Reactive Transport of Aqueous Protons in Porous Media

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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.

Keywords: protons, reactive transport, porous media, surface complexation, chromatography, acid-base chemistry

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 [1, 2, 3, 4, 5]. 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 [6, 7, 8, 5], but fail to capture the dependence of sorption on ionic strength and large pH variations [9, 10, 11]. 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 [12, 13, 14, 15, 16]. Proton transport 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 [17, 18, 19, 20]. However, chromatographic theory has not yet been extended to the surface complexation models most commonly used in reactive transport modeling, including CD-MUSIC [21].

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 [22, 23]. Even in the absence of competing metals, the sorption of protons leads to complex reaction fronts [19]. 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 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.

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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-fluid interface. The latter have been neglected in classical chromatographic theory [24] 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 [25]. The aqueous complexation of protons described by Equation (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 [4, 2, 7, 6].

The equilibrium distribution of species is given by the laws of mass action associated with Equations (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 $\Sigma SiO = S a \rho_s 10^{-3} / N_A$, 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

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

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

The total aqueous proton concentration, c , is generally referred to as *acidity*. The relationship between c and its constituent components is shown in Figure 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 [26]. 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.

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

2.1.2. Electrostatic interactions at the mineral interface

Surface complexation models determine Ψ_o in Equation (2b) from models of the electrostatic interactions at the mineral interface. Stern [27] combined the electrostatic theories of Helmholtz [28], Gouy, [29] and Chapman [30] to form the basis of modern surface complexation models. We will first introduce this 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.

Figure 2: **Surface complexation models.** a) A schematic representation of the mineral interface for the Basic Stern model and its limiting cases the Constant Capacitance and Diffuse Layer models. Electrical potential is shown as a function of distance from the mineral surface as segmented by charge accumulation planes. At a pH of 4 for the silica sand of this study b) shows the potential drop between the surface and IHP (blue) and within the diffuse layer (burnt orange) as a function of ionic strength as calculated by the Basic Stern model. c) shows the contributions to the total capacitance by the Helmholtz and diffuse layer component of the Basic Stern model, Equation (9).

Stern considered the mineral-liquid interface as discrete planes of charge and potential (Figure 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 . The region between the surface and IHP has a constant capacitance and the electrostatics are governed Helmholtz's theory,

$$\sigma_o = C_H (\Psi_o - \Psi_1), \quad (5)$$

where C_H is the capacitance density (F/m^2), referred to as capacitance for short. The Outer Helmholtz Plane (OHP) is the beginning of the diffuse layer and has potential Ψ_d and charge density σ_d . Strictly, the region between the IHP and OHP has a capacitance. Stern noted that little error was introduced into the total calculated integral capacitance by ignoring the contribution from this layer [27]. The Basic Stern model incorporates this simplification so that

$\Psi_1 = \Psi_d$. The Triple Layer model includes this additional layer as a second Helmholtz capacitance [31]. In the case of negligible outer sphere complexation, the inclusion of the second layer adds an adjustable parameter, but no new physics. For this reason we exclude the Triple Layer model from our analysis.

At the OHP a diffuse ion swarm experiences potential Ψ_d and balances the charge of the surface and IHP. The region beyond the OHP has a variable capacitance. The potential-charge relationship is given by Gouy-Chapman theory

$$\sigma_d = \sqrt{8 \cdot 10^3 RT I e_o e_w} \sinh \left(\frac{F \Psi_d}{2 RT} \right), \quad (6)$$

where I is the concentration of a 1:1 background electrolyte (mol/liter), e_o is the permittivity of free space (F/m), and e_w is the dielectric constant of water. For the simple monovalent electrolytes considered here I is the ionic strength of the solution. Divalent electrolytes require a more complex expression [32].

Finally, charge balance is enforced,

$$\sigma_o + \sigma_1 + \sigma_d = 0, \quad (7)$$

where the charge density of the mineral surface is related to the concentration of free sites by

$$\sigma_o = -\frac{F}{S_a} [\text{SiO}^-]. \quad (8)$$

This study does not consider outer sphere complexes, therefore $\sigma_1 = 0$.

We now consider the limiting cases of the Basic Stern model by an examination of the integral capacitance of the mineral-liquid interface,

$$\frac{1}{C_T} = \frac{1}{C_H} + \frac{1}{C_D}, \quad (9)$$

where C_T is the total capacitance, and $C_D = \partial \sigma_d / \partial \Psi_d$ is the capacitance of the diffuse layer [31]. As ionic strength increases the diffuse layer is compressed, its capacitance increases, and the potential drop across the diffuse layer declines (Figures 2b and 2c). Therefore, in the limit of large ionic strength, the system can be approximated by the Constant Capacitance model by setting $\Psi_1 = \Psi_d = \sigma_1 = \sigma_d = 0$. A strict charge balance is not possible with the Constant Capacitance model. As the ionic strength decreases, the diffuse layer grows wider, its capacitance diminishes, and the potential drop across it increases. In the limit of low ionic strength, the majority of the potential drop occurs in the diffuse layer and the system can be approximated by the Diffuse Layer model, assuming $\Psi_o = \Psi_1 = \Psi_d$ and $\sigma_1 = 0$. The diffuse layer charge must then balance the surface charge to maintain electroneutrality, $\sigma_o = -\sigma_d$.

