

The Density of Cement Phases
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ABSTRACT

The densities of principal crystalline phases occurring in Portland cement are critically assessed and tabulated, in some cases with addition of new data. A reliable and self-consistent density set for crystalline phases was obtained by calculating densities from crystallographic data and unit cell contents. Independent laboratory work was undertaken to synthesize major AFm and AFt cement phases, determine their unit cell parameters and compare the results with those recorded in the literature. Parameters were refined from powder diffraction patterns using CELREF 2 software.

A density value is presented for each phase, showing literature sources, in some cases describing limitations on the data, and the weighting attached to numerical values where an averaging process was used for accepted data. A brief discussion is made of the consequences of the packing of water to density changes in AFm and AFt structures.

Key words: Density; X-ray diffraction; Cement; Crystal Structure; Characterization

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1. Introduction

The densities of cement phases are fundamental parameter with many uses, for example, calculating space filling in pastes by solid cement substances as well as assessment of the potential for changes in dimension and porosity within hardened pastes undergoing phase changes. Yet it is difficult to access a self-consistent set of density data and values reported in the literature for the same substance can vary widely. The importance of having a self-consistent data set has long been recognized: for example Taylor [1] provided data for crystalline calcium silicate hydrates and, in a later publication, gave density and powder diffraction data for many of the main cement phases [2]. Richardson [3] published updated table of crystal data together with density values for calcium silicate hydrates and related phases, but previous compilations regarding other cement compounds are incomplete and somewhat out of date.

The substances comprising cement can be divided into two groups: crystalline and amorphous. The distinction is operational: in the present context, “crystalline” refers to substances having sufficiently regular internal structures, in terms of atomic, ionic and molecular arrangement, to enable characterization by classical crystallographic concepts.

Some of the relevant phases occur in nature and some can be obtained as single crystals, natural or synthetic. Classical methods of density measurement can often be applied to single crystals. But many cement substances, while crystalline, do not occur in adequate purity or size to apply classical methods. Therefore for most crystalline substances we rely on crystallochemical data for the calculation of densities, but with the cautions given below.

The principal amorphous substance of Portland cement is C-S-H. It presents particular problems in determining its density as it is insufficiently crystalline for application of conventional crystallographic methods: only experimentally-determined measurements are useful. Moreover uncertainties persist especially with respect to its water content and we note that only arbitrary distinctions between “bound” and “free” water are possible. Other phases may also be intercalated within C-S-H on a nanoscale *e.g.*, portlandite or AFm, thus affecting density. Uncertainty therefore exists over the Ca/Si ratio as well as extent of incorporation of other ions (alkali, alumina, sulfate...), all of which potentially affect the density. Finally, possible errors may arise from classical density measurements where, for example, a liquid used for density measurement by the Archimedes method may react with C-S-H. Thus for C-S-H we have no choice but to accept experimentally-determined data.

Crystalline solids, on the other hand, are amenable to calculation of density from crystallographic constants using the relationship:

$$D = (Z \times M)/(N_A \times V)$$

where: D = density in kg/m^3 , Z = number of formula units per unit cell, M = formula weight, V the unit cell volume and N_a = Avogadro's number.

Volumes of the unit cells were calculated for relevant crystal systems using standard formulae:

Isometric/cubic crystal system: $V = a^3$

Tetragonal crystal system: $V = a^2c$

Hexagonal/trigonal crystal system: $V = a^2c \sin(60^\circ)$

Orthorhombic crystal system: $V = abc$

Monoclinic crystal system: $V = abc \sin(\beta)$

Triclinic crystal system: $V = abc ((1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma) + 2(\cos(\alpha) \cos(\beta) \cos(\gamma)))^{1/2}$

where a , b , c are the unit cell axial dimensions and α , β , γ are the relevant angles. In some cases the unit cell contents require elucidation in order to establish the exact chemistry.

The crystallographic approach provides a uniform and consistent basis for calculation but many substances contain defects which result in real densities being slightly lower than calculated (usually the error is less than one part in 10×10^4). The occurrence of solid solution, in which for example substitution of Fe for Al occurs, also affects the mean atomic mass of ions occupying a particular lattice site or sites and hence the density. Many substances occur in several polytypes, each of which may differ in true unit cell size and symmetry and the possibility exists that preparations may contain mixtures of polytypes. Except where noted, isomorphic substitution is negligible in the selected data. We address polytypism by choosing a single subcell for the calculation and believe that this leads to the correct density, provided the subcell and Z are correctly matched. We also note that rhombohedral crystals have generally been treated on the basis of a larger hexagonal cell: again, no error results provided Z is chosen correctly.

Variable site occupancy may occur, with some sites left partially vacant. For example the subcell water (H_2O) content of ettringite attains a maximum of 36 but more commonly water contents lie in the range 30 to 32 H_2O per formula unit, but with little change in cell size occurring in this range. This uncertainty over composition is addressed by stating the formula used for calculation although we also develop density-composition relationships in selected cases. Where a particular phase is impurity-stabilized, the impurity is deemed to be minor but, although the presence of impurity is noted, we are often unable to include it in the formula because no analysis of the phase was recorded in the data source.

Temperature and pressure affect densities and the values shown here are nominally reported for 20° - $25^\circ C$ and ambient pressure, unless otherwise noted. The literature is often indefinite about the temperature used for collection of crystallographic data apart from stating that data were collected at "room temperature". We have assumed that "room temperature" lies within the range 20 - $25^\circ C$ and have not otherwise attempted corrections.

Where cell dimensions were determined from single crystal methods by the Weissenberg method, or from precession methods using photographic recording, cell dimensions thus obtained are probably only accurate to $\pm 1\%$. Therefore where a choice of methods for determination of cell parameters occurred, priority has been given to those made using calibrated powder X-ray diffraction or automated single-crystal methods with electronic recording.

In a few cases our recalculation of density does not agree with the author's own calculation. Where such disagreement exceeds the normal limits of arithmetic error, author's values are noted, but we have generally been unable to resolve the discrepancy between calculations.

This work is not complete because of multiplicity of phases, hydration states, and solid solution possibilities but it does include most of the significant compounds occurring in Portland cement and cement pastes. The order of data presentation divides substances into twelve main groups:

- Simple oxides and hydrated oxides
- Carbonates
- Sulfates and hydrated sulfates
- Tricalcium aluminate
- Tetracalcium aluminoferrite
- Tricalcium silicate
- Dicalcium silicate
- Aluminate-ferrite-trisubstituent phases
- Aluminate-ferrite-monosubstituent phases
- Hydrogarnet
- Selected crystalline calcium silicate hydrates structurally related to C-S-H (data including other calcium silicate hydrates presented by Richardson [3])
- Hydrotalcite and related phases

Experimental work was also undertaken to synthesize major AFm and AFt cement phases, determine their unit cell parameters and compare the results with those recorded in the literature. The preparative routes are described because of great interest amongst the cement community in accessing recipes. Results obtained from these preparations are included in the compilation.

[1] Taylor H.F.W., Crystallographic Data for the Calcium Silicates 1956, HMSO, London, UK

[2] Taylor H.F.W., Cement Chemistry 2nd edition 1997, Thomas Telford Publishing, London, UK

[3] I. G. Richardson, The calcium silicate hydrates, Cement and Concrete Research 38 (2008) 137-158

2. Synthesis and characterization of AFm and AFt phases

The synthesis of the relevant cement hydrates required several solid precursors. These were made from analytical reagent grade (AR) chemicals. Tricalcium aluminate, C₃A (Ca₃Al₂O₆), was prepared from a 3:1 molar ratio of CaCO₃ and Al₂O₃, fired in a platinum crucible at 1400°C for 3 days in an electrically heated furnace. Every 12 hours, the sample was cooled, reground in an agate mortar to achieve homogenization, placed back in the platinum crucible and reheated. Lime, CaO, was obtained by decarbonation of AR grade CaCO₃ at 1000°C for ~24 hours. Anhydrite, CaSO₄, was prepared by dehydration of AR gypsum (CaSO₄·2H₂O) in a muffle furnace at 550°C for 12 hours.

AFm phases

Using the above precursors, “hydroxy-AFm”, Ca₄Al₂(OH)₁₄·6-12H₂O, was synthesized by mixing CaO and C₃A in a 1:1 molar ratio. The solids were slurried in degassed, ultra pure CO₂ - free water (water/solid ratio ~ 10) and reacted at 5°C in a sealed system with stirring for the first 72 hours and thereafter periodically agitated at 5°C for 3 weeks. Finally the solid was vacuum filtered at 5°C under N₂ atmosphere.

“Monosulfoaluminate”, Ca₄Al₂(SO₄)(OH)₁₂·6H₂O, becomes more stable at temperatures above 40°C, therefore a 1:1 molar mixture of C₃A and CaSO₄ was suspended in ultra pure, CO₂ - free water (water/solid ratio ~ 10), and kept at 85°C. After 7 days the solid was vacuum filtered under N₂ atmosphere.

“Monocarboaluminate”, $\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH})_{12}\cdot 5\text{H}_2\text{O}$, was prepared by mixing C_3A and CaCO_3 in a 1:1 molar ratio with previously degassed ultra-pure water at 25°C and stored for 10 days with periodic agitation.

“Hemicarboaluminate”, $\text{Ca}_4\text{Al}_2(\text{CO}_3)_{0.5}(\text{OH})_{13}\cdot 5.5\text{H}_2\text{O}$, was made by addition of C_3A , CaCO_3 and CaO in stoichiometric quantities to previously degassed ultra pure water at 25°C at a w/s ratio about 10 and continuously stirred in plastic (HDPE) bottles for 14 days before filtration.

Strätlingite, $\text{Ca}_2\text{Al}_2\text{SiO}_2(\text{OH})_{10}\cdot 3\text{H}_2\text{O}$, was synthesized from a stoichiometric mix of CaO , $\text{Na}_2\text{Si}_2\text{O}_5\cdot 2\text{H}_2\text{O}$, NaAlO_2 and water at 25°C . The water :solid ratio was ~ 10 . The suspension was stirred for 5-6 weeks at 25°C . After filtration, sodium was washed out by flushing the remaining solid with double distilled water. From previous experience the sodium content of the washed solid is known to be negligible.

‘Friedel’s salt’ $\text{Ca}_4\text{Al}_2(\text{Cl})_2(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$ was made by mixing C_3A and $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ in a 1:1 molar ratio, which were dispersed in double distilled, CO_2 free water (w/s ~ 10), sealed in an airtight polythene bottle and left to age with stirring for 30 days. After ageing the solid was filtered under nitrogen atmosphere.

Aft phases

To prepare ‘sulfate ettringite’, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, two reactant solutions were initially made, solution (1) by adding 6.65 g $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ to 100 ml and solution (2) by dispersing 4.44 g $\text{Ca}(\text{OH})_2$ in 250 ml of ultrapure water ($>14\text{ M}\Omega\text{ cm}$). The two reactant solutions were transferred to a N_2 -filled glove box, mixed and diluted to 500 ml with additional reagent water to which 0.5 ml of 1 M NaOH had been added. The preparation was sealed in a 500 ml high density polyethylene (HDPE) bottle, removed from the dry box and placed on a 60°C hot plate, with stirring. After 48 hours, the contents were filtered under N_2 using a ceramic filter funnel and rapidly dried under N_2 using a poor vacuum.

‘Carbonate ettringite’, $\text{Ca}_6\text{Al}_2(\text{CO}_3)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, was prepared by precipitation from a stoichiometric mixture of CaO , NaAlO_2 and Na_2CO_3 in a 10% w/v sucrose solution. Previously-prepared slurries of sodium aluminate and sodium carbonate were added to the sucrose - portlandite mixture, stirred for 3 days and periodically agitated at 25°C for 2 weeks and thereafter filtered and washed. Experience of this preparation indicated that thorough washing was required to prevent retention of sucrose. The purified product should be free from sucrose, as determined by analysis.

Data collection.

A Bruker D8 advance powder diffractometer was used for characterisation and X-ray analysis. Data were collected using $\text{Cu K}\alpha$ radiation at room temperature ($25\text{-}30^\circ\text{C}$): the angular range was set between $5\text{-}55^\circ 2\theta$. Unit cell parameters were refined from the powder diffraction patterns using CELREF 2 software.

3. Results

The results and comments are presented in the form of work sheets, one for each phase or related group of phases. A summary of recommended values is provided in Table 1.

Index

<u>No</u>	<u>Phase</u>	<u>Page</u>
1	Lime.....	8
2	Periclase.....	8
3	Corundum.....	9
4	Quartz.....	10
5	Gibbsite.....	10
6	Brucite.....	11
7	Portlandite.....	12
8	Calcite.....	13
9	Aragonite.....	14
10	Vaterite.....	14
11	Magnesite.....	15
12	Dolomite.....	16
13	Anhydrite.....	17
14	'Soluble Anhydrite'.....	17
15	Hemihydrate.....	18
16	Gypsum.....	19
17	Arcanite.....	20
18	Thenardite.....	20
19	Aphthitalite.....	21
20	Syngenite.....	21
21	'Aluminosulfate' (calcium sulfoaluminate).....	22
22	'Silicosulfate' (calcium sulfosilicate).....	23
23	Tricalcium aluminate (cubic).....	23
24	Tricalcium aluminate (orthorombic).....	24
25	Tetracalcium aluminoferrite (brownmillerite).....	25
26	R-Tricalcium silicate (at 1200°C).....	26
27	R-Tricalcium silicate (stabilized with Sr).....	26
28	M3-tricalcium silicate (stabilized with Mg).....	27
29	M3-tricalcium silicate (less well ordered).....	27
30	T1-tricalcium silicate.....	28
31	α -dicalcium silicate (stabilized to ambient with Ba).....	29
32	α'_H -dicalcium silicate (1200°C, stabilized with P ₂ O ₅).....	29
33	α'_L -dicalcium silicate (stabilized with Sr).....	29
34	β -dicalcium silicate.....	30
35	γ -dicalcium silicate.....	30
36	Ettringite.....	31
37	'Carbonate Ettringite', 'CO ₃ -AFt'.....	34
38	'Iron Ettringite'.....	35
39	Thaumasite.....	35
40	Tetracalcium aluminate-13-hydrate (hydroxy AFm).....	37
41	Tetracalcium ferrite-13-hydrate (Fe-hydroxy AFm).....	37
42	α_1 -Tetracalcium aluminate-19-hydrate.....	38
43	α_2 -Tetracalcium aluminate-19-hydrate.....	38
44	Tetracalcium aluminate monosulfate-12-hydrate (monosulfoaluminate).....	39
45	Tetracalcium ferrite monosulfate-12-hydrate (Fe-monosulfoaluminate).....	40
46	Dicalcium aluminate monosilicate-8-hydrate (strätlingite).....	41
47	Tetracalcium aluminate carbonate-11-hydrate (monocarboaluminate).....	42

48	Tetracalcium ferrite carbonate-12-hydrate (Fe-monocarboaluminate).....	43
49	Tetracalcium aluminate hemicarbonat-12-hydrate (hemicarboaluminate).....	43
50	Dicalcium aluminate-8-hydrate.....	44
51	α -Tetracalcium aluminate dichloride-10-hydrate (Friedel's salt).....	44
52	β -Tetracalcium aluminate dichloride-10-hydrate (Friedel's salt).....	45
53	Tetracalcium ferrite dichloride-10-hydrate (Fe-Friedel's salt).....	46
54	Tetracalcium aluminate sulfate chloride-12-hydrate (Kuzel's salt).....	47
55	Tetracalcium ferrite sulfate chloride-12-hydrate (Fe-Kuzel's salt).....	47
56	Tricalcium aluminate-6-hydrate (hydrogarnet).....	48
57	Tricalcium ferrite-6-hydrate.....	49
58	'Siliceous' hydrogarnet.....	49
59	Jennite.....	50
60	Tobermorite (14 Å).....	51
61	Afwillite.....	52
62	Hydrotalcite.....	53
63	Fe-Hydrotalcite.....	53
64	Meixnerite.....	54
65	OH-Hydrotalcite.....	54

SIMPLE OXIDES AND HYDRATED OXIDES

1 Lime

Formula: CaO

Formula Weight: 56.08 g/mol

Space group: Fm3m

Conventional cement shorthand notation: C

1.1 Cell Dimensions: $a = 4.8105 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for cubic crystal system): 3345 kg/m^3

Reference: Morris M.C. et al., National Bureau of Standards Monograph 25 (1977), Vol. 14, 49

Cell parameters were determined at 298 K from X-ray powder patterns. The type of diffractometer and origin of the sample are not specified. The diffractometer was equipped with a focusing graphite monochromator; an internal standard (high purity 99.99% Si standard) and Cu $K\alpha$ radiation (1.5405 \AA) were used.

Density calculated by Morris, et al.: 3345 kg/m^3

1.2 Cell Dimensions: $a = 4.815 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for cubic crystal system): 3338 kg/m^3

Reference: Fiquet G. et al., Physics and Chemistry of Minerals (1999), Vol. 27, 103-111

Cell parameters were determined at 298 K from X-ray diffraction experiments with synchrotron radiation; type of diffractometer and origin of the sample are not given..

1.3 Mean density of lime: $D_x = 3341 \text{ kg/m}^3$

1.4 Comment:

Free lime is a minor constituent of most Portland cement clinkers. Large quantities (e.g., greater than a few percent) possibly indicate poor control in manufacture. Lime hydrolyzes in water to Ca(OH)_2 and to mixtures of CaCO_3 and Ca(OH)_2 in moist air.

2 Periclase

Formula: MgO

Formula Weight: 40.30 g/mol

Space group: Fm3m

Conventional cement shorthand notation: M

2.1 Cell Dimensions: $a = 4.211 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for cubic crystal system): 3581 kg/m^3

Reference: Hazen R.M., American Mineralogist (1976), Vol. 61, 266-271

Cell parameters were determined at 296 K, from single crystal X-ray structure refinements of synthetic periclase, using a Picker four circle diffractometer and Mo $K\alpha$ radiation.

- 2.2 Cell Dimensions:** $a = 4.210 \text{ \AA}$
Number of formula units in the unit cell: $Z = 4$
Density (calculated for cubic crystal system): 3587 kg/m^3
Reference: Fiquet G. et al., Physics and Chemistry of Minerals (1999), Vol. 27, 103-111

Cell parameters were determined at 298 K, from X-ray diffraction experiments with synchrotron radiation. The type of diffractometer and origin of the sample are not given.

- 2.3 Mean density of periclase:** $D_x = 3584 \text{ kg/m}^3$

2.4 Comment:

Occurs in some Portland cement clinkers. Hydrolyzes in water to Mg(OH)_2 and in air, to mixtures of hydroxide, carbonate and hydroxycarbonates.

3 Corundum

Formula: Al_2O_3

Formula Weight: 101.96 g/mol

Space group: $R\bar{3}c$

Conventional cement shorthand notation: A

- 3.1 Cell Dimensions:** $a = 4.758 \text{ \AA}$, $c = 12.991 \text{ \AA}$
Number of formula units in the unit cell: $Z = 6$
Density (calculated for hexagonal/trigonal system): 3988 kg/m^3
Reference: Swanson H.E. et al., National Bureau of Standards Circular 539 (1953), Vol. 2, 20

Cell parameters of a synthetic sample were determined at 300K, from X-ray powder patterns; X-ray intensities were collected with a Guiner-type camera using an internal standard and $\text{Cu K}\alpha$ radiation (1.5405 \AA).

