CEMENTITIOUS NATURAL ANALOGUES: SAFETY ASSESSMENT IMPLICATIONS OF THE UNIQUE SYSTEMS IN JORDAN

W.R.Alexander[1]*+, I.D. Clark[2], P.Degnan[3#], M.Elie[4], G.Kamei[5], H.Khoury[6], U.Mäder[7], A.E.Milodowski[8], K.Pedersen[9], A.F.Pitty[10], E.Salameh[11], J.A.T.Smellie[12], I.Techer[13] and L.Trotignon[14].

1. Bedrock Geosciences, Veltheimerstrasse 18, 5105 Auenstein, Switzerland. tel. +41 62 897 0538, email russell@bedrock-geosciences.com 2. Department of Earth Sciences, University of Ottawa, 365 Nicholas, Ottawa, Ontario, Canada K1N 6N5. tel. +1 613-562-5800 x6834, fax. +1 613-562-5192, email idclark@uottawa.ca 3. CSIRO Exploration & Mining, Queensland Centre for Advanced Technologies, Technology Court, Pullenvale, Qld 4069, Australia. tel. +61 7 3327 4174, fax. +61 7 3327 4455, email paul.degnan@btinternet.com 4. G2R, Nancy-Université, CNRS BP 239, 54506 Vandoeuvre Cedex, France. tel. +33 383 684 739, fax. +33 383 684 701, e-mail Marcel.Elie@g2r.uhp-nancy.fr 5. JAEA, Geological Isolation Research and Development Directorate, 4-33 Muramatsu, Tokai-mura, Ibaraki-ken, 319-1194, Japan.tel. +81-29-282-1111 ext.67700, fax. +81-282-9328, email kamei.gento@jaea.go.jp 6. Department of Geology, University of Jordan, Amman 11942 Jubeiha, Jordan. tel. +962 6 5341879, fax. +962 6 5348932, e-mail khouryhn@ju.edu.jo 7. Rock-Water Interaction Group, Institute of Geological Sciences, The University of Berne, Baltzerstrasse 3, 3012 Berne, Switzerland. tel: +41 31 631 45 63, fax: +41 31 631 48 43, e-mail: urs@geo.unibe.ch 8. British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, NG12 5GG, UK. tel +44 1159 363548, fax: +44 1159 363200, email aem@bgs.ac.uk 9. Göteborg University, Dept. of Cell and Molecular Biology, Box 463, 405 30 Göteborg, Sweden. tel. +46 31 786 25 78, fax. +46 31 335 13 07, email karsten.pedersen@cmb.gu.se 10. Pitty Consulting, 17 Black Horse Opening, Norwich, Norfolk, NR3 4EP, U.K. tel. +44 1603 410231, email alistair.pitty@btinternet.com 11. University of Jordan, Amman 11942 Jubeiha, Jordan. tel. +962 6 5355 000 ext. 22261, fax +962 6 5348 932, email salameli@ju.edu.jo 12. Conterra AB, Box 8180, 104 20 Stockholm, Sweden. tel/fax. +46-8-6500355, email john.smellie@conterra.se 13. CNRS UMR 6635 Labo GIS-CEREGE, 150 rue Georges Besses, Parc G. Besse, 30035 Nimes Cedex 1, France. tel. +33 4 66 70 99 73, fax. +33 4 66 70 99 89, email: isabelle.techer@unimes.fr 14. CEA, Cadarache, 13108 St Paul lez Durance, France. email trotignon@desdcad.cea.fr *To whom any correspondence should be addressed. +Formerly Nagra, Wettingen, Switzerland. #Formerly Nirex, Harwell, UK.

Abstract

Cement and concrete are extensively used to condition and isolate the waste in repositories for L/ILW (low and intermediate level wastes) and for construction in many HLW/SF/MOX (high level waste/spent fuel/mixed-oxide fuel) repositories. Consequently, in many repository designs, cement-based materials are expected to dominate the repository, ensuring long-term maintenance of hyperalkaline conditions which are predicted to suppress the solubility of key radionuclides in the waste and enhance their sorption on the cement.

Models of cement evolution predict that leaching 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 and CSH buffered (pH~12.5) leachates. It has also been predicted that, as the hyperalkaline porewater leaches out of the near-field, significant interaction with the repository host rock (and, where applicable, bentonite buffer and backfill) may occur. This could possibly lead to deterioration of those features for which the host rock formation and bentonite were originally chosen (*eg* low groundwater flux, high radionuclide retardation capacity etc).

