

Field assessment of the impacts of Aquifer Thermal Energy Storage (ATES) systems on chemical and microbial groundwater composition

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ABSTRACT

In the Netherlands, the total number of aquifer thermal energy storage (ATES) systems (or open loop underground thermal energy storage systems, UTES) has been growing exponentially during the last two decades, with a total of 2000 systems by the end of 2012. The exact number of borehole thermal energy systems (BTES, or closed loop UTES) is not clear, but the number of boreholes associated with these type of systems is about 200 times higher and also shows an exponential growth trend. Furthermore, current national and municipal ambitions in reducing CO₂ emissions, combined with rising energy prices, provide a driving force for further rapid expansion. With up to 10,000 additional ATES systems expected in the coming decade, concerns have been raised on their impact on overall groundwater quality, as this may adversely affect other groundwater uses such as drinking water production. As a consequence, several research programmes were initiated to assess the impact of UTES on groundwater composition. In particular, field monitoring campaigns provided insight in the processes that cause groundwater quality changes. Here, we provide an overview of the insight gained from the monitoring of the main processes that were observed to affect of field groundwater monitoring performed at UTES field sites for chemical and microbial parameters. To be able to acquire broad insight, the selected UTES sites consist of different types of UTES systems (borehole heat exchangers, doublet systems, monowell, recirculation, low and high temperature storage) in different geochemical circumstances (fresh/salt water, different redox conditions).

The results indicate that the impact of mixing of stratified groundwater from different depths in the aquifer is the predominant factor affecting

groundwater quality changes in low temperature ATES systems, with various site-specific aspects contributing to the mixing extent. Redox, salinity and pH- and alkalinity stratifications have identified and described as the main gradients over which mixing can impact groundwater chemistry. Temperature effects on mineral equilibria and reaction kinetics are generally minimal in thermally-balanced systems at temperatures below 25 °C, because the impact on the most sensitive parameters in the warm zone is largely compensated by the opposite effect in the cold zone. Of the chemical equilibria, particularly adsorption reactions are sensitive. With increasing temperatures the impacts on groundwater quality are progressively more pronounced, also because maintaining a thermally balanced system with respect to natural groundwater (~11°C) is no longer feasible. At higher temperatures the potential for organic matter mobilisation and mineral precipitation increases.

Large temperature increases can have an impact on the composition of the microbiological population, with shifts to mesophile and thermophile species at elevated temperatures. These effects may also be reversed on a functional level as observed after the abandonment of a high temperature ATES site, where the lowered temperature, resulted in a population similar (but not equal) to the original population, performing the same functions. No indications were found for risks of multiplication of pathogens. Biodiversity, as the number of different species appeared not to be affected at the studied sites (temperatures up to 39 °C).

1. INTRODUCTION

In the Netherlands, the total number of aquifer thermal energy storage (ATES, Figure 1) systems has been growing exponentially during the last two decades, with a total of 1,600 systems in 2012. The exact number of borehole thermal exchange systems (BTES, or closed loop UTES) is not clear, but estimated at

about 200 times higher and also shows an exponential growth trend. Furthermore, current national and municipal ambitions in reducing CO₂ emissions provide a driving force for further rapid expansion. With up to 10,000 additional ATEs systems expected in the coming decade, questions have been raised on their impact on overall groundwater quality. While under particular conditions ATEs improve the quality of contaminated groundwater (Zuurbier et al. 2013), ATEs systems may also negatively impact groundwater resources. Earlier research on changes in groundwater chemistry in ATEs systems mainly focussed on operational aspects such as clogging by mineral precipitation, particularly of carbonates and silica, due to the temperature effect on mineral equilibria (e.g. Brons et al., 1991; Griffioen and Appelo, 1993; Perlinger et al., 1987). Temperature is therefore one of the key factors (Figure 1) that may contribute to the overall effect on groundwater quality in ATEs systems.

