Determination of temperatures and cooled fractions by means of hydrolyzable thermo-sensitive tracers

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ABSTRACT

This work presents the development of improved tracer techniques for monitoring internal temperatures and cooled fractions in water saturated porous media. The analysis is based on reactive chemical compounds whose hydrolysis reactions allow for accurate temperature measurements. The tracers are designed to improve geothermal reservoir management procedures. Thermo-sensitive tracers will provide valuable information about the thermal state of the examined permeable media. This is demonstrated by means of laboratory experiments with sand-packed columns. The special heating/cooling setup provides a defined internal temperature distribution. In 70 independent experiments, tracer sensitivity was examined. Practical limitations in three different experimental schemes, flow-through, moving thermal front and push–pull, were investigated. The results show that thermo-sensitive tracers can be used to measure temperatures and cooled fractions with high precision and accuracy.

1. Introduction

The efficient exploitation of geothermal energy plays an increasing role in the context of climate change (Arvizu et al., 2011). A preferred reservoir management strategy to enhance geothermal energy extraction efficiency is the reinjection of the heat-exploited geothermal waters. Because the heat extracted usually exceeds the natural heat flow with time (O'Sullivan et al., 2010), an increasing fraction of the reservoir volume is cooled down. We denote this relative volume as the cooled fraction χ. Hence, reinjection bears the potential risk of thermal short-circuiting (Stefansson, 1997). Thus, there is a direct need for methods enhancing reservoir monitoring and characterization in order to control and mitigate this risk (Goldstein et al., 2011). One possibility is to use physical methods, e.g., with heat as a tracer (temperature as the state variable), to measure and forecast thermal drawdown (e.g., Kocabas, 2005; Maier and Kocabas, 2013). However, due to the slow propagation of the thermal front, either very large injection volumes are needed or the result is only representative for the vicinity of the injection well (e.g., Ghergut et al., 2011). In contrast, chemical methods based on the injection of organic molecules benefit from a faster transport of solutes compared to heat in porous media. For systems with a

known linear relationship between solute and heat transport, a relative retardation factor can be derived (Bodvarsson, 1972). Hence, with chemical tracers showing a conservative behavior (e.g., Rose et al., 2001), it is theoretically possible to gain early information on the thermal flow properties (e.g., Shook, 2001; Pruess and Doughty, 2010).

A very promising approach is the use of a new and specifically developed tracer group. These compounds are based on previously established conservative dye tracers. However, their tracer properties are expanded by the incorporation of a reactant group susceptible to a known temperature-dependent hydrolysis reaction while preserving their other advantageous properties, such as fluorescence, conservative transport and stability of the backbone moiety (e.g., Nottebohm et al., 2010; Schaffer et al., 2013). These recently developed and studied thermo-sensitive tracers (TSTs) can be used to predict in situ temperatures and temperature distributions (Maier et al., 2013, 2014, 2015). The underlying theory of TSTs was formulated in the mid 1980s (Robinson et al., 1984; Tester et al., 1986) and the increasing relevance of geothermal energy led to an intensive numerical/theoretical discussion (e.g., Behrens et al., 2009; Plummer et al., 2012). However, the assumptions and deductions from the governing equations describing energy (advection and conduction) and mass transport (advection and dispersion), as well as relevant couplings in a dynamic flow system lacked experimental validation (e.g., Plummer et al., 2010). Recent experiments, applying phenol acetate (PhAc) as TST, proved the transferability of the results from isothermal static batch tests (Nottebohm et al.,

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Nomenclature

∇	Nabla operator
A	Pre-exponential factor
c_i	Concentration of ith tracer
c_p	Fluid heat capacity at constant pressure
D	Dispersion coefficient
E_a	Activation energy
k	Rate constant
k_{eff}	Effective reaction rate constant
k_i	Bounding rate constants, the indices ($i = 1, 2$) relate to different temperatures
k_L	Thermal conductivity of the fluid
k_S	Thermal conductivity of the solid
k_{we}	Weighted thermal conductivity
Q	Thermal sink/source
R	Ideal gas constant
R_i	Solute sink/source term
T	Temperature
t	Time
T_{eq}	Equivalent temperature
T_{mean}	Mean temperature
$\boldsymbol{u}$	Darcy velocity vector
ρ	Fluid density
φ	Porosity
φ_S	Solid material's volume fraction
χ	Cooled fraction

2012) to isothermal dynamic flow experiments (Maier et al., 2013). A high precision and accuracy of the temperature estimates within ∼2 K was obtained (Maier et al., 2015). The choice of an appropriate TST is hereby crucial for a successful experiment. PhAc has Arrhenius parameters most suitable for low temperature environments. Nevertheless, the proposed evaluation procedure is independent of the actual reaction rate and thus, can be also applied to the evaluation of tracer compounds having much lower reaction rates.

