



Experimental method for determining mixed-phase precipitation kinetics from synthetic geothermal brine



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ABSTRACT

A batch reactor design for determining precipitation kinetics from an experimental (i.e. laboratory made) geothermal brine is presented. The purpose of the method is to improve techniques for predicting scaling risks in basin-hosted, enhanced geothermal systems (EGS). The method is applied to determining kinetic rate laws for alkali-earth metal sulfate precipitation in the Na–Ca–Ba–Sr–Cl–SO₄–H₂O system, which are a set of components commonly found in sedimentary basin brines, worldwide. The method of integral rates was used to determine alkali-earth metal precipitation kinetic rate laws for solutions reacting over 4 h at 75 °C and 150 °C. At 75 °C, the rate law for total sulfate precipitation is rate = 0.0137 * [SO₄²⁻]². At 150 °C, the rate law for total sulfate precipitation is rate = 0.011 * [SO₄²⁻]². All precipitants are found to be barite, with minor amounts of calcium and strontium incorporated into the barite structure. If only barite precipitation is considered, the rate coefficients become 0.045 and 0.025 at 75 °C and 150 °C, respectively. The precipitants' specific reactive surface areas are estimated for each time step and temperature and are qualitatively observed to decrease as the reactions progress. The (1) the reaction order, (2) the rate coefficient and (3) the change in specific reactive surface area over time are the three parameters required to develop reactive transport models of mineral precipitation in a geothermal power plant. All three of these parameters can be determined with the method employed in this study. Results from these experiments confirm previous results that precipitation kinetics are dependent on both starting concentrations and background salinities. Experiments designed to predict scaling risks in real geothermal systems require adjustments to the method presented herein, specifically (1) experimental fluids must more closely approximate real geothermal brines, (2) a larger reactor is required to produce a greater precipitant mass and (3) full quantitative assessment of the precipitants' specific reactive surface area are required to reduce the error of these measurements.

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1. Introduction

Over the last decade, sedimentary basins have received considerable attention as potential geothermal resources (e.g. Blackwell et al., 2007; Erdlac et al., 2007; Genter et al., 2003; Hartmann et al., 2008; Manning et al., 2007; MIT, 2006; Norden, 2009; Reyes and Jongens, 2005). *In situ* formation fluids in such basins can be produced and re-injected for sustainable production of heat and electricity. Due to their great age and extensive interaction with surrounding rock formations, these fluids (brines) are often characterized by a high concentration of dissolved mineral components (e.g. Bazin and Brosse, 1997; D'amore et al., 1997;

Eugster and Jones, 1979; Frape et al., 2004; Hanor, 1994; Kharaka et al., 1985; Kharaka and Hanor, 2004; Kuhn et al., 2003; Williams and McKibben, 1989). The high ionic strength of these fluids, combined with changes in temperature and pressure along its transport path in a geothermal installation, create a scaling risk during plant operation. Scaling, or process fouling by mineral growth on an industrial infrastructure, is a well-known hazard in many industries and has recently been the focus of much research in the geothermal community (e.g. Frick et al., 2011; Gunnarsson and Arnorsson, 2005; Kuhn et al., 2003; Minissale et al., 2008; Reyes et al., 2002; Wilson et al., 2007; Yanagisawa et al., 2005; Yanagisawa et al., 2008). Alkali earth metal sulfates, specifically anhydrite (CaSO₄; e.g. Opondo, 2002; Tulinius et al., 2000; Yanagisawa et al., 2011) and barite (BaSO₄; e.g. Kühn et al., 1997; Regenspurg et al., 2011) have previously been identified as particularly prominent scaling risks in geothermal systems.

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Accurate prediction of sulfate mineral scaling hazards is essential to the planning and operation of a basin-hosted geothermal system. Such predictions are often made with reactive transport models, which synthesize the mechanical, thermal and chemical parameters of the system into a holistic picture of fluid transport phenomena (e.g. MacQuarrie and Mayer, 2005; Steefel et al., 2005; Xu et al., 2005). The kinetic rate laws for expected mineral precipitants in a given system are required as input parameters in reactive-transport modeling software (e.g. Bethke, 2008; Parkhurst, 1995). While much previous work has been done on the issue of alkali-earth metal sulfate thermodynamics, solubility and precipitation/dissolution mechanics (e.g. Blount, 1977; Emmons et al., 2012; Fan et al., 2011; Raju and Atkinson, 1988; Raju and Atkinson, 1989; Templeton, 1960; Todd and Yuan, 1992), to date, no publications explicitly reveal kinetic rates laws for alkali-earth metal sulfate precipitation in the range of temperatures, pressures and compositions (T , p , x) often found in sedimentary basin hosted geothermal systems (e.g. Eugster and Jones, 1979; Frapé et al., 2004; Kharaka et al., 1985; Kharaka and Hanor, 2004; Williams and McKibben, 1989). Specifically, the parameters required for predicting sulfate mineral scaling risks in a geothermal system with reactive transport models are the (1) reaction rate coefficients (2) reaction orders and (3) the change in specific reactive surface areas (A_s) of multi-phase precipitants from a mixed-electrolyte brine. Currently, data for these parameters are essentially absent from the literature.