For over two decades, the precise implications of cement leachate/repository host rock interaction has been studied in the laboratory and in underground research laboratories (URLs) and this work has been supported by study of natural cements in Jordan. These natural cements have been produced by the combustion of organic-rich clay biomicrites and are very close analogues of industrial cement. Following interaction with groundwaters, natural hyperalkaline leachates are produced and these move out of the cement into the surrounding host rock, subsequently interacting with and altering it. Here, the conclusions of 15 years study of the Jordan Natural Cement Analogue are presented and the safety assessment (SA) implications of the interaction of cementitious hyperalkaline leachates on repository host rock and bentonite are discussed.

Key words

cementitious wastes, natural analogue, hyperalkaline leachates, clays

1. Introduction

The natural cements and associated hyperalkaline groundwater plumes of the Maqarin and Central Jordan areas are excellent natural analogues of cement-dominated repositories and provide the best sites currently known to examine the processes associated with the long-term behaviour of such systems (see Figure 1). The work carried out in Phases I to IV (see Alexander, 1992, Linklater, 1998, Smellie, 1998 and Pitty, 2007, for details) now provides a consistent picture explaining the origin of the hyperalkaline waters (with *in situ* pH values of up to 12.9, the highest ever measured for natural waters), the persistence of some of the plumes and the sequence of alteration occurring (See Figure 2) when such leachates interact with various host rock types.

The Maqarin Natural Analogue Project was initiated in 1989 with Phase I, continuing with Phase II in 1991, Phase III in 1993 and Phase IV in 2001. 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 high temperature-low pressure pyrometamorphism of marls (*ie* clay biomicrites) and limestones, producing a mineral assemblage which belongs to the sanidinite and pyroxene hornfels facies (Milodowski et al., 1992). These natural cements are a reasonable analogy of the industrial OPC (Ordinary Portland Cement) which is likely to be used in waste isolation and repository construction (Milodowski et al., 1998a,b, 2007).

In Jordan as a whole, at least three different types of hyperalkaline groundwater alteration have been identified and they appear to represent, by analogy, three different stages in the theoretical evolution of a cementitious repository for the disposal of radioactive wastes. They are:

Stage 1) early, currently active, high pH Na/KOH leachates (Western Springs, Maqarin)

Stage 2) intermediate, currently active, lower pH $Ca(OH)_2$ buffered leachates (Eastern Springs, Maqarin)

Stage 3) late, currently inactive, near-neutral pH, silica-dominated leachates (Daba and Khushaym Matruk regions in central Jordan).

Whilst Phase I and Phase II were very much site-specific and process oriented (*eg* studies of the source term and its interaction with the host rock; testing the applicability of available thermodynamic data to hyperalkaline conditions; predicting the extent of hyperalkaline water/rock interaction using coupled models *etc*), Phase III provided a more regional perspective to the geological and hydrogeochemical evolution of the entire cementitious system. Phase IV went on to better define the local hydrogeology (and the impact of the cement leachates on it), examine the impact of the leachates on matrix diffusion in the host rock, study the microbiology of the Maqarin site in further detail, look at the behaviour of Re (as an analogue of Tc IV and VII) and examine clay alteration (as an analogue of the alteration of bentonite buffer in a cementitious repository) at the newly studied Khushaym Matruk site. Finally, comparison of the long-term alteration of the advective-flow dominated Maqarin site with the diffusive-flow dominated Khushaym Matruk site allows better prediction of the likely affects the hyperalkaline leachates will have on a wide range of repository host-rock types.

2. Site description

The Maqarin study area is located in the Yarmouk River valley at the Syrian-Jordanian border, 16 km north of the provincial town of Irbid, and the Khushaym Matruk site is in central Jordan, about 75 km south-southwest of Amman. A generalised stratigraphic column is presented in Figure 2 and of most interest is unit B-3, known locally as the Bituminous Marl Formation, and units B-4 and B-5, the

Chalky Limestone Formation. The natural cement is formed by the local combustion of the B-3 unit which is regionally an aquaclude. It appears that fractures or joints in the B-3 to -5 units (or, in some cases, karstic dissolution of the B-4 and -5 units) allow penetration of air or oxygenated groundwater into the kerogen-rich (up to 15 wt%; Milodowski et al., 1998a,b) B-3 unit. Spontaneous combustion is thought to occur when the abundant pyrite (up to 1-2 wt%; Milodowski et al., 1992) in the B-3 unit oxidises exothermically, so igniting the kerogen (see also discussion in Linklater, 1998).

