CONTROLLED COLUMN EXPERIMENTS TO DETERMINE THE THEORY AND SENSITIVITY OF THERMO-SENSITIVE TRACERS

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ABSTRACT
The reinjection of abstracted thermal water is a common procedure in geothermal reservoir management. It provides several advantages e.g. disposal of geothermal wastewater, the maintenance of the reservoir strain and the reduction of the subsidence due to compaction. On the other hand, due to this practice the reservoir cools down since the extracted energy may exceed the natural heat flow. This limits the life time of a geothermal system. For an optimal reservoir management during geothermal power plant operation it is essential to locate and describe the thermal front in the subsurface. Currently, there is no method available for measuring this thermal drawdown. One promising tool to overcome this shortage is the application of thermo-sensitive tracers. Unfortunately, earlier reported field experiments failed due to inappropriate tracer compounds. Recently, new compounds were synthesized in our group with fluorescent properties allowing in-situ measurement of tracer breakthrough curves. These tracers have well known kinetic parameters, which is a prerequisite in tracking thermal fronts. According to the obtained pre-exponential factor \( A \) and the activation energy \( E_a \) of the Arrhenius law these thermo-sensitive tracers may already be used in short-term experiments (e.g. Push Pull) or low temperature reservoirs \( (T < 100 \, ^\circ C) \). This circumstance gave us the opportunity to conduct controlled laboratory experiments with focus on tracer breakthrough curve correlation to reservoir temperature. The experimental setup consists of two consecutively connected columns, where each is heated to a certain temperature using a rapid flow water bath. Preliminary results, with sieved sand as a packing material, show a precise estimate of the applied temperature from the recorded tracer breakthrough curve. It is the first time that reliable experiments were performed to evaluate the underlying theory.

INTRODUCTION
In the currently ongoing energy transition discussion, geothermal energy is considered to be one of the major potential sources for the worlds energy supply (IPCC, 2011). To enlarge the efficiency of the hereby used geothermal power plants, these facilities require a proper geothermal reservoir management. Common practice is the reinjection of abstracted thermal water, which provides a safe disposal of the geothermal wastewater, the maintenance of the reservoir strain and the reduction of the subsidence due to compaction. Unfortunately, this practice leads to a thermal drawdown in the exploited geothermal reservoir since the extracted energy exceeds the natural heat flow (O’Sullivan et al., 2010). To improve the reservoir management procedures and raise the efficiency of geothermal power generation knowledge on the thermal front’s position would be extremely valuable. In the broad range of available monitoring and characterisation tools e.g. geophysical, borehole and tracer methods, none of them is currently able to measure and/or quantify the thermal drawdown directly. The best available tool today is the analysis of tracer breakthrough curves using chemically inert tracers and the thermal retardation relation to estimate the position of the thermal front (Pruess and Doughty, 2010; Shook, 2001). To overcome this shortage one promising tool are thermo-sensitive tracers. This class of tracers were proposed for the first time in the mid-eighties (Robinson et al., 1984; Tester et al., 1986). Unfortunately, earlier reported laboratory and field experiments failed due to inappropriate compounds and measurement methods (Tester et al., 1987; Kwakwa, 1988). Recently, new compounds were synthesised and tested (Nottebohm et al., 2012). Their thermal dependency is described by a pseudo first order hydrolysis reaction (Nottebohm et al., 2010). The biggest advantage of these new tracers is that they show fluorescent properties hence, it is possible to perform online measurements under in-situ conditions. In analysis of their breakthrough
curve (BTC) a well studied kinetic behaviour is a prerequisite for tracking thermal fronts. Our experimental setup allows a reliable contribution in the currently ongoing discussion about the applicability and sensitivity of thermo-sensitive tracers (Behrens et al., 2009; Plummer et al., 2012). To answer the raised questions based on theoretical and numerical work this study presents results from laboratory experiments, which allow the application of thermo-sensitive tracers in flowing systems with an applied temperature field.

EXPERIMENTAL DESIGN

The scope of this laboratory work is to experimentally investigate the capability of thermo-sensitive tracers. These tracers extend the possibilities of tracer tests, as they provide estimates of spatial and temporal information on the reservoir temperature evolution. Hence the experimental setup should provide possibilities to examine temporal and spatial changes of temperature. Hereby, the reduction to a limited number of processes controlling the system and well defined and adjustable boundary conditions are essential in order to obtain reliable results (Schaffer et al., 2013). Every additional process, e.g. catalysis from column filling or column material, sorption or flow field heterogeneities influences the shape of the BTC and hence, will complicate the analysis. Vice versa, every deviation from the expected BTC tells the experimenter that additional processes are present (Schaffer et al., 2013) and must be considered or suppressed by setup changes. The understanding gained from these laboratory experiments is vital for interpreting later field experiments with thermo-sensitive tracers.

