

Reactive transport of aqueous protons in porous media



Colin J. McNeece, Marc A. Hesse*

The University of Texas at Austin, Department of Geological Sciences, 2275 Speedway Stop C9000, Austin, TX 78712-1722, United States

ARTICLE INFO

Article history:

Received 24 May 2016

Revised 20 September 2016

Accepted 23 September 2016

Available online 5 October 2016

Keywords:

Reactive transport

Porous media

Surface complexation

Chromatography

Acid-base chemistry

ABSTRACT

The sorption of protons determines the surface charge of natural media and is therefore a first-order control on contaminant transport. Significant effort has been extended to develop chemical models that quantify the sorption of protons at the mineral surface. To compare these models' effect on predicted proton transport, we present analytic solutions for column experiments through silica sand. Reaction front morphology is controlled by the functional relationship between the total sorbed and total aqueous proton concentrations. An inflection point in this function near neutral pH leads to a reversal in the classic front formation mechanism under basic conditions, such that proton desorption leads to a self-sharpening front, while adsorption leads to a spreading front. A composite reaction front comprising both a spreading and self-sharpening segment can occur when the injected and initial concentrations straddle the inflection point. This behavior is unique in single component reactive transport and arises due to the auto-ionization of water rather than electrostatic interactions at the mineral surface. We derive a regime diagram illustrating conditions under which different fronts occur, highlighting areas where model predictions diverge. Chemical models are then compared and validated against a systematic set of column experiments.

© 2016 Published by Elsevier Ltd.

1. Introduction

The transport of contaminants is affected by sorption onto mineral surfaces within the aquifer. Our basic understanding of solute transport with sorption stems from chromatographic concepts (Appelo and Postma, 2005; Charbeneau, 1981; Pope et al., 1978; Rhee et al., 2001; Valocchi et al., 1981). The classic chromatographic analysis considers surface chemistry models that provide an explicit relationship between the sorbed and aqueous concentration, often called isotherms, such as Freundlich and Langmuir, and has been extended to ion-exchange. These empirical models successfully capture the transport of major ions (Appelo and Postma, 2005; Charbeneau, 1988; Venkatraman et al., 2014; Voegelin et al., 2000), but fail to capture the dependence of sorption on ionic strength and large pH variations (Bethke, 2010; Tournassat et al., 2013; Zhu and Schwartz, 2011). Considerable effort has been extended to develop models suitable to these conditions by incorporating electrostatic interactions at the mineral-liquid interface, known as surface complexation models (Dzombak and Morel, 1990; Jeppu and Clement, 2012; Lützenkirchen et al., 2014; Schindler and Stumm, 1987; Yates et al., 1973). Proton trans-

port through clean, synthesized materials with well characterized surfaces has been predicted analytically using interpolations of titration data, and numerically in conjunction with the CD-MUSIC model (Filius et al., 1999; Meeussen et al., 1999; 1996; Scheidegger et al., 1994). However, chromatographic theory has not yet been extended to the surface complexation models most commonly used in reactive transport modeling, including CD-MUSIC (Goldberg et al., 2007).

In multicomponent systems the competition between proton and metal sorption leads to reaction fronts that are fundamentally different than those observed in classic competitive sorption (Gruber, 1995; Prigiobbe et al., 2013). Even in the absence of competing metals, the sorption of protons leads to complex reaction fronts (Scheidegger et al., 1994). However, it is unclear from previous work whether such reaction fronts arise due to electrostatic interactions at the mineral interface or the dissociation (auto-ionization) of water within the aqueous phase.

To identify the origin of the additional nonlinearity in proton transport we focus our analysis on the single component system. Here we present an extension of chromatographic theory to the surface chemistry models most often used in reactive transport, including surface complexation models. The theory identifies three different types of reaction fronts, and allows the construction of a regime diagram which summarizes their occurrence. Transport behavior can then be directly compared across chemical models and discrepancies in predicted behavior become apparent. We report a

* Corresponding author.

E-mail addresses: cmcneece@utexas.edu (C.J. McNeece), mhesse@jsg.utexas.edu (M.A. Hesse).

systematic set of transport experiments designed to test the ability of commonly used surface chemistry models to predict proton transport behavior through a natural porous media, over a wide range of chemical conditions.

2. Reactive transport model

The reactive transport model for protons couples the conservation laws for the chemical components to the equations describing local chemical equilibrium. Below, we first review the surface chemistry models most commonly used in reactive transport modeling and then the appropriate conservation laws.

2.1. Surface chemistry

Surface chemistry models contain two major components, the set of chemical reactions in the system and the description of electrostatic interactions at the mineral-liquid interface. The latter have been neglected in classical chromatographic theory (Rhee et al., 1971) and their effect on proton transport is considered here.

2.1.1. Chemical reactions and balance equations

The simplest model describing proton sorption must consider both the auto-ionization of water and the sorption of H^+ onto the silica surface



where SiO is the surface silicon oxide, and K_w and K_a are the respective equilibrium constants (Hiemstra et al., 1989). The aqueous complexation of protons described by Eq. (1a) is the key difference between the reactive transport of protons and that of metal cations, where aqueous complexation is often a second-order effect that can be neglected (Pope et al., 1978; Valocchi et al., 1981; Venkatraman et al., 2014; Voegelin et al., 2000).