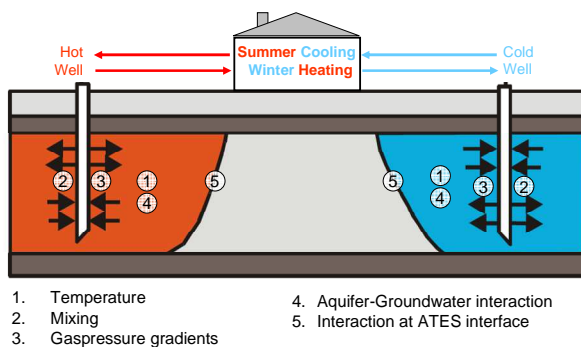


Figure 1: Principle of ATEs (or open loop underground energy storage systems, UTES) and the factors influencing groundwater quality.

In addition to temperature, other key factors may contribute to compositional changes of groundwater under the influence of ATEs systems, such as mixing and gas pressure changes (Figure 1). In this paper, we present the evaluation of effects of ATEs systems as observed through field monitoring.

2. METHODS

Effects of the various ATEs systems on the local groundwater quality were assessed through sampling monitoring wells as well as ATEs wells. Reference monitoring wells that were outside the influence zone of the ATEs systems were used to determine the reference groundwater composition. Groundwater samples were analysed for major ions, a wide range of trace metals, dissolved organic carbon (DOC), nitrate, ammonium and a selection of microbiological parameters. Temperature, alkalinity and the pH of the sampled groundwaters were determined in the field. PHREEQC (Parkhurst, et al., 1999) was used for all hydrogeochemical calculations.

3. RESULTS AND DISCUSSION

3.1 Temperature effects

Shallow (<50 m bgs) groundwater in the Netherlands typically has temperatures of about 11°C. Due to potentially detrimental effects, Dutch policy currently does not allow ATEs systems to inject water with temperatures above 25-30°C, nor does it allow thermal imbalances between the hot and cold wells. Due to this and operational aspects, most current ATEs systems in the Netherlands have relatively narrow temperature ranges ($\Delta T < 10^\circ\text{C}$). Earlier research on groundwater chemistry in ATEs systems mainly focussed on temperature-related operational aspects such as clogging by mineral precipitation, particularly of carbonates and silica, due to the temperature effect on mineral equilibria (e.g. Brons et al., 1991; Griffioen and Appelo, 1993; Perlinger et al., 1987). However, with respect to overall groundwater quality, many additional reactions are to be considered, many of which are not determined by chemical equilibrium but are driven by thermodynamic imbalances (e.g. Appelo and Postma, 1993). It has frequently been found that the rates of such (bio)geochemical reactions in groundwater systems are temperature-sensitive (Brons et al., 1991; Holm, 1986; Perlinger et al., 1987; Prommer and Stuyfzand, 2005), with higher rates observed at higher temperatures. Although not currently allowed under Dutch law, injection temperatures above 25 °C would allow further increases of overall energy efficiencies, by removing or reducing the need for heat pumps.

Temperature effects on geochemical equilibria

For the assessment of temperature effects on a wide range of equilibria the Van 't Hoff equation can be used:

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{-\Delta H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [1],$$

where K₁ is the equilibrium constant at temperature T₁ (in K, K = °C + 273,15) and K₂ at temperature T₂. Also included is ΔH^\ominus (cal) as the standard enthalpy change for a particular equilibrium and R as the universal gas constant (8.314 J/(mol K)). Using the Van 't Hoff equation, the relative impact of a particular temperature (T₂) with respect to a reference temperature (T₁) can be expressed as a function of different equilibrium reactions, as presented in Figure 2 for a reference temperature of 11 °C. As can be seen, the equilibrium constants of relatively soluble minerals (e.g. gypsum and halite) are affected minimally by temperature changes, in contrast with poorly soluble minerals (e.g. quartz and pyrite). Also, as ATEs systems store water both warmer and colder

