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Development and testing of a model for simulating weathering and trace elements release from fixated scrubber sludge utilized in abandoned coal mine reclamation site

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ABSTRACT

In this paper we present the first approximation to a fully coupled model for simulating chemical reactions between engineered coal combustion byproducts (specifically fixed scrubber sludge-FSS) and ambient groundwater. If FSS is placed at a mine site as a hydrologic barrier over pyritic refuse, it would interact with acidic mine water at the bottom and soil water at the top of the FSS. A coupled reactive transport model was developed for simulating reactions at the exposed edges of the FSS over long time frames. In our modeling, emphasis was placed on the release and fate of toxic trace elements such as arsenic, boron, barium, and zinc, which are commonly present in FSS. The parameters associated with dissolution of trace element hosts were calibrated and optimized using data from column leachate experiments on core samples extracted from a reclaimed abandoned mine land site in Indiana. In an effort to evaluate the leaching potential of these trace elements, reactive transport simulations were conducted and compared with historical chemistry data. The model successfully reproduced many characteristics observed in the field, such as initial rises in the concentrations of arsenic, boron, and zinc, following by continuous decline toward steady state by the end of simulation. Also, simulation results indicated that the weathering rate was slightly higher at the top of the FSS where it is in contact with ambient soil water than at the bottom of the FSS. While the preliminary modeling results are promising, comparisons between model calculations and historical data point to the fact that there must be other sources or mechanisms that accommodate rapid releasing of trace elements. Further model development will require explicit inclusion of mechanisms for sorption/desorption of the potentially toxic elements.

1. Introduction

Coal combustion byproducts (CCBs) including fly ash, bottom ash, and flue gas desulfurization (FGD) materials, are generated in vast quantities throughout the world. In 2014 alone, over 129 million tons of FGD and other CCBs were generated in the US; however, only 48% of these materials were being beneficially recycled into the environment while the remainders got stored in landfills and ash ponds (American Coal Ash Association, 2014). Previous studies have shown that when FGD sludge and fly ash are mixed, along with quick lime, a cementitious substance -fixated scrubber sludge (FSS) - is created. Beneficial physical properties of FSS include very high shear strength (>7000 kPa), and very low hydraulic conductivity ($<10^{-8}$ m/s) (Smith, 1992; Butalia and Wolfe, 1999). FSS has been used as liner materials for ponds and wetlands, embankments, and structural fills at mine sites (Stehouwer et al., 1995; Payette et al., 1997; Lamminen et al., 2001).

Many coal mining sites exhibit acid mine drainage (AMD) problems, which are caused by oxidation of sulfide bearing minerals in waste rocks. AMD has low pH, and contains high dissolved concentrations of toxic metals. The low hydraulic conductivity and moderate alkalinity of FSS and other engineered CCBs make them potentially useful as structural filling and capping materials in AMD settings. The virtually impermeable material prohibits oxygen diffusion and groundwater recharge, and thus helps to minimize acidic outflows from sulfide rich refuse. Previous field studies have reported the beneficial effects of using engineered CCBs at mine environments to abate acid mine drainage (Bulusu et al., 2005; Taerkaul et al., 2004; Rudisell et al., 2001). Long-term monitoring at one site documented improvement of groundwater quality beneath the FSS layer as well as in the surface water discharging from the reclaimed mine land site (Martin et al., 2012; Naylor et al., 2012).

Despite such documented beneficial effects, much concern exists about the potential to leach toxic elements from the fly ash contained

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in FSS. Laboratory leaching experiments are frequently conducted to demonstrate release and mobility of various trace elements from CCBs (Kost et al., 2005; Semeda and Zyrnicki, 2002; Fytianos and Tsaniklidi, 1998). Elements of concern include As, B, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Pb, Sr, V, and Zn. An overview by Izquierdo and Querol (2012) provided a detailed summary of major and minor element leaching behaviors based on over 90 publications. Most elements contained in ash displayed a pH-sensitive pattern. Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Th, Tl, U and Zn were poorly leached in the pH 7–10 region. By contrast, oxyanionic-forming species, such as As, B, Cr, Mo, Sb, Se, V and W, showed the maximum leachability in the pH 7–10 range.

Although necessary and useful, laboratory experiments and monitoring studies are not sufficient to address all the issues of how using engineered CCBs would affect groundwater quality, especially for the leaching potential of toxic elements over long time periods. Such questions can be addressed using coupled physical-chemical models, that allow numerical simulations to be conducted over long time spans (decades to centuries) in short order. An initial attempt by Cetin et al. (2012) combined data with a numerical analysis of trace elements leaching from fly ash-amended highway bases. Numerical simulations were conducted to predict concentrations of Ba, B, Cu, and Zn at different depths (4, 5 and 6 m to groundwater table) and times under field conditions. The simulation results indicated that concentrations decreased over time and depth due to dispersion in the vadose zone and that the modeled peak concentrations were much lower than those obtained in laboratory column leaching experiments. However, geochemical reactions were not taken into account in the modeling effort. In another study, Bin-Shafique et al. (2002) attempted to model the leaching potential of metals from fly ash applied in highway pavements using HYDRUS2D. The model was developed using transport parameters and data obtained from column tests and from field measurements. Although the model served as a quick and reasonable tool to predict metal concentrations based on Darcy flow, retardation, and dispersity, no specific toxic element was simulated and no geochemical reactions were explicitly considered. Van Herck et al. (2000) conducted numerical simulations to evaluate the leaching of heavy metals (Cd, Cu, Pb, and Zn) from fly ash using MINTEQA2. Their results illustrated the dissolved and precipitated forms of minerals at different pH values in phase diagrams. For example, at PH = 6, about 31% of total zinc remained in solution, whereas 26% and 20% precipitated as smithsonite and $ZnO \cdot \cdot SiO_2$, respectively, while about 23% still stayed in residual phase. Lead started to precipitate around pH = 3.4. Cadmium occurred as $CdCO_3$ or $Cd(OH)_2$ under basic conditions (pH > 8). However, their simulations were performed under equilibrium pH values, and do not necessary represent the realistic conditions that occur in an evolving geochemical system. Another study conducted by Mudd et al. (2004) focused on geochemical modeling of major and trace elements in fly ash leachate solutions using PHREEQC. Their results suggested that the concentrations of As, B, Ba, Mo, and Se were controlled by a variety of factors including mineral dissolution, co-precipitation, and possibly adsorption. However, the model was limited by assuming steady state equilibrium, so no kinetic reactions were taken into account.