Generally, the natural cement is found as localised 'pods' in the B-3 unit, but it can be found occasionally in the B-4 unit. Interaction of 'normal' (i.e. pH 7-8) groundwaters with the natural cements produces the hyperalkaline groundwaters (which are directly analogous to leachates from cementitious repositories) and these go on to interact with the B-3 unit, forming the so-called hyperalkaline plume downstream of the cement body (cf. Figures 1 and 3). As shown in Figure 3, at the cement/host rock interface, the hyperalkaline leachates have not yet reacted with the host rock and so have a high pH and high concentrations of Na, K and Ca, reflecting the cement porewater chemistry. As the plume reacts with the host (aluminosilicate-bearing) rock, the pH falls, as do the Na, K and Ca concentrations in the groundwater, while the concentrations of Al and Si rise fractionally. Beyond the distal edge of the plume, in the, as yet, undisturbed host rock, the groundwater pH is near neutral, the Na, K and Ca concentrations are lower and the concentrations of both Al and Si are higher than in the plume waters. This pattern has consequences for the secondary mineralogy (Figure 3, bottom): 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 leachate has not yet reacted with the host rock and is equilibrated with the C-S-H phases which make up the cement. As the leachate moves downstream and interacts with the aluminosilicates in the host rock (and the host rock groundwater and porewater), the Al concentration increases, precipitating C-A-S-H phases. At the distal edge of the plume, the leachate has reacted with an even larger volume of host rock (and the host rock groundwater and porewater) and eventually precipitates zeolites as the Al concentration in the groundwater becomes high enough and the pH low enough. As these secondary phases have much larger volumes than the primary phases they replace, the matrix porosity and flow porosity slowly decrease until being effectively sealed.

3. Methodology

All analytical methods are described in detail in Alexander (1992), Linklater (1998), Smellie (1998) and Pitty (2007).

4. Results and analyses

All results are described in detail in Alexander (1992), Linklater (1998), Smellie (1998) and Pitty (2007).

5. Discussion and conclusions

It is all but impossible to cover all of the areas of interest touched upon over the 15 years of the Jordan Natural Analogue Study so, here, focus is placed on those results which are of direct relevance to a cementitious radioactive waste repository safety assessment. These are split into two groups, quantitative and qualitative.

5.1 Quantitative conclusions

The conceptual model for the evolution of a cementitious repository-derived hyperalkaline plume in a generic host rock (see Figure 3) is largely consistent with observations at the sites, although the diffusive system at Khushaym Matruk still requires further, detailed study (Pitty, 2007).

Hyperakaline pore fluid conditions generated by minerals directly analogous to those in modern industrial cements are long-lived (in excess of tens of thousands of years) under the Maqarin advective flow conditions (Milodowski et al., 1998a,b).

The effects of the site hydrology (and tectonic/erosional processes) upon fracture sealing needs to be considered on a repository site-specific basis and fully integrated with the results of *in situ* experiments such as the HPF project when they become fully available (cf. Mäder et al., 2004). Only then can an estimate be made of the long-term impact of the hyperalkaline plume on radionuclide retardation in the geosphere.

Reactions between hyperalkaline waters and the host rock mostly have positive reaction volumes and thus open porosity (fractures or porous media) will be sealed by the precipitation of secondary phases.

Interaction between hyperalkaline waters and the host rock occur extensively and (small aperture) fracture sealing occurs within short timescales (years to hundreds of years). Further work is required at Khushaym Matruk to establish timescales of sealing under diffusive conditions (Pitty, 2007).

The altered rock matrix appears to be accessible to diffusion of aqueous species to a depth of several centimetres, but further study (e.g. on existing core material from Maqarin and in the laboratory with core infiltration experiments) is required to produce data of use to SA (cf. Pitty, 2007).

Sequences of minerals predicted by coupled (geochemical and transport) codes are very close to those observed in the hyperalkaline alteration zones at Maqarin, even if the specific phases cannot be represented due to a paucity of relevant thermodynamic and kinetic data (cf. Soler et al., 2004).

Thermodynamic databases of elements of interest to radioactive waste disposal provide conservative (*ie* solubilities are overestimated) estimates of solubility, despite the fact that the representation of the solubility controlling solid phases is too simplistic (Linklater et al., 1996).

The amounts of colloidal material generated at the cement zone/host rock interface appears to be low, although any future analogue and laboratory work would benefit from a common approach to minimise method-inherent differences, so allowing better comparison of data (Alexander and Möri, 2003).