with respect to reference, the effect of temperature on equilibrium constants is linearly opposite for temperature increases and decreases. For calcite, for example, the equilibrium constant is moderately sensitive to temperature changes in the ATES temperature range, as illustrated by the observed calcium concentrations at an ATES field site (Figure 3). For reactions that are kinetically controlled, such as the dissolution of poorly soluble minerals, this equilibrium-based evaluation is of limited use. However, many adsorption reactions are strongly endo- or exothermic (Figure 2). These equilibria are therefore particularly sensitive to temperature changes, as has been observed in ATES column experiments (Bonte et al., 2013). For example, arsenic sorption to ironoxides and clay is exothermic (Kersten and Vlasova, 2009; Mhoapatra et al., 2007) and thus increasing temperatures result in a decreasing sorption affinity to ironoxides for oxyanions. Contrary to the sorption behaviour of oxyanions, the sorption of divalent metals to ironoxides is endothermic and the actual enthalpy depends on the charge and the ratio of hydration number (number of H₂O molecules involved to form a ligand) and hydrated radius (Trivedi and Axe, 2000). Overall, ATES-induced temperature changes are therefore expected to significantly increase adsorption or desorption, depending on the enthalpy change associated with the particular adsorption reaction.

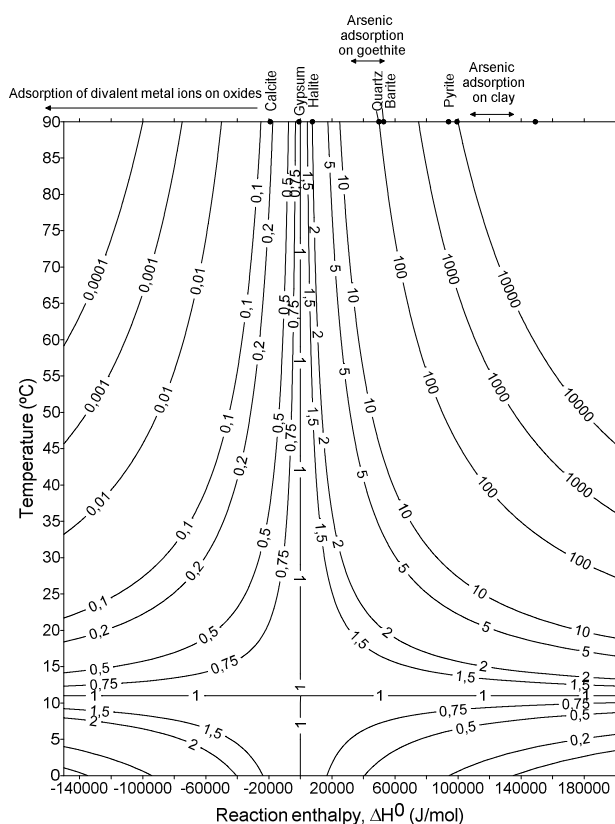


Figure 2: Effect of temperature on equilibrium constants for an ATES system with a reference temperature of 11°C. The contour values represent the relative factor with which the equilibrium constant for a certain standard enthalpy change

increases (>1) or decreases (<1). Mineral data is taken from the PHREEQC database (Parkhurst, et al., 1999). Ranges for desorption enthalpies are derived from various sorption studies (Kersten and Vlasova, 2009; Mhoapatra et al., 2007; Trivedi and Axe, 2000)

Temperature effects on geochemical reaction rates

Both chemical and microbial reaction rates are known to follow an exponential increase with temperature (Arrhenius, 1889). However, from the results of the field monitoring at ATES sites, temperature effects on reaction rates could not be observed. This was explained by the fact that for a thermally balanced SATES system, the temperature increase for groundwater in the warm bubble is balanced by the temperature decrease in the cold bubble. The expected rate increase in the warm bubble is therefore counteracted by a rate decrease in the cold bubble. As shown and discussed in a recent analytical study (Hartog, 2011) this net relative increase of the rate constant for thermally balanced ATES systems (f_{ATES}) can be expressed as:

$$f_{ATES} = \frac{1}{2} e^{\frac{Ea}{RT_{ref}}} \left(e^{\frac{-Ea}{R(-0.5\Delta T + T_{ref})}} + e^{\frac{-Ea}{R(0.5\Delta T + T_{ref})}} \right) [2]$$

