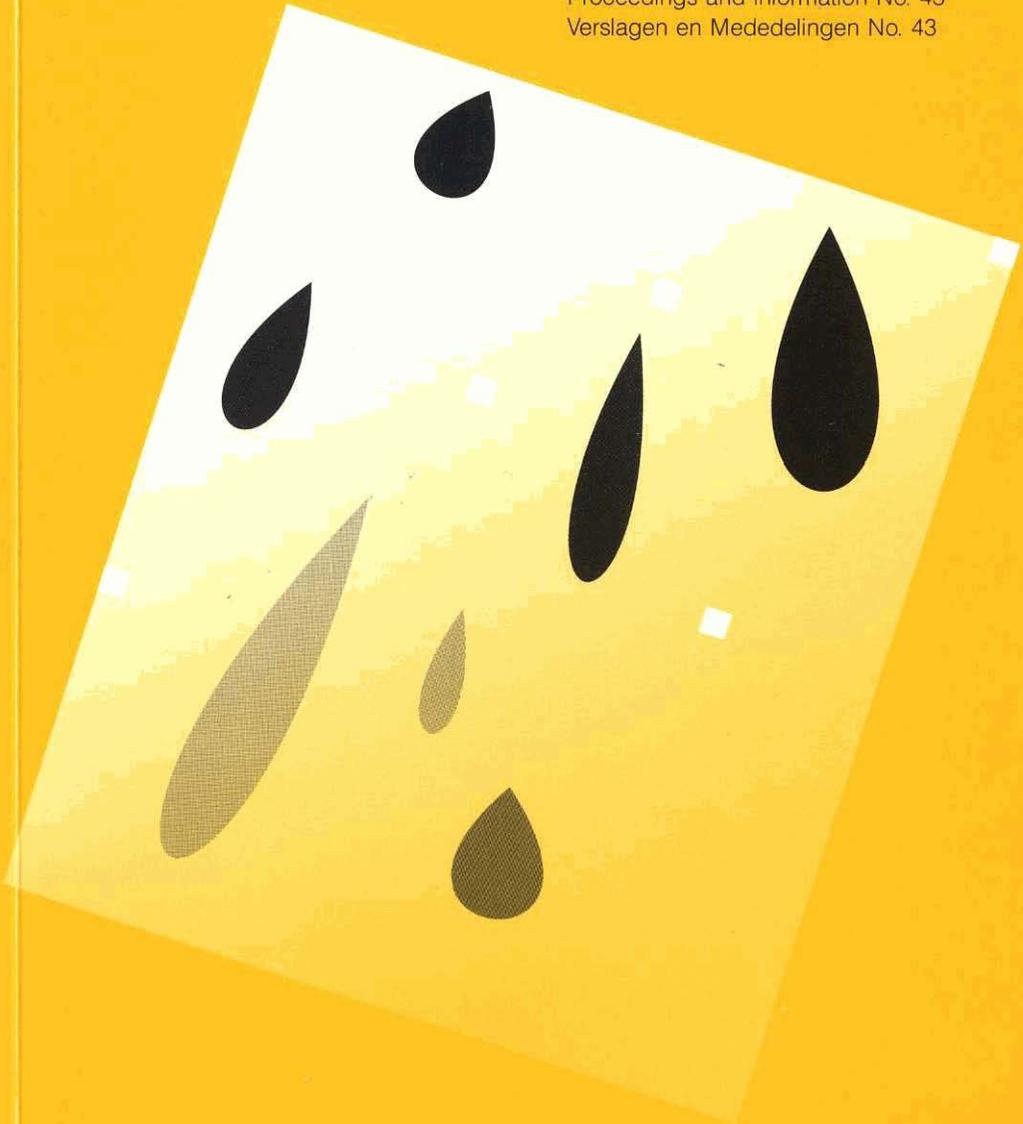


Netherlands
organization for
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research

TNO Committee
on Hydrological
Research

Hydrochemistry and energy storage in aquifers

Proceedings and information No. 43
Verslagen en Mededelingen No. 43



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The logo consists of the letters 'CHO' in a bold, sans-serif font, enclosed within a square border that is slightly rotated clockwise.

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INTRODUCTION

J.W. Lyklema

This volume of the series Proceedings and Information of the TNO Committee on Hydrological Research (CHO-TNO) contains the contributions as presented on the 48th technical meeting of the CHO-TNO, "Hydrochemistry and energy storage in aquifers".

During this symposium recent results have been presented on research which has been conducted within the framework of Annex VI of the International Energy Agency (IEA); Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods. The Dutch contribution within the IEA framework is coordinated and sponsored by the Netherlands Agency for Energy and the Environment (NOVEM BV) in the Dutch research program: National Research Program on Geothermal Energy and Energy Storage in Aquifers (NOAA).

Earlier research has shown that major problems can occur in operating plants when the effects of periodic changes in chemical equilibria due to heating and cooling are not correctly taken into account. A better understanding of the important chemical processes has been obtained by chemical modelling both empirically and theoretically in the laboratories and by computer experiments.

Also the interrelationship with microbiological processes has been studied extensively.

Of crucial importance are the water treatment methods. Clogging, scaling and corrosion processes can impair the system if no adequate techniques are used to avoid precipitation of various carbonates and oxides. Currently new, ecologically sound methods are being developed to counteract these precipitation processes.

The results on these topics have been presented to a broad audience with a background in heat and chill storage and water resources management. We expect that the presentations have contributed to a better understanding of the importance of hydrochemical and microbiological processes in the subsoil. We hope that this will be reflected in future research projects in this field and in other fields such as soil acidification and waste disposal studies.

G.J. van Mourik, A.L. Snijders.

ABSTRACT

The International Energy Agency (IEA) was founded in 1974 by a number of industrialized countries to secure energy supplies for both short and long term. To reach this goal, cooperative energy research, development and demonstration is encouraged by the IEA.

In the early eighties it was recognized that energy storage can play an important role in the saving of energy as well as the application of renewable energy sources. From the research carried out in this field, it turned out that aquifer thermal energy storage was both technically and economically feasible, but that the system reliability was questionable due to the water treatment methods applied.

So, in 1987 eight IEA countries decided to start a research activity, entitled "Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods".

1 INTRODUCTION

The papers in these proceedings deal with the results of basic research into the hydrochemical and microbiological processes in aquifers. This research has been executed at

the responsibility of the International Energy Agency.

At first sight it seems a little strange, a political institution like IEA engaged in this kind of research. This paper will enter into the background and the objectives of the IEA and will explain in which way basic hydrochemical and microbiological research fits within these objectives.

2 THE OECD

The OECD, the Organization for Economic Cooperation and Development, was founded in 1960 as a follow up of the OEEC (Organization for European Economic Cooperation). At this moment the OECD numbers 24 Member countries, including a number of industrialized non-European countries, namely: Canada, the United States, Japan, Australia and New Zealand.

The three basic aims of the OECD, given in Article 1 of the OECD Convention, are (Anonymous, 1985):

- * To achieve the highest sustainable economic growth and employment and a rising standard of living in Member countries, while maintaining financial stability, and thus contribute to the development of the world economy;
- * To contribute to sound economic expansion in Member as well as non-Member countries in the process of economic development;
- * To contribute to the expansion of world trade on a multilateral, non-discriminatory basis in accordance with international obligations.

The OECD is not a supranational organization but a centre for discussion where governments express their points of view, share their experiences and search for common ground.

The subjects they try to reach agreement upon concern: financial, fiscal and enterprise affairs; manpower, social affairs and education; agriculture and fisheries; science, technology and industry. A private staff of specialists belonging to the OECD, the OECD Secretariat, provides the basis by setting forward the problems and the possible remedies.

The International Energy Agency (IEA) was founded in 1974, directly after the first energy crisis, by a number of OECD countries to cope jointly with the energy problems. At present 22 countries participate in the activities of the IEA. The principal task of the IEA is to secure energy supplies for both short and long term.

The IEA has encouraged Member countries to conserve energy, to reduce dependence on oil, to develop alternatives to oil - like coal, nuclear power and renewable energy sources - and to pursue research and development. A current issue for the IEA is the effect of the growing environmental concerns on energy policy.

The joint energy Research, Development and Demonstration (RD&D) projects refer to (OECD, 1987) the application of fossil fuels, renewable energy forms, controlled thermonuclear fusion, and new technologies to achieve more efficient use of energy (energy conservation).

So the whole energy RD&D field is covered, except conventional nuclear energy. RD&D in this field is carried out by the Nuclear Energy Agency (NEA) of the OECD, that existed already before the establishment of the IEA.

Participation in energy RD&D activities takes place on voluntary basis. The intention to carry out research on a certain field is laid down in a so called "Implementing Agreement". Consequently there is an Implementing Agreement Energy Storage with the objective: "cooperative research, development, demonstrations and exchange of information regarding energy conservation through energy storage" (IEA, 1978).

After an Implementing Agreement has been drafted, separate RD&D projects are defined by two or more participating countries. In many cases the projects take place on a task sharing basis, in some cases, for instance when demonstration projects are executed, cost sharing is agreed upon.

The Implementing Agreement Energy Storage, in full: "Implementing Agreement for a Programme of Research and Development on Energy Conservation through Energy Storage", has been concluded in 1978. This Implementing Agreement has been concluded because it was recognized that energy storage can play an important role in the saving of energy as well as the application of renewable energy sources.

The first project within the framework of the Implementing Agreement Energy Storage concerned an evaluation of large scale energy storage systems. From this evaluation it appeared, among other things, that heat storage in aquifers is the least expensive technology for storage of thermal energy on a large scale, see figure 1 (IEA, 1981).

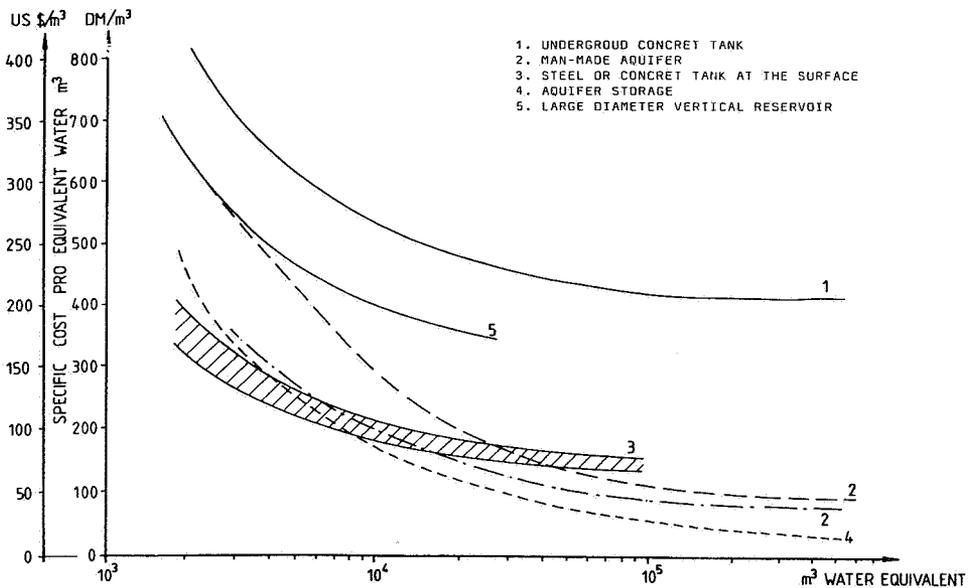


Figure 1 Cost of energy storage as a function of water volume

In addition to projects in the domain of short term storage in water and phase change materials, a pilot aquifer heat storage project has been executed within the framework of the IEA Energy Storage Programme (SPEOS project in Switzerland). Also exchange of information concerning pilot projects in Denmark (Hørsholm project) and in the United States (St. Paul Field Test Facility) has taken place.

Experience with these and other aquifer thermal energy storage projects had shown clearly that precipitation of chemical substances is the principal technical problem. Also the reliability of the water treatment methods applied was questionable because of the lack of information on slow underground chemical reactions and the possible interactions between microbiological and chemical processes.

As the storage of thermal energy in aquifers had proven to be both technically and economically feasible, high priority was attached to improve the reliability of the storage system by solving such bio-geochemical and environmental problems.

So, in 1987, eight countries decided to broaden the scope of the activities within the Implementing Agreement Energy Storage to the systematic investigation of the chemical, microbiological and environmental impacts of aquifer thermal energy storage and subsequently to the development of reliable, environmentally sound water treatment methods.

With this started the research entitled: "Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods" (IEA, 1987). The countries participating in this research are (in alphabetical order): Canada, Denmark, Finland, Germany, the Netherlands, Sweden, Switzerland and the U.S.A.

In this project the Netherlands have a relatively large part, because not only a part of the research activities is carried out by Dutch companies and research institutions, but also the coordination of the complete project rests with the Netherlands Agency for Energy and the Environment (NOVEM), see the organization scheme (Fig. 2).

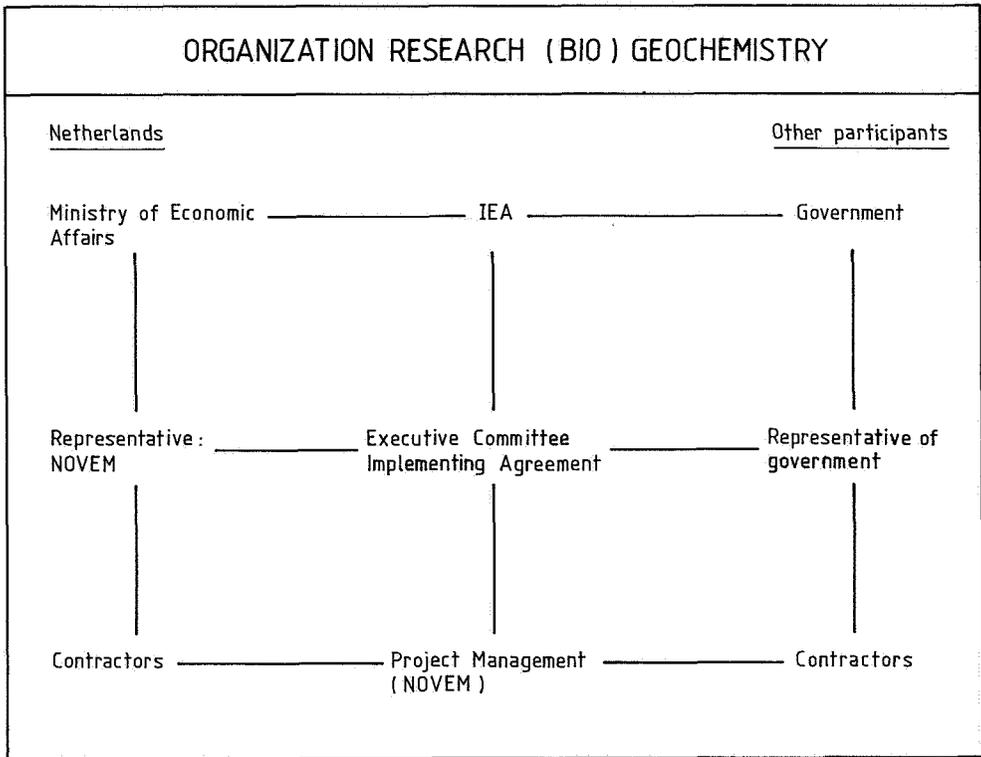


Figure 2 Organization scheme

REFERENCES

ANONYMOUS; 1985. OCDE-OECD, Paris, 31 pp.

IEA; 1978. Implementing Agreement for a Programme of Research and Development on Energy Conservation through Energy Storage. IEA, Paris, 33 pp.

IEA; 1981. Large scale thermal storage systems. Annex I, Final Report, Centre of Hydrogeology of the University of Neuchatel, Switzerland, 130 pp.

IEA; 1987. Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods. NOVEM, Utrecht, 22 pp.

OECD; 1987. A ten year review of collaboration in energy RD&D 1976 - 1986, OECD/IEA, Paris, 244 pp.

THE RELATION BETWEEN AQUIFER THERMAL ENERGY STORAGE AND HYDROCHEMISTRY; AN OVERVIEW

F.C. Dufour

1 INTRODUCTION

The underground storage of energy in the Netherlands is focused on storage of thermal energy in aquifers. This applies for heat storage as well as for cold storage. In view of the fact that the hydrochemistry of the groundwater is more influenced by large temperature fluctuations than by small temperature fluctuations, the hydrochemical consequences are more dominant in the case of heat storage ($\Delta T=50-80^{\circ}\text{C}$) than in the case of cold storage ($\Delta T=5-10^{\circ}\text{C}$). Consequently these proceedings are mainly dealing with heat storage in relation to hydrochemistry.

For an extensive overview of the geohydrological preconditions the reader is referred to Heederik, J.P. and Snijders, A.L., 1988, proceedings TNO Committee on Hydrological Research no. 40, p. 19-23.

2 PRINCIPLE OF HEAT STORAGE

Thermal energy storage in aquifers is essentially an integral part of an energy supply or energy saving system. In periods of heat surplus groundwater, extracted from aquifers, is heated in a heat exchanger, and afterwards returned into the aquifer. In periods of consumption the heated groundwater is re-extracted from the aquifer and cooled in the heat

exchanger.

Figure 1 presents the principle. The system always includes a heat supplier, a heat consumer, a hot and cold well and usually a heat exchanger to separate the groundwater circuit (brackish or salt water) from the surface, supplier/consumer, circuit (fresh water). The two wells are usually located in the same aquifer, so complications due to differences in groundwater composition are avoided. The hydrostatic equilibrium in the aquifer is maintained as well.

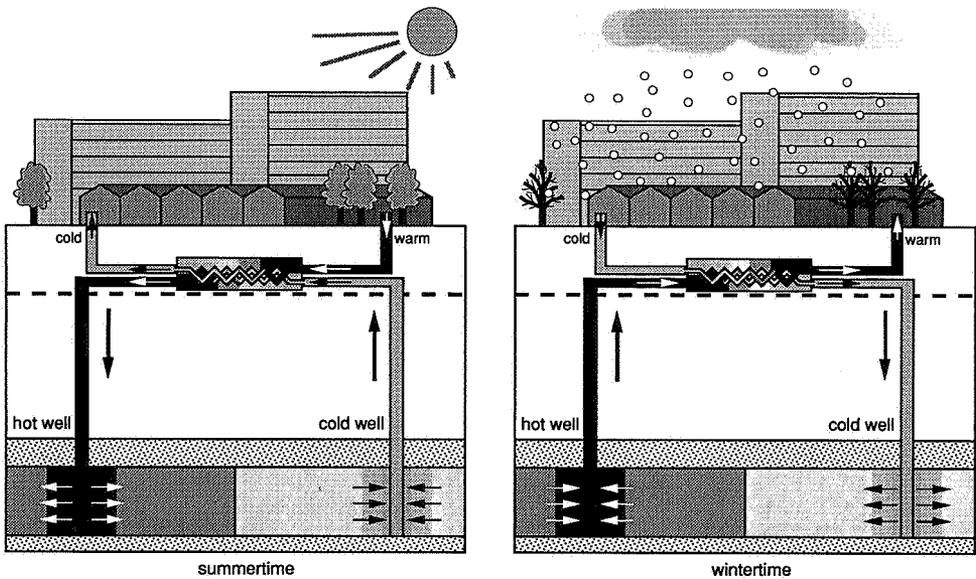


Figure 1 Principle of heat storage in aquifers

Aquifer thermal energy storage (ATES) can be connected to a building heating/cooling installation, to a greenhouse heating system or to a heat-power co-generating plant. A co-generating plant produces both electricity as well as heat. During summer periods heat demand is low consequently heat can be stored. The stored heat can be used during winter. In this configuration the temperature range of transferred groundwater in the heat exchanger is initially 10-90°C and after several cycles 40-90°C. The well temperature settles finally at 90°C (hot well) and 40°C (cold well) after several cycles.

ATES systems contribute to:

1. efficiency improvement of a heating/cooling installation;
2. reduction of primary energy (fuel) consumption;
3. reduction of environmental hazardous products (CO_2 , NO_x , heat etc.); which are related to power generation.

In view of the fact that renewable energy sources (wind-, solar energy etc.) cannot be tuned easily to energy consumption, energy storage systems are a prerequisite for the introduction of renewable energy sources.

GEOHYDROLOGICAL PRECONDITIONS OF AN ATES SYSTEM

The required aquifers characteristics, related to thermal energy storage, are presented in Figure 2.

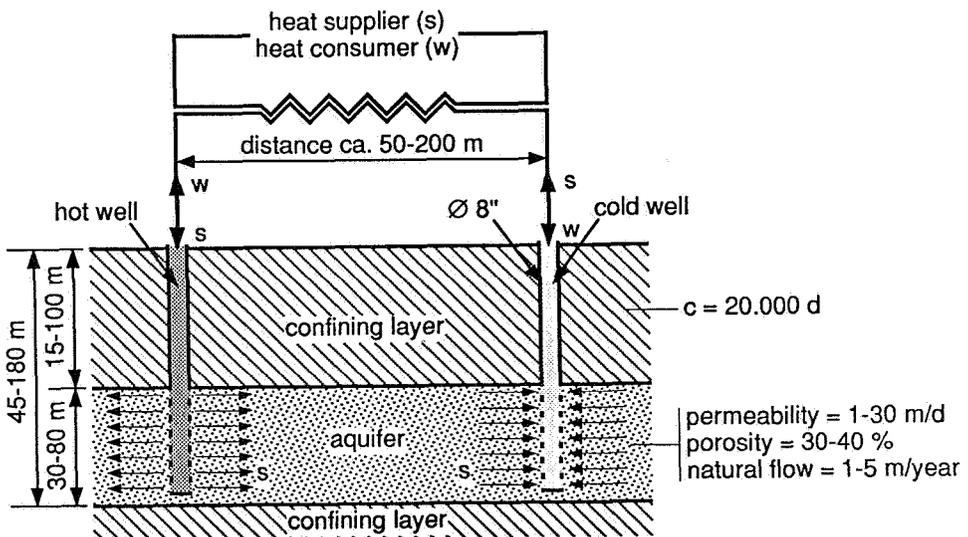
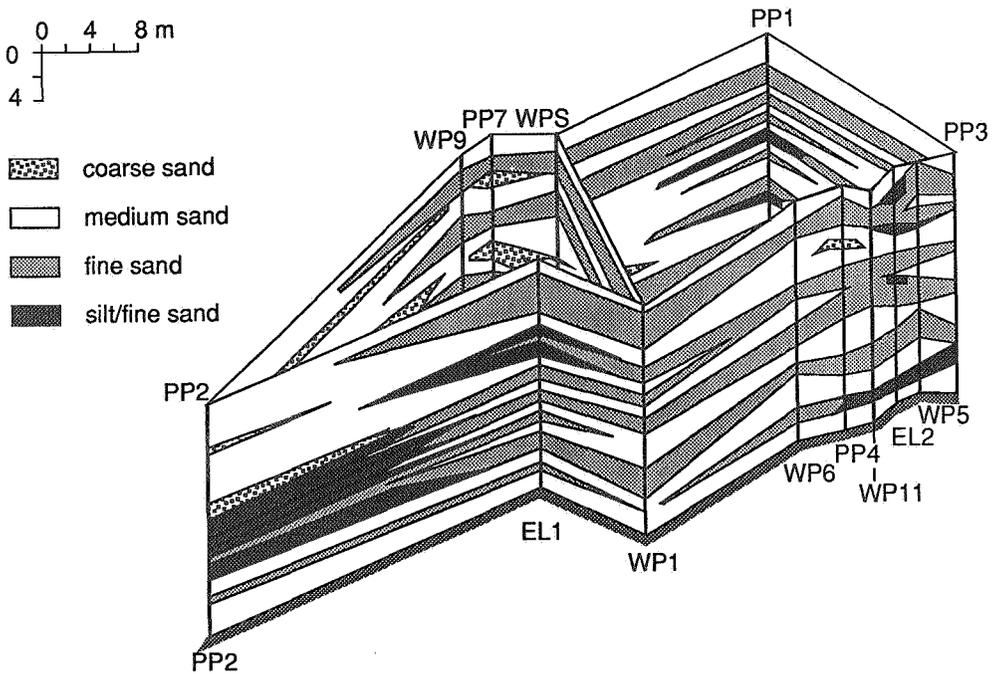


Figure 2 Aquifer characteristics

The most important required boundary conditions of the aquifer selected for thermal energy storage are depth, transmissivity and the hydraulic resistance of the confining layers. The flow directions are shown for the winter (w) and summer (s) season.

One has to realize that an aquifer (sand), in between two confining (clay) layers, is a result of a sedimentological process of deposition. Hence layers of finer and coarser material alternate with consequently a considerable variation in permeability and porosity in the aquifer. To illustrate this phenomenon, the lithological composition of the aquifer at the national test facility (for heat and cold storage) at Delft is shown in Figure 3.



5 TEMPERATURE VARIATIONS

The groundwater, acting as the energy transporting fluid, is subject to periodical heating and cooling. Figure 4 illustrates the temperature fluctuations of the transferred groundwater in time. In the case of aquifer storage coupled to a heat-power co-generating plant the temperature at the 'hot' side varies between 45 and 90°C during each yearly cycle.

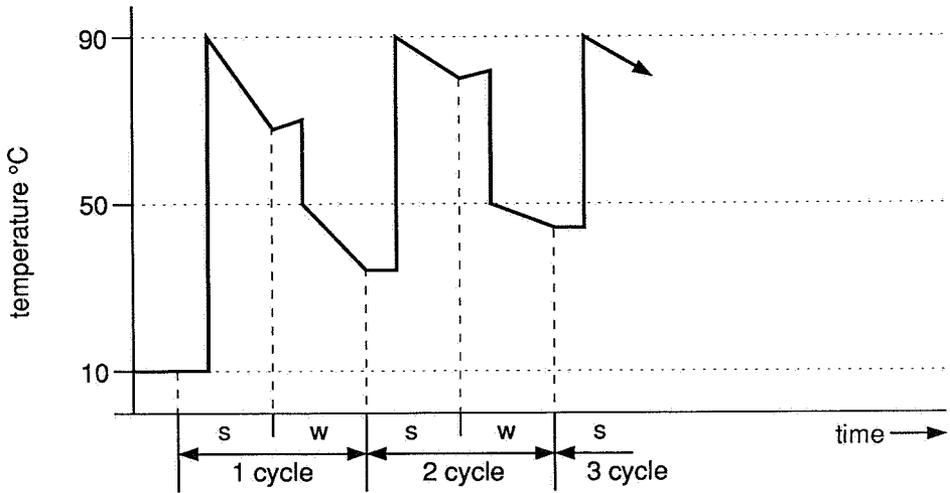


Figure 4 Temperature fluctuations of transferred groundwater

The sediment in the aquifer is subject to temperature fluctuations as well. Figure 5 illustrates the temperature variations on the surface of the sediments in the immediate neighbourhood of the 'hot' well. In view of the fact that the lowest temperature of (stored) heat extraction is 50°C, the temperature fluctuations remain restricted to the range 50-90°C.

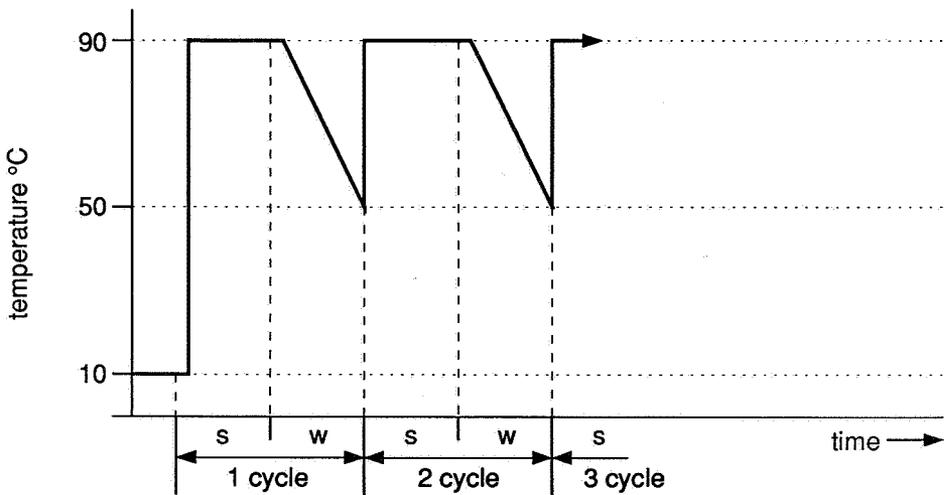


Figure 5 Temperature variations of sediment surface close to the hot well

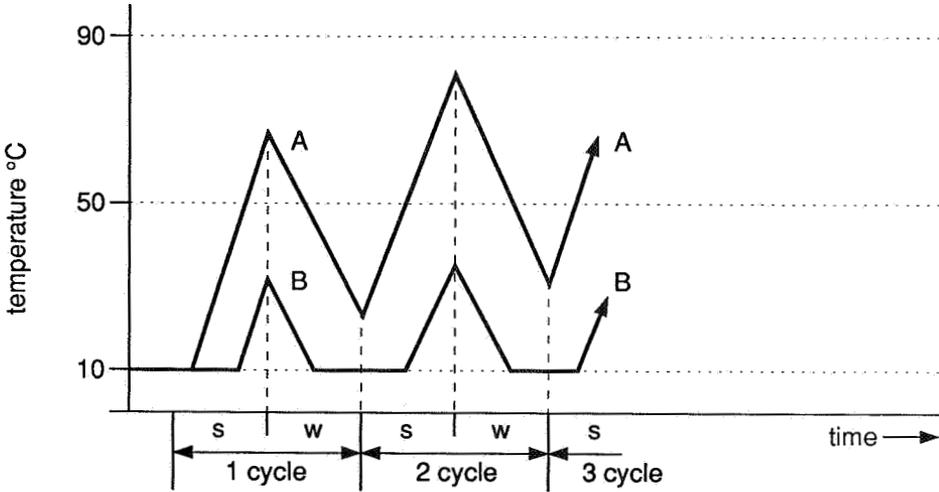


Figure 6 Temperature variations of sediment surface at distance of the hot well

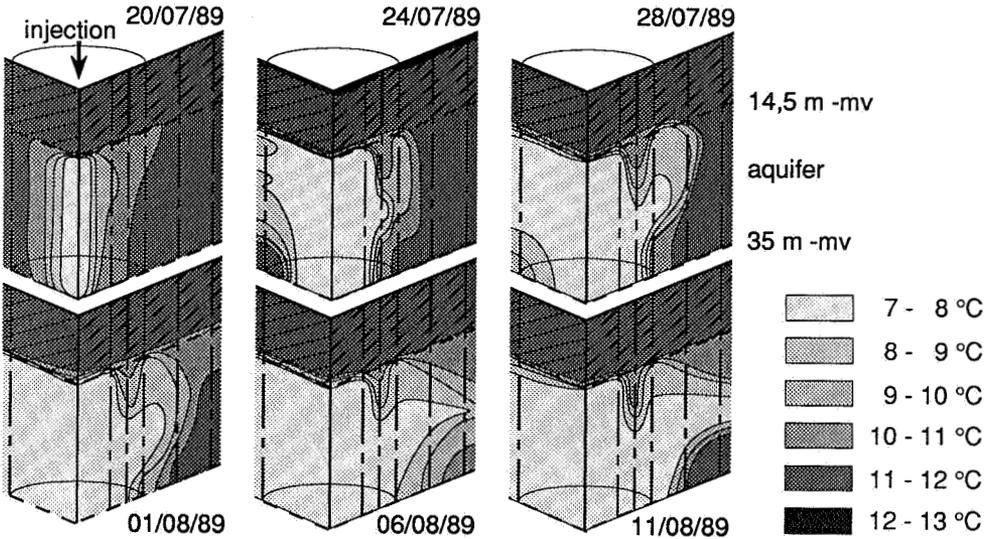


Figure 7 Temperature distribution as observed during cold storage at Delft

At a certain distance of the 'hot' well the temperature fluctuations on the sediment surface show a different regime. Figure 6 illustrates regimes for two different distances. In curve B (largest distance to the 'hot' well) the temperature drops to the initial aquifer temperature of

10°C between two cycles. We have to realize that at a certain distance, due to a gradual expansion of the sphere of influence, the lowest level as well as the top level of the temperature fluctuations raise. But in the mean time the initial temperature regime is transferred to an area at a larger distance from the 'hot' well. This creates a situation of different temperature regimes distributed throughout the aquifer related to the distance to the 'hot' well. Although the temperature levels are considerably lower, the same phenomenon of temperature fluctuations applies to the area around the 'cold' well.

The aquifer is not a homogeneous sand body (as shown in Figure 3), therefore, the temperature zones are not symmetric around the wells. As shown in Figure 7, based on observations during cold storage at the national test facility, the distribution of these temperature zones in the aquifer becomes erratic.

