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Structural characterization of C–S–H and C–A–S–H samples—Part I: Long-range order investigated by Rietveld analyses

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ABSTRACT

Rietveld analyses on samples belonging to C–S–H and C–A–S–H series ($0.8 \leq C/S \leq 1.7$) were realized on X-ray powder patterns. The tobermorite M model was successfully used to refine all the powder patterns from C–S–H samples whatever the C/S value. This gives clear indication on the steady change in a unique structural description, corresponding to a 'tobermorite M defect' model, when passing from C–S–H(I) ($C/S < 1.0$) to C–S–H(II) type ($C/S > 1.0$). The possibility for both C–S–H types (from polymerized silicate chains to isolated silicate dimers) to accommodate the same structural model is explained by the continuous evolution of the occupancies of the cationic sites: the interlayer Ca atoms, the Si atoms from paired and bridging silicates. Accurate refinements of the structural and microstructural parameters evidenced the well crystallized feature of C–S–H phase combined with a small coherent domain size. Insertion of Al atoms in the C–S–H structure (C–A–S–H phase) involves a clear disruption into the layered atomic framework. The large increase of layer spacing observed when incorporating aluminum into C–S–H indicates that Al atoms should be located in the interlayer region of the structure in new crystallographic sites. Aluminum atoms are not substituted silicon crystallographic sites or interlayer calcium crystallographic sites.

1. Introduction

Calcium Silicate Hydrate (C–S–H) is known to be the primary binding phase in Portland cement. Since late 19th century, the first studies were devoted to understand the setting and hardening of hydrated Portland cement [1–3]. C–S–H has been quickly identified as the principal binding phase. Its chemical composition has been subject to numerous studies [4–7]. However, difficulties to characterize the calcium silicate phase arose mainly from its poorly crystalline feature. Nevertheless two C–S–H types have been identified, respectively, named C–S–H(I) and C–S–H(II), according to their Ca/Si ratio [8], respectively, low (below 1.0) and high (above 1.0). According to Taylor C–S–H(I) and C–S–H(II) derive, respectively, from a tobermorite model and the jennite model [8,9]. More recently, Nonat proposed a different nomenclature based on solution equilibrium data with the existence of three different phases: α-C–S–H ($0.66 < Ca/Si < 1.0$), β-C–S–H ($1.0 < Ca/Si < 1.5$) and γ-C–S–H ($1.5 < Ca/Si < 2.0$) [10]. In 2008, Richardson has written a comprehensive review on the different structural models proposed by number of authors the last fifty-year [11]. C–S–H phase has a layered structure and a fibrous microstructure. X-ray powder patterns of C–S–H show similarities to tobermorite, a rare crystalline calcium silicate hydrate mineral which has the approximate chemical composition $Ca_4(Si_6O_{18}H_2) \cdot Ca \cdot 4H_2O$ (i.e. a Ca/Si ratio of 0.83) first described in 1956 [12]. The tobermorite structure contains layers of sevenfold coordinated (monocapped trigonal prisms) Ca^{2+} ions (labeled Ca_L in the text) linked on both sides to linear silicate chains of the 'dreierkette' form in such a way as to repeat a kinked pattern after every three tetrahedra (see Fig. 1). Two of the three tetrahedra, named paired tetrahedra (usually labeled Si_P), are linked together and share O–O edges with the central Ca–O part of the layer. The third tetrahedron, named bridging tetrahedron (usually labeled Si_B), shares an oxygen atom at the pyramidal apex of a Ca polyhedron and connects the dimers of paired tetrahedra. Additional calcium atoms (labeled Ca_I in the text) are inserted in the interlayer region of the structure. The Ca/Si ratio can increase by removing some bridging tetrahedra (decrease of the Si content) with the concomitant replacement by interlayer Ca atoms (increase of Ca content) [13]. Several structural types have been solved for crystalline tobermorite. By considering the interlayer distance,

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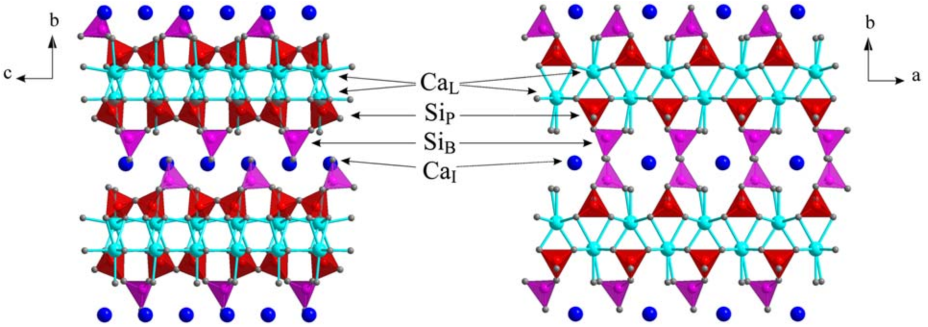

Fig. 1. Two projections (right: along the $\vec{a}$ axis; left: along the $\vec{c}$ axis) of the tobermorite M structural model given by Hamid [17]; using the conventional $\vec{b}$ unique monoclinic axis. Label Ca_L refers to layer calcium sites (i.e. the Ca1, Ca2, Ca3 and Ca4 crystallographic sites, seven coordinated light blue spheres), Ca_I refers to interlayer calcium sites (i.e. the Ca5 and Ca6 crystallographic sites, blue spheres), Si_P refers to the paired silicon tetrahedra (i.e. the Si1, Si2, Si4 and Si6 crystallographic sites, red tetrahedra) and Si_B refers to the bridging silicon tetrahedra (i.e. the Si3 and Si5 crystallographic sites, pink tetrahedra). (For interpretation of the references to the color in this figure legend, the reader is referred to the web version of this article).