Density calculated by Swanson, et al.: 3987 kg/m^3

- 3.2 Cell Dimensions:** $a = 4.758 \text{ \AA}$, $c = 12.996 \text{ \AA}$
Number of formula units in the unit cell: $Z = 6$
Density (calculated for hexagonal/trigonal system): 3987 kg/m^3
Reference: Fiquet G. et al., Physics and Chemistry of Minerals (1999), Vol. 27, 103-111

Cell parameters were determined at 298 K, from X-ray diffraction using synchrotron radiation; the origin of the sample is not specified.

- 3.3 Cell Dimensions:** $a = 4.7540 \text{ \AA}$, $c = 12.9820 \text{ \AA}$
Number of formula units in the unit cell: $Z = 6$
Density (calculated for hexagonal/trigonal system): 3997 kg/m^3
Reference: Maslen E.N. et al., Acta Crystallographica (1993), Vol. B49, 973-80

Cell parameters were determined at 293 K, from single crystal X-ray structure refinements of $\alpha\text{-Al}_2\text{O}_3$ crystals (origin: not specified), using a Syntex P2₁ four circle diffractometer (with graphite monochromator) and $\text{Mo K}\alpha$ radiation (0.7106 \AA).

Density calculated by Maslen, et al.: 3997 kg/m^3

3.4 Mean density of corundum: $D_x = 3990 \text{ kg/m}^3$

3.5 Comment:

Alumina, Al_2O_3 , occurs in various polymorphs. Alpha (corundum) is probably the only stable polymorph at 1 bar. Some of the 'polymorphs' are chemically stabilized: for example ' β Al_2O_3 ' is actually close in composition to $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. Corundum is not normally present in Portland cement clinkers but has sometimes been reported in special cement made using bauxite, for example in high-alumina or sulfoaluminate clinkers.

4 Quartz

Formula: SiO_2

Formula Weight: 60.08 g/mol

Space group: $P3_121$

Conventional cement shorthand notation: S

4.1 Cell Dimensions: $a = 4.9133 \text{ \AA}$, $c = 5.4053 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal system): 2648 kg/m^3

Reference: Gaines V.R. et al., *Dana's New Mineralogy*, eighth edition (1997), 1573-1586

Phase: synthesized α - quartz ('low' temperature form)

Details of the measurement are not given

The density given in *Dana's New Mineralogy*: 2660 kg/m^3

4.2 Cell Dimensions: $a = 4.92 \text{ \AA}$, $c = 5.42 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal system): 2634 kg/m^3

Reference: Glinnemann J. et al., *Zeitschrift für Kristallographie* (1992), Vol. 198, 177-212

Cell parameters were determined at 'room temperature', from X-ray structure refinements of a synthetic phase, using a Philips PW 1100 four circle diffractometer (with graphite monochromator) and Mo $K\alpha$ radiation (0.7106 \AA).

4.3 Mean density of α - quartz: $D_x = 2641 \text{ kg/m}^3$

4.4 Comment:

Two forms of quartz exist, alpha-quartz which is stable up to 573° C and beta-quartz, the high temperature form, stable between 573° and 867° C . High quartz cannot usually be quenched to ambient so "quartz" usually refers to the alpha phase. However some schemes use the reverse assignment, in which 'low' (temperature) form is designated beta.

Quartz is not nominally a phase found in Portland cement but is used in its manufacture, and is often added to autoclaved cements and oil well cements intended for high temperature service. On account of the sensitivity of X-ray diffraction to quartz and its almost universal presence in nature, it is frequently encountered as a trace impurity of Portland cement.

5 Gibbsite

Formula: $\text{Al}(\text{OH})_3$

Formula Weight: 78.00 g/mol

Space group: $P2_1/c$

Conventional cement shorthand notation: AH_3

5.1 Cell Dimensions: $a = 8.684 \text{ \AA}$, $b = 5.078 \text{ \AA}$, $c = 9.736 \text{ \AA}$, $\beta = 94.54^\circ$

Number of formula units in the unit cell: $Z = 8$

Density (calculated for monoclinic crystal system): 2421 kg/m^3

Reference: Saalfeld H. et al., Zeitschrift für Kristallographie (1974), Vol. 139, 129-135

Cell parameters were determined at 'room temperature', from X-ray structure refinements of a natural mineral from Langesunfjord, Norway, using an automated Siemens diffractometer and $Cu K\alpha$ radiation.

Identical values of the unit cell parameters were given by Balan E. et al, American Mineralogist (2006); Vol. 91, 115-119

5.3 Recommended density of gibbsite: $Dx = 2421 \text{ kg/m}^3$

5.4 Comment:

Gibbsite may be considered as the hexagonally-packed AX_3 layer structure but also has a cubic polymorph, bayerite. Many types of mixed stacking, some disordered and some ordered, are known as intermediates between gibbsite and bayerite.

6 Brucite

Formula: $Mg(OH)_2$

Formula Weight: 58.32 g/mol

Space group: $P\bar{3}m1$

Conventional cement shorthand notation: MH

6.1 Cell Dimensions: $a = 3.147 \text{ \AA}$, $c = 4.769 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1$

Density (calculated for hexagonal/trigonal crystal system): 2368 kg/m^3

Reference: Swanson H.E. et al., National Bureau of Standards Circular 539 (1956), Vol.6, 62

Cell parameters were determined at room temperature, 300 K, from X-ray powder patterns of a synthetic sample (from MgO and water held at 600°C and 1333 bars water vapour pressure for 3 days), using: a Guiner-type camera (with Ni filter), $Cu K\alpha$ radiation (1.5405 \AA) and an internal standard.

Density calculated by Swanson et al.: 2368 kg/m^3

6.2 Cell Dimensions: $a = 3.148 \text{ \AA}$, $c = 4.779 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1$

Density (calculated for hexagonal/trigonal crystal system): 2368 kg/m^3

Reference: Desgranges L. et al., Acta Crystallographica (1996), Vol. B52, 82-86

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of a natural sample (origin-not specified), using a four circle P110 neutron diffractometer at the Orphee Reactor (CEN-Saclay).

Density calculated by Desgranges et al.: **2360 kg/m³**

6.3 Mean density of brucite: $D_x = 2368 \text{ kg/m}^3$

6.4 Comment:

Brucite has been reported to occur as a hydration product of slag-cement blends and as an alteration product of Portland cement in sea water, brines, etc. A number of basic carbonates of general formula $x \text{Mg(OH)}_2 \cdot y, \text{MgCO}_3 \cdot \text{H}_2\text{O}$ also exist but differ in structure from brucite. The basic carbonates have not been reported to occur as Portland cement hydration products.

7 Portlandite

Formula: Ca(OH)_2

Formula Weight: 74.09 g/mol

Space group: $P \bar{3}m1$

Conventional cement shorthand notation: CH

7.1 Cell Dimensions: $a = 3.589 \text{ \AA}, c = 4.911 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1$

Density (calculated for hexagonal/trigonal crystal system): **2260 kg/m³**

Reference: Desgranges L. et al., Acta Crystallographica (1993), Vol. B49, 812-817

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of a synthetic sample (crystals were prepared by slow diffusion of calcium chloride into a sodium hydroxide solution), using a four circle P110 diffractometer (with Cu(220) monochromator) and Mo $K\alpha$ radiation (0.8330 \AA).

Density calculated by Desgranges et al.: **2260 kg/m³**

7.2 Cell Dimensions: $a = 3.593 \text{ \AA}, c = 4.909 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1$

Density (calculated for hexagonal/trigonal crystal system): **2242 kg/m³**

Reference: Swanson H.E. et al., National Bureau of Standards Circular 539 (1953), Vol.1, 95

Cell parameters were determined at room temperature, 300 K, from X-ray powder patterns; X-ray intensities were collected with a Guiner type camera (with Ni filter) using Cu $K\alpha$ radiation (1.5405 \AA) and an internal standard; the origin of the sample is not specified.

Density calculated by Swanson et al.: **2241 kg/m³**

7.3 Mean density of portlandite: $D_x = 2251 \text{ kg/m}^3$

7.4 Comment:

A major constituent of hydrated Portland cement. The structure consists of layers formed from rows of linked Ca(OH)_6 octahedra. Calcium hydroxide dehydrates to calcium oxide at about 400°C. It carbonates readily in humid air.

CARBONATES

8 Calcite

Formula: CaCO₃

Formula Weight: 100.09 g/mol

Space group: R $\bar{3}c$

Conventional cement shorthand notation: C \bar{C}

8.1 Cell Dimensions: $a = 4.991 \text{ \AA}$, $c = 17.062 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2710 kg/m³

Reference: Maslen E.N. et al., Acta Crystallographica (1993), Vol. B49, 636-641

Cell parameters were determined at 293 K, from single crystal X-ray structure refinements of CaCO₃ samples (crystals were grown from aqueous solution by slow diffusion), using a Syntex P3 four circle diffractometer with graphite monochromator and Mo K α radiation (0.7107 \AA).

Density calculated by Maslen et al.: 2709 kg/m³

8.2 Cell Dimensions: $a = 4.9896 \text{ \AA}$, $c = 17.0610 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2710 kg/m³

Reference: Effenberger H. et al., Zeitschrift für Kristallographie (1981), Vol. 156, 233-243

Cell parameters were determined at 'room temperature' from single crystal X-ray structure refinements of a natural sample (locality: Iceland), using a Philips PW 1100 four circle diffractometer with graphite monochromator and Mo K α radiation.

8.3 Cell Dimensions: $a = 4.990 \text{ \AA}$, $c = 17.002 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2722 kg/m³

Reference: Chessin H. et al., Acta Crystallographica (1965), Vol. 18, 689-693

Cell parameters were determined at 300K, from X-ray structure refinements of single crystals (origin: not specified); data were collected on an integrating Weissenberg camera using Mo K α radiation.

8.4 Recommended density of calcite: $D_x = 2710 \text{ kg/m}^3$

8.5 Comment:

On account of the lower accuracy of the Weissenberg method of determining cell parameters, the value in 8.3 is not preferred.

Calcite is the chief constituent of limestone, a basic raw material used in cement manufacture. It decomposes at about 900°C. In nature considerable substitution of Mg for Ca may occur. This random substitution gives rise to 'magnesian calcite', in which some Mg substitutes randomly on nominally Ca positions: it is not to be confused with dolomite, in which Ca-Mg ordering occurs.

9 Aragonite

Formula: CaCO₃

Formula Weight: 100.09 g/mol

Space group: Pmcn

Conventional cement shorthand notation: C \bar{C}

9.1 Cell Dimensions: $a = 4.96 \text{ \AA}$, $b = 7.97 \text{ \AA}$, $c = 5.74 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2929 kg/m³

Reference: De Villiers J.P.R, American Mineralogist (1971), Vol. 56, 758-767

Cell parameters were determined at 294 K, from single crystal X-ray structure refinements of a natural sample (locality: Grapevine Mountains, Nevada), using: a Super-Pace automated single crystal diffractometer and Cu K α radiation (1.5405 \AA).

9.2 Cell Dimensions: $a = 4.9614 \text{ \AA}$, $b = 7.966 \text{ \AA}$, $c = 5.740 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2931 kg/m³

Reference: Morris M.C. et al., National Bureau of Standards Monograph 25 (1977), Vol. 14, 44

Cell parameters were determined at 298 K, from X-ray powder patterns using: diffractometer with a focusing graphite monochromator, Cu K α radiation, and an internal standard (high purity 99.99% Si); origin of the sample is not specified.

9.3 Mean density of aragonite: $D_x = 2930 \text{ kg/m}^3$

9.4 Comment:

Aragonite is a stable high-pressure polymorph. It occurs in certain metamorphic rocks but is also formed metastably at low pressure. Thus it is frequently encountered as a product of rapid carbonation of cements. It is also commonly encountered in biological composites such as shells of marine organisms, where it is apparently stabilized by intercalation with protein-like substances. Upon heating in the air at 1 bar total pressure, aragonite converts to calcite prior to decomposition.

10 Vaterite

Formula: μ -CaCO₃

Formula Weight: 100.09 g/mol

Space group: P6₃/mmc

Conventional cement shorthand notation: C \bar{C}

10.1 Cell Dimensions: $a = 7.16 \text{ \AA}$, $c = 16.98 \text{ \AA}$

Number of formula units in the unit cell: $Z = 12$

Density (calculated for hexagonal/trigonal crystal system): 2664 kg/m³

Reference: Kamhi S.R., Acta Crystallographica (1963), Vol. 16, 770-773

Cell parameters were determined from single crystal X-ray structure refinements of synthetic crystals (grown by ionic diffusion in aqueous solution), using a Picker diffractometer equipped with a General Electric single crystal orienter. Crystal sizes and habits were

dependent upon the temperature at which experiment was performed (temperatures in the region 45°C to 60°C were found to give the best yields).

- 10.2 Cell Dimensions:** $a = 7.15 \text{ \AA}$, $c = 16.94 \text{ \AA}$
Number of formula units in the unit cell: $Z = 12$
Density (calculated for hexagonal/trigonal crystal system): 2659 kg/m^3
Reference: Meyer H.J., Zeitschrift für Kristallographie (1969), Vol. 128, 183-212

Cell parameters were determined from single crystal X-ray structure refinements of crystals (origin: not specified), using a Hilger & Watts microfocuss diffractometer and Cu $K\alpha$ radiation; temperature of the measurement is not specified.

- 10.3 Mean density of vaterite:** $D_x = 2661 \text{ kg/m}^3$

10.4 Comment:

Vaterite is a low density polymorph of CaCO_3 . It is believed to be metastable under all conditions. It may occur as a product of rapid precipitation often in mixtures with calcite, etc., as a product of cement carbonation. Upon heating in air, vaterite converts to calcite prior to decomposition.

11 Magnesite

Formula: MgCO_3
Formula Weight: 84.31 g/mol
Space group: $R\bar{3}c$
Conventional cement shorthand notation: $M\bar{C}$

- 11.1 Cell Dimensions:** $a = 4.632 \text{ \AA}$, $c = 15.007 \text{ \AA}$
Number of formula units in the unit cell: $Z = 6$
Density (calculated for hexagonal/trigonal crystal system): 3013 kg/m^3
Reference: Maslen E.N. et al., Acta Crystallographica (1995), Vol. B51, 929-939

Cell parameters were determined at 295 K, from single crystal X-ray structure refinements of a synthetic sample (prepared hydrothermally), using a four circle diffractometer and Mo $K\alpha$ radiation (0.7073 \AA).

Density calculated by Maslen et al: 3013 kg/m^3

- 11.2 Cell Dimensions:** $a = 4.632 \text{ \AA}$, $c = 15.013 \text{ \AA}$
Number of formula units in the unit cell: $Z = 6$
Density (calculated for hexagonal/trigonal crystal system): 3009 kg/m^3
Reference: Effenberger H. et al., Zeitschrift für Kristallographie (1981), Vol. 156, 233-243

Cell parameters were determined at 'room temperature' from single crystal X-ray structure refinements of a natural sample (locality: Oberdorf, Austria), using a Philips PW 1100 four circle diffractometer with graphite monochromator and Mo $K\alpha$ radiation.

- 11.3 Mean density of magnesite:** $D_x = 3011 \text{ kg/m}^3$

11.4 Comment:

See also brucite, for mention of 'hydroxycarbonates'.

12 Dolomite

Formula: CaMg(CO₃)₂

Formula Weight: 184.40 g/mol

Space group: R $\bar{3}$

Conventional cement shorthand notation: CM \bar{C}_2

12.1 Cell Dimensions: $a = 4.8312 \text{ \AA}$, $c = 16.166 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2811 kg/m³

Reference: Reeder R.J. et al., American Mineralogist (1989), Vol. 74, 1159-1167

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of a natural sample (locality: Erzberg, Austria), using a Picker four circle diffractometer equipped with a graphite monochromator and Mo K α radiation (0.7107 \AA).

12.2 Cell Dimensions: $a = 4.8069 \text{ \AA}$, $c = 16.002 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2868 kg/m³

Reference: Reeder R.J. et al., American Mineralogist (1986), Vol. 71, 795-804

Cell parameters were determined at 297 K, from single crystal X-ray structure refinements of a natural sample (locality: Eugui, Spain), using a Picker four circle diffractometer equipped with graphite monochromator and Mo K α radiation (0.7107 \AA).

12.3 Cell Dimensions: $a = 4.8064 \text{ \AA}$, $c = 16.006 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2868 kg/m³

Reference: Ross N.L. et al., American Mineralogist (1992), Vol. 77, 412-421

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of a natural sample (locality: Eugui, Spain), using a Picker four circle diffractometer equipped with graphite monochromator and Mo K α radiation (0.7107 \AA).

12.4 Cell Dimensions: $a = 4.812 \text{ \AA}$, $c = 16.020 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2859 kg/m³

Reference: Effenberger H. et al., Zeitschrift für Kristallographie (1981), Vol. 156, 233-243

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of a natural sample (locality: Oberdorf, Austria), using a Philips PW 1100 four circle diffractometer equipped with graphite monochromator and Mo K α radiation.

12.5 Mean density of dolomite: $D_x = 2852 \text{ kg/m}^3$

12.6 Comment:

Data are given for ideal dolomite, having Ca/Mg = 1. However natural dolomite exhibits a range of Ca/Mg ratios. Its synthesis has been reported but insufficient data are given to calculate a density [1,2].

[1] Usdowski E., Naturwissenschaften (1989), Vol. 76, 374-375

[2] Babcan J. et al., Geologica Carpathica (2001), Vol. 52, 139-146

SULFATES AND HYDRATED SULFATES

13 Anhydrite

Formula: CaSO₄

Formula Weight: 136.14 g/mol

Space group: Amma, Bbmm

Conventional cement shorthand notation: C $\bar{5}$

13.1 Cell Dimensions: $a = 7.006 \text{ \AA}$, $b = 6.998 \text{ \AA}$, $c = 6.245 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2952 kg/m³

Reference: Kirfel A. et al., Acta Crystallographica (1980), Vol. B36, 2881-2890

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of natural crystals (locality: Strassfurt, Germany), using a Syntex four circle diffractometer equipped with a graphite monochromator and Mo K α radiation (0,7106 \AA).

Density calculated by Kirfel et al.: 2952 kg/m³

13.2 Cell Dimensions: $a = 7.6993 \text{ \AA}$, $b = 6.995 \text{ \AA}$, $c = 6.245 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2988 kg/m³

Reference: Hawthorne F.C. et al., Canadian Mineralogist (1975), Vol. 13, 289-297

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of natural crystals (locality: Leopoldshall, Germany), using a Syntex four circle diffractometer equipped with a graphite monochromator and Mo K α radiation (0,7106 \AA).

13.3 Cell Dimensions: $a = 6.992 \text{ \AA}$, $b = 6.998 \text{ \AA}$, $c = 6.238 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2963 kg/m³

Reference: Hartmann R et al., European Journal of Mineralogy (1989), Vol. 1, 721-722

13.4 Mean density of anhydrite: $D_x = 2968 \text{ kg/m}^3$

13.5 Comment:

Active, or gamma, anhydrite is often added to Portland cement to regulate its set time in which application its readily-soluble properties are desirable. 'Active anhydrite' is characterized by having a high specific surface often with poor crystallinity: see 'soluble anhydrite' and is structurally different than anhydrite.