6 HYDROCHEMICAL AND MICROBIOLOGICAL ASPECTS

As a result of the chemical interaction between groundwater and the surrounding sediment material, groundwater contains a wide variety of dissolved inorganic chemical constituents in various concentrations. The solubility of the minerals depends upon temperature. Changes in temperature will result in shifts in chemical equilibrium, resulting in a possible dissolution or precipitation of elements.

An important equilibrium reaction for Dutch aquifers is:



In reality the equilibrium is influenced as well by the presence of other minerals as by specific combinations of minerals.

The microbiological equilibrium conditions as well are disturbed by a (sudden) change of temperature, by periodic temperature fluctuations, by the change of groundwater composition or by the increased groundwater flow. This may result in bacterial growth and slime production, or in bacterial mediated iron precipitation and metal corrosion by sulphate

reducing bacteria. These activities decrease groundwater quality in a serious way.

7 CORROSION AND SCALING

Scaling occurs due to the disturbance of the hydrochemical equilibrium and a change in mineral concentration, oversaturation and hence precipitation occurs consequently. A change in hydrochemical composition may also create a fluid which is more aggressive with consequently an increased risk of rapid corrosion of the installation.

The technical and economical performances of an aquifer thermal energy storage system are very sensitive to the consequences of corrosion and/or scaling. Corrosion of screens, casing, pipes and heat exchanger(s) may increase the depreciation beyond the economical limits. Scaling can cause clogging of screens and heat exchanger resulting in an unforeseen increase in cost of maintenance and increase of interruptions in the operation of the ATEs installation.

8 APPROACH AND SOLUTIONS

The most important approach to solve or to avoid the above stipulated problems related to aquifer thermal energy storage, is found in water treatment studies and experiments.

Two options under consideration at present are:

1. Addition of chemicals.
2. Microbiological and/or fluid bed methods and/or mechanical removal of solids.

Both methods are applied to compensate for the transition in hydrochemical composition of the (ground)water due to heating and (to a lesser extend) due to cooling.

The first option bears the insurmountable disadvantage that with each cycle more chemicals have to be added (the same groundwater is used periodically) and consequently an increase in concentration of added chemicals is unavoidable. This method risks to deteriorate the

groundwater quality so seriously that the operation will be forced to be terminated after a relative short period.

The methods mentioned as a second option offer a more promising solution due to the fact that the emphasis lies on extraction of those components which endanger the operation by clogging, scaling or corrosion. These methods do not contribute to an increasing deterioration of the (ground)water quality and hence do not have a negative impact on the environmental situation.

AQUIFER THERMAL ENERGY STORAGE: THE IMPORTANCE OF GEOCHEMICAL REACTIONS

E.A. Jenne

ABSTRACT

Aquifer Thermal Energy Storage (ATES) is a technology that uses waste heat to raise the temperature of groundwater until needed for heating during a season of greater demand. Geochemical problems encountered in ATES systems and the underlying geochemical processes are the subject of this paper.

Geochemical problems arise from the formation of precipitates that reduce the efficiency of heat exchangers and clog the pores of aquifers, reducing their permeability and maximum injection rates. Precipitates result from oversaturation of the water with solid phases because of changing temperature, changing partial pressures of oxygen and/or carbon dioxide, and/or displacement of Ca from cation exchange sites. Precipitates are generally composed of $\text{CaCO}_3(\text{s})$ or Fe and Mn oxyhydroxides. As storage temperatures in excess of 100°C are used, the likelihood increases that silicate scale will form during heat extraction. The infiltration of surface water through river and lake sediments commonly results in an increase in dissolved Fe and Mn because first oxygen then Mn(IV) and Fe(III) oxides serve as the electron acceptors for the products of microbial respiration. Thus, near-surface aquifers often contain significant levels of dissolved Fe and Mn that precipitate when exposed to oxygen. The water of ATES systems frequently calculates to be oversaturated with pure calcite as a result of the formation of solid solutions of calcite with Mg, Fe and Mn. The capability to model carbonate solid solutions empirically and theoretically has been

developed within Annex VI (Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment) of the International Energy Agency (Programme of Research and Development on Energy Conservation Through Energy Storage). However, the presence of crystal growth inhibitors (e.g., dissolved organic carbon, phosphate) may decrease precipitation rates of $\text{CaCO}_3(\text{s})$ and thereby cause oversaturation.

The formation of precipitates in ATEs systems can be avoided by appropriate selection of the storage aquifer, use of municipal water as initial source water, and/or continuous water treatment. Air and/or microbial oxidation can be used to lower dissolved Fe and Mn concentrations. Calcium and/or carbonate concentrations can be reduced by acidification, precipitation induced by increased pH, or by cation exchange. Any of these treatments can avoid clogging of the well and aquifer; however, certain treatments may cause local degradation of water quality.

This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

1 INTRODUCTION

A high degree of dependence on foreign sources of petroleum is of major economic and political concern to many countries. One expression of this concern is multi-national research, such as that carried out under Annex VI of the International Energy Agency, into alternative energy forms. Seasonal energy storage, e.g., aquifer thermal energy storage (ATES), is a technology that uses waste heat or electricity during low-cost periods (e.g., spring, fall) to heat water, which is stored in a groundwater aquifer until needed for heating during a season of greater demand. Economic benefits can accrue from using alternative energy forms during periods of peak demand by the avoidance, or at least the delay, of capital outlay for electric power plants.

Geochemical problems encountered in ATEs systems and the underlying geochemical processes are the subject of this paper. However, because certain mineralogic, geologic,

hydrologic, and mechanical factors relate to the geochemical problems encountered, the factors are briefly discussed here. For example, aquifer mineralogy may determine if water treatment is required to avoid carbonate precipitation within the ATES system. Local geology (e.g., aquifer thickness, depth below land surface, and nature of aquicludes) constrains those aquifers that may be used for heated water storage. Depth to the storage aquifer impacts both capital and operating costs. The presence and thickness of aquicludes are important in separating incompatible waters, in avoiding loss of the heated water from the storage aquifer to adjoining strata, and in allowing higher injection pressures and consequently higher injection rates. Inadequate structural integrity of an aquiclude has twice required abandoning ATES storage wells (Moltz et al., 1978; Schleisner-Ibsen and Qvale, 1988). Local hydrology (e.g., an excessive regional groundwater flow rate) can cause decreased efficiency because of losses of heated (or chilled) water or alternatively cause increased capital costs because additional wells are required (and associated maintenance and pumping costs) to hold the thermally altered water in position against the hydrologic gradient. Permeability, in conjunction with the screened thickness of the aquifer(s) and allowable injection pressures, determines if adequate injection rates can be achieved. Mechanical and material problems may be increased by water treatment (e.g., corrosion from acidification, dispersion of Na-saturated clays). However, these problems are less serious in ATES systems than in geothermal wells used for district heating (Ungemach and Turon, 1988).

The geochemical processes of primary interest are cation exchange, mineral equilibria (i.e., precipitation and dissolution), and redox reactions of sulfides, Fe, and Mn. The oxidation of organic carbon by microbial growth may affect mineral equilibria by increasing the $p\text{CO}_2$, thereby increasing the likelihood of carbonate precipitation, and by decreasing the redox potential.

2 CATION EXCHANGE PROCESSES

The total quantity of exchangeable Ca, which can be estimated from the cation exchange capacity (CEC) and relative quantities of exchangeable cations, is potentially important in three ATES situations. First, in aquifers where the water is in equilibrium with a solid

carbonate phase, the use of a high-Na (i.e., softened or saline) water may displace Ca and increase its pore water concentration enough to cause precipitation as the chromatographic front moves through the aquifer. Modelling the intrusion of very saline water (3 times sea-water concentration) into a fresh-water aquifer (assumed to be in equilibrium with calcite at a $p\text{CO}_2$ of 0.1 atm; $\text{CEC}=200$ miliequivalents(me)/L= 2.5 me/100 g) by Appelo and Willemsen (1987) indicated that dissolved Ca would increase by a factor of ≈ 3 as a result of displaced exchangeable Ca by Na, with resultant precipitation of $\text{CaCO}_3(\text{s})$. If the aquifer is of marginal permeability, the precipitate may cause some reduction in permeability, and if the storage time is not long enough for precipitation to go to completion, scaling may occur in the mechanical portion of the system ahead of the heat exchanger. Second, if only trivial quantities of carbonate minerals are present in the aquifer sediment, the quantity of exchangeable Ca, as well as an estimate of the probable extent of mixing with native groundwater, may be important for deciding if water treatment will be required. Third, if significant amounts of expansible clays are present in the aquifer, it is important that the Na exchange fraction be kept low enough to avoid dispersion of the clay fraction and attendant clogging of the injection well when the water is reinjected. Beekman and Appelo (1988a) found in column studies that the dispersivity value increased by a factor of 3 as freshwater replaced 50% sea water. In laboratory suspensions, Levy (1976) found montmorillonite crystallites tend to expand markedly when the exchangeable Na exceeded $\approx > 60\%$. The tendency of clays to swell and thereby reduce soil permeability as a result of increased saturation of cation exchange sites with Na is commonly evaluated by the "sodium adsorption ratio" of the water (Jackson, 1958), i.e.,

$$\text{Na} / (\text{Ca} + \text{Mg})^{0.5} \tag{1}$$

where the concentrations are in miliequivalents per liter. This ratio provides only a semi-quantitative estimate because the critical value also depends on the ionic strength of the water, on the expansible clay properties (e.g., charge density distribution), and the extent of cementation of aggregates.

Clay minerals generally exhibit a strong preference for divalent over monovalent cations. Mass-action selectivity coefficients for Ca-Na exchange decrease (by as much as a factor of 2) as exchangeable Na increases (Sposito and Fletcher, 1985). The Vanslow coefficients

vary more than Gapon coefficients (Beekman and Appelo, 1988b) as the Na exchange fraction varied from 0 to 0.25. Additionally, the selectivity coefficient for Ca decreases relative to that of Mg as exchangeable Na increases (Sposito and LeVesque, 1985; Beekman and Appelo, 1988a,b). Using the classical field injection data set of Valocchi et al. (1981), C.A.J. Appelo (manuscript in preparation) has evaluated the commonly used Gapon, Gaines-Thomas, and the Vanselow equations and concluded that the latter two give more satisfactory results than the Gapon equation.

A strong temperature dependence of Ca-Na exchange has been shown recently in column studies by J. Griffioen and C.A.J. Appelo (unpublished data). It seems likely that differences among cation exchange sites on the expansible clays (i.e., interlayer sites located on planer surfaces versus those on edge sites and sites on layers with significantly differing charge density) contribute to the variation in cation selectivity with changing temperature and Na exchange fraction. The edges of smectites (e.g., montmorillonite), which comprise ca. 20% of the CEC of these clay minerals, presumably have different selectivities than interlayer surfaces for heterovalent cation exchange. Thus, at < 20% Na saturation of montmorillonite, Na occupies primarily the exterior sites, while Ca dominates interlayer sites (Levy et al., 1983). High-charge exchangers, such as vermiculite and bidellite, may exhibit greater variation in selectivity than lower-charge smectites because of 12-fold coordination with certain mono-valent cations such as Cs, K, Rb, and NH_4 and also because of demixing. Demixing results from the tendency of cations of similar charge and hydrated radii to be found in interlayers of similar average charge and to prefer interlayers which are already predominately saturated with exchangeable cations of similar charge and hydrated radii.

3 MINERAL PRECIPITATION

3.1 Fe and Mn oxyhydroxides

Surface waters often contain significant levels of dissolved Fe and Mn, and they frequently gain additional quantities of these metals during recharge through soils and other surficial sediments. Surface water, and the soil and sediment through which the water infiltrates,

generally contain sufficient organic material to support an abundant microflora. Since oxygen serves as the initial electron receptor for microbial metabolism, a loss of oxygen and a lowering of the "system" redox potential of the infiltrating water generally occur during recharge. The loss of oxygen and lowering of the redox potential tend to increase the concentration of dissolved Fe and Mn in shallow groundwater. When this water subsequently encounters free oxygen in an ATES system, hydrous oxyhydroxides of Fe and Mn readily form. Such precipitates are frequently encountered in ATES systems in the Scandinavian countries, where a majority of the ATES systems have been located in shallow aquifers of glacial origin. These precipitates may decrease the maximum injection rate as at the Bunnik ATES site (Bredero Energy Systems, 1986) when a leaky connection allowed the entry of air into the system.

Traditional solutions to the problem of Fe- and/or Mn-rich water are to either remove these metals from the Fe- and Mn-bearing water or to totally exclude oxygen from the ATES system. Sufficient Fe and Mn may be removed by allowing the water to cascade onto a low-slope area where it flows in a thin layer over a rough surface, followed by slow sand filtration (Hatva et al., 1984). A more novel approach is to inject nitrate into the aquifer down gradient from the source well and allow microbial activity to promote the activity of Fe(II) oxidizing microflora and allow the Fe(III) oxides to precipitate in situ. This technique can reduce dissolved Fe to fractional milligrams per liter levels (Vanek, 1990). Alternatively, water containing elevated levels of Fe and Mn can be used without their removal where 1) the storage aquifer is isolated by aquicludes of low permeability and 2) atmospheric oxygen is totally excluded from the ATES system. The problem of Fe oxyhydroxide clogging at the Dutch Bunnik site was circumvented by using low-Fe municipal water for the initial heating and injection in conjunction with steps to prevent air from entering the system (Coevering and Appelo, 1988).

3.2 Carbonates

As carbonate minerals are nearly ubiquitous, the waters of many if not most ATES systems are close to equilibrium with calcite. This may be the case even when the mineral is only a minor constituent, e.g., < 0.4% of the aquifer matrix, as in the Fontainebleau sand at Saint Quentin (Yvelines, France) (Vinsot, 1987). The Plaisir site near Paris, France, is

exceptional in that after initial removal of carbonate by raising the pH, only minimal further softening is required, which is provided by an ion exchanger system (J. Despois, personnel communication, Oct. 1988).

The retrograde solubility of carbonate minerals (Garrels and Christ, 1965) generally results in their rapid precipitation when water that was in equilibrium with a carbonate mineral at some temperature is heated to some appreciably higher temperature. At the St. Paul (USA) site, major portions of the aquifer sediment are dolomitic. Thus, it is not surprising that the groundwaters are in approximate equilibrium with calcite (Holm et al., 1987). Copious amounts (600-800 kg per cycle) of aragonite precipitated (Walton, 1986) after rapidly heating the native groundwater to 87°C in the first short cycle.

The partial pressure of CO₂ may be much above atmospheric levels in confined aquifers. If CO₂ is allowed to escape from an ATES system, the carbonate equilibria will shift, as illustrated below to produce CO₂(g) and consume H⁺, resulting in a pH increase and possible carbonate precipitation:



The degree of oversaturation with pure calcite of a thermally altered water is affected by the formation of solid solutions, the presence of nucleation and crystal growth poisons, and temperature and complexation of Ca by dissolved organic carbon (DOC). The formation of solid solutions between calcite and other metal carbonates that form the same rhombohedral structure can cause large deviations from the equilibrium solubility of pure calcite (E.A. Jenne and R.W. Smith, unpublished data). Nucleation and crystal growth poisons can also cause oversaturation of calcite and its solid-solutions. These factors are thought to account for the observed oversaturation with respect to pure calcite of various ATES waters.

At some ATES installations, moderate oversaturation with calcite, even accounting for solid-solution effects, does not result in scaling of the heat exchanger. The rate of calcite

precipitation from solutions at near-neutral pH values without nucleation and crystal growth poisons is such that equilibrium is generally closely approached within several hours (Reddy et al., 1981; Inskeep and Bloom, 1986). One concludes, therefore, that the oversaturation of calcite solid solutions is due to inhibitors that may reduce the rate of precipitation or even prevent the precipitation of CaCO_3 . Known inhibitors include PO_4^{3-} , Mg^{2+} , SO_4^{2-} , Sr, Ba, Pb, glycerophate, phosphonic acids, organic ligands, and organic acids (Reddy, 1977; Berner et al., 1978; Reynolds, 1978; Reddy and Wang, 1980; Matty and Tomson, 1988). Bricker and Myers (1969) proposed that the adsorption of hydroxyl complexes of metals, such as Fe(III) and Th(IV), that readily hydrolyze at circumneutral pH values affect crystal growth rates of BaSO_4 . In accord with the inhibition observations for calcite, it has been observed that the poisons noted above are removed in pellet reactors along with the calcium carbonate (Graveland et al., 1983). Indeed, when phosphate and DOC are in excessive concentrations in the pellet reactors ($> 1 \text{ mg L}^{-1}$ and KMnO_4 consumption $> 50 \text{ mg L}^{-1}$, respectively), both the density of the pellets and carbonate removal efficiency decreases. Organic inhibitors appear to be noticeably more effective at low concentrations than are PO_4^{3-} , Mg^{2+} , or SO_4^{2-} (Reddy, 1977; Berner et al., 1978; Reynolds, 1978; Reddy and Wang, 1980). The ability of organic compounds to inhibit or prevent carbonate precipitation is used to prevent scale in industrial water processing equipment and in the petroleum industry (Walton, 1967). Inhibitors are effective at concentrations of a few parts per million where the degree of supersaturation is not too great, i.e., considerably less inhibitor is required to inhibit crystal growth than to prevent nucleation from high oversaturations (Matty and Tomson, 1988).

The preceding qualitative results require a quantitative framework to be useful in reliable prediction of the likelihood of calcite precipitation and resultant need for water treatment for individual ATEs sites and temperatures. Importantly, Ferguson (1984) found that the quantity of inhibitor required to control calcite precipitation in a once-through cooling tower was linearly proportional to the degree of calcite oversaturation, and Matty and Tomson (1988) found that the combined effects of DOC, PO_4^{3-} , Mg^{2+} , and SO_4^{2-} on calcium carbonate precipitation were linearly additive. Inskeep and Bloom (1986) determined the effect of several concentrations of DOC on calcite precipitation from oversaturated solutions. It seems likely that the effectiveness of the DOC in a water extract of a soil that is lower than purified fulvic acid in inhibiting calcite precipitation on seed crystals was a result

of different effective charge properties of the two sources of DOC. Unfractionated, unpurified DOC of surface waters has an apparent charge of about 3.6 meq.g^{-1} of carbon (Johannessen, 1980; Cronan and Aiken, 1985) whereas purified fulvic acid has an average charge of 10.7 meq.g^{-1} (Oliver et al., 1983). When the quantity of DOC charge is normalized to unit surface area of the seed crystals used in the experiments and plotted versus the reaction rate constant, the two sets of data are observed to scatter about the same curve (Figure 1). A similar calculation was made for the inhibition of hydroxyapatite precipitation by fulvic acid and humic acid (7.7 meq.g^{-1} ; Oliver et al., 1983) reported by Inskeep and Silvertooth (1988). However, the precipitation of hydroxyapatite is inhibited to a much greater extent than calcite at the same DOC charge to surface ratios (Figure 1).

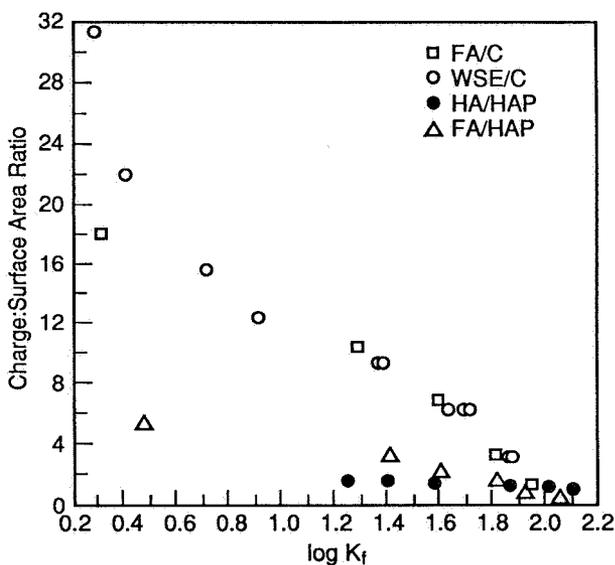


Figure 1 Effect of estimated Dissolved Organic Carbon Charge (DOC) to surface area of Calcite or Hydroxyapatite Seed Crystals on the reaction rate constant (C=Calcite, FA= Fulvic Acid, HA=Humic Acid, WSE=Water Soluble Extract, and HAP=Hydroxyapatite)

Water treatments used to avoid carbonate precipitation in ATEs systems include acidification of the water (with or without removal of evolved CO_2), removal of carbonate by precipitation pre-treatment of sufficient Ca carbonate to avoid precipitation within the ATEs system, and lowering of Ca and Mg concentrations by cation exchange before heating

of the water for storage. These treatments run the gambit of preferential removal of $\text{HCO}_3^- + \text{CO}_3^{2-}$, both Ca + Mg and $\text{HCO}_3^- + \text{CO}_3^{2-}$, or Ca + Mg. Acid treatment (with stripping of the evolved CO_2) was used at Horsholm (Denmark) (Schleisner-Ibsen and Qvale, 1988) where, over the course of several high-temperature (up to 100°C) injection cycles, there was considerable corrosion of the monitoring equipment, which was located close to the acid-addition apparatus. Acidification (without air stripping of evolved CO_2) has been used for a number of years at the SPEOS (Switzerland) system to control carbonate precipitation (Saugy, 1989). However, lowering of pH by acid addition increases both the rate and extent of dissolution of minerals (including carbonate) in a storage aquifer following injection of heated water. Thus, the pH must be lower in each succeeding storage cycle to avoid carbonate precipitation. This is a major limitation on the use of acidification in ATEs systems and effectively eliminates the use of acids for other than remedial action. The Plaisir high-temperature experimental ATEs system in France was designed for carbonate removal, preceding heating, by $\text{Ca}(\text{OH})_2$ addition in a batch reactor designed to allow precipitate removal at the bottom. A sand filter removed suspended precipitate before passage through the heat exchanger and reinjection into the storage well. On one occasion, an equipment malfunction resulted in the injection of high-pH water which resulted in carbonate precipitation upon mixing of injected water with groundwater with attendant loss of permeability. Permeability was restored by an acid treatment.

3.3 Silicates

Silica (SiO_2) scaling has not proved to be a problem in ATEs. Although Si constituted 7.5 to 11% of the scale formed on the Horsholm (Denmark) heat exchanger (C.T. Boesen, personal communication, 1989), it is not known if this represents SiO_2 precipitation or entrapment of Si-bearing particles. To date, none of the ATEs systems have operated at a sufficiently high storage temperature (i.e., $> 120^\circ\text{C}$) and with sufficient temperature drop during heat extraction to have caused significant silica precipitation on the heat exchanger. Because of the planned storage temperature of 180°C at the Plaisir site, Si removal was part of the design. This treatment method is novel: addition of Al to form an amorphous compound with Si, addition of Fe(III) to scavenge the Al-Si precipitate, sedimentation of precipitate in the batch reactor, and polishing with a sand filter. Information on the success of this treatment strategy is not yet available.

The heterogeneous reactions of SiO_2 generally involve an activated complex; the dissolution reactions are zero-order whereas precipitation is first-order with regard to dissolved silica (Rimstidt and Barnes, 1980; Bird et al., 1986) (see Equations 4 - 7).



where the * indicates the activated complex.

The slower rate of precipitation as opposed to dissolution has led to the widespread use of dissolved Si as a geothermometer (Fournier and Rowe, 1966; Arnorsson, 1975) of water temperatures at depth in geothermal exploration. This reaction rate differential minimizes SiO_2 scaling.

3.4 Temperature dependent modelling

Scaling is to be avoided in ATEs systems because it results in increased maintenance costs and decreased efficiency. Similarly, unnecessary capital costs for treatment should be avoided. The avoidance of scaling requires that saturation indices for pertinent minerals be calculated with a significantly greater reliability than is normally required by geochemists and environmental chemists for interpretative studies. Therefore, a major aspect of the U.S. contribution to Annex VI of the International Energy Agency collaborative research has been focused on this problem. Solid solution modelling of carbonates and ATEs-groundwater mixing models have already been mentioned. The initial effort was to improve the temperature competence of our geochemical modelling (Smith, 1988). Calculation of saturation indices can be no more reliable than the aqueous speciation calculations on which they are based. However, thermodynamic data are conventionally determined at 25°C and require adjustment for use at higher temperatures. These adjustments can be estimated with the Van 't Hoff relationship but this estimation procedure often leads to significant error at

the higher ATES temperatures. Therefore, experimental data need to be used for reliable temperature compensation. An extensive search for available temperature dependence data below 350°C was made and the results used to calculate coefficients for functions of the form

$$\log K_T = a_0 + a_1 \ln T + a_2 T + a_3 + a_4 \quad (9)$$

for 57 aqueous species and 60 minerals (where T is temperature in Kelvin and a_0 through a_4 are reaction-specific coefficients) (Smith 1988). The extent of the change in aqueous speciation as a result of using experimental data in conjunction with equation 8, as opposed to using the Van 't Hoff estimation of the temperature correction is shown in Figure 2. The changes for CO_3^{2-} , Fe^{2+} , SO_4^{2-} and Mg^{2+} were important. The important consequences of the improved database (MINTEQP3) versus use of the Van 't Hoff approximation (MINTEQP2) for calculation of calcite and quartz saturation indices are shown in Figures 3 and 4.

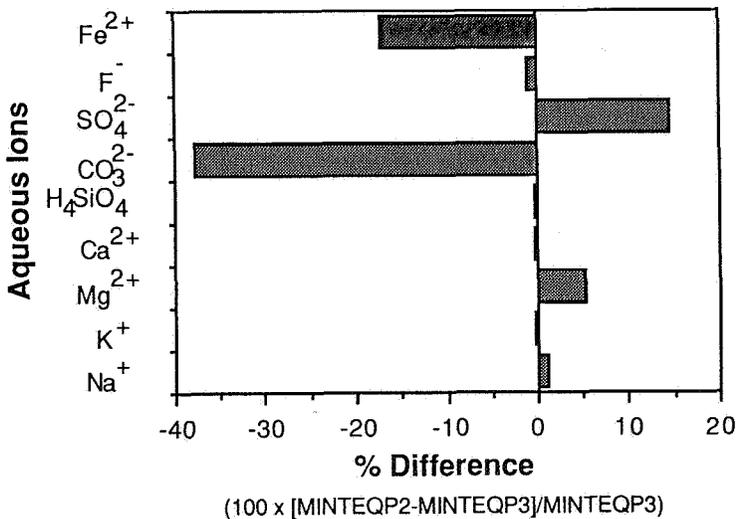


Figure 2 Differences in ion activities calculated 120°C with and without increased temperature competence added to the MINTEQ(P3) geochemical model.

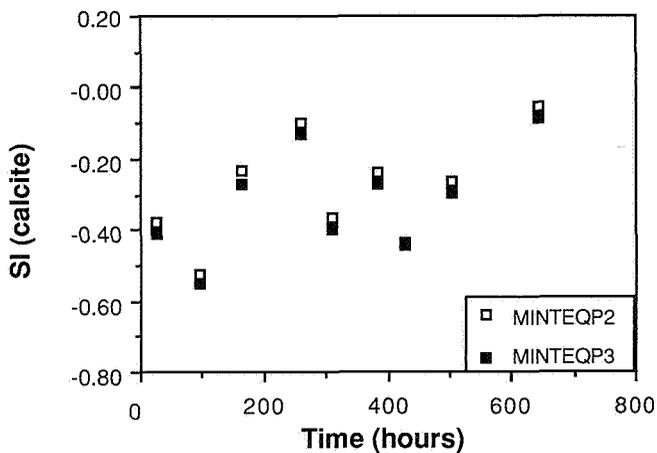


Figure 3 Saturation index for Calcite calculated at 120°C with and without increased temperature competence added to the MINTEQ(P3) geochemical model.

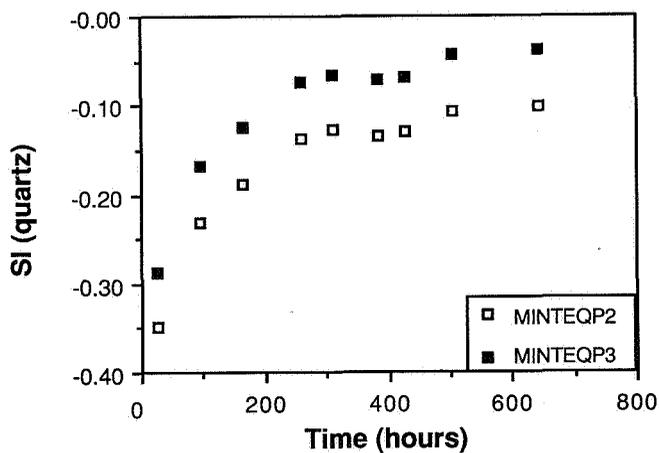


Figure 4 Saturation index for Quartz calculated at 120°C with and Without increased temperature competence using the MINTEQ(P3) geochemical model.

One of our research objectives is to approximate the dissolved concentrations of scale-forming components as a function of time and temperature. Thus, the solubility limiting form of SiO_2 is of importance. Groundwater distant from recharge areas is generally found to be in equilibrium with chalcedony, a micro-crystalline form of SiO_2 , (Coudrain-Ribstein and Goblet, 1987; Vinsot, 1987; Fisher and Eckstein, 1989*); E.A. Jenne unpublished data). J.P. McKinley and E.A. Jenne (unpublished data) found that water injected at $> 100^\circ\text{C}$ at the St. Paul, Minnesota, ATEs site was in all cases oversaturated with quartz (using the temperature dependence of thermodynamic data reported by Smith, 1988), whereas the earlier reports of Holm et al. (1987) and Perlinger et al. (1987) reported that the withdrawn water from short- and long-term cycles at St. Paul (with injection temperatures of $55\text{-}115^\circ\text{C}$) was "not far from equilibrium with quartz." In general, temperature and reaction time determines whether chalcedony or quartz is the equilibrium phase (Roy et al., 1989).

4 CONCLUDING REMARKS

The likelihood of decreased effectiveness or even failure of ATEs systems can be significantly reduced by a knowledge of the geochemical processes involved in the formation of precipitates which frequently decrease the efficiency of heat exchangers and may reduce hot-water injection rates. Problems arising from the formation of precipitates and clay dispersion are now largely avoidable by using appropriate geochemical calculations. For these reasons, cation exchange is included in the transport modelling of dissolved constituents in ATEs systems (Appelo and Willemsen, 1987; Willemsen and Nienhuis, 1988). Some uncertainty remains in the region of modest oversaturation due to inhibitors. A significant aspect of the geochemical research by the U.S. Department of Energy is the reduction in the uncertainty with which reliable predictions of precipitation are made. In cases where calcium carbonate calculated oversaturation is due to solid solution and inhibition of precipitation, capital costs for water treatment can be avoided which otherwise would be required to ensure freedom from troublesome precipitates.

*) Fisher, D.S. and Eckstein, Y., 1989. Simulated hydrogeochemical processes in a glacial drift basin. Unpublished ms. presented at Metals Speciation in Ground Water. Jekyll Island, Georgia. May 24-26, 1989.

REFERENCES

- APPELO, C.A.J. and WILLEMSSEN, A.; 1987. Geochemical calculation and observations on salt water intrusions: I. A combined geochemical/mixing cell model. *J. Hydrol.* 94, pp. 313-330.
- ARNORSSON, S.; 1975. Application of the silica geothermometer in low temperature hydrothermal areas in Iceland. *American Journal Science* 275, pp. 763-784.
- BEEKMAN, H.E. and APPELO, C.A.J.; 1988a. Fresh- and salt-water intrusion: Laboratory experiments and geochemical transport modelling. 10th Salt Water Intrusion Meeting, Ghent, Belgium, 14-20 May, 1988.
- BEEKMAN, H.E. and APPELO, C.A.J.; 1988b. Ion chromatography of fresh- and salt-water displacement: Laboratory experiments and multicomponent transport modelling. Proceedings of the International Conference and Workshop on the Validation of Flow and Transport Models for the Unsaturated Zone, New Mexico State University.
- BERNER, R.A., et al.; 1978. Inhibition of aragonite precipitation from super saturated seawater: A laboratory study and field study. *Am. J. Sci.* 278, pp. 816-837.
- BIRD, G., et al.; 1986. Silica transport during steam injection in to oil sand 1. Dissolution and precipitation kinetics of quartz: New results and review of existing data. *Chemical Geology* 54, pp. 69-80.
- BREDERO ENERGY SYSTEMS; 1986. Office Building at Bunnik: Aquifer Storage of Solar Energy. Bredero Energy Systems, Bunnik, The Netherlands.
- BRICKER, C.E. and MYERS, D.J.; 1969. The effects of iron and thorium ions on the kinetics of precipitation of BaSO₄. Project Completion Report, Kansas Water Resources Institute, University of Kansas, Manhattan.
- COEVERING, F. VAN DE and APPELO, C.A.J.; 1988. Putverstopping bij Warmte-opslag in ondiepe aquifers; drinkwaterinjectie. Heidemij Adviesbureau & Instituut voor Aardwetenschappen Vrije Universiteit.
- CRONAN, C.S. and AIKEN, G.R.; 1985. Chemistry and Transport of Soluble Humic Substances in Forested Watersheds of the Adirondack Park, New York. *Geochim. Gosmochim. Acta* 49:1697-1705.