Microbes are present in the hyperalkaline groundwaters, although their precise activity is currently difficult to define (Pedersen et al., 2004).

5.2 Qualitative conclusions

The natural cement at Maqarin and Khushaym Matruk may be considered a good analogy to an industrial cement and the leaching behaviour of both cement types is very similar (Pitty, 2007).

All fractures examined within the plume at Maqarin (other than those currently water conducting) are sealed (Pitty op. cit.). However, as the apertures of the fractures examined to date are generally small (mm to cm), it is currently possible to state only that thin fractures in a repository host will be probably self-healing.

As a consequence of the fast rate of interaction between hyperalkaline waters and the wallrocks, it seems likely that radionuclides released from a cementitious repository will migrate through rock that has already been altered by the high-pH plume (although it must be emphasised that the radionuclide release scenarios for most repositories are still somewhat unclear here). This alteration affects both the geochemical (mineralogy) as well as the physical (porosity, connectivity) properties of the rocks.

Once a fracture is sealed, no further alteration can take place unless new pore-space is created by fracture reactivation. In this case, the fracture may then ”see” a pulse of hyperalkaline leachate with a composition no longer in equilibrium with the existing fracture infill (*ie* secondary minerals) and this will initiate further interaction with both the host rock and the fracture infill (Milodowski et al., 1998a,b), possibly releasing any radionuclides associated with the original secondary mineralogy. The numerous phases of fracture precipitation (and dissolution) identified at Maqarin bear witness to recurrent events of alteration/precipitation, sealing and reactivation as does the range of ages so far reported for infill mineralogy.

In a highly porous rock (or flow system), it is possible that reaction will not rapidly seal the flow porosity. In this case, the distal part of the plume may be over-run by the middle part which may, in turn, be over-run by the proximal part of the plume (see Figure 3). Partial to complete replacement of previous secondary phases is to be expected, with the potential implications this has for radionuclide retardation. Such flow systems are probably of little relevance to deep repository host rocks.

Where very wide fractures are present, the same processes described immediately above may also occur and this could be of more significance to a repository (Pitty, 2007).

Due to the high permeability in this surficial environment, the length of the hyperalkaline plumes downstream of the cement zones appear to be on the order of hundreds of metres. In the lower advection rate systems of relevance to deep repository host rocks, plume lengths will probably be much smaller.

Re, studied as an analogue of Tc, is leached from the natural cement and, in some cases, is re-deposited in secondary fracture filling minerals (especially calcite and gypsum), possibly in the Re-VII form (Trotignon et al., 2006).

I retardation in the altered host rock is currently under investigation and preliminary results suggest an enrichment in the host rock (T.Ishidera, *pers comm*, 2007). These data need to be integrated with the information on matrix diffusion in the altered host rock before a detailed assessment of I retardation can be made.

In those parts of the flow system which may be defined as 'open' (in the geochemical sense), or groundwater dominated, C-S-H phases are seen to dominate the secondary mineral assemblage whereas 'closed', or rock dominated, parts are zeolite dominated. By comparison with Maqarin and Khushaym Matruk, deep repository host rocks with low groundwater fluxes might be expected to be zeolite dominated.

Cement carbonation studies: this could effectively protect a cementitious repository from significant groundwater leaching and can be clearly seen in certain areas of the Maqarin site but has not, to date, been studied in detail

Clay alteration by the hyperalkaline leachates has been observed at Khushaym Matruk and would appear to show a decrease in expandibility of mixed layer illite-smectite following interaction with the leachates. However, the number of samples analysed to date is small so care must be taken with the extrapolation of these results to SA.

Despite major differences between the rock types at the Eastern and Western Springs sites at Maqarin and between Maqarin and Khushaym Matruk, the mineralogical composition of the secondary minerals at all sites is very similar, implying that similar reactions could be expected to occur at a repository host rock, *ie* the mineralogical information from Jordan appears to be directly transferable to repository conditions.

