Numerical simulation of cation exchange in fine-coarse seawater slurry pipeline flow

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A B S T R A C T

Slurry pipelines transporting a coarse—the comminution product—and a fine fraction, both in the presence of seawater, can cause an alteration of the liquid phase chemical composition. In the present paper, we present the result of two-dimensional numerical simulations using a mixture model using the OpenFOAM library solving the momentum equations for both the coarse and fine species, the liquid phase, mass transport equations for three ionic species (Ca^{2+}, Na^+ and Mg^{2+}) and the mean flow continuity. The flow is assumed turbulent, and to this purpose, the k- model is used. The mass transport has been modeled using a two-species first order kinetic model derived from the Gaines-Thomas exchange equation, assuming the relation between the rate of Ca^{+2}–Na^+ and that between Na^{+2}–Mg^{+2}. The presence of an inhomogeneous concentration distribution in the vertical and the fine fraction vertical mobility via settling, reveals a strongly inhomogeneous mass transfer characteristic within the pipe section. In particular, the higher particle concentration near the bottom along with lower local velocities of the continuous phase compared to the mid-section imply larger residence times, as confirmed by the numerical results. Both aspects in combination, promote higher Ca^{2+}–Na^+ and Mg^{2+}–Na^+ exchange rates near the bottom than in the axis of the pipe. This observation suggests that particle flow heterogeneity may promote or hinder adsorption-desorption processes when compared to homogeneous slurry flows. Results also reveal the potential for the control of the electrolyte structure given the cation exchange capacity (CEC), type and concentration of clays and coarse phase concentration, the latter conditioning the flow structure.

1. Introduction

In the mining industry, transport systems of slurry and water are of primary importance since there are many unit operations that rely on them, especially in mineral processing plants. Pipelines are a common system used in mineral processing because it is extremely flexible and is used in short or long distance for concentrate and tailings. These mixtures contain solid particles that, depending on various aspects, can behave as an equivalent homogeneous fluid or a heterogeneous mixture due to the formation of a bed particles in the bottom of pipe, bringing a non-uniform distribution of particles (Jacobs, 2003; Wilson et al., 2006; Shook and Roco, 2015). Such solid content has a specific size distribution where coarse particles might alter the motion of the fine particles and the liquid phase in the pipe. It is known that when particles are close to the colloidal size, surface forces begin to affect the behavior of the particles in the fluid (Rhodes and Ebrary, 2008).

The presence of clays has various implications in the process. In particular, it affects the pump efficiency in the transport of pulp due its fine size and capacity to change the pulp rheology (Nguyen and Boger, 1998; Ndlovu et al., 2013). On the other hand, it alters the froth stability and surface chemistry of particles in flotation, thus modifying the mineral recovery (Bulatovic, 2007; Farrokhpay and Bradshaw, 2012; Peng and Zhao, 2011). Downstream the process, clays may impact the level of separation of solid from liquid in thickeners *via* the yield stress and the settling characteristics of particles and flocs (Ndlovu et al., 2011; Au and Leong, 2013). In most of the cases, the behavior of clay depends on the electrolyte where it is immersed. In fact, the presence of ions at certain pH develop different process such as sorption, ion exchange and precipitation in the clay surface. In particular, there are many studies that describe the adsorption of heavy metals on clays (*e.g.* Kraepiel et al., 1999; Al-Qunaibit et al., 2005) and some that describe the ion exchange with major cations (Atesok et al., 1988; Carroll and Starkey, 1958). In general, clays interact with cations because the surface charge or zeta potential is a negative product of the isomorphic substitutions of cations of a lower valence. For instance, in the case of montomorillonite, some Al^{+3} are substituted by Mg^{+2} or Fe^{+2}, whereas Si^{+4} are substituted by Al^{+3} (Zarzycki et al., 2007). Thus, cations are adsorbed on the particle surface or exchanged with another

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ion to compensate the surface charge. Taking advantage of this feature, clays are used for cleaning wastewater and are considered complex minerals provided that changes in the particle surface can cause changes in the hydrodynamics, rheology, flocculation and sedimentation stability (Zhou et al., 2001; Boger, 2009; Zhang and Peng, 2015).

