The crystal structure of Magnesium Silicate Hydrate (M-S-H) andits relation with talc-like clay mineral

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In the framework of a geological disposal of radioactive waste, cement-based materials will be highly used; the deep geological disposal facilitywill imply large amounts of concrete in the clayrock formation. In this context, low pH cementitious materials are considered, especiallyfor sealingrequirements, in order to minimize chemical interactions at the interfaces between cementitious materials and the clay surrounding rock formations and/or engineered clay materials. The target is to reach a concrete pore solutionpH more compatible with the clay materials or rock formation (pH ~7-7.5) for reducing the detrimental impact of the alkali plume from the cement-based materials. Recent studies[1–3] have proposed low-pH formulations based on ternary and quaternary mixes of Portland cement with supplementary cementitious materials (SCMs) such as blast furnace slag (BFS) andfly ash (FA).For these formulations, the pHis controlledby low C/S C-S-H.

However, if forOrdinary Portland Cement (OPC) concrete formulations, the hydration products are well characterized with suitable constrained kinetic/thermodynamic models[4] [4], , the mineralogical control of elements in solution have to be discussed for low pH formulations because of their higheraluminum and magnesium contents[5]. In particular, for the hydration of MgO, which is mainly introduced by the BFS, Zhang et al.[6]have mentioned the precipitation of brucite ($MgOH_2$) which reacted with the silica fume to produce a magnesium silicate hydrate (M-S-H). The calculated pH in equilibrium with this mineralogical assemblage is around 10.5 and satisfies the requirement of low pH condition.

The occurrence of M-S-H has been mentioned in many environments[6–9], and was described as low crystalline phases according to the low intensity and broad peaks signals. Despite this abundance of M-S-H evidences and characterizations, the structure of M-S-H is not well known. Some authors have explained the precipitation of such Mg-silicate hydrates according to Ca/Mg isomorphic substitution in the calcium silicate hydrates (C-S-H). The present study aims to determine this crystal structure and to define their nature (cement phase or phyllosilicate). Two low temperature synthesis of M-S-H have been made, with Mg/Si ratios of 0.6 and 1.2, close to the talc composition ($Mg_3Si_4O_{10}OH_2$) and consistent to the Ca/Si ratio of the C-S-H phases. Crystal chemistry of M-S-H was determined by combining TGA, electron probe micro-analysis (EPMA), TEM, NMR and powder X-ray diffraction. These experimental investigations of poorly crystalline Mg-silicates showed a 2:1 magnesium phyllosilicate-like structure with short range stacking order, identified as a talc-like structure. All the talc structure crystallographic evidences described in previous studies are in agreement with the characterization of the talc synthesis performed for short synthesis time[10]. In that case, the M-S-H particles display a low crystallinity and a small size. XRD patterns were successfully modelled according to the modelling approach developed by Plançon[12,13]and used by Grangeon et al[11], providing meaningful and accurate structural information, including structure defects, despite the weak modulation of the profiles. A full structure model is then proposed for M-S-H.

(1) García Calvo, J. L.; Alonso, M. C.; Hidalgo, A.; Fernández Luco, L.; Flor-Laguna, V. Development of Low-pH Cementitious Materials Based on CAC for HLW Repositories: Long-Term Hydration and Resistance against Groundwater Aggression. *Cem. Concr. Res.***2013**, *51*, 67–77.

(2) García Calvo, J. L.; Hidalgo, A.; Alonso, C.; Fernández Luco, L. Development of Low-pH Cementitious Materials for HLRW Repositories. *Cem. Concr. Res.***2010**, *40*, 1290–1297.

(3) Cau Dit Coumes, C.; Courtois, S.; Nectoux, D.; Leclercq, S.; Bourbon, X. Formulating a Low-Alkalinity, High-Resistance and Low-Heat Concrete for Radioactive Waste Repositories. *Cem. Concr. Res.***2006**, *36*, 2152–2163.

(4) Matschei, T.; Damidot, D.; Marchand, J.; Lothenbach, B. Thermodynamic Modelling: State of Knowledge and Challenges. *Adv. Cem. Res.***2010**, *22*, 211–223.

(5) Lothenbach, B.; Le Saout, G.; Ben Haha, M.; Figi, R.; Wieland, E. Hydration of a Low-Alkali CEM III/B–SiO2 Cement (LAC). *Cem. Concr. Res.***2012**, *42*, 410–423.

(6) Zhang, T.; Cheeseman, C. R.; Vandeperre, L. J. Development of Low pH Cement Systems Forming Magnesium Silicate Hydrate (M-S-H). *Cem. Concr. Res.***2011**, *41*, 439–442.

(7) Ono, H.; Wada, S. I. Properties of Layer Silicates Formed from MgO-SiO2-H2O Mixtures at 25 Degree C. *J. Fac. Agric. Kyushu Univ.***2007**, *52*, 159–162.

(8) Dumas, A.; Martin, F.; Le Roux, C.; Micoud, P.; Petit, S.; Ferrage, E.; Brendlé, J.; Grauby, O.; Greenhill-Hooper, M. Phyllosilicates Synthesis: A Way of Accessing Edges Contributions in NMR and FTIR Spectroscopies. Example of Synthetic Talc. *Phys. Chem. Miner.***2013**, *40*, 361–373.

(9) Brew, D. R. M.; Glasser, F. P. Synthesis and Characterisation of Magnesium Silicate Hydrate Gels. *Cem. Concr. Res.***2005**, *35*, 85–98.

(10) Dumas, A.; Martin, F.; Ferrage, E.; Micoud, P.; Le Roux, C.; Petit, S. Synthetic Talc Advances: Coming Closer to Nature, Added Value, and Industrial Requirements. *Appl. Clay Sci.***2013**, *85*, 8–18.

(11) Grangeon, S.; Claret, F.; Lerouge, C.; Warmont, F.; Sato, T.; Anraku, S.; Numako, C.; Linard, Y.; Lanson, B. On the Nature of Structural Disorder in Calcium Silicate Hydrates with a Calcium/silicon Ratio Similar to Tobermorite. *Cem. Concr. Res.***2013**, *52*, 31–37.

(12) Plançon, A. Diffraction by Layer Structures Containing Different Kinds of Layers and Stacking Faults. *J. Appl. Crystallogr.***1981**, *14*, 300–304.

(13) Plancon, A. New Modeling of X-Ray Diffraction by Disordered Lamellar Structures, such as Phyllosilicates. *Am. Mineral.***2002**, *87*, 1672–1677.

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