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# A natural cement analogue study to understand the long-term behaviour of cements in nuclear waste repositories: Maqarin (Jordan)

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## ABSTRACT

The geological storage of nuclear waste includes multibarrier engineered systems where a large amount of cement-based material is used. Predicting the long term behaviour of cement is approached by reactive transport modelling, where some of the boundary conditions can be defined through studying natural cement analogues (e.g. at the Maqarin natural analogue site). At Maqarin, pyrometamorphism of clay biomicrites and siliceous chalks, caused by the in-situ combustion of organic matter, produced various clinker minerals. The interaction of infiltrating groundwater with these clinker phases resulted in a portlandite-buffered hyperalkaline leachate plume, which migrated into the adjacent biomicrite host rock, resulting in the precipitation of hydrated cement minerals.

In this study, rock samples with different degrees of interaction with the hyperalkaline plume were investigated by various methods (mostly SEM-EDS). The observations have identified a paragenetic sequence of hydrous cement minerals, and reveal how the fractures and porosity in the biomicrite have become sequentially filled. In the alkaline disturbed zone, C-A-S-H (an unstoichiometric gel of Ca, Al, Si and OH) is observed to fill the pores of the biomicrite wallrock, as a consequence of reaction with a high pH Ca-rich fluid circulating in fractures. Porosity profiles indicate that in some cases the pores of the rock adjacent to the fractures became tightly sealed, whereas in the veins some porosity is preserved. Later pulses of sulphate-rich groundwater precipitated ettringite and occasionally thaumasite in the veins, whereas downstream in the lower pH distal regions of the hyperalkaline plume, zeolite was precipitated.

Comparing our observations with the reactive transport modelling results reveals two major discrepancies: firstly, the models predict that ettringite is precipitated before C-A-S-H, whereas the C-A-S-H is observed as the earlier phase in Maqarin; and, secondly, the models predict that ettringite acts as the principal pore-filling phase in contrast to the C-A-S-H observed in the natural system. These discrepancies are related to the fact that our data were not available at the time the modelling studies were performed. However, all models succeeded in reproducing the porosity reduction observed at the fracture–rock interface in the natural analogue system.

## 1. Introduction

The accumulating nuclear waste from power plants, medical and research facilities must be stored safely for $10^5$–$10^6$ years until the radioactivity has decayed to a level below which any release of radionuclides to the environment no longer poses an unacceptable risk. In several concepts for nuclear waste storage, the galleries in which the waste containers are emplaced will be back-filled and sealed with cementitious mortars, as the highly alkaline cement pore waters are expected to limit the solubility and mobility of radionuclides, and they also provide favourable conditions for the

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long-term stability and inhibit corrosion of the steel waste containers (www.nagra.ch, 2013: Entsorgungsprogramm und Standortgebiete für geologische Tiefenlager). Therefore, there is a need to understand the interaction of a high pH pore water plume migrating from the cement into the host rock in order to assess its impact on porosity, permeability and groundwater flow, and consequently the radionuclide transport.

Long-term predictions for the interaction of a hyperalkaline plume in contact with the host rock in a nuclear waste repository are approached by reactive transport models. However, in order to have an accuracy control for such models, they should be compared with processes occurring in natural analogue systems such as the Maqarin cement analogue site, where the interaction between a host rock and a hyperalkaline plume occurred over >100,000 years (Linklater, 1998; Smellie, 1998; Pitty and Alexander, 2014). Thus studying natural analogue systems provides the potential to understand the processes which could occur along a fracture system in a nuclear waste repository and increase the confidence in the extrapolation of data to greater time and distance scales, as indicated by Savage (2011).

Within the framework of the Long-Term Cement Study (LCS) project, data from various reports that investigated the Maqarin cement analogue site (Jordan) were compiled in order to understand the geochemical long-term processes occurring in this natural cement analogue system (Jordan Natural Analogue Project Phase I to IV: Alexander, 1992; Linklater, 1998; Smellie, 1998; Pitty and Alexander, 2014). To extrapolate the long-term effects, various studies modelled the interaction of a hyperalkaline plume along a single fracture system similar to that at the Maqarin site, in order to predict which processes occur along a fracture (e.g. Steefel and Lichtner, 1998; Shao et al., 2013; Soler, 2016; Watson et al., 2016). Within the scope of this work, the existing database on Maqarin has been extended by studying additional mineral alteration samples from Adit A6. This tunnel was constructed for the Jordan–Syria unity dam project in 1979 (Alexander, 1992; Milodowski, 1994a, b, c, d, 1998, 2013; Linklater, 1998; Smellie, 1998) and is located about 60 m above the Yarmouk river and has been driven southward along N358° for 450 m horizontally into the hill side (for details see Steefel and Lichtner, 1998). The aim of this study was to develop a conceptual model of the processes that influenced the mineralogical and geochemical evolution along the fracture flow system in Adit A6 (i.e. the mineral precipitation sequence, interaction of the hyperalkaline plume with the host rock and its impact on porosity), and further to compare the observations from the natural samples with modelling results.