where A is a pre-exponential factor, Ea the activation energy for a reaction (J mol⁻¹) and R is the gas constant (8.314 J K⁻¹ mol⁻¹). In addition, for a particular ATES system, f_{ATES} depends on the reference temperature of groundwater (T_{ref}) and the temperature difference (ΔT) within the ATES system. As illustrated in Figure 4, rate increases for reactions with low activation energies (labile compounds) are limited at typical ATES temperatures, particularly when counteracted by rate decreases in the cold bubble. In contrast, the rates of reactions that occur on geological time scales (recalcitrant compounds) are strongly affected by temperature increases but are however unlikely to be expressed during the typical operational lifetime of an ATES system (~25 yrs). Overall, although thermally balanced ATES will result in a net increase of the overall rate due to the exponential dependence of rates on temperature, this effect is very small (<1%) for the temperature conditions ($\Delta T < 15$ °C) under which SATES systems are generally operated. However, for heat storage systems or thermally unbalanced ATES systems, the effect of temperature on reaction rates is increasingly significant (Figure 4).

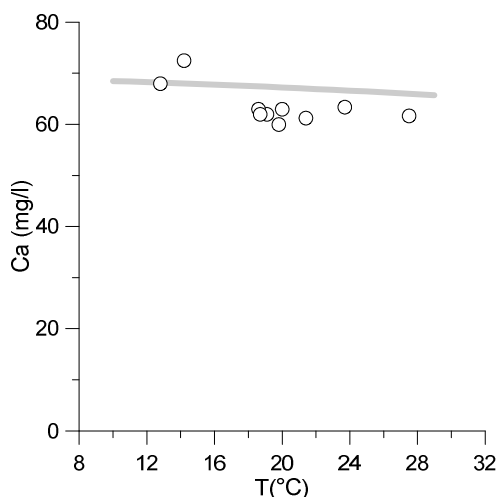


Figure 3: Relation between temperature and calcium concentrations at an ATEs field site. The line shows the predicted temperature dependence of the calcite equilibrium at a partial CO₂ pressure of 10^{-2.26} using PHREEQC (Parkhurst, et al., 1999).

Temperature effects on microbiology

The microbial composition of groundwater is an important quality that affects the value of groundwater, for example as a resource for drinkingwater production. However, for the temperature range of groundwater at monitored ATEs sites (11–35 °C), the quantities and composition of detected bacteria and archaea vary within the natural variation as observed outside of the influence of the ATEs systems and did not depend on the temperature (Figure 5). Microbial communities, as quantified on a functional level (e.g. based on functional genes for for instance sulphate reduction) differed more between ATEs systems than within these systems regardless of the existing temperature differences. On one site only, where temperatures rose up to 39 °C, the number of archaea was significantly higher than on the other wells on the site (data not shown). The numbers of micro-organisms on the different locations could not be linked to the concentrations of TOC (total organic carbon) as an explanation of growth constraints unrelated to the temperature but to carbon sources. This may be explained by the low natural concentrations or the poor quality of TOC in these groundwaters. No indications were found that elevated temperatures may give rise to increases in pathogenic microorganisms as no *E. coli* or *Legionella pneumophila* were detected. On a few locations, only very low numbers of *Clostridium perfringens* were found. Additional lab tests showed that larger temperature increases can have an impact on the composition of the microbiological population, with shifts between mesophile and thermophile species at elevated temperatures. These effects may also be reversed on a functional level as observed after the abandonment of a high temperature (> 80 °C) ATEs site, where at a lowered temperature (28 °C) resulted in a population similar (but not equal) to the original

population, performing the same functions. No indications were found for risks of multiplication of pathogens. Biodiversity, as the number of different species appeared not to be affected at the studied sites (temperatures up to 39 °C).