14 'Soluble Anhydrite'

Formula: γ - CaSO₄, Ca(SO₄)·<0.05 H₂O

Formula Weight: 136.14 g/mol

Space group: P₆22

Conventional cement shorthand notation: γ -C $\bar{5}$

14.1 Cell Dimensions: $a = 6.9695 \text{ \AA}$, $c = 6.3033 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

N.B The formula used for calculation assumes 0.00 H₂O

Density (calculated for hexagonal/trigonal crystal system): 2958 kg/m³

Reference: Lager G.A. et al., American Mineralogist (1984), Vol. 69, 910-918

Cell parameters were determined at 295 K, from single crystal X-ray photography of synthetic crystals using a Guiner- type focusing camera.

14.2 Recommended density of ‘soluble anhydrite’: $D_x = 2958 \text{ kg/m}^3$

14.3 Comment:

Considerable controversy exists in the literature concerning existence of the γ phase or ‘active anhydrite’, as distinct from normal anhydrite. However, it would appear to be established as a distinct compound. It rehydrates readily to mixtures of hemihydrate and gypsum in the presence of water.

15a Hemihydrate

Formula: Ca(SO₄)·0.5 H₂O

Formula Weight: 145.14 g/mol

Space group: I2

Conventional cement shorthand notation: C $\bar{5}$ H_{0.5}

15a.1 Cell Dimensions: $a = 6.930 \text{ \AA}$, $b = 12.062 \text{ \AA}$, $c = 12.66 \text{ \AA}$, $\alpha = 90.0^\circ$

Number of formula units in the unit cell: $Z = 12$

Density (calculated for monoclinic crystal system): 2733 kg/m³

Reference: Lager G.A. et al., American Mineralogist (1984), Vol. 69, 910-918

Cell parameters were determined at 295 K, from single crystal X-ray photography of synthetic crystals (grown from aqueous NaCl, and chemically analyzed with an electron microprobe), using a Guiner-type focussing camera.

15a.2 Recommended density of hemihydrate: $D_x = 2733 \text{ kg/m}^3$

15a.3 Comment:

Also known as ‘plaster of Paris’. It is made by partial dehydration of gypsum and is often produced in Portland cement during intergrinding of clinker to which gypsum has been added: the heat generated by grinding leads to its partial dehydration. The structure of hemihydrate is closely related to that of its precursor, gypsum, and in the presence of liquid water, it readily re-hydrates to gypsum.

There is uncertainty as to the maximum H₂O water content of hemihydrate. Kuzel [1] found that variation was continuous from 0.53-0.62 H₂O, but that a miscibility gap existed at 0.03-0.53 H₂O. Abriel [2] reported a crystal structure refinement for a preparation with 0.8 H₂O: see subsequent sheet and comment. The water content used in density calculations is stated in the formula.

[1] Kuzel H.J., Neues Jahrbuch für Mineralogie Abhandl. (1987), Vol. 156, 155

[2] Abriel W., Acta Crystallographica (1983), Vol. C39, 956-958

15b Hemihydrate

Formula: $\text{Ca}(\text{SO}_4) \cdot 0.8 \text{H}_2\text{O}$

Formula Weight: 150.54 g/mol

Space group: $P3_121$

Conventional cement shorthand notation: $\text{C}\bar{\text{S}}\text{H}_{0.8}$

15b.1 Cell Dimensions: $a = 6.968 \text{ \AA}$, $c = 6.410 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2783 kg/m^3

Reference: Abriel W., Acta Crystallographica (1983), Vol. C39, 956-958

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements (origin of the crystals: not specified), using a Huber RHD-402 diffractometer equipped with graphite monochromator) and Mo $K\alpha$ radiation (0.7107 \AA).

Density calculated by Abriel: 2630 kg/m^3

Note: even assuming the high water content, the reported density seems low.

15b.2 Recommended density of hemihydrate: $D_x = 2783 \text{ kg/m}^3$

16 Gypsum

Formula: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Formula Weight: 172.17 g/mol

Space group: $I2/a$

Conventional cement shorthand notation: $\text{C}\bar{\text{S}}\text{H}_2$

16.1 Cell Dimensions: $a = 5.679 \text{ \AA}$, $b = 15.202 \text{ \AA}$, $c = 6.522 \text{ \AA}$, $\beta = 118.43^\circ$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for monoclinic crystal system): 2310 kg/m^3

Reference: Pedersen B.F., Acta Crystallographica (1982), Vol. B38, 1074-1077

Cell parameters were determined at 294 K, from single crystal X-ray structure refinements of a natural sample (locality: Hampshire, England), using a Siemens CIRCUS four circle diffractometer.

Density calculated by Pedersen: 2300 kg/m^3

16.2 Cell Dimensions: $a = 5.6765 \text{ \AA}$, $b = 15.1952 \text{ \AA}$, $c = 6.5243 \text{ \AA}$, $\beta = 118.49^\circ$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for monoclinic crystal system): 2312 kg/m^3

Reference: Schofield P.F. et al., American Mineralogist (1996), 847-851

Cell parameters were determined at 300 K, from X-ray structure refinements of a natural sample (locality: Tuscany, Italy), using a neutron powder diffraction data, which were collected on a medium resolution Polaris diffractometer.

16.3 Mean density of gypsum: $D_x = 2311 \text{ kg/m}^3$

16.4 Comment:

Interground with Portland cement clinker to retard set. Its dehydration in air at 70-200°C gives hemihydrate ($\text{CaSO}_4 \cdot \sim 0.5\text{H}_2\text{O}$), or γ - CaSO_4 ('soluble anhydrite'), or mixtures.

17 Arcanite

Formula: K_2SO_4

Formula Weight: 174.26 g/mol

Space group: Pnam

Conventional cement shorthand notation: $\text{K}\bar{\text{S}}$

17.1 Cell Dimensions: $a = 7.476\text{\AA}$, $b = 10.071\text{\AA}$, $c = 5.763\text{\AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2668 kg/m^3

Reference: McGinnety J.A., Acta Crystallographica (1972), Vol. B28, 2845-2852

Cell parameters were determined at 291 K, from single crystal X-ray structure refinements (origin of crystals: not specified), using a Picker (Hilger & Watts) four circle diffractometer and Mo $\text{K}\alpha$ radiation (0,7093 \AA).

17.2 Recommended density of arcanite: $\text{Dx} = 2668\text{ kg/m}^3$

17.3 Comment:

" K_2SO_4 " is often reported as vapour- phase condensates on clinker or as having crystallised from sulfate-rich interstitial sulfate-rich melts trapped within clinker. It is likely that the formulation is approximate because at elevated temperature, extensive solid solution occurs with substitution of sulfate by carbonate. K_2SO_4 is also polymorphous. Data reported here are for the low-temperature phase although the high temperature phase is frequently reported to occur in clinker. Since this composition is not quenchable to ambient as the "high temperature" polymorph, its frequent occurrence in clinker is probably stabilized by solid solution. Solid solution will of course affect the density so the value given here may require appropriate adjustment.

18 Thenardite

Formula: Na_2SO_4

Formula Weight: 142.04 g/mol

Space group: Fddd

Conventional cement shorthand notation: $\text{N}\bar{\text{S}}$

18.1 Cell Dimensions: $a = 5.861\text{\AA}$, $b = 9.815\text{\AA}$, $c = 12.307\text{\AA}$

Number of formula units in the unit cell: $Z = 8$

Density (calculated for orthorhombic crystal system): 2665 kg/m^3

Reference: Mehrotra B.N. et al., Neues Jahrbuch für Mineralogie Monatshefte (1978), 408-421

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of synthetic crystals, grown from aqueous solution, using a Siemens automatic diffractometer and Mo $\text{K}\alpha$ radiation.

- 18.2 Cell Dimensions:** $a = 5.868 \text{ \AA}$, $b = 9.829 \text{ \AA}$, $c = 12.302 \text{ \AA}$
Number of formula units in the unit cell: $Z = 8$
Density (calculated for orthorhombic crystal system): 2659 kg/m^3
Reference: Hawthorne F.C., Canadian Mineralogist (1975), Vol. 13, 181-187

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of natural crystals (locality: Borax Lake, California); the type of diffractometer is not given.

- 18.3 Mean density of thenardite:** $D_x = 2662 \text{ kg/m}^3$

19 Aphthitalite

Formula: $\text{K}_3\text{Na}(\text{SO}_4)_2$
Formula Weight: 332.27 g/mol
Space group: $P\bar{3}m1$
Conventional cement shorthand notation: $\text{K}_3 \text{N}\bar{S}_2$

- 19.1 Cell Dimensions:** $a = 5.680 \text{ \AA}$, $c = 7.309 \text{ \AA}$
Number of formula units in the unit cell: $Z = 1$
Density (calculated for hexagonal/trigonal crystal system): 2703 kg/m^3
Reference: Okada K. et al., Acta Crystallographica (1980), Vol. B36, 919-921

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of synthetic crystals, using a Philips PW 1100 automated four-circle diffractometer equipped with graphite monochromator.

Density calculated by Okada et al.: 2690 kg/m^3

- 19.2 Recommended density of aphthitalite:** $D_x = 2703 \text{ kg/m}^3$

19.3 Comment:

Density is calculated for the ideal formula. Some variation in Na/K ratio occurs as result of solid solution, cell parameters decreasing with increasing Na/K ratio.

20 Syngenite

Formula: $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$
Formula Weight: 328.42 g/mol
Space group: $P2_1/m$
Conventional cement shorthand notation: $\text{KC}\bar{S}_2\text{H}$

- 20.1 Cell Dimensions:** $a = 6.225 \text{ \AA}$, $b = 7.127 \text{ \AA}$, $c = 9.727 \text{ \AA}$, $\beta = 104.153^\circ$
Number of formula units in the unit cell: $Z = 2$
Density (calculated for monoclinic crystal system): 2607 kg/m^3
Reference: Bokii G.B. et al., Soviet Physics Crystallography (1978), Vol. 23, 141-143

Cell parameters were determined at 153 K, from single crystal X-ray structure refinements of natural crystals (locality: not specified), using a Syntex $P2_1$ four circle diffractometer equipped with graphite monochromator.

Density calculated by Bokii G.B. et al.: **2607 kg/m³**

20.2 Cell Dimensions: $a = 6.25 \text{ \AA}$, $b = 7.15 \text{ \AA}$, $c = 9.77 \text{ \AA}$, $\beta = 104^\circ$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for monoclinic crystal system): **2575 kg/m³**

Reference: Corazza E. et al., Zeitschrift fur Kristallographie (1967), Vol. 124, 398-408

Cell parameters were determined at 'room temperature', from single crystal X-ray structure refinements of natural crystals (locality: Kalusz, Galicia); intensity data were collected using an integrating Buerger precession camera.

Density calculated by Corazza E. et al.: **2575 kg/m³**

20.3 Cell Dimensions: $a = 6.251 \text{ \AA}$, $b = 7.156 \text{ \AA}$, $c = 9.775 \text{ \AA}$, $\beta = 104^\circ$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for monoclinic crystal system): **2575 kg/m³**

Reference: Aruja E., Mineralogical Magazine (1958), Vol. 31, 943-946

Powder photographs were taken in at 18-cm diameter Debeye-Scherrer camera as well as on a focusing camera (Cu radiation) at 'room temperature'; a synthetic sample was prepared by immersing gypsum plaster in shallow dish of aqueous K₂SO₄ for 2 weeks.

20.4 Recommended density of syngenite: **D_x = 2575 kg/m³**

20.5 Comment:

Syngenite may form in cement during storage by reaction of potassium sulfate with gypsum. It has also been found in secondary deposits in deteriorating concrete.

The values by Corazza E. et al. and Aruja et.al value are preferred because the coefficients of thermal dilation, necessary to correct data (obtained at 154 K) to ambient are not available.

21 'Aluminosulfate' (calcium sulfoaluminate)

Formula: Ca₄(Al₆O₁₂)(SO₄)

Formula Weight: 610.26 g/mol

Space group: I4₁32; I23 also proposed

Conventional cement shorthand notation: C₄A₃ \bar{S}

21.1 Cell Dimensions: $a = 18.39 \text{ \AA}$

Number of formula units in the unit cell: $Z = 16$

Density (calculated for cubic crystal system): **2607 kg/m³**

Reference: Halstead P.E. et al., Journal of Applied Chemistry (1962), Vol. 12, 413-417

Cell parameters were determined from X-ray powder data of a synthetic sample (mixtures of CaO, Al₂O₃ and CaSO₄ in appropriate proportions were heated in platinum containers), X-ray powder data were obtained using a diffractometer equipped with a Geiger counter detector and Cu K α radiation; temperature of measurement was not specified.

Density calculated by Halstead et al.: **2607 kg/m³**

21.2 Recommended density of calcium sulfoaluminate: **D_x = 2607 kg/m³**

21.3 Comment:

The phase occurs in commercial calcium sulfoaluminate cement clinkers as a principal clinker mineral, probably with some Fe(III) substituting for Al(III). It has also been manufactured as an expansive admixture intended to produce shrinkage-compensated or expansive formulations in mixtures with Portland or calcium aluminate cements.

22 'Silicosulfate' (calcium sulfosilicate)

Formula: $\text{Ca}_5(\text{SiO}_4)_2(\text{SO}_4)$

Formula Weight: 480.58 g/mol

Space group: Pcmn

Conventional cement shorthand notation: $\text{C}_5\text{S}_2\bar{5}$

22.1 Cell Dimensions: $a = 10.182 \text{ \AA}$, $b = 15.398 \text{ \AA}$, $c = 6.850 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2972 kg/m^3

Reference: Brotherton P.D. et al., Australian Journal of Chemistry (1974), Vol. 27, 657-660

Cell parameters were determined at 'room temperature', from X-ray structure refinements of a synthetic phase (found coating from a lime kiln), using a Syntex four circle diffractometer equipped with Ni filter and Cu $K\alpha$ radiation.

Density calculated by Brotherton et al.: 2973 kg/m^3

22.2 Recommended density of calcium sulfosilicate: $D_x = 2972 \text{ kg/m}^3$

22.3 Comment:

It is obtained on heating mixtures of appropriate composition in air of ordinary humidity, and in this environment, it is stable up to 1298°C at which point it decomposes with loss of sulfur. The phase is also known as "sulfospurrite" on account of its similarity with spurrite, calcium silicocarbonate, with which it may form solid solution.

23 Tricalcium aluminate (cubic)

Formula: $\text{Ca}_3\text{Al}_2\text{O}_6, 3\text{CaO}\cdot\text{Al}_2\text{O}_3,$

Formula Weight: 270.19 g/mol

Space group: Pa3

Conventional cement shorthand notation: C_3A (cubic)

23.1 Cell Dimensions: $a = 15.263 \text{ \AA}$

Number of formula units in the unit cell: $Z = 24$

Density (calculated for cubic crystal system): 3028 kg/m^3

Reference: Mondal P. et al., Acta Crystallographica (1975), Vol. B31, 689-697

Cell parameters were determined from single crystal data, which were collected on a Nonius integrating camera using Cu $K\alpha$ radiation (1.5405 \AA); temperature of the measurement is not given.

Density calculated by Mondal et al.: 3027 kg/m^3

23.2 Cell Dimensions: $a = 15.262 \text{ \AA}$

Number of formula units in the unit cell: $Z = 24$

Density (calculated for cubic crystal system): 3030 kg/m^3

Reference: Swanson H.E. et al., National Bureau of Standards Circular 539 (1955), Vol. 5

Cell parameters of a synthetic sample were determined at 298 K, from X-ray powder patterns, using: a Guiner-type camera with Ni filter, an internal standard and Cu $K\alpha$ radiation (1.5405 \AA).

23.3 Cell Dimensions: $a = 15.268 \text{ \AA}$

Number of formula units in the unit cell: $Z = 24$

Density (calculated for cubic crystal system): 3030 kg/m^3

Reference: Lee, F. et.al, Journal of Applied Crystallography (1979), Vol. 12, 407- 410

X-ray examinations of the synthetic samples were done at 'room temperature'. Three graduated exposures were taken on a Guinier camera (Incentive Research and Development, Model XDC 700) with Cu $K\alpha$ radiation. The films were read with a scanning microdensitometer specially developed at Aberdeen for reading powder films; it had a relative accuracy of ± 3 parts in 10^5 .

23.4 Mean density of cubic tricalcium aluminate: $D_x = 3030 \text{ kg/m}^3$

23.5 Comment:

Tricalcium aluminate reacts strongly with water, and it is the most reactive of all the Portland clinker phases. Its rapid hydration to form phases of the type $\text{Ca}_2\text{AlO}_3(\text{OH}) \cdot n\text{H}_2\text{O}$ leads to the phenomenon of "flash set", and a large amount of heat is generated in the course of hydration.

24 Tricalcium aluminate (orthorombic)

Formula: $\text{Ca}_3\text{Al}_2\text{O}_6, 3\text{CaO} \cdot \text{Al}_2\text{O}_3,$

Formula Weight: 270.19 g/mol

Space group: Pcaa

Conventional cement shorthand notation: C_3A (orthorombic)

24.1 Cell Dimensions: $a = 10.873 \text{ \AA}, b = 10.851 \text{ \AA}, c = 15.115 \text{ \AA}$

Number of formula units in the unit cell: $Z = 12$

Density (calculated for orthorombic crystal system): 3023 kg/m^3

Reference: Lee, F. et.al, Journal of Applied Crystallography (1979), Vol. 12, 407- 410

X-ray examinations of the synthetic samples were done at 'room temperature'. Three graduated exposures were taken on a Guinier camera (Incentive Research and Development, Model XDC 700) with Cu $K\alpha$ radiation. The films were read with a scanning microdensitometer specially developed at Aberdeen for reading powder films; it had a relative accuracy of ± 3 parts in 10^5 .

24.2 Mean density of orthorhombic tricalcium aluminate: $D_x = 3023 \text{ kg/m}^3$

24.3 Comment:

The orthorhombic polymorph is stabilized by Na₂O. Cubic Ca₃Al₂O₆ is stable with contents of up to 2% by weight of Na₂O and the orthorhombic phase is stable between 3.5 and 4.5% Na₂O in the temperature range 293 to 1810 K. Thus the exact composition of the orthorhombic phase is not known but probably contained about 4 wt% sodium oxide (above 7.85 wt% Na₂O monoclinic form reported). The sodium substitution mechanism is believed to involve replacement of 1 calcium by 2 sodium, one of which occupies an otherwise vacant site. The mass change is however slight Ca = 40, 2 Na = 46, so the partial substitution does not much affect the density.