The equilibrium distribution of species is given by the laws of mass action associated with Eqs. (1a) and (1b)

$$K_w = \{H^+\}\{OH^-\}, \quad (2a)$$

$$K_a e^{(F\Psi_o/RT)} = \hat{K}_a = \frac{[SiO^-]\{H^+\}}{[SiOH]}, \quad (2b)$$

where F is Faraday's constant (C/mol), Ψ_o is the electrostatic potential at the mineral surface (V), R is the gas constant (J/(°K mol)), and T is temperature (°K). Quantities in $[-]$ and $\{-\}$ correspond to concentrations and activities, respectively. The electrostatic potential, Ψ_o , must be determined using one of the models for the electrostatic interactions at the mineral interface reviewed in Section 2.1.2.

The total molar concentrations of the three linearly independent basis components is given by

$$\Sigma H = [H^+] - [OH^-] + [SiOH], \quad (3a)$$

$$\Sigma H_2O = [H_2O] + [OH^-], \quad (3b)$$

$$\Sigma SiO = [SiO^-] + [SiOH], \quad (3c)$$

and must be specified to determine the concentrations of all five species. The total concentration of surface sites is given by $\Sigma SiO = Sa\rho_s 10^{-3}/N_A$, where S is the specific surface area (m^2/kg), a is the mass of solid per volume of pore space (kg/m^3), ρ_s is the density of surface sites ($\#/m^2$) and N_A is Avagadro's constant.

In the formulation of the conservation law in Section 2.2, it is useful to distinguish the total aqueous proton concentration, c , and total surface proton concentration, s , so that $\Sigma H = c + s$, where

$$c = [H^+] - [OH^-], \quad (4a)$$

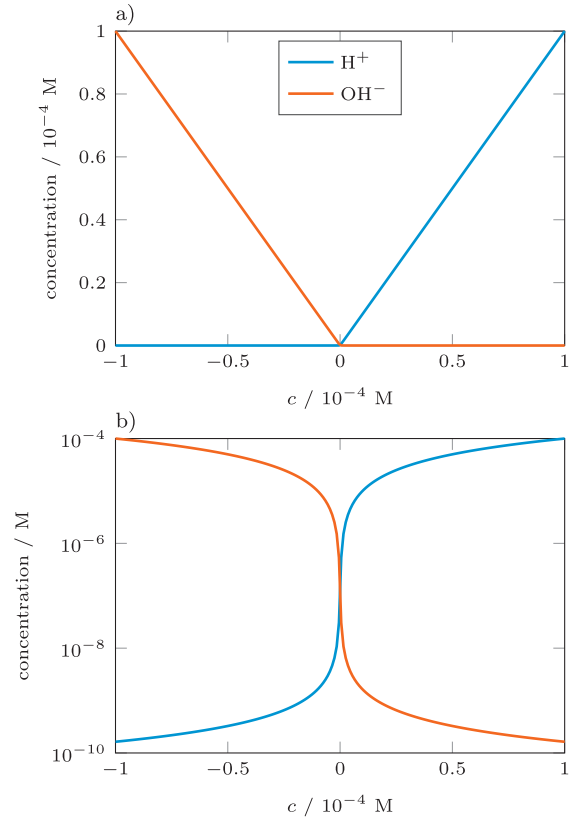


Fig. 1. Aqueous acidity. The distribution of H^+ and OH^- as a function of acidity, c , on a linear a), and \log_{10} scale b).

$$s = [SiOH]. \quad (4b)$$

The total aqueous proton concentration, c , is generally referred to as *acidity*. The relationship between c and its constituent components is shown in Fig. 1. The acidity represents OH^- concentration under basic conditions and H^+ concentration under acidic conditions. At local chemical equilibrium and constant pressure, temperature, and ionic strength, s is a uniquely defined function of c .

The Non-electrostatic model (NEM) considers the limit of negligible surface potential, $\Psi_o = 0$. In this case $\hat{K}_a = K_a$ is a parameter sensitive to pH. A single parametrization is typically able to represent sorption data over a ~ 2 pH unit range (Westall et al., 1995). However, as we aim to highlight the effect of electrostatic assumptions, we keep a single parametrization for the Non-electrostatic model despite the larger pH range considered here.

2.1.2. Electrostatic interactions at the mineral interface

Surface complexation models determine Ψ_o in Eq. (2b) from models of the electrostatic interactions at the mineral interface. Stern (1924) combined the electrostatic theories of Helmholtz (1853), Gouy (1910) and Chapman (1913) to form the basis of modern surface complexation models. We will first introduce the Basic Stern model (BSM) and then consider its limiting cases, the Constant Capacitance (CCM) and Diffuse Layer models (DLM) for high and low ionic strengths respectively.

Stern considered the mineral-liquid interface as discrete planes of charge and potential (Fig. 2a). The mineral surface has charge density σ_o (C/ m^2) as determined by the direct sorption of ions like H^+ to the mineral surface, so called inner sphere complexes. At the Inner Helmholtz Plane (IHP) sorbed ions are separated from the surface by their waters of hydration and form outer sphere complexes with the surface. The IHP has potential Ψ_1 and charge σ_1 .

Download English Version:

<https://daneshyari.com/en/article/6380607>

Download Persian Version:

<https://daneshyari.com/article/6380607>

[Daneshyari.com](https://daneshyari.com)