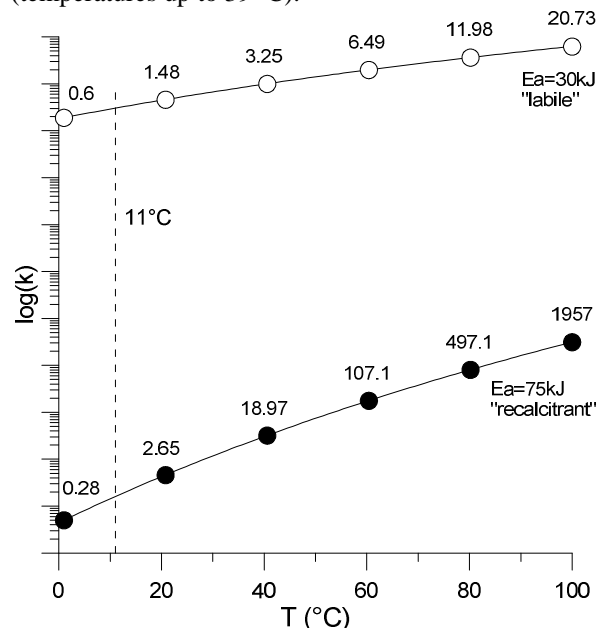


Figure 4: The effect of temperature on the kinetic rate constants for labile (30 kJ) and recalcitrant (75 kJ) reactions. Kinetic rate constants are shown on an arbitrary logarithmic scale. The labels (f_{ATES}) indicate the relative increase of the reaction rate constants for a reference temperature of 11 °C

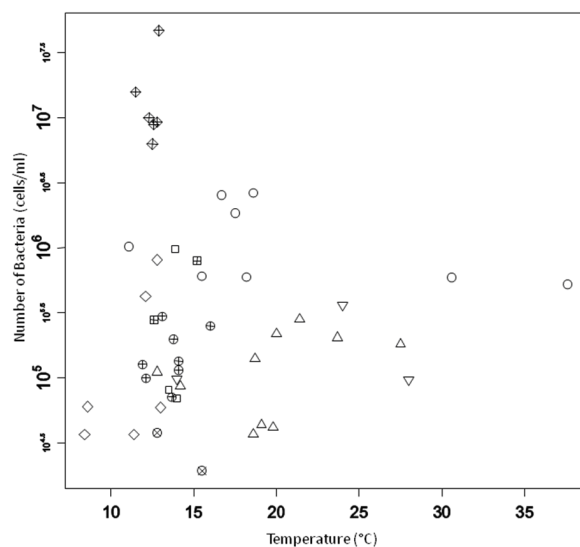


Figure 5: Total number of bacteria (10 log cells/ml groundwater) related to the groundwater temperatures at different pilot locations.

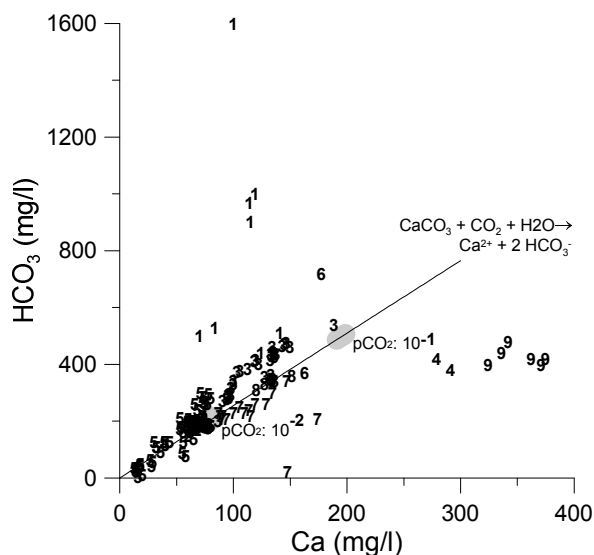


Figure 6: Carbonate equilibrium in the groundwaters of the studied ATEs systems, as reflected by measured calcium concentrations and alkalinity. The line reflects the dissolution of calcite under the influence of increased CO₂ pressures. Temperature effects are marked gray for the temperature range of 10-20 °C at a p CO₂ of 10⁻¹ and 10⁻² atm.

