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Study on the transformation mechanism of nitrate in a loose-pore geothermal reservoir: Experimental results and numerical simulations

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ABSTRACT

Concentration of NO_2^-–N in 26% of geothermal water samples collected from Kaifeng city, Henan province, China exceeds the national groundwater quality standard (0.02 mg/L). Thus there is a need to investigate the transformation mechanism of nitrate in a loose-pore geothermal reservoir. Column experiments were performed at temperatures from 20 °C to 65 °C and the computer code CXTFIT was used to fit the experimental data and to determine the transport parameters. The results revealed that the assumption of first-order reaction kinetics in convection–dispersion equation (CDE) resulted in a closer agreement between the model results and the data than the CDE model without reaction when Darcy's flux was decreased from 3.67 to 1.23 cm/h. The nitrate reduction rate, the removal efficiency of nitrate, and nitrite and ammonium accumulation all increased with temperature between 20 °C and 65 °C, which was accompanied by the decrease of Eh with temperature after 144 h. NO_3^-–N reduction rate and nitrite accumulation amount also increased upon NO_3^-–N loading. With limited types and amounts of carbon sources and bacteria, denitrification was incomplete at all the six experimental temperatures, giving a maximum nitrate reduction efficiency of 81.28% and a maximum ΣN removal efficiency of 37.75% at 65 °C after 144 h. 37.6% of the nitrate was converted to nitrite and 5.93% of the nitrate was converted to ammonium through dissimilatory nitrate reduction to ammonium (DNRA). High levels of nitrite and ammonium in the geothermal water of the study area also indicated the incomplete denitrification.

1. Introduction

The geothermal water in Kaifeng city, Henan province, China, is mainly exploited from a loose-pore geothermal reservoir which is composed of the Minghuazhen Formation in the Neogene Period with the depths between 600 m and 1400 m. Geothermal water has been intensively used since the early 1990s because it can be used for drinking, bathing, medical treatment, and health care (Wang and Huang, 2009; Yang et al., 2004). The geothermal water is of the HCO_3^-–Na^+ type and is categorized as alkalescent and soft water. SO_4^{2-} concentrations vary from 14.89 mg/L to 122.48 mg/L.

Overextraction of geothermal water in some areas of Kaifeng city has caused engineering and environmental problems over the last few years, such as reduced well water levels and flow, and deterioration of water quality (Wang et al., 2013; Yuan et al., 2006). Nitrite-nitrogen concentrations were measured in the water of 28 geothermal wells with depths that range between 300 m and 1300 m in Kaifeng city, North China Plain between 1992 and 1998. Increase of nitrite content was found in 65% of the geothermal water samples after exploitation (Yuan et al., 2006). The reason for this is still unclear, although Yuan et al. (2006) inferred that elevated nitrite in the geothermal water was related to denitrification or nitrification, which may be largely due to changes in geochemical and hydrogeological conditions. Through column experiments, Wang et al. (2012, 2013) demonstrated that nitrification could be neglected during NH_4^+–N transport in a loose-pore geothermal reservoir at the Darcy fluxes of 2.8 cm/h and 6.34 cm/h. Thus, efforts should be made to explore the transformation mechanism of nitrate in the study area, which is fundamental to understand what happens to nitrate and beneficial to investigate processes related to the N cycle in a loose-pore geothermal reservoir.

Biological denitrification is an anoxic microbial process in which nitrate is converted into N_2 through four enzymatic steps via nitrite intermediates [NO_2^-, nitric oxide (NO) and nitrous oxide (N_2O)]: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ (Hamlin et al., 2008). Denitrification manifests in autotrophic and heterotrophic ways and develops under anaerobic conditions (Soares, 2000). For denitrification, a first-order reaction and a zero-order reaction has been assumed (Greenan et al., 2006; Shah and Coulman, 1978). Nitrite accumulation is a reliable marker of nitrate overloading, insufficient electron donors, or insufficient contact time and can result in incomplete heterotrophic and autotrophic denitrification (Ge et al., 2012; Moon et al., 2008; Sahinkaya et al., 2011; Wang et al., 2009; Y. Zhao et al., 2011). Vega-Jarquin et al. (2008) speculated that under aerobic conditions, nitrite or ammonium is produced through