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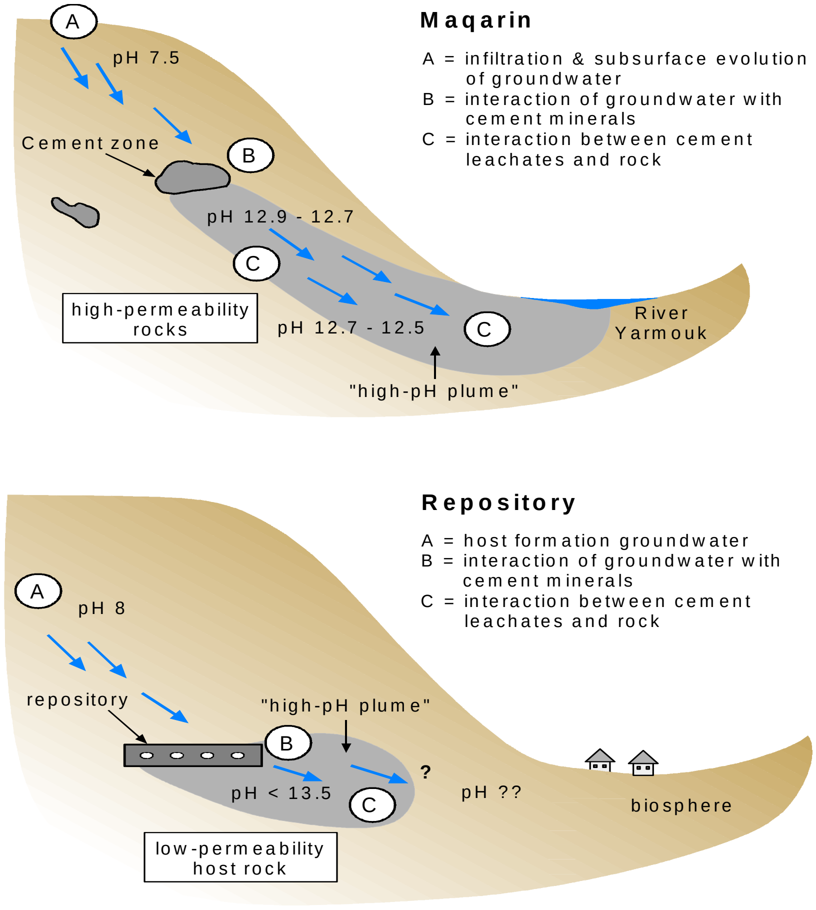

Figure 1: The basis of the analogy (from Alexander et al., 1998)

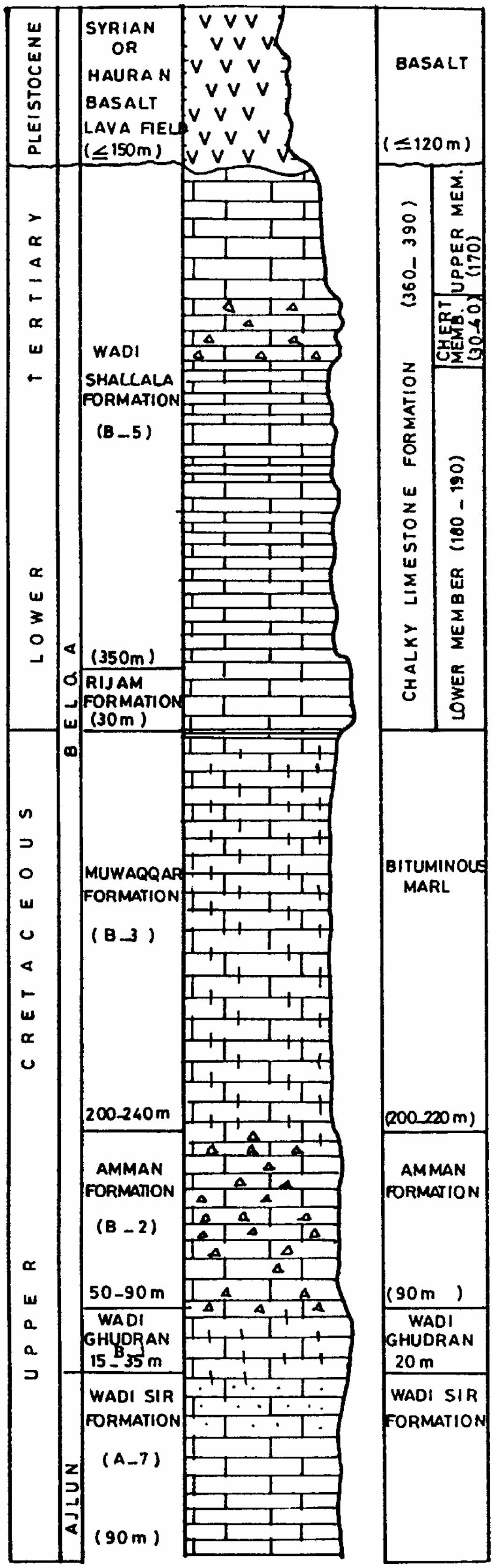

Figure 2: Regional lithostratigraphic correlation chart (from Khoury et al., 1998)