A summary of the site and the hydrology are provided by Steefel and Lichtner (1998). Here we would like to highlight the key points which are important for understanding the processes which occurred along the fracture systems in Adit A6. The stratigraphy of the site is described by Khoury et al. (1998) and a detailed description of these rocks is provided by Alexander (1992) and Milodowski et al. (1994a, b, 1998). The pyrometamorphic rocks that represent the cement analogue are located in the upper part of the Bituminous Marl Formation and the base of the Chalky Limestone Formation (Upper Cretaceous). The background host rocks are classified as bituminous clay-biomicrites (Folk, 1959; Pettijohn, 1975) with up to 20% organic matter (immature kerogen, Smellie, 1998). In-situ combustion of organic matter within the clay biomicrite resulted in thermal metamorphism (pyrometamorphism) which calcined the limestone and produced various minerals analogous to cement clinker phases (Alexander, 1992; Milodowski, 1994a; b, 2013). Infiltrating groundwater interacting with these "clinker" phases produced a portlandite-buffered hyperalkaline leachate plume that emanates from the "cement zone", and leads to the formation of hydrated cement phases such as ettringite ($Ca_6Al_2(SO_4)_3(OH_{12}\cdot 26(H_2O))$, thaumasite ($Ca_3Si(CO_3)$ $(SO_4)$ $(OH)_6\cdot 12(H_2O))$, tobermorite ($Ca_5Si_6O_{16}(OH)_2\cdot 2{-}8(H_2O))$, afwillite ($Ca_3(SiO_3OH)_2\cdot 2H_2O)$, jennite ($Ca_9H_2Si_6O_{18}(OH)_8\cdot 6H_2O$, and unstoichiometric calcium-aluminium-silicate-hydrates (C-A-S-H), and amorphous calcium-aluminium-silicate-hydrate (C-A-S-H) gels.

For details about the hydrogeological setting and water geochemistry of the Maqarin site within the context of the regional flow system of northern Jordan, see Waber et al. (1998). Two distinct hyperalkaline groundwater systems have been recognized at Maqarin, referred to as the Eastern Springs and the Western Springs, respectively. Adit A6 is located within the Eastern Springs area. Both systems are Ca-OH-dominated groundwaters. However, the Western Springs groundwater are more mineralized and contain a high concentration of Na and K in addition to a higher concentration of $Ca(OH)_2$, which results in a pH up to 13 in comparison to about 12.5 for the Eastern Springs area. The difference in composition of the groundwaters between the Eastern and Western springs can be explained by a difference in the extent and duration of water–rock interaction (Waber et al., 1998). The Eastern Springs groundwater is considered to be more evolved, as having more extensively leached away the more soluble and K-Na-rich metamorphic silicates that are the earliest minerals to hydrate and dissolve in the pyrometamorphic rocks (Milodowski et al., 2013). This has resulted in the Eastern Springs now having a lower pH. Therefore, the question arises whether the Western Springs represent an analogue of the "early" hyperalkaline cement pore fluid with NaOH-KOH-$Ca(OH)_2$-dominated leachate of pH up to 13 that is still in the process of leaching the very soluble K-Na-rich phases, whereas the Eastern Springs (exemplified by the groundwater discharging into Adit A6) correspond to a more evolved "later" $Ca(OH)_2$-buffered cement pore fluid with low NaOH and KOH, and a pH around 12.5 (Smellie et al., 2013). Based on stable isotope and $^{14}C$ analyses, it is assumed that temperatures were near ambient at the time when hydration, recarbonation and sulphatisation occurred (Clark et al., 1993).

Average saturation indices for the high pH groundwater for the Western Springs area, which corresponds to the early water chemistry of the hydration of the natural clinker in Adit A6, suggest that the early Maqarin groundwater is strongly undersaturated with silicon, and will consequently tend to dissolve silicate and aluminosilicate phases (Waber et al., 1998). Furthermore, the undersaturation of $CO_2$ with the atmosphere explains the abundant tufa precipitates on the fracture walls in Adit A6 and at spring discharge points. With regard to this $CO_2$ undersaturation, carbonation could be an issue for the preservation of the hydrated cement phases. The principal seepages of hyperalkaline groundwater into the Adit A6 occur in a wide, highly brecciated fracture zone in the pyrometamorphic rocks that is intersected by the tunnel between 110 and 305 m from the entrance (Fig. 1S, Supporting Material). The abundant fractures between 110 and 140 m, which are now largely sealed by secondary calcite, C-A-S-H, ettringite and thaumasite, indicate that the extent of hyperalkaline groundwater flow in these fractures was originally much wider (Milodowski et al., 1994b). Further towards the back of the tunnel (318–370 m) there are several small fracture-controlled groundwater inflows. All major groundwater inflow zones in Adit A6 are fracture-controlled and occur within the highly brecciated, high-temperature pyrometamorphic zones intersected by the tunnel (Milodowski et al., 1994b, 2013). At around 110 m, the bituminous clay biomicrites appear to be very extensively altered and very friable. In this region, the clay biomicrite is cut by abundant, closely-spaced, fine anastomosing networks of white veinlets containing cross-fibrous to fine-powdery ettringite–thaumasite, and occasionally veins of grey white calcite (Milodowski et al.,