- COUDRAIN-RIBSTEIN, A. and GOBLET, P.; 1987. Modelisation des Phenomenes Geochimiques Lies a un Stockage Thermique en Aquifere: 2 - Modelisation Spatio-Temporelle des Reactions Eau-Roche, in M. Sardin and D. Schweich (eds), Impact de la physico-chimie sur l'etude, la conception et l'optimisation des precedes en milieu poreus natural. Nancy, France, 10-12 juin 1987.
- FERGUSON, R.J.; 1984. A kinetic model for calcium carbonate deposition. *Materials Performance*, November, 25-34.
- FOURNIER, R.O. and ROWE, J.J.; 1966. Estimation of underground temperatures from the silica solubility water from hot springs and wet-steam wells. *American Journal Science* 264, pp. 685-697.
- GARRELS, R.M. and CHRIST, C.L.; 1965. *Solutions, minerals, and equilibria*. Harper & Row, New York.
- GRAVELAND, A., et al.; 1983. Development in water softening by means of pellet reactors. *J. Am. Water Works Assoc.* 75, pp. 619-625.
- HATVA, T., et al.; 1984. Removal of iron and manganese from groundwater by re-infiltration and slow sand filtration. *Aqua Fennica* 15, pp. 211-225.
- HOLM, T.R., et al.; 1987. Groundwater geochemistry of short-term aquifer thermal energy storage test cycles. *Water Resources Research* 23, pp. 1005-1019.
- INSKEEP, W.P. and BLOOM, P.R.; 1986. Kinetics of calcite precipitation in the presence of water-soluble organic ligands. *Soil Sci. Soc. Amer. J.* 50, pp. 1167-1172.
- INSKEEP, W.P. and SILVERTOOTH, J.C.; 1988. Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic and tammic acids. *Soil Sci. Soc. Amer. J.* 52, pp. 941-946.
- JACKSON, M.L. *Soil Chemical Analysis*; 1985. Prentice Hall, Englewood Cliffs, N.J., p. 258.
- JOHANNESSEN, M.; 1980. Aluminum, a buffer in acidic waters, in *Proceedings of the International Conference on Ecological Impacts of Acid Precipitation*, D. Drablos and A. Tollan, eds., Oslo, Norway, SNSF Project Report, pp. 222-223.
- LEVY, R.; 1976. Size of sodium-calcium montmorillonite crystallites. *J. Colloid Interface Sci.* 57, pp. 572-574.
- LEVY, R., et al.; 1983. Effect of precipitation of alkaline earth carbonates and magnesium hydroxide on Na-Ca-Mg exchange in Wyoming bentonite. *Soil Sci. Soc. Am. J.* 47, pp. 906-912.

- MATTY, J.M. and TOMSON, M.B.; 1988. Effect of multiple precipitation inhibitors on calcium carbonate nucleation. *Applied Geochemistry* 3, pp. 549-556.
- MOLTZ, F.J., et al.; 1978. Aquifer storage of heated water: Part I - A field experiment. *Groundwater* 16, pp. 234-241.
- OLIVER, B.G., et al.; 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochim. et Cosmochim. Acta* 4, pp. 2031-2035.
- PERLINGER, J.A., et al.; 1987. Groundwater geochemistry of aquifer thermal energy storage: long-term test cycle. *Water Resources Research* 23, pp. 2215-2226.
- REDDY, M.M.; 1977. Crystallization of calcium carbonate in the presence of trace concentrations of phosphorus-containing anions. *J. Cryst. Growth* 41, pp. 287-295.
- REDDY, M.M., et al.; 1981. Crystal growth of calcite from calcium bicarbonate solutions at constant $p\text{CO}_2$ and 25°C; A test of a calcite dissolution model. *Geochim. Cosmochim. Acta* 45, pp. 1281-1289.
- REDDY, M.M. and WANG, K.K.; 1980. Crystallization of calcium carbonate in the presence of metal ions. I. Inhibition by magnesium ion at pH 8.8 and 25°C. *J. Cryst. Growth* 50, pp. 470-480.
- REYNOLDS, R.C., Jr.; 1978. Polyphenol inhibition of calcite precipitation in Lake Powell. *Limnol. Oceanogr.* 23, pp. 585-597.
- ROY, W.R., et al.; 1989. Geochemical interactions of hazardous wastes with geological formations in deep-well systems. *Environmental Geology Notes* 130, Illinois State Geological Survey, Champaign, Illinois.
- RIMSTIDT, J.D. and BARNES, H.L.; 1980. The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta* 44, pp. 1683-1699.
- SAUGY, B., et al.; 1989. A seasonal aquifer heat store: Results after five years of tests and running. *JIGASTOCK* 88, Versailles, France.
- SCHLEISNER-IBSEN, L. and QVALE, B. (Editors); 1988. The Danish Aquifer Thermal Energy Storage Project: Demonstration Plant. *Risø-M-2764*, Risø National Laboratory, Roskilde, Denmark.
- SMITH, R.W.; 1988. Calculation of equilibria at elevated temperatures using the MINTEQ geochemical code. PNL-6700, Pacific Northwest Laboratory, Richland, Washington.
- SPOSITO, G. and FLETCHER, P.; 1985. Sodium-calcium-magnesium exchange on a montmorillonitic soil: III. Calcium-magnesium exchange selectivity. *Soil Sci. Soc. Amer. J.* 49, pp. 1160-1163.

- SPOSITO, G, and LeVESQUE, C.S.; 1985. Sodium-calcium-exchange on Silver Hill Illite. Soil Sci. Soc. Amer. J. 49, pp. 1153-1159.
- UNGEMACH, P. and TURON, R.; 1988. Geothermal well damage in the Paris Basin: A review of existing and suggested workover inhibition procedures. Society Petroleum Engineers, preprint no. SPE 17165.
- VALOCCHI, A.J., et al.; 1981. Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation. Water Resources Research 17, pp. 1517-1527.
- VANEK, V.; 1990. In situ treatment of iron-rich groundwater by the addition of nitrate. ISSN 1100-6366, Department of Ecology, University of Lund, Lund, Sweden.
- VINSOT, A.; 1987. Modelisation des phenomenes geochemiques lies a un stockage thermique en aquifere. M. Sardin and D. Scheich (eds), Impact de la physicochimie sur l'etude, la conception et l'optimisation des precedes en milieu poreus natural. Nancy, France, 10-12 juin 1987.
- WALTON, A.G.; 1967. The formation and properties of precipitates. Interscience Publishers. 232 p.
- WALTON, M., et al.; 1986. University of Minnesota aquifer heat storage project. STES Newsletter VIII, pp. 1 - 7.
- WILLEMSSEN, A. and NIENHUIS, P.R.; 1988. CHARMI chemical aquifer reaction model with 1-dimensional transport. Heidemij Adviesbureau, Arnhem, The Netherlands.

LABORATORY EXPERIMENTS ON BEHALF OF THE TNO-DGV TEST FACILITY FOR AQUIFER THERMAL ENERGY STORAGE AT DELFT, THE NETHERLANDS

J. Griffioen

ABSTRACT

An aquifer thermal energy storage (ATES) cycle was simulated by injecting groundwater in a sediment column at 90°C and, subsequently, injecting it in a column at 11°C to study aspects of the hydrogeochemical processes associated with ATES. For the heat storage cycle, no thermodynamic equilibrium with end-member carbonates was found after a reaction time of 44 hours at 90°C. Fast precipitation occurs as long as Fe remains in solution. Prolonged precipitation of Ca, eventually with Mg, appears inhibited by o-PO_4 and organic acids. Desorption of K, NH_4 and Fe upon temperature increase of the system, occurs initially. This buffering mechanism against precipitation of carbonate is not sufficient, because of the small CEC of the sediment in combination with the high hardness of the injected groundwater. Weathering of silicates leads to the release of Na, Ca and Mg. K and Si appear to be incorporated in secondary minerals. ReInjection of heated groundwater in a cold column does only induce desorption of Fe and Mn.

1 INTRODUCTION

Hydrogeochemical processes during the operation of an ATES system need to be considered because they may seriously affect the system. Especially the potential of carbonate precipitation upon heating of groundwater needs attention, because many groundwaters show

saturation with respect to calcite and will become supersaturated when temperature is increased. Thermodynamic equilibrium computations to calculate the expected amount of mineral precipitation, as done by Palmer and Cherry (1984) and Holm et al. (1987), might not be operative in a natural ATES system. Hydrochemical experiments on natural systems are needed to determine in an empirical way the amount of precipitation, as governed by the degree of supersaturation, kinetics, occurrence of inhibition, weathering of other minerals and ion-exchange processes.

Purpose of the laboratory experiments was to investigate which hydrogeochemical processes really occur when groundwater is heated and injected in the sediment, subsequently withdrawn, cooled and reinjected in the sediment. The experiments simulate an ATES cycle to a large extent: both temporary reactions and continuous reactions are observed when groundwater flows through a sediment.

2 ATES TEST FACILITY

Both sediment and groundwater originate from the Dutch ATES test facility, constructed on the terrain of the TNO-DGV Institute of Applied Geoscience in Delft, West Netherlands. The first aquifer, the Kreftenheije aquifer, is the storage aquifer. The Westland Formation forms the upper confining layer and the Kedichem Formation forms the lower confining layer (Fig. 1). The Pleistocene Kedichem Formation dominantly consists of fluvial silt-containing fine sands and clay. The Kreftenheije Formation is also of Pleistocene, fluvial origin from a braided river system. The aquifer consists mainly of medium coarse sands with interspersed coarse sands. At the test-site, the aquifer ranges from 14 to 34 m. below surface. The Holocene, perimarine Westland Formation consists mainly of an alternation of clay and peat layers (Haak, 1989).

Sediment was sampled at a depth of about 16 meters at the production side (Fig. 1) with the 'shrew-mouse' technique, an anaerobic sampling procedure (Appelo et al., 1990). The sediment can be characterized as medium coarse, quartz-rich sand with mainly chlorite and illite as clay minerals. The mean $C_{organic}$ content is 770 ppm \pm 300 and the mean N-content is 17.6 ppm \pm 8.1. The grain size distributions show an arithmetic mean of about 0.35 mm.

and a standard deviation of 0.14 mm. The $< 53 \mu\text{m}$. content is 0.9 to 2.3%, the $< 2 \mu\text{m}$. content is 0.1 to 0.3%. Several water samples from both the production side and the storage side have been analysed. In general, the groundwater can be characterized as hard, brackish and anaerobic with a high CO_2 pressure. CH_4 gas has been shown in the groundwater at concentrations up to 7.2 mmol/l. The salinity increases with depth, as is shown by stiff diagrams (Fig. 1).

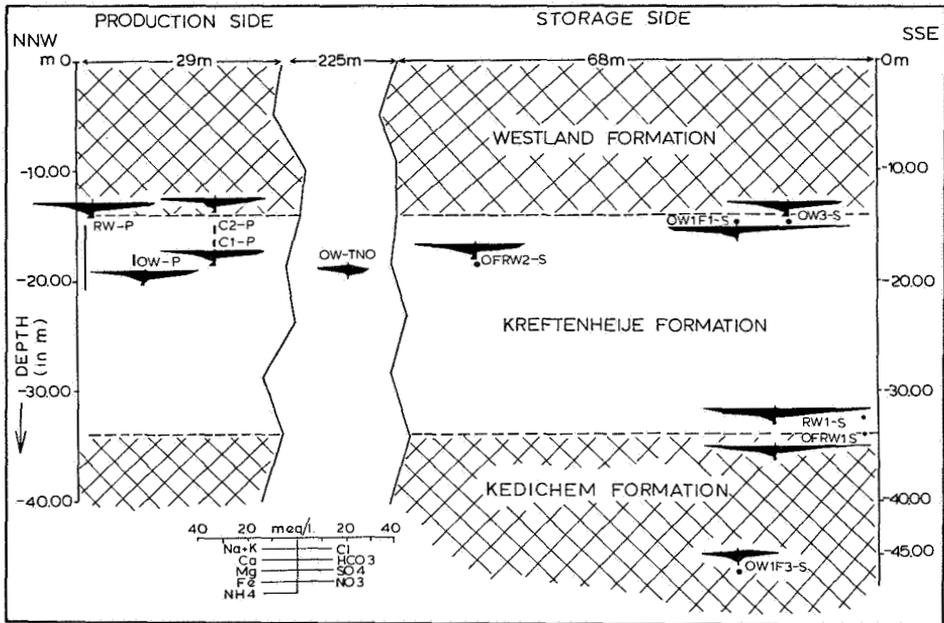


Figure 1 (Hydro)geological schematization with stiff diagrams of water samples at TNO test facility

3 MATERIALS AND METHODS

Sampled sediment was installed in airtight flow-through column chambers in a procedure described by Appelo et al. (1990) and Griffioen (1989). The whole set-up must be closed for gas transfer to simulate the closed environment of the aquifer: lack of such a closed

system would influence the hydrochemistry in a large extent (Griffioen, 1989). Two columns were set in a waterbath at 90°C and a third in a waterbath at 11°C (Fig. 2).

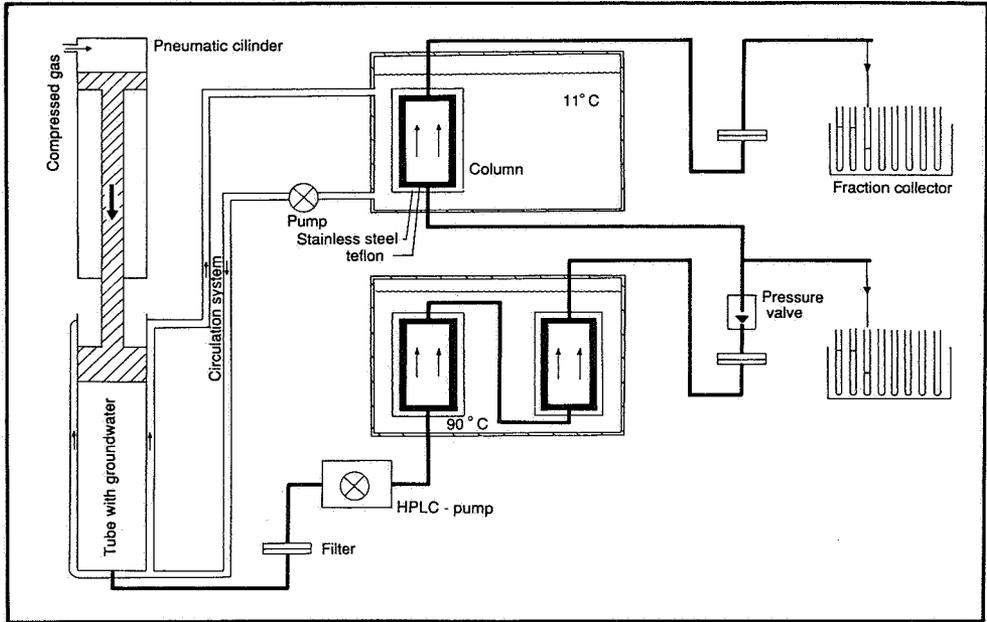


Figure 2 Laboratory set-up

Groundwater, sampled in an airtight tube, was filtered through a 0.45 μm filter before it was injected with a HPLC-pump. Effluent was filtered through a 0.45 μm filter before sampling or flowing to the cold column. A pressure valve, set at 2 bar, after the warm columns prevented degassing of the solution. At the end of the experiments, the columns were opened and sediment samples were prepared for scanning electron microscope (SEM) examination. The data of the experimental conditions are: cation exchange capacity (CEC) is 0.5 meq/100 g. dry sediment, pore water velocity is 1.07 or 0.34 cm/hr., column length is 70 mm., column width is 60 mm. and porosity is 35%.

4.1 Concentration curves

Figure 3 shows the effluent curves for the first part of the experiment on injection of groundwater in the 90°C columns. It should be kept in mind that in the beginning the

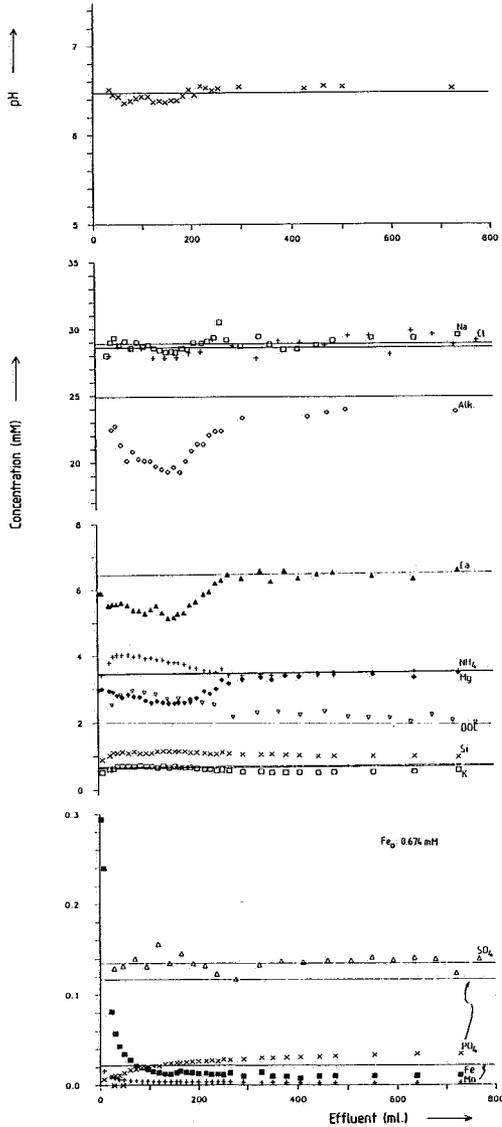


Figure 3 Effluent curves for the first part of heat storage experiment. Solid lines represent injection concentrations

columns were heated from 11°C to 90°C. The first 175 ml. of effluent were affected by this stage. The temperature of the injected groundwater was 90°C at the entrance of the column for the remainder.

The initial increases in K and NH_4 have to be attributed to a re-establishment of the cation-exchange equilibria upon temperature increase (Griffioen and Appelo, 1990). The temporary increase in Si may also be attributed to a shift in sorption equilibria. The sharp decline in Fe and Mn concentration and the value of the o-PO_4 concentration, which lies below the original value, point towards precipitation of carbonate and phosphate. So do the initial drops, within the first 300 ml., in Ca and Mg concentration. This cannot be solely attributed to cation-exchange: the calculated amounts of released K and NH_4 are respectively 0.039 and 0.077 meq, whereas the amounts of removed Ca and Mg are respectively 0.424 and 0.348 meq. The decrease in alkalinity also excludes a decrease in Ca and Mg merely by cation-exchange.

A combination of two facts indicates that precipitation of carbonates must occur during the entire period of injection of groundwater in the heated column. The first is the constant decrease in Fe. This shows that precipitation occurs constantly in time. The second is the average Ca to Fe ratios in the precipitate (see Section 4.2). As the ratios are more than one, the precipitated amount of Ca must be higher than of Fe. Therefore, Ca must have been co-precipitated with Fe during the entire period of injection of groundwater.

The increase in Ca and Mg from 170 ml. on, must be caused by an additional reaction: weathering of silicates. The increase in Na also indicates weathering of silicates as a significant process. The influence of weathering on the concentrations, just after 170 ml. have been collected, is a consequence of the heating stage. In the first period, the residence time of the pore water solution was too short to result in a significant amount of silicate weathering. On the opposite, the rapid decrease in Fe, Ca, Mg and alkalinity during heating indicates that, as long as Fe is present in solution, the precipitation process is a fast reaction. Similar findings were given by Van der Weiden and Appelo (1988).

Table 1 gives saturation indices at different stages of the experiments. Comparison of the data with data on model compositions in equilibrium with (combinations of) carbonates

Table 1 Composition and saturation indices of injected groundwater and effluent samples.

Sample	groundwater	warm column*)			cold column
		(1)	(2)	(3)	
A. Composition (in mM, except when stated otherwise)					
Temperature	11	90	90	90	11
pH	6.63	6.39	6.52	6.52	6.68
Na	28.6	28.3	29.2	29.3	28.8
K	0.642	0.6675	0.490	0.525	0.486
Mg	3.47	2.58	3.44	3.48	3.44
Ca	6.45	5.18	6.44	6.07	6.25
NH ₄	3.45	3.78	3.44	3.41	3.37
Fe	0.674	0.014	0.013	0.0169	0.035
Mn	0.022	0.0039	0.0029	0.0111	0.010
Si	0.022	0.0039	0.0029	0.0111	0.010
Cl	28.9	28.4	28.9	28.8	29.0
Alk. #	24.9	19.4	24.0	22.9	23.7
SO ₄	0.14	0.14	0.14	0.13	0.131
PO ₄	0.117	0.025	0.038	0.043	0.0037
DOC	2	2.7	2.0	2.5	2.1
Sum cat.	53.92	48.34	52.89	52.36	52.15
Sum an	54.19	48.07	53.13	52.03	52.88
Balance	-0.2%	0.3%	-0.2%	0.3%	0.7%
B. Saturation indices					
Calcite	1.80	7.00	13.24	12.07	1.87
Aragonite	1.37	5.41	10.22	9.32	1.43
Dolomite	1.58	71.4	275.0	245.0	1.74
Siderite	18.5	6.08	8.84	11.01	1.09
Rhodochrosite	0.48	0.18	0.21	0.78	0.22
OH-apatite	5.58	594	16262	19112	0.0047
Quartz	14.5	1.92	1.47	1.57	15.8
Chalcedony	4.24	1.03	0.79	0.84	4.55
SiO ₂ (am.)	0.61	0.17	0.13	0.14	0.65
PCO ₂	0.24	1.06	0.97	0.92	0.18

*) (1) at 170 ml. (concentration minima for carbonate species), (2) after 14 hr. reaction time (high flow rate), (3) after 44 hr. reaction time (low flow rate).

in meq/kg.

(Table 2), clearly shows that the injected groundwater does not reach equilibrium with any simple carbonate mineral, even after 44 hours of reaction time. The effluent remains supersaturated with the carbonates, except for rhodochrosite. The decrease in Ca and alkalinity upon reaction time also gives a small decrease in the supersaturation with the Ca-bearing carbonates, reflecting a slow carbonate precipitation process. The effluent is also supersaturated with quartz, chalcedony and OH apatite, and undersaturated with amorphous silica. No control of the o-PO_4 concentration by other Ca phosphates was indicated by the thermodynamic calculation of the saturation indices.

Table 2 Composition and saturation indices of groundwater at 90°C, with or without carbonate equilibrium

	Ground-water at 90°C	Calcite	Calcite Siderite	Dolomite	Dolomite Siderite
pH	6.47	6.14	6.10	6.05	6.01
Mg (mM)	3.47	-	-	0.48	0.61
Ca "	6.45	1.58	1.81	3.47	3.60
Fe "	0.674	-	0.0059	-	0.0084
Alk. (meq/kg H ₂ O)	24.9	15.3	14.4	13.0	13.3
Saturation indices					
Calcite	12.0	1	1	1.58	1.43
Aragonite	9.30	0.77	0.77	1.22	1.10
Dolomite	229	6.38	5.58	1	1
Siderite	415	131	1	93.1	1
Rhodochrosite	1.47	0.48	0.42	0.34	0.30
PCO ₂	1.13	1.54	1.58	1.64	1.67

4.2 Scanning electron microscope-examination

The SEM was used to study both (carbonate) precipitates and surfaces of feldspars. Precipitates were only observed in samples from the first three centimeter of the first warm

column. This means that, for a flow rate of 0.96 or 0.31 cm/hr., precipitation occurs within 3 or 10 hours. This confirms the findings from the water analyses. The precipitates appear as a coating on CaCO₃ grains (Plate 1) and as small grains (< 20 μm.) on quartz grains (Plate 2). Two kinds of precipitate can be distinguished on chemical composition. The first is a Ca-Fe precipitate with some P and Mn. The second is a Ca-Mg-Fe-Mn precipitate without P. The cation percentages are for the first 60 ± 16, 38 ± 15 and 2 ± 1, and for the second 33 ± 10, 30 ± 15, 32 ± 19 and 5 ± 3.

Both the observed large variation in molar ratios of the precipitated cations and the partly amorphous, partly crystalline appearance of the precipitated aggregates (Plate 3 and 4) point to a great kinetic control of the precipitation process. Even within one precipitated aggregate, large variations in chemical composition were found within distances of a few μm.

The feldspars were studied to look whether the surface morphology of grains from the heated sediment was different from that of grains from the non-heated sediment. No unambiguous differences were observed as the differences between individual grains from one stage were larger than the differences between the two stages. However, on the average a more angular surface was observed on the heated grains (Plate 5 and 6).

4.3 Discussion

4.3.1 Kinetics of carbonate precipitation

The results show that precipitation of carbonate is a slow process, after Fe has been nearly completely removed, in spite of the existing high supersaturation with carbonates. Although dolomite is the thermodynamically stable Ca carbonate, attention will be focused on calcite precipitation. Precipitation of dolomite is an extremely slow process; precipitation of calcite as an intermediate product is more likely. The time span during which precipitation of calcite occurs down to saturation can be calculated according to the Plummer et al. (1978) model. For groundwater with a near-neutral pH and a high CO₂ pressure, the rate of precipitation will be controlled by dissolved CO₂. The following differential can be derived for a closed system, assuming that 1) the activities in the surface layer of the precipitate are equal

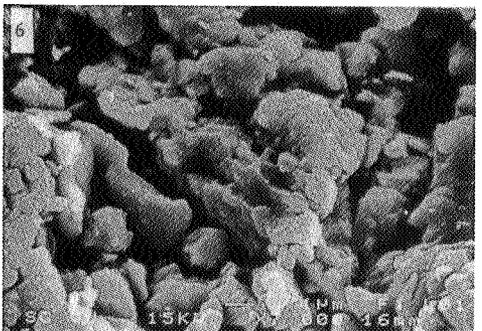
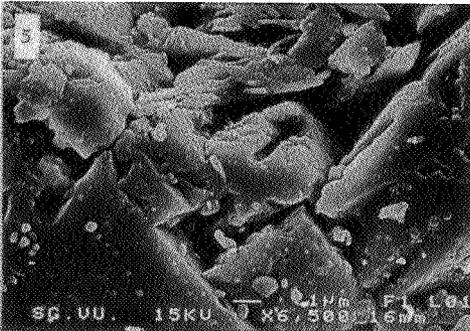
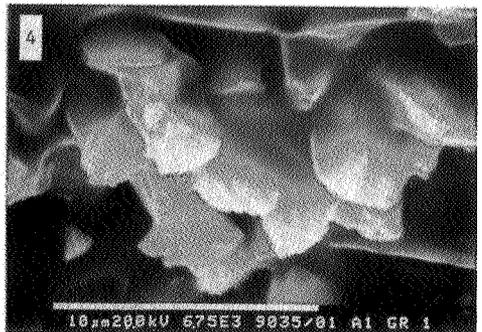
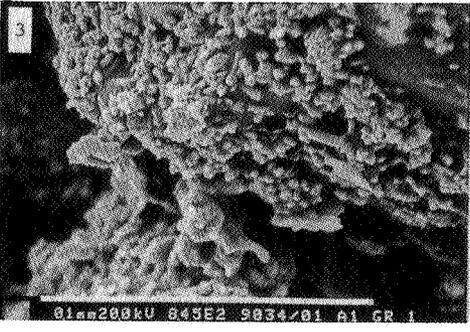
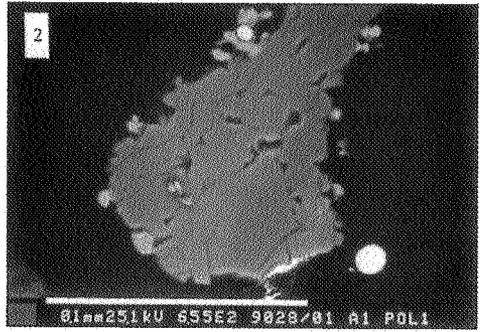
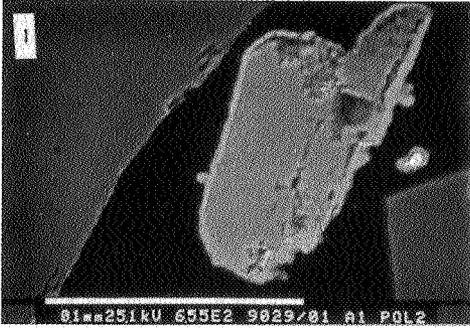


Plate 1: CaCO₃ grain from first centimeter of 90°C column with a solid-solution precipitate. Plate 2: Quartz grain from first centimeter with solid-solution precipitate (light grey) and FeS particles (white). Plate 3 and 4: Precipitates on grains at two different enlargements. Note the combination of smooth and sharp edged surfaces of the precipitates. Plate 5: Na feldspar from heated sediment. Plate 6: Na feldspar from non-heated sediment.

to the activities in the bulk solution and 2) the activity coefficients are constant during the precipitation process:

$$\frac{d(\text{Ca}^{2+})}{dt} = -k_2 \cdot s_v \cdot \left[\frac{(\text{H}_2\text{CO}_3^*)_{\infty} (\text{Ca}^{2+}) \{ (\text{HCO}_3^-)_0 + 2(\text{Ca}^{2+}) - 2(\text{Ca}^{2+})_0 \}^2}{(\text{Ca}^{2+})_{\infty} (\text{HCO}_3^-)_{\infty}^2} - (\text{H}_2\text{CO}_3^*)_0 - (\text{Ca}^{2+})_0 + (\text{Ca}^{2+}) \right]$$

where

s_v is the surface area of precipitation per pore volume,

k_2 is the reaction rate constant,

0 and ∞ represent the initial and equilibrium concentration, respectively.

The latter are known or can be easily calculated with computer programs. The reaction time to reach near-saturation was calculated numerically. The surface area was set equal to the average surface area, assuming spherical particles, multiplied by the CaCO_3 content of the sediment (1.5%). The calculated time span is 2 minutes. This calculation clearly shows that the precipitation rate can not be calculated by this model.

The presence of Mg gives a decrease in precipitation rate (Nancollas and Sawada, 1982; Mucci and Morse, 1983). An evaluation of experimental results indicates that for an aqueous Mg to Ca ratio of 1 to 2, the precipitation rate decreases twofold (Griffioen, 1989). Mg, thus, slightly influences the kinetics of precipitation.

The large discrepancy between the calculated precipitation rate and the actual rate clearly shows that the decrease in Ca cannot be described by calcite precipitation models which are based on simple systems. Several factors may explain the observed slow decrease of Ca in time, which will now be discussed. Complexation between cations and organic acids is not considered in the geochemical calculations. This implies that the actual Ca^{2+} activity will be lower than the calculated one, due to non-consideration of Ca-organic acids complexation. For groundwaters with DOC concentrations of about 2.2 mM, complexation will certainly be of importance on the activity of Ca^{2+} (Stumm and Morgan, 1981). However, a tenfold

decrease in Ca^{2+} activity, to reach a saturated solution instead of a supersaturated one, would require a nearly complete complexation of 6.4 mM Ca by 2.2 mM DOC. This is entirely impossible as indicated by results of Brons (in prep.).

In case of solid-solution control of the Ca concentration instead of control by end-member carbonates, attention has to be drawn to Mg calcite. Other ions will not influence the solubility of Ca-containing carbonate. The solubility of Mg calcites does not deviate strongly from the solubility of calcite for aqueous Mg to Ca ratios smaller than one (Mackenzie et al., 1983). Extrapolation of the Mg calcite solid-solution model of Busenberg and Plummer (1989) towards the temperature range of 10° to 100°C gives a thermodynamic constant for an aqueous solution with a Mg to Ca ratio of 0.5, which is even smaller than the value for calcite. The control of Ca concentrations by equilibrium with Mg calcites instead of calcites, will only result in calculated saturation indices with respect to calcite, smaller than about 2.

Studies on inhibition of calcite precipitation show that strong inhibition occurs at low concentrations of o-PO_4 (Mucci, 1986) and/or organic acids (Inskeep and Bloom, 1986). As the o-PO_4 concentration in the 90°C effluent is 0.04 mM and the DOC is about 2.2 mM, these concentrations will be sufficient to give significant inhibition. It is therefore believed that this factor is the most important in controlling the Ca concentration: precipitation of calcite is strongly inhibited by surface poisoning of present CaCO_3 grains by o-PO_4 and organic acids.

