

## **A new natural analogue study of the interaction of low-alkali cement leachates and the bentonite buffer of a radioactive waste repository**

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### **ABSTRACT**

Bentonite plays a significant barrier role in many radioactive waste repository designs, where it has been chosen due to its favourable properties such as plasticity, swelling capacity, colloid filtration, low hydraulic conductivity and its stability in relevant geological environments. However, bentonite is unstable at high pH meaning that it could lose its favourable properties if interacted with hyperalkaline leachates from concrete construction materials (e.g. tunnel liners, grouts, etc.), seals and plugs and/or cementitious wastes in a repository. This fact has forced several national programmes to assess alternative construction and sealing materials such as low alkali cements. Recently, it has been assumed that the lower pH (typically pH 10-11) leachates of such cements will degrade bentonite to a much lesser degree than 'standard' OPC-based cement leachates (generally with an initial pH>13).

To date, few laboratory or *in situ* URL (underground rock laboratory) data are available to support the use of low alkali cements in conjunction with bentonites, partly because of the very slow kinetics involved. Consequently, a new project has focussed on finding an appropriate natural analogue site to provide long-term supporting data which will avoid the kinetic constraints of lab and URL experiments. Early results have identified an initial, very promising site at Mangatarem in the Philippines, where a quarry excavating bentonite and zeolites is found in the sedimentary carapace of the Zambales ophiolite. In the immediate vicinity of the quarry, ophiolite-derived hyperalkaline groundwaters are present and further field work (including geophysics surveys and borehole drilling) are now being planned to assess regional bentonite/hyperalkaline groundwater interaction. This paper presents an overview of the current status of the project and assesses the relevance of the study to improving understanding of low-alkali cement leachate/bentonite interaction.

### **INTRODUCTION**

Bentonite is one of the most safety-critical components of the engineered barrier system for the disposal concepts developed for many types of radioactive waste (radwaste) [1]. The choice of bentonite results from its favourable properties – such as plasticity, swelling capacity, colloid filtration, low hydraulic conductivity, high retardation of key radionuclides – and its stability in relevant geological environments. However, bentonite – especially the swelling clay component that contributes to its essential barrier functions – is unstable at high pH. This led to some repository designs, especially for disposal of HLW (high-level waste) or SF (spent fuel) [e.g.2], that specifically exclude the use of concrete from any sensitive areas containing bentonite, due to the fact that cementitious materials react with groundwater to produce initial leachates with pH >13, later falling to around pH 12.5 [3].

Such an option of avoiding the problem by constraining the design was considered acceptable during early, generic studies but, as national radwaste programmes move closer to implementation, it is increasingly recognised that constructing extensive facilities underground without concrete – a staple of the engineering community – would be difficult, expensive and potentially dangerous for workers [4]. This is especially the case in countries like Japan, where a volunteering approach to siting a HLW repository [5] means that repository construction could be in a technically challenging host rock.

A further area of concern involves ILW (long-lived intermediate level waste, also called TRU), particularly if this is co-disposed (or co-located) with HLW/SF. ILW contains large inventories of cementitious materials and hence, in principle, could pose a risk to the EBS (engineered barrier system) of HLW/SF, even if concrete was excluded from the HLW part of the repository (e.g. scenarios discussed in [2]). Indeed, some designs of the EBS for various kinds of ILW include a bentonite layer [e.g. 6], which is planned to act as an external barrier around concrete structures. To date, there has been no comprehensive demonstration that the performance of such a barrier can be assured for relevant periods of time [e.g. 7].

Recently, therefore, there have been extensive efforts to better understand the interactions of hyperalkaline fluids with bentonite [8,9], coupled with studies aimed at reducing the risk by development of low alkali cement formulations [e.g. 10]. The greatest challenge is bringing the information produced by laboratory (conventional and URL – underground rock laboratory) and modelling studies together to form a robust safety case. This is complicated by the inherently slow kinetics of such reactions and the commonly observed persistence of metastable phases for geological time periods (for a good overview of the issues involved, see [8]). Clearly, this is an area where natural analogues (see [11,12] for definition and examples) could play a valuable role – bridging the disparity in realism and timescales between laboratory studies and the systems represented in repository performance assessment [13].

