

HIGH TEMPERATURE AQUIFER THERMAL ENERGY STORAGE (HT-ATES): WATER TREATMENT IN PRACTICE

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Introduction

The application of Underground Thermal Energy Storage (UTES) has proven to be a cost effective way to save energy for heating and cooling of buildings or industrial processes. This has resulted in an exponential growth of this technology in The Netherlands. The registered number of open systems (ATES, Aquifer Thermal Energy Storage) has grown from 5 in 1990 to 214 in 200 and more than 1300 in 2010. The Dutch government wants to stimulate this growth. Important arguments are reducing the dependency on fossil fuel producing countries (security of energy supply), finiteness of fossil fuels and the reduction of CO₂-emissions (limit greenhouse effect). Different growth scenarios predict an increase between 3500 (autonomous growth) and 18000 ATES systems (accelerated growth) in 2020.

The rapid growth of UTES has resulted in questions on the related impact on soil (eco)systems and interference with soil use. Bioclear, Deltares, IF Technology and Wageningen University have initiated a research program to answer these questions. In the framework of this research program the effects on the subsurface are investigated together with opportunities to combine UTES with applications for other goals (for instance remediation). The research program should help to achieve a sustainable growth of UTES in the Netherlands. The program is supported by national, regional and local authorities and companies that recognise the importance of a sustainable growth of UTES.

One of the subtasks of the project is high temperature aquifer thermal energy storage (HT-ATES). HT-ATES has a number of

important advantages compared to low temperature heat storage. High temperatures are suitable for more applications. The use of the heat pump can be eliminated or reduced significantly (strong improvement of the energy efficiency). Finally the relatively large temperature difference between the hot and the cold well increases the thermal power of the system significantly.

Despite these advantages, the number of HT-ATES systems is insignificant compared to the total amount of ATES systems. Worldwide only three commercial projects with storage temperatures > 60 °C (that we know of) have been made (Sanner, 1999). Two of these projects are located in The Netherlands (University of Utrecht and De Bruggen in Zwammerdam) and both are not active any more. The only active HT-ATES is The Reichstag Building in Berlin (Germany), where heat of 70 °C is stored.

The main reason for the lack of HT-ATES systems are the operational problems that have to be solved. In the period 1976-1988 six experimental HT-ATES systems were initiated in different countries (USA, Switzerland, Denmark, Sweden, France), partly in the framework of the ECES (Energy Conservation through Energy Storage) research projects from the International Energy Agency (IEA). The idea was to use the projects for thermal energy supply after the experimental phase, but due to serious operational problems this did not occur. The main problems encountered were (Sanner, 1999; Snijders, 2000):

- large heat losses (low thermal efficiency)
- clogging due to particles, gas bubbles and precipitation of minerals (clogging of wells, heat exchanger, piping, etc.)
- corrosion of components in the ground water system

- automatic control of the groundwater system

In the period 1985-1995 much research was focused on solving these problems, partially within national research programmes and partly within the framework of the IEA Storage Programme. The research has demonstrated that the technical problems encountered can be solved. Furthermore, it has made clear that the technical problems faced in low temperature storage are much smaller than those met in high temperature heat storage (Snijders, 2000).

This paper focuses on the solution to one of these problems: water treatment to prevent clogging by mineral precipitation.

Theory

For most minerals the solubility increases when the temperature rises, but for carbonates this is not the case. The result is well known from daily practice: scaling in kettles or at heating elements in washing machines. In theory a limited rise in temperature of water that is initially saturated with calcite, the most common carbonate (CaCO_3), leads to oversaturation and should result in calcite precipitation. In practice however calcite precipitation does not occur when the temperature rise is limited. In literature different temperatures are mentioned, varying from 50 °C (Heidemij, 1987), 40-60 °C (Snijders, 1991, 1994) and 60 tot 70 °C (Knoche et. al, 2003). The fact that no precipitation occurs despite significant oversaturation is attributed to the presence of inhibitors.

