

Scawt Hill (Northern Ireland)

Description: Tertiary alkaline olivine dolerite volcanic plugs penetrated the Upper Cretaceous Chalk (Ulster White Limestone Formation) at Scawt Hill, near Larne, and at the Carneal Plug, near Carrickfergus, County Antrim, Northern Ireland. High-temperature (~1100°C), low-pressure (<700 m cover) metamorphism of the limestone and included flint nodules resulted in the formation of a complex assemblage of calcsilicate mineral phases including larnite. Subsequently, reactions under falling temperatures and in the presence of groundwater resulted in retrograde metamorphism and hydration of some of the high temperature calcsilicate phases to form a number of calcium-silicate-hydrate (CSH) gels.

These processes of high temperature heating of limestone plus silicates to form larnite and other calcsilicates followed by hydration to form CSH phases occur in the formation and hydration of Ordinary Portland Cement (OPC) and other cementitious materials. Thus the Scawt Hill is a natural analogue of cement phases, in particular CSH gels, and provides the opportunity to study the longevity of CSH phases and their reaction processes.

The intrusion event has been dated at 58 Ma (Sabine et al., 1982). Dating the hydration event is more complex. Two phases of carbonate formation were recognised by Milodowski et al. (1989). The earliest phase of carbonate formation appeared to be texturally contemporaneous with the CSH gel formation. A study of the stable C and O isotopes of these early carbonate phases showed them to be comparable with the carbonates formed during metamorphism. In contrast, a later Fe-stained calcite event showed a more meteoric stable isotope signature and is believed to have formed at shallower depths and much later when the CSH phases were in contact with meteoritic waters. This evidence was interpreted by Milodowski et al. (1989) to infer an age for the formation of the CSH phases as shortly after intrusion (i.e. close to 58 Ma).

Secondary carbonates (calcite and scawtite) associated with the larnite hydration are very limited in distribution. They occur only as fracture infills in the calcsilicate nodules and around the margins of the nodules. This is interpreted by Milodowski et al. (1989) as due to the rapid reaction of exposed CSH phases with CO₂ and (HCO₃)⁻ in groundwater. The calcite appears to armour the CSH phases.

Relevance: Some repository concepts for LLW or ILW incorporate large volumes of cementitious materials either to provide individually or in combination i) structural integrity; ii) buffer material in waste packages; or iii) large-volume backfill around the containers. Furthermore, in some concepts the high-pH leachate from cementitious materials is considered beneficial in acting as a 'chemical barrier' to limit solubility of some radionuclides. In the short term, high-pH buffering is provided by the leaching of NaOH and KOH from the cement followed by the leaching of Ca(OH)₂. In the longer term it is the leaching of CSH phases that provides the high-pH buffer. Evidence for the long-term stability of CSH phases is therefore important in this context.

The Scawt Hill analogue study helps to answer the question: How long would the CSH phases last in a repository?

Studies of Portland cement concrete in industrial analogue sites up to 100 years old in Sweden and the UK have demonstrated that CSH gels remain stable over this time-scale (Jull & Lees, 1990; Lagerblad, 1996). Archaeological cement analogues can be used to extend the time-scales considered to at least 2,000 years, but early cements were lime-based and did not always contain siliceous materials and hence CSH phases (Miller et al., 1994). The Romans did incorporate siliceous materials (pozzuolans) in some cements and CSH gels have been preserved in some but not all Roman cements of this type (Jull & Lees, 1990). CSH gels have also been preserved in the impure lime mortars used in the construction of Hadrian's Wall, built by the Romans around A.D.120 (Atkinson & Hearne, 1989).

Scawt Hill demonstrates that CSH gels are stable over geological time periods measured in tens of Ma. However, it also demonstrates that high-pH buffering capacity of CSH phases may be

reduced by the formation of carbonate armouring from reaction with CO₂ and (HCO₃)⁻ in incoming groundwaters or by reaction with CO₂ formed by degradation of organic wastes in the repository.

There have also been suggestions that carbonation of CSH gels may be a process capable of removing ¹⁴C substituted CO₂ generated from biodegradation of contaminated wastes. Again the formation of carbonate armouring may limit the volume of CSH available for reaction.

Position(s) in the matrix tables: The Scawt Hill analogue belongs to the Wasteform Cement-Physical Integrity box of the near-field matrix table. It could also belong to the Waste Package Concrete-Physical Integrity box and the Buffer/Backfill Concrete-Physical Integrity box in the same matrix table.

Limitations: The Scawt Hill analogue study did not date the CSH gels directly, but it appears reasonable to assume that they formed soon after the date of intrusion at 58 Ma. It is possible that the Scawt Hill site has never been buried very deeply (<700 m) and so the CSH phase longevity is only relevant to conditions where contact with low salinity groundwater is expected.

Quantitative information: CSH gels are capable of remaining stable for periods measured in tens of millions of years.

Uncertainties: As noted in the limitations entry above, the exact age of the CSH formation event is unknown. However, it is almost certain to be older than the time-scales considered relevant to repository performance assessments (>1 Ma).

Time-scale: The analogue is relevant to the archaeological (1000 – 10,000 years) and geological (Quaternary <2 Ma and >2Ma) time-scales.

PA/safety case applications: SKB's 1999 SFR PA for the SFR repository at Forsmark in Sweden, used the Scawt Hill analogue information to support the long-term durability of a concrete barrier system (IAEA, 1999).

Communication applications: None known.

References:

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Sabine PA, Beckinsale RD, Evans JD and Walsh JN. 1982. Geochemical and strontium-isotope studies of reactions between basic magma, Chalk, and flint, and the role of groundwater, in the Carneal Plug, Co. Antrim, Northern Ireland. Journal of Petrology, 23, 427-446.

Added value comments: This analogue has the potential to support arguments for the long term stability of CSH phases and the associated long-term buffer to high pH.

Potential follow-up work: None proposed.

Keywords: Scawt Hill, Carneal Plug, CSH, cement, durability

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