4.3.2 Silicate weathering

The increase in Na and the effluent curves for Ca and Mg indicate that enhanced weathering of silicates occurs upon temperature increase. The K and Si data point towards the same. The decrease in K shows that K becomes entrapped in secondary silicates, like illite.

The observed increase in Na concentration in the experiments is larger than the increase with similar sediment in artificial CaCl_2 solutions. This leads to the suggestion that natural humic acids catalyse the dissolution process of silicates, as has been observed by others (Huang and Kiang, 1972; Petersen, 1988). Derivation of a thermodynamic model in which the stabilities of silicates are considered, is hindered by the absence of thermodynamic and

mineralogical data for the smectite. Construction of stability diagrams for K-minerals at 11° and 90°C shows that muscovite becomes a more stable mineral upon temperature increase (Griffioen, 1989). This also makes illitization of clay minerals not unlikely (Aagaard and Helgeson, 1983).

5 HEAT SUBTRACTION PHASE

After reaching a steady-state in the composition of the effluent from the warm columns, effluent was injected in a cold column at 11°C. Effluent was injected both at the high flow velocity and at the low flow velocity.

The compositions of the injected heated groundwaters are given in the fourth and fifth column of Table 1. Figure 4 shows the effluent curves for the injection of heated groundwater in the column at 11°C. The first 66 ml. of effluent have to be considered as the native pore water solution. The concentrations remain constant in time, except for Fe, Mn and o-PO₄.

The Fe concentration increases to a maximum of 0.220 mM after 100 ml. has been injected; it subsequently decreases to about 0.035 mM. The last is higher than the injected effluent concentration from the warm side (Table 1). The Mn concentrations show a similar pattern. The changes in concentration of Fe and Mn are a consequence of desorption from the sediment due to a shift in the cation-exchange equilibria as result of the lowered concentrations in the injected heated groundwater. o-PO₄ is low at the beginning of the experiment and increases slowly in time to a maximum of 5.5 μM at 360 ml. The solution is under-saturated with respect to Fe²⁺, Mn²⁺ and Ca phosphates. Most likely, o-PO₄ is controlled by sorption processes instead of mineral equilibria.

6 CONCLUSIONS

The experiments on the simulation of an ATEs cycle indicate that carbonate precipitation occurs upon heating and reinjection of native groundwater, but not to the extent as predicted

by thermodynamic equilibrium calculations or existing kinetical models, assuming precipitation down to equilibrium with respect to pure carbonates.

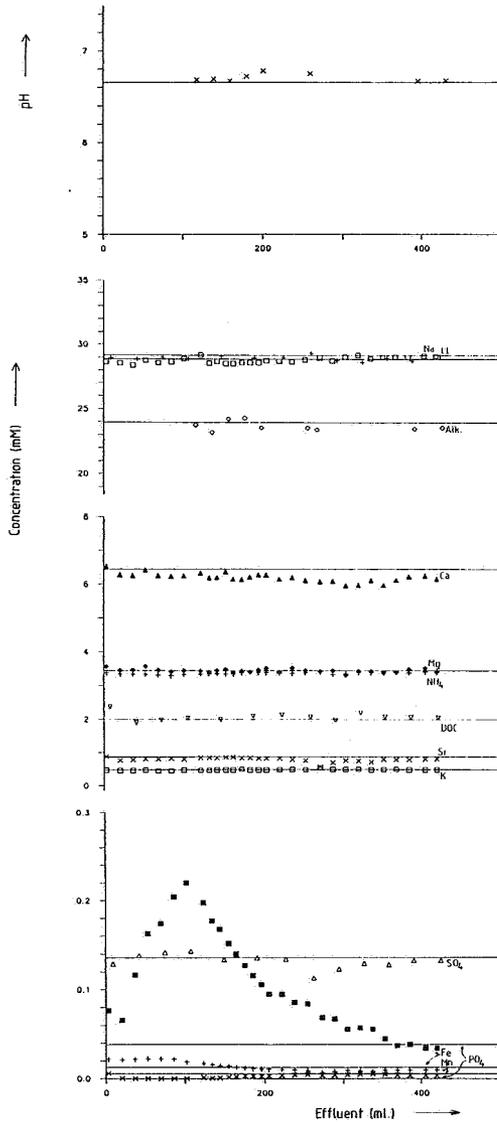


Figure 4 Effluent curves for the heat subtraction phase. Solid lines represent injection concentration from 90°C column

The results show precipitation within three hours of Fe-containing solid-solutions. The precipitates have large variations in cation composition and are partly amorphous, which mean that the process is strongly kinetically controlled. The precipitation rate must be

controlled by inhibition through surface poisoning of the growth sites on calcite by o-PO_4 and organic acids, after Fe has been nearly completely removed. The tenfold supersaturation with calcite after 44 hours reaction time can neither be explained by control of the solubility of Ca by Mg calcites, nor neglect of complex-forming between Ca and organic acids in the thermodynamic computations, or a combination of these two.

Buffering of the sediment against Ca (and Mg) precipitation by cation-exchange is of small importance as result of the low CEC of the sediment. The release of Ca by enhanced weathering upon temperature increase is of small importance for the carbonate precipitation process.

REFERENCES

- AAGAARD, P. and HELGESON, H.C.; 1983. Activity/composition relations among silicates and aqueous solutions: II chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites, and mixed-layer clays. *Clays and Clay Min.* (31), 207-217.
- APPELO, C.A.J., WILLEMSEN, A., BEEKMAN, H.E. and GRIFFIOEN, J.; 1990. Geochemical calculations and observations on salt water intrusions. II. Validation of a geochemical model with laboratory experiments. *J. Hydrol.*, in press.
- BRONS, H.; (in prep.). Ph.D-thesis.
- BUSENBERG, E. and PLUMMER, L.N.; 1989. Thermodynamics of magnesian calcite solid-solutions at 25°C and 1 atm. total pressure. *Geochim. Cosmochim Acta* (53), 1189-1208.
- GRIFFIOEN, J.; 1989. Hydrogeochemical column experiments with sediment from the Dutch ATES test-facility. I.E.A. Annex VI, Report 33-B, Free University, Amsterdam, 103 pp.
- GRIFFIOEN, J. and APPELO, C.A.J.; 1990. A potassium - calcium multi-component exchanger model from elution curves of column experiments at 25°, 60° and 90°C. Submitted to *Soil Sci. Soc. Am. J.*
- HAAK, A.M.; 1989. Testfaciliteit voor opslag van koude en warmte in aquifers - ontwerp en realisatie. TNO-Dienst Grondwaterverkenning, rapport no. OS 89-08, 122 pp.

- HOLM, T.R., EISENREICH, S.J., ROSENBERG, H.L. and HOLM, N.P.; 1987. Groundwater geochemistry of short-term aquifer thermal energy storage test cycles. *Wat. Resour. Res.* (23), 1005-1019.
- HUANG, W.H. and KIANG, W.C.; 1972. Laboratory dissolution of plagioclase feldspars in water and organic acids at room temperature. *Am. Mineral.* (57), 1849-1859.
- INSKEEP, W.P. and BLOOM, P.R.; 1986. Kinetics of calcite precipitation in the presence of water-soluble organic ligands. *Soil Sci. Soc. Am. J.* (50), 1167-1172.
- MACKENZIE, F.T., BISCHOFF, W.D., BISHOP, F.C., LOIJENS, M., SCHOONMAKER, J. and WOLLAST, R.; 1983. Magnesian calcites: low temperature occurrence, solubility and solid-solution behaviour. In: 'Reviews in mineralogy vol. 1: Carbonates: mineralogy and chemistry', ed. by Reeder, R.J. *Miner. Soc. Am.*, p. 97-144.
- MUCCI, A. and MORSE, J.W.; 1983. The incorporation of Mg^{2+} and Sr^{2+} into calcite overgrowths: influences of growth rate and solution composition. *Geochim. Cosmochim. Acta* (47), 217-233.
- MUCCI, A.; 1986. Growth kinetics and composition of magnesian calcite overgrowths precipitated from seawater: quantitative influence of orthophosphate ions. *Geochim. Cosmochim. Acta* (50), 2255-2265.
- 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.
- PARKHURST, D.L., THORSTESON, D.C. and PLUMMER, L.N.; 1980. PHREEQE - a computer program for geochemical calculations. *U.S. Geol. Surv. Water Res. Inv.* 80-96, 210 pp.
- PETERSEN, A.; 1988. Laboruntersuchungen zum Einfluss organischer Komplexbildner auf die Kinetik der Feldspatverwitterung. *Berichte no. 21, Geol.-Paläont. Inst., Univ. Kiel, BRD*, 195 pp.
- PLUMMER, L.N., WIGLEY, T.M.L. and PARKHURST, D.L.; 1978. The kinetics of calcite dissolution in CO_2 -water systems at $5^\circ C$ and $60^\circ C$, and 0.0 to 1.0 atm. CO_2 . *Am. J. Sci.* (278), 179-216.
- VAN DER WEIDEN, M.J.J. and APPELO, C.A.J.; 1988. Batch experiments with sediment from a Dutch ATES test facility. I.E.A. Annex VI, report 21-B. *Heidemij Adviesbureau, Arnhem/ Vrije Universiteit, Amsterdam, The Netherlands*, 79 pp. (in Dutch).

SCALING AND CORROSION IN SUBSURFACE THERMAL ENERGY STORAGE SYSTEMS

O. Andersson

ABSTRACT

At first sight the ATES concept seems quite simple to design, construct and run. However, worldwide experiences show that severe problems related to water composition and system design often occur.

In this paper, a brief overview of the most common scaling and corrosion processes are described and some preventive methods are discussed.

As a part of scaling special consideration is given to hydro- and biochemically induced clogging, preferably in forms of iron compounds and carbonates. Another source of clogging is by solid particles and in this respect well drilling and completion methods are discussed.

Corrosion might be a severe problem in any ATES application, especially if oxygen is allowed to enter the system. In this paper some simple measures to avoid corrosion are pointed out.

As a general conclusion it is stated that most of the potential scaling and corrosion problems can be prevented or at least minimized by means of a proper design. For that reason much attention has to be payed to this in the pre-investigation phase of any ATES plant.

The use of aquifers for thermal energy storage (ATES) is still in an early development stage.

The applications look simple on paper, but experiences so far show several technical and legal obstacles that have to be solved before the concept enters a more commercial phase.

One such not yet fully understood field of problems is connected to scaling and corrosion processes. Indeed, this subject has proved to be so serious that it has been an item for international research and development within the IEA-program (IEA - Conservation Through Energy Storage - Annex VI).

As a matter of fact most of the material in this paper has its origin from one of the subtasks in Annex VI, Subtask E - Scaling and Corrosion.

The art of hydrochemically induced problems that might be expected is shown in Figure 1 (Andersson, 1990). In this figure a typical ATES set-up is drawn, showing the groundwater system connected to a heat exchanger. Through one of the wells hot groundwater is stored ("the storage well") with the same flow as water is extracted from the second well ("the source well"). The energy is transferred through the heat exchanger. In the aquifer a hot water front is expanding around the storage well while the front with colder water is moving towards the source well.

When discharging the system, the flow is reversed and the same goes for the thermal fronts in the aquifer.

During charging, storing and discharging, different processes take place. The main part of those are underlined in Figure 1 and are actually those who can bring birth to the scaling and corrosion problems dealt with in this paper.

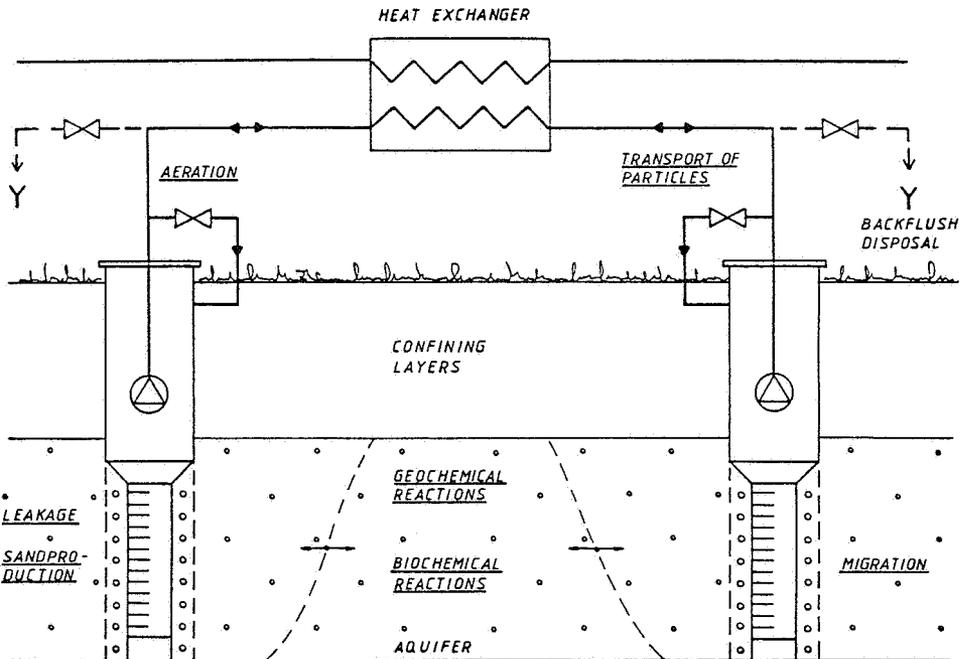


Figure 1 A typical ATEs system showing different processes (underlined) that might lead to scaling, clogging and corrosion problems

The most common problems, as they are experienced in existing subsurface energy systems, are listed in Table 1.

Table 1 The most common scaling and corrosion problems in ATEs applications and their main causes

PROBLEM	CAUSED BY
Carbonate scaling in heat exchangers	Increased temperature or drop of pressure
Clogging of wells by particles or precipitates	Sandproduction, drop of pressure or uncontrolled aeration
Thinning and pitting corrosion in system components	Uncontrolled aeration, material selection or improper treatment

As can be seen "clogging" has been separated from scaling and describes processes connected to the aquifer and the wells while the term "scaling" stands for carbonate precipitation in tubings and fittings.

Below each one of the scaling, clogging and corrosion considerations are discussed separately and from an ATES system's point of view.

2 SCALING

Experiences have shown that the most sensitive part for scaling would be in the heat exchanger. As such, it can easily be traced by a decreasing thermal efficiency and furthermore by an increased pressure drop over the exchanger (Andersson 1990). In a later stage it can also be found in tubes, fittings and injection wells.

The scaling process will form a continuous growing "skin" on metal surfaces and will eventually totally plug narrow channels like in a plate heat exchanger or a well screen.

The scaling products might vary from case to case, but the absolute dominating ones are different forms of carbonates. This is true not only for high temperature ATES plants but also in other branches handling subsurface waters, like the geothermal systems and waterflooding within the oilfield industry.

What makes carbonate to precipitate is fairly well understood. In technical applications there are mainly two different causes that will bring the water in a supersaturated condition with respect to carbonates:

- 1) increased temperature
- 2) decreased hydraulic pressure.

So far practically all high temperature ATES plants have suffered from carbonate scales preferably due to the increased temperature in the heat exchanger (ATES Newsletter).

So far no severe problems with scaling due to pressure drops have been reported. This

might indicate that the plants have proper design from this point of view, However, one week point would still be production wells, see next Section.

Potential scaling caused by increased temperature can be predicted and considered in the designing stage. In the IEA-annex VI project some treatment methods have been suggested and field tests are on its way.

Those methods are described in the paper of A. Willemsen, 1990 (this Volume) and therefore only summarised here:

- Inhibitors can be added that will prevent carbonate crystals to form. Some of those might even be in the water natural.
- Ion exchange might be an other solution. In this case a proven technology is to have calcium replaced with sodium.
- pH-adjustment, i.e. by adding carbonate dioxide is a third way of methods that aim to keep the carbonates in solution.
- Mechanical removal by using scraper balls or special constructed heat exchanger form another group of treatment techniques.

3 CLOGGING

3.1 General

Clogging is mainly a problem located to the well system.

It might involve "true" scaling caused by an inescapable drop of pressure when a well is used for production. But it also involves a lot of other possibilities.

Whatever the reason is a well clogging process can quite easy be traced by measuring the

specific capacity of the well and compare that with the original value, see Figure 2 (Andersson 1988 a).

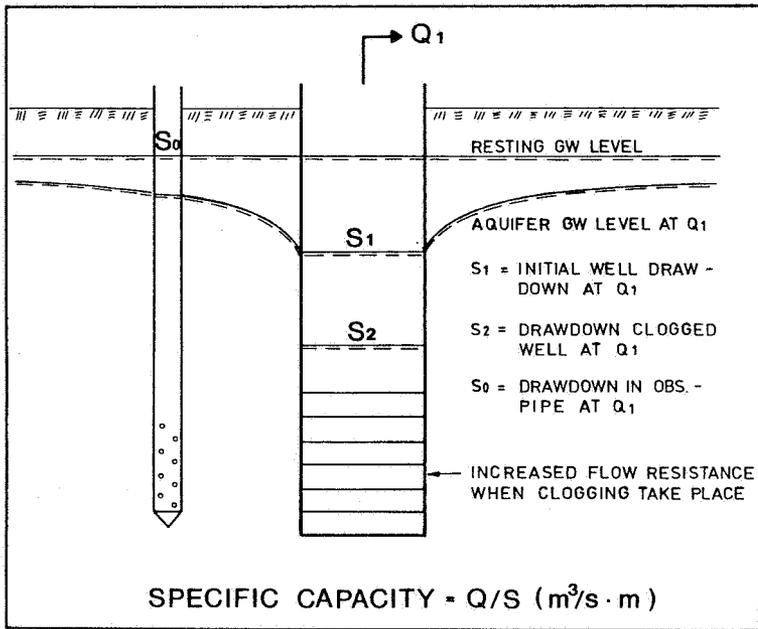


Figure 2 Clogging can be traced by a monitoring of specific capacity. A lowered watertable in the well but not outside indicates that clogging takes place

Since clogging will increase the skin of the well and hence cause an increased entrance resistance, clogging is bound to show up as a drop of specific capacity. What has to be measured now and then is the flow (Q) and the drawdown (s). The third parameter would be the groundwater level outside the well that will give a more precise value, but this is not of greater importance.

The processes involved forming the clogging agent are far from being perfectly understood. However, by experiences the causes of clogging can be divided into four main sources:

- solid particles or fines
- precipitates
- organic slime
- gas bubbles.

Already while drilling a well in an unconsolidated formation, a certain risk for clogging will occur, especially if a non selfdestructed mud is used as a drilling fluid. It has been shown that fine sand can invade more permeable parts of the formation and get trapped there (Glenn and Slusser 1970), see Figure 3.

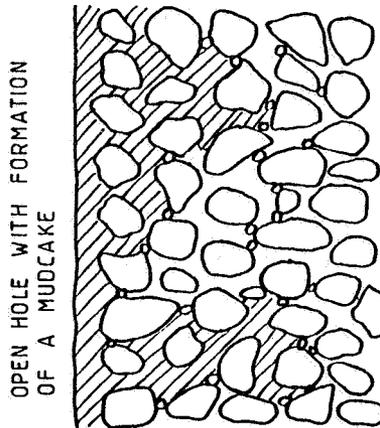


Figure 3 During drilling mud and fine grained cuttings will invade more permeable parts of the formation (after Glenn and Slusser 1970)

A second source of hardly treatable clogging could occur while setting the screen and gravelpack. If not carefully performed there is a good chance that the walls of the wellbore will get eroded during that operation and hence the gravelpack will be mixed with particles from the formation (Andersson, 1988 a).

Another reason for particle clogging might be migration and bridging of fines within the formation, especially at high flowrates. This has been suggested to explain a slow but continuous drop of capacity of certain wells in Sweden, but only at injection (Andersson, 1988 a). This clogging phenomena might also be one of several explanations to the fact that injection capacity often is lower than production capacity in equal wells.

However, the most pronounced cause for particle clogging in injection wells has its origin in

the water being injected. The reason for this is that recharge water never is perfectly clean. Even the smallest concentration of solids will sooner or later build up a clogging skin against the screen, gravelpack or the wall of the wellbore. Those particles might be fines from the aquifer (in a closed system) but another important source is corrosion products (Driscoll, 1986).

The most simple way to restore a plugged injection well is by backflushing. As shown in Figure 4 the backflush method normally brings back the initial capacity quite easy. Naturally, it is advisable to design any such well with a permanent back-flush system.

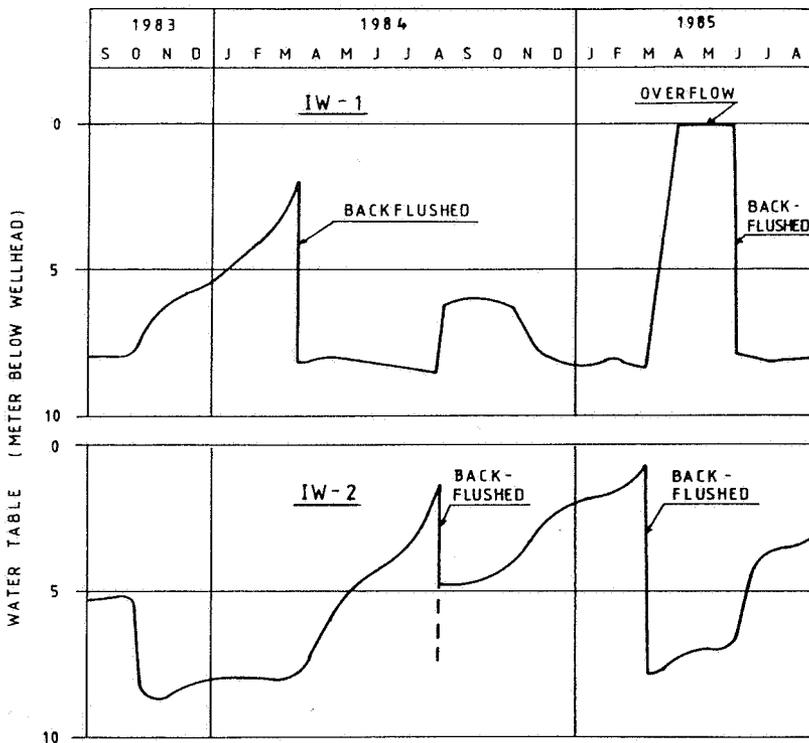


Figure 4 Clogged injection wells can be redeveloped by backflushing (Andersson, 1988b)

To avoid damages during drilling and well construction there are three important things to consider:

- 1) Avoid usage of clay minerals like bentonite in the drilling fluid. Selfdestroyed polymers are available on the market.
- 2) Before setting screen and gravelpack, circulate the hole clean with a special completion mud that also is available on the market.
- 3) To prevent sand or fines flowing in the system, the wells have to be designed properly with respect to screens and gravelpacks. They have also to be perfectly developed by airlift pumpage or likewise.

3.3 Clogging by precipitates

A very common phenomena in water-production wells is that capacity slowly drops as the well gets older. In many cases this decreasing yield can be explained by iron or manganese precipitation in screens, fractures or porespace around the well (Driscoll, 1986).

From a "clean" hydrochemical point of view precipitation of iron and manganese compounds, normally referred to as incrustations, are a result of changing the chemical balance in the water. As shown in Figure 5 the incrustation can be explained by changes of redox or acidity. Three possible ways for the water to be oxidized have been suggested (Andersson, 1988 a):

- 1) The water picks up oxygen that increases the Eh-value (displacement from A to B in Figure 5).
- 2) Different type of waters (Eh-status) are mixed entering the well (A to B).
- 3) Carbon dioxide escapes from the water that will increase the pH-value (A to C).

In practice it has been stated that most cases of iron or manganese incrustations are caused by stripping of carbon dioxide (point 3 above) as a result of a too high drawdown (Driscoll, 1986).

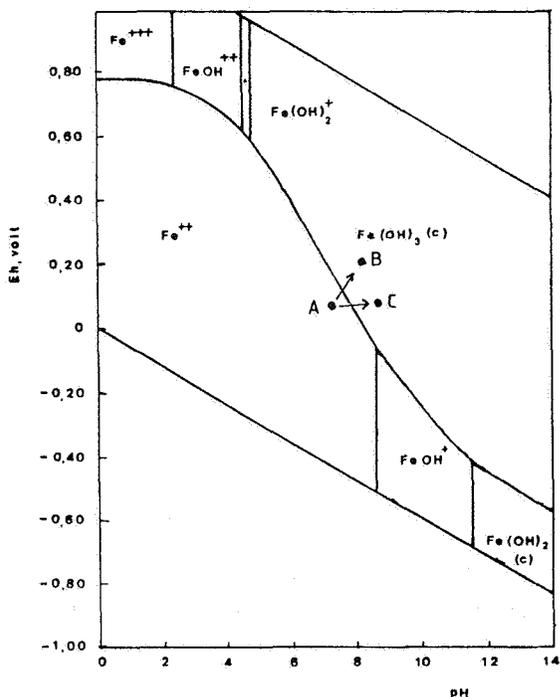


Figure 5 Simplified stability diagram for the iron system. The points A, B and C have been added, see further in the text

Escaping carbon dioxide is also believed to be one of the main factors for having precipitation of carbonates in a well. If the water also keeps iron in solution precipitation of iron carbonate might be added, something that is quite common and very hard to treat (FAO, 1980).

The clogging processes involved for a production well compared to an injection well have been illustrated in Figure 6.

As shown injection wells react somewhat different when it comes to hydrochemical processes. Those wells are working under an increased pressure and the water quality normally differs compared to the water in the aquifer. This means that the chances for precipitation of carbonates or hydroxides as a result of supersaturation should be very small.

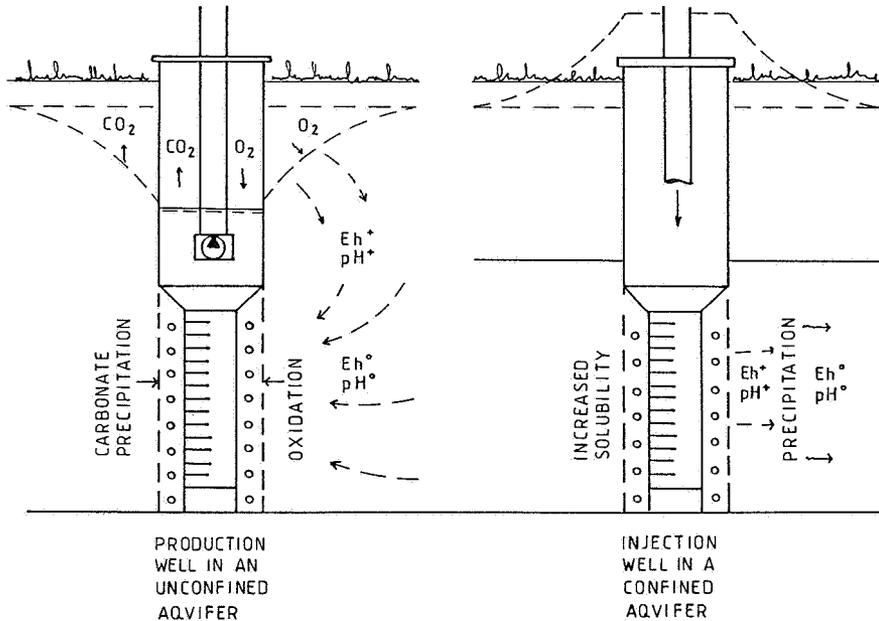


Figure 6 Potential causes for chemical precipitations in a production well compared to an injection well

Theoretically injection of oxidized water might lead to clogging of the formation in the long run, but such examples have not yet been reported. This is probably due to the fact that the zone of precipitation will move to a bigger and bigger distance from the well along with the injection phase (Andersson, 1988 a). However, in ATES applications a more fixed zone could be established due to the cyclic usage of such a system.

For prevention of chemically induced clogging of wells in an ATES system at least two designing measures can be stated:

- 1) From a hydrogeological point of view confined aquifers should be chosen prior to unconfined. This will reduce the potential for mixing reduced water with oxidized.
- 2) Stripping of carbon dioxide must be prohibited by keeping the system overpressured and to have the drawdown in production wells as small as possible.

3.4 Clogging by organic slime

Clogging by a growing biofilm or slime, produced by micro-organisms, is a well known phenomena in the water-well industry.

Experiences show that problems with preferably iron bacteria have a worldwide extension. Those bacteria exist natural in groundwater and under certain conditions will grow to form a biofilm, slime or lumps in wells and tubings.

The development of a biofilm may be divided into three phases (Trulear and Characklis, 1982):

- 1) Surface colonization (first 10 hours).
- 2) Biofilm growth (next 40 hours).
- 3) Biofilm maintenance (further on).

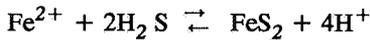
From a clogging point of view phase 3 is the important one. Two mechanisms are known to influence the further growth or thickness of the film, shearing and sloughing. Normally, the thickness remains constant by shearing (cells are sheared of by fluid erosion in the same speed as new cells are growing). However, under certain flow conditions parts of the film could be sloughed away (Pedersen and Hallbeck, 1985). In that case accumulation in narrow spaces is probable and the risk for clogging is obvious, especially in injection wells.

However, forming of slime or lumps must be considered as a much greater risk for clogging. It has been shown that this form of bacteria growth can clog a well totally and in a very short time, preferably caused by growing of stalks on the *Galionella* bacteria (Driscoll, 1986).

Treatment with acids and biocides is commonly used in clogged wells normally with a good result. However, experiences show that the effect of treatment only is temporary (Driscoll, 1986).

Another group of micro-organisms that sometimes create clogging in wells is the sulphur bacteria. In the water well industry they are known to produce iron sulfide according to the

formula (Driscoll, 1986):



It is also known that different types of sulphur bacteria under certain circumstances can produce a black-white coloured slippy mass that will form a skin on well installations. Experiences also show that occurrence of sulphur bacteria can be tightened to wells that produce highly reduced groundwater (Driscoll, 1986).

Finally, it has been showed that biomass (and iron sulfide) tend to accumulate in the aquifer surrounding a production well, rather than in the gravel pack or well screen (van Beck, 1984).

As a special remark, it shall be underlined that clogging by slime will be a potential problem mainly in low temperature ATEs systems.

3.5 Clogging by gas

It is a well known fact that water that is supersaturated with respect to gas drastically will decrease the capacity of any well.

There is very little written information on the subject, but some experiences have been reported from the Netherlands (Rijkswaterstaat, 1986). According to that investigation gas is responsible for at least one and possibly three sets of clogged injection wells. (The study involved 18 sites.)

In all three cases the cause of the problem was concluded to be a release of methane gas from production wells that entered the injection wells. It was also shown by experiments that such type of clogging can be prevented by the installation of effective degasification equipment or by maintaining the water under pressure.

4 CORROSION

4.1 Forms of corrosion

In ATEs applications, mainly two forms of corrosion can be expected:

- chemical and
- electrochemical.

As known from different branches dealing with groundwater systems the main constituents responsible for a "pure" chemical corrosion are:

- carbon dioxide (CO_2)
- oxygen (O_2)
- hydrogen sulfide (H_2S)
- hydrochloride (HCl)
- chloride (Cl) and
- sulfuric acid (H_2SO_4).

Those constituents are all known to have caused severe damage in wells and surface equipments. However, the number of wells affected by chemical corrosion is small compared to damages by clogging (Driscoll, 1986).

The most frequent areas for corrosion seem to be in screens (enlarging of slots) and pumps (shafts and impellers).

The electrochemical form of corrosion is mainly caused by mixing different metals, but there are also corrosion experiences from monometalic places like:

- heat-affected areas around welded joints and torch-cut slots (on screens)
- work-hardened areas around machine-cut slots
- cut surfaces of exposed threads at pipe joints and
- at breaks in surface coatings such as paint and mill scale.

Bimetallic corrosion is experienced whenever different metals are in contact and immersed in an electrolyte such as:

- low-carbon steel contra stainless steel
- steel contra lead
- steel contra bronzes, copper or brasses.

The experiences are, generally, that electrochemical corrosion is more frequent than chemical. Further, it seems that electrochemical corrosion causes loss of material only on parts of well screens and casings. Usually it occurs in water that is slightly acidic and with total dissolved solids (TDS) greater than roughly 1000 mg/l (Driscoll, 1986).

4.2 Prevention and protection

In the water well industry efforts have been made to prevent most types of corrosion. By example many screen manufactures have most of their products built out of stainless steel, type 304 or 316. This is because stainless steel is proved to be more resistant to underground environment and to chemicals added during well rehabilitation than low-carbon steel.