In summary, the risk of carbonate precipitation depends on the degree of saturation of the original groundwater, the temperature increase and the presence and concentrations of inhibitors. Since most groundwater in The Netherlands is saturated with respect to calcite, precipitation of calcite is likely in case of HT-ATES if no countermeasures are taken. The necessity to avoid calcite precipitation is illustrated by the initial experiences at the University of Minnesota in St. Paul (USA), where the heat exchanger of an experimental HT-ATES plant had to be cleaned with acid after every 40 hours of operation (Miller and Delin, 2002).

Water treatment methods

A number of different water treatment methods have been tested in the national and IEA research projects. Two of these methods have

been applied in commercial projects: ion exchange (Utrecht University) and addition of acid (De Bruggen in Zwammerdam). At the Reichstag Building no water treatment is used. Apparently the groundwater composition is favourable at this site.

Ion exchange was used at the University of Utrecht and at the experimental plant of the University of Minnesota. Groundwater is led through a column filled with a resin: charged solid particles that are capable of binding ions with the opposite charge. In this case the resin was negatively charged and could bind cations (positively charged ions). First the column is flushed with a NaCl solution, so that the resin is charged with Na^+ . After that, groundwater is led through the column, cations from the groundwater are exchanged for Na^+ and bound to the resin. The calcium (Ca^{2+}) concentration in the groundwater drops, which prevents scaling when the water is heated. After a while the exchange capacity is reduced and the exchanger has to be regenerated, using the NaCl solution.

In both projects the water treatment worked, but had some serious disadvantages. Firstly the operation requires much attention. At the Utrecht University the intensity of treatment had to be adjusted constantly, based on frequent water analysis. Secondly the method is sensitive to overtreatment (risk of clogging by clay swelling) and undertreatment (risk of clogging by carbonates). The hot well at the Utrecht University has become severely clogged over the years. Although there is no proof, the critical water treatment is a possible cause. Thirdly both in St. Paul and in Utrecht huge amounts of salt (NaCl) were needed: in St. Paul 684 kg/day (Sanner, 1999).

For the project in Zwammerdam water treatment with hydrochloric acid (HCl) was chosen, partly based on the experiences in Utrecht. Adding acid lowers the concentration of carbonate by converting it to bicarbonate ($\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$) thus reducing the saturation index of carbonates.

The experiences in Zwammerdam are positive. During 5 years of operation there was no indication of clogging. The addition of HCl was automatically controllable based on pH measurement. Disadvantages were handling the HCl (hazardous fluid when concentrated: for instance fluid tight floors were needed), the need for large amounts of acid (delivery by trucks) and the control based on pH proved fragile (limited accuracy of pH meters).

Water treatment Zwammerdam

In Zwammerdam the calcite saturation index (SI_{cc}) was used as a steering parameter: the SI_{cc} of the natural groundwater should not be exceeded. Before heating the water the right amount of acid is added, which results in the natural SI_{cc} after heating. Adding less acid could result in clogging risks and adding more would unnecessarily increase the HCl consumption and geochemical impact.

Adding hydrochloric acid lowers the pH and increases the chloride content of the groundwater. In Zwammerdam a 30% HCl solution was used. In the first four years on average about 0.2 liter of HCl solution was used for every m^3 of groundwater that was heated, which corresponds to a dilution with a factor 5000. After the addition of acid and heating, the water is stored in the hot well. When there is heat demand, hot water is extracted and injected in the cold well with a lower temperature. Cooling the water reduces the SI_{cc} , which means that calcite present in the aquifer will be dissolved. Because the dissolved calcite concentration in the water extracted from the cold well is higher, more HCl is needed to prevent calcite precipitation due to heating than in the cycle before. Extrapolating this sequence would mean that each cycle more acid is needed per m^3 of groundwater, more calcite is dissolved and the pH drops more and more.