25 **Tetracalcium aluminoferrite (brownmillerite)**

Formula: Ca₂(Al,Fe)₂O₅·4CaO·Al₂O₃·Fe₂O₃

Formula Weight: 242.97 g/mol

Space group: Ibm2

Conventional cement shorthand notation: C₄AF

25.1 Cell Dimensions: $a = 5.584 \text{ \AA}$, $b = 14.60 \text{ \AA}$, $c = 5.374 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): **3684 kg/m³**

Reference: Colville A.A. et al., Acta Crystallographica (1971), Vol. B27, 2311-2315

Cell parameters were determined from single crystal data, which were collected on a Buerger-Supper-Pace-Picker automatic diffractometer using Cu K α radiation (1.5405 \AA); temperature of the measurement and origin of the sample were not specified.

Density calculated by Colville et al.: **3684 kg/m³**

25.2 Cell Dimensions: $a = 5.5672 \text{ \AA}$, $b = 14.521 \text{ \AA}$, $c = 5.349 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): **3732 kg/m³**

Reference: Morris M.C. et al., National Bureau of Standards Monograph 25 (1979), Vol.16, 186

Cell parameters were determined at 298 K, from X-ray powder patterns of the sample (origin - not specified), using: diffractometer equipped with a focusing graphite monochromator, Cu K α radiation (1.540598 \AA) and an internal standard (high purity 99.99% Si standard).

25.3 Mean density of tetracalcium aluminoferrite: $D_x = 3708 \text{ kg/m}^3$

25.4 Comment:

C₄AF is a member of a solid solution series based on C₂F (Ca₂Fe₂O₅). At 1 bar pressure, solid solution extends continuously from C₂F to ~ 70 mol % C₂A. The C₄AF composition is thus an arbitrary composition in this series and is not a discrete compound, as is often claimed. However a gradual symmetry change occurs in the solid solutions, from P₆m₂ at C₂F to Ibm2 at the C₄AF composition and higher Al substitutions. Data are only given for C₄AF composition free from other substituents: the ferrite in Portland cement is often a complex solid solution, containing significant Mg, Ti and Si. These substituents affect the crystallography; polytypism is also common. In general, substitution of Mg and Ti increase the resemblance of the overall structure to a perovskite-like arrangement.

TRICALCIUM SILICATE

Tricalcium silicate is the major, and characteristic, mineral constituent in Portland cement, responsible for setting and development of "early" strength.

At high temperatures, Ca_3SiO_5 is rhombohedral (R). However, in the course of cooling, a series of phase changes occurs spontaneously. This sequence is sensitive to solid solution. The lower temperature phases are distorted rhombohedral with actual monoclinic (M) or triclinic (T) symmetry. Several variants of M and T are known. It is agreed that impurity stabilizes the M and R phases to ambient, but that relatively high levels of doping, several wt%, may be required to obtain R at ambient. Therefore data given here for R are for the pure phase, but obtained at high temperature, while data for the other polymorphs and polymorphic variants are at ambient.

A summary of the polymorphs of tricalcium silicate, Ca_3SiO_5 , is as follows:

>1070°C :	R, Rhombohedral
1060-1070°C :	M3, Monoclinic
990-1060°C :	M2, Monoclinic
980-990°C :	M1, Monoclinic
920-980°C :	T3, Triclinic
620-920°C :	T2, Triclinic
<620°C	T1: Triclinic

26 R-Tricalcium silicate (at 1200°C)

Formula: $\text{Ca}_3\text{SiO}_5, 3\text{CaO} \cdot \text{SiO}_2$

Formula Weight: 228.32 g/mol

Space group: R3m

Conventional cement shorthand notation: R-C₃S

26.1 Cell Dimensions: $a = 7.135 \text{ \AA}$, $c = 25.586 \text{ \AA}$

Number of formula units in the unit cell: $Z = 9$

Density (calculated for hexagonal/trigonal crystal system): 3025 kg/m³

Reference: Nishi F. et al., Zeitschrift für Kristallographie (1984), Vol. 168, 197-212

Cell parameters were determined at temperature 1473 K from X-ray structure refinements of a synthetic phase, using a Syntex four circle diffractometer (equipped with graphite monochromator) and Mo K α radiation (0.7106 Å).

26.2 Recommended density of R-tricalcium silicate at 1200°C: $D_x = 3025 \text{ kg/m}^3$

27 R-Tricalcium silicate (stabilized with Sr)

Formula: $\text{Ca}_3\text{SiO}_5, 3\text{CaO} \cdot \text{SiO}_2$,

Formula Weight: 228.32 g/mol

Space group: R3m

Conventional cement shorthand notation: R-C₃S

27.1 Cell Dimensions: $a = 7.0767 \text{ \AA}$, $c = 24.974 \text{ \AA}$

Number of formula units in the unit cell: $Z = 9$

Density (calculated for hexagonal/trigonal crystal system): 3168 kg/m^3

Reference: Ilyinets A.M. et al., 8th International Congress on the Chemistry of Cement, Vol. 6, (1986), 489- 491

Cell parameters were determined from single-crystal X-ray structure refinements of synthetic crystals stabilized with Sr (Sr content was not given, hence the formula is shown without Sr); details of the measurement are not specified, but are believed to have been obtained at ambient temperature.

27.2 Recommended density of R-tricalcium silicate stabilized with Sr: $D_x = 3168 \text{ kg/m}^3$

28 M3-tricalcium silicate (stabilized with Mg)

Formula: $\text{Ca}_3\text{SiO}_5, 3\text{CaO} \cdot \text{SiO}_2$

Formula Weight: 228.32 g/mol

Space group: Cm

Conventional cement shorthand notation: M3-C₃S

28.1 Cell Dimensions: $a = 33.083 \text{ \AA}$, $b = 7.027 \text{ \AA}$, $c = 18.499 \text{ \AA}$, $\beta = 94.12^\circ$

Number of formula units in the unit cell: $Z = 36$

Density (calculated for monoclinic crystal system): 3182 kg/m^3

Reference: Nishi F. et al., Zeitschrift für Kristallographie (1985), Vol. 172, 297-314

Cell parameters were determined from X-ray structure refinements of a synthetic phase (mixture of C₃S, MgO and CaCl₂-flux component), using a Rigaku AFC-5 diffractometer equipped with a graphite monochromator and Mo K α radiation; temperature of the measurement is not specified but is believed to be at ambient temperature. The Mg content is not known and is therefore not shown in the formula.

28.2 Recommended density of M3-tricalcium silicate stabilized with Mg: $D_x = 3182 \text{ kg/m}^3$

29 M3-tricalcium silicate (less well ordered)

Formula: $\text{Ca}_3\text{SiO}_5, 3\text{CaO} \cdot \text{SiO}_2$,

Formula Weight: 228.32 g/mol

Space group: Cm

Conventional cement shorthand notation: M3-C₃S

29.1 Cell Dimensions: $a = 12.235 \text{ \AA}$, $b = 7.073 \text{ \AA}$, $c = 9.298 \text{ \AA}$, $\beta = 116.31^\circ$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for monoclinic crystal system): 3153 kg/m^3

Reference: Mumme W.G., Neues Jahrbuch für Mineralogie Monatshefte (1995), 145-160

Cell parameters were determined from single crystal X-ray structure refinements of a synthetic C₃S crystals (extracted from a sample of cement clinker provided by British Cement Association), using a Siemens AED diffractometer and Mo K α radiation (0.710687 \AA); temperature of the measurement is not specified but is believed to be at ambient

29.2 Recommended density of M3-tricalcium silicate (less well ordered): $D_x = 3153 \text{ kg/m}^3$

29.3 Comment:

At high temperatures tricalcium silicate is rhombohedral. However, in the course of cooling to ambient, several minor phase transformations occur. These lower the symmetry of C_3S . But the nature, sequence and temperature at which transformations occur are variable depending on amount and chemical nature of impurity. As a consequence, the phase obtained at ambient typically has a large unit cell although of course retaining a simple rhombohedral pseudocell. Moreover, quenched in disorder may persist. But while doubts may persist over the symmetry unit cell and order-disorder state of the product, it is likely that the density is not significantly affected and it is appropriate to use densities in the range $3168 \pm 15 \text{ kg/m}^3$. See also data for the triclinic (T1) phase.

30 T1-tricalcium silicate

Formula: $\text{Ca}_3\text{SiO}_5, 3\text{CaO} \cdot \text{SiO}_2$

Formula Weight: 228.32 g/mol

Space group: $P\bar{1}$

Conventional cement shorthand notation: T1- C_3S

30.1 Cell Dimensions: $a = 11.67 \text{ \AA}, b = 14.24 \text{ \AA}, c = 13.72 \text{ \AA}, \alpha = 105.5^\circ, \beta = 94.3^\circ, \gamma = 90.0^\circ$

Number of formula units in the unit cell: $Z = 18$

Density (calculated for triclinic crystal system): 3120 kg/m^3

Reference: Golovastikov N.I. et al., Soviet Physics Crystallography (1975), Vol. 20, 441-445

Cell parameters were determined from X-ray structure refinements of a synthetic phase (C_3S containing traces of $\text{MgO}, \text{Al}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{Ge}$), using an integrating Weissenberg camera and $\text{Mo K}\alpha$ radiation; temperature of the measurement is not specified but probably ambient.

30.2 Recommended density of T1-tricalcium silicate: $D_x = 3120 \text{ kg/m}^3$

30.3 Comment:

The reported density of T1, 3120 kg/m^3 is close to that reported for less well ordered C_3S (sheet - 29), density of 3153 kg/m^3 also to that of M3 (3182 kg/m^3). The preparations differ slightly in chemistry and it is not possible to deconvolute differences in density arising from composition and structure. Also, many cements contain mixtures of C_3S variants.

DICALCIUM SILICATE

Dicalcium silicate is a major component of Portland cement and is believed to be responsible for the development of strength at later ages.

As bar pressure and as e temperature changes, dicalcium silicate passes through several polymorphic states. The higher temperature polymorphs cannot normally be preserved by cooling to room temperature unless stabilized by substituent ions. Thus several of the polymorphs are normally encountered at ambient as impurity-stabilised phases. For pure dicalcium silicate, the sequence of phase transformations and stability range of polymorphs is shown below. Rapidly reversible phase transitions are marked *:

- * $>1425^\circ\text{C}$: $\alpha \text{ Ca}_2\text{SiO}_4$
- * $1160\text{-}1425^\circ\text{C}$: $\alpha'_H \text{ Ca}_2\text{SiO}_4$
- * $680\text{-}1160^\circ\text{C}$: $\alpha'_L \text{ Ca}_2\text{SiO}_4$

500-680°C: β Ca₂SiO₄
<500°C: γ Ca₂SiO₄

31 α -dicalcium silicate (stabilized to ambient with Ba)

Formula: Ca₂SiO₄, 2CaO·SiO₂,

Formula Weight: 172.24 g/mol

Space group: P6₃/mmc

Conventional cement shorthand notation: α -C₂S

31.1 Cell Dimensions: $a = 5.579 \text{ \AA}$, $c = 7.150 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 2968 kg/m³

Reference: Udagawa S. et al., Review of the 34th General Meeting, Cement Association of Japan, Tokyo (1980), 37

The original reference has not been consulted. These data are taken from: Taylor H.F.W., "Cement Chemistry" 2nd edition 1997, Thomas Telford Publishing, London, UK

31.2 Recommended density of α -dicalcium silicate: $D_x = 2968 \text{ kg/m}^3$

32 α'_H -dicalcium silicate (1200°C, stabilized with P₂O₅)

Formula: Ca₂SiO₄, 2CaO·SiO₂,

Formula Weight: 172.24 g/mol

Space group: Pcmn

Conventional cement shorthand notation: α'_H -C₂S

32.1 Cell Dimensions: $a = 9.49 \text{ \AA}$, $b = 5.59 \text{ \AA}$, $c = 6.85 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 3148 kg/m³

Reference: Saalfeld H. et al., American Mineralogist (1975), Vol. 60, 824-827

Cell parameters were determined at 1723 K, from single crystal X-ray structure refinements of a synthetic phase, using an integrating Weissenberg camera and Mo K α radiation.

32.2 Recommended density of α'_H - dicalcium silicate at 1723K : $D_x = 3148 \text{ kg/m}^3$

33 α'_L -dicalcium silicate (stabilized with Sr)

Formula: Ca₂SiO₄, 2CaO·SiO₂,

Formula Weight: 172.24 g/mol

Space group: Pcn₂1

Conventional cement shorthand notation: α'_L -C₂S

33.1 Cell Dimensions: $a = 20.871 \text{ \AA}$, $b = 9.496 \text{ \AA}$, $c = 5.6 \text{ \AA}$

Number of formula units in the unit cell: $Z = 12$

Density (calculated for orthorhombic crystal system): 3092 kg/m³

Reference: Ilyinets A.M. et al., 8th International Congress on the Chemistry of Cement, Vol. 6, (1986), 489- 491

Cell parameters were determined from single-crystal X-ray structure refinements of synthetic crystals stabilized with Sr. The Sr content is not given and details of the measurement are not specified.

33.2 Recommended density of α'_L -dicalcium silicate : $D_x = 3092 \text{ kg/m}^3$

34 β -dicalcium silicate

Formula: $\text{Ca}_2\text{SiO}_4, 2\text{CaO} \cdot \text{SiO}_2$,

Formula Weight: 172.24 g/mol

Space group: $P2_1/n$

Conventional cement shorthand notation: $\beta\text{-C}_2\text{S}$

34.1 Cell Dimensions: $a = 5.502 \text{ \AA}$, $b = 6.745 \text{ \AA}$, $c = 9.297 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 3326 kg/m^3

Reference: Jost K.H. et al., Acta Crystallographica (1977), Vol. B33, 1696-1700

Cell parameters were determined at 293 K, from single crystal X-ray structure refinements of synthetic crystals (grown from a CaCl_2 flux without other stabilizing reagents, at 1300°C), using a Hilger four circle diffractometer equipped with graphite monochromator and Mo $K\alpha$ radiation.

Density calculated by Jost et al: 3326 kg/m^3

34.2 Cell Dimensions: $a = 5.48 \text{ \AA}$, $b = 6.76 \text{ \AA}$, $c = 9.28 \text{ \AA}$, $\beta = 94.33^\circ$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for monoclinic crystal system): 3326 kg/m^3

Reference: Midgley C.M., Acta Crystallographica (1952), Vol. 5, 307-312

Cell parameters were determined from single crystal X-ray structure refinements of a synthetic phase, using an integrating Weissenberg camera; temperature of the measurement is not specified but probably ambient.

34.3 Mean density of β -dicalcium silicate: $D_x = 3326 \text{ kg/m}^3$

34.4 Comment:

See discussion on γ -dicalcium silicate, entry No. 35

35 γ -dicalcium silicate

Formula: $\text{Ca}_2\text{SiO}_4, 2\text{CaO} \cdot \text{SiO}_2$,

Formula Weight: 172.24 g/mol

Space group: Pbnm

Conventional cement shorthand notation: $\gamma\text{-C}_2\text{S}$

35.1 Cell Dimensions: $a = 5.081 \text{ \AA}$, $b = 11.224 \text{ \AA}$, $c = 6.778 \text{ \AA}$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for orthorhombic crystal system): 2960 kg/m^3

Reference: Udagawa S. et al., Cement Concrete Research (1980), Vol. 10, 139-144

Cell parameters were determined from powder diffraction X-ray structure refinements of a synthetic phase, using a Rigaku four circle diffractometer equipped with a graphite monochromator) and using Mo K α radiation; temperature of the measurement is not specified.

35.2 Recommended density of γ -dicalcium silicate : $D_x = 2960 \text{ kg/m}^3$

35.2 Comment:

α , α'_H and α'_L polymorphs of Ca_2SiO_4 are only stable at elevated temperatures. These polymorphs can only be obtained at ambient if stabilised by solid solution and consequently, uncertainty about the unit cell contents. The normal sequence of cooling results in a reconstructive transformation to the γ polymorph. Its structure is markedly less dense than those of the other polymorphs. However, formation of the γ polymorph during cooling is often slow; γ persists metastably to $\sim 650^\circ\text{C}$ at which temperature, a metastable transformation to β occurs. The beta phase has a slightly collapsed version of the α' type structure and its density, 3326 kg/m^3 , is markedly higher than for the γ polymorph. Preservation of α'_L below its normal stability limit, allowing β to form, is assisted by ions in solid solution: Mg, Al, Fe, etc. The resulting complex series of transformations are partially manifesting by a complex internal structure of beta marked by several types of twinning and also by exsolution of other phases as the belite host composition approaches the ideal Ca_2SiO_4 formula. Crystals are frequently strained as a result. Densities given are therefore approximate on account of the presence of exsolution lamellae in the β phase.

ALUMINATE - FERRITE - TRISUBSTITUENT PHASE (Aft)

36 Ettringite

Formula: $[\text{Ca}_3\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot (24+2)\text{H}_2\text{O}$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

Formula Weight: 1255,11 g/mol

Space group: P31c

Conventional cement shorthand notation: $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$

36.1 Cell Dimensions: $a = 11.23 \text{ \AA}$, $c = 21.50 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1775 kg/m^3

Reference: Struble L.J., 8th International Congress on the Chemistry of Cement, Vol. 6, (1986), 582-588

Cell parameters were determined at 'room temperature', from X-ray powder patterns of a synthetic ettringite, using an internal standard (high purity 99.99% Si standard); other details of the measurement are not specified.

36.2 Formula: $[\text{Ca}_3\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot (24+2)\text{H}_2\text{O}$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

Formula Weight: 1255,11 g/mol

Space group: P31c

Conventional cement shorthand notation: $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$

Cell Dimensions: $a = 11.23 \text{ \AA}$, $c = 21.44 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1780 kg/m^3

Reference: Swanson H.E. et al., National Bureau of Standards Circular 539 (1959), Vol. 8, 3

Cell parameters were determined at 300 K, from X-ray powder patterns of a sample (origin-not specified), using: a Guiner-type camera with Ni filter, an internal standard and Cu K α radiation (1.5405 Å).

Density calculated by Swanson et al.: **1754 kg/m³**

36.3 Formula: $[\text{Ca}_3\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot (24+2)\text{H}_2\text{O}, 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

Formula Weight: 1255,11 g/mol

Space group: P31c

Conventional cement shorthand notation: C₆A $\bar{3}$ H₃₂

Cell Dimensions: $a = 11.22 \text{ \AA}, c = 21.48 \text{ \AA}$

Number of formula units in the unit cell: Z = 2

Density (calculated for hexagonal/trigonal crystal system): 1780 kg/m³

Reference: Pöllmann H., 'Characterization of Different Water Contents of Ettringite and Kuzelite', proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

Cell parameters were determined by X-ray diffraction of a synthetic phase at 35 % relative humidity (CO₂ free conditions) at room temperature, using analytical X-Pert and Bruker D5000 diffractometers.

36.4 Formula: $[\text{Ca}_3\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot (24+2)\text{H}_2\text{O}, 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

Formula Weight: 1255,11 g/mol

Space group: P31c

Conventional cement shorthand notation: C₆A $\bar{3}$ H₃₂

Cell Dimensions: $a = 11.23 \text{ \AA}, c = 21.52 \text{ \AA}$

Number of formula units in the unit cell: Z = 2

Density (calculated for hexagonal/trigonal crystal system): 1774 kg/m³

Reference: Pöllmann H., Cement Concrete Research (1993), Vol. 23, 422 - 430

Cell parameters were determined from X-ray powder patterns of a synthetic sample made by the 'sucrose method' (using sugar to enhance solubilities) and measured at relative humidity 35%; an internal Si standard ($a_0 = 5.4308 \text{ \AA}$) and Cu K α radiation were used; measurements made at 297 K.

