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POTENTIAL EFFECTS OF HYPERALKALINE LEACHATES ON CEMENTITIOUS REPOSITORY HOST ROCKS: AN EXAMPLE FROM MAQARIN, NORTHERN JORDAN

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1. Introduction

The extensive use of cementitious materials is a feature of many repository designs for the deep disposal of radioactive waste. In addition to the straightforward structural uses, these materials are commonly used to provide physical and/or chemical containment. The use of within-package, cementitious waste encapsulants, for instance, immobilises the waste, isolates it from its surroundings and provides chemical containment by supplying sites on minerals and gel surfaces where radionuclides can sorb. Further chemical containment can be provided, as in the Nirex repository design, by surrounding the waste packages with a specially formulated, porous cement backfill. This reduces the solubility of key radionuclides by establishing hyperalkaline near-field conditions and provides abundant surfaces on which radionuclides can be sorbed. Models of cement evolution (eg Atkinson, 1985) predict that hydration of the cementitious material in the repository by groundwater will produce an initial stage of hyperalkaline (pH>13.3) leachates, dominated by alkali hydroxides, followed by a longer period of portlandite buffered (pH~12.5) leachates.

Such hyperalkaline leachates may react chemically with the repository host rock and have the potential to lead to a modification of those features for which the formation was originally chosen (eg low groundwater flux, high radionuclide retardation capacity etc). The extent of these reactions can be calculated (eg Haworth et al., 1987), but it is clear that the calculations need to be tested against relevant data, not least because the geochemical codes upon which the calculations are based may be incomplete or otherwise inadequate. The prime sources of data are laboratory experiments (eg Rochelle, 1995) which, while valuable, cannot fully represent all the complexities present at a real site. Perhaps more importantly, laboratory experiments are unable to reproduce directly the long time periods which are of interest to a repository post-closure safety assessment.

Consequently, Nirex, along with Nagra, the UK Environment Agency (formerly Her Majesty`s Inspectorate of Pollution; HMIP), SKB and Ontario Hydro have sought, in addition to laboratory data, means of testing the models by observations of similar processes which have occurred in nature - the so-called natural analogue approach (see Miller et al., 1994, for details). The most suitable natural analogue to constrain the effects of possible interactions between the host rock of a cementitious repository and hyperalkaline leachates is the natural cements and their associated hyperalkaline groundwaters at Maqarin in Northern Jordan (Figure 1).

2. Background to the Maqarin natural analogue study

The Maqarin site appears to be unique in that the hyperalkaline groundwaters in the area are the product of leaching of an assemblage of natural cement minerals produced as a result of the high temperature-low pressure metamorphism of the marls and limestones of the area (see Alexander, 1992, for details of groundwater chemistry). At least three different sites of hyperalkaline groundwaters have been identified in Jordan (see Figure 1) and they appear to represent the three main stages in the theoretical evolution of a cementitious repository (cf Atkinson, 1985):

1. Early: alkali hydroxide groundwaters (Western Springs, Maqarin). The pH (maximum 12.9) and the high Na/KOH (content with relatively high Ca) suggests that this site is analogous to an initial cement leachate (ie high pH, Na/KOH dominated).

2. Intermediate: portlandite buffered system (Eastern Springs, Maqarin). A pH of ~12.5 and portlandite saturation indicate a very good analogy of the $Ca(OH)_2$ buffered cement leachate.

3.Late: lower pH, silica dominated system (Daba region in central Jordan,). No groundwaters have been found in this area to date, but the mineral assemblage strongly resembles the theoretical late stage (pH 10.5) leachate.

The basis of the analogy between the Maqarin site and a cementitious repository is quite simple: at Maqarin, infiltrating groundwaters percolate through the rock until they meet the zone containing the natural cement minerals where rock/water interaction produces hyperalkaline groundwaters. It is assumed that the same course of events will be followed at a cementitious repository, with the local groundwaters leaching the cement, producing hyperalkaline leachates (or groundwaters). At Maqarin, the hyperalkaline groundwaters have been observed to then continue their percolation through the fractured rock, interacting with the fractures and rock matrix as they migrate. This sequence of events is also likely downstream of a cementitious repository and thus the observations from Maqarin can be used to provide a guide to the possible long-term effects of the repository leachates on the host rock.

