Alteration, adsorption and nucleation processes on clay–water interfaces: Mechanisms for the retention of uranium by altered clay surfaces on the nanometer scale

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Abstract

Nano-scale processes on the solid–water interface of clay minerals control the mobility of metals in the environment. These processes can occur in confined pore spaces of clay buffers and barriers as well as in contaminated sediments and involve a combination of alteration, adsorption and nucleation processes of multiple species and phases. This study characterizes nano-scale processes on the interface between clay minerals and uranyl-bearing solution near neutral pH. Samples of clay minerals with a contact pH of $\sim$6.7 are collected from a U mill and mine tailings at Key Lake, Saskatchewan, Canada. The tailings material contains Cu-, As-, Co-, Mo-, Ni-, Se-bearing polymetallic phases and has been deposited with a surplus of $Ca(OH)_2$ and Na_2CO_3 slaked lime. Small volumes of mill-process solutions containing sulfuric acid and U are occasionally discharged onto the surface of the tailings and are neutralized after discharge by reactions with the slaked lime. Transmission electron microscopy (TEM) in combination with the focused ion beam (FIB) technique and other analytical methods (SEM, XRD, XRF and ICP-OES) are used to characterize the chemical and mineralogical composition of phases within confined pore spaces of the clay minerals montmorillonite and kaolinite and in the surrounding tailings material. Alteration zones around the clay minerals are characterized by different generations of secondary silicates containing variable proportions of adsorbed uranyl- and arsenate-species and by the intergrowth of the silicates with the uranyl-minerals cuprosklodowskite, $Cu[(UO_2)_2(SiO_3OH)_2](H_2O)_6$ and metazeunerite, $Cu[(UO_2)(AsO_4)_2](H_2O)_8$. The majority of alteration phases such as illite, illite–smectite, kaolinite and vermiculite have been most likely formed in the sedimentary basin of the U-ore deposit and contain low amounts of Fe (<5 at.%). Iron-enriched Al-silicates or illite–smectites (Fe >10 at.%) formed most likely in the limed tailings at high contact pH ($\sim$10.5) and their structure is characterized by a low degree of long-range order. Adsorption of U and nucleation of metazeunerite and cuprosklodowskite are strongly controlled by the presence of the adsorbed oxy-anion species arsenate and silica on the Fe-enriched silicates. Heterogeneous nucleation of nano-crystals of the uranyl minerals occurs most likely on adsorption sites of binary uranyl-, arsenate- and silica-complexes as well as on ternary uranyl–arsenate or uranyl–silicate complexes. The uranyl minerals occur as aggregates of misoriented nano-size crystals and are the result of supersaturated solutions and a high number of nucleation sites that prevented the formation of larger crystals through Oswald ripening. The results of this study provide an understanding of interfacial nano-scale processes between uranyl species and altered clay buffers in a potential Nuclear Waste repository as similar alteration conditions of clays may occur in a multi-barrier system.

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1. INTRODUCTION

Clay minerals play an important role in the Nuclear Fuel cycle. Clays and argillites are considered in some countries as possible host rocks for deep geological disposal of radioactive waste (e.g. Switzerland and France; Claret et al., 2004; Delage et al., 2010). The use of compacted swelling clays (bentonites) as engineered barriers is also considered within the framework of the multi-barrier concept (Madsen, 1998; Delage et al., 2010; Sellin and Leupin, 2013). Furthermore, geosynthetic clay liners are widely used in waste barrier systems such as in constructed Uranium mine and mill tailings facilities (Bouazza et al., 2002; Cameco, 2010; Lottermoser, 2010). Clay minerals play also an important role in the retention of radionuclides in contaminated sediments at the Hanford site (Catalano et al., 2006) and Savannah River (Bertsch et al., 1994; Dong et al., 2012).