The CD-MUSIC model (CDM) couples a mechanistic determination of K_a with the Basic Stern model [25] and keeps only C_H as an adjustable parameter. The charging

behavior of surface sites in the CD-MUSIC model is also determined mechanistically, however, for silica surfaces the valence does not differ from the assumptions of Equation (1b). In this study, K_a is kept as an adjustable parameter for all models except CD-MUSIC.

2.2. Proton transport equation

The reactive transport model requires a conservation equation for each of the basis components of Equation (3). In dilute solutions with negligible dissolution/precipitation the total concentrations of surface and water components are constant, and their respective conservation laws are trivially satisfied. Therefore, only the conservation law for the proton component must be considered.

At local chemical equilibrium the transport of protons in a saturated sand packed column of constant porosity is given by

$$\frac{\partial}{\partial \tau} (c + s(c)) + \frac{\partial c}{\partial z} - \text{Pe}^{-1} \frac{\partial^2 c}{\partial z^2} = 0. \quad (10)$$

Here, $\tau = tv/L$, $z = x/L$, and $\text{Pe} = vL/D$ is the Peclet number, where v is the average fluid velocity, L is the column length, and D is the hydrodynamic dispersion coefficient [5]. Note that both c and s are dimensional and have units of molarity, i.e., moles per liter of water (Appendix A). The dimensionless time τ corresponds to pore volumes injected. The column flood experiments presented in Section 4 can be represented by the following piecewise-constant initial condition

$$c(z, \tau = 0) = \begin{cases} c_{\text{inj}} & z < 0, \\ c_{\text{ini}} & z > 0, \end{cases} \quad (11)$$

where c_{ini} is the acidity of the initial solution in the column, and c_{inj} is the acidity of the injected solution which is introduced at $\tau = 0$.

Equation (10) shows that $s(c)$ is the non-linearity that determines the behavior of protons during reactive transport [19, 23]. Below we will refer to $s(c)$ as the *equilibrium constraint*, because it represents the constraints that local chemical equilibrium imposes on the transport of protons. The chromatographic analysis presented in Section 3 shows that the entire reactive transport behavior can be deduced from the shape of this equilibrium constraint.

2.3. Comparison of surface chemistry models

Section 2.1 has introduced five different surface chemistry models for the sorption of H^+ onto oxide surfaces. The direct comparison of these models is impeded by the differing graphical representations in the literature [21]. In particular, it is not possible to gain an intuitive understanding of the effect of surface complexation models on reactive transport, because the equilibrium constraint required for chromatographic analysis is rarely shown. To bridge this gap, Figure 3 shows the model predictions in several common graphical representations. To illustrate the connection between surface complexation models and

sorption isotherms we substitute (2b) into (3c) to obtain the following expression for the equilibrium constraint,

$$\frac{s}{\Sigma \text{SiO}} = \frac{\{\text{H}^+\}}{\hat{K}_a + \{\text{H}^+\}} = \frac{K\{\text{H}^+\}}{1 + K\{\text{H}^+\}}, \quad (12)$$

where $K = 1/\hat{K}_a$ is the equilibrium constant for the adsorption reaction. In the Non-electrostatic model Equation (12) is an explicit function and reduces to the Langmuir isotherm [33, 24, 5]. This behavior arises because the surface has a finite number of sites that can be either free or occupied. For surface complexation models, Equation (12) must be solved together with the electrostatic relationships given by Equations (5) to (7).

Figure 3a compares the fraction of occupied sites, predicted by surface chemistry models, as a function of aqueous hydrogen ion activity, $s = s(\{\text{H}^+\})$. This representation is suggested by the form of Equation (12) and therefore commonly used to illustrate sorption isotherms [5]. For all models the fraction of occupied sites initially increases very rapidly but then saturates slowly.

In studies of interfacial chemistry the surface charge density is often measured experimentally as a function of solution $p\text{H}$. This relationship is therefore commonly used to compare surface complexation models with experimental data and is shown in Figure 3b. This representation allows a better comparison of the models under basic conditions than the isotherms shown in Figure 3a.

However, neither of these two representations are suitable to infer the transport behavior of protons [19, 23], which depends on the equilibrium constraint, $s = s(c)$, discussed in the previous section. This relationship is obtained by substituting,

$$\{\text{H}^+\} = \frac{1}{2} \left(\gamma_{\text{H}^+} c + \sqrt{\frac{\gamma_{\text{H}^+} 4K_w}{\gamma_{\text{OH}^-}} + c^2 \gamma_{\text{H}^+}^2} \right) \quad (13)$$

into Equation (12), where γ_{H^+} and γ_{OH^-} are activity coefficients. In this study, these coefficients are determined by the Davies Equation [34]. The resulting relationship is shown in Figure 3c. All chemical models predict a sigmoidal relationship which leads to the complex transport behavior of protons, discussed below. Under acidic conditions $c \approx [\text{H}^+]$ and the shape of the equilibrium constraint is similar to the isotherms shown in Figure 3a. Under basic conditions $c \approx -[\text{OH}^-]$ and Figure 3c shows a similar trend towards desaturation of surface sites.

The surface chemistry models shown in Figure 3c are parametrized against the experimental data discussed in Section 4.3. Model parameter values are given in Table 1. The equilibrium calculations presented in this study were verified for the Diffuse Layer and CD-MUSIC models by comparison with the USGS maintained software PHREEQC [35], see Appendix B.

