Alteration of nanocrystalline Calcium Silicate Hydrate (C-S-H) at pH 9.2 and room temperature

Nicolas C.M. Marty¹, Sylvain Grangeon¹, Fabienne Warmont² and Catherine Lerouge¹
1. BRGM, 45060 Orléans Cedex 2, France
2. CRMD, FRE 3520- CNRS – Université d’Orléans, 45071 Orléans Cedex 2, France

In the French design of deep underground radioactive waste disposal, cementitious materials will be used to build access structures, galleries, vaults and waste packages for Intermediate Level Long-lived Waste (ILLW). Part of these cementitious materials will be in physical contact with the Callovian-Oxfordian clay host rock formation (COx). The pH of the COx pore water is around 7 and its composition is very different from the cementitious pore water. Due to this chemical contrast, a chemical gradient will develop at the cement/clay interfaces and will induce mineralogical transformations.

Nanocrystalline calcium silicate hydrates (C-S-H) are the main constituents of concretes and are essential for cohesion of cement paste. It is therefore fundamentally important that we be able to reliably estimate C-S-H weathering/dissolution rates if we wish to estimate the durability of various cementitious materials. In order to mimic a clay/concrete interface, C-S-H alteration was studied with flow-through experiments at 25 °C and pH 9.2. Three materials with apparent Ca/Si ratios of 1.47, 1.38 and 0.86 were investigated. Physical (TGA/DTA), mineralogical (XRD) and chemical (EPMA, TEM/EDX) analyses were performed to characterize the reacting minerals. Initial stoichiometric Ca/Si ratios (C/S) were 1.22, 1.22 and 0.85, respectively. The excess of calcium is attributed mainly to the presence of CH intimately mixed in with C-S-H particles. Under our experimental conditions the stoichiometric C/S ratios decreased continuously with time. C-S-H compositions were monitored during flow-through experiments in order to know the mineral stoichiometry. The kinetics were found to be a function of the C/S. A decrease in layer-to-layer distance in the early stage of the alteration process is interpreted as interlayer Ca/Na exchange. A second dissolution step, marked by the stoichiometric release of calcium and silicate, certainly results from layer dissolution.