## **NATURAL ANALOGUE CONCEPT**

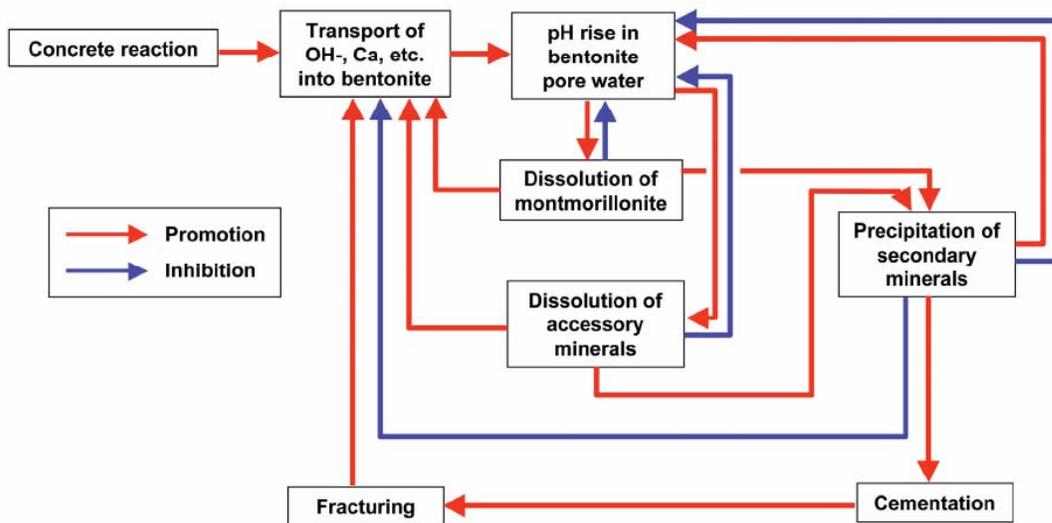
Although both hyperalkaline (i.e. groundwaters with pH 12.5 and above) and alkaline systems (target pH of 10 to 11) have previously been examined as natural analogues of cementitious repositories [9, 14, 15], neither produced data of relevance to the questions now being posed with regard to low alkali cements. The natural cements in Jordan [9, 14] are closely representative of the OPC (Ordinary Portland Cement) based materials traditionally used in repository designs and, although it is likely that a period of cement evolution similar to that of low alkali cements exists at the study sites, no data are currently available. An appropriate low alkali cement analogue was studied in Oman [15] but, as the focus of the work was on hydro- and biogeochemistry, no data of relevance to bentonite alteration were collected here either.

As such, an initial literature study was sponsored by RWMC of Japan with search parameters that include both aspects of the target geology and also themes of relevance to radwaste management programmes. Factors considered include:

- ophiolite terrains
- hyperalkaline groundwaters
- bentonites
- H<sub>2</sub> or CH<sub>4</sub> gas in groundwaters
- thermal groundwaters
- tuffaceous deposits

- coastal sites
- logistics (e.g. potential support from local mining operations, ease of transport etc)
- use in training junior staff

and indicated that no useful information on this topic could be “mined” from any past studies and hence the option of a new project was examined. The basic idea was to use a “top-down” approach to identify sites where bentonite deposits have been exposed to relevant hyperalkaline water for very long periods. Especially given the interest in low pH (or, more precisely, low alkali) cements, the focus was on sites that have natural waters with pH in the appropriate range (around 10-11). As indicated in Figure 1, the cement leachate is simulated by natural hyperalkaline water, which, if the timescale of interaction can be determined, allows the models that are being developed to quantify the specific processes shown in the figure to be tested.



**Figure 1: Some of the important processes involved in bentonite alteration (from [8]); at the natural analogue site, natural hyperalkaline groundwaters simulate concrete leachates.**

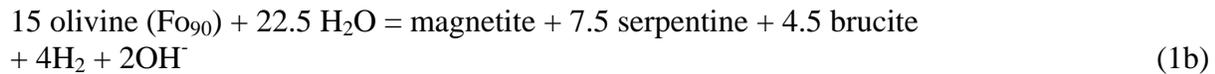
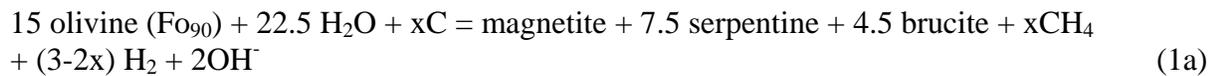
The challenge is to maximise the value of this test, by assuring that materials and boundary conditions are as similar as possible to those in a repository. Nevertheless, it must be emphasised that such sites are no more than an analogy of a repository, not a copy, and hence certain differences are inevitable (discussed below). Currently, the technical focus is on:

- long-term bentonite stability in low alkali cement leachates
- if possible, same system interacting with seawater/brines for a coastal repository (NB this may also provide indicators of site stability)
- low alkali cement leachate/host rock interaction – is there any?
- BPM (blind predictive modelling – see [16]) of the chemistry of safety relevant elements (eg Se), including *in situ* speciation
- microbiology of the system (cf. 15)
- staff training, including mentoring by experienced (in radwaste) international staff

In principle, there are a number of locations worldwide where such an analogue might be found, including Cyprus, Oman, California, Bosnia, Papua New Guinea, Japan and the

Philippines. Based on a multi-attribute analysis, considering factors such as probability of finding suitable locations, relevance to Asian programmes, opportunity for training, low risk of disrupting calls for volunteer sites in Japan and cost-effectiveness, the Philippines is now under consideration as one of the preferred options for the Japanese programme and has recently been the focus of more detailed literature studies and a limited number of field investigations to confirm fundamental feasibility.