36.5 Cell Dimensions: $a = 11.23 \text{ \AA}, c = 21.49 \text{ \AA}$

Number of formula units in the unit cell: Z = 2

Density (calculated for hexagonal/trigonal crystal system): 1776 kg/m³

Reference: this study

Cell parameters were determined at ambient pressure and 303 K, from X-ray powder diffraction diagrams of a synthetic sample. Data were collected using a Bruker D8 advance powder diffractometer, Cu K α radiation (1.54060 Å). The angular range was set between 5-55° 2 θ . Unit cell parameters were refined from the powder diffraction patterns (71 selected reflections) using CELREF 2 software; mean square deviation: $M_D = 0.00816$

36.6 Mean density of ettringite: Dx = 1778 kg/m³

36.7 **Comment:**

Ettringite (shorthand: AFt (aluminate-ferrite-trisubstituted) type compound) typically grows in needle-shaped morphologies, hexagonal prisms, ect. Its water content ranges between 30 and 32 H₂O and water within this range is zeolitic: it can be gained or lost without significant change in structure or cell dimensions. Consequently, there is always slight uncertainty about the water contents, and hence the density. The calculations assume 32 H₂O.

Water contents below 30 H₂O are also reported but Zhou and Glasser showed that the structure degraded and 'metaettringite' was obtained [1]. Pöllmann describes a 36 H₂O variant at 100% relative humidity [2]

See also the carbonate and iron analogues included in this compilation.

[1] Zhou Q., Glasser F.P, Lachowski E.E., Cement and Concrete Research (2004), Vol. 34, 703- 710

[2] Pöllmann H, Proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

36.8a **Ettringite low water content**

Formula: [Ca₃Al(OH)₆]₂(SO₄)₃·24 H₂O, 3CaO·Al₂O₃·3CaSO₄·30H₂O

Formula Weight: 1219,11 g/mol

Space group: P31c

Conventional cement shorthand notation: C₆A $\bar{3}$ H₃₀

36.8a₁ Cell Dimensions: $a = 11.14 \text{ \AA}$, $c = 21.30 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1768 kg/m³

Reference: Pöllmann H, 'Characterization of Different Water Contents of Ettringite and Kuzelite', proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

Cell parameters were determined by X-ray diffraction of synthetic, acetone-dried sample (CO₂ free conditions) at room temperature, using analytical X-Pert and Bruker D5000 diffractometers.

36.8a₂ Recommended density of ettringite with 30 H₂O: $D_x = 1768 \text{ kg/m}^3$

36.8b **Ettringite with high water content**

Formula: [Ca₃Al(OH)₆]₂(SO₄)₃·(24+6) H₂O, 3CaO·Al₂O₃·3CaSO₄·36H₂O

Formula Weight: 1327,11 g/mol

Space group: P31c

Conventional cement shorthand notation: C₆A $\bar{3}$ H₃₆

36.8b₁ Cell Dimensions: $a = 11.26 \text{ \AA}$, $c = 21.56 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1861 kg/m³

Reference: Pöllmann H, 'Characterization of Different Water Contents of Ettringite and Kuzelite', proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

Cell parameters were determined by X-ray diffraction of synthetic, (100% relative humidity, CO₂ free conditions) at room temperature, using analytical X-Pert and Bruker D5000 diffractometers.

36.8b₂ Cell Dimensions: $a = 11.255 \text{ \AA}$, $c = 21.54 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1865 kg/m^3

Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic wet sample (100% relative humidity) covered with Mylar foil to prevent water loss and carbonation. Data were collected by a Bruker D8 advance powder diffractometer, using Cu K α radiation (1.54060 \AA). The angular range was set between $5\text{-}55^\circ$ 2θ . Unit cell parameters were refined from the powder diffraction patterns (38 selected reflections) using CELREF 2 software, mean square deviation: $M_D = 0.00918$

36.8b₃ Mean density of ettringite with 36 H₂O: $D_x = 1863 \text{ kg/m}^3$

37 'Carbonate Ettringite', 'CO₃-Aft'

Formula: $[\text{Ca}_3\text{Al}(\text{OH})_6]_2(\text{CO}_3)_3 \cdot (24+2)\text{H}_2\text{O}$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCO}_3 \cdot 32\text{H}_2\text{O}$

Formula Weight: 1146.94 g/mol

Space group: P31c (determined using X-ray powder pattern)

Conventional cement shorthand notation: $\text{C}_6\text{A}\bar{\text{C}}_3\text{H}_{32}$

37.1 Cell Dimensions: $a = 10.834 \text{ \AA}$, $c = 21.25 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1763 kg/m^3

Reference: Struble L.J., 8th International Congress on the Chemistry of Cement, Vol. 6, (1986), 582- 588

Cell parameters were determined at 'room temperature', from X-ray powder patterns of a synthetic ettringite, using an internal standard (high purity 99.99% Si standard); other details of the measurement are not specified.

37.2 Cell Dimensions: $a = 10.851 \text{ \AA}$, $c = 21.257 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1757 kg/m^3

Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic sample. Data were collected by a Bruker D8 advance powder diffractometer (xx reflections), using Cu K α radiation (1.54060 \AA). The angular range was set between $5\text{-}55^\circ$ 2θ . Unit cell parameters were refined from the powder diffraction patterns (35 selected reflections), using CELREF 2 software, mean square deviation: $M_D = 0.00818$

37.3 Mean density of carbonate ettringite: $D_x = 1760 \text{ kg/m}^3$

37.4 Comment:

Carbonate ettringite appears to be stabilized by low temperatures, close to 0°C. It accommodates limited sulfate in solid solution. However sulfate ettringite can accommodate up to ~ 50 mol % of “carbonate ettringite” at 20°-25°C.

38 ‘Iron Ettringite’

Formula: $[\text{Ca}_3\text{Fe}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot (24+2)\text{H}_2\text{O}$, $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$

Formula Weight: 1312.84 g/mol

Space group: P31c (determined using X- ray powder pattern)

Conventional cement shorthand notation: $\text{C}_6\text{F}\bar{3}\text{H}_{32}$

38.1 Cell Dimensions: $a = 11.182 \text{ \AA}$, $c = 22.008 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1830 kg/m^3

Reference: Struble L.J., 8th International Congress on the Chemistry of Cement, Vol. 6, (1986), 582- 588

Cell parameters were determined at ‘room temperature’, from X-ray powder patterns of a synthetic ettringite, using an internal standard (high purity 99.99% Si standard); other details of the measurement-not specified.

38.2 Cell Dimensions: $a = 11.1817 \text{ \AA}$, $c = 22.007 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1830 kg/m^3

Reference: McMurdie et.al, Powder Diffraction, Vol. 2 (1), (1987), 41- 52

Cell parameters were determined at ‘room temperature’, from X-ray powder patterns of a synthetic ettringite.

38.3 Mean density of iron ettringite: $D_x = 1830 \text{ kg/m}^3$

38.4 Comment:

The extent of iron substitution in the ettringite of Portland cement is believed to be small and we have not found reports of natural ettringite containing much Fe. The extent of solid solution between Al/OH- ettringite and Fe/OH- ettringite is not known.

39 Thaumaside

Formula: $\text{Ca}_3(\text{SO}_4)(\text{CO}_3)[\text{Si}(\text{OH})_6] \cdot 12\text{H}_2\text{O}$

Formula Weight: 622.62 g/mol

Space group: $\text{P}\bar{6}_3$

Conventional cement shorthand notation: $\text{C}_3\text{S}\bar{6}\bar{3}\text{H}_{15}$

39.1 Cell Dimensions: $a = 11.030 \text{ \AA}$, $c = 10.396 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): 1888 kg/m^3

Reference: Effenberger H. et al., Neues Jahrbuch für Mineralogie Monatshefte (1983), 60-68

Cell parameters were determined at 293 K, from single-crystal X-ray structure refinements of natural crystals (locality: Langban, Sweden), using a Syntex four circle diffractometer equipped with a graphite monochromator and Mo K α radiation (0.7107 Å).

Density calculated by Effenberger H. et al.: **1876 kg/m³**

39.2 Cell Dimensions: $a = 11.0538 \text{ \AA}$, $c = 10.4111 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): **1876 kg/m³**

Reference: Jacobsen S.D. et al., *Physics and Chemistry of Minerals*, (2003), Vol. 30, 321-329

Cell parameters were determined at 298 K, from single-crystal X-ray structure refinements of natural thaumasite (locality: not specified), using a Siemens P4 four circle diffractometer equipped with a graphite monochromator and Mo K α radiation (0.7109 Å)

Density calculated by Jacobsen S.D. et al: **1876 kg/m³**

A discrepancy exists between data presented in Gaines V.R. et al., *Dana's New Mineralogy*, Eighth edition (1997); the density data for thaumasite on page 671 differ from those on page 568 although both appear to rest on the same dataset.

39.3 Mean density of thaumasite: Dx = 1882 kg/m³

39.4 Comment.

Thaumasite is a naturally occurring mineral, usually found in hydrothermally- altered rocks, as a late stage, low temperature mineral. It is very similar to ettringite: limited solid solutions occur between the two minerals[1]. Thaumasite is also well known as a product of sulfate and carbonate attack on concrete. Thaumasite is noteworthy because it contains Si(OH)₆ groups yet does not require high pressure for its formation. The phase relations and extent of solid solution between thaumasite, carbonate ettringite and sulfate ettringite are not known in detail.

[1] Macphee D.E. et al., *Cement and Concrete Research* (2004), Vol. 34, Issue 9, 1591-1598

ALUMINATE-FERRITE-MONOSUBSTITUENT PHASE (AFm)

Phases in this family are comprised of a layer structure containing the basic unit Ca₂(Al,Fe^{III})(OH)₆⁺. The positive charge is balanced in interlayer positions by either monovalent (OH,Cl) or divalent (SO₄²⁻, etc.) ions. Additional water is present in the interlayer. The phases listed here are those the most relevant to cement hydration but others occur in nature, for example with Fe and Cr(III) in the layer. Solid solution between different AFm phases is always incomplete when the substituent anion differs in charge and may be incomplete even when the charge is the same, as with (OH, Cl). The water content much affects the c axis spacing, for example, C₄AH₁₉ and C₄AH₁₃. However the preservation for analysis is often difficult: C₄AH₁₉ readily loses water and often appears in XRD as C₄AH₁₃ having lost water in the course of specimen preparation and handling. The stacking of layers can differ leading to polytypism. The polytypes have not been classified but it is believed that while the existence of different stackings may affect the true symmetry and intensity of X-ray reflections, its effect on density is not significant.

40 Tetracalcium aluminate-13-hydrate (hydroxy AFm)

Formula: $\text{Ca}_4\text{Al}_2(\text{OH})_{14}\cdot 6\text{H}_2\text{O}, 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$

Formula Weight: 560.47 g/mol

Space group: R--

Conventional cement shorthand notation: C_4AH_{13}

40.1 Cell Dimensions: $a = 5.752 \text{ \AA}, c = 95.27 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2046 kg/m^3

Reference: Fischer R. et al., Cement Concrete Research (1982), Vol. 12, 517-526

Cell parameters were determined at 295 K, from X-ray powder diffraction diagrams of a synthetic phase (all chemicals used were of reagent quality), using an internal standard (high purity 99.99% Si standard); when single crystals were available, lattice constants were determined using a Weissenberg camera. Precise determination of space group was not possible.

40.2 Cell Dimensions: $a = 5.758 \text{ \AA}, c = 95.226 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2042 kg/m^3

Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic sample. Data were collected by a Bruker D8 advance powder diffractometer, using Cu $K\alpha$ radiation (1.54060 \AA). The angular range was set between $5\text{-}55^\circ$ 2θ . Unit cell parameters were refined from the powder diffraction patterns (22 selected reflections) using CELREF 2 software. Refinement was made for the space group $R\bar{3}$, mean square deviation: $M_D = 0.02030$

40.3 Mean density of hydroxy-AFm: $D_x = 2044 \text{ kg/m}^3$

41 Tetracalcium ferrite-13-hydrate (Fe-hydroxy AFm)

Formula: $\text{Ca}_4\text{Fe}_2(\text{OH})_{14}\cdot 6\text{H}_2\text{O}, 4\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot 13\text{H}_2\text{O}$

Formula Weight: 618.19 g/mol

Space group: R--

Conventional cement shorthand notation: C_4FH_{13}

41.1 Cell Dimensions: $a = 5.89 \text{ \AA}, c = 7.902 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1/2$

Density (calculated for hexagonal/trigonal crystal system): 2162 kg/m^3

Reference: Schwiete H.E. et al., Zement-Kalk-Gips (1964), Vol. 17, 379-386

Cell parameters were determined at 'room temperature', from X-ray powder pattern of a synthetic phase.

41.2 Recommended density of Fe-hydroxy AFm: $D_x = 2162 \text{ kg/m}^3$

41.3 Comment:

Believed to form a continuous series of solid solutions with $\text{Ca}_4\text{Al}_2(\text{OH})_{14}\cdot 6\text{H}_2\text{O}$. As in the corresponding system with Al_2O_3 , the phase was coexisting in solution with the 19- hydrate phase.

42 α_1 -Tetracalcium aluminate-19-hydrate

Formula: $\text{Ca}_4\text{Al}_2(\text{OH})_{14}\cdot 12\text{H}_2\text{O}, 4\text{CaO}\cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$

Formula Weight: 668.48 g/mol

Space group: $R\bar{3}c$ or $R3c$

Conventional cement shorthand notation: $\alpha 1 - \text{C}_4\text{AH}_{19}$

42.1 Cell Dimensions: $a = 5.77 \text{ \AA}, c = 64.08 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 1804 kg/m^3

Reference: Aruja E., Acta Crystallographica (1961), Vol. 14, 1213-1216

Cell parameters were determined at 'room temperature', from X-ray powder diffraction diagrams of a synthetic phase, using a Guiner-type focusing camera; specimens were made in a glove box under controlled atmospheric conditions and exposed to X-rays in a sealed envelope to avoid carbonation.

Density calculated by Aruja: 1804 kg/m^3

42.2 Recommended density of α_1 -Tetracalcium aluminate-19-hydrate: $D_x = 1804 \text{ kg/m}^3$

43 α_2 -Tetracalcium aluminate-19-hydrate

Formula: $\text{Ca}_4\text{Al}_2(\text{OH})_{14}\cdot 12\text{H}_2\text{O}, 4\text{CaO}\cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$

Formula Weight: 668.48 g/mol

Space group: $P6_3/m$ or $P6_322$

Conventional cement shorthand notation: $\alpha 2 - \text{C}_4\text{AH}_{19}$

43.1 Cell Dimensions: $a = 5.77 \text{ \AA}, c = 21.37 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1$

Density (calculated for hexagonal/trigonal crystal system): 1802 kg/m^3

Reference: Aruja E., Acta Crystallographica (1961), Vol. 14, 1213-1216

Cell parameters were determined at 'room temperature', from X-ray powder diffraction diagrams of a synthetic phase, using a Guiner-type focusing camera; specimens were made in a glove box under controlled atmospheric conditions and exposed to X-rays in a sealed capsule to avoid carbonation.

Density calculated by Aruja: 1802 kg/m^3

43.2 Recommended density of α_2 -Tetracalcium aluminate-19-hydrate: $D_x = 1802 \text{ kg/m}^3$

43.3 Comment:

C_4AH_{19} is structurally derived from C_4AH_{13} by the addition of an extra H_2O molecules.

Two polytypes (α_1 and α_2) are distinguished.

44 Tetracalcium aluminate monosulfate-12-hydrate (monosulfoaluminate)

Formula: $\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 6\text{H}_2\text{O}, 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$

Formula Weight: 622.52 g/mol

Space group: $R\bar{3}$

Conventional cement shorthand notation: $\text{C}_4\text{A}\bar{3}\text{H}_{12}$

44.1 Cell Dimensions: $a = 5.758 \text{ \AA}, c = 26.794 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3/2$

Density (calculated for hexagonal/trigonal crystal system): 2020 kg/m³

Reference: Allmann R., Neues Jahrbuch für Mineralogie Monatshefte (1977), 136-144

Cell parameters were determined at 'room temperature', from single-crystal X-ray structure refinements of a synthetic phase, using a Philips PW 1100 four circle diffractometer (equipped with graphite monochromator) and Mo K α radiation.

Density calculated by Allmann R: 2020 kg/m³

44.2 Cell Dimensions: $a = 5.76 \text{ \AA}, c = 53.66 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2014 kg/m³

Reference: Pöllman H. et al., American Mineralogist (1998), 909 (abstract only)

Cell parameters were determined at room temperature, from X-ray powder pattern of a synthetic phase, using Cu K α radiation.

44.3 Cell Dimensions: $a = 5.76 \text{ \AA}, c = 26.79 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3/2$

Density (calculated for hexagonal/trigonal crystal system): 2014 kg/m³

Reference: Pöllmann H, 'Characterization of Different Water Contents of Ettringite and Kuzelite', proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

Cell parameters were determined by X-ray diffraction of synthetic, sample at 25°C (CO₂ free conditions), using analytical X-Pert and Bruker D5000 diffractometers.

44.4 Cell Dimensions: $a = 5.763 \text{ \AA}, c = 53.661 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2014 kg/m³

Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic sample. Data were collected by a Bruker D8 advance powder diffractometer, using CuK α radiation (1.54060 Å). The angular range was set between 5-55° 2 θ . Unit cell parameters were refined from the powder diffraction patterns (23 selected reflections) using CELREF 2; software gave a mean square deviation: $M_D = 0.01361$

44.5 Mean density of monosulfoaluminate (12 H₂O): $D_x = 2015 \text{ kg/m}^3$

44.6 Monosulfoaluminate with high water content (14 H₂O)

Formula: Ca₄Al₂(SO₄)(OH)₁₂·8H₂O, 3CaO·Al₂O₃·CaSO₄·14H₂O

Formula Weight: 658.52 g/mol

Space group: R $\bar{3}$

Conventional cement shorthand notation: C₄A $\bar{3}$ H₁₄

Cell Dimensions: $a = 5.748 \text{ \AA}$, $c = 28.69 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3/2$

Density (calculated for hexagonal/trigonal crystal system): 1998 kg/m³

Reference: Pöllmann H, 'Characterization of Different Water Contents of Ettringite and Kuzelite', proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

Cell parameters were determined by X-ray diffraction of synthetic phase at 25°C (below 100% relative humidity, CO₂-free conditions), using analytical X-Pert and Bruker D5000 diffractometers.

