Montmorillonite colloid size heterogeneity – Fractionation and Characterization

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Highly compacted bentonite is planned to be one component of the engineered barrier system in many spent nuclear fuel final repository designs. The potential release of montmorillonite colloids, acting as carriers, may enhance the transport of radionuclides in case of a leaching canister. During transport, size exclusion/filtration may occur, resulting in migration of specific size fractions only. Therefore, it is necessary to determine the size heterogeneity of the mobile bentonite clay colloid and its radionuclide association.

In this study, unpurified MX-80 bentonite consisting mainly of smectite with impurities of quartz, plagioclase, orthoclase, muscovite as well as calcite/dolomite, gypsum and pyrite, was sedimented in low ionic strength carbonated synthetic ground water (SGW) at 10g/L. Thereafter, seven colloidal suspensions of various size fractions were obtained by sequential and direct centrifugation. Their particle size distributions were measured by PCS and AsFlFFF/UV-Vis/LLS/ICP-MS. The concentrations of colloids and other elements present in the suspensions were measured by IC and ICP-OES. The mineralogical composition was analyzed by XRD.

The mean particle size is decreasing with the number of fractionation steps, from ~500 down to ~50 nm. The presence of predominantly montmorillonite colloids is confirmed by: i) XRD results, for all colloidal fractions and ii) the Si/Al and Al/Mg mole ratios. There is an instant release of Na and SO_4^{2-} to the SGW while adding the bentonite indicating the dissolution of accesory minerals and cation exchange processes. An increasing release of natural ^{238}U with decreasing size fractions (i.e. larger exposed surface area) is evidenced. The results are discussed with respect to the implication on radionuclide speciation and transport.

Activities and volatilities of trace components in CaO-MgO-FeO-Al₂O₃-SiO₂ melts

CaO-MgO-FeO-Al_2O_3-SiO_2 melts

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Knowledge of the activities of trace components in silicate melts is extremely important for addressing such problems as (a) degassing in volcanic systems (b) volatilities in protoplanetary systems and (c) the effect of melt composition on trace element partitioning. Nevertheless these activities are very difficult to measure by conventional phase equilibrium techniques except under circumstances where the metallic element is stable in a readily accessible f_{O_2} range[1]. We have modified the "metal-saturation" approach by measuring the partitioning of a large number of elements (V, Cr, Cu, Zn, Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl, Pb and Bi) between liquid Fe alloys and liquid silicate at 1.5 GPa and 1650°C. The data provide activity coefficients for oxide components relative to the activity of FeO, whose partitioning between metal and silicate is also measured. Use of graphite capsules means that the silicate melt composition can be varied over a wide range, but also means that the metal is carbon-saturated, a factor which has a profound effect on the activities of some components (e.g Pb, Ag, W) in the liquid metal.

We find that the activity coefficients of a number of the most important trace components, notably WO_3, MoO_2, GeO_2, $TlO_{0.5}$, $GaO_{1.5}$, $BiO_{1.5}$ and $SbO_{1.5}$ are strongly dependent on melt composition each showing variations of 1-2 orders of magnitude over the accessible range of silicate melt compositions. Values for $CuO_{0.5}$ are in excellent agreement with previous experimental data[2] on Cu-saturated compositions which shows that the method is viable. When combined with thermodynamic data on the gas species we find that volatilities under solar nebula conditions are displaced relative to those of the "conventional" condensation sequence[3].

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