3.Summary of the secondary mineral distribution

Milodowski et al., (1996) have described the secondary phases formed in the fractures and associated rock matrix downstream from the Maqarin cement zone in great detail. The mineralogy is dominated by several CSH and CASH[1] phases with occasional zeolites and up to 11 successive stages of fracture mineralisation. Generally, the fractures are completely sealed by the secondary CSH/CASH/zeolites and are then often tectonically re-activated, so producing manifold repetition and reversals of the fracture filling mineral succession. In this paper an attempt is made to place the alteration pattern in the framework of the conceptual model for the development of a hyperalkaline plume downstream of a cementitious repository (figure 2).

In the cement zone (the proximal part of the plume), the hyperalkaline groundwaters have not reacted with the host rock and so have a high pH and high concentrations of Na, K and Ca . As the plume reacts with the host (aluminosilicate-bearing) rock, the pH falls as do the Na, K and Ca concentrations while the concentrations of Al and Si rise fractionally. Beyond the distal edge of the plume, the host rock groundwater pH is near neutral, the Na, K and Ca concentrations are low, while the concentrations of both Al and Si are high. This pattern has consequences for the secondary mineralogy: C-S-H phases will be found in the fractures (through which the plume has migrated) in the proximal part of the plume, reflecting the fact that the groundwater has not yet reacted with the host rock and is equilibrated with the CSH phases which make up the cement. As the alkaline groundwater moves downstream and interacts with the aluminosilicates in the host rock, the Al concentration increases, precipitating CASH phases. At the distal edge of the plume, the alkaline groundwater has reacted with an even larger volumes of host rock and eventually precipitates zeolites as the Al concentration in the groundwater becomes high enough and the pH low enough (Savage, 1996)[2].

If this evolutionary pattern could be observed from a fixed point in a fracture, the theoretical sequence (assuming an infinite source of cement pore water) of mineral precipitates, as the plume migrates past the observation point (X in Figure 2), would then be: at point **a** (in Figure 2) in the plume evolution, zeolites first, followed by, at point **b** in the plume evolution, CASH phases and then, finally, at point **c** in the plume, C-S-H phases. In the following sections, the observations from Maqarin are presented and described according to the above conceptual model.

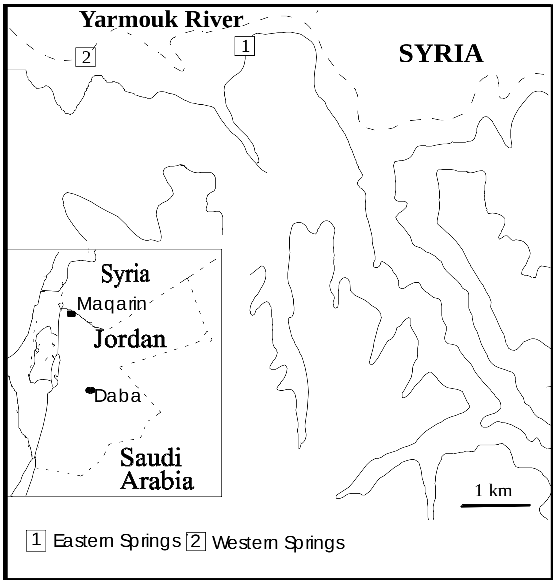
Briefly, the Western Springs sampling site is a porous colluvium and shows a succession of secondary minerals which begins with zeolite which is then overlain by CASH phases which in turn are overlain by CSH phases (ettringite-thaumasite, due to the high sulphate content of the groundwater). These data may be interpreted as representing a system which remains open (eg in a fractured rock in a tectonically highly active region or in a porous rock) where the middle part of the plume may over-run the distal edge which may then be over-run by the proximal portion, with each new portion of the plume replacing wholly, or in part, the previous mineral assemblage (cf Figure 2)

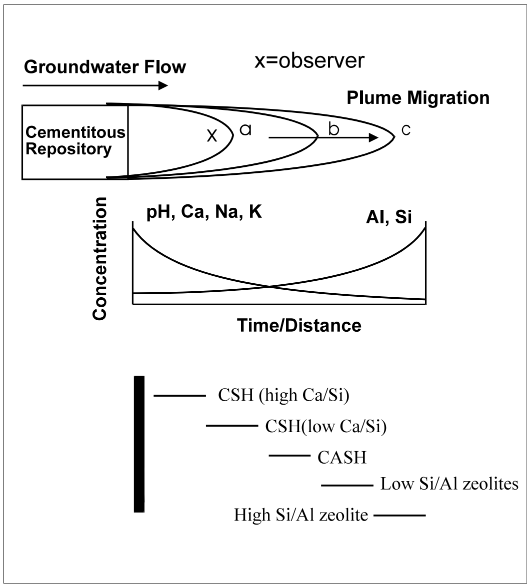
Figure 1: Maqarin site, northern Jordan

Figure 2: Theoretical development of the hyperalkaline plume in a host rock (after Savage, 1996)

[1] Following the standard cement industry shorthand: C=CaO; A=Al_2O_3 ;S=SiO_2 ; H=H_2O:

[2] See Savage (1996) for a discussion of zeolite and CSH stability fields. Briefly, in the presence of elevated Al levels in solution, zeolites will form preferentially due to limited ability of CASH/C-S-H to incorporate Al in the mineralogical structure.