3.2 Gas pressure effects

Total gas pressure can vary for different groundwater types but are typically above atmospheric. To prevent operational issues, such as gas clogging, ATEs systems are typically operated under overpressure. Also, the degassing of CO₂ can trigger carbonate precipitation that can also contribute to well clogging. As the CO₂ pressure affects carbonate equilibria, it is also important with respect to the general quality of groundwater.

As shown in Figure 6, CO₂ partial pressures range from atmospheric to about 15% (0.15 atm) for the various monitored ATEs sites. Within this range, the effect of variations in CO₂ partial pressures on the calcite equilibrium far exceed the effects of temperature within the typical range of ATEs systems (10–20 °C). Most of the observed groundwater compositions reflect the increase of calcite solubility with increasing CO₂ partial pressures, with increasing alkalinity and calcium concentrations in a 2:1 ratio (following: $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$). Deviations from this stoichiometric ratio indicate the occurrence of additional processes. For example, the high calcium concentrations for an former high-temperature ATEs site (site 9 in Figure 6) reflect the operational use of hydrochloric acid to treat or prevent carbonate scaling.

3.3 Mixing effects

Mixing effects during ATEs occur when water of different compositions is extracted. Three common

types of vertical “chemical gradients” were identified in the evaluation of the field monitoring results:

- pH- and alkalinity gradients, e.g. carbonation levels
- salinity gradients
- redox gradients, such as oxic-anoxic transitions

pH- and alkalinity gradients

As shown in (Figure 6), a considerable range in CO₂ pressures was present in the groundwater of each ATEs site monitored. Mixing of such groundwaters will enhance carbonate dissolution, as carbonate-saturated groundwater results from mixing groundwaters that have carbonate-saturated at different CO₂ pressures. However, the amounts of carbonate dissolved in each cycle are minimal and are only likely to be significant in carbonate-poor aquifers. The carbonate equilibrium is also affected by replacement of groundwater with a different chemical composition (e.g. replacement of NaCl by CaHCO₃ type water) due to cation-exchange processes. This is illustrated by the BTEs site (site 1, Figure 6), high storage temperatures (up to 60 °C) induced density driven flow. Here, subsequent freshening of the aquifer results in cation-exchange, as reflected by lowered calcium concentrations and increased alkalinity values.

Salinity gradients

With greater proximity to the North Sea, as well as at greater depths, groundwater in the Netherlands is generally more saline, and a wide range of groundwater salinities were present at the various ATEs sites (Figure 7). Obviously, fresh groundwater is a valuable resource, e.g. for public water supply. When ATEs systems mix groundwaters with too large of a salinity contrast, this can result in the net loss of fresh groundwater (typically < 150 mg/l Cl). Therefore regulations prohibit salinization of fresh groundwater by ATEs systems. At two of the ATEs sites studied, such salinity contrasts were present.

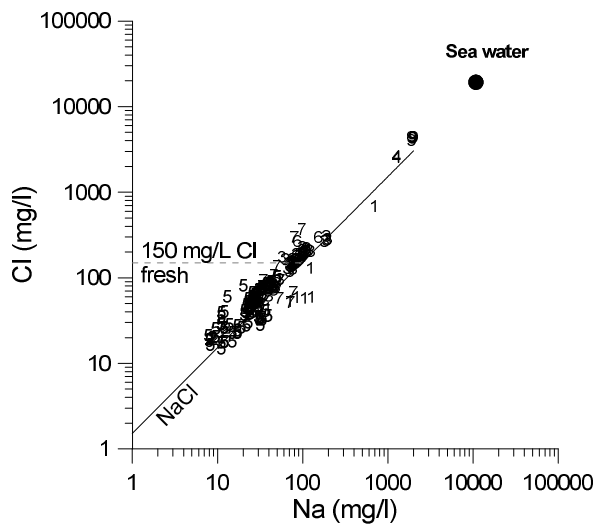


Figure 7: Variation and mixing of various salinity levels in the ATES groundwaters.