Experimental setup

Due to the above mentioned spatial and temporal requirements the experimental setup should be capable of providing a non-isothermal flow field. Therefore the selected experimental setup is governed by the advection-dispersion-reaction-equation,

\[
\frac{\partial c}{\partial t} = D_l \frac{\partial^2 c}{\partial l^2} - v \frac{\partial c}{\partial l} - kc
\]  

(1)

where the flow field is determined by Darcy’s law and the thermal dependency is given by the first order reaction rate \( k \) expressed by Arrhenius law

\[
k = Ae^{-\frac{E}{RT}}.
\]  

(2)

Note that for inert tracers \( k = 0 \), where all other processes are still valid. The presented results were conducted under steady state flow and isothermal conditions. That operation mode of the system, as a plug-flow-reactor, allows us initially to compare results directly with isothermal batch experiments (Nottebohm et al., 2012). This is done to gauge the system prior to more complex operations modes, e.g. applied temperature field, unsteady flow, change of flow direction and others.

The experimental system consists of three separated flow systems. On the one hand, the tracer system in which tracer solute is pumped from the tracer reservoir through two columns, mounted in separate chambers to the fluorescence detector. On the other hand, the two temperature-controlled water reservoirs which are connected to the column chambers via thermally insulated pipes. Note that each thermostat corresponds to one chamber and therefore one column only (Figure 1).

Figure 1: Upper: Initial sketch of the experimental setup. From left to right the tracer solute flows from the reservoir via the pump through two differentially heated columns. At the outlet the BTC is recorded. Lower: Final column experimental design. From left to right the fluorescence detector connected to the PC, the pumping module, the vertically standing column setup and two temperature water reservoirs (one for each column)
The core of the system comprises of two stainless steel columns 0.5 m each with \( \Phi = 3E^{-2} \) m. They are coupled together in series via interconnecting pipes and are positioned vertically. The use of stainless steel ensures that the applied temperatures of the surrounding water bath is conducted into the porous media packed columns and maintain a fixed thermal boundary condition. The columns where filled with sieved sand of grain sizes between 125–250 \( \mu m \). The uniform size of the sieved sand provides a homogeneous porous media packing, which maintains its hydraulic properties over a number of experiments. It further reduces the influence of dispersion towards an ideal plug flow regime. Natural materials (e.g. reservoir sediments and sand) showed no influence on the reaction speed of hydrolysis (Nottebohm et al., 2012). The packing was done after the slurry method which provides best results for natural materials. The packed columns are mounted coaxially in the thermally insulated column chambers (Figure 2). Finally the experimental core is connected to external devices (Figure 1):

- Two thermostats which allow differential heating/cooling of the two columns
- The pump with adjustable flow rate and back pressure control
- Fluorescence spectrophotometer together with a tempered flow-through cell allowing simultaneous online measurements of multi-compound tracer solutions.

The operating procedure of the experimental setup starts with heating the inner columns bearing the porous media packing. After regulating the temperature of the water in the temperature reservoirs, the fluid will start circulating around the stainless steel columns and transmit the heat. Then the flow through cell inside the fluorescence detector is also pre-heated to the same temperature as the outlet from the upper column, in order to maintain isothermal conditions and accurate reading (Figure 3). Experiments are started once the system is in thermal equilibrium. The presented results were conducted under steady state flow and isothermal conditions. The tracers to be considered are uranine as an inert reference tracer (similar to an internal standard) and phenyl acetate as thermo-sensitive tracer (Nottebohm et al., 2012). Due to the experimental design it takes almost one week to exchange the columns. Hence one aim is to maintain stable conditions, so that several thermo-sensitive tracer experiments can be conducted with one set of mounted columns.

**RESULTS**

**Hydraulic characterisation**

Prior to the thermal experiments the packed columns where hydraulically characterised. This is done by classic step input tests using only uranine. Beside the estimation of the hydraulically relevant parameters (Table 1) e.g. effective porosity, interstitial velocity or dispersion coefficient the analysis of BTCs produced from each column separately is an inherent control that the packing is reproducible.