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assimilatory nitrate reduction in glucose-amended alkaline saline soil. Previous studies mainly focused on the effects of pH, carbon-to-nitrogen (C/N) ratio, types of carbon sources, types of electron donors such as reduced iron and pyrite, nitrate concentration, hydraulic retention time (HRT), oxygen concentration, and temperature on nitrate removal (Boaventura an Rodrigues, 1997; Her and Huang, 1995; Korom, 1992; Majumder et al., 2008; Rivett et al., 2008; Schwientek et al., 2008; Thayalakumaran et al., 2008; Yin et al., 2002; Zhao et al., 2012). However, few studies have focused on the effects of temperature on nitrate reduction and nitrite and ammonium accumulation during denitrification in the porewater of groundwater at depths below 600 m. Wang et al. (2013) performed column experiments to investigate the effect of temperature on nitrate transport and ammonium adsorption parameters in a geothermal reservoir. However, denitrification of nitrate was neglected in their study, because of the short test duration and the very good mass recovery (>0.98) in the effluent from the columns. The CDE can be used to describe the nitrate transport process at the Darcy fluxes of 2.72 cm/h, 6.71 cm/h and 10.99 cm/h under low-temperature geothermal experimental conditions (Wang et al., 2013). However, when the Darcy flux was decreased to some extent in our later column experiment studies, the NO_2^-–N concentration in the effluent increased and the NO_3^-–N concentration decreased in spite of the low organic carbon content in the matrix (0.745 mg/g) (L. Zhao et al., 2011).

Nitrite in the intestine is believed to cause several cancers, and it may cause methemoglobinemia, which is also known as blue baby syndrome, in infants. Furthermore, nitrite may form carcinogenic compounds such as nitrosamines in the stomach (Gómez et al., 2000; Kapoor and Viraraghavan, 1997). Under aerobic or anaerobic conditions, nitrate can be reduced to ammonium (NH_4^+) through DNRA. NH_4^+ can lead to nitrite formation, which may negatively affect the smell and taste of drinking water (World Health Organization, 1993). In view of these problems, numerous countries have promulgated specific regulations to set the maximum contamination levels of nitrite and ammonium in drinking water. In China, the allowable nitrite and ammonium levels are 0.02 and 0.2 mg/L, respectively (China State Bureau of Quality and Technical Supervision, 1993).

There is a basic need for simulating transport and transformation processes of nitrogen compounds in groundwater systems in order to assess baseline conditions and explore remediation schemes. The numerical reactive transport models, which are also widely used in many other scientific fields (Alt-Epping and Zhao, 2010; Awadh et al., 2013; Charifo et al., 2013; Hobbs et al., 2000; Mugler et al., 2012; Zhao et al., 2008a, 2010), are appealing approaches for such a purpose. For example, the water flow and nitrate transport global model (WNGM) was developed to simulate three-dimensional variably-saturated groundwater flow coupled with the transformation and transport of nitrogen compounds in the aquifer at a local scale (Bonton et al., 2012). A reaction module for the reactive transport in three-dimensional (RT3D) code was presented to describe transformations and transport of nitrogen compounds in a saturated groundwater aquifer and was successfully applied to study the field-scale nitrogen transformations at a cattle feedlot site (Clement et al., 1998; Lee et al., 2006). Then a modified version of the reactive transport model RT3D linked to the unsaturated-zone flow (UZF) package and MODFLOW (i.e. UZF-RT3D) was proposed to simulate multispecies reactive solute transport in variably saturated large-scale subsurface systems (Bailey et al., 2013a). Most recently, the model was successfully used to reproduce observed measurements of Se and NO_3^- concentrations in agricultural groundwater systems (Bailey et al., 2013b). Moreover, Hydrus-2D and other two-dimensional models can also be used to describe water and nitrate flow in multiple spatial dimensions (Tafteh and Sepaskhah, 2012). Although the models in two and three dimensions are suitable for applications at the field scale, they are more complicated than one-dimensional models and not easily accessible. In this work, we addressed the longitudinal transport and transformation of nitrate in a loose-pore geothermal reservoir, where the gravitational one-dimensional flow may be prevailed so that water and nitrate flow in deeper matrix profile might be described by a one-dimensional model. Tafteh and Sepaskhah (2012) also reported that a one-dimensional flow model could be suitable for simulation of nitrogen leaching at a higher soil depth (1.0 m). Thus, a one-dimensional reactive-transport model, which has been widely used for field and laboratory simulations (Chun et al., 2009; Clement et al., 1997; Peyrard et al., 2011; Tafteh and Sepaskhah, 2012), was used to simulate the transport and transformation of nitrate through column experiments in this study.