The present paper represents an effort to develop a more realistic model for the time-dependent release of trace elements from FSS in contact with groundwater. Data used for model calibration and field testing came from laboratory studies (Martin et al., 2013; Zhang et al., 2016) and long-term monitoring (Martin et al., 2012) at an abandoned mine land (AML) site where the FSS was utilized as a hydrologic barrier over the pyritic refuse. Our current emphasis was placed on the mobilization of As, B, Ba, and Zn in FSS when in contact with ambient soil water and acidic mine water that are typically encountered at AML sites. The physical-chemical model was calibrated using data from column leachate experiments involving sediment cores extracted from the study site. When the calibrated model output was compared to historical chemistry data from the study site the match was reasonable. Additionally, the model was used to investigate changes in aqueous chemical composition, and relevant mineral alterations in the system over a time frame of 17 years. Although some aspects of system behavior remain uncertain, or inadequately addressed, no previous studies have employed such extensive empirical data nor addressed the issues of long-term mobility, transport and fate the trace elements contained in engineered CCBs applied at AML sites. Ultimately, the coupled physico-chemical model will facilitate predicting the probable outcomes of using FSS as a remediation material at AML sites and particularly the potential risk of releasing trace elements into the local groundwater.

2. Modeling approach

2.1. Governing equations for reactive transport modeling

Chemical reactions and fluid flow transport are coupled through the general governing equation to describe fluid-rock interactions (Steefel and Lasaga, 1994; Xu et al., 2004; Xiao et al., 2009):

$$\frac{\partial}{\partial t}\varnothing C_i = \frac{\partial}{\partial x}\left(\varnothing \mathbf{D}\frac{\partial C_i}{\partial x}\right) - \varnothing \upsilon \frac{\partial C_i}{\partial x} + \varnothing r_i \qquad (1)$$

where C_i is the concentration of a specific species in the pore fluid ($mol \cdot m^{-3}$) and $\varnothing$ is the porosity of the porous media. **D** represents the combined molecular diffusion ($D\times$) and mechanical dispersion coefficient (Dh) for the porous media ($D = D\times + D_h$; Marsily, 1986; Bear, 1979) ($m^2 \cdot s^{-1}$), υ is the average linear fluid velocity of the flow ($m \cdot s^{-1}$), and r_i is the reaction rate of species i in solution ($mol \cdot m^{-3} \cdot s^{-1}$) - positive values of r_i indicate dissolution, and negative values indicate precipitation. Note that the first two terms on the right hand side of Eq. (1) describe the transport process (diffusion and advection, respectively), whereas the last term describes the effect of geochemical reactions between solid and liquid phases. The reaction rates are calculated using the following general equation to describe the surface-controlled mechanisms (Lasaga et al., 1994):

$$r = k * A * \left[1 - \left(\frac{Q}{K}\right)^{\theta}\right]^{\vartheta} \qquad (2)$$

where r is the kinetic rate of precipitation/dissolution of a specific mineral ($mol \cdot m^{-3} \cdot s^{-1}$). Note that $r > 0$ indicates dissolution and $r < 0$ indicates precipitation of the solid phase. In Eq. (2), k is the kinetic rate constant for the reaction ($mol \cdot m^{-2} \cdot s^{-1}$) and A is the reactive surface area ($m^2 \cdot m^{-3}$). Q is the dimensionless reaction quotient and K is the equilibrium constant for mineral-water reaction in the form of destruction of 1 mol of mineral. θ and ϑ are fitting parameters that can be determined from experiments, but which are usually assumed to equal unity.

Reactive transport modeling is an important tool for the analysis of coupled physical, chemical, and biological processes of water-rock interactions (Steefe et al., 2005). Solutions have been achieved for the migration of contaminants in aquifers (Steefe et al., 2005; Mayer et al., 2002) and estimation of elemental and nutrient fluxes (C, O, N, S, Fe, and Mn) in coastal marine environments (Wang and Van Cappellen, 1996). However, due to lack of critical geochemical information, such models have not been applied to environments where engineered CCBs are in contact with ground and surface waters.

2.2. Simulation method overview

Numerical simulations in this study were performed using the computer program TOUGHREACT v2, which is capable of modeling up to three-dimensional geologic domains with physical and chemical heterogeneity (Xu et al., 2011). The TOUGHREACT source code was developed as an extension of the non-isothermal multi-phase fluids and heat flow code TOUGH2 v2, and include general chemical speciation and reactive chemistry based on EQ3/6 (Xu et al., 2004; Pruess, 2004;