44.7 Recommended density of monosulfoaluminate (14 H₂O): D_x = 1998 kg/m³

44.8 Monosulfoaluminate with high water content (16 H₂O)

Formula: Ca₄Al₂(SO₄)(OH)₁₂·10H₂O, 3CaO·Al₂O₃·CaSO₄·16H₂O

Formula Weight: 694.52 g/mol

Space group: R $\bar{3}$

Conventional cement shorthand notation: C₄A $\bar{3}$ H₁₆

Cell Dimensions: $a = 5.73 \text{ \AA}$, $c = 30.67 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3/2$

Density (calculated for hexagonal/trigonal crystal system): 1983 kg/m³

Reference: Pöllmann H, 'Characterization of Different Water Contents of Ettringite and Kuzelite', proc. XII International Congress on the Chemistry of Cement, 8-13 July 2007, Montreal, Canada

Cell parameters were determined by X-ray diffraction of synthetic phase at 25°C (100% relative humidity, CO₂-free conditions), using analytical X-Pert and Bruker D5000 diffractometers.

44.9 Recommended density of monosulfoaluminate (16 H₂O): D_x = 1983 kg/m³

44.10 Comment:

Monosulfoaluminate forms solid solutions in which the SO₄²⁻ is partly replaced by OH⁻ at ~ 25°C; solid solution extends to ~ 50 mole % replacement.

45 Tetracalcium ferrite monosulfate-12-hydrate (Fe-monosulfoaluminate)

Formula: Ca₄Fe₂(SO₄)(OH)₁₂·6H₂O, 3CaO·Fe₂O₃·CaSO₄·12H₂O

Formula Weight: 680.24 g/mol

Space group: R $\bar{3}$

Conventional cement shorthand notation: C₄F $\bar{3}$ H₁₂

- 45.1 Cell Dimensions:** $a = 5.888 \text{ \AA}$, $c = 26.625 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3/2$
Density (calculated for hexagonal/trigonal crystal system): 2119 kg/m^3
Reference: Kuzel H.J., Zement-Kalk-Gips (1968), Vol. 21, 463-469

Cell parameters were determined at 298 K, from X-ray powder pattern of a synthetic phase (prepared under CO₂-free conditions) and using an internal standard (high purity 99.99% Si).

- 45.2 Cell Dimensions:** $a = 5.889 \text{ \AA}$, $c = 26.669 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3/2$
Density (calculated for hexagonal/trigonal crystal system): 2115 kg/m^3
Reference: Ecker M. et al., Mineralogical Institute of University, Erlagen, Germany, PDF 41-1472, ICDD, Grant in Aid (1991)

Cell parameters were determined at 'room temperature', from X-ray powder pattern of a synthetic phase using diffractometer with Ni filter and Cu K α radiation (1.5405 \AA).

- 45.3 Mean density of Fe-monosulfoamate:** $D_x = 2117 \text{ kg/m}^3$

- 45.4 Comment:**
C₄F $\bar{3}$ H₁₂ forms solid solutions with C₄A $\bar{3}$ H₁₂. Solid solution is continuous at 100°C but at 25 and 50°C, a miscibility gap exists; at ~25°C, solid solution extends to ~50 mole %.

46 Dicalcium aluminate monosilicate-8-hydrate (strätlingite)

Formula: Ca₂Al₂SiO₇ · 8H₂O, 2CaO · Al₂O₃ · SiO₂ · 8H₂O
Formula Weight: 418.21 g/mol
Space group: R $\bar{3}$ or R 3
Conventional cement shorthand notation: C₂ASH₈

- 46.1 Cell Dimensions:** $a = 5.747 \text{ \AA}$, $c = 37.64 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3$
Density (calculated for hexagonal/trigonal crystal system): 1936 kg/m^3
Reference: Kuzel H.J., Neues Jahrbuch für Mineralogie Monatshefte (1976), 319-325

Cell parameters were determined at 'room temperature' from single-crystal X-ray structure refinements of a synthetic phase (crystals were prepared by hydration of a glass of the gehlenite composition), using: X-ray rotation and precession cameras, Cu K α radiation and an internal standard (high purity 99.99% Si standard).

Density calculated by Kuzel: 1940 kg/m^3

- 46.2 Cell Dimensions:** $a = 5.737 \text{ \AA}$, $c = 37.59 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3$
Density (calculated for hexagonal/trigonal crystal system): 1948 kg/m^3
Reference: Hentschel G. et al., Neues Jahrbuch für Mineralogie Monatshefte (1976), 326-330

Cell parameters were determined at room temperature, from single-crystal X-ray structure refinements of a natural mineral (limestone inclusion of a basalt from the Bellerberg /Mayen region (Germany)), using X-ray rotation and precession cameras and Cu K α radiation.

Density calculated by Kuzel et al: **1950 kg/m³**

46.3 Cell Dimensions: $a = 5.745 \text{ \AA}$, $c = 37.77 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): **1930 kg/m³**

Reference: Rinaldi R. et al., European Journal of Mineralogy (1990), Vol. 2, 841-849

Cell parameters were determined at 'room temperature', from single-crystal X-ray structure refinements of natural crystals (locality: Montalto di Castro, Italy), using a Philips PW 1100 four circle diffractometer equipped with a graphite monochromator and Mo K α radiation.

Density calculated by Rinaldi R. et al.: **1960 kg/m³**

46.4 Cell Dimensions: $a = 5.747 \text{ \AA}$, $c = 37.638 \text{ \AA}$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for hexagonal/trigonal crystal system): **1936 kg/m³**

Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic sample. Data were collected using a Bruker D8 advance powder diffractometer, CuK α radiation (1.54060 \AA). The angular range was set between 5-55 $^\circ$ 2 θ . Unit cell parameters were refined from the powder diffraction patterns (29 selected reflections) using CELREF 2 software; mean square deviation: $M_D = 0.01183$.

46.5 Mean density of strätlingite: $D_x = 1937 \text{ kg/m}^3$

46.6 Comment:

Has been called "gehlenite hydrate. It is an AFm phase including silicate anions in interlayer positions. The identity of natural phases including stratlingite and vertumnite, with the synthetic is not proven. Gehlenite hydrate is a commonly- occurring constituent of lime- pozzolan, cement - pozzolan and slag-blended cements. Its low physical density suggests that it is partly responsible for the good space filling and low permeability characteristic of well- cured blends.

47 Tetracalcium aluminate carbonate-11-hydrate (monocarboaluminate)

Formula: $\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH})_{12} \cdot 5\text{H}_2\text{O}$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$

Formula Weight: 568.29 g/mol

Space group: $P\bar{1}$ or $P1$

Conventional cement shorthand notation: $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$

47.1 Cell Dimensions: $a = 5.781 \text{ \AA}$, $b = 5.744 \text{ \AA}$, $c = 7.855 \text{ \AA}$, $\alpha = 92.61^\circ$, $\beta = 101.96^\circ$, $\gamma = 120.09^\circ$

Number of formula units in the unit cell: $Z = 1/2$

Density (calculated for triclinic crystal system): **2170 kg/m³**

Reference: Fischer R. et al., Cement Concrete Research (1982), Vol. 12, 517-525

Cell parameters were determined at 295 K, from X-ray powder diffraction diagrams of a synthetic phase (all chemicals used were of reagent quality), using an internal standard (high purity 99.99% Si standard); when single crystals were available, lattice constants were determined using rotation and Weissenberg methods.

- 47.2 Cell Dimensions:** $a = 5.742 \text{ \AA}$, $b = 5.744 \text{ \AA}$, $c = 15.09 \text{ \AA}$, $\alpha = 92.29^\circ$, $\beta = 87.45^\circ$, $\gamma = 119.54^\circ$
Number of formula units in the unit cell: $Z = 1$
Density (calculated for triclinic crystal system): 2182 kg/m^3
Reference: Renaudin G. et al., Cement Concrete Research (1999), Vol. 29, 63-69

Cell parameters were determined at 293 K, from a single crystal (prepared by hydrothermal synthesis), mounted in an automatic Nonius diffractometer.

- 47.3 Cell Dimensions:** $a = 5.768 \text{ \AA}$, $b = 5.742 \text{ \AA}$, $c = 7.862 \text{ \AA}$, $\alpha = 92.68^\circ$, $\beta = 101.89^\circ$, $\gamma = 120.01^\circ$
Number of formula units in the unit cell: $Z = 1/2$
Density (calculated for triclinic crystal system): 2174 kg/m^3
Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic phase. Data were collected by a Bruker D8 advance powder diffractometer, using $\text{CuK}\alpha$ radiation (1.54060 \AA). The angular range was set between $5\text{-}55^\circ$ 2θ . Unit cell parameters were refined from the powder diffraction patterns (27 selected reflections) using CELREF 2 software; mean square deviation: $M_D = 0.01253$.

- 47.4 Mean density of monocarboaluminate:** $D_x = 2175 \text{ kg/m}^3$

48 Tetracalcium ferrite carbonate-12-hydrate (Fe-monocarboaluminate)

Formula: $\text{Ca}_4\text{Fe}_2(\text{CO}_3)(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$, $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{CaCO}_3\cdot 12\text{H}_2\text{O}$
Formula Weight: 644.11 g/mol
Space group: $R\bar{3}c$
Conventional cement shorthand notation: $\text{C}_4\text{F}\bar{\text{C}}\text{H}_{12}$

- 48.1 Cell Dimensions:** $a = 5.917 \text{ \AA}$, $c = 47.679 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3$
Density (calculated for hexagonal/trigonal crystal system): 2219 kg/m^3
Reference: Simon G. , Erlagen, Germany, Thesis, (1984)

Cell parameters were determined at room temperature, from X- ray powder patterns of a synthetic sample; using a diffractometer equipped $\text{Cu K}\alpha$ radiation (1.5405 \AA)

- 48.2 Recommended density of Fe- monocarboaluminate:** $D_x = 2219 \text{ kg/m}^3$

49 Tetracalcium aluminate hemcarbonate-12-hydrate (hemicarboaluminate)

Formula: $\text{Ca}_4\text{Al}_2(\text{CO}_3)_{0.5}(\text{OH})_{13}\cdot 5.5\text{H}_2\text{O}$
Formula Weight: 564.45 g/mol
Space group: $R\bar{3}c$ or $R3c$
Conventional cement shorthand notation: $\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_{12}$

- 49.1 Cell Dimensions:** $a = 5.77 \text{ \AA}$, $c = 49.159 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3$
Density (calculated for hexagonal/trigonal crystal system): 1984 kg/m^3
Reference: Fischer R. et al., Cement Concrete Research (1982), Vol. 12, 517-526

Cell parameters were determined at 295 K, from X-ray powder diffraction diagrams of a synthetic phase (all chemicals used were of reagent quality), using an internal standard (high purity 99.99% Si); when single crystals were available, lattice constants were determined using rotation and Weissenberg cameras.

- 49.2 Cell Dimensions:** $a = 5.761 \text{ \AA}$, $c = 49.252 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3$
Density (calculated for triclinic crystal system): 1986 kg/m^3
Reference: this study

Cell parameters were determined at ambient pressure, 303 K, from X-ray powder diffraction diagrams of a synthetic phase. Data were collected by a Bruker D8 advance powder diffractometer, using $\text{CuK}\alpha$ radiation (1.54060 \AA). The angular range was set between $5\text{-}55^\circ$ 2θ . Unit cell parameters were refined from the powder diffraction patterns (22 selected reflections) using CELREF 2 software mean square deviation: $M_D = 0.01904$.

- 49.3 Mean density of hemicarboaluminate:** $D_x = 1985 \text{ kg/m}^3$

49.4 Comment:

Most commercial Portland cements contain sufficient carbonate to form hemicarboaluminate. However, cements blended with calcium carbonate normally contain monocarboaluminate, which is more stable than AFm phases with $(\text{OH}, \text{SO}_4^{2-})$.

50 Dicalcium aluminate-8-hydrate

Formula: $\text{Ca}_2\text{Al}_2(\text{OH})_{10}\cdot 3\text{H}_2\text{O}$, $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$
Formula Weight: 358.23 g/mol
Space group: $R\bar{3}c$
Conventional cement shorthand notation: C_2AH_8

- 50.1 Cell Dimensions:** $a = 5.74 \text{ \AA}$, $c = 10.7 \text{ \AA}$
Number of formula units in the unit cell: $Z = 1$
Density (calculated for hexagonal/trigonal crystal system): 1950 kg/m^3
Reference: Scheller T. et al., 6th International Congress on the Chemistry of Cement (Moscow) (1976), Vol. 2, part 1, 217

Reference cannot be traced.

- 50.2 Recommended density of dicalcium aluminate-8-hydrate:** $D_x = 1950 \text{ kg/m}^3$

51 α -Tetracalcium aluminate dichloride-10-hydrate (Friedel's salt)

Formula: $\text{Ca}_4\text{Al}_2(\text{Cl})_2(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$, $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{CaCl}_2\cdot 10\text{H}_2\text{O}$
Formula Weight: 561.34 g/mol
Space group: $C2/c$ or Cc
Conventional cement shorthand notation: $\alpha\text{-C}_3\text{A CaCl}_2 \text{H}_{10}$

- 51.1 Cell Dimensions:** $a = 9.98 \text{ \AA}$, $b = 5.74 \text{ \AA}$, $c = 16.79 \text{ \AA}$, $\beta = 110.2^\circ$
Number of formula units in the unit cell: $Z = 2$
Density (calculated for monoclinic crystal system): 2065 kg/m^3
Reference: Kuzel H.J., Neues Jahrbuch für Mineralogie Monatshefte (1966), 193-200

Cell parameters were determined at 298 K, from single-crystal X-ray structure refinements of synthetic crystals (prepared hydrothermally), using a Philips Norelco diffractometer.

51.2 Cell Dimensions: $a = 9.979 \text{ \AA}$, $b = 5.751 \text{ \AA}$, $c = 16.320 \text{ \AA}$, $\beta = 104.53^\circ$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for monoclinic crystal system): 2056 kg/m^3

Reference: Terzis A. et al., Zeitschrift für Kristallographie (1981), 29-34

Cell parameters were determined at room temperature, from single-crystal X-ray structure refinements of synthetic crystals.

51.3 Cell Dimensions: $a = 9.960 \text{ \AA}$, $b = 5.744 \text{ \AA}$, $c = 16.268 \text{ \AA}$, $\beta = 104.471^\circ$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for monoclinic crystal system): 2068 kg/m^3

Reference: Rapin J.P. et al., Cement and Concrete Research (2002), Vol. 32, 513-519

Cell parameters were determined at 20°C , from crystalline samples prepared by hydrothermal synthesis. Compound was studied by synchrotron radiation using the WDIF4C powder diffractometer on the DW22 beamline of LURE.

51.4 Cell Dimensions: $a = 9.955 \text{ \AA}$, $b = 5.748 \text{ \AA}$, $c = 16.754 \text{ \AA}$, $\beta = 110.02^\circ$

Number of formula units in the unit cell: $Z = 2$

Density (calculated for monoclinic crystal system): 2070 kg/m^3

Reference: this study

Cell parameters were determined at ambient pressure, 300 K, from X-ray powder diffraction diagrams of a synthetic phase. Data were collected using a Bruker D8 advance powder diffractometer, $\text{CuK}\alpha$ radiation (1.54060 \AA). The angular range was set between $5-55^\circ 2\theta$. Unit cell parameters were refined from the powder diffraction patterns (23 selected reflections) using CELREF 2 software.

51.5 Mean density of Friedel's salt: $D_x = 2064 \text{ kg/m}^3$

51.6 Comment:

The monoclinic low temperature phase is transforms to a trigonal phase at $28 \pm 2^\circ \text{C}$, therefore two phases (α and β) are distinguished. Friedel's salt - $\text{Ca}_4\text{Al}_2(\text{Cl})_2(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$ ($\text{C}_3\text{A CaCl}_2 \text{H}_{10}$) is a product of chloride interaction with a cement paste [1-2].

[1] Nielsen E., Denmark, DTU, Ph.D thesis (2004)

[2] Glasser F.P, Kindness A., Stronach A., Stability and solubility relationships in AFm phases: Part I. Chloride, sulfate and hydroxide, Cement and Concrete Research (1999), Vol. 29, 861-866

52 β -Tetracalcium aluminate dichloride-10-hydrate (Friedel's salt)

Formula: $\text{Ca}_4\text{Al}_2(\text{Cl})_2(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$, $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{CaCl}_2\cdot 10\text{H}_2\text{O}$

Formula Weight: 561.34 g/mol

Space group: $R\bar{3}c$ or $R3c$

Conventional cement shorthand notation: $\beta\text{-C}_3\text{A CaCl}_2 \text{H}_{10}$

52.1 Cell Dimensions: $a = 5.74 \text{ \AA}$, $c = 46.88 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2090 kg/m^3

Reference: Kuzel H.J., Neues Jahrbuch für Mineralogie Monatshefte (1966), 193-200

Cell parameters were determined at 308 K, from single-crystal X-ray structure refinements of synthetic crystals, prepared hydrothermally, using a Philips Norelco diffractometer.

52.2 Cell Dimensions: $a = 5.739 \text{ \AA}$, $c = 46.87 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2092 kg/m^3

Reference: Kuzel H.J., Zement-Kalk-Gips (1968), Vol.21, 463-469

Cell parameters were determined at 298 K, from X-ray powder pattern of a synthetic phase (prepared under CO_2 -free conditions) and using an internal standard (high purity 99.99% Si).

52.3 Cell Dimensions: $a = 5.724 \text{ \AA}$, $c = 46.689 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for hexagonal/trigonal crystal system): 2111 kg/m^3

Reference: Renaudin G., Cement and Concrete Research (1999), Vol.29, 1937-1942

Cell parameters were determined at 310 K, from a single crystal (prepared by hydrothermal synthesis), using INEL CPS 120 diffractometer equipped with a high temperature system.

52.4 Cell Dimensions: $a = 5.75 \text{ \AA}$, $c = 46.89 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3$

Density (calculated for monoclinic crystal system): 2083 kg/m^3

Reference: Rapin J.P. et al., Cement and Concrete Research (2002), Vol. 32, 513-519

Cell parameters were determined at 40°C , from crystalline samples prepared by hydrothermal synthesis. Compound was studied by synchrotron radiation using the WDIF4C powder diffractometer on the DW22 beamline of LURE.

52.5 Mean density of β -Friedel's salt: $D_x = 2094 \text{ kg/m}^3$

53 Tetracalcium ferrite dichloride-10-hydrate (Fe-Friedel's salt)

Formula: $\text{Ca}_4\text{Fe}_2(\text{Cl})_2(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$, $3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$

Formula Weight: 619.07 g/mol

Space group: $R\bar{3}$, $R3$, $R\bar{3}m$, $R3m$ or $R32$

Conventional cement shorthand notation: $\text{C}_3\text{F CaCl}_2 \text{H}_{10}$

53.1 Cell Dimensions: $a = 5.858 \text{ \AA}$, $c = 23.267 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3/2$

Density (calculated for hexagonal/trigonal crystal system): 2230 kg/m^3

Reference: Kuzel H.J., Zement-Kalk-Gips (1968), Vol.21, 463-469

Cell parameters were determined at 298 K, from X-ray powder pattern of a synthetic phase (prepared under CO_2 -free conditions) and using an internal standard (high purity 99.99% Si).

53.2 Cell Dimensions: $a = 5.861 \text{ \AA}$, $c = 23.279 \text{ \AA}$

Number of formula units in the unit cell: $Z = 3/2$

Density (calculated for hexagonal/trigonal crystal system): 2226 kg/m³

Reference: F. Götz Neunhoeffler, Ph.D thesis (in german) (1996), University of Erlagen Nürnberg, Germany, 124-135

Cell parameters were determined at room temperature (relative humidity 35%), from X-ray powder pattern of a synthetic phase.