This paper presents a method for experimentally determining these three parameters for potential sulfate scale forming minerals in mixed-electrolyte brines at (T , p , x) conditions associated with basin-hosted geothermal systems. To approximate a real-world environment, the conditions used in the experiments herein were designed to resemble, but not replicate, the conditions found at the Groß Schönebeck *in situ* Geothermal Laboratory (GrSk) near Berlin, Germany (e.g. Feldbusch et al., 2013; Frick et al., 2011; Giese et al., 2002; Regenspurg et al., 2011). Located in the Northeast German Basin (NEGB), a sub-basin of the extensive Central European Basin System (CEBS), the GrSk site is considered to be representative of basin-hosted geothermal systems worldwide (Huenges, 2002; Huenges et al., 2004; Hurter, 2002). Thus, the experiments presented in this work investigated precipitation from a Na–Ca–Ba–Sr–Cl–SO₄–H₂O brine (see Table 1, below) with ~5 molal (mol/kg) background Cl⁻ concentration at 75 °C and 150 °C.

A batch reactor design similar to that of Sparks et al. (1996) was developed. Precipitation rates were determined by measuring the mass fraction of precipitants (compared to the total system's mass) formed in the experimental solution over time. The chemistry of the precipitated phase(s) was determined via X-ray fluorescence spectrometry (XRF), and the rate laws were calculated via the method of integrated rates. The change in the A_s was determined semi-quantitatively with a scanning electron microscope (SEM). The main purpose of this paper is to demonstrate a method for determining rate laws, not to predict scaling risks in any one particular geothermal system. Therefore, it was not necessary that the experimental concentrations directly replicate a real system, such as the GrSk system.

2. Methods

2.1. Experimental apparatus

A batch reaction system was used to determine alkali-earth metal sulfate precipitation rates in an experimental geothermal brine. Experiments were performed in a Berghof® BR-300 high-pressure reactor treated with a tantalum coating to prevent corrosion. The vessel has an internal volume of ~280 ml. As shown in Fig. 1, the apparatus consisted of a reactor vessel (Fig. 1a), a nitrogen (N₂) bottle for supplying pressure (Fig. 1b, behind the safety wall), a syringe pump for injecting fluid into the pressure vessel (Fig. 1c), a filter assembly (Fig. 1d) and a sampling cylinder (Fig. 1e). The vessel can operate at up to 200 °C and 20 MPa and can be stirred at up to 1000 rpm. In addition to the fittings for the pump, gas tank and sampling line (Fig. 1), the pressure vessel's lid was also equipped with an analogue manometer, a manual gas release valve and an over-pressure relief valve set to 1.5 MPa.

The vessel was pressurized via an external N₂ tank attached to the vessel with a 1/8" stainless steel (SS 316) capillary. For safety purposes, the gas tank was housed in a closet (Fig. 1b). The 1.5 MPa pressure relief valve prevented the reactor pressure from exceeding the pressures found in the GrSk plant, upon which these experiments were based (e.g. Frick et al., 2011). A syringe pump with a flow resolution of 0.001–204 ml/min (±0.1%) was used for fluid injection (Fig. 1c). The sampling line consisted of a 1/8" titanium (Grade 5) capillary inserted to the bottom of the pressure vessel that terminated outside the vessel at a 1/8" Alloy 400 dosing valve. The dosing valve was connected to a polyetheretherketone (PEEK) 50 mm membrane filter housing with a 1/8" perfluoroalkoxy (PFA) capillary. Cellulose acetate (CA) filters with a pore size of 0.2 μm were used in this study. The filtered fluid was collected in a 300 ml, PTFE lined, stainless steel (SS-304) sampling cylinder that was also connected to the filter housing with a 1/8" PFA capillary. The PFA capillaries used to connect the vessel to the filter unit and the filter unit to the sampling cylinder reduced the system's operating pressure to 2 MPa. The closed nature of the sampling cylinder prevented any vapor phase from escaping the system during depressurization and cooling.

2.2. Experimental procedure

The ionic concentration and the density of the experimental solution used in this study are shown in Table 1. The solution's density was required for converting the rate coefficient units derived in this study into standard rate coefficient units, as explained in 2.3, below. The measured concentrations of the pristine (i.e. before any reservoir stimulations) GrSk fluid are also shown for comparison in Table 1. Single distilled water was used as the aqueous phase in all solutions. All solutes were Merck™ brand analytical reagent grade salts. Two experimental solutions were prepared. The first solution, the "matrix," was a brine containing alkali and alkali-earth chloride salts. The second solution, the sulfate additive, was a 1 mol/kg sodium sulfate solution. The densities were measured at 25 °C with a hand-held density meter. Due to the non-routine nature of measuring pH in high ionic strength solutions, especially at elevated temperature (see, e.g.

Table 1
Molal (mol/kg) concentrations of ionic species in the experimental solution.

| Ion (mol/kg) | Na ⁺ | Ca ²⁺ | Sr ²⁺ | Ba ²⁺ | Cl ⁻ | SO ₄ ²⁻ | Density |
|---|-----------------|------------------|------------------|------------------|-----------------|-------------------------------|---------|
| Experimental (mixed) | 1.90 | 1.41 | 0.05 | 0.005 | 4.81 | 0.01 | 1.17 |
| Groß Schönebeck (converted from Giese et al., 2002) | 1.80 | 1.46 | 0.022 | 0.00022 | 5.10 | .002 | 1.19 |

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