On the other hand, this effect might be limited by the extraction of a mixture of the injected water and surrounding groundwater. Mixing causes dilution of the injected water (relatively high calcite and chloride content and low pH compared to the surrounding groundwater). Important processes that are responsible for dilution are dispersive mixing, natural groundwater flow, buoyancy flow and an imbalance between the amount of water injected and extracted annually.

Thermal and geochemical modelling

To better understand the processes that occur geothermal and geochemical modelling was performed for the Zwammerdam project. First an estimation of the amount of mixing is needed. The extraction temperatures can be used as a tracer, when they are corrected for thermal losses by heat conduction to the confining layers. The available data on the amounts of water that were pumped each season and the corresponding extraction and injection temperatures were used as model input. The system has effectively been active

only five years (1998-2002). Only the data on the first four years (1998-2001) were available. These four years were modelled with the computer code HstWin-3D, a code specially developed for heat and solute transport in porous media. The code takes into account the dependency of fluid properties such as viscosity and density on temperature and concentration changes. To be able to distinguish the temperature losses by heat conduction to the confining layers from the temperature losses by mixing with surrounding groundwater, two scenarios were modelled: one scenario with heat conduction in the confining layers and another one without (thermal conductivity = 0). The calculated temperatures for both scenarios are shown in figure 1. The results show that the main part of the decrease in the extraction temperature compared to the injection temperature is caused by dilution (dispersive mixing, natural groundwater flow, buoyancy flow).

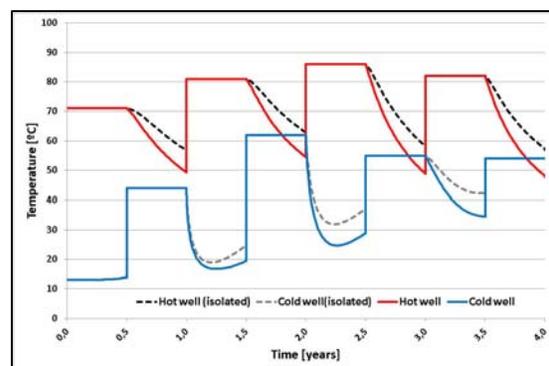


Figure 1 – Calculated temperatures in the “hot” and the “cold” well.

Based on the results from the thermal model a geochemical model was built in PHREEQC. To be able to simulate long term geochemical effects it was assumed that the system continues operation for 20 years in total. For the first four years actual data were used combined with the results from the thermal calculations. For the following years, it was assumed that heat demand is increased significantly, resulting in a larger temperature difference between the hot well and the cold well (assumed injection temperatures are 84 and 40 °C). The results for the pH and chloride content are shown in figure 2.

The calculations show that the pH of the water that is injected in the hot well (after the addition of acid) varies between 6.3 and 6.4 in the first years, and finally stabilizes at about 6.2. The water that is extracted from the cold well has an initial pH of 7 which decreases and

stabilizes around 6.6. Field measurements during the first four years show a drop in pH between 0.0 and 0.5 in the cold well, which corresponds well to the model results. The chloride content increases from 3900 mg/l to a maximum value of about 4100 mg/l. In 2002 and 2003 (latest data available) the chloride concentrations were 3900 and 4000 mg/l, also in good agreement with the model.

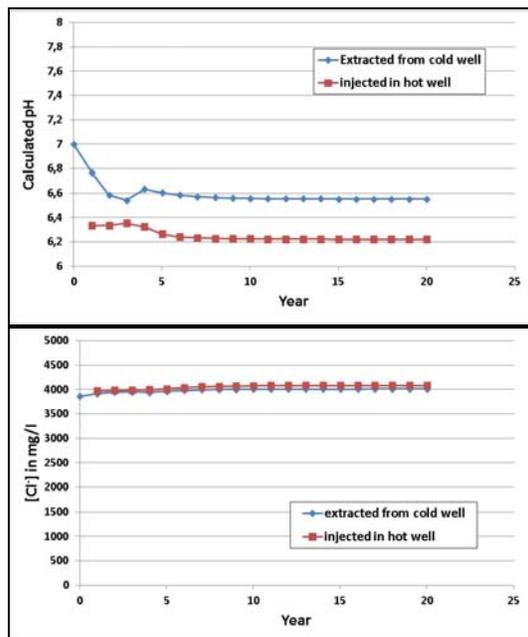


Figure 2 – Calculated pH and chloride content of the water extracted from the “cold” well and injected in the hot well.