53.3 Mean density of Fe- Friedel's salt: $D_x = 2228 \text{ kg/m}^3$

54 Tetracalcium aluminate sulfate chloride-12-hydrate (Kuzel's salt)

Formula: $\text{Ca}_4\text{Al}_2(\text{SO}_4)_{1/2}(\text{Cl})(\text{OH})_{12} \cdot 6\text{H}_2\text{O}, 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \frac{1}{2} \text{CaSO}_4 \cdot \frac{1}{2} \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$

Formula Weight: 610.07 g/mol

Space group: R3c or R $\bar{3}c$

Conventional cement shorthand notation: $\text{C}_3\text{A} \frac{1}{2} \text{C}\bar{\text{S}} \frac{1}{2} \text{CaCl}_2 \text{H}_{12}$

54.1 Cell Dimensions: $a = 5.750 \text{ \AA}, c = 100.62 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2110 kg/m³

Reference: Kuzel H.J., Zement-Kalk-Gips (1968), Vol.21, 463-469

Cell parameters were determined at 298 K, from X-ray powder pattern of a synthetic phase (prepared under CO₂-free conditions) and using an internal standard (high purity 99.99% Si).

54.2 Cell Dimensions: $a = 5.74 \text{ \AA}, c = 100.6 \text{ \AA}$

Number of formula units in the unit cell: $Z = 6$

Density (calculated for hexagonal/trigonal crystal system): 2118 kg/m³

Reference: Kuzel H.J., Neues Jahrbuch für Mineralogie Monatshefte (1966), 193-200

Cell parameters were determined at 298 K, from single-crystal X-ray structure refinements of synthetic crystals (prepared hydrothermally), using a Philips Norelco diffractometer.

54.3 Mean density of Kuzel's salt: $D_x = 2114 \text{ kg/m}^3$

54.4 Comment:

Kuzel's salt - $\text{Ca}_4\text{Al}_2(\text{SO}_4)_{1/2}(\text{Cl})(\text{OH})_{12} \cdot 6\text{H}_2\text{O}$ ($\text{C}_3\text{A} \frac{1}{2} \text{C}\bar{\text{S}} \frac{1}{2} \text{CaCl}_2 \text{H}_{12}$) is an ordered compound containing both mono and divalent anions, with ratio 1:1 Cl⁻ and SO₄²⁻ [1]. It was reported as a product of chloride attack at lower CaCl₂ concentrations [2].

[1] Glasser F.P, Kindness A., Stronach A., Stability and solubility relationships in AFm phases: Part I. Chloride, sulfate and hydroxide, Cement and Concrete Research (1999), Vol. 29, 861-866

[2] Hirao H. et. al, Journal of Advanced Concrete Technology (2005), Vol. 3, 77-84

55 Tetracalcium ferrite sulfate chloride-12-hydrate (Fe-Kuzel's salt)

Formula: $\text{Ca}_4\text{Fe}_2(\text{SO}_4)_{1/2}(\text{Cl})(\text{OH})_{12} \cdot 6\text{H}_2\text{O}, 3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \frac{1}{2} \text{CaSO}_4 \cdot \frac{1}{2} \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$

Formula Weight: 667.71 g/mol

Space group: R*c

Conventional cement shorthand notation: $\text{C}_3\text{F} \frac{1}{2} \text{C}\bar{\text{S}} \frac{1}{2} \text{CaCl}_2 \text{H}_{12}$

- 55.1 Cell Dimensions:** $a = 5.876 \text{ \AA}$, $c = 50.08 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3$
Density (calculated for hexagonal/trigonal crystal system): 2222 kg/m^3
Reference: Kuzel H.J., Zement-Kalk-Gips (1968), Vol.21, 463-469

Cell parameters were determined at 298 K, from X-ray powder pattern of a synthetic phase (prepared under CO₂-free conditions) and using an internal standard (high purity 99.99% Si).

- 55.2 Recommended density of Fe-Kuzel's salt:** $D_x = 2222 \text{ kg/m}^3$

HYDROGARNET PHASES

56 Tricalcium aluminate-6-hydrate (hydrogarnet)

Formula: $\text{Ca}_3\text{Al}_2(\text{OH})_{12} \cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$
Formula Weight: 378.28 g/mol
Space group: Ia3d
Conventional cement shorthand notation: C₃AH₆

- 56.1 Cell Dimensions:** $a = 12.5755 \text{ \AA}$
Number of formula units in the unit cell: $Z = 8$
Density (calculated for cubic crystal system): 2527 kg/m^3
Reference: Kuzel H.J., Neues Jahrbuch für Mineralogie Monatshefte (1969), 397-404

Cell parameters were determined at 300 K, from single-crystal X-ray structure refinements of synthetic crystals, prepared hydrothermally, using a Philips powder diffractometer and a Si internal standard.

- 56.2 Cell Dimensions:** $a = 12.56 \text{ \AA}$
Number of formula units in the unit cell: $Z = 8$
Density (calculated for cubic crystal system): 2535 kg/m^3
Reference: Brandenberger E., Schweizerische Mineralogische und Petrographische Mitteilungen (1933), 569 (abstract)

Details of the measurement - not given

- 56.3 Cell Dimensions:** $a = 12.5695 \text{ \AA}$
Number of formula units in the unit cell: $Z = 8$
Density (calculated for cubic crystal system): 2529 kg/m^3
Reference: Lager G.A. et al., American Mineralogist (1987), Vol. 72, 756-765

Cell parameters were determined at 300 K, from single-crystal X-ray structure refinements of synthetic crystals, using an Enraf Nonius diffractometer equipped with a graphite monochromator and Mo K α radiation.

- 56.4 Mean density of hydrogarnet:** $D_x = 2530 \text{ kg/m}^3$

56.5 Comment:

An end -member of the hydrogrossular solid-solution series, having the general formula $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$; $x = 1.5-3.0$ for katoite. Hydrogarnet is not normally a product of

modern OPC hydration, although reported to occur in older Portland cements, in calcium aluminate cements (CAC) and in heat cured Portland cements. See also section 58.

57 Tricalcium ferrite-6-hydrate

Formula: $\text{Ca}_3\text{Fe}_2(\text{OH})_{12}, 3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot 6\text{H}_2\text{O}$,

Formula Weight: 436.02 g/mol

Space group: Ia3d

Conventional cement shorthand notation: C_3FH_6

57.1 Cell Dimensions: $a = 12.73 \text{ \AA}$

Number of formula units in the unit cell: $Z = 8$

Density (calculated for cubic crystal system): 2809 kg/m^3

Reference: Taylor, H.F.W. (1989), "Cement Chemistry" 2nd edition 1997, Thomas Telford Publishing, London, UK, 171

Details of the measurement are not given

57.2 Cell Dimensions: $a = 12.74 \text{ \AA}$

Number of formula units in the unit cell: $Z = 8$

Density (calculated for cubic crystal system): 2801 kg/m^3

Reference: Flint E.P et al., Journal of Research of the National Institute of Standards and Technology U.S., (1941), Vol. 26, 13-33

Cell parameters were determined at room temperature, from X-ray powder patterns of the synthetic phase (hydrothermal preparations). The samples were mounted on fine glass rods in the center of cylindrical cameras having radii of about 5.7 cm, and were rotated during exposure; $\text{CuK}\alpha$ radiation was used. The absolute accuracy of this method is however relatively low.

57.3 Recommended density of Fe-hydrogarnet: $D_x = 2809 \text{ kg/m}^3$

58 'Siliceous' hydrogarnet

Formula: $\text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})_8$

Formula Weight: 402.37 g/mol

Space group: Ia3d

Conventional cement shorthand notation: C_3ASH_4

58.1 Cell Dimensions: $a = 12.358 \text{ \AA}$

Number of formula units in the unit cell: $Z = 8$

Density (calculated for cubic crystal system): 2832 kg/m^3

Reference: Rinaldi E. et al., Bulletin de Mineralogie (1984), Vol. 107, 606-618

Cell parameters were determined at 298 K, from single-crystal X-ray structure refinements of natural crystals from Lazio, Italy, using: a Philips diffractometer, $\text{CuK}\alpha$ radiation (1.54051 \AA) and an internal standard. Natural crystal contained various inclusions (Mg, S) but these are not believed to affect measurements. Formula determined in above reference nearly corresponded to the idealized formula, $\text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})$, therefore minor elements were not included in the calculation.

Density calculated by Rinaldi et al.: 2760 kg/m^3

58.2 Cell Dimensions: $a = 12.32 \text{ \AA}$

Number of formula units in the unit cell: $Z = 8$

Density (calculated for cubic crystal system): 2858 kg/m^3

Reference: Flint E.P et al., Journal of Research of the National Institute of Standards and Technology U.S., (1941), Vol. 26, 13-33

Cell parameters were determined at room temperature, from X-ray powder patterns of the synthetic phase (hydrothermal preparations). The samples were mounted on fine glass rods in the center of cylindrical cameras having radii of about 5.7 cm, and were rotated during exposure; $\text{CuK}\alpha$ radiation was used. This method has relatively poor absolute accuracy.

58.3 Recommended density of siliceous hydrogarnet: $D_x = 2832 \text{ kg/m}^3$

58.4 Comment:

Jappy et.al reported that at 1 bar pressure $\text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})_8$ forms only limited solid solution with $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$. Numerous mineralogical investigations of siliceous hydrogarnets report weak optical birefringence and the cubic symmetry may be only a pseudo-symmetry.

[1] Jappy T.G. et. al, Advances in Cement Research, (1991/1992), Vol. 4, 1-8

CRYSTALLINE CALCIUM SILICATE HYDRATES RELATED TO C-S-H GEL

Although crystalline calcium silicate hydrates do not occur in constructional concretes, our knowledge of the structure of the semi amorphous C-S-H is in part modelled on the known structures of several crystalline calcium silicate hydrates. These phases also occur in autoclaved or heat treated cements and on that account, three hydrates, tobermorite, jennite and afwillite have been selected for inclusion in this compilation. The three structures can be considered as layer structures with Ca-OH layers resembling those in portlandite ($\text{Ca}(\text{OH})_2$) and the silicate layer being more or less complete, to achieve the Ca/Si ratios characteristic of each phase.

Afwillite has an essentially fixed stoichiometry, while tobermorite has a defect structure which can tolerate some variation in Ca/Si ratio. Jennite is believed to be close to stoichiometric, although the evidence is as yet inconclusive.

59 Jennite

Formula: $9\text{CaO} \cdot 6\text{SiO}_2 \cdot 11\text{H}_2\text{O}$

Formula Weight: 1063.44 g/mol

Space group: $P1$ or $P\bar{1}$

Conventional cement shorthand notation: $\text{C}_9\text{S}_6\text{H}_{11}$

59.1 Cell Dimensions: $a = 9.96 \text{ \AA}$, $b = 3.64 \text{ \AA}$, $c = 21.36 \text{ \AA}$, $\alpha = 91.8^\circ$, $\beta = 101.8^\circ$, $\gamma = 89.6^\circ$

Number of formula units in the unit cell: $Z = 1$

Density (calculated for triclinic crystal system): 2332 kg/m^3

Reference: Taylor H.F.W. (1989), Data published in Cement Chemistry 2nd edition 1997, Thomas Telford Publishing, London, UK, 130

Details of the measurement-not given

Density given by Taylor: 2332 kg/m^3

- 59.2 Cell Dimensions:** $a = 10.593 \text{ \AA}$, $b = 7.284 \text{ \AA}$, $c = 10.839 \text{ \AA}$, $\alpha = 99.67^\circ$, $\beta = 97.65^\circ$, $\gamma = 110.11^\circ$
Number of formula units in the unit cell: $Z = 1$
Density (calculated for triclinic crystal system): 2336 kg/m^3
Reference: Gard J.A. et al., American Mineralogist (1977), Vol. 62, 365-368

Cell parameters were determined from X-ray powder patterns of a natural (Crestmore) sample, using a Guiner- type camera, an internal standard (high purity 99.99 % Si standard) and Cu $K\alpha$ radiation; temperature of the measurement is not specified.

Density calculated by Gard et al: 2330 kg/m^3

- 59.3 Cell Dimensions:** $a = 10.576 \text{ \AA}$, $b = 7.265 \text{ \AA}$, $c = 10.931 \text{ \AA}$, $\alpha = 101.30^\circ$, $\beta = 96.98^\circ$, $\gamma = 109.65^\circ$
Number of formula units in the unit cell: $Z = 1$
Density (calculated for triclinic crystal system): 2325 kg/m^3
Reference: Bonaccorsi E. et al., Cement and Concrete Research (2004), Vol. 34, 1481-1488

Cell parameters were determined from single crystal X-ray diffraction of a natural (Fuka, Japan) sample, using synchrotron radiation at the Elettra facility (Trieste, Italy).

- 59.4 Mean density of jennite:** $D_x = 2331 \text{ kg/m}^3$

60 Tobermorite (14 \AA)

Formula: $5\text{CaO} \cdot 6\text{SiO}_2 \cdot 8\text{H}_2\text{O}$
Formula Weight: 785.03 g/mol
Space group: B11b
Conventional cement shorthand notation: $\text{C}_5\text{S}_6\text{H}_8$

- 60.1 Cell Dimensions:** $a = 56.735 \text{ \AA}$, $b = 7.425 \text{ \AA}$, $c = 27.987 \text{ \AA}$, $\beta = 123.25^\circ$
Number of formula units in the unit cell: $Z = 2$
Density (calculated for monoclinic crystal system): 2228 kg/m^3
Reference: Bonaccorsi E. et. al, Journal of the American Ceramic Society (2005), Vol. 88, 505-512

Cell parameters were determined at room temperature, from single-crystal X-ray structure refinements of natural crystals (Crestmore). Two polytypes were detected but reflections of the other polytype were too weak to be used in a structure refinement and only approximate cell parameters of second polytype are given (space group: F2dd, $a \sim 11.2 \text{ \AA}$, $b \sim 7.3 \text{ \AA}$, $c \sim 56 \text{ \AA}$)

- 60.2 Cell Dimensions:** $a = 5.624 \text{ \AA}$, $b = 3.670 \text{ \AA}$, $c = 27.97 \text{ \AA}$
Number of formula units in the unit cell: $Z = 1$
Density (calculated for orthorhombic crystal system): 2224 kg/m^3
Reference: Taylor H.F.W. (1989), Data published in Cement Chemistry 2nd edition 1997, Thomas Telford Publishing, London, UK, 130

Details of the measurement are not given. Idealized formula postulated: $5\text{CaO} \cdot 6\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ but the actual formula given in the reference is near $5\text{CaO} \cdot 5.5\text{SiO}_2 \cdot 9\text{H}_2\text{O}$. Calculation of density was performed for $5\text{CaO} \cdot 5.5\text{SiO}_2 \cdot 9\text{H}_2\text{O}$.

Density given by Taylor: 2224 kg/m^3

Uncertainty regarding composition therefore value given by Bonaccorsi et al. preferred.

60.3 Recommended density of tobermorite 14 Å: $D_x = 2228 \text{ kg/m}^3$

61 Afwillite

Formula: $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}_3\text{Si}_2\text{O}_4(\text{OH})_6$

Formula Weight: 342.45 g/mol

Space group: Cc

Conventional cement shorthand notation: $\text{C}_3\text{S}_2\text{H}_3$

61.1 Cell Dimensions: $a = 16.278 \text{ \AA}$, $b = 5.6321 \text{ \AA}$, $c = 13.236 \text{ \AA}$, $\beta = 134.898^\circ$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for monoclinic crystal system): 2646 kg/m^3

Reference: Malik K.M.A. et al., Acta Crystallographica (1976), Vol. B32, 475-480

Cell parameters were determined at room temperature, from single-crystal X-ray structure refinements of natural crystals (Kimberly, South Africa), using a Hilger and Watts Y290 four-circle automatic diffractometer and Mo $K\alpha$ radiation (0.70926 Å).

61.2 Cell Dimensions: $a = 16.27 \text{ \AA}$, $b = 5.632 \text{ \AA}$, $c = 13.23 \text{ \AA}$, $\beta = 134.80^\circ$

Number of formula units in the unit cell: $Z = 4$

Density (calculated for monoclinic crystal system): 2644 kg/m^3

Reference: Megaw H.D., Acta Crystallographica (1952), Vol. 5, 477-491

Unit cell dimensions were determined at room temperature, from oscillation photographs with Cu $K\alpha$ radiation (1.5405 Å). Natural crystals from the Scawt Hill (Northern Ireland) were generally used but later compared with crystals from Kimberley (South Africa), which had identical unit cell dimensions. However unit cell dimensions determined by this method have low absolute accuracy.

Density calculated by Megaw: 2634 kg/m^3

61.3 Mean density of afwillite: $D_x = 2645 \text{ kg/m}^3$

HYDROTALCITE TYPE AND RELATED PHASES

“Hydrotacite” refers both to a single mineral and a family of minerals with related structures. Structural relations are not completely known for all members of the group and therefore we should strictly regard phases other than hydrotacite itself as “hydrotalcite-like”.

The hydrotalcite structure is derived from that of brucite, $\text{Mg}(\text{OH})_2$. The brucite structure consists of electrically neutral sheets of net composition $\text{Mg}(\text{OH})_2$; the Mg is in octahedral coordination. In derivative structures such as hydrotalcite, part of the Mg is replaced by a trivalent ion, typically Al, on an ordered basis. The unbalance of charge is accommodated by introducing anions in interlayer positions: sufficient space also exists for water molecules. The ratio $\text{Mg}/(\text{Mg} + \text{Al})$ varies from 0.67 to 0.75. While both natural and synthetic products exhibit variable ratios, natural specimens tend to have ratios close to 0.75 (Taylor H.F.W) while the synthetics tend to have lower ratios, close to 0.67. The stacking plan of constituent layers can also vary, giving rise to polytypes.

Analysis of the synthetic is handicapped by the fine-grained nature of hydrotalcite crystals. Electron microprobe methods do not enable distinction and quantification of OH/CO₃ ratios and furthermore, are frequently not reliable for Mg/Al ratios. Therefore a degree of uncertainty exists about the number of phases in this family and their properties. We have included a number of examples relevant to cement and where composition, crystallography and hence unit cell contents seem to be well established.

62 Hydrotalcite

Formula: Mg₄Al₂(OH)₁₂CO₃·3H₂O

Formula Weight: 469.32 g/mol

Space group: R $\bar{3}$ m or R3m

Conventional cement shorthand notation: M₄A \bar{C} H₉

62.1 Cell Dimensions: $a = 3.054 \text{ \AA}$, $c = 22.81 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1/2$

Density (calculated for hexagonal/trigonal crystal system): 2117 kg/m³

Reference: Allmann R. et al., Jahrbuch für Mineralogie Monatshefte (1969), 544-551

Cell parameters were determined from X-ray structure refinements of natural crystals (Vezna, Western Moravia), using Cu K α radiation; other details of the measurement are not specified.