The objective of the current work is to investigate the tracer behavior in non-isothermal environments under controlled laboratory conditions. The laboratory experiments that were performed are based on common field tracer test designs (continuous, pulse, and push–pull injections). A defined thermal front position was applied in order to explore the feasibility and limitations of the proposed tracer methods by a differentially heated setup. As a result, the general ability of TSTs to estimate system temperatures and χ can be assessed and valuable implications for future field tests can be derived.

2. Material and methods

2.1. Experimental design

The laboratory column setup as described by Maier et al. (2015) was slightly modified to allow the examination of tracer behavior in non-isothermal flow environments. The system consists of two serially connected stainless steel columns that are filled with sieved sand (fraction between 125 and 250 μm) providing a homogeneous flow field. Each column was individually heated by an external water jacket. In addition to the setup described in Maier et al. (2015), a switching valve was installed to enable reversed flow inside the two columns. Hence, different operation modes for various tracer applications can be investigated. In the experiments, solutions containing both a conservative tracer and a TST were injected into the column system. All of the tracers have flu-

orescent properties, allowing their online recording at the column inlet and outlet, respectively.

2.2. Chemicals

The TST solution was prepared using phenol acetate (PhAc, CAS: 122-79-2) from Acros Organics, Geel, Belgium dissolved in water to produce a concentration c of 10 mg/L. PhAc was chosen because it reacts sufficiently fast under the applied laboratory conditions. Furthermore, an extensive dataset on the hydrolysis reaction kinetics of PhAc is available in Nottebohm et al. (2012). For internal referencing, PhAc was accompanied by $c = 0.4$ mg/L of the tracer 2-naphthol-3,6-disulfonic acid (2-OH-3,6-NDS, CAS: 135-51-3) (Nottebohm and Licha, 2012) purchased from TCI Europe, Zwijndrecht, Belgium. Sulfonic acids are known to be non-reactive and conservative tracers (Schaffer and Licha, 2015). Both tracers were dissolved in a buffered (pH 7 at room temperature) aqueous solution containing 0.01 M aqueous N,N-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES, CAS: 10191-18-1) (Good et al., 1966) and 5 g/L NaCl.

2.3. Governing equations

The reactive transport of (thermo-sensitive) tracers in non-isothermal porous media can be described with a set of coupled partial differential equations. The transport of the tracers follows the advection–dispersion–reaction–equation:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D \nabla c_i) - \frac{\boldsymbol{u}}{\varphi} \cdot \nabla c_i + R_i \tag{1}$$

where c_i is the tracer concentration, t the time, ∇ the nabla operator, D the dispersion coefficient, $\boldsymbol{u}$ the Darcy velocity vector, φ the porosity, and R_i a sink/source term. The temperature sensitivity is given by an OH^- catalyzed, and thus pOH dependent pseudo-first order hydrolysis reaction contributing to Eq. (1) as follows:

$$R_i = \begin{cases} -k c_i & \text{for} & \text{TST} \\ 0 & & \text{conservative tracer} \end{cases} \tag{2}$$

here k is the reaction rate constant expressed by the Arrhenius' law:

$$k = A e^{-\frac{E_a}{RT}} \tag{3}$$

where A is the pre-exponential factor, E_a the activation energy, R the ideal gas constant, and T the temperature. Hence, Eqs. (2) and (3) enables the coupling of Eq. (1) with the following equation for the energy transport:

$$\left(\varphi_S \rho_S c_{S,p} + \varphi \rho c_p \right) \frac{\partial T}{\partial t} = \nabla \cdot (k_{we} \nabla T) - \rho c_p \boldsymbol{u} \cdot \nabla T + Q \tag{4}$$

where ρ is the fluid density, c_p the fluid heat capacity at constant pressure, k_{we} is the weighted thermal conductivity, and Q is the heat sink/source. The subscript S denotes the solid parameters while k_{we} is related to the conductivity of the solid, k_S and to the conductivity of the fluid, k_L by:

$$k_{we} = \varphi_S k_S + \varphi k_L \tag{5}$$

with the solid material's volume fraction φ_S related to φ by:

$$\varphi_S + \varphi = 1 \tag{6}$$

For the presented experiments with an applied thermal distribution, the temperature is in steady state and, thus, the term on the left-hand side of Eq. (4) disappears. Note that minor couplings due to temperature dependent material parameters are not discussed.