Both for the pH and chloride the calculations show a stabilisation after 5 to 10 years. Apparently the increase in decrease in H⁺ and Cl⁻ concentrations due to the addition of HCl is balanced by the decrease due to dilution (mixing).

Geochemical impact

The increase of the chloride concentration in this salt water aquifer from 3900 to 4100 mg/l is considered insignificant. On the other hand, the same rise can be critical if a fresh water aquifer is used: a rise of 200 mg/l would change fresh water to brakish.

Although the drop in pH is also limited (a pH of 6.2 is not exceptional in natural groundwater), a decrease in pH can have consequences. The possible impact of a pH decrease has been investigated in relation with the potential risks for shallow groundwater resources when leakage from a geological CO₂-storage would occur. An extensive review of the existing

knowledge is given by Lemieux (2011). Effects that can occur are:

- enhanced mineral dissolution, including minerals that contain hazardous trace elements;
- influence on adsorption/desorption.

Lemieux states that despite important knowledge gaps, most of the available information shows that a minor impact is expected. Arsenic is considered the most critical parameter, for which the drinking water limit could be exceeded. Other, less critical, parameters that could be relevant are lead, zinc and cadmium. An important conclusion is that the risks depend on the aquifer mineralogy and mineral composition (presence of hazardous trace elements). For the Dutch situation mainly pyrite is considered relevant. According to Stuyfzand et al. (2006), the mean composition of pyrite in Dutch fluvial sands is Fe_{0.98}Co_{0.0037}Ni_{0.01}Zn_{0.01}S_{1.9947}As_{0.0053}. Based on this composition monitoring of Ni, Zn and As is recommended, when water treatment with acid is applied (for Co no drinking water limit is available).

In the framework of the research program the groundwater in Zwammerdam was sampled in June 2011. The temperature measured in the hot well was 28 °C. The results are shown in table 1. The parameters As, Ni and Zn show relatively high values in the hot well, which suggests dissolution of pyrite. An important note is that none of the concentrations exceed the drinking water limit.

Table 1 Measured concentrations of potentially critical parameters 8 years after shutdown.

Parameter	Reference	Cold well	Hot well	Drinking water limit (NL)
As [µg/l]	1	1	10	10
Cd [µg/l]	0	0	0	5
Pb [µg/l]	0	0	0	10
Ni [µg/l]	1	1	4	20
Zn [µg/l]	0	1	13	3000

Conclusions

Currently two water treatment methods to prevent scaling have been used in commercial HT-ATES projects. Ion exchange was used at the Utrecht University and has some serious disadvantages. Partly because of these drawbacks, another method was used in Zwammerdam: addition of HCl.

The geochemical impact of the Zwammerdam water treatment was modelled and compared with field measurements. Addition of HCl

results in a rise in chloride content (3900⇒4100) and a decrease in pH (7⇒6.2). In this case the rise in chloride content is insignificant compared to the initial concentration in the salt water aquifer. However, for fresh water aquifers the same rise in chloride content can result in brackish groundwater.

The calculated decrease in pH in itself is not a concern. However, it can enhance the dissolution of minerals, including those that contain hazardous trace elements. In the Dutch situation it particularly concerns pyrite, containing trace elements like As, Ni and Zn. The results of recent field measurements in Zwammerdam, 8 years after shutdown of the system, show relatively high concentrations of these trace elements in the warm well. These results suggest enhanced dissolution of pyrite in the warm well. Nevertheless the concentrations do not exceed the drinking water limit. Monitoring of these trace elements is recommended for projects where HT-ATES is combined with the addition of acid.

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