Figure 3: **Proton equilibrium constraint.** a) classic representation for sorption isotherms: fraction of occupied sites vs. activity of H^+ in solution; b) common representation for surface complexation models: surface charge density vs. solution pH ; and c) the equilibrium constraint for chromatography: total sorbed proton concentration vs. total aqueous proton concentration (acidity).

3. Chromatographic analysis

Here we first identify different types of reaction fronts that can occur in the reactive transport of protons, by an analysis of the Riemann problem. We then present the solution to the transport model by the method of characteristics. A regime diagram of predicted transport behavior is derived, highlighting areas of model divergence. The chemical mechanisms of reaction front formation is later discussed in Section 5.

Model	pK_a	C
Non-electrostatic	$-10.1 \ (-8 \pm 0.5)^{36}$	-
Constant Capacitance	$-6.2 \ (-6 \pm 0.5)^{37}$	$0.8 \ (1)^{37}$
Diffuse Layer	$-8.5 \ (-8.2)^{37}$	-
Basic Stern	$-6.0 \ (-7.5)^{25}$	$1.35 \ (3.9)^{25}$
CD-MUSIC	-7.5^{25}	$4.7 \ (3.9)^{25}$

Table 1: **Model parameters.** Parameter values for each surface chemistry model. These values are determined by optimization against experimental data discussed in Section 4.3. Published values are shown in parenthesis.

3.1. Proton reaction fronts

To identify the different types of reaction fronts that occur during proton transport we analyze the reactive transport model, in the limit of large Peclet number, $Pe \gg 1$. Differentiating the accumulation term, the governing equation can be written in quasi-linear form

$$R(c) \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial z} = 0, \quad (14a)$$

where the retardation of the acidity is given by

$$R(c) = 1 + \frac{ds}{dc}. \quad (14b)$$

Figure 4: **Acidity retardation.** The retardation of acidity traveling through the silica sand packed column of this study, as computed by Equation (14b) for each surface chemistry model.

The retardation is the inverse of the propagation velocity and therefore corresponds directly to the pore volumes at which a concentration elutes. For all surface chemistry models considered here $R(c)$ is not monotonic (Figure 4). This is due to the inflection point in $s(c)$ (Figure 3c).

In contrast, the classic chromatographic analysis considers concave downward equilibrium constraints, $d^2s/dc^2 < 0$, such as the Langmuir and Freundlich isotherms [24, 5, 38, 39]. In these models, $R(c)$ is monotonic and only two types of transport behaviors are observed:

- A spreading front with a gradual change in c occurs when the injected concentration is lower than the initial

concentration. Such waves are called rarefactions and are denoted $\mathcal{R}$.

- A self-sharpening front with an abrupt change in c occurs when the injected concentration is higher than the initial concentration. Such waves are called shocks and are denoted $\mathcal{S}$.

A third of type of behavior is observed in proton transport due to the inflection point in $s(c)$ [19, 40, 23]: a single reaction front, which is composed of an initial rarefaction followed by a shock, denoted $\mathcal{RS}$.

3.2. Solution by the method of characteristics

The retardation $R(c)$ depends only on the unknown c , so that Equation (14a) is quasi-linear and allows solution by the method of characteristics [1, 41, 38, 39]. Each acidity travels along a curve in space-time given by the characteristic equation

$$z = z_0 + \frac{\tau}{R(c)}, \quad (15)$$

where z_0 is the initial location of the acidity. One characteristic emerges from both the initial and injected acidity and can be visualized in the τz -plane. Along each characteristic c is constant, so that the time of elution of each c at the end of the column, $z = 1$, can be determined. A closed form analytic solution $c = c(z, \tau)$ can be found only if the equilibrium constraint $s(c)$ can be inverted [42]. For the equilibrium relations considered here this is not possible and solutions are semi-analytic. In this case, the solution is constructed by the determination of the breakthrough time τ for a given c from the function $R(c)$. Figure 5 illustrates the solution construction for the three types of proton reaction fronts with the method of characteristics.

Figure 5a shows the τz -plane for a rarefaction, $\mathcal{R}$, and the corresponding elution history is shown in Figure 5d. A rarefaction occurs when $R(c)$ increases monotonically from c_{ini} to c_{inj} such that the initial acidity travels faster than the injected acidity. The characteristics emerging from the discontinuity form a spreading fan and illustrate the growth of the rarefaction with time as concentrations move further apart from one another.

Figure 5b shows the τz -plane for a shock, $\mathcal{S}$, and the corresponding elution history is shown in Figure 5e. A shock occurs when $R(c)$ decreases monotonically from c_{ini} to c_{inj} such that the initial acidity travels slower than the injected acidity. The characteristics of the discontinuity will then converge and overlap resulting in a triple valued elution history. This solution is non-physical and replaced by a shock [42, 41]. The retardation of the shock can be found by the Rankine-Hugoniot jump condition,

$$R_s(c_{\text{ini}}, c_{\text{inj}}) = 1 + \frac{s(c_{\text{ini}}) - s(c_{\text{inj}})}{c_{\text{ini}} - c_{\text{inj}}}. \quad (16)$$

The retardation of the shock, R_s , is always intermediate to $R(c_{\text{ini}})$ and $R(c_{\text{inj}})$, so that the characteristics converge onto the shock.

