

Reaction of bentonite in low-alkali cement leachates: an overview of the Cyprus Natural Analogue Project (CNAP)

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ABSTRACT

The Cyprus Natural Analogue Project was carried out due to the requirement to support ongoing laboratory and modelling efforts on the potential reaction of the bentonite buffer with cementitious leachates in the repository engineered barrier system. Although it is known that the higher pH (12.5–13) leachates from ordinary Portland cement will degrade bentonite, it is unclear if this will also be the case for the lower pH (10–11) leachates typical of low alkali cements. Ongoing laboratory and underground rock laboratory programmes, which are currently investigating this, face the obstacle of slow kinetics and the production of short-lived metastable phases, meaning obtaining unambiguous results may take decades. It was therefore decided to implement a focussed natural analogue study on bentonite/low alkali cement leachate reactions to provide indications of the probable long-term reaction products and reaction pathways to provide feedback on the existing short-term investigations noted above and to ascertain if any critical path research and development needs to be instigated now. The results of the analyses presented here, in this short overview of the project, suggest that there has been very limited alkaline groundwater reaction with the bentonite. This is generally supported by both the geomorphological evidence and the natural decay series data which imply groundwater/rock interaction in the last 10^5 a.

KEYWORDS: low alkali cement, engineered barrier systems.

Introduction

BENTONITE is one of the most safety critical components of the engineered barrier system in the disposal concepts developed for many types of radioactive waste. The choice of bentonite results from its favourable properties (including plasti-

city, swelling capacity, colloid filtration, low hydraulic conductivity and high retardation of key radionuclides) and its stability in relevant geological environments. However, bentonite is unstable in alkaline conditions and, due to the fact that cementitious materials react with groundwater to produce initial leachates with pH >13, this has driven recent interest in low alkali cements, because the pH of the leachate is somewhat lower than standard ordinary Portland cement (OPC), at around pH 10–11. It is hoped

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that this lower pH will reduce, or even eliminate, bentonite degradation, so allowing the use of low alkali cements in close proximity to bentonite.

Assuring the long-term stability of bentonite in contact with such alkaline fluids under conditions representative of a deep geological repository requires complementary laboratory, modelling and *in situ* studies. In particular, to build a robust safety case, it is important to have supporting natural analogue data to confirm understanding, and validate models, of the likely long-term performance of bentonite (see discussion in Miller *et al.*, 2000). In general, natural analogue studies can: (1) provide quantitative information on alteration rates, the products of such alteration and their safety relevance to the performance of the engineered barrier system; (2) allow testing of current models and databases used to assess such alteration; (3) provide input to a range of supporting documents for safety cases. However, due to the extremely slow kinetics of the bentonite reaction in low alkali cement leachates, natural analogues would appear to be the only viable method of studying this reaction. As a result of a literature review and recent geological investigations by the authors, several sites in Cyprus were selected as particularly promising for this purpose; field investigations (Alexander and Milodowski, 2011) confirmed the presence of alkaline springs (with a pH of 10–12) in the vicinity of bentonites and clay-rich soils at a wide range of sites.

All alkaline groundwaters studied so far in Cyprus originate from the Troodos ophiolite or the Mamonia terrain (cf. Neal and Shand, 2002). The alkaline pH values (generally between pH 10 and 12) in the groundwaters are a product of the serpentinization of the ophiolites, a reaction which has several possible pathways with the exact reaction pathway depending on the Mg content of the precursor olivine/pyroxene or serpentine product, CO₂ fugacity, water-rock ratio and Ca²⁺ content of groundwater (Moody, 1976). The nomenclature of the Penrose Conference of 1972 (Anonymous, 1972) has been adopted herein and, from top to bottom, the ophiolites consist of: deep (abyssal) marine sediments (including bentonites)/pillow lavas (basalt)/sheeted dyke complex/high level, isotropic gabbro/layered mafic cumulates (gabbro)/layered ultramafic cumulates (herzbergites)/transition zone dunites and residual peridotites. Geomorphological evidence suggests that low temperature serpentinization of the ophiolite

was initiated around 850 ka BP and has been ongoing since, albeit with climatic-induced interruptions at various times in the past. This report presents a short overview of the two years of field work, laboratory analysis and data interpretation of this project, full details of which are provided elsewhere (Alexander and Milodowski, 2011; Alexander *et al.*, 2011).

Field area

The bentonite deposits of the Troodos area are located at the contact between the pillow lavas and the overlying carbonate sedimentary rocks, around the margins of the Troodos ophiolite complex, particularly within the Campanian-age Kannaviou and Moni Formations, in southern and southwestern Cyprus. However, bentonites also occur within the older (Turonian) Perapedhi Formation that forms scattered outcrops, typically only a few metres thick (but locally as much as 35 m), filling hollows in the highly irregular topographic surface of the pillow lavas. The Perapedhi Formation bentonites (and associated alkaline groundwaters) studied here were collected in the vicinity of Parsata, an abandoned village in the Limassol Forest area of southern Cyprus. Samples were collected from four shallow boreholes and a 2 m deep trench in the valley WSW of Parsata and returned to the British Geological Survey (BGS) and Scottish Universities Environmental Research Centre (SUERC) for analysis.