Clay minerals have either one (TO) or two sheets (TOT) of polymerized silicate tetrahedra (T) sandwiching either a gibbsite or brucite-type sheet with polymerized octahedra containing trivalent (Al, Fe, V; dioctahedral) and divalent cations (e.g. Mg, Fe, Mn; trioctahedral), respectively (Grim, 1968). Surface terminations along the edges of the sheets are Lewis bases or acids and protonate or deprotonate depending on the pH of the solution in contact with the clay mineral (Stumm, 1992). In the case of the common clay minerals montmorillonite, (Na, K, Ca)$_{0.33}$[(Al, Mg, Fe)$_2$((Al,Si)$_4$O$_{10}$(OH)$_2$](H$_2$O)$_n$ and kaolinite, Al$_2$Si$_2$O$_5$(OH)$_4$, aluminol (>AlO), silanol (>SiO) and >Al–O–Si< terminations exhibit amphoteric acid/base behavior and provide adsorption sites for inner and outer-sphere complexes with solute species. In addition, isomorphic substitution of Al for Si and divalent cations (Mg, Fe, Mn) for octahedrally coordinated trivalent cations (Al, Fe) may result in a negative charge of the TO or TOT units, which is (partially) compensated by exchangeable cations occurring in the interlayer between the units (Grim, 1968). The ability of clays to admit and accommodate cations from aqueous solution within their interlayers is commonly referred as the cation exchange capacity. The interactions of uranyl-bearing aqueous species with clay surfaces is thus more complex in comparison to those with oxides and hydroxides as (UO$_2$)$^{2+}$-species can sorb to cation exchange sites within the interlayer or to >AlO, >SiO, >MgO, >FeO terminations along the edges of the T and O units.

The interaction of uranyl-bearing solutions with clay–mineral mixtures such as bentonite is of great interest as the latter material is considered as a buffer material in nuclear waste repositories due to its excellent physicochemical properties such as high specific surface area, large cation exchange and sorption capacity, and good swelling and sealing nature (Madsen, 1998; Delage et al., 2010; Sellin and Leupin, 2013). Bentonite was originally named for clay of the upper cretaceous tuff near Fort Benton, Wyoming and contains mainly montmorillonite (80–90%) with minor quartz, feldspars, sulfides and carbonates (Liu and Neretnieks, 2006). Maximum adsorption of uranyl aqueous-species onto bentonite occurs in the pH range of pH

5–8 with a maximum at pH 6.5 (Boult et al., 1998; Bachmaf and Merkel, 2011). The adsorption of uranyl-species is however strongly controlled by oxy-anion species present in solution as lower adsorption occurs in the presence of sulfate and carbonate species and higher adsorption in the presence of phosphate species (Bachmaf and Merkel, 2011).

The adsorption of uranyl aqueous-species onto swelling clay minerals such as montmorillonite and non-swelling clays such as kaolinite have been examined in greater detail with respect to the type of adsorption complexes and changes in pH, ionic strength of the electrolyte solution and concentrations of U and (CO$_2$)$_{aq}$ (e.g. McKinely, 1995; Pabalan and Turner, 1996; Turner et al., 1996; Sylwester et al., 2000; Chisholm-Brause et al., 2001, 2004; Kowal-Fouchard et al., 2004; Catalano and Brown, 2005; Bachmaf and Merkel, 2011; Dong et al., 2012; Marques Fernandes et al., 2012, and many more). These studies showed that

(a) Maximum adsorption of uranyl aqueous-species occurs commonly under near neutral pH conditions (all references) and decreases in the presence of negative-charged uranyl–carbonate complexes in solution (e.g. Bachmaf and Merkel, 2011; Dong et al., 2012; Marques Fernandes et al., 2012).

(b) Adsorption of uranyl aqueous-species occur predominantly *via* outer sphere complexes on the cation exchange sites under weak acidic conditions (pH ~4–5; all references).

(c) The adsorption of uranyl aqueous-species onto cation exchange sites is strongly affected by the strength of the electrolyte solutions NaCl and NaClO$_4$ as Na$^+$ and uranyl aqueous-species compete for the same adsorption sites (Pabalan and Turner, 1996; Catalano and Brown, 2005; Bachmaf and Merkel, 2011).

(d) Uranyl aqueous-species predominantly sorb to surface terminations along edge sites via inner sphere complexes at higher pH values (pH >5); and their sorption is preferred onto >FeO over >AlO terminations (Catalano and Brown, 2005) and onto >SiO over >AlO with increasing pH (McKinley et al., 1995; Chisholm-Brause et al., 2004).

(e) In the absence of uranyl–carbonate aqueous species (i.e. the solution is not in equilibrium with the atmosphere), the amount of adsorbed U is independent from its speciation in solution (Chisholm-Brause et al., 2001) and depending on the total U concentration in solution, surface complexes on edge sites can be composed of uranyl-ions (>AlO-UO$_2^+$; >SiO-UO$_2^+$) and polymerized uranyl-aqueous species; e.g. SiO-[(UO$_2$)$_3$(OH)$_5$]^0 (McKinley et al., 1995; Chisholm-Brause et al., 2004; Kowal-Fouchard et al., 2004).

(f) At equilibrium with the atmosphere, uranyl–carbonate rather than uranyl–hydroxy-hydrate species sorb to surface terminations along the edges (Catalano and Brown, 2005; Dong et al., 2012; Marques Fernandez et al., 2012).