Figure 5c shows the τz -plane for a composite wave, $\mathcal{RS}$, and the corresponding elution history is shown in Figure 5f. A composite wave forms when $R(c)$ is non-monotonic between c_{ini} and c_{inj} such as when they straddle the inflection point c_I . The characteristics of the monotonically increasing portion of $R(c)$ form a spreading fan as above, however, as the reaction front crosses the inflection point, the retardation decreases, and the characteristics of c_{inj} intersect those of the rarefaction. The triple valued segment is replaced by a tangent shock connecting c_{tan} to c_{inj} [41, 43]. The tangent point, c_{tan} , is found by equating the retardation of the rarefaction and the retardation of the shock, so that

$$R_s(c_{\text{tan}}, c_{\text{inj}}) = R(c_{\text{tan}}). \quad (17)$$

The tangent construction is illustrated in Figure 6 for various initial conditions. As the injected acidity decreases, the retardation of the shock decreases, resulting in an earlier arrival. This trend is verified experimentally in Section 4. Irrespective of the choice of c_{ini} and c_{inj} , the composite wave will always comprise a fast rarefaction followed by a slow shock, because $R(c)$ has a local maximum [23].

3.3. Transport regime diagram

The chromatographic analysis identifies three different types of reactions fronts, allowing for the construction of a regime diagram that summarizes the conditions under which these fronts occur. Such a regime diagram for proton transport behavior is shown in Figure 7, and allows the comparison of predicted transport behavior between surface chemistry models and the design of validation experiments. This is particularly important in reactive transport modeling, given the abundance of model choices.

The 1:1 line represents no change in injected acidity and separates the $\mathcal{S}$ and $\mathcal{R}$ regimes. Therefore, these single fronts predominantly occur when the injected and initial acidity have like sign. In contrast, composite fronts can only occur if the injected and initial acidity have opposite sign. The vertical boundary separating the $\mathcal{R}$ and $\mathcal{RS}$ regimes marks the inflection point of the equilibrium constraint. This boundary is visually indistinguishable between models and is therefore plotted as a single line. The chromatographic analysis shows that only the $\mathcal{S}$ - $\mathcal{RS}$ boundary, determined by c_{tan} , is sensitive to the choice of surface chemistry model. The predictions for systems initially equilibrated with circumneutral solutions are the most sensitive to model choice and are shaded gray in Figure 7. This area widens rapidly as the injected acidity increases. The column experiments in Section 4 have been designed to clarify the behavior in this region.

4. Column experiments

The chromatographic analysis presented in Section 3 allows the targeted design of column flow experiments to validate model predictions. First, the material characterization and experimental procedures are reported in

Figure 5: **Characteristic fields of proton reaction fronts.** Characteristics fields are shown for the three types of wave structures observed in proton transport, as calculated from the Basic Stern model: a) $\mathcal{R}$, b) $\mathcal{S}$, and c) $\mathcal{RS}$. The corresponding calculated elution histories are shown in d), e), and f) respectively. The end of the column $z = 1$, is denoted by a horizontal dashed line. Construction of the characteristic field is discussed in Section 3.2.

Figure 6: **Construction of composite waves.** The solution structure for various initial conditions which result in a $\mathcal{RS}$ based on the Basic Stern model are shown. As the injected acidity is lowered, the slope of the shock path decreases and therefore the shock travels faster.

Sections 4.1 and 4.2. The determination of the equilibrium constraint from transport experiments is discussed in Section 4.3. Finally, design and results of the column experiments are presented in Section 4.4 and compared to model predictions via the regime diagram (Figure 7).

4.1. Material characterization

Silica sand, product name #1 Dry Unground Silica, was obtained from US SilicaTM. The average grain diameter and specific gravity are reported as $1.2 \cdot 10^{-4}$ m and 2650

Figure 7: **Regime diagram for proton transport.** Numbered markers correspond to elution histories shown in Figures 12 and 13. Closed and open circles represent experimentally observed single and composite fronts respectively (Table 2). Colored lines separating the $\mathcal{S}$ and $\mathcal{RS}$ regions represent the value of c_{tan} predicted by each model as a function of the injected acidity. Grey shading represents the region of divergent model predicts.

kg/m³ respectively (Figure 8a). The major mineralogical constituents of the sand as reported by US SilicaTM are SiO₂ (99.8%), Al₂O₃ (0.09%), K₂O (0.04%), and Fe₂O₃ (0.017%) with less than 0.01% of TiO₂, CaO, MgO, and Na₂O. CT-Scan and energy spectral density analysis confirm that the trace oxides do not appear as a surface coating (Figures

8b and 9). Prior to use, the silica sand was washed in a solution of 10^{-4} M NaOH for 30 minutes, rinsed, and then washed in a 10^{-4} M HCl solution for 30 minutes. The slurry was then rinsed with ultrapure water until a neutral pH was achieved. The specific surface area, determined by multi-point BET sorption with N_2 at -196 °C, was $50 \text{ m}^2/\text{kg}$.

Figure 8: **Silica sand images.** a) compound microscope image of the cleaned silica sand used in this study and b) CT scan of packed column used in transport experiments. Column porosity was measured by dry and wet mass weight as 0.325. Pure white regions are iron oxides.

Figure 9: **Silica sand surface chemistry.** Energy spectral density of the sand used in this study. The analysis was done over $2.5 \cdot 10^{-5} \text{ m}^2$ with grain density similar to Figure 8a. Sand grains were mounted on carbon tape resulting in a carbon peak.