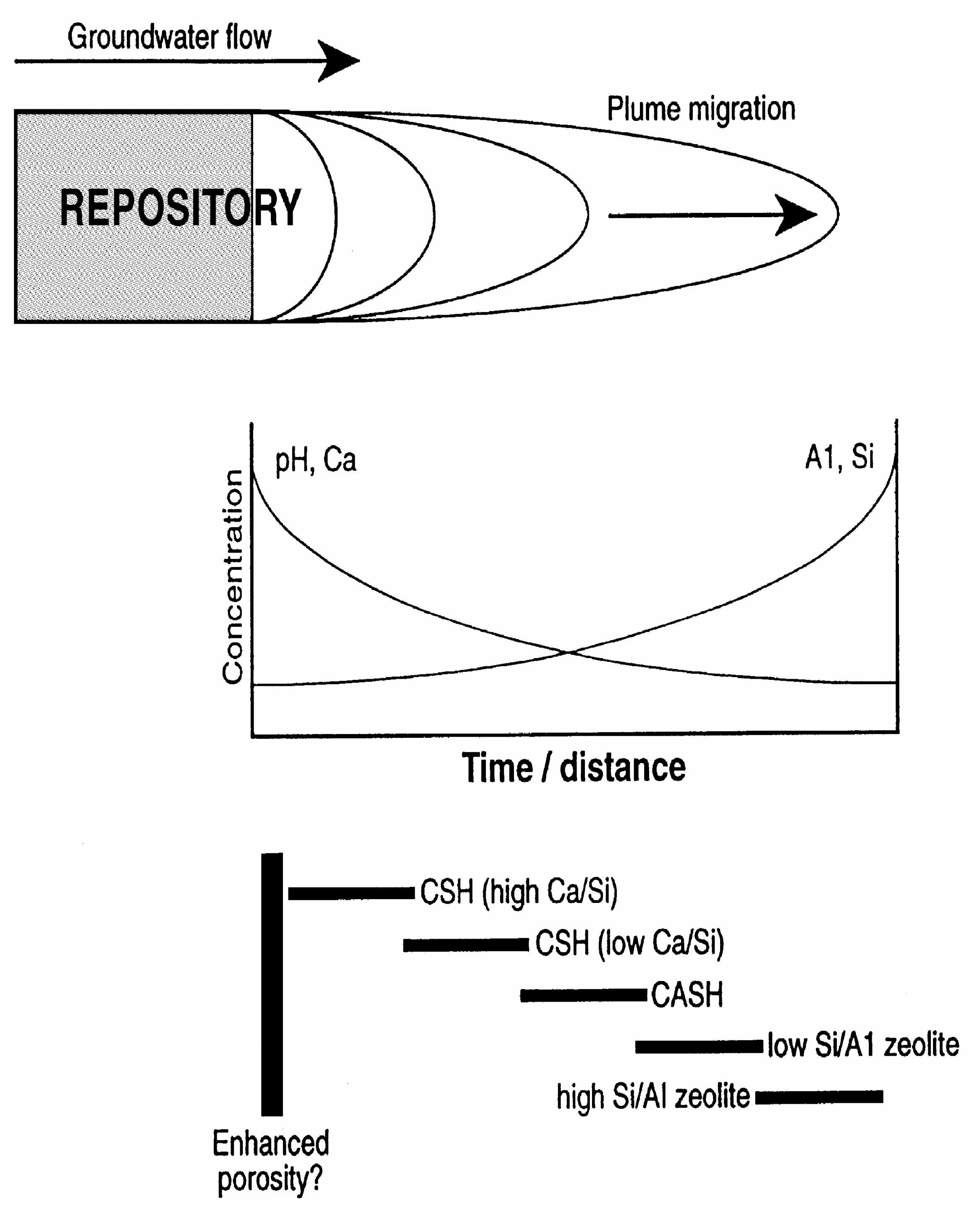

Figure 3: Conceptual model of the hyperalkaline plume evolution (from Smellie, 1998). As the hyperalkaline leachates leave the cement (top) and enter the host rock, the groundwater pH (middle) increases to around 13.3 (initially) and Ca levels climb dramatically. As the leachates interact with the host rock, pH and Ca levels drop as CSH and CASH secondary phases form in the host rock and Al and Si levels increase (middle) as aluminosilicate minerals in the host rock dissolve. This gradual buffering

action of the host rock means that the secondary phases which precipitate in the host rock vary with distance away from the cement source (bottom).