However, at certain occasions, the "passive film" that protects the stainless steel surface might be broken. This has proved to be the case in an environment with halogen salts, primarily chlorides. Under this circumstances pitting corrosion most certainly will occur, see Figure 7.

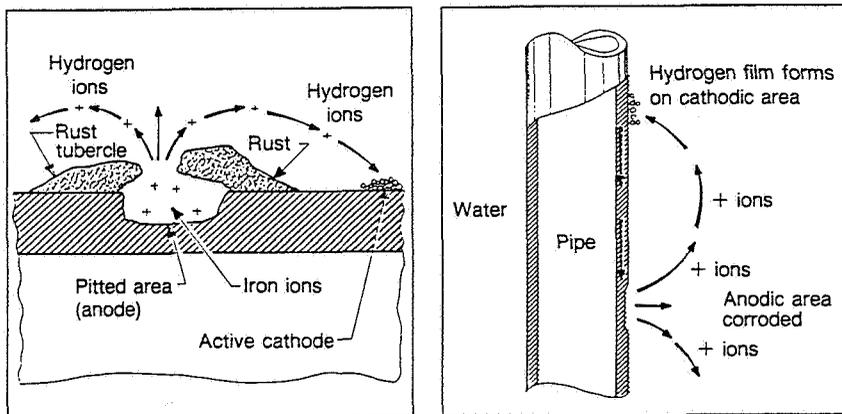


Figure 7 Anodes and cathodes development lead to pitting corrosion (from Driscoll, 1986)

When halogens are known to be present alloyed stainless steel qualities are used. An increased pitting resistance has been experienced by using molybdenum, chromium and nickel alloys (Driscoll, 1986).

A worldwide method for galvanic corrosion protection of wells is to use a cathodic protection system. As shown in Figure 8 this is normally done by installation of a sacrificial anode that is connected to the casing by a copper wire.

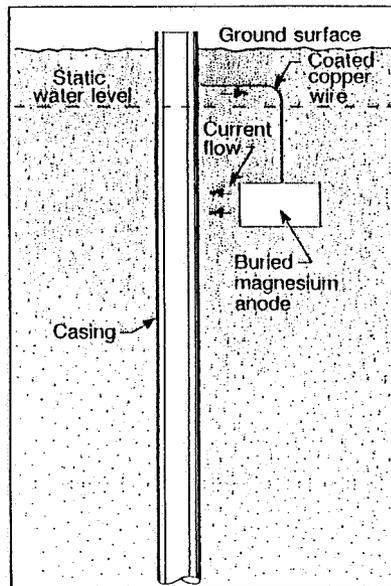


Figure 8 Example of cathodic protection of a cased well (Driscoll, 1986)

The choice of using special alloys and/or a cathodic protection system would also be applicable in ATEs systems.

Unexpected corrosion might sometimes occur, normally as a result of a drastic change of the corrosiveness of the water. This would often be the case if the water for one reason or another gets aerated. One example of such an event is illustrated in Figure 9.

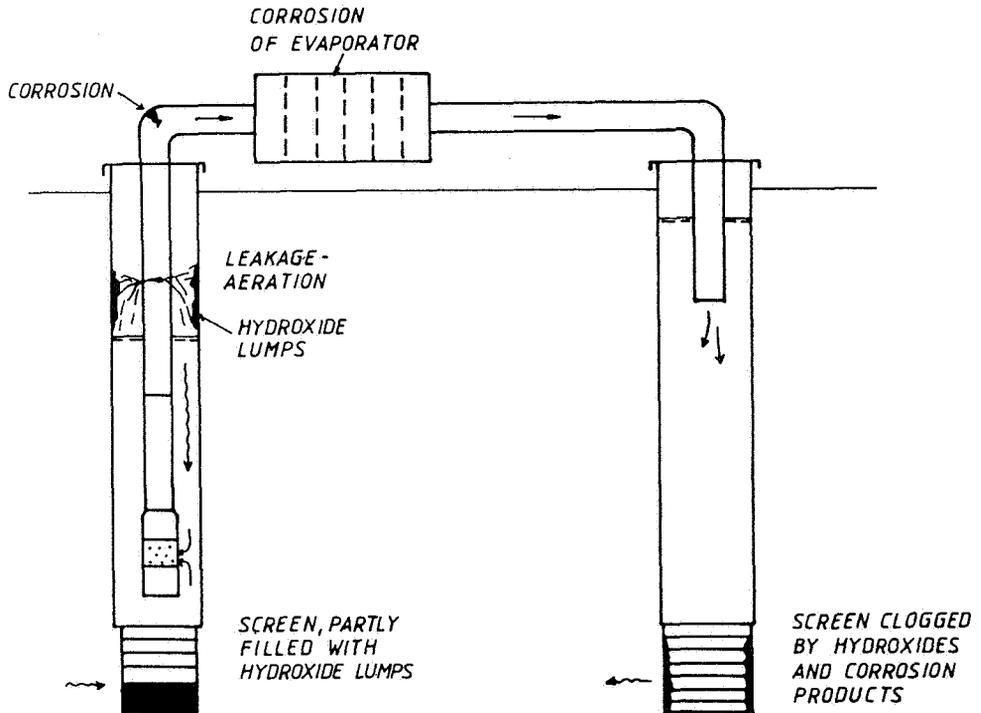


Figure 9 A leakage in a riser pipe on a production well caused severe corrosion and clogging damages in Flädie (Andersson, 1990)

In this case the water was aerated through a leakage on the riser pipe. The leakage also caused a smaller portion of the water to be recirculated. All together this lead to severe corrosion of the total system and further more clogging of the injection wells. The leakage was hardly detectable since it took place in a narrow space some 10 m below surface. Further on, it was located to a thread that was not perfectly tight.

From this case study it could be learned that down-the-hole threaded pipe connections should be locked by welded points to secure that unthreading does not occur.

To trace changes of water quality that makes it more corrosive, it is advisable to install a corrosion detector in the system. Such equipment is well proved in different industries and

available on the market.

5 SOME CONCLUSIONS

Most of the hydrochemically related scaling, clogging and corrosion problems that can be expected in ATEs systems can be predicted and taken into consideration when a plant is developed.

However, this statement assumes a comprehensive and carefully performed pre-investigation phase of any project. Furthermore each project has to be looked upon as site specific. Therefore it is not possible to state any detailed generally applicable set of rules for how a specific project should be investigated and designed. Still some general and simple designing guidelines can be recommended and those are:

- a) To detect scaling, install temperature and pressure meters to measure changes of delta temperature and delta pressure over narrow channels like plate heat exchangers.
- b) To detect and avoid clogging of injection wells:
 - have the injection water controlled by means of solids
 - have an injection pressure control
 - install a permanent back-flush system
 - install a safety valve
 - prevent oxygen to enter the system at any point.
- c) To detect and prevent clogging in production wells:
 - use confined aquifers prior to unconfined
 - monitor the specific capacity
 - do not allow carbon dioxide to strip
 - keep the drawdown as small as possible.
- d) To detect and avoid severe corrosion:
 - do not mix metals or alloys with an electrochemical potential with too far distance

- do not allow oxygen to enter the system at any point
- consider to install a corrosion detector.

REFERENCES

- ANDERSSON, O.; 1988 a. Injection well designing requires special concerns. Symposium on Geohydrology in Practice, 4th of May 1988, VIAK AB, Stockholm.
- ANDERSSON, O.; 1988 b. The Flådie groundwater heatpump plant. Experiences from the first years of operation. Swedish Council for Building Research, Doc. D9.
- ANDERSSON, O.; 1990. Scaling, clogging and corrosion experiences in the water well industry. VIAK AB, Malmö. Special reports 1.
- ATES NEWSLETTER; 1979-1989. A Quarterly Review of Seasonal Thermal Energy Storage, vol I-XI, Earth Science Div. Lawrence Berkely Laboratory, Univ. of California - till 1986. International Council for Thermal Energy Storage, Public Works Canada - from 1987.
- BECK VAN, C.G.E.M.; 1984. Restoring well yield in the Netherlands. Journal of American Water Works Assoc. 76 (10).
- DRISCOLL, F.G.; 1986. Groundwater and wells. Second Edition. Johnson Division, St Paul, Minnesota.
- FAO; 1980. Corrosion and incrustation in water wells. FAO Irrigation and Drainage Papers, FAO of UN, Rome.
- GLENN, E.E. and SLUSSER, M.L.; 1970. Factors affecting Well Productivity. Serie of articles in "Well Completions", Petro. Trans. Reprint, Serie No 5.
- PEDERSEN, K. and HALLBECK, E.; 1985. Rapid Biofilm development in deep groundwater by *Gallionella ferruginea*. Vatten 41.
- TRULEAR, M.G. and CHARACKLIS, W.G.; 1982. Dynamics of biofilm processes. Journal of the Water Pollution Control Federation 54 (9).
- RIJKSWATERSTAAT; 1986. Groundwater infiltration with bored wells. Rijkswaterstaat Communications, No 39, The Hague, The Netherlands.

BIOGEOCHEMICAL ASPECTS OF AQUIFER THERMAL ENERGY STORAGE

H.J. Brons and A.J.B. Zehnder

ABSTRACT

A good understanding of biogeochemical reactions is an important aspect of aquifer thermal energy storage (ATES) processes. For the prediction of biogeochemical reactions an electron free energy diagram is presented involving microbially mediated redox reactions with organic carbon. In this respect the most important processes detrimental to ATES are iron precipitation and anaerobic metal corrosion by sulphate reducing bacteria. The factors that control the solution chemistry and the redox cycle of iron in aquifers are outlined. The generally accepted mechanism by which sulphate-reducers initiate ferrous metal corrosion is described and a remedial *in situ* treatment technique is proposed.

1 INTRODUCTION

Confined aquifers that are used for thermal energy storage are isolated from the soil's gas phase. Hence, oxygen consumption by hydrochemical and microbiological activities cannot be replenished by oxygen diffusion. When the dissolved oxygen concentration in groundwater is depleted, thermodynamic considerations predict that the bacterial reduction of inorganic electron acceptors at the expense of organic carbon oxidation should proceed in the order: nitrate, manganese (IV), ferric iron, sulphate and carbon dioxide (Stumm and Morgan, 1981). In other words, in the biologically catalyzed oxidation of organic carbon

more energy yielding reactions precede processes that are less energy yielding.

Consequently, when the rate of oxidant depletion exceeds the rate of oxidant import the redox potential ($p\epsilon$) will decrease. In this respect Figure 1 is to be interpreted as an electron free energy diagram for biologically mediated redox reactions with organic carbon (CH_2O) as an electron donor. The ordinates in Figure 1 denoted ΔG° (kJ/mol e^-) and $p\epsilon$ -units represent the energy that is required for the transfer of electrons from one free energy level to another.

The free energy levels in Figure 1 are useful tools for the prediction of microbially mediated redox reactions in soils and sediments. For example, Figure 1 predicts that oxygen respiration can proceed concomitantly with denitrification whereas dissimilatory nitrate reduction to ammonium cannot. According to the literature the latter process is repressed by oxygen (Stouthamer, 1988) while aerobic denitrification is considered rule rather than exception (Lloyd et al., 1987).

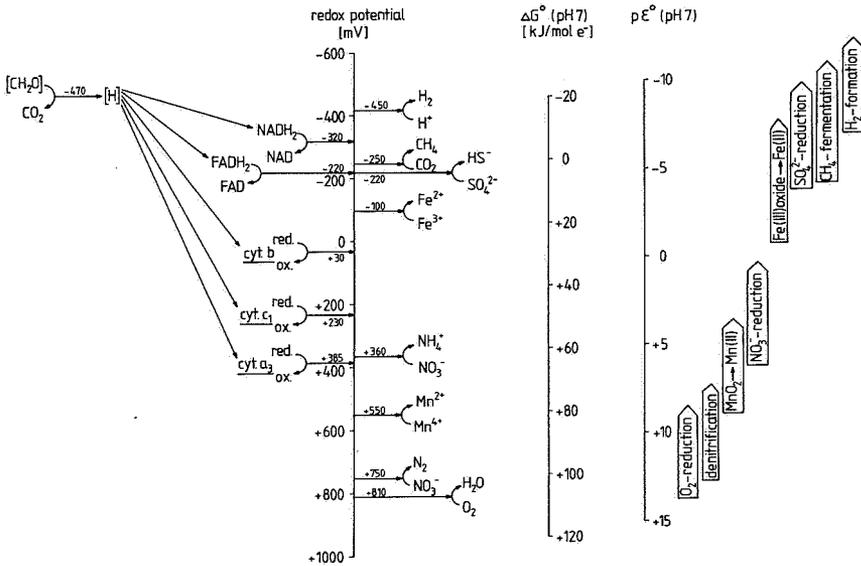


Figure 1 Electron free energy diagram for microbially mediated redox reactions in aquifers with organic carbon (CH_2O) acting as an electron donor. Calculated for standard conditions at $\text{pH}=7$; (CH_2O) represents one-sixth of glucose (i.e. -153 kJ/mol). After Zehnder and Stumm, 1988.

In accordance with Figure 1 manganese IV reduction coincides with denitrification (Klinkhammer, 1980) while ferric iron reduction does not (Sørensen, 1982), although thermodynamically possible ferrous iron is as yet unknown as an electron donor for denitrifying bacteria. On the other hand, sulphide driven denitrification in *Thiobacillus denitrificans* has been well established (Kuenen and Tuovinen, 1981).

The thermodynamic biochemical data in Figure 1 only provide evidence with regard to direction and extent rather than the actual reaction rates. Consequently, when low oxygen concentrations (0.1-1.0 mgO₂/l) prevent the chemical oxidation of both ferrous iron and sulphide some intriguing forms of chemotrophic bacteria may develop. In marine sediments for instance the chemosynthetic sulphur bacterium *Beggiatoa* can successfully compete with abiotic reactions in sulphide-oxygen gradients that are present at redox potentials between -100 and +200 mV (Jørgensen, 1977). The iron bacterium *Gallionella ferruginea* is another typical example of an organism that is particularly well adapted to gradients of ferrous iron and oxygen that occur in groundwater in the redox potential range of +200 to +320 mV (Seppänen, 1988).

During the process of aquifer thermal energy storage considerable fluctuations of the *in situ* groundwater temperature occur. As a consequence the biogeochemical reactions mentioned above will markedly change the groundwater quality. A decrease in groundwater quality may affect the performance of wells, pipes and heat exchangers. The most important biogeochemical phenomena in this respect are iron precipitation and anaerobic metal corrosion by sulphate reducing bacteria.

2 IRON PRECIPITATION

In anaerobic waterlogged soils that contain organic carbon the poorly soluble ferric iron is usually reduced to the more mobile ferrous form (Van Veen et al., 1978). The translocation of iron can be significant during the discharge of groundwater through drainpipes or wells. As oxygen near drainpipes and groundwater wells causes the oxidation of ferrous iron the subsequent formation of ochreous depositions of ferric hydroxides and organic matter may hamper or entirely clog the discharge system.

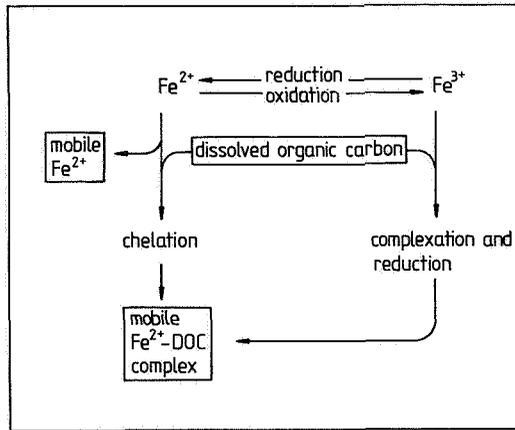


Figure 2 Schematic representation of the biogeochemical reactions in aquifers that are involved in the mobilization of ferrous iron in groundwater

With regard to the mobilization of iron (Fig. 2) it is important to understand the processes that control the solution chemistry and the redox cycle of iron in aquifers. Iron reduction in anaerobic environments is a complex biogeochemical process involving both enzymatic and abiotic factors. Ferric iron can be reduced chemically by metabolic end products such as sulphide and formate as well as by lowering the p_e and the pH of the environment (Nealson, 1983). In the presence of dissolved organic carbon ferrous iron may occur as soluble complexes of fulvic acids or other organic soil constituents derived from the break down of plant material such as polyphenols (Moore, 1988). Some of these compounds not only keep the chelated ferrous iron in the reduced state but they can reduce ferric iron to the ferrous form as well (Stevenson, 1982).

Biochemical studies on ferric iron reducing enzyme systems indicate that respiratory pathways can be involved (Dailey and Lascelles, 1977). Iron-respiration driven proton translocation and coupling to oxidative phosphorylation is possible in some cases (Lovley and Phillips, 1988).

Spontaneous oxidation of ferrous iron does not occur below $pH=3$ and in such cases precipitation of ferric iron can be solely accounted for with the acidophilic chemolithotroph *Thiobacillus ferrooxidans* (Kuenen and Tuovinen, 1981). Spontaneous ferrous iron oxidation

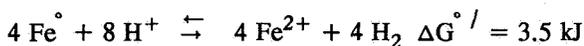
at a neutral pH is kinetically determined at low oxygen concentrations ($< 1 \text{ mg O}_2/\text{l}$), under such circumstances *Gallionella ferruginea* poses an important well clogging problem (Pedersen and Hallbeck, 1985). Anaerobic ferrous iron oxidation is possible during the process of biological denitrification. Under anaerobic conditions ferrous iron can be oxidised to ferric iron with a concomitant formation of nitric oxide. Nitric oxide is chemically formed from the reduction of nitrite (from nitrate reduction) with ferrous iron (Brons and Zehnder, 1990).

3 ANAEROBIC METAL CORROSION

3.1 Biogeochemical reactions and corrosion

The most important metal corroding microbes are the sulphate-reducing bacteria (Hamilton, 1983). Anaerobic corrosion of iron caused by this group of bacteria constitutes an economic problem of massive proportions. Therefore, it is important to understand the eco-physiology of sulphate-reducers if we want to minimize their corrosive impact. The generally accepted explanation by which sulphate-reducers provoke ferrous metal corrosion (Widdel, 1988) is based on the classic cathode depolarization theory of Von Wolzogen Kühn and Van der Vlugt, 1934. According to this theory, iron immersed in water releases ferrous cations, as a result of which the iron surface becomes negatively charged by the remaining electrons (Fig. 3).

Only when the electrons or ferrous ion are removed the dissolving process continues; under aerobic conditions this is achieved by rust formation. In the absence of oxygen, anodic dissolution of iron coupled to hydrogen formation is not energetically favored at $\text{pH} = 7.0$ and 25°C (Daniels et al., 1987):



Hydrogen adsorbs on the iron surface and thus a dynamic equilibrium is established which keeps the elemental iron polarized. The principle mechanism of anaerobic corrosion is cathodic depolarization of the iron surface by hydrogen scavenging sulphate-reducers, as

was shown with hydrogenase-positive strains of *Desulfovibrio vulgaris* (Pankhania et al., 1986). In addition, it should be noted that the production of H_2S and FeS is corrosive as well (Hamilton, 1983).

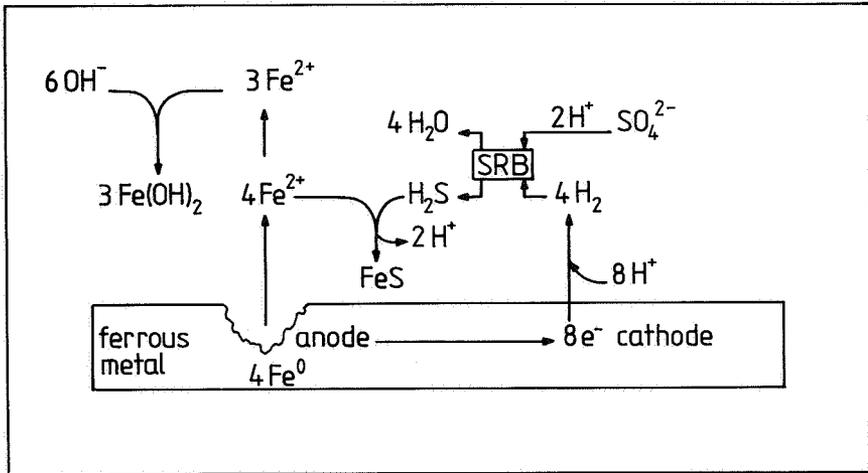


Figure 3 Proposed cathodic depolarization reactions for pitting corrosion of ferrous metals by sulphate-reducing bacteria (SRB) according to Von Wolzogen Kühr and Van der Vlugt, 1934. Adapted from Widdel, 1988.

3.2 Control of sulphate-reducers

Under limited access of oxygen growth of sulphate-reducing bacteria can be expected in groundwaters that contain organic carbon and sulphate. Moreover, in aerobic aquatic environments biofilms attached to surfaces may become oxygen depleted through microbial respiration within a short distance (10-25 μm) and thus provide microniches that are conducive to sulphate-reducers (Costerton and Geesey, 1979). In analogy to the offshore oil and gas industry (Battersby et al., 1985) control of growth and activity of sulphate-reducing bacteria during aquifer thermal energy storage can be achieved by cathodic protection using a rather expensive sacrificial magnesium anode. A less expensive preventive measurement would be the use of protective coating in pipes with fiber glass, rubber derivatives and other inert materials. Biocides such as quaternary ammonium compounds and glutaraldehyde are widely used in the offshore industry (Battersby et al., 1985). Obviously, the general toxicity

of such biocides used against desulphuricants militates against their use in aquifers. A treatment technique more suitable for practical application against sulphate-reducers in aquifers might be the Vyredox method (Braester and Martinell, 1988) which comprises the aeration and *in situ* injection of oxygenated groundwater.

REFERENCES

- BATTERSBY, N.S., STEWART, D.J. and SHARMA, A.P.; 1985. Microbiological problems in the offshore oil and gas industries. J. Appl. Bact. Symp. Suppl.: 227-235.
- BRAESTER, C. and MARTINELL, R.; 1988. The Vyredox and Nitredox methods of *in situ* treatment of groundwater. Water Sci. Tech., 20: 149-163.
- BRONS, H.J. and ZEHNDER, A.J.B.; 1990. The inhibition of sulphate reduction by nitric oxide in marine enrichment cultures. Appl. Environ. Microbiol. Submitted.
- COSTERTON, J.W. and GEESEY, G.G.; 1979. Microbial contamination of surfaces. In: Surface Contamination vol 1: 211-221. Plenum Publishing, New York.
- DAILEY, H.A. and LASCELLES, J.; 1977. Reduction of iron synthesis of protoheme by *spirillum itersoni* and other organisms. J. Bacteriol, 129: 815-820.
- DANIELS, L., BELAY, N. RAJAGOPAL, B.S. and WEIMER, P.J.; 1987. Bacterial methanogenesis and growth from CO₂ with elemental iron as the sole source of electrons. Science, 237: 509-511.
- HAMILTON, W.A.; 1985. Sulphate-reducing bacteria and anaerobic corrosion. Ann. Rev. Microbiol., 39: 195-217.
- JØRGENSEN, B.B.; 1979. Bacterial sulphate reduction within reduced microniches of oxidised marine sediments. Mar. Biol., 41: 7-17.
- KLINKHAMMER, G.P.; 1980. Early diagenesis in sediments from the eastern equatorial Pacific II. Pore water metal results. Earth Planet. Sci. Lett., 49: 81-101.
- KUENEN, J.G. and TUOVINEN, O.H.; 1981. The genera of Thiobacillus and Thiomicrospira. In: The Prokaryotes. A handbook on habitats, isolation and identification of bacteria. Volume 1: 1023-1036. Springer Verlag, Berlin.
- LLOYD, D., BODDY, L. and DAVIES, K.J.P.; 1987. Persistence of bacterial denitrification capacity under aerobic conditions: the rule rather than the exception. FEMS microbiol. Ecol., 45: 185-190.

- LOVELY, D.R. and PHILLIPS, E.J.P.; 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Appl. Environ. Microbiol.*, 54: 1472-1480.
- MOORE, T.R.; 1988. Dissolved iron and organic matter in northern peatlands. *Soil Sci.*, 145: 70-76.
- NEALSON, K.H.; 1983. The microbial iron cycle. In: *Microbial Geochemistry*: 159-190. Blackwell Scientific Publications, London and Melbourne.
- PANKHANIA, I.P., MOOSANI, A.N. and HAMILTON, W.A.; 1986. Utilization of cathodic hydrogen by *Desulfovibrio vulgaris* (Hildenborough). *J. Gen. Microbiol.*, 132: 3357-3365.
- PEDERSEN, K. and HALLBECK, E.L.; 1985. Rapid biofilm development in deep groundwater by *Gallionella ferruginea*. *Vatten*, 41: 263-265.
- SEPPÄNEN, H.; 1988. Groundwater- a living ecosystem. *Water Sci. Tech.*, 20: 95-100.
- SØRENSEN, J.; 1982. Reduction of ferric iron in anaerobic, marine sediment and interaction with reduction of nitrate and sulfate. *Appl. Environ. Microbiol.*, 43: 319 -324.
- STEVENSON, F.J.; 1982. Humus chemistry: genesis, composition, reactions, 420-431. John Wiley and Sons, New York.
- STOUTHAMER, A.H.; 1988. Dissimilatory reduction of oxidized nitrogen compounds. In: *Biology of anaerobic microorganisms*, 245-303. John Wiley and Sons, New York.
- STUMM, W. and MORGAN, J.J.; 1981. Aquatic chemistry, 448-463. Wiley-Interscience New York.
- VAN VEEN, W.L., MULDER, E.G. and DEINEMA, M.H.; 1978. The *Sphaerotilus - Leptothrix* group of bacteria. *Microbiol. Rev.*, 42: 329-356.
- VON WOLZOGEN KÜHR, C.A.H. and VAN DER VLUGT, L.S.; 1934. De grafitering van gietijzer als elektrobiochemisch proces in anaerobe gronden (in Dutch). *Water*, 16: 147-165.
- WIDDEL, F.; 1988. Microbiology and ecology of sulfate- and sulfur reducing bacteria. In: *Biology of anaerobic microorganisms*, 496-586. John Wiley and Sons, New York.
- ZEHNDER, A.J.B. and STUMM, W.; 1988. Geochemistry and biogeochemistry of anaerobic habitats. In: *Biology of anaerobic microorganisms*, 1-38. John Wiley and Sons, New York.

HYDROGEOCHEMICAL TRANSPORT MODELLING

C.A.J. Appelo

ABSTRACT

Reactions which determine water quality can be simulated with geochemical models. The models include corrections for complexes and activity-coefficients, which make hand-calculations excessively laborious, but are necessary to obtain the right results. For example, calculating the dissolution of calcite with a model gives about twice higher concentrations than a hand-calculation in which the corrections are neglected. The models compute water-composition in a batch, but can be incorporated in a transport code and thus permit dynamic modelling of hydrological situations. Cation exchange is an important reaction which is easily introduced in the models. Examples are given of 1) a column experiment in which cation exchange, proton buffering and slow calcite dissolution occur, 2) aquifer thermal energy storage at St. Paul (USA), where major cation concentrations in recovered water can be adequately modelled.

1 INTRODUCTION

The propulsion of space rockets appears to be the first problem for which a comprehensive chemical equilibrium model was developed. Product and reactant gasses in the rocket fuel can be calculated, as a function of temperature and pressure, knowing that the Gibbs Free Energy of the mixture should be minimal at equilibrium. Equilibrium among the gasses

gives a set of non-linear equations which are solved with Newton-Raphson iteration (Smith and Missen, 1982). Reactions in natural water are about as complex, and involve even more components, so that use of similar equilibrium models serves to show the evolution of water quality influenced by silicate weathering (Helgeson, et al., 1970; Fritz, 1975), carbonate reactions in groundwater (Plummer et al., 1983), acidification (Eary et al., 1989; Appelo, 1985), ore deposition or waste leaching (Garven and Freeze, 1984; Liu and Narasimhan, 1989), cation exchange with salt/fresh water displacements in aquifers (Appelo and Willemsen, 1987), complexation of heavy metals in water and adsorption on solids (Westall and Hohl, 1978; Felmy et al., 1984), or water treatment for aquifer thermal energy storage (Willemsen, 1990, this volume).

Figure 1 shows the types of reactions which influence the chemical composition of water. Dissolution and precipitation, oxidation and reduction, exchange of cations among water and solids, and of gasses among water and air, are the prominent reactions. An equilibrium analysis helps to predict the direction and possible extent of the reactions. For Aquifer Thermal Energy Storage (ATES), the reactions induced by seasonal heating and cooling of aquifer water are important. These may lead to clogging of heat exchangers and injection wells, or reduce the porosity and permeability of the aquifer. Important reactions are precipitation of carbonates, and exsolution of gas when water is heated (Appelo et al., 1990b). When the hot water temperature raises above 120°C, precipitation of silicate-minerals upon cooling may also become important.

An equilibrium analysis can be performed with a geochemical model. Geochemical models go a step beyond the computer models which calculate the saturation state with respect to minerals for a given water analysis, such as WATEQF (Plummer, 1976). A geochemical model can additionally calculate how water composition changes in response to reactions (dissolution of minerals, gasses, etc.), and exactly this capability makes them so useful for modelling natural water quality, including ATES-related processes. The following pages should provide an idea of the possibilities and restrictions of modern hydrogeochemical modelling. An example of calcite dissolution at a given CO₂ pressure is used to introduce the basic chemical formulae. The general geochemical models are meant for reactions in a batch, but many hydrogeochemical problems, including ATES, relate to flow and transport. Introduction of the models in a transport code is thus necessary, but poses some problems.

The complexity of the models with a large number of adjustable parameters, requires due assessment of the validity of the assumptions. Such may only be obtained by comparison with carefully obtained experimental data. Two examples are given, one is a column experiment with sediment from the Dutch ATES test site, the other is a model of the first long term storage cycle at the St. Paul ATES field site.

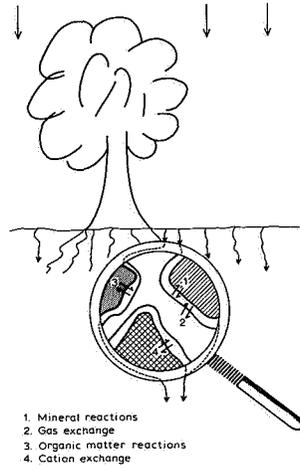
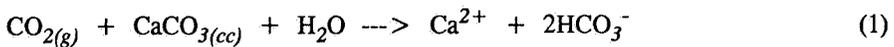


Figure 1 A close-up view of reactions which are important for natural water quality

2 GEOCHEMICAL MODELS, WHAT CAN THEY DO?

A geochemical model can calculate the composition of water in a batch when minerals dissolve or precipitate, reactants are added, temperature is changed, or pressure of gasses alters. We may consider, as an example, dissolution of calcite in a glass of water, at a given temperature and pressure of CO₂ gas. Calcite then dissolves according to the reaction:



for which the mass-action equation is:

$$K_{(1)} = \frac{[\text{Ca}^{2+}] [\text{HCO}_3^-]^2}{P_{\text{CO}_2}} \quad (2)$$

where

[i] is activity of i in water (molal concentration m_i times activity coefficient γ_i),

K is equilibrium constant of the reaction, and

P_i is gas pressure of i (atm).

Other ions and complexes which exist in solution besides the molecules and ions of reaction (1) are H^+ , OH^- , $CaHCO_3^+$, CO_3^{2-} , H_2CO_3 . However, we may neglect their existence and try to calculate the composition of the solution by hand. Electroneutrality in solution then requires that:

$$2m_{Ca} = m_{HCO_3} \quad (3)$$

Combination of (2) and (3), and setting activity [i] = m_i , allows the calculation of Ca-concentration as a function CO_2 -pressure; the outcome can be compared with the calculation of a geochemical model in which the same $K_{(1)}$ is used, and in which moreover due account is given of the existence of activity coefficient corrections, and of all other complexes and ions in solution. Table 1 gives the result, when CO_2 pressure is 0.01 atm.

Table 1 Calcite dissolution at $P-CO_2 = 0.01$ atm; comparison of hand calculation with a geochemical model

Hand $Ca^{2+} = 10^{2.1}(P_{CO_2})^{1/3}$	Numerical model, includes activity-corrections; complexes
$HCO_3^- = 1.76$	$= 3.24$ mmol/l (*)
$Ca^{2+} = 0.88$	$= 1.65$ " (*)
$CaCO_3^0 = -$	$= 0.005$ " (\$)
$CaHCO_3^+ = -$	$= 0.40$ " (\$)
EC $= 176$	$= 324$ μ mho/cm

(*) total concentration, including complexes;

(\$) actual complex concentration.