Redox gradients

Mixing of oxic and anoxic groundwater is usually avoided when designing ATES systems, as this increases clogging risks due to the potential precipitation of iron hydroxides. However, at one of the studied ATES sites (a mono-well ATES system), the effects of pyrite oxidation were observed in several of the shallowest monitoring wells. This was inferred from the elevated sulphate for these wells and the associated trace metal concentrations, such as for nickel (Figure 8). As can be seen there is a distinct mixing line for chloride and sulphate concentrations, reflecting the composition of water in the ATES wells and the monitoring wells that receive it.

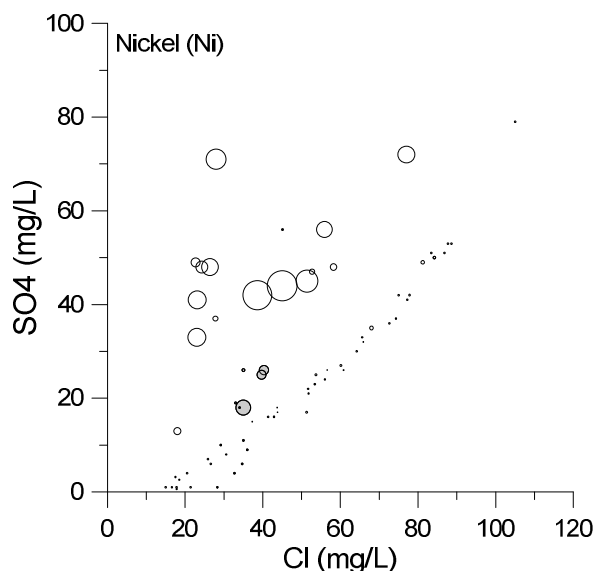


Figure 8: Bubble plot of chloride and sulfate concentrations with the symbol size indicating the relative nickel concentrations. The concentrations in the reference filters are marked grey.

As the shallow sulphate and nickel concentrations near the ATES system are elevated, as compared with

shallow reference wells, may suggest that pyrite oxidation is enhanced. This may occur during the additional drawdown that occurs when the extraction of the shallow filter of this mono-well ATES system. However, ATES-induced mixing dilutes the elevated sulphate and associated trace metal concentrations to the extent that these do not affect the overall quality of the groundwater within ATES system.

Controlling factors of mixing in ATES systems

Groundwater mixing is shown to be the predominant process affecting groundwater quality changes in the ATES systems studied. However, the extent and impact of mixing is location-specific. Foremost, the extent to which mixing in ATES systems affects groundwater quality depends on the presence and type of hydrochemical gradients present in the groundwater that is extracted by the ATES system. Also, the level of sedimentary heterogeneity affects the extent of mixing, as permeability differences and relative thicknesses affect the relative contribution of groundwater to the mixed groundwater in the ATES system.

As illustrated in Figure 9, three aspects contributing to the extent and temporal variation of groundwater mixing in ATES systems are discerned:

1. **Startup of ATES system:** initial mixing of groundwater gradients in the ATES groundwater volume.
2. **Background groundwater flow:** mixing of the ATES groundwater with inflowing groundwater under influence of (regional) background groundwater flow.
3. **Dispersion:** mixing through dispersion in the transition zone between the injected ATES groundwater volume and the surrounding groundwater. The significance of dispersive mixing is dependent on operational factors (injection rates and volume) as well as the heterogeneity (Sommer, 2011) of the aquifer sediment along the ATES filter screens.

Also, during operations mixing ratios may vary as shown by detailed temporal monitoring at an ATES site, where several monitoring wells and the ATES production wells were sampled with a monthly frequency for a period of 1.5 years (Figure 10). The screens of the ATES wells are set in a semi confined aquifer that consists of two geological formations. The groundwater in the upper formation contains elevated chloride and sulphate concentrations of about 70 and 60 mg/l, respectively. In contrast, the concentrations in the lower geological formation are relatively low with 10 and 6 mg/l, respectively. The ATES system

extracts both water types, mixes them and re-injects the mixture back into the aquifer. This causes freshening of the upper and salinization of the lower formation. Based on the chloride and sulfate concentrations of the two end members, the water quality in the ATEs well, reflects a mixture of about 90% from the lower formation and about 10% from the upper formation. This can be attributed to a lower permeability of the upper geological formation. However, the mixing ratio for the extracted groundwater varies within each ATEs cycle (Figure 10). Moreover, the relative contribution of the extracted fresher groundwater from the lower geological formation, seem to increase further with each consecutive cycle. These observations could be linked to both to operational differences between injection and extraction regimes, and between cycles. In addition, temporal well development, e.g. partial preferential clogging of the filter in the upper formation.