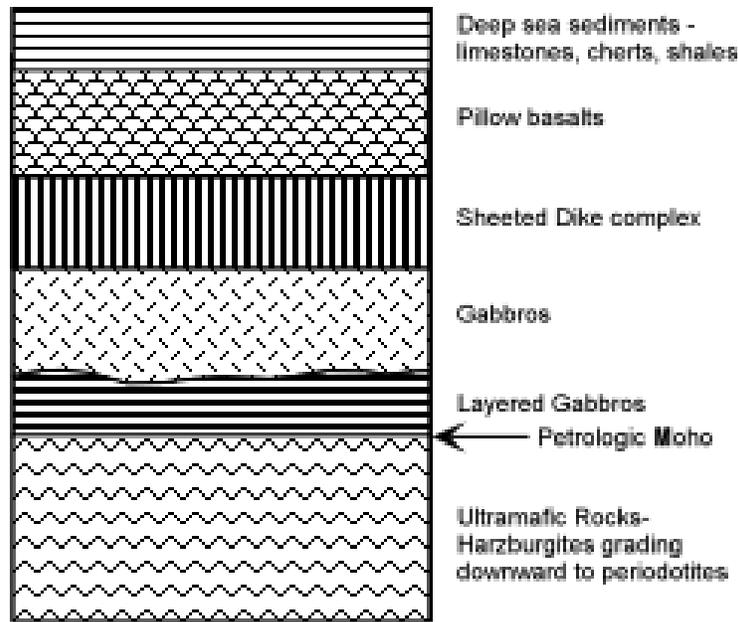
The hyperalkaline pH values (generally between pH 10 and 11, see [17] for examples) observed in the groundwaters are a product of the serpentinisation of ultramafic rock, in this case usually the ophiolites (Figure 2), a reaction which has several possible pathways (e.g. equation 1, from [18 after 19]) with the exact reaction pathway depending on Mg content of the precursor olivine/pyroxene or serpentine product, CO<sub>2</sub> fugacity, water-rock ratio, Ca<sup>2+</sup> content of groundwater, etc.



Equation 1a is for systems open with respect to carbon input and equation 1b is for closed systems. The serpentinite mineral assemblages are very strongly reducing and the hyperalkaline waters are often effervescent with H<sub>2</sub> and/or CH<sub>4</sub> gas (see above). Some of the reaction pathways are also strongly exothermic, frequently producing hydrothermal groundwaters which are often used as therapeutic springs.

## RESULTS AND DISCUSSION

All hyperalkaline groundwaters studied so far in the Philippines originate from the 20 or so known ophiolite bodies which are widely scattered throughout the archipelago. Several ophiolites on the islands of Panay (around E121,000 N012,500), Luzon (around E120,500 N014,500) and Palawan (around E118,000 N010,000) have been examined as part of a preliminary assessment of suitable sites and, to date, the Mangatarem area (E120,180 N015,047) in the province of Pangasinan on the west central area of the island of Luzon in northern Philippines appears the most promising. This area hosts the largest known bentonite deposits in the country, with reserves of approximately four million tonnes. Here, bedded bentonites and zeolites belong to the Eocene Aksitero Formation (and most probably extend to the finer members of the overlying Moriones Formation), the sedimentary carapace of the Eocene Zambales ophiolite, and which (un)conformably overlie the cherts and upper pillow lavas of the ophiolite. The well-bedded tuffaceous members of the formations have been authigenically transformed after deposition into bedded zeolite (mordenite [20]) and a bentonite dominated by montmorillonite and quartz which is similar in chemistry to the MX-80 bentonite which is under consideration as an EBS material in many national programmes (e.g. [1, 5, 6 and 8] - see also Table I). Individual beds range in thickness from a few centimetres to several metres and range in colour from light cream, beige, off-white, light to medium brown and greenish. Texture closely resembles a tuff, but sometimes exhibits finer grains.



**Figure 2. Cross section through an ‘average’ ophiolite. The serpentinisation reaction can take place in any of the igneous members of the entire sequence, hence leading to slightly different leachate chemistries.**

In the immediate vicinity of the bentonite deposit, hyperalkaline groundwaters come to the surface as a hot spring and the chemistry is clearly that of an serpentinisation-derived (presumably from the nearby ophiolite) groundwater which has similarities to low alkali cement leachates (see Table II).