The comparison shows that inclusion of complexes and activity-corrections gives almost twice as high total concentrations (which would be analyzed chemically) as the simple hand calculation. This illustrates that use of a geochemical model may be a worthwhile step to a more accurate description of chemical reactions. A number of the models are, what is called 'user-friendly', and there is no reason not to perform a more reliable and in many instances quicker calculation with a computer model.

2.1 Governing equations

The example of calcite which dissolves to equilibrium, shows that we must calculate complexes, activity-coefficients, equilibria with minerals and gas pressures, as a function of temperature. We can deduce formally, that the geochemical model should minimize residuals R_i in the following equations:

Mass-balance for components i:

$$\sum_i (R_1)_i = \text{Tot. conc}_i - \sum_j \text{complex}_j \cdot d_{i,j} - m_i \quad (4)$$

Electroneutrality:

$$R_2 = \sum \text{complex}_j \cdot z_j + \sum m_i \cdot z_i \quad (5)$$

Electron-balance:

$$R_3 = \text{Tot. e} - \sum \text{complex}_j \cdot e_j - \sum m_i \cdot e_i \quad (6)$$

Mineral-equilibria for minerals m:

$$(R_4)_m = \log(\text{IAP})_m - \log K_m \quad (7)$$

with

$$(\text{IAP})_m = \prod_i (m_{i,m} \cdot \gamma_i)^{d_{i,m}} \quad (8)$$

where

Tot. conc_i is total (molal) concentration of component i,

complex j is obtained as molal concentration from the mass-law equation:

$$\text{complex}_j = K_j \prod_i (m_{i,j} \cdot \gamma_i)^{d_{i,j} / \gamma_j} \quad (9)$$

K_j is association constant for complex j, or the solubility-product of a mineral,

m_i is (molal) concentration of free, uncomplexed i,

γ_i is activity coefficient,

$d_{i,j}$ is stoichiometric coefficient of i in the jth complex or mth mineral,

z_i is charge of i, and

e_i is redox-status of i.

The problem to reduce the residuals $R_1 \dots R_4$ to within some preset limit, involves solution of the non-linear equations, for example with Newton-Raphson iteration. The non-linearity stems from inclusion of complexes, and from mineral-equilibria. The fulfilment of equilibrium with a mineral m may require dissolution or precipitation of an amount of mineral MIN_m , and hence the total concentration of i is augmented with $\text{MIN}_m \cdot d_{i,m}$. Likewise, a reaction-term simply adds an amount to a concentration. The activity coefficients γ can be considered perturbation factors which are calculated separately from the Newton-Raphson iterations. The electroneutrality equation and electronbalance can be used to calculate concentrations of two components, for which usually pH (or concentration of H^+), and pe (or 'availability' of electrons) are chosen.

The definition of a 'component' requires some discussion; components in the thermodynamical sense are the independent entities from which the chemical system under consideration can be constructed. In the hydrological literature the term 'moiety' has been introduced (Rubin, 1983), which is identical to the more common thermodynamic term. For thermodynamic purposes, the choice of components of a system is often arbitrary and depends upon the range of conditions for the problem under consideration (Pitzer and Brewer, 1961). The elements of the periodic systems with their usual valence, and additionally the oxidation potential (or pe) would be sufficient as components for a general hydrogeochemical system. In PHREEQE (Parkhurst et al., 1980) and EQ3/6 (Wolery, 1982)

the component O₂ (Oxygen) has been replaced by the component H₂O, and O₂ is calculated as complex from the reaction:



or

$$P_{\text{O}_2} = (K_{(10)} \cdot \frac{[\text{H}_2\text{O}]}{[\text{H}^+]^2[\text{e}]^2})^2 \quad (11)$$

The component N₂ has similarly been replaced in both models by the component NO₃, which is advantageous since NO₃ is normally the analyzed form of nitrogen in water. The nitrogen forms are of interest to illustrate the difference of component-concentration, and the complex or species which is actually analyzed. The 'component' NO₃ actually consists of the species (or complexes) NH₄⁺, N_{2(g)}, NO₂⁻, and NO₃⁻. With given pe and pH the model calculates the distribution over these species. Thus, when at pH=7, pe has been set to 0, the thermodynamically stable (i.e. highly predominant) form is NH₄⁺. Although in such case an input concentration of NO₃ has been defined, the output concentration of NO₃⁻ may be surprisingly low for the inexperienced user of the model. When equilibrium among the different species of a component is unrealistic, it is possible to separate them and define additional components. For example, the denitrification reactions of NO₃⁻ can be rapid and lead to N₂ gas, but production of NH₄⁺ may be sluggish. Two components may then be defined: a component NO₃, with species NO₃⁻, NO₂⁻ and N₂, and a second component NH₄, which consists of NH₄⁺ (and complexes of NH₄⁺ such as NH₄SO₄⁻) only.

2.2 Available models

A number of models have been developed which all have the ability to equilibrate a given aqueous solution with minerals, add reactants and calculate pH and pe as function of reactions, change temperature and gas pressures, and again calculate solution composition in response to such additions or changes. Table 2 lists the models which are freely available and known to be operational. The availability is in itself a tribute to the development of science, and it is certainly right to honor the developers. Selection may be based on specific features which have been incorporated, or on the extensiveness of the database.

Table 2 Available geochemical computermodels

Model	Features	Reference
PHREEQE	fast convergence on carbonate-problems. efficient & modular program.	Parkhurst et al., 1980.
EQ3	fast convergence; mineral equilibrium fixes component-concentration; EQ6 has path-finding ability. Bulky & not very clear program. Large database.	Wolery, 1983
GEOCHEM	slow convergence. Bulky output, new version available (1988). Database with species of interest for soil science.	Sposito & Mattigod, 1979
MINTEQ	Large database, aimed at complexing of heavy metals. Fancy models for adsorption on solid surfaces.	Felmy et al., 1984.

2.3 Database comparison

The model results are completely depending on values for the thermodynamic constants which are used in the database. Each complex and mineral must be given values for the equilibrium-constant at 25°C, and either the enthalpy of the reaction via the Van 't Hoff-equation, or a power series for the temperature dependency. A comparison of speciation models (Nordstrom et al., 1979) gives some insight in deviations in the database. A speciation model calculates the speciation, ion-activities and saturation indices for a given water-analysis, but cannot do the more refined job of calculating water compositions in response to reactions, mineral equilibria, etc. which a geochemical model can perform. The actually used database can be completely identical for both types of models, however, so that the comparison of Nordstrom et al. (1979) is still valid for geochemical models as well. It may be noted that the Environmental Protection Agency of the USA has directed a considerable effort into providing MINTEQ with an extensive and critical database.

The results of a recent solubility product-comparison by Lichtner and Engi (1989) at two temperatures is shown in Figure 2. It can be seen that there is convergency of values for a large number of minerals; these values apply to well-defined minerals under laboratory conditions. However, the actual mineral encountered in the field may be less well-defined, both as regards composition and crystallinity.

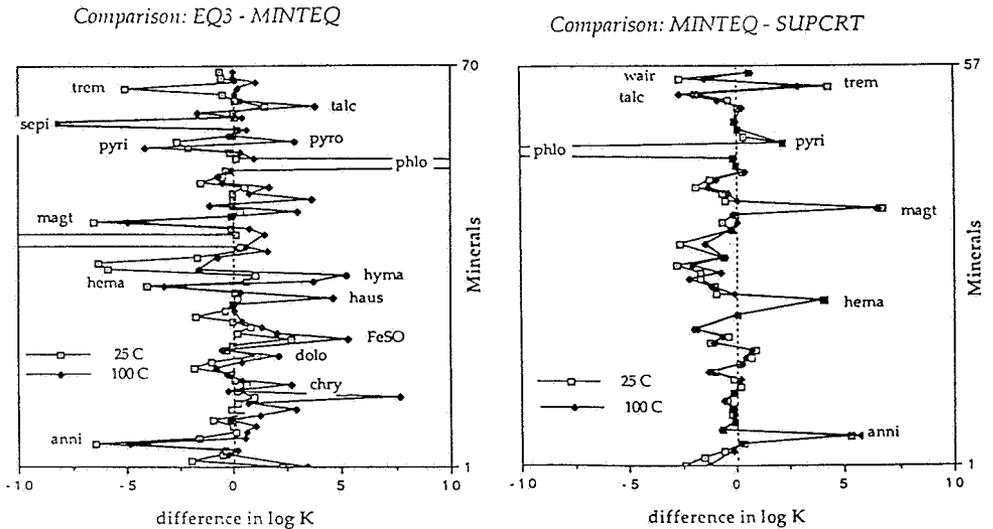


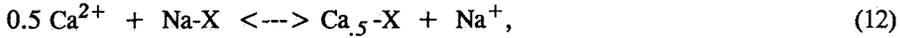
Figure 2 Comparison of solubility-products used in the models MINTEQ and EQ3, at two temperatures. From Lichtner and Engi, 1990.

2.4 Cation exchange in the geochemical models

The models offer either a refined electrostatic model to calculate ion exchange reactions as in MINTEQ (Westall and Hohl, 1980; Felmy et al., 1984), a Langmuir-type formulation (Bryant et al., 1986), or approximations which are not exactly in agreement with exchange phenomena (Parkhurst et al., 1980, suggest a 'mineral' reaction which effectively fixes the ion ratios in water; Sposito and Mattigod (1979) give a relationship which is difficult to link to observable ion exchange relationships).

All the models use an ion-association model to calculate complexes in solution. It is possible

to incorporate ion-exchange in such model, without adaption of the solution algorithm, simply by writing the ion-exchange reaction as two 'half-reactions' (Appelo, 1985; Shaviv and Mattigod, 1985; Appelo and Willemssen, 1987). This can be illustrated for the Na/Ca exchange reaction:



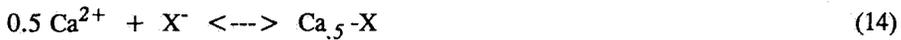
for which a mass-action equation can be written:

$$K_{G\text{Ca}\backslash\text{Na}} = \frac{[\text{Na}^+] [\text{Ca}_{.5}\text{-X}]}{[\text{Ca}^{2+}]^{.5} [\text{Na-X}]} \quad (13)$$

where

[i-X] is activity on the exchanger-surface (equivalent fraction), and
 $K_{G\text{Ca}\backslash\text{Na}}$ is the exchange coefficient.

Reaction (12) uses the exchange-sites filled with a given cation as basis for calculating the activity of the exchangeable cation (Gapon convention). The reaction can be written as a subtraction of two association reactions:



and



The amount of exchange capacity can be expressed in the total concentration of X^- . The 'free X^- ', which does not exist in a pure exchange model, can be made negligibly small when the association constants for reactions 14 and 15 are set to a high value, and the amount of cations associating with X^- is larger than the total amount of X^- . All surplus charge is then tied up in neutral species, so that effects on ionic strength are minimal, and other calculations of the ion association model are not affected.

The neutral "exchangeable" complex is conventionally expressed as a fraction, which implies that concentration must be divided by the cation exchange capacity (CEC). This correction is not necessary when the Gapon convention has been chosen, since each complex has a single X^- associated with a cation, irrespective of its charge: the contributions of CEC cancel when the two association equations are added to give the exchange reaction.

The strength of an ion exchange reaction can be expressed in the relative value of the association constant with respect to the value for a reference cation, say Na^+ . For example with the Gapon convention, when the exchange constant for Ca\Na exchange (reaction 12) is $K_{(12)}$, and $K_{(15)}$ is y , then $K_{(14)} = K_{(12)} \cdot y$ (add reaction (15) to reaction (12), to obtain reaction (14)). The value of y typically must be larger than 10^{12} , to obtain a free activity $[X^-]$ smaller than 10^{-9} moles dm^{-3} . It is possible to include the Gaines & Thomas convention for cation exchange in a similar way.

2.5 Incorporation in a transport code

The geochemical models calculate the composition in a batch of water; transport can be simulated by calculating the movement of total concentrations with a hydrological model, and calculating the equilibrium composition in a grid-cell, or -element. Transport and chemistry are then solved separately, and this technique is therefore referred to as the 'uncoupled' formulation (Kirkner and Reeves, 1988). The alternative is to write transport equations for all components, species, as well as the imposed equilibrium relations (Miller and Benson, 1983; Lichtner, 1985). The equations are solved simultaneously over the finite difference grid; such a 'coupled' procedure requires large amounts of computer storage, and a reformulation of the chemical equations for each problem. An important point is that the equations are solved algebraically correct, and results should thus be considered as a reference for the decoupled models. Engesgaard (1989) for example, has compared the dissolution of a calcite-front as calculated with an uncoupled model with results from the Miller and Benson (1983) model. It appears necessary to iterate among transport and chemical models to prevent numerical dispersion due to retardation (Herzer and Kinzelbach, 1989). More prolonged iteration may be necessary when chemical reactions give rise to jumps (sharp fronts), such as with precipitation-dissolution reactions (Rubin, 1983), or with oxidation-reduction fronts (Engesgaard, 1989).

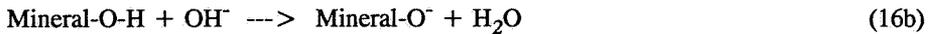
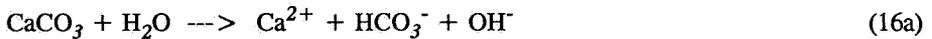
A number of uncoupled models have been published, where numerical dispersion has been neglected, or is corrected for one component (normally a conservative component) only (Van Ommen, 1985; Appelo and Willemssen, 1985; Nienhuis et al., 1988; Jauzein et al., 1989). This approach, based on the mixing cell approach, is particularly loved by chemical engineers (Vermeulen et al., 1984; Jauzein et al., 1989), and has produced a number of workable models in which basic chemical requirements such as mass balances, electroneutrality, etc. are easily conserved. There is a formal problem, however, when sharpening fronts are calculated with these models. Willemssen (1990) has worked out techniques which can lead to correction for numerical dispersion without iteration.

3 APPLICATION AND VALIDATION

Geochemical models are typically used in situations where many and interdependent processes, reactions and parameters, prohibit the use of simple approximations. Or, rather, the fact that a geochemical model is available which can simulate all the equilibrium reactions, gives an easy possibility to gain insight in the complex chemistry of natural water. Applications have been mentioned in the introduction, but these refer mainly to theoretical studies. The availability of carefully measured data under exactly known conditions which could be used to validate the possibilities of geochemical transport models is despairingly small. The following cases have been obtained in the course of research for aquifer thermal energy storage (ATES). This research is fit to provide a classical action/reaction analysis, in that temperature increase and water treatment provoke reactions between water and aquifer sediment which are intricate enough to warrant the use of geochemical transport models. A column experiment where sediment from the Dutch ATES test facility at TNO-Delft has been flushed with a SrCl_2 solution shows the effects of cation exchange, proton buffering and slow calcite dissolution (Appelo et al., 1990a). Injection of hot water, from which the cations have been exchanged for Na^+ , at the St. Paul ATES test facility shows how the aquifer sediment reacts with cation exchange (Appelo et al., 1990b).

3.1 SrCl₂ elution of Delft sediment, showing proton buffering and calcite dissolution

Native groundwater was displaced in a column experiment by 0.022 N SrCl₂ to determine original groundwater composition, CEC of the sediment and absorbed amounts of individual cations. The experimental conditions (column set-up) and sediment characteristics are described by Griffioen (1990, this volume). When a neutral SrCl₂ solution is used to flush a sediment with calcite, the alkalinity becomes nearly zero and pH increases to 10. This pH is attained when water with a very low CO₂ pressure equilibrates with calcite. However, the alkalinity in the experiment remained significantly non-zero: at the end of the experiment, after 500 ml SrCl₂ solution had percolated the column, the solution had 0.37 meq/l alkalinity and a pH of 7.15. The alkalinity is attributed to dissolution of CaCO₃ as a result of proton-buffering of the sediment in reaction to the pH-increase during displacement:



The total amount of proton-buffering for an increase in pH from 6.83 to 7.15 was calculated, from the measured alkalinity, to be 0.07 meq/100g (as compared with a CEC = 0.51 meq/100g at pH = 6.83). Calcite saturation indices show undersaturation in the tailing part of the elution curve.

The exchangeable quantity of an individual cation is calculated from the total eluted amount minus the amount in native groundwater. The amount of Ca is also corrected for calcite dissolution by subtracting the measured alkalinity. Summation of all cations gives the CEC at native pH (6.83), and the model exchange constants can be easily calculated from the experimental results. Calcite dissolution in combination with proton buffering is manifest in this sample and the following text emphasizes this aspect of the modelling exercise.

Measured and modelled Ca concentrations are shown in Figure 3. Modelling of the Ca elution as an exchange process gives the lowermost curve (curve A) in Figure 3. The model-curve adequately follows the experimental Ca peak, but gives too low concentrations

in the tail. Inclusion of calcite equilibrium in the model hardly improves the results (curve B), since only limited amounts of calcite can dissolve in the CO₂-free SrCl₂ solution. Moreover, the modelled eluate pH increases to 9.6, which is far higher than the observed pH of 7.1. Clearly, proton-buffering has to be included as an additional reaction. It was assumed that proton buffering by the sediment could be modelled as a cation-exchange reaction:

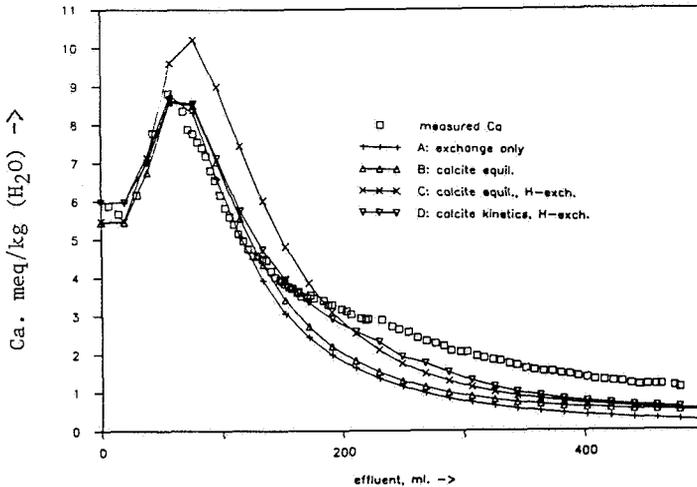
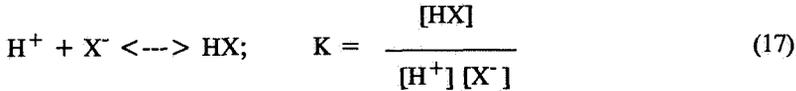


Figure 3 Modelling Ca elution from Delft sediment with different options

The model value of the association constant was calculated from the pH of native groundwater (gives [H⁺]), and the observed amount of proton buffering (gives [HX]). Inclusion of this reaction together with calcite equilibrium gives curve C in Figure 3. The amounts of Ca which are eluted from the column are now identical in experiment and model, since the assumptions underlying the model calculation are wholly obtained from experiment. However, the calculated initial Ca peak is too high and Ca concentrations in the tail are too low; this suggests that calcite dissolution is slower in practice and does not reach equilibrium (undersaturation was calculated with respect to calcite in the eluate). Dissolution kinetics were then introduced to the model as a last reasonable step to try and fit the experimental data. The geochemical model calculates saturation ratios (Ω), which are defined as:

$$\Omega = IAP/K \tag{18}$$

The saturation ratios can be used in rate equations describing calcite dissolution which are of the form (Morse, 1983):

$$\frac{d(\text{Ca})}{dt} = kA (1 - \Omega) \tag{19}$$

where

$d(\text{Ca})/dt$ is rate of calcite dissolution or precipitation, and

kA is rate of the reaction, which incorporates a rate constant k , and a surface area A .

With a value for the term kA of $5E-8 \text{ mol l}^{-1} \text{ s}^{-1}$, the fourth modelled line D in Figure 3 results. This gives a reasonable description of the measured data. Curves for Mg and Sr are given together with the data for Ca in Figure 4.

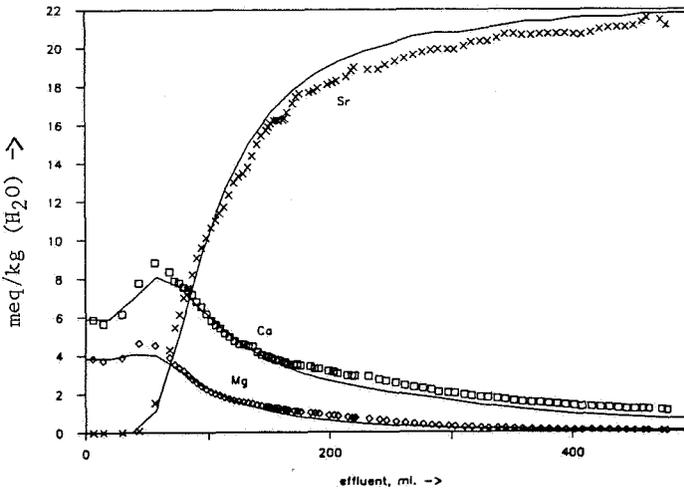


Figure 4 Experimental points and modelled curves for Ca and Mg elution from Delft by SrCl_2 , with proton buffering and slow calcite dissolution

It is appropriate to recall here that the use of more variables makes model applicability more haphazard. Even though the step by step modelling sequence shown here has a logical, and intuitively reasonable background, the assumed values for the constants are derived by

experiment and are therefore not of universal value. It appears that the kinetics of mineral dissolution and precipitation might indeed be the most formidable task to resolve before general geochemical models can be applied to environmental problems.

3.2 An ATES field experiment: St. Paul

A high temperature ATES field test site has been constructed on the campus of the University of Minnesota in St. Paul. Water is injected in a quartzitic aquifer at 180 m depth. The local stratigraphy and mineralogy of the aquifer sediments is shown in Figure 5. A number of tests with injection of hot water up to 110°C have been performed and were described in the literature (Holm et al., 1987; Perlinger et al., 1987). Scaling of the injection well was initially prevented by installment of a calcite precipitator after the heat exchanger during four short test cycles (Holm et al., 1987). For a long term test during which about 92000 m³ was injected, water was softened to a NaHCO₃-type water by ion exchange before the heat exchanger (Perlinger et al., 1987).

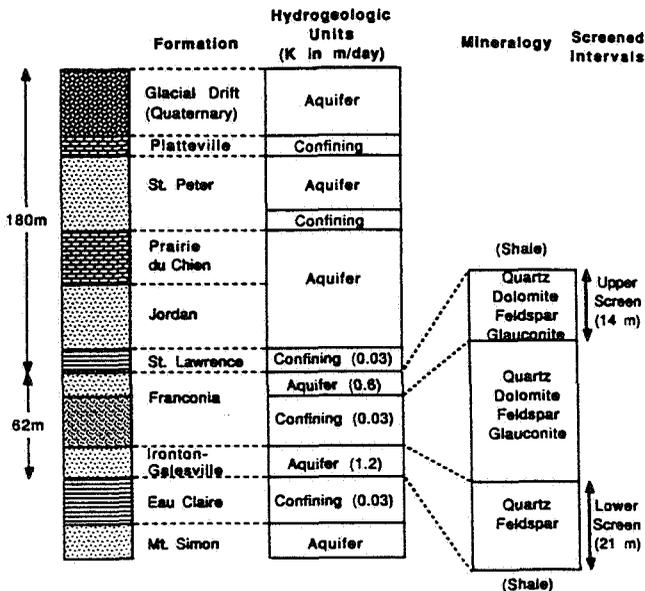


Figure 5 Stratigraphy and hydraulic conductivity at the St. Paul ATES test facility (Perlinger et al., 1987)

Recovered water in the long term test showed an increase in Ca and Mg concentrations, and a decrease in Na concentrations. The changing composition of recovered water has been described on the basis of carbonate and silicate reactions, but not quite successfully (Perlinger et al., 1987). The increase of Mg could not be explained, and in fact a decrease is normally observed when H_4SiO_4 increases through silicate weathering, possibly as a result of precipitation of a Mg silicate (Willemsen and Appelo, 1987; Holm et al., 1987). The Mg decrease has also been observed in batch experiments with the aquifer sediments performed by McKinley et al., (1988).

The possibility of cation exchange influencing the water quality has not been considered in the interpretation of the observed composition changes. Perlinger et al. noted that about 1/3 of Na from the softened water was not recovered, although the same amount of water was withdrawn which had been injected. The discrepancy was explained to be a result of dispersion (Perlinger et al., 1987). However, cation exchange with a non-linear isotherm gives a similar dispersion which depends on flow direction.

3.2.1 Modelling cation exchange in recovered water at St. Paul

The cation exchange characteristics of the St. Paul aquifer have not been determined, and neither are the hydraulic parameters (dispersivity, bulk density of the sediment) given in the literature. A few testruns with a geochemical transport model (Nienhuis et al., 1988) have been made with commonly encountered selectivity constants and a varying CEC and dispersivity, using the water quality of source groundwater given by Perlinger et al (1987). The parameters are given in Table 3 (the value for porosity has been provided by Jenne, pers. comm.). A CEC of 60 meq l^{-1} , was adequate to obtain a reasonable fit with observed data (which translates to $0.83 \text{ meq (100g)}^{-1}$ when bulk density is 1.9 g cm^{-3} , and porosity is 25%). The composition and relative amount of the exchange complex in equilibrium with ambient groundwater, and with injected water is shown in Figure 6.

Table 3 Parameters used for modelling chemistry of the long term test cycle at St. Paul.

Basic assumptions

Hydraulic parameters

Aquifer thickness : 30 m	Injected, c.q. recovered : 92100 m ³
Porosity : 0.25	Maximal injection radius, without dispersion : 62.5 m

Water quality, c.q. exchangeable cations

	Na	K	Mg	Ca	
groundwater	0.25	0.2	1.4	2.6	meq dm ⁻³
exchangeable	0.2	1.2	35.0	63.6	% of CEC
injected	4.35	0.05	0.1	0.1	meq dm ⁻³
exchangeable	14.8	1.2	36.0	48.0	% of CEC

Fitted parameters

CEC : 60 meq dm ⁻³	dispersivity : 3.4 m
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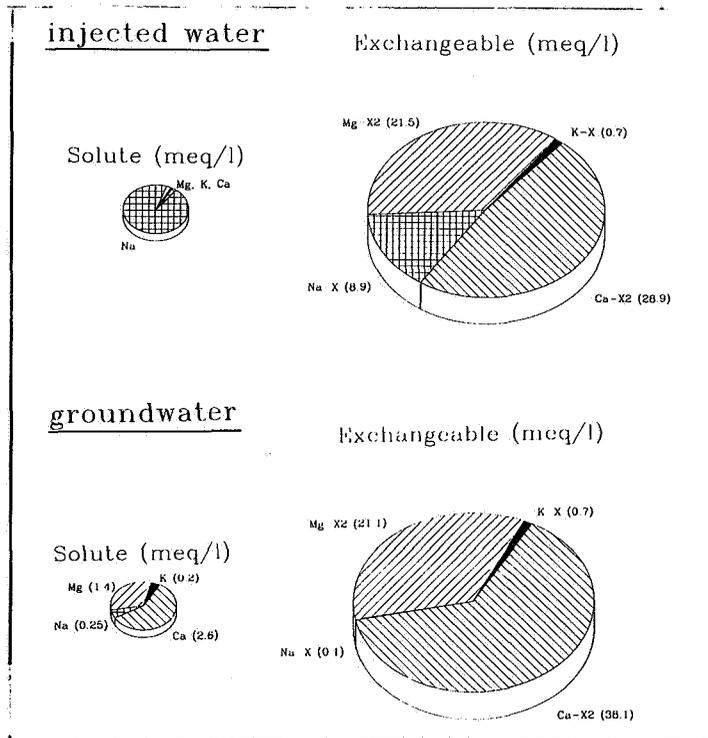


Figure 6 Solute and exchangeable cations in the St. Paul ATES field site

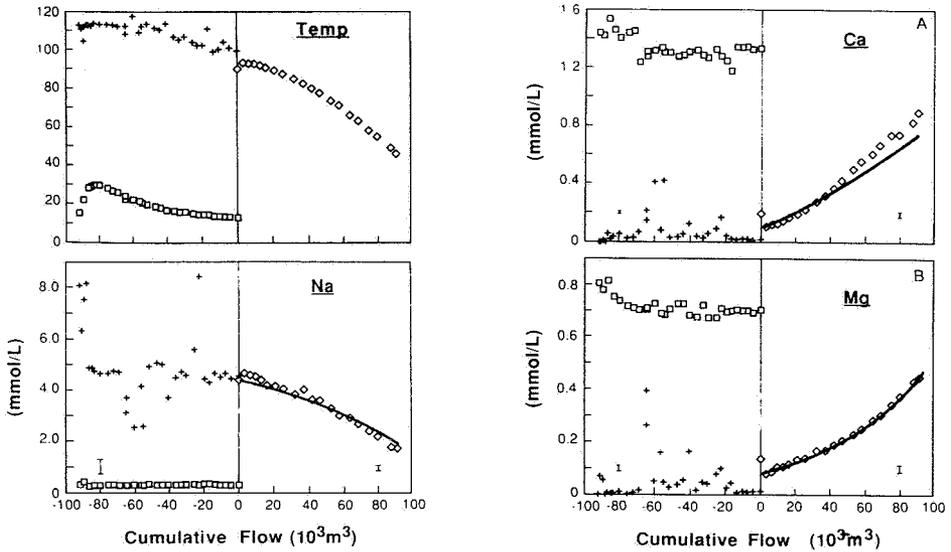


Figure 7 Observed concentrations of Na, Mg and Ca during injection resp. recovery of softened and heated groundwater at St. Paul. Crosses indicate concentrations in source-water, squares idem in injection water after ion exchange, and diamonds idem in recovered water. Drawn lines are modelled concentrations. Also shown the measured temperature of injected and recovered water.

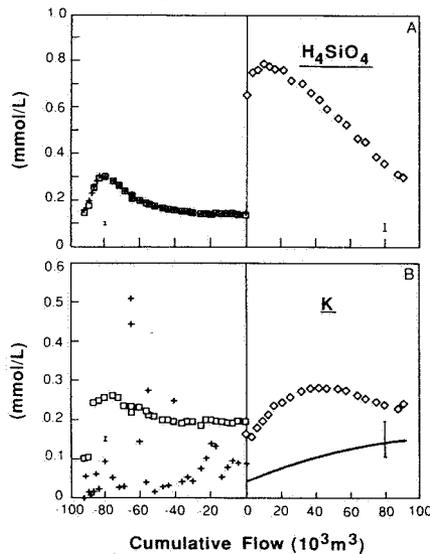


Figure 8 Observed K and Si concentrations in injected and recovered water during the long test cycle at St. Paul (Perlinger et al., 1987). Symbols as explained with Figure 7.

The exchange coefficients have been assumed constant over the range of temperatures encountered when injected water is recovered (decreasing from 100 to 40°C). The observed and simulated concentrations of Na, Mg and Ca are shown in Figure 7, and agree quite closely.

Modelled K concentrations are compared with observed concentrations in Figure 8. The observed increase with respect to model-concentrations is probably caused by dissolution of K feldspar, or K-containing clay minerals, or variation of the K/Ca exchange coefficient as found for Delft sediment (Griffioen, 1990, this volume). In batch experiments reported by McKinley et al. (1989) an increase of K was accompanied by increase of Si, a relation which is not obvious in the field test (Fig. 8). It seems logical that part of the released K is also active in the exchange process, but amounts are small, and of not much influence on exchange of the other cations. The Si concentrations were found to be limited by quartz saturation, so that actual amounts of dissolving K feldspar cannot be calculated without additional assumptions regarding the amount of quartz precipitation.

4 FINAL REMARKS

The model results discussed so far make clear that processes which affect major cation transport in aquifers can now be calculated by computer simulation. An amazingly good fit between experiment and model is possible for processes such as cation exchange and calcite dissolution. These are fairly rapid processes, which achieve equilibrium within the time-span available with slow groundwater flow (less than 100 m yr⁻¹). For calcite a simple, but empirical kinetic model may be adequate to describe dissolution.

Precipitation of calcite is another story, as clearly illustrated in the contributions by Griffioen and Jenne (1990, this volume). Precipitation is hindered by inhibition, by surface poisoning, by formation of solid solutions, and perhaps even other processes induced by components which are active at low concentrations found in natural water. Precipitation of other minerals may be about as complex, at least in the dynamic environment created during ATEs, where large temperature changes cause large supersaturation, and hence may induce precipitation of ill-defined, or amorphous solids. These processes are too complex to be readily modelled at this time.