As stated above, the transport mechanism of the tracer is dominated by advection and hydrodynamic dispersion (eq. 1). Hydrodynamic dispersion leads to smearing of the tracer front, or in other words a wider band of tracer residence times with higher dispersion coefficients. As the end concentration of thermo-sensitive tracers depend on the residence time in the system maximizing the Peclet number

\[
Pe = \frac{vL}{D_0 + \alpha v}
\] (3)

is essential in order to ease the analysis. For the presented experimental system molecular diffusion can be neglected since \( D_0 \) is in the order of \( 1E^{-9} \) whereas \( \alpha v \) is of order \( 1E^{-7} \). With a total of one

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**Figure 2:** Installation of isothermal insulation; In gray is the column chamber surrounded by insulation (green) and coating (orange).

**Figure 3:** Temperature dependency of the uranine and phenol fluorescence signals. The correction factor applies for deviations of the sample temperature from the reference temperature.
Table 1: Hydraulic parameters of the packed columns. The spherical glass beads provide a slightly better packing in terms of eff. porosity than sand. The columns were characterised ($Q = 3 \text{ ml/min}$) separately as well as in the later mounted serial configuration. The $R^2$ refers to nonlinear curve fitting to the analytical solution of eq. 1.

<table>
<thead>
<tr>
<th>Packing</th>
<th>Column</th>
<th>Velocity [m/s]</th>
<th>Dispersion coefficient [m$^2$/s]</th>
<th>Eff. porosity [1]</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass beads</td>
<td>1</td>
<td>1.83E-4</td>
<td>1.77E-7</td>
<td>0.39</td>
<td>.998</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.76E-4</td>
<td>0.99E-7</td>
<td>0.38</td>
<td>.995</td>
</tr>
<tr>
<td></td>
<td>1+2</td>
<td>1.78E-4</td>
<td>2.99E-7</td>
<td>0.39</td>
<td>.986</td>
</tr>
<tr>
<td>Sand</td>
<td>1</td>
<td>1.79E-4</td>
<td>0.50E-7</td>
<td>0.40</td>
<td>.999</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.72E-4</td>
<td>0.46E-7</td>
<td>0.40</td>
<td>.998</td>
</tr>
<tr>
<td></td>
<td>1+2</td>
<td>1.76E-4</td>
<td>0.50E-7</td>
<td>0.40</td>
<td>.999</td>
</tr>
</tbody>
</table>

meter column length the system is clearly advection dominated since $Pe$ is in the order of 1000. Systems with high $Pe$ numbers show a sharp and fast breakthrough with a small bandwidth of tracer residence time. This allows in turn estimating a mean residence time for the analysis of the BTC.

Isothermal experiment - Static batch experiments

The solute to be used in the column experiments contains phenyl acetate ($c = 10 \text{ mg/l}$), uranine ($c = 0.05 \text{ mg/l}$) and phosphate buffer ($1 = 0.014 \text{ mol/L, pH} = 7$). Note that the hydrolysis product of phenyl acetate is measured, since phenol has fluorescent properties but not its ester. Here uranine will be used as reference compound as it is stable and inert under the applied temperature conditions. The adjusted $pH = 7$ allows the comparison with the results from Nottebohm et al. (2012). Note that the kinetic parameters are extremely sensitive to the $pH$. For any decrease of $pH$ by 1 unit, between $pH = 6–8$, the reaction rate of the reactive tracer reduces approximately one order of magnitude (Nottebohm et al., 2012). The buffer is used to maintain a constant $pH$ of the solute, hence to maintain a stable dependency of reaction rate on temperature (eq. 2). The kinetic parameters, for the used $pH$ of the solute where $E_a = 77 \text{ kJ/mol}$ and $\ln A = 25.5 \text{ h}^{-1}$ (Nottebohm et al., 2012). These parameters where verified again for the used tracer solute and packing material using batch experiments. For sand a small scattering around the values reported by Nottebohm et al. (2012) of the estimated reaction rates was obtained (Figure 4). This demonstrates the quality and robustness of the data set presented in Nottebohm et al. (2012).

In addition to the sand as packing material glass beads of comparable size were also tested. Their spherical shape combined with their smooth surface leads to even better packing (Table 1) as well as reproducible hydraulic conditions between experiments. However, it turned out that the artificial material showed a higher reaction rate then natural materials (Figure 4). Therefore the data transferability to geothermal systems may be limited.

![Figure 4: The obtained reaction rates of the used tracer solute and tracer solute / sand mixture matches the values obtained from Nottebohm et al. (2012), in contrast reaction rates from the tracer solute / glass beads mixture are clearly of the line.](image)

![Figure 5: Relation between residence time and tracer reaction for different isothermal temperatures](image)
**Table 2:** Comparison of the estimated temperature with the applied temperature. The sand packing provides precise estimates for single experiments. Due to more scatter (Fig. 5) the glass packing was analysed using mean values for the reaction rate ($n = 3,5,4$ for $T = 40,50,60$ °C).

