Modeling uranium(VI) adsorption onto montmorillonite under varying carbonate concentrations: A surface complexation model accounting for the spillover effect on surface potential

C. Tournassat [a,b,*], R.M. Tinnacher [b,c], S. Grangeon [d], J.A. Davis [b]

[a] UMR 7327 Institut des Sciences de la Terre d'Orléans (ISTO), Université d'Orléans−CNRS/INSU−BRGM, Orléans, France
[b] Earth and Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[c] Department of Chemistry & Biochemistry, California State University East Bay, Hayward, CA 94542, USA
[d] BRGM, French Geological Survey, Orléans, France

Abstract

The prediction of U(VI) adsorption onto montmorillonite clay is confounded by the complexities of: (1) the montmorillonite structure in terms of adsorption sites on basal and edge surfaces, and the complex interactions between the electrical double layers at these surfaces, and (2) U(VI) solution speciation, which can include cationic, anionic and neutral species. Previous U(VI)-montmorillonite adsorption and modeling studies have typically expanded classical surface complexation modeling approaches, initially developed for simple oxides, to include both cation exchange and surface complexation reactions. However, previous models have not taken into account the unique characteristics of electrostatic surface potentials that occur at montmorillonite edge sites, where the electrostatic surface potential of basal plane cation exchange sites influences the surface potential of neighboring edge sites ('spillover' effect).

A series of U(VI) – Na-montmorillonite batch adsorption experiments was conducted as a function of pH, with variable U(VI), Ca, and dissolved carbonate concentrations. Based on the experimental data, a new type of surface complexation model (SCM) was developed for montmorillonite, that specifically accounts for the spillover effect using the edge surface speciation model by Tournassat et al. (2016a). The SCM allows for a prediction of U(VI) adsorption under varying chemical conditions with a minimum number of fitting parameters, not only for our own experimental results, but also for a number of published data sets. The model agreed well with many of these datasets without introducing a second site type or including the formation of ternary U(VI)-carbonato surface complexes. The model predictions were greatly impacted by utilizing analytical measurements of dissolved inorganic carbon (DIC) concentrations in individual sample solutions rather than assuming solution equilibrium with a specific partial pressure of CO_2, even when the gas phase was laboratory air. Because of strong aqueous U(VI)-carbonate solution complexes, the measurement of DIC concentrations was even important for systems set up in the 'absence' of CO_2, due to low levels of CO_2 contamination during the experiment.

 * Corresponding author at: UMR 7327 Institut des Sciences de la Terre d'Orléans (ISTO), Université d'Orléans−CNRS/IN-SU−BRGM, Orléans, France.
 E-mail address: c.tournassat@brgm.fr (C. Tournassat).

1. INTRODUCTION

Due to mining, milling and fuel processing operations, numerous sites have been contaminated with uranium in the past, with 38 proposed or final Superfund sites on the EPA National Priority List in the U.S. alone (NIH, 2016). In the future, the long-term storage of nuclear waste has the potential to create additional sources of uranium contamination affecting subsurface environments and drinking water resources. Chemically-induced, acute effects of uranium in humans, such as an inflammation of the kidneys (nephritis), have been reported (Hursh and Spoor, 1973), while chronic health effects and carcinogenicity are less well understood (World Health Organization, 2004). At this point in time, the World Health Organization has proposed a provisional guideline value of 15 μg U·L^{-1} in drinking water (World Health Organization, 2004); the current U.S. EPA Maximum Contaminant Level (MCL) is set at 30 μg U·L^{-1} (U.S. Environmental Protection Agency, 2001). A sound scientific understanding of uranium mobility is needed in order to evaluate risks to humans and the environment, to optimize the management of nuclear waste and to take appropriate remediation actions if necessary.

The most relevant factors controlling uranium transport in saturated porous media are uranium solubility in pore water solutions and uranium adsorption reactions to mineral surfaces. Uranium can exist at oxidation states of IV or VI, but U(VI) is the most relevant oxidation state in most surface waters and in oxic groundwaters (Choppin, 2006). In reducing environments, the low solubility of U (IV) mineral phases greatly decreases uranium mobility.