Dissolution of silicates is in much the same way not well understood at present. Silicate reactions are certainly too slow to assume equilibrium, at least when temperature is not appreciably above 100°C. Many silicates have a flexible crystal structure which allows for a range of solid solutions. Clay minerals are especially notorious in providing a generous accommodation of a variety of cations, in addition to a continuous adaption to environmental changes. Such behaviour is impossible to capture with a model built on simple equilibrium thermodynamics alone. The shortcomings of geochemical modelling are obvious; more empirical laboratory and field study is necessary to further expand the applicability of the model description of nature's variation. Nevertheless, the geochemical models offer the great advantage of showing possible reactions, e.g. indicating the reactions which may be detrimental for heat storage as such. Research on clogging of heat exchangers or injection wells is far easier, when it is based on predictions of possible reactions made by a geochemical model. This same advantage is, of course, valid for research on all hydrochemical processes, also when the puzzles of nature are subject of study.

REFERENCES

- APPELO, C.A.J.; 1985. CAC, Computer Aided Chemistry, or calculating the composition of groundwater with a geochemical computer model. *H₂O* 18, 557-562 (in Dutch).
- APPELO, C.A.J., and WILLEMSSEN, A.; 1987. Geochemical calculations and observations on salt water intrusions. I A combined geochemical/mixing cell model. *J. Hydrol.* 94, 313-330.
- APPELO, C.A.J., WILLEMSSEN, A., BEEKMAN, H.E. and GRIFFIOEN, J.; 1990. Geochemical calculations and observations on salt water intrusions. II Validation of a geochemical transport model with column experiments. *J. Hydrol.*, in press.
- APPELO, C.A.J., GRIFFIOEN, J. and VAN DER WEIDEN, M.J.J.; 1990b. (Bio)geochemical reactions. Subtask B of IEA-Annex VI, 89 p. restricted.
- BRYANT, S.L., SCHECHTER, R.S. and LAKE, L.W.; 1986. Interactions of precipitation/dissolution waves and ion exchange in flow through permeable media. *AIChE J.*, 32, 751-764.

- EARY, L.E., JENNE, E.A., VAIL, L.W. and GIRVIN, D.C.; 1989. Numerical models for predicting watershed acidification. *Arch. Environ. Contam. Toxicol.* 18, 29-35.
- ENGESGAARD, P., and CHRISTENSEN, T.; 1988. A review of chemical solute transport models. *Nordic Hydrol.*, 19, 183-216.
- ENGESGAARD, P.; 1989. Multicomponent solute transport with equilibrium chemistry: tracking a dissolution front. Techn. Univ. Denmark, research note.
- FELMY, A.R., GIRVIN, D.C. and JENNE, E.A.; 1984. MINTEQ - A computer program for calculating aqueous geochemical equilibria. U.S. Environm. Protection Agency, Athens.
- FRITZ, B.; 1975. Etude thermodynamique et simulation des reactions entre mineraux et solutions. *Sci. Geol. Univ. Strasbourg Mém.* 41, 153 p.
- GARVEN, G., and FREEZE, R.A.; 1984. Theoretical analysis of the role of groundwater flow in the genesis of stratabound ore deposits. *Am. J. Sci.* 284, 1085-1174.
- GRIFFIOEN, J.; 1989. Hydrogeochemical column experiments with sediment from a Dutch ATES test facility. Amsterdam, Institute of Earth Sciences, Free University, 103 pp., restricted.
- GROVE, D.B., and STOLLENWERK, K.G.; 1987. Chemical reactions simulated by groundwater quality models. *Water Resour. Bull.*, 23, 601-615.
- HELGESON, H.C., BROWN, T.H., NIGRINI, A. and JONES, T.A.; 1970. Calculation of mass transfer in geochemical processes involving aqueous solutions. *Geochim. Cosmochim. Acta* 34, 569-592.
- HERZER, J., and KINZELBACH, W.; 1989. Coupling of transport and chemical processes in numerical transport models. *Geoderma* 44, 115-127.
- HOLM, T.R., EISENREICH, S.J., ROSENBERG H.L. and HOLM, N.P.; 1987. Groundwater geochemistry of short-term aquifer thermal energy storage test cycles. *Wat. Resour. Res.* (23), 1005-1019.
- HOYER, M.C. and WALTON, M.; 1986. Aquifer thermal energy storage experiments at the university of Minesota, St. Paul, Minesota U.S.A. 21th Intersociety energy conversion engineering conference, San Diego, California, August 25 - 29, 1986. pp. 708-713.
- JAUZEIN, M., ANDRE, C., MARGRITA, R., SARDIN, M. and SCHWEICH, D.; 1989. A flexible computer code for modeling transport in porous media: IMPACT. *Geoderma* 44, 95-113.

- KIRKNER, D.J., and REEVES, H.; 1988. Multicomponent mass transport with homogeneous and heterogeneous reaction: effect of the chemistry on the choice of numerical algorithm I. Theory. *Water Resour. Res.* 24, 1730- 1739.
- LICHTNER, P., and ENGI, M.; 1989. Data bases of thermodynamic properties used to model thermal energy storage in aquifers. IEA-Annex VI, restricted.
- LICHTNER, P.; 1985. Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochim. Cosmochim. Acta* 49, 779-800.
- LIU, C.W., and NARASIMHAN, T.N.; 1989. Redox-controlled multiple species chemical transport. *Water Resour. Res.* 869-882, 883-910.
- McKINLEY, J.P., JENNE, E.A. and SMITH, R.W.; 1988. Experimental investigation of interaction between heated groundwater and sandstone. *Proc. Jigastock 88*, Versailles, France, Vol. (2), 687-691.
- MILLER, C.W., and BENSON, L.V.; 1983. Simulation of solute transport in a chemically reactive heterogeneous system: model development and application. *Water Resour. Res.*, 19, 381-391.
- MORSE, J.W.; 1983. The kinetics of calcium carbonate dissolution and precipitation. In: *Reviews in Mineralogy*, Vol. 11. Carbonates; mineralogy and chemistry, ed. by Reeder, R.J. *Miner. Soc. Am.*, p. 227-264.
- NIENHUIS, P.R., APPELO, C.A.J. and WILLEMSSEN, A.; 1988. Adaptation of PHREEQE in a mixing cell flow tube: PHREEQM. User manual etc., Free University, Amsterdam.
- NORDSTROM, D.K. et al.; 1979. A comparison of computerized chemical models for equilibrium calculations in aqueous systems. in: E.A. JENNE (ed.), *Chemical modelling in aqueous systems*. *Am. Chem. Soc. Symp. Ser.* 93, 857-892.
- PARKHURST, D.L., THORSTENSON, D.C. and PLUMMER, L.N.; 1980. PHREEQE - a computer program for geochemical calculations. *U.S. Geol. Surv., Water Resour. Inv.* 80-96, 210 p.
- 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, 2215-2226.
- PITZER, K.S. and BREWER, L.; 1961. *Thermodynamics*, 2nd ed. (rev. of Lewis and Randall). McGraw-Hill.

- PLUMMER, L.N., et al.; 1976. WATEQF - a FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. US Geol. Surv. Water Resour. Inv. 76-13, 63 p.
- PLUMMER, L.N., PARKHURST, D.L. and THORSTENSON, D.C.; 1983. Development of reaction models for groundwater systems. *Geochim. Cosmochim. Acta* 47, 665-686.
- RUBIN, J.; 1983. Transport of reacting solutes in porous media: relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resour. Res.* 19, 1231-1252.
- SHAVIV, A., and MATTIGOD, S.V.; 1985. Exchange equilibria in soils expressed as cation-ligand complex formation. *Soil Sci. Soc. Am. J.* 49, 569-573.
- SMITH, W.R., and MISSEN, R.W.; 1982. *Chemical reaction equilibrium analysis*. Wiley, New York, 364 p.
- SPOSITO, G. and MATTIGOD, S.V.; 1979. GEOCHEM: a computer program for calculating chemical equilibria in soil solutions and other natural water systems. Univ. California, 110 p.
- VAN OMMEN, H.C.; 1985. The "mixing cell" concept applied to transport of non-reactive and reactive components in soils and groundwater. *J. Hydrol.*, 78, 201-213.
- VERMEULEN, Th., et al.; 1984. Adsorption and ion exchange. in: *Perry's Chemical engineer's handbook*, 6th ed. McGraw-Hill.
- WALTON, M., et al.; 1986. University of Minnesota Aquifer Thermal Energy Storage (ATES) project. Report on the first long-term cycle (draft). St. Paul, Minnesota, PNL, UESP Contractnr. B-97601-A-0.
- WESTALL, J.C., and HOHL, H.; 1980. A comparison of electrostatic models for the oxide/solution interface. *Adv. Colloid Interface Sci.*, 12, 265-294.
- WILLEMSSEN, A., and APPELO, C.A.J.; 1985. Chemical reactions during heat storage in shallow aquifers in the Netherlands: laboratory experiments and geochemical modelling. *Int. Ass. of Hydr.-Ass. Int. des Hydr. Hydrology in the services of man, part 4: energy sources and groundwater control*, pp. 68-78.
- WILLEMSSEN, A.; 1990. Coupled geochemical transport model. Subtask A of IEA-Annex VI, 74 p, (restricted).
- WOLERY, T.J.; 1982. EQ3NR: a computer program for geochemical aqueous speciation-solubility calculations. Lawrence Livermore Lab., California.

A. Willemsen

ABSTRACT

Precipitation of carbonates is a common problem encountered in many cases where hard water is heated. Problems can be prevented by an adequate water treatment. When water treatment is used for ATEs account should be taken of the effects of the resulting change in composition on the water quality. The cyclic nature of ATEs causes a reuse of a part of the water each cycle. Calculations show that for treatment techniques that remove ions a decrease of treatment intensity can be expected. For techniques that only add ions (acid addition) an increase is calculated.

New environmentally sound techniques that have been investigated are addition of chemicals that can be removed (CO_2 addition and degassing) and removal of precipitation after their formation.

When iron containing and oxygenated water are both present in the aquifer, precipitation of ironhydroxide will occur when the water mixes in the well. This precipitate generally causes rapid clogging of production and injection wells.

For those iron related problems two new treatment techniques have emerged from the work in Annex VI: in situ iron removal with nitrate and iron removal with a bioreactor.

From existing ATEs projects (Holm et al, 1987; Perlinger et al, 1987; Qvale et al, 1988; Saugy et al, 1988) and from experiments (Appelo et al, 1990a) it is known that problems due to precipitation of iron and/or carbonates occur frequently. In the following we will assume that water treatment against calcite precipitation will be the adequate treatment against all carbonate scaling. In some cases however, FeCO_3 precipitation may be more troublesome than CaCO_3 precipitation. In that case one should consider whether the treatment against calcite scaling will work against FeCO_3 scaling. In general that will be the case.

Water treatment against calcite scaling is different from water treatment against iron-hydroxide precipitation. Therefore these two are treated separately.

2 CALCITE

2.1 Conventional techniques

Precipitation of calcite ("calcite-scaling") is a very common problem encountered during heating of water. Many different techniques have been developed and used to soften the water before heating in order to prevent scaling. Table 1 gives an overview of possible chemical techniques against scaling. This table has been presented earlier in a less complete form (Willemsen, 1988). The table is organised according to the ion it operates on and the reaction mechanism (homogeneous: in water phase only; hetero-geneous: adsorption/desorption, precipitation of solids, formation of gasses). In all but one cases the free Ca^{++} and/or CO_3^{--} concentration is lowered by the water treatment. Only inhibition does not effect the Ca^{++} and/or CO_3^{--} concentration but instead influences the crystallization process.

Techniques that are frequently used are acid addition, Na exchange, H^+ exchange combined with degassing, precipitation of CaCO_3 by Ca(OH)_2 or NaOH and inhibition with (poly)phosphates or (recently) acrylates.

Table 1 Overview of chemical treatment techniques against calcite scaling

ion \ reaction	solution	ion-exchange	gasses	solids
Ca ⁺⁺	Ca ⁺⁺ + 2L → CaL ₂	Ca ⁺⁺ + 2NaX → → CaX ₂ + 2Na ⁺	X	other Ca-salts e.g. 5Ca ⁺⁺ + 3HPO ₄ ⁻ + H ₂ O → → Ca ₅ (PO ₄) ₃ OH(s) + 4H ⁺
Both	Ca ⁺⁺ + 2HL + CO ₃ ⁻ → → CaL ₂ + H ₂ CO ₃	2HX + Ca ⁺⁺ + CO ₃ ⁻ → → H ₂ CO ₃ + CaX ₂	X	Ca ⁺⁺ + Ca(OH) ₂ + 2HCO ₃ ⁻ → → 2CaCO ₃ (s) + 2H ₂ O Ca ⁺⁺ + NaOH + HCO ₃ ⁻ → → CaCO ₃ (s) + Na ⁺ + H ₂ O
CO ₃ ⁻	2H ⁺ + CO ₃ ⁻ → H ₂ CO ₃	2ClX + CO ₃ ⁻ → → CO ₃ X ₂ + 2Cl ⁻	H ₂ CO ₃ → CO ₂ (g) + H ₂ O	other carbonates e.g. Fe ⁺⁺ + CO ₃ ⁻ → FeCO ₃ (s)

L = Ligand (complexing solute) ; X=Exchanger ; (g) = Gas ; (s) = Solid

A number of factors play a role in heat storage which are quite anomalous in comparison to the application of water treatment for industrial cooling processes or the softening of drinking water for example. During ATES the treated water is injected into an aquifer. By dispersion (mixing), free convection, and regional groundwater flow, part of the water injected is lost from the store. This means that account should be taken of the consequences of the treatment for the groundwater quality, especially when an aquifer containing fresh water is used. A portion of the treated water is recovered and used again in the subsequent cycles. It is not impossible that the treatment intensity will increase because of re-dissolution of calcite on cooling. Both aspects (losses and reactions) play an important role in the determination of the suitability of treatment techniques for heat storage.

2.2 Processes in the aquifer

2.2.1 Losses

The losses of water can be divided in losses that are caused by dispersion (and diffusion) and losses that are caused by groundwater flow through the store (by buoyancy flow or regional flow). The losses that are due to dispersion gradually decrease because the gradient

at the store boundary decreases by the presence of water losses from previous cycles. In the 'equilibrium - situation' (which might or might not be reached in the life-time of a store) all losses (including those due to buoyancy and regional flow) are stable. A third type of losses of water occurs due to the fact that the amount of water injected in the store might not be the same as the amount withdrawn. These amounts are determined by the supply and demand of energy to and from the store and will in general not result in equal volumes of water for injection and production. This type of losses is minimal if injection and production wells are close to each other (short circuiting of water). The losses due to dispersion and buoyancy flow can be estimated with a transport model like HST3D (Kipp, 1987) or HST2D (Hagoort, 1989). Losses due to regional flow and unequal volumes of injection and recovery can be modelled with HST2D as well, but these effects can also (easier) be estimated with a streamline model like ATESSS (Vail et al, 1988) or MFLOP (Van den Akker et al, 1986).

2.2.2 Reactions

Water that is treated, heated and injected into an aquifer will react with the aquifer material due to the temperature change and due to the change in composition caused by the treatment. Experiments in the laboratory and in the field (see Appelo et al, 1990a) have demonstrated that the most important reactions are the precipitation and dissolution of carbonates (especially Ca, Mg and Fe carbonates) and ion exchange.

All reactions will tend to counteract the change that is driving the reaction. Therefore a treatment that reduces the Ca concentration might be counteracted by the dissolution of calcite and the release of Ca from the cation exchange complex (CEC). Because the water that is injected into the aquifer is partly reused in the next cycle (after cooling and injection in the 'cold' well) these reactions together with the losses from the store, determine the water quality before treatment in the next cycle. This water quality again determines the intensity of the treatment (e.g. the amount of Ca that has to be removed) in next cycles. For the design, the exploitation costs and the environmental effects of the treatment it is important to know whether a treatment will increase or decrease in intensity and how fast it will increase or decrease. Different treatment techniques will cause different counteracting reactions and will have a different increase or decrease in intensity. These effects can be

calculated with a computer model that couples heat and solute transport to chemical reactions.

2.3 Modelling of geochemical reaction

In order to identify the differences between treatment techniques and to present (if possible) some general rules, calculations have been performed with the coupled chemical transport model CHARM1. For a general description of this model we refer to Appelo and Willemssen (1987), Willemssen et al (1988), Appelo et al (1990b) and Willemssen (1990). In this model chemical reactions can be calculated for up to 20 minerals simultaneously as long as equilibrium between minerals and solution holds. Kinetic calculations can be performed for one mineral. The model also includes cation exchange. Transport of heat and solute is calculated along one streamline. A 2D coupled chemical transport model called HSTAR which replaces CHARM1 has been developed recently (Willemssen, 1990).

CHARM1 is used to calculate the trends in water quality using the following water treatments: HCl addition, CO₂ degassing after HCl addition, Ca-Na exchange and removal of the amount of CaCO₃ supersaturated at the injection temperature.

During the calculations only equilibrium with calcite and (temperature dependent) ion-exchange are assumed to be active as chemical processes. Further, the following assumptions were made:

- * constants for cation exchange are as in Table 2
- * water composition is as in Table 3
- * CEC = 0.5 meq/100 gram (coarse sand)
- * 4 cycles of storage
 - cycle 1: charging of 12.000 m³ from 10 to 60°C during 3 weeks, storage for 3 weeks and discharging of 12.000 m³ in 3 weeks to the 'cold' side with cooling to 50°C (as far as applicable).
 - cycle 2,3,4: charging of 12.000 m³ from the 'cold side' temperature (appr. 40 to 50°C) to 90°C (in 3 weeks time), storage during three weeks and discharging of 12.000 m³ as in the 1st cycle.
- * transport and reactions in both 'hot' and 'cold' side are modelled. There is no 'short

circuiting' between the two sides. A schematic representation of the application of CHARM1 for this situation is given in Figure 1.

Table 2 Cation exchange constants fitted to the results from column experiments (see Willemsen, 1990). Values are for exchange with respect to NaX ($\text{NaX} = 10^{14}$)

Adsorbed complex	K	dH_r (Kcal/mol)
KX	10.0	- 2.0
$\text{Ca}_{\frac{1}{2}}\text{X}$	2.0	1.0
$\text{Mg}_{\frac{1}{2}}\text{X}$	1.6	1.0
NH4X	5.0	- 0.5

Table 3 Water composition used in the calculations (in mmol/l; except pH)

pH (-)	6.38
Ca	10.1
Mg	2.98
Na	30.5
K	0.35
NH_4	1.10
HCO_3	15.6
SO_4	0.15
Cl	40.1

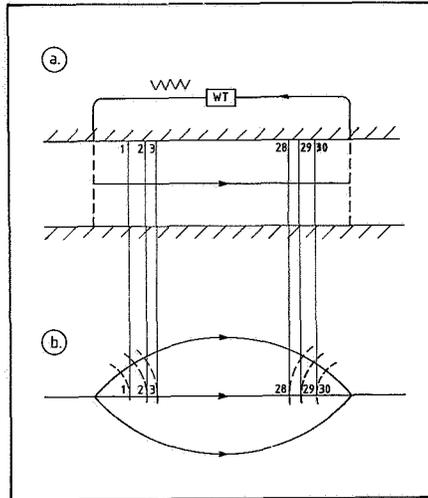


Figure 1 Schematic representation of application of CHARM1 for calculations on water treatment

Figure 2 shows some of the results for two of the four treatment techniques. For decarbonation (Figure 2a) the assumption is made that CO_2 is removed after addition of HCl. The amount of CO_2 produced from the cold well determines the intensity of treatment. It is clear that the CO_2 concentration produced from the cold well diminishes as the number of cycles increases.

When the degassed water is injected (Figure 2b) calcite is dissolved around the hot well. During production from the hot well calcite precipitates in the aquifer around the hot well due to water being heated by the grain skeleton. The amount of calcite dissolved is greater than the amount precipitated, so clogging of the aquifer by calcite deposits is not likely.

Water treatment by precipitation of calcite during heating (e.g. in a fluidized bed heat exchanger) or after heating (as applied by St. Paul, see Holm et al, 1987) results in a certain amount of calcite being deposited in the precipitator (Figure 2c). Surprisingly, the amount of calcite precipitating around the hot well (Figure 2d) is about the same as the amount in the precipitator. This is caused by the supply of Ca from the cation exchange complex (CEC). The quantity precipitated (3 mmol/l, about 0.01% of the porosity per time step) is such that

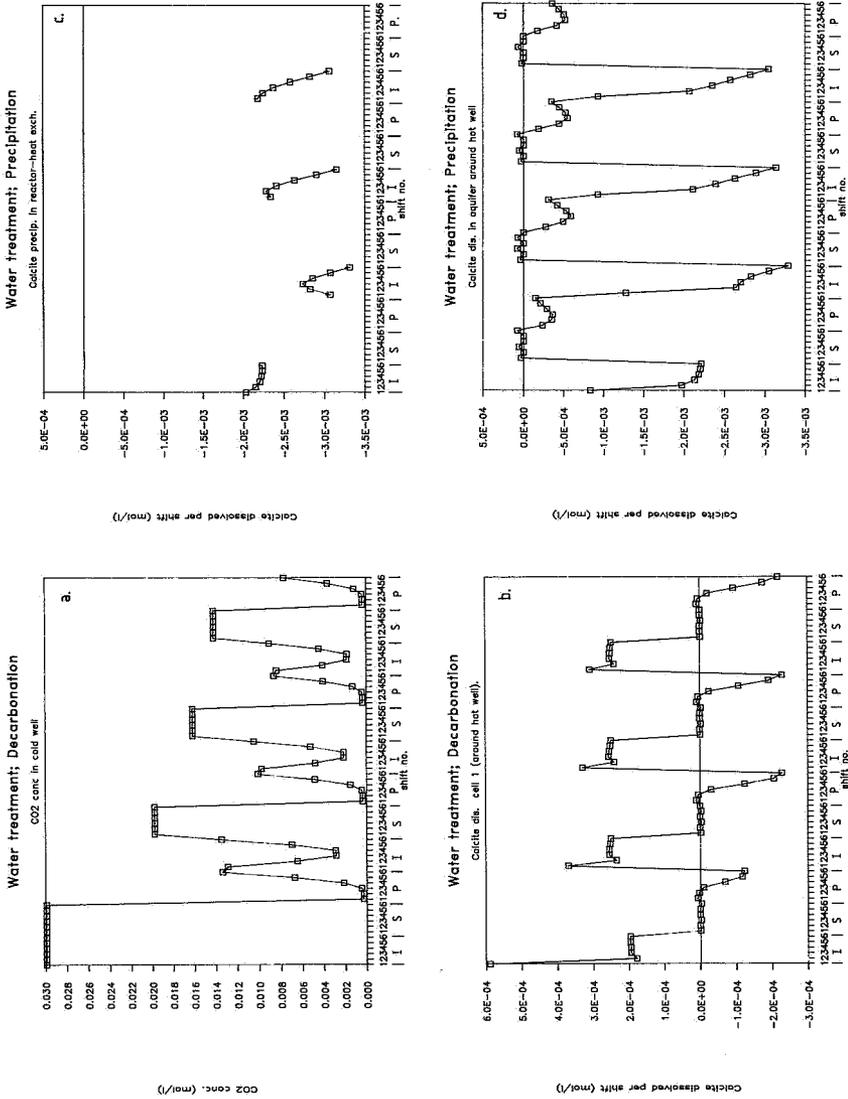


Figure 2 Computed effects of water treatment during heat storage. a and b: decarbonation. c and d: precipitation. a: CO₂ concentration in cold well. b: calcite dissolution in aquifer around hot well. c: calcite dissolution in precipitator (negative = precipitation). d: see b. I: charging S: storage P: discharging

after a long period of operation of the store some clogging may occur around the well. To draw conclusions on this issue it will be necessary to make more detailed computations which also includes the kinetics of the precipitation reaction.

A comparison of the amounts of chemicals added for the four treatment-techniques is given in Figure 3 and 4.

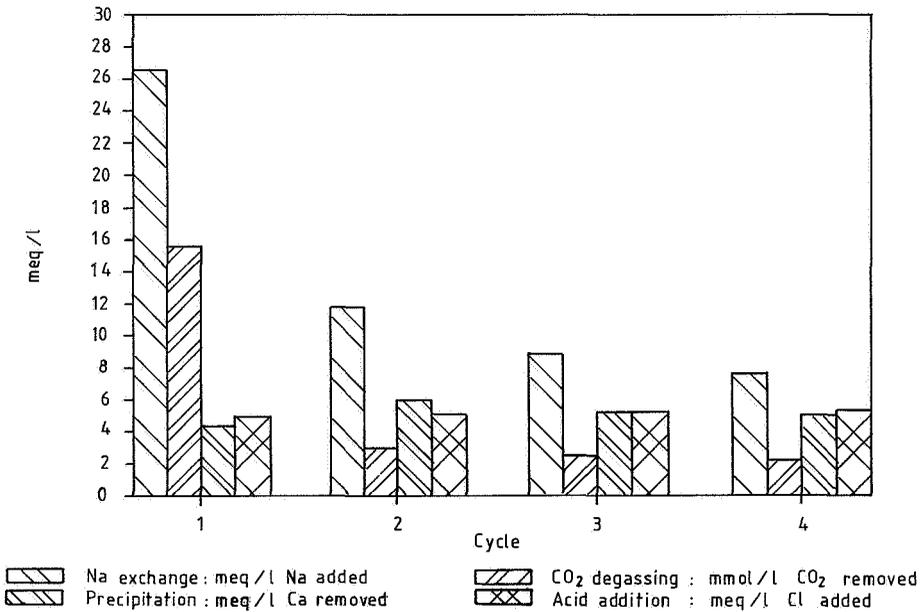


Figure 3 Calculated amount of chemicals added/removed for 4 different treatment techniques for the first 4 cycles

Figure 3 shows that Na exchange requires the most equivalents, due to the fact that apart from Ca, also Mg is exchanged. During the first cycle CO₂ degassing requires the most treatment (after Na exchange), while after the first cycle CO₂ degassing requires the least treatment. During the fourth cycle acid addition is the treatment that requires the most equivalents after Na exchange. During the second cycle, acid addition requires the least treatment. Precipitation of calcite only removes the excess amount of calcite.

Figure 4 shows the relative amounts of treatment (relative to the amount in the first cycle). Decarbonation and Na exchange show a clear decreasing amount of treatment, while acid

addition shows an increase in necessary amounts of treatment. Precipitation of calcite is the only treatment that is sensitive to the storage temperature.

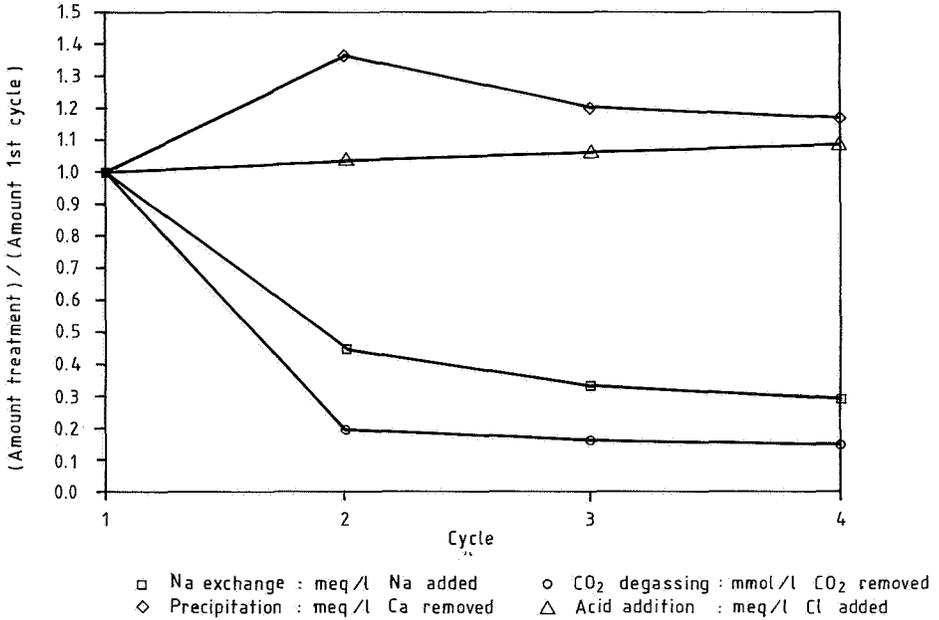


Figure 4 As Figure 3; amounts divided by the amount for the first cycle

In the first cycle only the amount supersaturated at 60°C is removed. During the following cycles the amount supersaturated at 90°C is removed. With constant storage temperature, the amount of calcite removed per cycle decreases slightly.

From the scheme in Table 1 and the previous results we can derive several classes of treatment techniques that have similar effects when used for ATEs.

- Class 1. Acid addition and complexation, are techniques that operate on the water phase, and these techniques will increase in required dosage each cycle, because the added chemical will move with the water to the cold side, where dissolution of calcite will occur. H⁺ exchange without degassing also belongs to this class.
- Class 2. Cation exchange (generally Na⁺ exchange). When Na exchange is used the required treatment decreases each cycle. The slope of the decrease is dependent

on three parameters: the amount of dissolution of calcite at the cold side (can be minimized using split treatment), the losses of water from the store (the higher the losses the less the decrease) and, probably most important, the CEC in the aquifer. For the treatment to decrease to zero, all other cations will have to be removed from the CEC in the aquifer.

Class 3. CO₂ degassing can be performed after H⁺ exchange or after acid addition. As shown in Figure 7a and 7b, this techniques shows the strongest decrease in required treatment, because practically no dissolution of calcite can occur in a solution free of CO₂ and because CO₂ is not buffered in the aquifer by the CEC (It may however be buffered by organic material).

Class 4. CaCO₃ precipitation.

In this case it is assumed that only the amount supersaturated at the higher temperature is removed. This may be hard to achieve using (Ca or Na) hydroxide dosing, but it can be achieved with the proposed fluid bed water treatment/heat exchanger (see under 2.5). Using hydroxide dosing, generally more calcite will be removed then is supersaturated at the required temperature. With calcite precipitation Ca⁺⁺ is the only cation removed from the solution. This implies that there will be an important amount of buffering of Ca from the CEC in the aquifer, as with Na exchange. However, Na exchange also removes Mg from solution, which means that the CEC will buffer Mg and Ca, causing a lower buffering of Ca then in the case of Calcite precipitation. An other important difference is that Na exchange removes more Ca then calcite precipitation. Both phenomena cause a lower decrease of treatment intensity for CaCO₃ precipitation.

2.4 Environmental effects of water treatment

The environmental effects of the water treatment consist mainly of a change in the groundwater composition and, when using ion exchange in a disposal of salts to surface water. Other possible effects (constructions, risk of leakage of chemicals, etc.) are not investigated, they depend mainly on local circumstances.

Table 4 summarizes the primary environmental effects of some treatment techniques.

The techniques are ranked approximately according to increasing environmental effects. Softening with precipitation of calcite with Ca(OH)_2 only results in a decrease of Ca and CO_3 concentrations. This also holds for H^+ exchange (where Mg also decreases), but with H^+ exchange salts (neutralized acids) have to be disposed of to surface water. Of course the local environmental effects will depend on the local natural groundwater quality (e.g. brackish or fresh) and surface water availability and quality. Local circumstances might therefore change the order in Table 4. The ranking in Table 4 according to environmental effects (lowest effects on top) coincides with an inverse ranking according to costs (highest on top). For heat storage it is important to have affordable environmentally sound treatment techniques available. Therefore some new techniques were proposed.

Table 4 Effects on the waterquality of different water treatment techniques against calcite scaling.

Technique	Groundwater	Surface water
1. precipitation with Ca(OH)_2	$\text{Ca, CO}_3 <$	-
2. precipitation with NaOH	$\text{Ca, CO}_3 < , \text{Na} >$	-
3. H^+ exchange with CO_2 degassing	$\text{Ca, Mg, CO}_3 <$	Ca, Mg-salt disposal
4. Na^+ exchange	$\text{Ca, Mg} < , \text{Na} >$	Na, Ca, Mg-Cl disposal
5. HCl addition + CO_2 degassing	$\text{CO}_3 < , \text{Cl} >$	-
6. HCl addition	$\text{pH} < , \text{Cl} >$	-

2.5 New techniques

Two ways have been followed to come to other treatment techniques:

1. Use additives that can be removed. These techniques can then follow the cyclic character of ATES (add when heating, remove when cooling).
2. Use techniques that remove the precipitate after having formed. This principle has led to the following techniques:
 - a. remove the precipitate discontinuously from the heat exchanger by dissolution with a (non-corrosive) acid in a separate closed loop;
 - b. remove the precipitate continuously from (or prevent it from forming in) the heat exchanger with the aid of (fluidized) scraping solid particles;
 - c. let the precipitation take place on a (removable, fluidized) bed of solid particles in the heat exchanger.