At both the Palawan and Panay sites, no exposed bentonite has yet been discovered and it seems likely that drilling would be required at these sites. However, it is not necessary to cover all technical questions at one site so it is likely that the focus at Palawan will be on coastal repository processes due to the close proximity (<1 km) of the site to the sea whereas a seemingly highly active microbial community at Panay (here microbial mats in and around the groundwater springs and seeps are the simplest way to find the alkaline groundwaters, backed up by establishing the groundwater pH) might prioritise this site for microbial studies. An intercomparison of the BPM work at all three sites would, based on the intrinsic differences in the groundwater chemistry, increase confidence in the results of the modelling.

## CONCLUSIONS

Although still at a preliminary stage, the results of the project to date are very encouraging and indicate the potential of the sites in the Philippines to address the long-term alteration of bentonite (and possible repository host rocks) by low alkali cement leachates. Currently, the Mangatarem site looks the most promising for the study of bentonite/leachate interaction, but further work may be carried out at the Palawan and Panay sites, as these provide better examples of a coastal repository analogue and microbiological processes respectively. As each site will provide a different challenge in terms of site characterisation, logistics and interpretation, this project is particularly suitable for staff training.

Indeed, the proposed International Philippines Hyperalkaline Analogue Project (IPHAP) aims to maximise the extent of transfer of experience to younger staff [21], which is widely acknowledged to be a critical problem in many national waste management programmes [e.g. 22]. Participation in this project is open to radwaste implementing, regulating and R&D organisations and may be particularly suitable for the developing nuclear programmes in Asia.

**Table I: Geochemical (XRD) analysis of the Mangatarem bentonite and MX-80 bentonite [23]**

<b>Parameter (%)</b>	<b>Untreated Mangatarem</b>	<b>Average treated MX-80 (Wyoming)</b>
<b>SiO<sub>2</sub></b>	<b>50.3 - 69.8</b>	<b>58.5</b>
<b>TiO<sub>2</sub></b>	<b>0.40 - 0.64</b>	<b>nd</b>
<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>2.8 - 6.8</b>	<b>3.8</b>
<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>12.1 - 13.2</b>	<b>19.1</b>
<b>CaO</b>	<b>0.1 - 5.8</b>	<b>1.4</b>
<b>MgO</b>	<b>1.9 - 3.1</b>	<b>2.4</b>
<b>K<sub>2</sub>O</b>	<b>0.4 - 1.2</b>	<b>0.5</b>
<b>Na<sub>2</sub>O</b>	<b>1.2 - 1.3</b>	<b>2.1</b>
<b>CEC</b>	<b>55.2 - 102.5 meq/100 g</b>	<b>72.0 meq/100 g</b>

**Table II: Hydrochemistry of hyperalkaline groundwaters: examples from around the world [24] for comparison with the new Philippines groundwater data and low pH cement leachates [25]. All data in ppm (nd: no data bdl: below detection limit).**

<b>Location</b>	<b>pH</b>	<b>Na</b>	<b>K</b>	<b>Ca</b>	<b>Mg</b>	<b>Cl</b>	<b>SO<sub>4</sub></b>	<b>SiO<sub>2</sub></b>
Cyprus 3a	11.5	385.0	15.1	1.0	0.3	420.0	251.0	24.0
Cyprus 3b	11.2	163.0	1.2	93.0	0.5	190.0	207.0	3.4
Greece	11.3	24.0	1.0	34.0	0.3	15.0	3.0	2.0
Bosnia	11.7	35.0	1.5	29.0	7.0	20.0	2.0	0.9
Oman	11.5	132.5	4.8	34.0	1.3	127.5	22.5	3.0
New Caledonia	10.8	15.0	3.0	14.0	2.3	22.0	0.8	0.4
Western USA	11.5	19.0	1.0	40.0	0.3	63.0	0.4	0.4
<b>Narra 1</b>	<b>10.8</b>	<b>158.3</b>	<b>0.9</b>	<b>3.1</b>	<b>0.0</b>	<b>95.0</b>	<b>nd</b>	<b>nd</b>
<b>Narra 2</b>	<b>10.3</b>	<b>158.3</b>	<b>0.9</b>	<b>3.1</b>	<b>0.1</b>	<b>95.0</b>	<b>bdl</b>	<b>43.8</b>
<b>Narra 3</b>	<b>10.3</b>	<b>157.4</b>	<b>0.9</b>	<b>2.4</b>	<b>0.1</b>	<b>80.0</b>	<b>bdl</b>	<b>44.2</b>
<b>Mangatarem</b>	<b>11.1</b>	<b>28.0</b>	<b>0.5</b>	<b>18.6</b>	<b>0.2</b>	<b>17.4</b>	<b>5.1</b>	<b>nd</b>
Cement	11.03	42	7.3	20	<0.5	52	12	49.2

leachate ALL-MR f63								
3Cement leachate OL- SR f63	10.05	4400	150	4300	0.56	13000	247	32.1

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