While the Western Springs colluvium gives a clear picture of the effects of a hyperalkaline plume in a dynamic, open system, the data from the eastern springs are probably of more direct relevance to a repository host rock. The overall mineral succession in the fractured host rock at the Eastern Springs is not so different from that at the Western Springs, but the site straddles an active anticline which induces continuous re-opening of previously sealed fractures. The new hyperalkaline water which then flows through the re-opened fractures may no longer be in equilibrium with the previous fracture infill and so reaction begins again. Usually, replacement of the previous generation of infill is only partially completed before the fracture seals again, resulting in a complex pattern which makes interpretation difficult. However, what is clear is that the fractures always seal (and relatively quickly too according to the data of Clark et al., 1994a; see below) and, in a tectonically quieter regime such as a repository host rock, will presumably remain sealed.

Finally, it is worth noting that work on the changes in the fracture wallrock porosity is currently ongoing. Although the petrological data (including porosity determinations) tend to suggest that the matrix porosity behind the fracture is being reduced via blocking of the pore space by secondary minerals, geochemical data (including natural decay series data; Milodowski et al.,1996) indicate that the rock matrix is still open to rock-water interaction when the fracture is open, even when the matrix porosity is reduced. This is a significant result as it indicates that non-sorbing radionuclides advecting through the open fractures with the hyperalkaline waters can be retarded via matrix diffusion.

4. Age of the hyperalkaline groundwater/host rock interaction

As a scoping exercise, a few vein minerals (and associated fracture wallrock) from sealed fractures in Adit A-6 have been analysed for natural decay series radionuclides and dates can be very tentatively assigned to the hyperalkaline groundwater alteration (Milodowski et al., 1994). A diagenetic calcite vein has been dated by the ^{230}Th ingrowth method at between 500ka and 2Ma, providing a maximum age for the metamorphism which produced the cement zone mineral assemblage. This will be compared with an ongoing goemorphological assessment of uplift and erosion in the Yarmouk Valley area which should also provide an estimate for the time of metamorphism.

Tobermorite vein filling and jennite-ettringite vein filling produced ages of 90ka and 80ka respectively and a zeolite altered rock matrix an age of 160ka. The zeolitic sample is almost certainly contaminated with detrital ^{230}Th, producing an overestimate of the age and questions remain on the the tobermorite and jennite ages. Although fission-track registration and BSEM petrography strongly suggest that no wallrock was present nor was there any detrital U-bearing components in the vein materials (Milodowski et al., 1994), the samples certainly contain ^{232}Th. This was possibly introduced as colloidal Th, incorporated from the groundwater by the cement phases during formation (Clark, pers. comm., September, 1994). If this were the case, it might also be expected that at least some of the ^{230}Th present in the veins was also originally groundwater supplied so indicating that the calculated ^{230}Th ingrowth ages are a maximum. It is not, however, possible to correct these maximum ages for a potential Th colloidal input as it is impossible to assess any previous (or, indeed, current) $^{230}Th/^{232}Th$ ratios for the colloids. Also, no meaningful correction can be applied to the zeolitic rock matrix age as no natural decay series data exist for the undisturbed, unaltered host rock. Clark et al., (1994a; 1996) quote a ^{14}C age of less than 650a for recarbonated cement zone material from Adit A-6. This does not necessarily contradict the ^{230}Th ingrowth ages, rather simply confirms the scenario of repeated re-activation of fractures with consequent mutli-phase fracture infill.

5. Conclusions

Study of the secondary fracture minerals at Maqarin suggests that the hyperalkaline plume released from a cementitious repository will seal groundwater pathways in the host rock. Dating of the material at Maqarin suggests that, once sealed, the secondary fracture-filling mineralogy in the hyperalkaline disturbed zone can remain stable for safety assessment relevant timescales - with the implication that radionuclides associated with these secondary phases also can be isolated from the evolving groundwaters. In addition, the presence of secondary minerals on the fracture walls do not necessarily seal off the matrix to radionuclide diffusion from the fracture.

6. Acknowledgements

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