4.2. Column experiment set-up and procedure

All experiments were conducted through a cylindrical glass column of length 0.37 m and inner diameter 0.015 m, packed with silica sand, with a porosity $\phi = 0.325$ and pore volume of $2.13 \cdot 10^{-5} \text{ m}^3$. A slurry density a of 5503 kg/m^3 was calculated by

$$a = \frac{1 - \phi}{\phi} \rho, \quad (18)$$

where ρ is the specific gravity of the silica sand. Solution ionic strength and pH were adjusted by the addition of

NaCl and NaOH or HCl to ultrapure, degassed water. All experiments were conducted at a temperature of 23 °C and ionic strength of 0.1 M. Effluent pH was recorded by an in-line probe. In an effort to exclude CO_2 , solutions were kept under N_2 gas and passed through an in-line Jasco™ de-gasser before entering the column. Flow was controlled by two Jasco™ HPLC pumps. A flow through valve allowed the influent solution to be changed instantaneously without disturbing the flow field. The experiment flow rate was set to $3 \cdot 10^{-6} \text{ m}^3/\text{min}$, corresponding to an average fluid velocity of $5.2 \cdot 10^{-2} \text{ m/min}$, which leads to a replacement of the pore volume every ~ 7.6 minutes. Tracer breakthrough curves suggest a longitudinal dispersivity coefficient equal to the grain diameter sufficiently matches the data (Appendix C). Together with published literature values for the molecular diffusion of H^+ results in a Pe-number of $O(10^3)$. The behavior within the column is therefore well approximated by the hyperbolic limit of the transport equation [5, 44, 45], and smoothing observed in elution curves is due primarily to mixing within the pH probe holder.

The initial and injected solution chemistry have been varied systematically to capture transitions in front morphology as shown in Figure 7. Experiment initial conditions as well as the resulting front morphology are given in Table 2.

Exp #	initial solution		injected solution		front morphology
	$c / 10^{-4}$	pH	$c / 10^{-4}$	pH	
1	1.000	4.107	0.672	4.279	$\mathcal{R}$
2	1.000	4.107	0.338	4.578	$\mathcal{R}$
3	1.000	4.107	0.095	5.131	$\mathcal{R}$
4	1.000	4.107	0.036	5.547	$\mathcal{R}$
5	1.000	4.107	-0.157	9.089	$\mathcal{RS}$
6	1.000	4.107	-0.504	9.595	$\mathcal{RS}$
7	1.000	4.107	-0.882	9.839	$\mathcal{RS}$
8	0.659	4.288	1.000	4.107	$\mathcal{S}$
9	0.337	4.579	1.007	4.104	$\mathcal{S}$
10	0.094	5.132	0.987	4.112	$\mathcal{S}$
11	0.037	5.534	1.000	4.107	$\mathcal{S}$
12	-0.154	9.082	1.000	4.107	$\mathcal{S}$
13	-0.492	9.585	1.000	4.107	$\mathcal{RS}$
14	-0.868	9.832	1.010	4.103	$\mathcal{RS}$

Table 2: **Experiment information.** Chemical information for initial and injected solution of each experiment as well as the resulting front morphology. Column packing, size, and flow conditions were identical between experiments and are given in Section 4.2.

4.3. Flow derived equilibrium constraint

For natural porous media, such as sands, experimental determination of sorption behavior is difficult, given the low surface area density. This excludes the use of zeta-potential as the material is not colloidally stable and batch titration methods due to the large volume of material needed [15, 46]. To overcome this obstacle, we determine the equilibrium constraint from flow through data directly. This method has been used to determine the charge density of silica sand [47], but can also be used to determine the equilibrium constraint of protons.

Figure 10: **Construction of transport derived equilibrium constraint.** The equilibrium constraint is derived by the integration of rarefaction fronts in basic (circles, experiment 7) and acidic (squares, experiment 14) regions. The data sets are related to each other by the breakthrough time of the shock components of the composite waves. The width of the shock fronts introduces uncertainty in the slope of the shock cords.

Rarefaction fronts sample $R(c)$ directly and therefore the breakthrough time of an acidity can be integrated to obtain the equilibrium constraint shown in Figure 3c by

$$s(c) = \int \tau(c) - 1 dc. \quad (19)$$

However, due to the inflection point, no single rarefaction can sample the entire equilibrium constraint. Therefore, $s(c)$ must be assembled from two rarefaction-shocks experiments, one that transitions from acidic to basic and one from basic to acidic. The two rarefaction derived curves are separated by an unknown constant of integration. In principle this constant can be determined by the shock speed of the composite front, which is a direct measure of the slope of the shock cord connecting the two curves. However, the diffuse nature of the experimentally observed shock fronts introduces some uncertainty in the reconstructed equilibrium constraint and is shown by error bars in Figure 10. The shock speed of the composite fronts is sensitive to the separation of these two curves. While it is possible to fit any individual experiment, the constant has been chosen to best represent the entire experimental sequence.

The values for model parameters were obtained by a least squares minimization against the flow derived equilibrium constraint and are given in Table 1. The surface site density ρ_s has been kept constant ($4.6 \cdot 10^{18}$ sites/m²) [48], while equilibrium constants, and the capacitance density have been fit for each model individually. A comparison of the flow through derived equilibrium constraint and surface chemistry model calculations is shown in Figure 11.