<table>
<thead>
<tr>
<th>Packing</th>
<th>Q [ml/min]</th>
<th>residence time [h]</th>
<th>T estimated [°C]</th>
<th>T applied [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.4</td>
<td>11.56</td>
<td>59.7</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>6.76</td>
<td>60.0</td>
<td>60</td>
</tr>
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<td></td>
<td>3.0</td>
<td>1.57</td>
<td>62.8</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.51</td>
<td>62.5</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.62</td>
<td>61.5</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.19</td>
<td>63.7</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>1.18</td>
<td>63.6</td>
<td>60</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td></td>
<td>62.0 ± 1.6</td>
<td>60</td>
</tr>
<tr>
<td>Glass beads</td>
<td>Mean values</td>
<td></td>
<td>40.5 ± 16</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48.5 ± 15</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>63.0 ± 5</td>
<td>60</td>
</tr>
</tbody>
</table>

**Isothermal experiment - Dynamic column experiments**

Initially, isothermal experiments were conducted for system temperatures of 40, 50, 60 °C with various pumping rates. Under these isothermal conditions it was possible to obtain the fundamental relationship of phenyl acetate concentration to tracer residence time according to the decay equation which states that for longer residence times more thermo-sensitive tracer reacts (Figure 5). Furthermore the temperature dependency is clearly seen, which states that for higher temperature, the reaction rate is higher and hence more thermo-sensitive tracer reacts. By applying eq. 2 the obtained tracer concentrations can be transformed into a system temperature estimate (Table 2). The system temperature estimates show a high accuracy and in the case of sand packing a very good reproducibility.

**CONCLUSIONS**

During the last decades, thermo-sensitive reactive tracers are considered as a method to obtain in-situ information about geothermal reservoir temperature and temperature evolution. In theory, the reaction rate is proportionally related to the temperature of the reservoir. Hence the measured concentrations are a function of temperature and residence time. Based on the relationship an evaluation of the thermal drawdown of geothermal reservoirs should be possible. This work contributes experimental results to the ongoing discussion.

This laboratory work is the first successful experimental trial, known so far, to validate the underlying theory in a flow system. The two main assumptions that for longer residence times and higher temperatures more thermo-sensitive tracer reacts are proven. Furthermore we obtain a high accuracy and good reproducibility of the estimated system temperature. The outcome from the experiments has validated the proportionality of the reaction rate to the temperature of thermal sensitive tracers. The residence time alone was the driving factor that determined the end concentration, and thus the system temperature, when the system was operated under isothermal conditions. Furthermore it turned out that for a reliable analysis of thermo-sensitive tracers and therefore better understanding of the investigated systems, the simultaneous injection of an inert reference tracer is essential. The inert tracer provides comparable spatial and temporal information and hence the combined analysis allows an improved specification of influences e.g. dispersion, retardation, flow path heterogeneities, tracer loss etc. which are important for the analysis. Such influences must be considered and cannot be detected by tracer tests using only thermo-sensitive tracers.

The use of artificial material (glass beads) showed that the estimation of the system temperature is possible, but due to very different kinetic constants, possibly caused by catalytic effects from the glass beads, the transferability to geothermal systems is limited. The use of glass beads for testing thermo-sensitive tracers based on hydrolysis is not recommended. Further experiments will be conducted with sand filled columns.

The experimental setup allows examining the influencing processes on thermo-sensitive tracers as it provides known boundary conditions e.g. temperature, pumping rate, geometry and material...
properties. Next steps planned are the analysis of a wider temperature spectrum as well as the application of non-isothermal temperature fields. Additionally, the application of different compounds and multiphase experiments is considered. Finally, the experimental setup aims to contribute solving questions about sensitivity in terms of temperature front estimation and interpretability of pumping and injection schemes (Push-Pull, Slug injection etc.).

**NOMENCLATURE**

- \( \alpha \) = dispersivity
- \( A \) = pre-exponential factor
- \( c \) = concentration
- \( D_0 \) = molecular diffusion coefficient
- \( D_L \) = longitudinal dispersion coefficient
- \( E_a \) = activation energy
- \( l \) = ionic strength
- \( k \) = 1st order reaction rate
- \( I \) = spatial coordinate
- \( L \) = column length
- \( Q \) = pumping rate
- \( R \) = ideal gas constant
- \( t \) = time
- \( T \) = temperature
- \( v \) = interstitial velocity

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**REFERENCES**