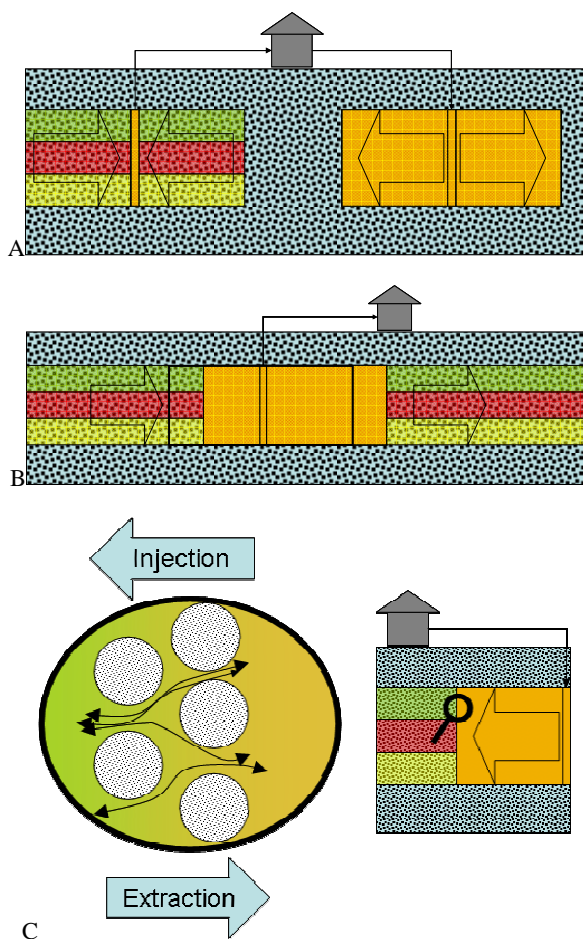


Figure 9: Three aspects contributing to mixing effects in ATEs system. Initial mixing (A), mixing through the inflow of native groundwater (B) dispersive mixing at the boundaries of the injection volume (C).

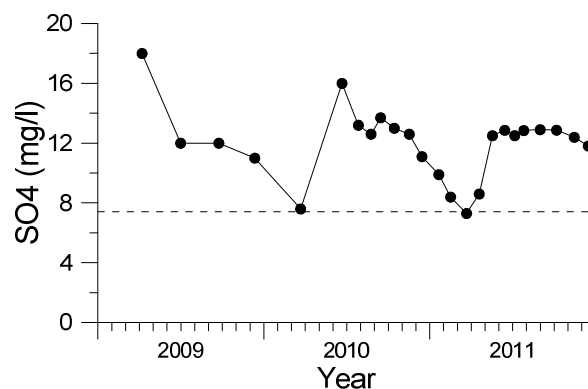


Figure 10: Temporal evolution of sulfate concentrations in an ATEs well during 3 yearly extraction and injection cycles. Dashed line represents sulphate concentration in lower formation.

4. CONCLUSIONS

This study illustrates that several processes contribute to groundwater quality effects of ATEs systems, in which the effect of mixing is predominant for the low-temperature ATEs systems studied. Only for ATEs systems in aquifers with relatively homogeneous groundwater quality, minor temperature effects could be observed. At higher temperatures (>30 C) groundwater quality is expected to be more significantly affected, due to the exponential temperature-dependence of both geochemical equilibria and rate constants.

Overall, mixing was the predominant process affecting groundwater quality at the studied ATEs sites, particularly, where groundwater gradients were strongest.

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