Minimal alteration of montmorillonite following long-term reaction in natural alkali solutions: implications for geological disposal of radioactive waste

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Bentonite is one of the more safety-critical components of the engineered barrier system in the disposal concepts developed for many types of radioactive waste. Bentonite is utilised because of its favourable properties which include plasticity, swelling capacity, colloid filtration, low hydraulic conductivity, high retardation of key radionuclides and stability in geological environments of relevance to waste disposal. However, bentonite is unstable under the highly alkaline conditions induced by Ordinary Portland Cement (OPC: initial porewater pH>13) and this has driven interest in using low alkali cements (initial porewater pH9-11) as an alternative to OPC. To build a robust safety case for a repository for radioactive wastes, it is important to have supporting natural analogue data (see Alexander et al., 2015 for discussion) to confirm understanding of the likely long-term performance of bentonite in these lower alkali conditions.

Recently, therefore, there have been extensive efforts to better understand the interactions of alkaline fluids with bentonite (e.g. Savage et al., 2010; Sidborn et al, 2015), coupled with studies aimed at reducing the potential risk by development (cf. NDA, 2010) and testing (e.g. Vourinen et al., 2005) of low alkali cement formulations which typically have leachates with a pH of 9-11. Attempts to examine potential reaction of bentonite at these lower pH values has been complicated by the inherently slow kinetics of such reactions (e.g. Heikola et al., 2013). Clearly, this is an area where studying natural systems could play a valuable role – bridging the disparity in realism in temporal and spatial scales between laboratory studies and the systems represented in repository performance assessment (see discussion in Alexander et al., 1998, 2014, 2015; Miller et al., 2000). Indeed, in this case, the particularly slow kinetics of bentonite reaction in low alkali cement porewaters suggests natural system studies would appear to be the only viable method of assessing bentonite reaction within a timescale which would allow input to current repository safety cases.

In Cyprus, the presence of natural bentonite in association with natural alkaline groundwater (Figure 1) permits the zones of potential bentonite/alkaline water reaction to be studied as an analogy of the potential reaction between low alkali cement leachates and the bentonite buffer in the repository. Here, the results (Milodowski et al., 2015) indicate that a cation diffusion front has moved some metres into the bentonite whereas the bentonite reaction front is restricted to a few millimetres into the clay. This reaction front shows minimal volumetric reaction of the bentonite, with production of a palygorskite secondary phase following reaction of the primary smectites over time periods of 10^5-10^6 a.

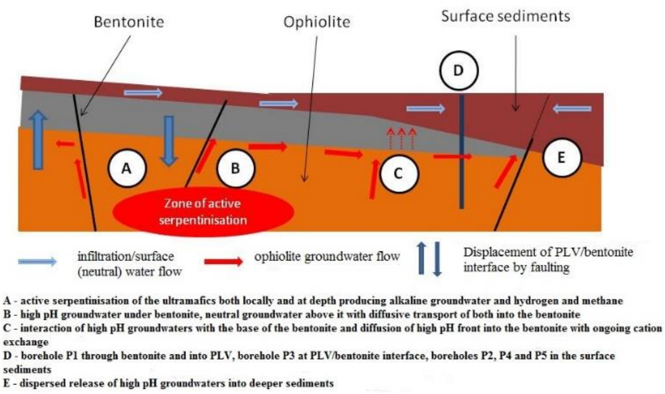

Figure 1: ***conceptual model of groundwater flow in the Troodos ophiolite. The ophiolite-derived, natural alkali (high pH) groundwaters are in contact with the base of the bentonite while surficial (neutral pH) groundwaters flow across the top (Alexander & Milodowski, 2015)***

The physical and temporal similarities between the natural bentonite/ophiolite groundwater environment studied in Cyprus and that expected for processed bentonite in a repository exposed to low alkali cement leachates argues strongly for limited reaction in the repository environment. That Mg-silicate reaction phases have not been considered in previous waste disposal studies is simply a reflection of the limited range of repository EBS designs and host rock types examined to date. In any case, the precise nature of the secondary phase may well prove less important to the long-term performance of the repository than the limited extent of alteration of the bentonite, something which points to an EBS which is robust enough to survive for the timescales of concern to the repository safety assessment.

References

W.R.Alexander and A.E.Milodowski (*eds*) (2015). Cyprus Natural Analogue Project (CNAP) Phase IV Final Report. Posiva Working Report WR 2014-02, Posiva, Eurajoki, Finland.

W.R.Alexander, A.Gautschi and P.Zuidema (1998). Thorough testing of performance assessment models: the necessary integration of *in situ* experiments, natural analogues and laboratory work. Sci. Basis Nucl. Waste Manag. XXI, 1013-1014.

W.R.Alexander, I.G.McKinley and H.Kawamura (2014). The process of defining an optimal natural analogue programme to support national disposal programmes. Proc. NEA-GRS Workshop on natural analogues for Safety Cases of repositories in rock salt. 4 – 6 September, 2012, Braunschweig, Germany. NEA/OECD, Paris, France.

W.R.Alexander, H.M.Reijonen and I.G.McKinley (2015). Natural analogues: studies of geological processes relevant to radioactive waste disposal in deep geological repositories. Swiss Journal of Geosciences, 108, 75-100.

T.Heikola, S.Kumpulainen, U.Vuorinen, L.Kiviranta and P.Korkeakoski (2013). Influence of alkaline and saline solutions on chemical, mineralogical and physical properties of two different bentonites – batch experiments at 25 °C. Clay Mins 48, 309-329.

A.E.Milodowski, S.Norris & W.R.Alexander (2015). Minimal alteration of montmorillonite following long-term reaction in natural alkali solutions: implications for geological disposal of radioactive waste. Appl. Geochem. (*in prep*).

E.B.A.Moyce, C.A.Rochelle, K.Morris, A.E.Milodowski, X.Chen, S.Thornton, J.S.Small and S.Shaw. (2014). Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste. Appl. Geochem. 50, 91-105.

NDA (2010). Geological disposal: geosphere status report. NDA Report No. NDA/RWMD/035. RWM Ltd, Harwell, UK.

D.Savage, S.Benbow, C.Watson, H.Takase, K.Ono, C.Oda and A.Honda (2010). Natural systems evidence for the alteration of clay under alkaline conditions: an example from Searles Lake, California. Applied Clay Science, vol. 47, pp. 72-81.

M.Sidborn, N.Marsic, J.Crawford, S.Joyce, L.Hartley, A.Idiart, L.M. de Vries, F.Maia, J.Molinero, U.Svensson, P.Vidstrand and W.R.Alexander (2015). Potential alkaline conditions for deposition holes of a repository in Forsmark as a consequence of OPC grouting. SKB R-12-17, SKB, Stockholm, Sweden.

U.Vuorinen, J.Lehikoinen, H.Imoto, T.Yamamoto and M.C.Alonso (2005). Injection grout for deep repositories. Subproject 1: Low pH cementitious grout for larger fractures, leach testing of grout mixes and evaluation of the long-term safety. Posiva Working Report 2004-46, Posiva, Eurajoki, Finland.