4.4. Experimental validation of regime transitions

Here we present two series of column flow experiments that determine the boundaries of the $\mathcal{RS}$ regimes. Figure 12a and 12c show elution histories sampling the transition

Figure 11: **Model and data equilibrium constraint.** A comparison of the flow through derived equilibrium constraint shown in markers to the various models considered in this study.

in behavior from $\mathcal{R}$ to $\mathcal{RS}$ by increasing the pH of the injected solution, as shown in Figure 7. Both the initial and injected solutions in experiments 1-4 are in the acidic regime. The desorption of H^+ leads to a classic rarefaction front, which grows as the injected pH increases. As the pH of the injected solution increases further, in experiments 5-7, the desorption rarefaction persists, however, the neutralization of desorbing H^+ under basic conditions leads to a trailing shock and hence a $\mathcal{RS}$ front. The shock speed increases with injected pH , as the ability of desorbing H^+ to neutralize the OH^- in solution decreases. The regime diagram of Figure 7 shows that all chemical models predict the $\mathcal{R}$ - $\mathcal{RS}$ transition.

Figure 12b and 12d show elution histories sampling the transition in behavior from $\mathcal{S}$ to $\mathcal{RS}$ by increasing the pH of the initial solution. Both the injected and initial solutions of experiments 8-11 are in the acidic regime, resulting in a sorption shock. The shock speed decreases with increasing initial pH , as more surface sites are initially available for H^+ adsorption. As the initial pH continues to increase, the shock speed stabilizes and is preceded by a growing rarefaction as water is ionized to supply enough H^+ to reach chemical equilibrium with the surface. Within the sampling density of our experimental series, only the electrostatic models with the Helmholtz component are capable of capturing this transition.

In areas of the regime diagram where models predict similar behavior a more detailed comparison of front features is useful. Figure 11 shows the Constant Capacitance and Basic Stern models offer similar fits to the transport derived equilibrium constraint across the range of acidity considered in this study. Therefore, these models also produce the best overall match to the experimental elution histories in Figures 12 and 13.

There is a considerable mismatch in the models prediction of composite waves which occur near neutral pH (experiments 5-6). Under these conditions the shock speed

Figure 12: **Elution histories of column experiments.** Two sets of elution histories demonstrating the emergence of composite reaction fronts. a) and c) transition from $\mathcal{R}$ to $\mathcal{RS}$ by an increase in the injected solution pH. b) and c) transition from $\mathcal{S}$ to $\mathcal{RS}$ by a decrease in the initial solution pH. Analytic solutions from the Basic Stern model are shown in dashed lines for comparison.

of composite waves is very sensitive to the curvature of the equilibrium constraint near neutral conditions, as shown by Equation (17) and Figure 6. Unfortunately, this is also the region where dispersion and mixing in the experiment affect the reconstruction of the equilibrium constraint via Equation (19) the most.

5. Discussion of the reaction front mechanisms

In general, adsorption of a solute leads to the formation of a self-sharpening front $\mathcal{S}$ and desorption to a spreading front $\mathcal{R}$ [42, 38, 5]. For proton sorption, the inflection point of $s(c)$ near neutral pH leads to a reversal of the front type under basic conditions, so that H^+ desorption produces a sharp front, while adsorption produces to a spreading front. While the chromatographic analysis in Section 3 predicts the occurrence of this reversal, it does not give insight into the underlying chemical mechanism. Here we discuss differences in the adsorption and desorption mechanisms under acidic and basic conditions that leads to this reversal.

The key to understanding this reversal is the recognition that the acidity, c , represents either $[\text{H}^+]$ under acidic conditions and $[\text{OH}^-]$ under basic conditions, see Figure 1. Therefore, reaction fronts under acidic conditions are H^+ fronts while reaction fronts under basic conditions are OH^- fronts, as illustrated in Figure 14.

Acidic reaction fronts are dominated by H^+ that sorb onto the mineral surface and the equilibrium constraint is concave downwards (Figure 3c), similar to the classic sorption isotherms (Figure 3a). Rarefactions arise when the injected acidity is lower than the initial acidity (Figure 14a). The spreading front develops as H^+ desorbs from the surface, raising the acidity of

the aqueous phase until the surface is in equilibrium with the injected solution. Shocks form when the injected acidity is higher than the initial acidity (Figure 14b). The sharp front develops as H^+ adsorbs onto the surface, decreasing the acidity of the aqueous phase until the surface has taken up sufficient H^+ to be in equilibrium with the injected solution.

Basic reaction fronts are dominated by OH^- which do not sorb onto the surface, due to their negative charge. The interaction of the solution with the surface is therefore mediated by the auto-ionization of water, which links the H^+ and OH^- concentrations (Equation 1a). Mathematically this is achieved by expressing the isotherm in terms of the acidity, by inserting Equation (13) into Equation (12). This gives rise to the concave upwards equilibrium constraint under basic conditions that leads to the reversal in the front formation mechanism (Figure 3c).

Rarefactions form when the injected acidity is higher than the initial acidity (Figure 14c). The surface must uptake H^+ to reach equilibrium with the injected solution. However, very little H^+ exists. Therefore, water ionizes to form H^+ and OH^- . The H^+ subsequently adsorbs to the mineral surface, until the surface is in chemical equilibrium with the higher acidity injected solution. The OH^- produced by auto-ionization remains in solution and increases the OH^- concentration. The combination of auto-ionization of water and H^+ adsorption therefore has the same net effect as if OH^- had desorbed from the mineral surface.