The theoretical analysis and numerical simulation of fluid flow in geological systems of crustal scales have been studied extensively and systematically in the emerging computational geoscience field (Zhao et al., 2008a, 2009 and the references therein included). Based on the finite element method, Zhao et al. (2009) developed advanced numerical methods and algorithms for solving coupled problems between fluids mixing, heat transfer and redox chemical reactions in fluid-saturated porous rocks within the crust of the Earth (Charifo et al., 2013; Schmidt Mumm et al., 2010). Such advanced numerical methods and algorithms have been widely used for solving both multi-dimensional ore-forming problems (Gow et al., 2002; Ju et al., 2011; Lin et al., 2006; Liu and Zhao, 2010; Liu et al., 2005, 2008, 2011; Ord et al., 2002; Schaubs and Zhao, 2002; Sorjonen-Ward and Zhang, 2002; Zhang et al., 2003, 2008) and many other types of multi-dimensional geoscience problems (Lin et al., 2003, 2008, 2009; Xing and Makinouchi, 2008; Zhang et al., 2011; Zhao, 2009). By considering the complexity of the interactions, some simplified conceptual models were also proposed to describe the controlling processes associated with the ore forming system (Zhao et al., 2009 and the references therein included). Because no mineral dissolution and precipitation are involved in our study, the instability phenomena of chemical dissolution fronts, which may occur in a mineral forming system (Zhao et al., 2008b, 2010), were neglected in this paper.

The current study aims to (1) evaluate the importance of flow rate on nitrate transport and reduction in a simulated loose-pore and low-temperature geothermal reservoir through column experiments and numerical simulations; (2) quantify the impact of temperature and nitrate loading on nitrate transformations under simulated geothermal conditions; and (3) determine the variation of nitrate, nitrite, and ammonium concentrations with depth and temperature in a loose-pore geothermal reservoir in Kaifeng city, North China Plain.

2. Materials and methods

2.1. Column design

The loose-pore geothermal reservoir matrix used for the tests was obtained from a 60 m-deep valley in the village of Wang-Gou, Qu-Liang town, in Xin-Mi county, China (Wang et al., 2013). Before use, all samples were air dried and ground to pass through a 2 mm screen.

Two columns (with a diameter and a height of 11 and 85 cm, respectively) were prepared for the experiments, which were larger in scale than those used in previous studies (Wang et al., 2013). These columns were identical and run as duplicates. The structure of the column and the method of packing of air-dried fine sand were similar to those used in previous studies (Wang et al., 2013). The column setups were placed in darkness inside an incubator. The incubator structure was already introduced in the literature (Wang et al., 2013). The nitrate elution experiments were performed at Darcy fluxes of 1.23, 2.64, and 3.67 cm/h, respectively, and at 35 °C for 252 h after saturation and the electrical conductivity of the outflow less than 100 μs/cm. At the end of each experiment, the porous medium in the column was leached for at least 7 d with deionized water to remove residual salinity caused by the nitrate solution. After each nitrate displacement experiment at 35 °C and at a Darcy flux of 3.67 cm/h, transformation experiments were performed for 144 h at temperatures of 20, 35, 45, 55, 60, and 65 °C respectively, with an average Darcy flux of 0.08 cm/h. As seen in