Results and discussion

On the basis of petrographic observations a paragenetic sequence of mineralization and mineralogical alteration is illustrated in Fig. 1. However, it should be noted that this is speculative to a degree because it is difficult to evaluate the temporal–fabric relationships between all of the secondary minerals in these very fine-grained rocks and many of the mineral relationships have ambiguous interpretations. Analysis of the clay mineral fraction X-ray diffraction (XRD) data from the Parsata bentonites revealed no evidence of denaturing or decomposition of the montmorillonite component(s). However, detailed scanning electron microscope (SEM) petrographic observations identified a secondary Mg-rich fibrous clay mineral, with a palygorskite-like (or Fe-rich palygorskite) composition, to be forming on the surfaces of altering

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Cyprus Natural Analogue Project III Mudstone Paragenetic Sequence

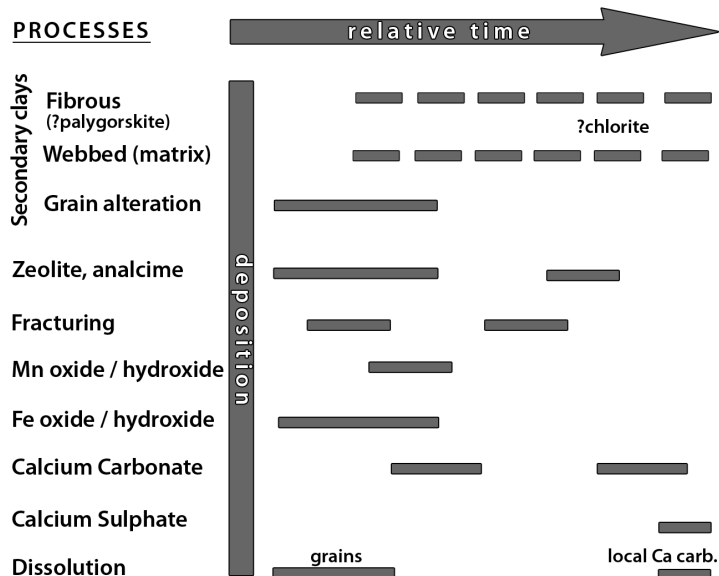


FIG. 1. Bentonite paragenetic sequence (Alexander *et al.*, 2011)

sheet-like montmorillonite particles. The SEM revealed that the surface layers of montmorillonite particles were exfoliating and breaking down to form the fibrous secondary Mg-rich silicate phase.

Palygorskite can also be formed by pedogenic processes, and is found as an authigenic mineral under evaporative conditions, commonly associated with calcrete formation, in arid environment soils and palaeosols. It is also found in highly saline, playa and alkaline lake sediments, where it may form as an alteration product of smectite. The formation of palygorskite in these environments appears to be favoured by the alkaline conditions and high concentration of Mg. The destabilization of smectite and its breakdown to palygorskite in saline/alkaline lake environments is also encouraged by increasing Mg:Ca ratios in the porewater.

Although it was not possible to quantify the palygorskite distribution, qualitative evaluation of the XRD intensities suggested that palygorskite forms a greater proportion of the clay assemblage in the deepest clay sampled from the Parsata trench. The whole-rock geochemical profile in the trench indicates a progressive increase in Mg with depth through laminated bentonite, with a very sharp increase in both Mg and Ca concentration in

the highly fractured bentonite immediately above the contact with the pillow lavas. This Mg enrichment would be consistent with the greater abundance of palygorskite indicated qualitatively by XRD at the base of the sequence. Although this does not conclusively prove that the observed alteration of smectite to palygorskite is the result of interaction with alkaline groundwater, it would be consistent with reaction with low-temperature hydrothermal alteration by Mg-rich fluids associated with serpentinization from the underlying pillow lava sequence and ophiolite assemblage. This is consistent with the natural decay series data which indicate that there has been uptake of uranium (presumably from the groundwater) throughout the sediment column, indicating ongoing reaction for the last 10^5 a. In particular, trench sample 964, from just above the pillow lavas, shows evidence of long-term uranium deposition, indicating a zone of long-term groundwater–bentonite reaction.

Conclusions

The results of the analyses presented here suggest that there has been some form of limited alkaline groundwater reaction with the bentonite. However, ambiguity in some of the boundary

conditions means that it is not yet possible to conclude with absolute certainty that the cause of reaction is alkali groundwater. Nevertheless, the alternative thesis, that the presence of palygorskite at the base of the bentonite is due to reaction with Mg-rich hydrothermal fluids, would appear to be unlikely on the basis of the natural decay series results and the geomorphological interpretation. As noted in Alexander *et al.* (2011), two, or perhaps three, hydrothermal events can be traced in the bentonite mineralogy, but these are probably early stage, sub- and supra-marine processes (i.e. when the ophiolite was still part of the ocean crust), whereas the smectite-to-palygorskite transformation observed here appears to be a very late stage event. This is generally supported by both the geomorphological evidence and the natural decay series data which imply activation of groundwater circulation and groundwater/rock interaction in the last 10^5 a.

That the bentonite reaction is confined to a thin zone at the base of the bentonite suggests that the physical properties of the bentonite which are of importance to its barrier role in a repository have not been compromised following production of palygorskite, but this will be investigated in detail in a new phase of work planned for 2012.

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