Shocks arise in the basic regime when the injected acidity is lower than the initial acidity (Figure 14d).

Figure 13: **Comparison of model predictions.** a) rarefaction front, $\mathcal{R}$, due to H^+ desorption, b) shock front, $\mathcal{S}$, due to H^+ adsorption, and c) a composite rarefaction-shock front, $\mathcal{RS}$ due to auto-ionization of water under basic conditions. Experimental elution histories and the predicted transport behavior of surface chemistry models are compared. Inset numbers correspond to the experimental conditions on the regime diagram shown in Figure 7 and Table 2.

The surface desorbs H^+ to reach equilibrium with the injected solution. The desorbed H^+ is subsequently neutralized by OH^- , therefore consuming both species. This neutralization has the same effect that adsorption of OH^- onto the surface would have had, by eliminating OH^- from the solution.

The combination of H^+ adsorption/desorption from the surface with auto-ionization/neutralization in the aqueous phase has the same effect on the OH^- concentration as if OH^- would be adsorbing/desorbing onto the surface. The reversal of the front formation mechanism under basic conditions can therefore be thought of as an OH^- front with effective OH^- adsorption/desorption.

This discussion shows that the auto-ionization of water is the key mechanism that leads to the reversal of the front formation mechanism under basic conditions. It is therefore also the mechanism that leads to the formation of composite waves if the front crosses neutral pH . The electrostatic interactions at the mineral surface are not required to produce this behavior, as even the Non-electrostatic model

Figure 14: **Reaction front mechanisms.** The four reaction front mechanisms described in Section 5 are illustrated. In the acidic regime a) a rarefaction is produced by H^+ desorption and b) a shock is formed by H^+ adsorption. In the basic regime c) a rarefaction is formed by H^+ formation through the ionization of water and subsequent adsorption while d) a shock is formed by H^+ desorption and subsequent neutralization.

leads to a s-shaped equilibrium constraint [23].

6. Conclusions

This study extends the theory of chromatography to standard surface complexation models and demonstrates the importance of the equilibrium constraint in determining the transport behavior of protons. The theoretical framework enables the construction of a regime diagram identifying different types of reaction fronts and their occurrence. This allows a full comparison of different chemical models and hence the design of validation experiments that target conditions of divergent model predictions.

The application of this approach to protons has shown that the unique transport behavior is due to the auto-ionization of water rather than electrostatic effects at the mineral surface. The aqueous reaction leads to a reversal in the transport behavior under basic conditions, so that desorption of H^+ leads to a shock rather than a rarefaction, the opposite of the classic behavior. All models which account for the auto-ionization of water can predict the three types of reaction fronts. However, only the electrostatic models with the Helmholtz component capture the boundary between $\mathcal{S}$ and $\mathcal{RS}$ fronts and generally give the best

fit to the data. This has been confirmed by an extensive set of column experiments.

The chromatographic framework can be extended to multicomponent systems which require more robust surface chemistry models [6, 23]. With increasing complexity, the types of behaviors and the disagreement between different model predictions will likely increase. Therefore, conducting strategic experiments is essential to sample the full range of transport behaviors required to validate reactive transport models. The chromatographic analysis presented here is therefore a useful tool to understand reactive transport in porous media.

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Appendix A. Transport equation

All concentrations in this study, including sorbed species, are given in units of molarity (moles per liter of water). Therefore the dimensional transport equation for the mass of protons is

$$\frac{\partial}{\partial t} (\phi c + \phi s(c)) + \phi v \frac{\partial}{\partial x} c - \phi D \frac{\partial^2}{\partial x^2} c = 0, \quad (\text{A.1})$$

where ϕ is the porosity of the porous medium. However, it is common to report the concentration of surface bound chemical species in units of moles per kilogram of solid. In this case the transport equation is

$$\frac{\partial}{\partial t} (\phi c + (1 - \phi) \rho_s \bar{s}(c)) + \phi v \frac{\partial}{\partial x} c - \phi D \frac{\partial^2}{\partial x^2} c = 0, \quad (\text{A.2})$$

where $\bar{s}(c)$ has units of moles per kg solid and can be converted to $s(c)$ by

$$s(c) = \nu \rho_s \bar{s}(c), \quad (\text{A.3})$$

where $\nu = (1 - \phi)/\phi$ is the ratio of solid to void volume and ρ is the bulk density of the solid in kilograms per liter. Scaling space and time gives

$$\left(1 + \nu \rho_s \frac{d\bar{s}}{dc}\right) \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial z} - \text{Pe} \frac{\partial^2 c}{\partial z^2} = 0. \quad (\text{A.4})$$

Appendix B. Comparison with PHREEQC

Equilibrium calculations for the Diffuse Layer and CD-MUSIC model were verified by comparison with PHREEQC (Figure B.15a) [35]. In PHREEQC electrostatics for the CD-MUSIC model are governed by the Triple Layer model [35]. We mimic the Basic Stern model within the PHREEQC code by setting the capacitance of the second layer (between the IHP and OHP) to a very large number. This is done using the `capacitances` keyword. Transport calculations of the advective conservation law were also carried out in PHREEQC, which employs an explicit finite difference scheme [35]. A comparison of the numerical transport simulations of PHREEQC with the analytical solutions are shown in Figure B.15b for the Diffuse Layer model.

