CRYSTAL STRUCTURE OF A METASTABLE PHASE OF CEMENT CLINKER, Ca-CHLORORTHOSILICATE Ca$_{3}$[SiO$_{4}$]Cl$_{2}$

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Abstract

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CRYSTAL STRUCTURE OF A METASTABLE PHASE OF CEMENT CLINKER, Ca-CHLORORTHOSILICATE $Ca_3[SiO_4]Cl_2$

The use of $CaCl_2$ as an additive to cement clinker (for the purpose of regulating the hardening process of concrete) often causes corrosion of the reinforcement with subsequent destruction of concrete products. The viewpoint is sufficiently well founded that, upon interaction of calcium silicates with $CaCl_2$ (or HCl) in Portland-cement clinker, metastable Ca-chlorsilicates are formed, which decompose upon hydration. The active Cl (or HCl) that is released becomes a destructive agent, and interest in the structure of these unstable compounds is natural, in particular in the synthesized* Ca-chlorsilicate
$Ca_2SO_4 \cdot CaCl_2 = Ca_3[SiO_4]Cl_2$.

Table 1

Coordinates of the basis atoms of $Ca_3[SiO_4]Cl_2$

Atoms	x	y	z	Atoms	x	y	z
Ca	0.1955	0.7428	0.0453	Si	0.1209	0.2493	0.0306
Ca	0.0789	0.4565	0.2715	O_1	0.235	0.416	0.109
Ca	0.4286	0.2230	0.1118	O_2	0.022	0.069	0.003
Cl_1	0.5078	0.7899	0.1240	O_3	0.017	0.199	0.121
Cl_2	0.2833	0.8233	0.3174	O_4	0.017	0.189	0.393

Single crystals of $Ca_3[SiO_4]Cl_2$ were rapidly destroyed under the action of x-rays and upon hydration, and in order to preserve them the samples were coated with a protective lacquer film. Nevertheless, to obtain initial information on the cell and a three-dimensional set of experimental intensities, it was necessary to use several samples. The monoclinic cell with parameters $a = 9.79$, $b = 6.76$, $c = 10.96$ Å, $\beta = 105°24'$ contains $Z = 4$ units of $Ca_3[SiO_4]Cl_2$. The Fedorov group is $C_{2h}^5 = P\frac{2_1}{c}$.

The three-dimensional Patterson function $P(uvw)$ was constructed from ~ 1400 nonzero reflections $h0l - h5l$, $0kl - 1kl$ (MoKα radiation, $\max \sin\theta/\lambda = 0.95$

Figure 1

Figure 1: Figure 1

$Å^{-1}$; intensities were estimated on the $\sqrt[4]{2}$ blackening scale). Absorption was not taken into account because of the isometry of the samples.

The large number of overlaps and the concentration of peaks in two planes at $v = 0$ and $v = 1/2$ (which appears to be a consequence of a more regular arrangement of the "average" Ca, Si, Cl atoms) did not permit analysis of the Patterson function by ([1]). The basic system was selected from the vector set by the method of multiple peaks. Of the 6 atoms of the basic system (3Ca, 2Cl, Si), 5 were selected directly with a discrepancy coefficient at the first stage equal to 0.53. These 5 atoms (on the assumption of identical scattering power for all average atoms) were the starting ones for construction of the first synthesis of the electron density $\rho(xyz)$. Refinement of the coordinates of the initial five reduced R to 0.40, addition of the sixth cation —to 0.32, and the subsequent differentiation of them into three "varieties" —to 0.28. The remaining atoms were subsequently localized from a series of electron-density maps $\rho(xyz)$. Least-squares refinement reduced R_{hkl} from 0.19 to 0.11 ($\max \sin\theta/\lambda = 0.95$ $\mathring{A}^{-1}$ with an isotropic thermal correction $B_{hkl} = -0.82$ $\mathring{A}^{2}$).

The final coordinates of the basis atoms are given in Table 1, and the interatomic distances calculated from them—in Table 2.

For the Si atom in an almost regular tetrahedron the distances are $\mathrm{Si-O} =$ 1.64-1.66 Å (mean 1.647), with tetrahedron edges $\mathrm{O-O} =$ 2.61-2.83 Å. Of the three independent Ca cations, the first, Ca_{I}, has 7 neighbors situated at the vertices of a rather ordinary polyhedron: a trigonal prism plus a semioctahedron. In the environment of Ca_{I}, a near coordination sphere is clearly distinguished (anions O^{2-}) at distances of 2.29-2.41 Å, and Cl^{1-} anions, more distant at 2.88-2.96 Å. The two other cations, Ca_{II} and Ca_{III}, although having the same coordination number 6, have different environments. Whereas around Ca_{II} six oxygen ligands form a slightly distorted trigonal prism, the coordination polyhedron for Ca_{III} is a strongly distorted octahedron, which is formed by four Cl^{1-} anions (2.80-3.03 Å) and two O^{2-} anions (2.29 and 2.30 Å).

The structure of calcium chlororthosilicate is shown in Fig. 1.

The principal architectur—

Fig. 1. $Ca_3[SiO_4]Cl_2$. Projection of the structure on the *xz* plane in polyhedra. Highlighted are columns of Ca_{II}-polyhedra (a), Ca_{I}-polyhedra (b), a ribbon of $Ca_{I} + Ca_{III}$ (c), and a wall (d). Cl anions are marked by circles.