When modeling the competitive sorption of major cations a common approach is the definition of cation exchange reactions with constant exchange stoichiometry based on equivalent charges. An example is the Gaines-Thomas relation (Voegelin et al., 2000). In the case of pipe flow, CFD is a valid option for modeling two-phase systems. However, to the knowledge of the authors, there are no studies that treat fine and coarse particles in high Reynolds number flows concurrently with a chemical process such as adsorption or ion exchange that may alter the composition of the liquid phase. In this paper, we treat this topic studying its effects on the ion exchange in terms of the chemical and hydrodynamic properties of the system.

2. Governing equations

2.1. Momentum equations

The suspension is modeled as a continuum with solid velocity, density and volume fraction fields $\mathbf{u}_s, \rho_s$ and ϕ_s, respectively, superimposed to the liquid with velocity ($\mathbf{u}_l$), density ρ_l and volume fraction $\phi_l = 1 - \phi_s$. The momentum conservation equations are

$$\frac{\partial(\phi_i\rho_i\mathbf{u}_i)}{\partial t} + \nabla\cdot(\phi_i\rho_i\mathbf{u}_i\mathbf{u}_i) + \nabla\cdot(\phi_i\tau_i) = -\phi_i\nabla p + \nabla\cdot(\phi_i p_{s,i}) + \phi_i\rho_i\mathbf{g} + \mathbf{f}_i,$$
(1)

where the subindex i stands for solid s or liquid l. The pressure is assumed common to both phases. An additional solid pressure contribution $p_s\phi_s$, which sharply increases around the maximum packing fraction ϕ_{max}, is added on the momentum equation for the solid in order to bound the volume fraction of solid ϕ_s below ϕ_{max}. This extra pressure term in the liquid equation is zero $p_{s,l} = 0$. It is important to note that the volume fraction of fines, ϕ_f, and salt concentration, $C = \sum_i C_i$, affect the liquid density, resulting in a liquid density $\rho_l = \phi_f\rho_f + \phi_{l,C}\rho_{l,C}$, where ρ_s is the solid density and $\rho_{l,s} = \rho_{l,0}(1 + \alpha C)$ is defined as the salt liquid density with $\rho_{l,0}$ the density of fresh water and α an expansion coefficient. The shear stress tensor for each phase is given by Enwald et al. (1996):

$$\tau_i = \mu_i\left(\frac{\nabla\mathbf{u}_i + (\nabla\mathbf{u}_i)^T}{2} - \frac{2}{3}(\nabla\cdot\mathbf{u}_i)\mathbf{I}\right),$$
(2)

where the effective viscosity of the solid μ_s is obtained from the expression for the slurry, $\mu_{mix} = \phi_s\mu_s + \phi_l\mu_l = \mu_l\left(1 + \frac{\phi_s}{\phi_{max}}\right)^{-[\eta]\phi_{max}}$, where $[\eta] = 5/2$ is the intrinsic viscosity of a sphere suspension (e.g. Shook and Roco, 2015). Here, $\mu_l = \mu_{l,0}(1 + [\eta]\phi_f)$ corresponds to the suspension viscosity equation, with $\mu_{l,0}$ the dynamic viscosity of the liquid phase. Both can be revised in Enwald et al. (1996). The volumetric forces between phases, denoted by the last term of the right hand side of (2) are given by $\mathbf{f}_i = \mathbf{f}_D + \mathbf{f}_L + \mathbf{f}_{WL} + \mathbf{f}_{TD}$ (Ekambara et al., 2009 and references therein), where $\mathbf{f}_D$ is the drag force, $\mathbf{f}_L$ is the lift force, $\mathbf{f}_{WL}$ is the lubrication wall force and $\mathbf{f}_{TD}$ is the turbulent dispersion force. Here, $\mathbf{f}_i = \mathbf{f}_s = -\mathbf{f}_i$ is the force per unit volume the fluid applies on the solid. For these interfacial forces, we consider same expressions and parameters used in the non-cohesive three-dimensional slurry flow modeling by Ekambara et al. (2009) using ANSYS-CFX.