2.5.1 Removable additives

An additive that can be removed is CO_2 . Addition of CO_2 results in a lowering of pH and a higher solubility of carbonates. Addition should take place before heating, removal can be accomplished through degassing after cooling. Addition of CO_2 to prevent carbonate scaling is used frequently in oil- and geothermal industry (see Greulich, 1988). Degassing is also a known technique, so the combination should be quite feasible. A potential problem of this technique is the corrosiveness of CO_2 gas.

2.5.2 Removal of precipitates after formation

a. Dissolution.

A schematic representation of a system that removes scale from the heat exchanger discontinuously is as follows. If a heat exchanger is clogged, or if its thermal power is reduced below a certain limit, the ATES system will use the other exchanger (or stop in the case of one exchanger). The exchanger can now be cleaned with acid (preferably HNO_3 , because it is hardly corrosive; with H_2SO_4 gypsum might form). The acid is reused until it is saturated with salts, or until the pH has risen too much. The heat exchanger will have to be overdimensioned to permit the scaling in the exchanger. The

costs for this overdimensioning may be an important part of the costs for this treatment method.

b. Mechanical removal of scale.

Scale can be removed by mechanical abrasive actions like scrubbing and scraping. Known methods are the 'Taprogge'-system for 'shell and tube' heat exchangers. This system uses rubber balls that move in the tubes. This system is in use especially for condensers of power plants that use river water. Bio-fouling in the exchanger is prevented with this system. A similar system is the 'Technos'-system, that uses small plastic balls to scrape the surface (see Figure 5). This system can be used both in 'shell and tube' and in plate heat exchangers. It has been tested at SPEOS (Switzerland), on a scaling plate heat exchanger. The tests showed that the balls scaled and then clogged the heat exchanger. In future this system will be tried out in combination with a regular cleaning of the balls with acid. Both in the 'Taprogge' and in the 'Technos' system two baskets in the tubes hold the balls. Regular switching of the baskets move the outgoing balls to the incoming flow.

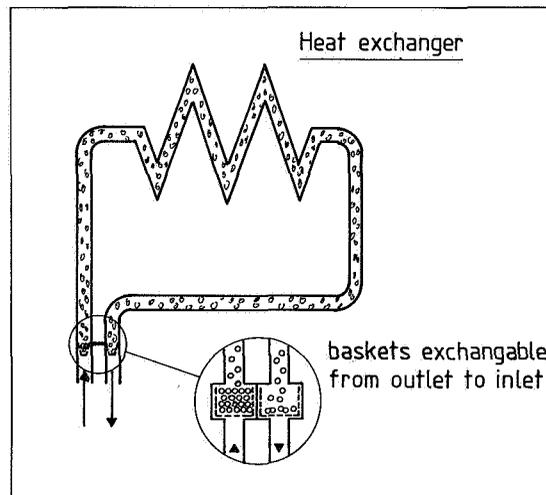


Figure 5 Schematic representation of the 'Technos system' for continuous mechanical cleaning of a heat exchanger

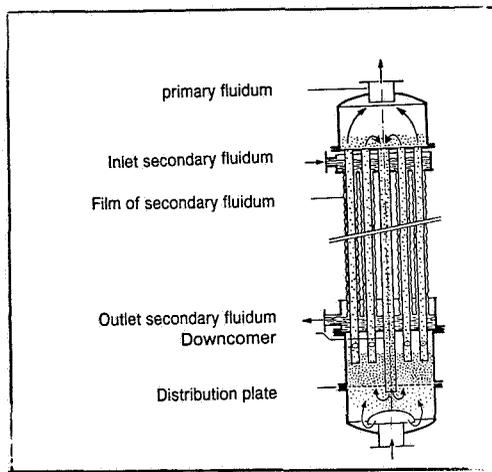


Figure 6 FBHX with falling liquid film on secondary side (from Klaren and Bailie, 1988)

Another type of mechanical removal of scale is the fluidized bed heat exchanger (FBHX) developed by Klaren (1975), and produced by Scheffers/ESKLA in the Netherlands. A schematic representation of the FBHX is given in Figure 6. This heat exchanger can be used in (strongly) fouling and scaling environments.

The scraping effect of the fluidized particles prevents the adherence of solids on the surfaces in the exchanger. The particles also create a larger heat transfer across the tubes than would be the case without particles. A possible disadvantage of the use of this heat exchanger for ATEs is that the scale might form after the heat exchanger. This has also been measured at some places where this heat exchanger is used for scaling waters. During ATEs the scale might cause clogging of the wells and the aquifer.

2.5.3 Precipitation of scale on pellets in the heat exchanger

Scaling after the heat exchanger can be prevented by letting the precipitation take place on a fluidized bed of solid particles in the heat exchanger (see Figure 7). The difference between the FBHX by Scheffers/ESKLA and this combined FBHX and reactor lies primarily in the flow velocity of the scaling fluid.

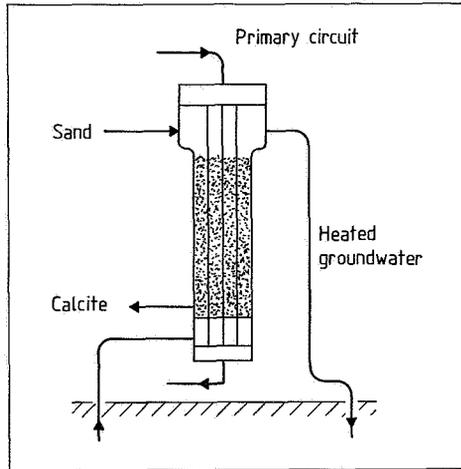


Figure 7 Reactor-FBHX for precipitation of scale on pellets in the exchanger. (Patent applied for by IF Technology)

The residence time of the scaling fluid in the reactor is much larger than the residence time in a FBHX. As fluidized solid particles sand can be used. Once the particles have grown with calcite to a certain size, the particles can be removed (and sold to users of calcite). New sand is then added to the reactor. In fact this reactor-FBHX is closely related to the Fluidized Bed Pellet reactor installed at the Amsterdam Municipal Drinking Water Plant (see Graveland et al, 1983).

In the pellet reactors at Amsterdam NaOH is added and calcite precipitates on a fluidized bed of sand particles. In the Reactor-FBHX heat is added instead of NaOH. The Reactor-FBHX is now in development by IF Technology in cooperation with ESKLA/Scheffers (sponsored by NOVEM, the Netherlands Agency for Energy and the Environment). Experiments in the laboratory are in progress.

2.6 Investment costs

Investment costs for the different treatment techniques depend strongly on local conditions like safety regulations, choice of materials, temperature levels, water quality etc. Because it

is important to be able to compare techniques also on costs an indication of investment costs is summarized in Table 5.

Table 5 Indication of the range of investment costs (in Dutch guilders per m³/h capacity) for water treatment against calcite scaling for 30 to 300 m³/h capacity, without split treatment.

Technique	Investment costs
Acid addition	500 to 1.000
Pellet reaction softening	2.000 to 4.000
H ⁺ , Na ⁺ exchange	2.000 to 4.000
CO ₂ degassing (CO ₂ towers)	2.000 to 4.000
FBHX ^{*)}	1.000 to 3.000
Reactor-FBHX ^{*)}	1.000 to 3.000

^{*)} also dependent on the temperature difference (dT) between primary and secondary circuit

This table shows that acid addition will often be the cheapest technique. However, because of corrosion risks and environmental effects an other treatment technique will often be selected. Without split treatment the other chemical treatment techniques cost about the same, and the selection will depend on all kinds of local circumstances (of which the available space will often be important). The two thermal techniques will often be cheaper then chemical techniques (without split treatment), provided the dT across the exchanger is high enough.

3 IRON

Precipitation of iron is a known problem when anaerobic groundwater comes into contact with oxygen. Prevention of the entrance of oxygen (air) into the system is possible by maintaining an overpressure (with respect to atmospheric) in the system at all places.

Problems with iron precipitation can still occur when iron-containing and oxygenated waters are both present in the storage aquifer and mix in or near the wells. In that case iron removal is necessary. A conventional treatment to remove iron consists of aëration and filtration. This treatment however has high investment costs. An other (existing) treatment method is the 'Vyredox' iron removal technique that precipitates iron in the aquifer by injection of oxygenated water in boundary wells (see Hallberg and Martinell, 1976). However, this method does not always work (see Appelo et al, 1990a), and until now it has been unpredictable whether the method would work or not under given circumstances. New techniques have therefore been investigated within Annex VI.

3.1 New techniques

Two new techniques have emerged that are promising: 'Vyredox' treatment with NO_3^- instead of O_2 (Vanek, 1989) and a so called bioreactor (see Greulich, 1988).

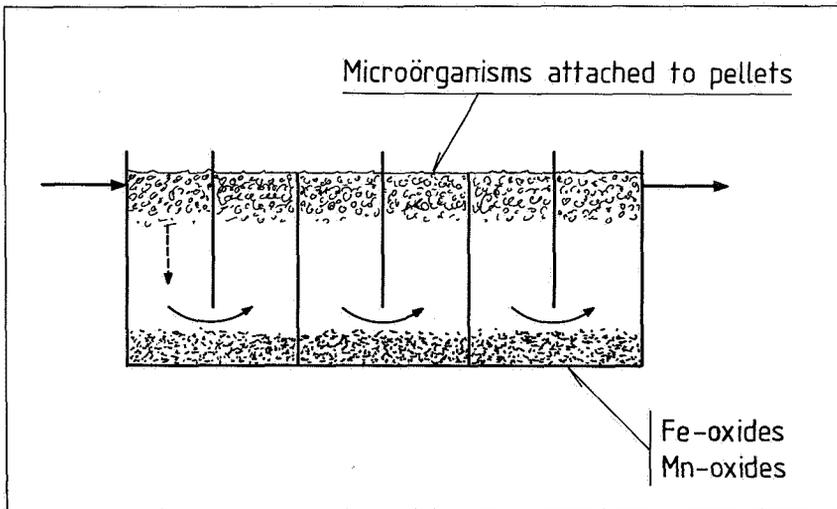


Figure 8 Bioreactor for the removal of iron (and manganese). Developed in Finland.

With the 'NO₃ method' NaNO_3 is added to boundary wells. Results from a field test in Sweden (Vanek, 1989) indicate that the method might work well. Further research will be necessary before this technique could be implemented commercially. One of the aspects to

be studied further is the environmental effect of the addition of NO_3 .

A bioreactor has been developed in Finland (see Greulich, 1988). A schematic representation of the reactor is given in Figure 8. The principle of the reactor is that microorganisms that oxidize iron are attached to floating pellets. This makes the process considerably faster than in normal aeration reactors. For the bioreactor a patent is applied for by a Finnish company.

REFERENCES

- APPELO, C.A.J., GRIFFIOEN, J. and V.D. WEIDEN, M.J.J.; 1990a. Environmental and chemical aspects of thermal energy storage in Aquifers and Research and Development of Water treatment Methods. Subtask B (Bio)geochemical reactions - 91 pp.
- APPELO, C.A.J. and WILLEMSEN, A.; 1987. Geochemical calculations and observations on salt water intrusions I. A combined geochemical mixing all model. *J.Hydrol.* 94, p. 313-330.
- APPELO, C.A.J., WILLEMSEN, A., BEEKMAN, H.E., and GRIFFIOEN, J.; 1990b. Geochemical calculations and observations on salt water intrusions II. Validation of a geochemical model with laboratory experiments *J.Hydrol.* (In press).
- GRAVELAND, A., VAN DIJK, J.C., DE MOEL, P.J., OOMEN, J.H.C.M.; 1983. Developments in water softening by means of pellet reactors. *Journal AWWA* (75) 12.
- GREULICH, R.H.; 1988. Progress in the development of new water treatment methods related to groundwater heat storage. *Proc. Jigastock Conference Versailles, October 1988, Volume II* p. 663 - 673.
- HAGOORT; 1989. HST2D-PC. Heat and solute Transport simulation for personal computers. Hagoort, Delft, The Netherlands.
- HALLBERG, R.O. and MARTINELL R.M.; 1976. Vyredox - in situ purification of groundwater. *Groundwater* 14 (2).
- HOLM, T.R.; EISENREICH, S.J., ROSENBERG, H.L. and HOLM N.P.; 1987. Groundwater geochemistry of short-term aquifer thermal energy storage test cycles.

Water Resour. Res. 23(6):1005-1019.

- KIPP, K.L.;1987. HST3D: A computer code for simulation of heat and solute transport in three-dimensional groundwater flow systems. USGS-water Resour. Inv. Rep. 86-4095.
- KLAREN, D.G.; 1975. Development of a vertical flash evaporator. Ph. D. Thesis - Delft, The Netherlands.
- KLAREN, D.G. and BAILIE, E; 1988. Fluid bed heat exchangers solve fouling problems. American papermaker, february 1988 p. 32-33
- PERLINGER, J.A., ALMENDINGER, J.E., URBAN, H.R. and EISENREICH, S.J.; 1987. Groundwater geochemistry of aquifer thermal energy storage: long term test cycle. Water Resour. Res. 23 (12) 2215-2226.
- QVALE, B., SCHLEISNER-IBSEN, L., and JØRGEN ANDERSEN, L.;1988. The Danish aquifer energy storage project - operational experience. Proc. Jigastock Conference, Versailles, October 1988, vol. I p 287-290.
- SAUGY, B., MISEREZ, J.J., and MATTHEY, B; 1988. Stockage saisonnier de chaleur dans l'aquifère (SPEOS). Resultats de 5 ans de fonctionnement Proc. Jigastock Conference, Versailles, October 1988 vol. I p 325-336.
- VAIL, L.W., KANNBERG, L.D. and KINCAID, C.T.; 1988. Aquifer thermal energy storage system simulator (ATESSS). User's manual and report (Draft) - Pac. Northwest Lab. PNL - UC - 94e.
- VAN DEN AKKER, C., VERRUIJT, A. and HEMKER C.J.; 1986. Microcomputer Flow Pattern Analysis. Free University Amsterdam.
- VANEK, V.;1989. In situ treatment of iron - rich groundwater by the addition of nitrate in Knislinge, Sweden - Final report. 35 pp VIAK AB Malmö, Sweden.
- WILLEMSEN, A.; 1988. Geochemistry and environmental effects of heat storage in aquifers. Proc. and Inf. TNO Comm. Hydrol. Res.; no 40 pp 31-45.
- WILLEMSEN, A.; 1990. Environmental and chemical aspects of thermal energy storage in aquifers and research and development of water treatment methods; Subtask A: coupled geochemical transportmodel.
- 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. Proc. Jigastock, Versailles, October 1988 Volume II p. 591 - 597.

RESEARCH ON HYDROCHEMISTRY AND WATER TREATMENT FOR HEAT STORAGE IN AQUIFERS: STATE OF THE ART

A.L. Snijders

ABSTRACT

In 1987 eight IEA countries decided to start a research activity, entitled "Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods". During the first Phase of this research activity, a coupled geochemical-transport model has been developed and basic research was conducted to the hydrochemical and microbial processes in the aquifer as a result of aquifer thermal energy storage (ATES). Furthermore conventional water treatment methods to prevent precipitation were evaluated with respect to effectiveness and environmental effects. Eight techniques with little or no adverse environmental effects are identified for further testing. Some of these treatment methods are based on new concepts. Field testing of these water treatment techniques will be performed as part of Phase II of this IEA research activity. As part of this second Phase, two generally applicable procedures will be developed also. One procedure to select the best water treatment method for a new ATES site and the other to assess the environmental impacts of an ATES project.

1 INTRODUCTION

In the early eighties several projects have been realized with storage of high temperature heat in an aquifer. Most of these projects started as a pilot project with the aim to get

experience with this new technology and to integrate the aquifer storage in an energy system later on. Examples are the following projects:

- The SPEOS project in Lausanne, Switzerland. The maximum storage temperature is about 90°C (Saugy et al, 1988).
- The Hørsholm project in Denmark with a storage temperature of about 100°C (Qvale et al, 1988).
- The St. Paul Field Test Facility in USA, maximum storage temperature about 140°C (Hoyer et al, 1985).

From experience with aquifer thermal energy storage (ATES) at high temperatures, the following conclusions can be drawn:

- Heating the groundwater often results in precipitation of dissolved minerals. This precipitation mainly consists of carbonates and takes place inside and after the heat exchanger.
- Precipitation of iron hydroxide can be prevented by avoiding oxygen to enter into the system. However, iron hydroxide (and also manganese hydroxide) may precipitate when different water types are withdrawn from the same well.
- The application of a precipitator for calcite prevents well clogging, but does not solve the clogging problem for the heat exchanger.
- Current water treatment methods like addition of hydrochloric acid or ion exchange are effective to prevent calcification. However, the reliability of these methods over a longer period of time is questionable, because of the lack of information on the interaction between the treated water and the aquifer material.
- The addition of chemicals to the groundwater may deteriorate the groundwater quality, and render the water unsuitable for other purposes. This applies particularly when heat is stored in an aquifer that is used also for the production of tap water.
- The addition of hydrochloric acid as a water treatment method has resulted in system operation failures due to corrosion.
- Well clogging due to biomass, as encountered for instance at the infiltration of surface water into aquifers, has not occurred at high temperature ATES projects so far.
- There is lack of knowledge on the effect of heat storage on the development of (pathogeneous) micro organisms. This may obstruct the implementation of aquifer heat storage.

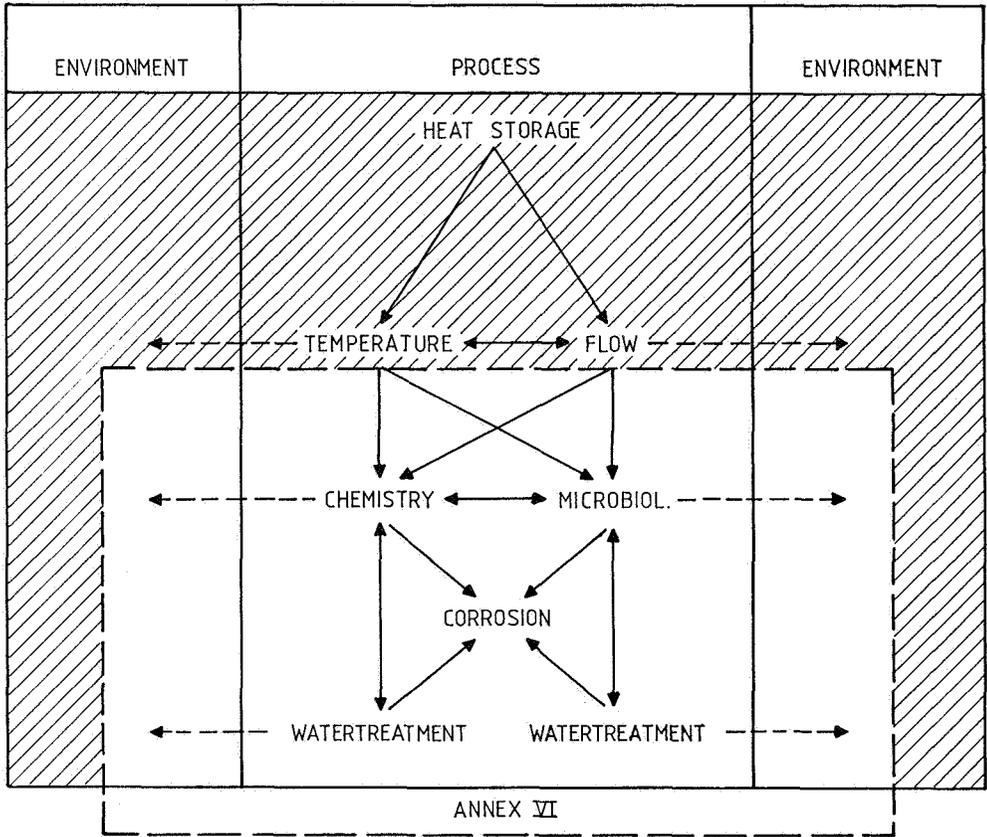


Figure 1 Relation and interaction between the processes at aquifer heat storage.

Figure 1 gives the relation and interaction between the processes taking place at heat storage. In the aquifer there is an equilibrium between the chemical species in the solid phase and the solution. Heating the water causes the equilibrium to change. Moreover, there is also a balance between the micro organisms in the aquifer and the availability of nutrients. This balance, too, is disturbed by temperature change and also by groundwater flow.

The relation between water treatment against precipitation and groundwater composition on

one hand and corrosion on the other hand was mentioned before. Water treatment to avoid undesired microbial effects results in the same kind of interactions.

Adverse environmental effects may result from the change of temperature and the induced groundwater flow themselves, the water treatment methods applied, and the change of the chemical and microbial equilibria.

2 IEA RESEARCH

As a result of the experience with the pilot aquifer heat storage projects, in 1987 eight IEA countries decided to start a systematic investigation to the chemical, microbial and environmental impacts of ATEs and consequently to the development of reliable, environmentally sound water treatment methods. This research is conducted in the framework of the IEA "Implementing Agreement for a Programme of Research and Development on Energy Conservation through Energy Storage". The countries participating in this so called Annex VI (the sixth R&D task under the Energy Storage Agreement), are Canada, Denmark, Finland, Federal Republic of Germany, The Netherlands, Sweden, Switzerland and the United States of America.

The distribution of groundwater and heat in the soil does not form a part of the research within the framework of Annex VI (see also figure 1). About these aspects, sufficient information is available already from other sources.

The objectives of Annex VI are (IEA, 1987):

- A. To develop and verify a coupled geochemical-transport model.
- B. To analyse the (bio)geochemical reactions and related environmental impacts caused by heat storage in different aquifers.
- C. To classify and analyse different water treatment techniques for heat storage, both existing techniques and new concepts.
- D. To analyse by theory and experiment the microbiological processes during thermal energy storage.
- E. To analyse scaling and corrosion problems in installations connected to aquifer heat

stores.

F. To test selected water treatment techniques and evaluate their environmental effects.

G. To develop generically applicable procedures for the choice of an optimized water treatment method and to assess the environmental impacts for an ATEs site.

The first Phase of the Annex VI research covers the above-mentioned objectives A to E. This Phase started in 1987 and most of the work has been completed now. The second Phase (objectives F en G) will take about two years. The activities of the second Phase will be described in more detail later on.

Section 3 gives some preliminary conclusions from Phase I. It is emphasized that these conclusions are preliminary, because of the fact that evaluation and reporting of the experimental data is still under way.

3 ACTIVITIES AND PRELIMINARY CONCLUSIONS PHASE I

3.1 Development coupled model (A)

The two dimensional coupled model that has been developed describes the transport of heat, groundwater and solutes. Solute concentrations may change due to mineral equilibrium dissolution and precipitation processes and cation exchange. For this coupling, the HST2D code (Hagoort, 1989) was used to describe the transport processes, the PHREEQUE code (Parkhurst et al, 1980) to simulate the geochemical reactions.

The above mentioned transport code is able to describe the transport of groundwater and heat in the aquifer and the confining layers, including the buoyancy of flow. For a correct description of the processes during heat storage, the geochemical part of the coupled model had to be extended. A temperature dependent geochemical database is required, because of the temperature variations of the groundwater during the heat storage and production cycle. This temperature dependence not only applies to equilibrium constants, but also to cation exchange capacities. With the coupled model it is not only possible to calculate the equilibrium dissolution and precipitation for up to 20 minerals simultaneously, but also to

calculate the kinetic dissolution and precipitation. At the moment, calculations including kinetics are possible for only one mineral. Extension of the model with this respect is foreseen, because it is important to know when and where precipitation will occur in order to predict clogging.

When developing the coupled model, special attention had to be paid to the errors due to numerical dispersion calculating the transport of retarded (reacting) solutes. Comparison of the results of the coupled model with analytical solutions for conservative and retarded transport shows that the numerical dispersion was suppressed successfully.

The coupled geochemical-transport model was used during the IEA Annex VI research to simulate and extrapolate the results of the geochemical experiments and to predict the effect of several water treatment methods over a longer period of time.

3.2 Geochemical research (B)

As a part of the geochemical research both field experiments and laboratory experiments have been performed. For the laboratory experiments flow columns were constructed and used to study the geochemical interactions between water and sediment at flow velocities and temperatures relevant to ATES. The column experiments were carried out for geochemically different combinations of sediment and groundwater, as can be found in aquifers suitable for ATES.

Some conclusions from the geochemical research are:

- For a correct laboratory simulation of the geochemical reactions during heat storage, the exchange of gasses has to be prevented during sampling, sample handling and experiments in the laboratory. Escape of carbon dioxide for instance, will result in too high values of the saturation indices for carbonates.
- Precipitation of iron and manganese hydroxide can be almost completely blamed to the entrance of air into the installation or to withdrawal of different, chemically incompatible water types from the same well. In the latter case, water treatment seems the only solution to avoid iron and manganese hydroxide clogging.
- The precipitation of carbonates sometimes appears to be dominated by the formation of

(Fe, Ca, Mg) solid solutions. The prediction of the equilibrium composition of the solid solutions is still a not completely resolved problem.

- Carbonate precipitation is inhibited in groundwater containing organic matter or phosphates. A saturation index for calcite up to one is found without precipitation of carbonates.
- Depending on the sediment, cation exchange may play an important role when the water composition is changing, for instance due to water treatment.
- At high temperatures dissolution of silicates takes place. Problems due to silicate precipitation at decreasing temperatures have not been encountered.

3.3 Water treatment (C)

The research on water treatment methods has started with an evaluation of conventional water treatment methods applied so far for ATES systems. This evaluation addresses the efficiency, the cost and the environmental impacts of these treatment methods. Furthermore, the applicability to ATES was studied for several other water treatment methods, whether commercially available or not. This study implied some small scale tests also.

The efficiency and the environmental effects of conventional treatment methods may differ significantly, not only as compared to each other, but also as a result of local factors, like the chemical composition of sediment and groundwater and like groundwater flow velocity (Willemsen, 1990). For instance, an increase of the chloride concentration due to water treatment may render fresh water unsuitable for human consumption, but might be considered as an acceptable environmental impact in case of an aquifer containing brackish or salt groundwater.

Under those circumstances that it is impossible to avoid iron and/ or manganese oxidation, both in situ oxidation and iron/manganese removal by a bioreactor seem to be environmentally sound techniques for water treatment. To avoid precipitation of carbonates, also some water treatment methods have been selected with minor environmental effects, because of the fact that no chemicals are added to the groundwater permanently. Some examples: periodical and automatic cleaning of the heat exchanger for situations where only little precipitation is envisaged; temperature dependent addition and removal of CO₂ to and

from the groundwater; controlled carbonate precipitation using an integrated fluidized bed water treatment/heat exchanger (Willemsen, 1990).

3.4 Microbiological research (D)

Also for the microbiological research both laboratory experiments and field experiments were carried out. The main objective of the laboratory research was to quantify the parameters governing the development and change of bacteria populations. The field research has focused on the presence and development of pathogenic micro organisms at existing ATES projects.

The microbial research of the first Phase of the IEA research is expected to be completed by the end of 1990. Although the final results are not yet available, some preliminary conclusions may be drawn:

- Without oxygen in the groundwater and at very low oxygen concentrations, bacteria play a decisive role at the reduction and oxidation of iron and manganese.
- Normally the availability of nutrients (assimilatable organic carbons) is the parameter restricting the development of micro organisms in aquifers. Dissolved organic carbon is often mobilised at higher temperatures, so an increase of the number of micro organisms may be expected. However, on the other hand the fluctuating groundwater temperature seems to suppress the bacterial growth.
- No excessive biomass growth (resulting e.g. in biomass clogging) was encountered during the experiments, not even when assimilatable organic carbons were added to the groundwater.
- Up to now, no adverse health effects were encountered. Additional laboratory experiments are scheduled with groundwater that is artificially contaminated with pathogenic micro organisms.

3.5 Scaling and corrosion (E)

The scaling and corrosion part of the Annex VI research has started with the assessment of the experience in related branches of industry, like oil industry, geothermal industry, and district heating. Furthermore, laboratory and field tests were carried out to determine

corrosion and scaling rates under different circumstances.

The inhibition phenomenon, mentioned already in Section 3.2, was confirmed by the fact that at some experiments no scaling was found although it was expected.

Anaerobic conditions, as often found in groundwater, are favourable with respect to corrosion. It may be concluded that corrosion rates are much lower than in the case of oxygen containing water, although not much experimental data are available at this moment. However, corrosion may be acceptable from the system lifetime point of view, sometimes will it be not acceptable for system operation: corrosion products easily clog infiltration wells (Fouillac et al, 1988).

4 ACTIVITIES PHASE II

The objectives of Phase II of the IEA Annex VI research are mentioned in Section 2 under F and G. The Phase II activities will start by the middle of 1990 and will be completed by the middle of 1992.

During Phase I, eight water treatment methods with little or no adverse environmental effects were identified to prevent clogging due to precipitation. Some of these treatment methods are based on new concepts and require a further development in the laboratory. After this laboratory stage, for the most promising techniques pilot treatment installations will be designed, constructed and used for field testing. For these tests existing field test facilities will be used. All these activities, starting from the laboratory development until the evaluation of the results of the field tests, are covered by Phase II.

The last activity under the second Phase is the development of two generally applicable procedures. One procedure will describe the method to select the best water treatment method for given new ATES site, as well as the provisions to be made to avoid or reduce corrosion problems. The other procedure outlines how to assess the environmental impacts of a new ATES project. As an example, this procedure will be applied to a new or existing ATES site.

What are the prospects for thermal energy storage in aquifers based on the IEA Annex VI research results up to now?

One of the main obstructions to the large scale implementation of this technology was formed by the adverse environmental effects of conventional water treatment methods. The inhibition to carbonate precipitation, that is found in many natural groundwaters, will reduce the treatment requirement and thus the adverse environmental impacts of treatment. It is expected that in the presence of inhibitors, a reduced treatment is required for heat storage at higher temperatures (above 40°C) and no treatment at all at lower temperatures (below 40°C). Furthermore, several water treatment methods have been selected to prevent problems due to precipitation of carbonates, iron and manganese without the addition of undesired chemicals to the groundwater.

Operational nor environmental problems due to micro organisms were found up to now. Further research will be conducted to the survival of pathogens in a contaminated aquifer, because such an aquifer might be used for ATEs in the future. Well clogging due to biomass is not anticipated at higher temperatures (injection temperature over 50°C). At lower temperatures the conditions for biomass development are more favourable, although excessive biomass growth was not found in the experiments and the existing heat storage projects so far.

The final reports from the IEA Annex VI research will be available for the participating countries after clearance by the IEA. It is envisaged that the results presented in these reports will be applied to other fields of science and technology rather soon. In fact, the coupled geochemical-transport model has been used already to describe the effects of acid rain on the groundwater composition for several types of soil. Further application to soil and ground water pollution is expected to follow. The know-how on the phenomena governing well clogging will contribute to reduce the use of good quality ground water for cooling purposes. This reduction may be obtained by reinjection of the groundwater into the aquifer. As a last example, it is also expected that the environmentally sound water-treatment methods under development, in the future will be used for the treatment of groundwater for

the industry. For this treatment nowadays chemical additives are used.

REFERENCES

- FOUILLAC, C., CRIAUD, A., CZERNICHOWSKI-LAURIOL, I. and VUATAZ, F.D.; 1988. Chimie et exploitation géothermique de basse enthalpie. Proceedings Jigastock 88: 629 - 633.
- HAGOORT & ASSOCIATES and U.S. GEOLOGICAL SURVEY; 1989. HST2D-PC. Heat and Solute Transport simulator for personal computers. Hagoort, Delft, 32 pp.
- HOYER, M.C., WALTON, M., KANIVETSKY, R. and HOLM, T.R.; 1985. Short-term Aquifer Thermal Energy Storage (ATES) Test Cycles, St. Paul, Minnesota, USA. Proceedings Enerstock 85: 75 - 79.
- IEA; 1987. Environmental and Chemical Aspects of Thermal Energy Storage in Aquifers and Research and Development of Water Treatment Methods. NOVEM, Utrecht, 22 p.
- PARKHURST, D.L., THORSTENSON, D.C. and PLUMMER, L.N.; 1980. PHREEQUE - A computer program for geochemical calculations. USGS Water Resour. Inv.: 80 - 96.
- QVALE, B., SCHLEISNER IBSEN, L. and JØRGEN ANDERSEN, L. ; 1988. The Danish aquifer energy storage project - Operational experience. Proceedings Jigastock 88: 287 - 290.
- SAUGY, B., MISEREZ, J.J. and MATTHEY, B.; 1988. Stockage saisonnier de chaleur dans l'aquifère SPEOS. Résultats de 5 ans de fonctionnement. Proceedings Jigastock 88: 325 - 336.
- WILLEMSSEN, A.; 1990. Water treatment and environmental effects. This volume.

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