Figure B.15: **Equilibrium and transport comparison with PHREEQC.** a) comparison of equilibrium constraint for the Diffuse Layer model and CD-MUSIC model as calculated by PHREEQC and this study. b) analytic solutions by the method of characteristics compared to numerical transport simulations by PHREEQC's ADVECTION keyword data block using the Diffuse Layer model.

Appendix C. Experimental set-up and tracer test

All solutions were prepared with degassed, ultrapure water. Water was degassed under vacuum with constant agitation until bubble formation stopped, ~ 3 hours. During experiment runs, typically lasting 1-3 hours, solutions were

stored in airtight HDPE vessels under an inert N_2 head space.

Figure C.16: **pH probe housing.** pH probe housing and 1 cm stir bar placed at column effluent. Total housing volume with probe and stir bar in place was ~ 2 ml.

The silica sand was packed into a 0.37×0.015 m Omnifit BenchmarkTM glass column. The porosity of the column was calculated, by dry and wet mass weighing, as 0.325.

The column was saturated by first pulling a vacuum at -101 kPa for 1 hour. Ultrapure water was then allowed to enter the column to fill the void space. Ultrapure, degassed water was then pumped through the column for 24 hours at 10^{-6} m³/min to ensure the column was saturated and the sand surface was in chemical equilibrium with the solution [15]. A set of two JascoTM HPLC pumps set at constant flow rate moved the solutions through the set-up. Solutions were passed through an in-line JascoTM degasser to remove any remaining dissolved gases. The pH was measured by an inline Endress HauserTM pH probe set at the column effluent. The pH readings were relayed to a PC and recorded at 1 Hz. The pH probe was housed in an airtight custom built glass enclosure, with room for a 1 cm stir bar, which ensured the solution in the housing was well mixed, pictured in Figure C.16. The inclusion of this stir bar dramatically improved the sharpness of the elution histories. During column experiments solutions were pumped at a constant flow rate of $3 \cdot 10^{-6}$ m³/min, resulting in an average fluid velocity, v , of $5.2 \cdot 10^{-2}$ m/min. The hydrodynamic dispersion coefficient was calculated by

$$D = \alpha_L v + D^*, \quad (C.1)$$

where α_L is the longitudinal dispersivity of the sand pack, and D^* is the molecular diffusion of hydronium. Assuming $D^* = 4.2 \cdot 10^{-7}$ m²/min and the longitudinal dispersivity is equivalent to the grain diameter results in a $Pe = 2.8 \cdot 10^3$ [45].

Tracer test were conducted in the column using a dilute NaCl solution at a pH of 4. Under these conditions the silica sand surface should have a neutral charge, therefore minimizing Na^+ sorption. A step change in salt content was introduced into the column under identical flow conditions to Experiments 1-14. Two in-line DionexTM ion chromatographs measured Na^+ content every ~ 2 minutes.

The results of these experiments are shown in Figure C.17. The salinity front breaks through the column at ~ 7.6 minutes, which is in good agreement with the calculated pore volume displacement time. The experimental breakthrough curves are also in good agreement with the analytic solution to the advection-diffusion equation,

$$C = \frac{C_{inj} - C_{ini}}{2} \left[\operatorname{erf} \left(\frac{x - vt}{2\sqrt{Dt}} \right) + \exp \left(\frac{vx}{D} \right) \operatorname{erf} \left(\frac{x + vt}{2\sqrt{Dt}} \right) \right] + C_{ini} \quad (C.2)$$

where C is the concentration of Na^+ in mol/L, D is the hydrodynamic dispersion for Na^+ , and C_{ini} and C_{inj} are the initial and injected sodium concentrations respectively [49]. D is calculated as above with $D^* = 7.8e - 6$ m²/min [50]. The results of the tracer breakthrough tests reinforce the conclusion that the hyperbolic limit is appropriate for transport behavior within the column, as well as the assumption that the majority of smoothing observed in proton effluent histories occurs within the pH probe holder.

Figure C.17: **Tracer breakthrough curves.** Effluent histories for column experiments with step changes in sodium concentration. The analytic solution for the advection-diffusion equation is also shown.

Appendix D. Supplementary data and code

- **TransportData.zip**

ZIP file containing comma separated data of experimental and model predictions for all experiment runs. All data is given in terms of pore volumes injected. Values of both acidity and pH are provided.

- **EquilConDDL.txt**

PHREEQC input file which calculates the equilibrium constraint by the Diffuse Layer model. The equilibrium calculation will output to the file EquilConDDL.sel.

- **EquilConCDMUSIC.txt**

PHREEQC input file which calculates the equilibrium constraint by the CD-MUSIC model. In

PHREEQC electrostatics for CD-MUSIC are governed by the Triple Layer Model. The Basic Stern model approximated by setting the capacitance of the region between IHP and OHP to a very large value. The equilibrium calculation will output to the file `EquilConCDMUSIC.sel`.

• `Proton_Transport.txt`

Example PHREEQC input file for the transport of acidity given by the Diffuse Layer model. This file shows the example of a solution of pH 4 being injected into a column initially equilibrated with a solution of pH 10. The output is saved to the file `Proton_Transport.sel`.

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