Evolution of reaction and alteration of mudstone with cement leachate: Flow experiments and reactive-transport modelling

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The construction of a repository for geological disposal of radioactive waste will include the use of cement-based materials. Following closure, groundwater will saturate the repository and the use of cement will result in the development of a highly alkaline porewater, pH >12.5 in the case of Ordinary Portland cement (OPC). The fluid will migrate into and react with the host rock. The chemistry of the migrating fluid will evolve over time, initially being high in Na and K, evolving to a Ca rich fluid and finally returning to the groundwater composition. This evolving fluid chemistry will affect the long-term performance of the repository altering the physical and chemical properties, including radionuclide behaviour. Understanding these changes forms the basis for modelling the long-term evolution of the repository. This study focused on the alteration due to OPC-type leachates on mudstone from the Horonobe URL, Hokkaido, Japan.

It was anticipated that the mudstone would react with the high pH fluids and that silicate minerals present would provide buffering together with the formation of secondary mineral phases which would evolve with time; this study was aimed at determining the specific nature and extent of these reactions. The flow experiments described here reacted in succession, fluids representing a 'young' OPC leachate, with high pH and high levels of Na and K. This was followed by an 'evolved' leachate (portlandite saturated) and finally Horonobe ground water (HGW). In addition, the experimental data were used as test cases for reactive transport geochemical modelling, to both assess and validate the predictive capability of the model.

The experiments were conducted using a small flow cell constructed from acrylic plastic, 10 mm long and 20 mm in diameter. The experiments used a dry density of 1 g/cm^3, with a typical volumetric flow rate ≈ 0.5 ml per hour. The evolution of the fluid chemistry was tracked by chemical analysis and mineralogy by characterisation of the reacted solids. A combination of PHREEQC and the 1-D reactive transport 'CABARET' geochemical codes were used to simulate the experiments.

Initially with the 'young' fluid, there was a reduction in [Na] and [K] due to ion exchange reactions with the clay mineral in the mudstone but these quickly returned to close to the initial concentrations. Si levels increased whilst Ca decreased. With the change to the 'evolved' leachate, [Ca] increased but remained below that of the 'evolved' fluid. Both [Na] and [K] decreased as did [Si]. The pH with both OPC leachates showed only a small decrease (≈ 0.2) from the initial values. With the change to the HGW, the pH returned to close to that of the HGW, as did both Na and K. Ca levels remained slightly lower than the HGW but Si levels increased.

The changes in Ca and Si with the OPC leachates were due to the formation of secondary C-S-H phases. This was confirmed by the mineralogical analysis, examination of the saturation indices (SI) for the reacted fluids and the output of the reactive transport modelling This showed continued dissolution of the primary minerals in the clay together with the saturation and hence precipitation of a variety of C-S-H phases. With the HGW, the secondary C-S-H phases re-dissolved releasing Si into solution and Ca levels were

controlled by the formation of calcite by reaction with bicarbonate in the HGW.

In summary, the reaction of the mudstone with the successive OPC leachates demonstrated its chemical buffering capacity, leading to a reduction in pH, the dissolution of primary minerals with Ca and Si concentrations being controlled by C-S-H phase precipitation. However, when the fluid returns to the natural background groundwater composition the C-S-H phases re-dissolve, which would potentially release any sorbed radionuclides. The experimental data has been used to help validate a 1-D reactive transport geochemical model generating increased confidence in its predictive capabilities.

Keywords: Radioactive waste, Mudstone, Geochemistry, Modelling, Flow experiments