Numerous studies have demonstrated the impacts of pH, bicarbonate and calcium concentrations on U(VI) solution speciation, adsorption and transport behavior (Davis et al., 2004; Curtis et al., 2004; Fox et al., 2006; Hartmann et al., 2008). Potential changes in chemical solution conditions and contaminant solution speciation over time and space are especially relevant for uranium, given the long half-lives of uranium isotopes and complex transport pathways in engineered systems and the natural environment. For instance, in nuclear waste repositories, pore water pH is buffered at values between 7 and 8 in the bentonite backfill material of engineered barrier systems surrounding waste canisters and/or in the clay host-rock (Muurinen and Lehikoinen, 1999; Bradbury and Baeyens, 2003; Wersin, 2003; Wersin et al., 2004; Tournassat et al., 2015c). However, more alkaline pH conditions are expected in close proximity to steel canisters (pH 8–11) due to corrosion processes (Bildstein and Claret, 2015), as well as in cementitious leachates at bentonite-concrete boundaries (pH > 13 for Ordinary Portland Cement and pH 9–11 for low alkali cement) due to the chemical degradation of cement (Savage et al., 1992; Gaucher and Blanc, 2006; Gaboreau et al., 2012b; Milodowski et al., 2016). Furthermore, dissolved calcium concentrations may also vary over time and space due to the progressive degradation of cement-based engineered barriers, the specific calcite contents in clay host rocks or changing concentrations in carbonate minerals along transport pathways (Hartmann et al., 2008; Gaboreau et al., 2012a; Adinarayana et al., 2013).

These chemical gradients in waste scenarios are important for the fate and transport of uranium, since U(VI) aqueous speciation is very complex. For instance, the uranyl cation (UO_2^{2+}) typically dominates speciation at low pH, while neutral and anionic U(VI)-hydroxyl and carbonate complexes become predominant at higher pH conditions. In a dilute U(VI) solution at pH 7 in the absence of carbonate, the predominant U(VI) species is the neutral $UO_2(OH)_2^0$. In comparison, for the same solution in equilibrium with atmospheric CO_2, the predominant species is the anion $(UO_2)_2CO_3(OH)_3^-$ (for a 1 μmol·L^{-1} solution). However, groundwater solutions are typically in equilibrium with partial pressures of CO_2 (pCO_2) at 1 % or greater, and may contain considerable concentrations of calcium due to the presence of carbonate minerals. At 1 % pCO_2, pH 7 and in the *absence* of Ca, U(VI) solution speciation is dominated by the anion $UO_2(CO_3)_2^{2-}$ (Fig. EA-1, Electronic Annex). For a comparable solution in equilibrium with calcite, the predominant U(VI) species is the neutral $Ca_2UO_2(CO_3)_3^0$ (Fig. EA-2, Electronic Annex).

Clay minerals are important minerals to consider in uranium contaminant transport because of the proposed use of bentonite or clay-rocks as a buffer material in engineered and natural barrier systems at future nuclear waste disposal sites (Tournassat et al., 2015b). Furthermore, there is the possibility that colloid-facilitated transport of uranium adsorbed on clay or bentonite particles may occur near granite waste repositories (Geckeis et al., 2004; Schäfer et al., 2004; Missana et al., 2008). Last, clay contents in soils and sediments are often high at uranium-contaminated sites (Grawunder et al., 2009; Graham et al., 2011).

Sodium-montmorillonite is the focus of this study because this mineral is the major component of bentonite in barrier systems. Montmorillonite is a smectite, a 2:1-layer-type dioctahedral phyllosilicate with a large specific surface area (∼750 m^2·g^{-1}) and cation exchange capacity (∼1 mol$_c$·kg^{-1}). Each montmorillonite layer has a thickness of ∼1 nm and carries negative surface charges due to isomorphic substitutions of Al(III) for Si(IV) and Mg(II)/Fe (II) for Al(III) in its phyllosilicate framework (Brigatti et al., 2013). Due to its crystal structure, montmorillonite provides two types of surfaces and surface site types: (1) cation exchange sites, with a permanent surface charge, on basal planar surfaces, and (2) surface complexation sites, with variable surface charges as a function of pH, on edge surfaces of clay particles (Borisover and Davis, 2015).

Many research groups have investigated the surface speciation of adsorbed U(VI) on montmorillonite with EXAFS spectroscopy (Dent et al., 1992; Chisholm-Brause et al., 1994; Giaquinta et al., 1997; Sylwester et al., 2000; Hennig et al., 2002; Catalano and Brown, 2005; Schlegel and Descostes, 2009; Marques Fernandes et al., 2012; Troyer et al., 2016). Analysis of the data obtained at various ionic strengths reveals the presence of U(VI) outer-sphere complexes at low pH and/or low ionic strengths, and of U(VI) inner-sphere complexes at other conditions. These interpretations of EXAFS data are in qualitative agreement with the duality of adsorption mechanisms on montmorillonite surfaces, i.e. cation exchange on basal planar surfaces at low pH/ionic strength and surface