Fig. 2. Chains of Ca-prisms along the twofold screw axis $2_1[010]$.

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Figure 2

Figure 2: Figure 2

···the structural elements of $Ca_3[SiO_4]Cl_2$ may be considered to be infinite columns—chains of Ca polyhedra, each column being composed of polyhedra of one kind. These are, first of all, chains extending along [001], in which translationally identical Ca_{III} octahedra at one level ($\sim b/4$, and parallel ones at $\sim 3b/4$) alternate with those reflected in their "own" glide plane ($b/4$ and, respectively, $3b/4$). These octahedra are joined to one another by vertices Cl_1. In an analogous manner, i.e., situated almost at one level on both sides of their "own" glide plane c,

Table 2

Interatomic distances in $Ca_3[SiO_4]Cl_2$

Polyhedron / bond	Distance, Å
Si tetrahedron	
$Si - O_1$	1.66
$Si - O_2$	1.65
$Si - O_3$	1.64
$Si - O_4^*$	1.64
mean	**1.647 Å**
Ca_I **polyhedron**	
$Ca_I - O_1$	2.33
$Ca_I - O_2^*$	2.29
$Ca_I - O_3^*$	2.41
$Ca_I - O_4^*$	2.38
$Ca_I - Cl_1$	2.96
$Ca_I - Cl_2$	2.93
$Ca_I - Cl_2^*$	2.88
Ca_{II} **polyhedron**	
$Ca_{II} - O_1$	2.65
$Ca_{II} - O_2^*$	2.56
$Ca_{II} - O_3$	2.37
$Ca_{II} - O_3^*$	2.36
$Ca_{II} - O_4$	2.44
$Ca_{II} - O_4^*$	2.39
Ca_{III} **polyhedron**	
$Ca_{III} - O_1$	2.29
$Ca_{III} - O_2$	2.30
$Ca_{III} - Cl_1^*$	2.82
$Ca_{III} - Cl_1^*$	2.83
$Ca_{III} - Cl_1^*$	3.03
$Ca_{III} - Cl_2^*$	2.80

Polyhedron / bond	Distance, Å

they are arranged into denser columns (parallel to those just described) and semi-polyhedra Ca_I. But whereas the chains of Ca_{III} octahedra (Fig. 1a) are located one above another (two along the period b), the columns of Ca_I semi-polyhedra are shifted away from the middle Ca_{III} chains, alternately to the left (at the level $b/4$) and to the right (at the level $3b/4$) (Fig. 1b). At each level, with its own Ca_{III} chain, the Ca_I semi-polyhedra are tightly connected by edges, so that one may speak of strips, each made up of two parallel columns of different kinds. The seventh vertices of the Ca_I polyhedra and the sixth (Cl) vertices of the Ca_{III} octahedra allow them to be connected less tightly with the Ca_{III} chains of the strips lying above and below (through the plane c, alternately with the lower and the upper one). As a result, parallel to the plane yz (100) there arise walls of Ca_{III} and Ca_I polyhedra, somewhat open-work in character, with central "slabs" (beams) of Ca_{III} octahedra and with "stiffening ribs" – columns of Ca_I semi-polyhedra–projecting alternately to one side (along [100]) and to the other.

Between translationally identical (along [100]) and not directly connected walls, in narrow openings, rectangular faces of Ca_{II} prisms continue one another along $b = [010]$, the bodies of these prisms facing in different directions (along [100]); as a result, columns of Ca_{II} prisms are obtained, strung on screw axes 2_1 parallel to $b = [010]$ (Fig. 2). Two neighboring such columns are connected to one another by centers of symmetry, which, as often in monoclinic structures, are situated in empty octahedra; orthotetrahedra SiO_4 adjoin the walls of the latter, and together with the Ca_{II} prisms they also form thinner and more open-work walls, parallel to the walls of $Ca_{III} + Ca_I$ polyhedra.

Table 3

Valence balance in the structure of $Ca_3[SiO_4]Cl_2$

	Si	Ca_I	Ca_{II}	Ca_{III}	Σ
O_1	${}^{4}/_{4}$	${}^{2}/_{7}$	${}^{2}/_{6}$	${}^{2}/_{6}$	$2 - {}^{2}/_{42}$
O_2	${}^{4}/_{4}$	${}^{2}/_{7}$	${}^{2}/_{6}$	${}^{2}/_{6}$	$2 - {}^{2}/_{42}$
O_3	${}^{4}/_{4}$	${}^{2}/_{7}$	$2 \times {}^{2}/_{6}$	–	$2 - {}^{4}/_{42}$
O_4	${}^{4}/_{4}$	${}^{2}/_{7}$	$2 \times {}^{2}/_{6}$	–	$2 - {}^{4}/_{42}$
Cl_1	–	${}^{2}/_{7}$	–	$3 \times {}^{2}/_{6}$	$1 + {}^{2}/_{7}$
Cl_2	–	$2 \times {}^{2}/_{7}$	–	${}^{?}/_{6}$	$1 - {}^{4}/_{24}$

The jointly alternating walls are consolidated into a three-dimensional framework filling the entire crystal space.

With the very diverse environment of the large cations, equilibration of the local valence balance (Table 3) is achieved by means of participation at each vertex necessarily of three Ca polyhedra. With substantially different Ca–O and Ca–Cl bond lengths, this leads to distortion of the polyhedra and, as a consequence, to low stability of the framework, and causes the breaking of Ca–Cl bonds upon hydration of the compound.

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