2.2. Particle transport equations

The mass transport equation for the solid phase, including fine particles, is:

$$\frac{\partial(\phi_i\rho_s)}{\partial t} + \nabla\cdot(\phi_i\rho_s\mathbf{u}_s) = \kappa\nabla^2\phi_i\rho_s,$$
(3)

Here, κ is the mass diffusivity coefficient, and $i = f$ or s. It has been assumed that the clay particles move with the liquid, except on the vertical velocity, where the sedimentation is allowed. This assumption has been proven reasonable in comparison with the full set of coarse and fine equations, and allows saving significant computational times. The fine particle velocity is defined as $\mathbf{u}_{s,f} = -w_{s,f}\hat{\mathbf{k}}$, and corresponds to the Stokes velocity corrected by a hindrance function (Richardson and Zaki, 1954):

$$w_{s,f} = \frac{1}{18}\frac{(\rho_s - \rho_l)d_f^2}{\mu_{l,0}}(1 - \phi_T)^{4.65},$$
(4)

where d_f is the fine fraction diameter (the clay fraction) and $\phi_T = \phi_f + \phi_s$ is the total volume fraction of particles.

2.3. Salt transport equations

The salt concentration satisfies the advection-diffusion equation

$$\frac{\partial(\phi_l\rho_l C_i)}{\partial t} + \frac{dS_i}{dt} + \nabla\cdot(\phi_l\rho_l C_i\mathbf{u}_l) = D\nabla^2(\phi_l\rho_l C_i),$$
(5)

where D is the salt diffusivity coefficient, which is taken as $D = 25\kappa$ (Schulte et al., 2016), $i = $ Na,Mg,Ca or Cl. The term dS_i/dt is the source term (in the case of Cl is 0) and refers to the ion exchange of the ion pair within the liquid and the fine solid phase, and is defined as:

$$\frac{dS_j}{dt} = w_{m,j}\left(\frac{\partial S_j^*}{\partial t} + \nabla\cdot(S_j^*\mathbf{u_f})\right) = w_{m,j}(R_{1,j}^* + R_{2,j}^*),$$
(6)

where $w_{m,j}$ is a unit conversion factor from mol to grams, S_j is the concentration of the ion $j = $ Mg or Ca in kg/m³, S_j^* is the ion concentration, in mol/m³, $R_{1,j}^*$ and $R_{2,j}^*$ are derived from the Gaines-Thomas equilibrium equation for ion exchange (Voegelin et al., 2000). For the case of calcium (or magnesium, replacing Ca by Mg):

$$R_{1,Ca}^* = -k_1\frac{S_{Ca}^* z_{Ca}}{CEC_c}\left(\frac{a_{s,Na}}{c_0}\right)^2$$
(7)

$$R_{2,Ca}^* = k_2\left(\frac{S_{Na}^* z_{Na}}{CEC_c}\right)^2\frac{a_{s,Ca}}{c_0},$$
(8)

with k_1 and k_2 the kinetic constant, in mol/m³ s, and z_i is the charge of the ion i. Here, c_0 is a reference unit that equals 1 M (Voegelin et al., 2000). On the other hand, $R_{1,Ca}^*$ is defined as the rate of exchange of calcium in particles with liquid. It also corresponds to the rate of exchange of sodium in the liquid phase with particles. If $R_{2,Ca}^*$ is higher than $R_{1,Ca}^*$, then calcium (or magnesium) can go to the particles. Otherwise, the sodium goes to the particles. In (7) and (8), $a_{s,i} = a_{b,i}\exp\left(\frac{-z_i e\zeta}{k_b T}\right)$, where e is the charge of an electron, ζ is the zeta potential, k_B is the Boltzmann constant, T is the absolute temperature and $a_{b,i} = \gamma_i C_i w_{m,i}$ is the surface ion activity, in mol/m³. Here, $w_{m,i}$ is the molecular weight and γ_i is the activity coefficient, determined by B-dot Model (Bethke, 2007) as:

$$\log\gamma_i = -\mathscr{A}z_i^2\left(\frac{\sqrt{I}}{1 + a_i B_i\sqrt{I}} - \dot{B}_i I\right).$$
(9)

Here, $\mathscr{A}$ is a constant, a_i, B_i and $\dot{B}_i$ are ion-dependent constants, and I is the ionic force determined by $I = \sum_i z_i mC_i$ with mC_i the molal concentration of ion i. On the other hand, CEC_c is the calculated cation exchange capacity determined by $\sum z_i S_i$. It is noted that k_1 and k_2 are critical on fixing the timescale of the exchange process. Given a constant mean flow velocity, this implies that the kinetic constant may have a strong relevance on the cation exchange entry length within pipeline (Section 4). For this system, it was assumed that calcium and magnesium ions exchange moles with ion sodium but there is not a