Table 1
Starting material amounts and calculated compositions of the synthesized phases.

	Nominal composition: Ca/Si ratio					
	0.8	1.0	1.1	1.3	1.5	1.7
C–S–H						
CaO (mmol)	41.25	45.71	47.86	51.96	55.18	58.03
SiO_2 (mmol)	49.83	45.67	43.66	39.83	36.83	34.17
Solution (mL)	265.14	265.19	265.04	265.10	265.25	265.02
Experimental Ca/Si ratio[a]	0.82	0.98	1.08	1.24	1.40	1.59
Water amount[b] (%)	14.6	20.5	19.8	19.3	21.7	20.8
Composition[c]	$C_{0.8}SH_{1.0}$	$C_{1.0}SH_{1.7}$	$C_{1.1}SH_{1.7}$	$C_{1.2}SH_{1.7}$	$C_{1.4}SH_{2.1}$	$C_{1.4}SH_{1.9}$
C–A–S–H						
CaO (mmol)	16.95	21.19	23.30	27.54	31.78	36.01
SiO_2 (mmol)	21.17	21.17	21.17	21.17	21.17	21.17
Al_2O_3 (mmol)	1.06	1.06	1.06	1.06	1.06	1.06
Solution (mL)	500	500	500	500	500	500
Experimental Ca/(Si+Al) ratio[a]	0.71	0.82	0.92	1.04	1.17	1.24
Experimental Al/Si ratio[a]	0.10	0.10	0.10	0.10	0.10	0.10
Experimental Ca/Si ratio[a]	0.78	0.90	1.01	1.14	1.29	1.36
Water amount[b] (%)	22.6	20.2	20.5	19.4	19.6	19.7
Composition[c]	$C_{0.7}A_{0.05}S_{0.9}H_{1.6}$	$C_{0.8}A_{0.05}S_{0.9}H_{1.5}$	$C_{0.9}A_{0.05}S_{0.9}H_{1.6}$	$C_{1.0}A_{0.05}S_{0.9}H_{1.5}$	$C_{1.2}A_{0.05}S_{0.9}H_{1.7}$	$C_{1.2}A_{0.05}S_{0.9}H_{1.6}$

C_3A saturated solution with $[Ca]=5.24\,mmol\,L^{-1}$ and $[Al]=4.24\,mmol\,L^{-1}$.

[a] Verified indirectly by chemical analysis of the solutions.

[b] Total weight loss determined by TGA analyses between room temperature and 1100 °C.

[c] Composition of the C–S–H (C–A–S–H) phases; taken into account the experimental Ca/Si ratio (Ca/(Si+Al) ratio) and the thermal contribution of the secondary $Ca(OH)_2$ (C–S–H_1.5 and C–S–H_1.7 samples) and $C_4A\overline{C}H_{11}$ (C–A–S–H_1.7 sample) phases.

three main tobermorite families are distinguished: the tobermorite 14, 11 and 9 Å. The two tobermorite 14 and 11 Å families are compatible with the interlayer distance observed in C–S–H formed in hardened Portland cement [14]. Amongst these two families, nine different structural types were described: tobermorite 14 Å [15], tobermorite 11 Å Mdo1 [16], tobermorite 11 Å Mdo2 [16], tobermorite O [17], tobermorite M [17] and four clinotobermorite types [18–20]. Due to the poorly resolved X-rays powder patterns of C–S–H in hardening cement pastes, its characterization has been mainly and largely realized by ^{29}Si NMR spectroscopy during the last twenty years [21–26]. Most studies agree that, upon composition change, a continuous structural evolution occurs between the two previously described C–S–H(I) and C–S–H(II) types. This paper presents a comprehensive Rietveld analysis realized from Laboratory X-rays powder diffraction patterns to investigate the structural features of C–S–H and C–A–S–H samples with a Ca/Si, or Ca/(Si+Al), ratio ranging from 0.8 to 1.7. The results support the tobermorite M-like structure. The apparent lack of long-range order in C–S–H is attributed to the nanometric size of the coherent domains rather than to a poorly ordered or quite amorphous compound. However, the insertion of aluminum into C–S–H to form C–A–S–H leads to the formation of a poorly crystallized material coming from a highly disorganized stacking sequence.

2. Experimental

2.1. *C–S–H and C–A–S–H syntheses*

C–S–H_*n* samples with n, the nominal Ca/Si atomic ratio,=0.8, 1.0, 1.1, 1.3, 1.5 and 1.7 were synthesized from silica (Degussa, Aerosil 380) and calcium oxide (Aldrich, 99.9% pure) freshly decarbonated 3 h at 900 °C. Demineralized and decarbonated water added to reach a water/solid ratio of 50.

C–A–S–H_n samples with a nominal Al/Si atomic ratio of 0.1 and a nominal Ca/Si atomic ratio *n*=0.8, 1.0, 1.1, 1.3, 1.5 and 1.7 were synthesized from silica (Degussa, Aerosil 380) and calcium oxide (Aldrich, 99.9% pure) freshly decarbonated for 3 h at 900 °C