Density calculated by Allmann R. et al.: 2117 kg/m³

62.2 Cell Dimensions: $a = 3.051 \text{ \AA}$, $c = 22.81 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1/2$

Density (calculated for hexagonal/trigonal crystal system): 2119 kg/m³

Reference: Sato T. et al., Reactivity of Solids (1988), Vol. 5, 219-228

Cell parameters were determined by X-ray powder diffractometry of synthetic phases; Ni-filtered CuK α radiation was used. Lattice constants were calculated using silicon as an internal standard.

62.3 Cell Dimensions: $a = 3.046 \text{ \AA}$, $c = 22.772 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1/2$

Density (calculated for hexagonal/trigonal crystal system): 2129 kg/m³

Reference: Bellotto M. et al., Journal of Physical Chemistry (1996), Vol. 100, 8527-8534

Cell parameters were determined for synthetic phases (composition checked by XRF); X-ray diffraction powder patterns were measured using a Siemens D501 diffractometer with Cu K α radiation and a graphite diffracted monochromator.

62.4 Mean density of hydrotalcite : D_x = 2122 kg/m³

63 Fe-Hydrotalcite

Formula: Mg₄Fe₂(OH)₁₂CO₃·3H₂O

Formula Weight: 527.06 g/mol

Space group: R $\bar{3}$ m or R3m

Conventional cement shorthand notation: M₄F \bar{C} H₉

- 63.1 Cell Dimensions:** $a = 3.104 \text{ \AA}$, $c = 23.12 \text{ \AA}$
Number of formula units in the unit cell: $Z = 1/2$
Density (calculated for hexagonal/trigonal crystal system): 2269 kg/m^3
Reference: Sato T. et al., *Reactivity of Solids* (1988), Vol. 5, 219-228

Cell parameters were determined by X-ray powder diffractometry of synthetic phases; Ni-filtered Cu $K\alpha$ radiation was used. Lattice constants were calculated using silicon as an internal standard.

- 63.2 Recommended density of Fe-hydrotalcite:** $D_x = 2269 \text{ kg/m}^3$

64 Meixnerite

Formula: $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 4\text{H}_2\text{O}$
Formula Weight: 577.99 g/mol
Space group: $R\bar{3}m$
Conventional cement shorthand notation: M_6AH_{13}

- 64.1 Cell Dimensions:** $a = 3.046 \text{ \AA}$, $c = 22.93 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3/8$
Density (calculated for hexagonal/trigonal crystal system): 1953 kg/m^3
Reference: Koritnig S. et al., *American Mineralogist* (1976), Vol. 61, 176 (abstract)

Cell parameters were determined from X-ray structure refinements of natural crystals (Ybbs-Presenberg, Austria); other details of the measurement are not specified.

- 64.2 Formula:** $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 4.5\text{H}_2\text{O}$
Formula Weight: 586.99 g/mol
Space group: $R\bar{3}m$

Cell Dimensions: $a = 3.054 \text{ \AA}$, $c = 23.40 \text{ \AA}$
Number of formula units in the unit cell: $Z = 3/8$
Density (calculated for hexagonal/trigonal crystal system): 1934 kg/m^3
Reference: Mascolo G. et al., *Mineralogical Magazine* (1980), Vol. 43, 619-621

Cell parameters were determined from the X-ray powder patterns obtained by using Guiner de Wolff camera with Cu $K\alpha$ radiation; $\text{Pb}(\text{NO}_3)_2$ was used as a reference material. Synthetic samples were prepared under CO_2 -free conditions.

- 64.3 Mean density of meixnerite:** $D_x = 1945 \text{ kg/m}^3$

64.4 Comment:

The density seems to decrease as the ratio $\text{Mg}/(\text{Mg}+\text{Al})$ increases.

65 OH-Hydrotalcite

Formula: $\text{Mg}_4\text{Al}_2(\text{OH})_{14} \cdot 3\text{H}_2\text{O}$
Formula Weight: 443.33 g/mol
Space group: $R\bar{3}m$ or $R3m$
Conventional cement shorthand notation: M_4AH_{10}

65.1 Cell Dimensions: $a = 3.038 \text{ \AA}$, $c = 22.62 \text{ \AA}$

Number of formula units in the unit cell: $Z = 1/2$

Density (calculated for hexagonal/trigonal crystal system): 2036 kg/m^3

Reference: Mascolo G. et al., Mineralogical Magazine (1980), Vol. 43, 619-621

Cell parameters were determined from the X-ray powder patterns obtained by using Guiner de Wollf camera with $\text{CuK}\alpha$ radiation; $\text{Pb}(\text{NO}_3)_2$ was used as a reference material. Synthetic samples were prepared under CO_2 -free conditions.

65.2 Recommended density of OH-hydroxalcite: $D_x = 2036 \text{ kg/m}^3$

4. Discussion

The classification of cement phases as ‘important’ (and hence worthy of inclusion) is partly a matter of opinion and partly a matter of the availability of data. For example data on solid solutions at well-spaced intervals are largely absent.

The compilation therefore rests on the values critically extracted from the literature but with a special focus on AFm and AFt phases. Where multiple data were available, and admitted into the compilation, an averaging process was used and density described as ‘mean density’. If some methods had relatively poor absolute accuracy and data were rejected or not heavily weighted, the density is expressed as ‘recommended density’. Review shows that quality of data reported in the literature varies. One of the principal difficulties of determining the densities of substances experimentally by classical methods is in providing assurance that preparation is phase-pure. This assurance is often given by using single crystals, or handpicking enough smaller crystals, for analysis. With cement phases, this is often not possible: not only are crystals too small to select, but an ever-present inaccuracy arises because bulk preparations may contain significant content of amorphous material which escapes detection by X-ray powder analysis, etc.

Regarding natural samples we have to take into consideration solid solution as well as possible physical inclusions which may affect density. However by determining unit cell sizes, coupled with the known cell contents, errors arising from physical inclusions, adhering impurities, etc. are eliminated: unit cell sizes as determined by refinement of the powder pattern are also insensitive to the presence of non-crystalline impurities.

The use of crystallographic methods also calls into question the definition of a ‘phase’. For example, the cement literature tends to treat ‘AFm’ as though it were a single phase, but we know that this is an oversimplification: recent studies have disclosed that several AFm phases may coexist, which form limited solid solutions. Thus the density classification reflects current knowledge and, as data permit, densities are also given for AFm phases differing in water content e.g. 13 and 19 H_2O states (hydroxy-AFm), for different trivalent substituents in the principle layer e.g. with octahedral Al or Fe (III) and with different anions, e.g. sulfate, chloride, carbonate and hydroxide. Data are however available for only a few permutations; indeed not all the permutations may be stable and in at least two known examples, phase development is further complicated by ordering of anionic substituents, as occurs in Kuzel’s salt (distinguished by ordering of Cl and SO_4) and in hemicarboaluminate (distinguished by ordering of OH and CO_3). It appears that ordered AFm arrangements require both a mono- and divalent anionic substituent and it is possible that other, as yet undiscovered, anion-ordered AFm phases exist.

Problems of assessing the impact of solid solution on densities have been noted. For example, as expected from the relative formula weights, the density of Al-AFm is much less than the density of corresponding Fe(III) -AFm (Al=27 g/mol, Fe = 55.8 g/mol). Given that the two AFm phases are isostructural, or very nearly isostructural, the density difference is expected. In the absence of data on intermediate compositions, Vegard's law has to be assumed that density is a linear function of composition.

However a number of systems are known in which significant departure from Vegard's law occurs: for example in the Al-AFm series with (OH, SO₄) anions, where solid solution is incomplete but no ordered compound occurs, analysis of the thermodynamic data discloses that sulfate has a strong stabilizing action on the OH-AFm phase [1], i.e., that the solid solutions are non-ideal. It may be that similar non-ideal changes are reflected in the density function.

Other possibilities occur for non-ideal solid solution. For example, carbonate can replace other anions in AFm. While some anions, e.g. chloride and hydroxide appear to behave as simple spherical ions, carbonate can appear either as a spherical ion or as a trigonal planar group. Depending on carbonate orientation, the two possibilities differ in the effective molar volume of the anionic substituent and hence differ in their contribution to density. Fig 1 shows the densities in the series of AFm phases with OH and CO₃. Of course changing composition influences density but the density of hemi- and monocarboaluminate are also affected by the orientation of the trigonal planar carbonate group. It is most efficiently packed in monocarboaluminate, in which it is sub-parallel to the principal layer spacing [2,3], hence the high density, whereas in hemicarboaluminate, it is perpendicular to the principal layers. Thus the density of hemicarboaluminate falls much below the trend line, as deduced for its end-members. These differences in carbonate orientation also affect the basal spacings (d_{001}), numerical values of which are shown in the Fig 1.

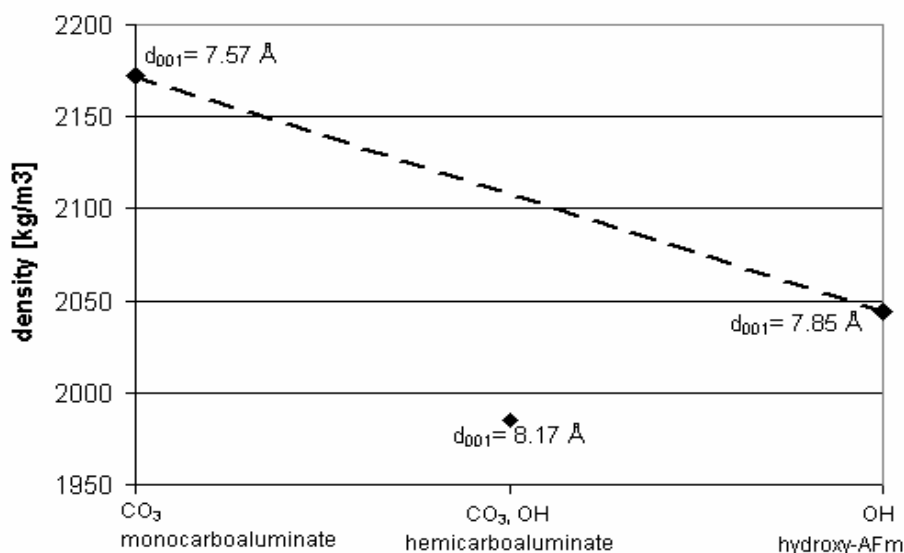


Figure 1. Density trends in the (OH, CO₃) AFm phases.

Interesting relations exist between the composition and density relationships in the AFm and AFt families, as shown in Fig 2. The two structures, of AFm and AFt, differ in bonding requirements. The layer spacings in AFm are easily increased to allow variable water contents, as a result of which the density decreases as the water content increases. This relation appears, by definition to be linear for OH-AFm but it is also observed to be approximately linear for the SO₄-AFm series, where we have three datum. The structural role

of water is relatively well-defined: we can for example have the 13 H₂O state or 19 H₂O state but not, apparently, intermediate water contents, which can only be achieved by having a mixture of discrete AFm phases. For that reason, trend lines are shown as dashed, to emphasize that water contents are not continuously variable within a single AFm phase. Similarly, sulfate AFm at room temperature exhibits three hydrate states: 12 H₂O, 14 H₂O and 16 H₂O, depending on relative humidity. Pöllmann has established three additional lower hydration states, the densities of which are not sufficiently well established to show in Fig 2(b).

However the three examples of sulfate AFm phases show a linear trend of decreasing density with increasing water content, with a much lower slope than observed for OH-AFm.

The actual hydration state achieved by AFm in cement is not always well known: as we have described, loss of water may occur in the course of specimen preparation unless special precautions are taken in the course of specimen preparation and handling. However it is apparent that large potential volume changes can occur in AFm, should its hydration state change. The greatest potential seems to occur for OH-AFm, where the transition from 13 H₂O to 19 H₂O results in an increase in specific volume of more than 10%. For sulfate AFm, a comparable change occurs but is less marked, only a few %. It appears that the more strongly bonded water occupies less effective volume than more weakly bonded, space requirements of which approach that of free water.

The calculated volume change cannot be associated with an actual expansion or contraction: it is best regarded as indicating a *potential for change*. This potential might, for example, be achieved in the course of thermal cycling because, other factors being equal, the highest hydration states are achieved at low temperatures. Nevertheless, the potential for expansion can be minimized by inclusion of sufficient sulfate to convert all AFm to its sulfated form with perhaps a sufficient reserve to stabilize AFt in the cement. Because sufficient sulfate is usually added to Portland cement to achieve this mineralogical state, the problem of dimensional instability resulting from changing AFm hydration states is unlikely to arise in commercial Portland cements. The arguments continue about optimum sulfate content in cement but we note that there are good reasons, more than just control of set times, why cement should not be under-sulfated: in this instance, to avoid potential dimensional instability resulting from the presence of OH-AFm in different hydration states.

The hydration states of AFt show a non-linear density trend in response to changing water content, Fig 2(c). However the density trend shows a slope opposite to that of AFm: intercalation of more water in the AFt structure *increases* the physical density. This state is believed to arise because AFt is a three dimensional structure; it is not easy to expand or contract its framework so water in excess of 30 H₂O per formula unit has to fit into a relatively unchanged physical space. However between 30 and 32 H₂O the volume change per water molecule changes much less than between 32 and 36. Probably water in excess of 32 occupies a different set of sites than between 30 and 32, thus impacting differently on cell dimensions.

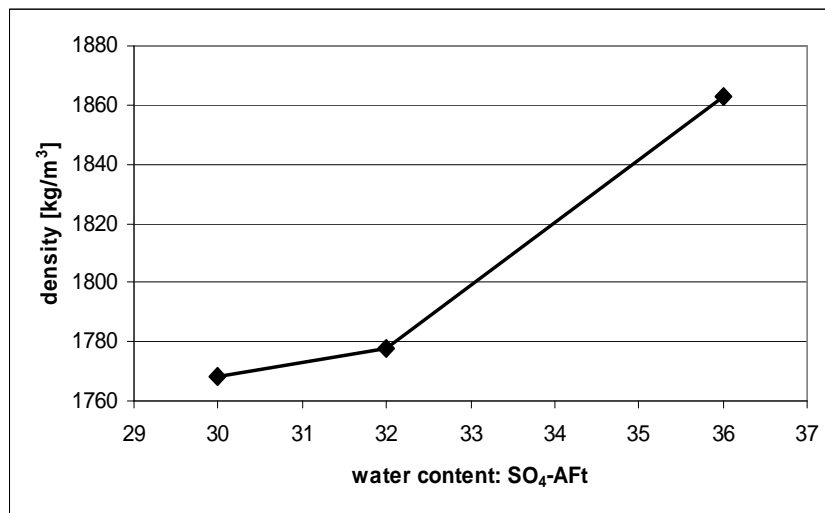
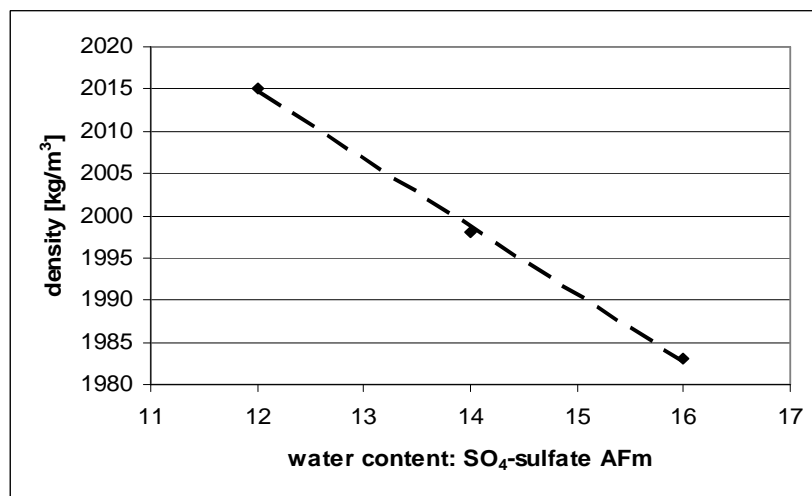
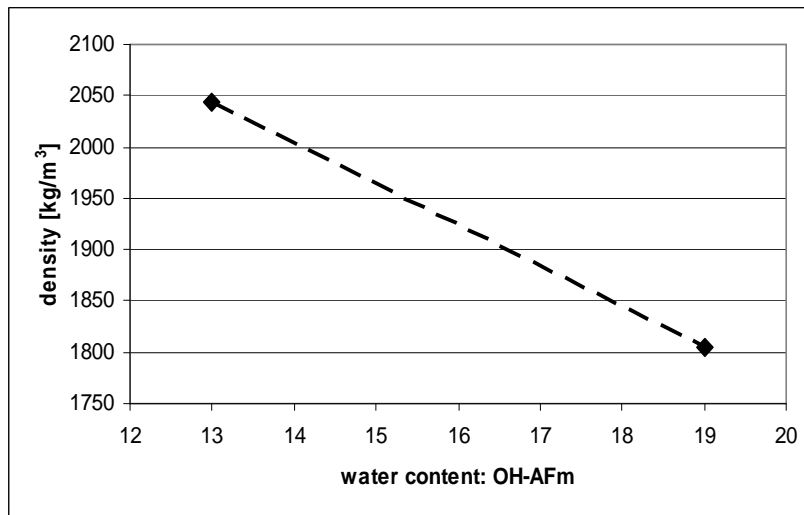


Figure 2. Relation between water content and density of: OH-AFm (a ,top), SO₄-AFm (b, middle) and (c), SO₄-AFt (bottom).

Many reactions occurring in cementitious systems are isochemical: that is, the chemistry remains constant but a redistribution of ions occurs amongst coexisting phases. This compilation might serve as a benchmark to enable the precise calculation of volume changes to be made in the course of isochemical mineralogical changes. Reactions between cement and its service environment generally involve exchange of mass: that is, they are not isochemical. In these conditions, the database presented forms the basis of calculation but requires application of more sophisticated calculations, taking into account the impact of mass balance changes.

- [1] H.F.W.Taylor, Cement Chemistry 2nd edition 1997, Thomas Telford Publishing, London, UK
 [2] T. Matschei, B. Lothenbach, F.P. Glasser, The AFm phase in Portland cement, Cement and Concrete Research 37 (2007) 118-130
 [3] G. Renaudin, Ph.D thesis (1998), Nancy, France, p 150

Table 1. Density of Selected Cement Phases at 20-25°C

Mineral or Chemical Name	Formula	Density [kg/m ³]
lime	CaO	3341
periclase	MgO	3584
corundum	Al ₂ O ₃	3990
quartz	SiO ₂	2641
gibbsite	Al(OH) ₃	2421
portlandite	Ca(OH) ₂	2251
brucite	Mg(OH) ₂	2368
calcite	CaCO ₃	2710
aragonite	CaCO ₃	2930
vaterite	μ-CaCO ₃	2661
magnesite	MgCO ₃	3011
dolomite	CaMg(CO ₃) ₂	2852
anhydrite	CaSO ₄	2968
'soluble anhydrite'	CaSO ₄ ·<0.05H ₂ O	2958
hemihydrate	CaSO ₄ ·0.5H ₂ O	2733
hemihydrate	CaSO ₄ ·0.8H ₂ O	2783
gypsum	CaSO ₄ ·2H ₂ O	2311
arcanite	K ₂ SO ₄	2668
thenardite	Na ₂ SO ₄	2662

Mineral or Chemical Name	Formula	Density [kg/m ³]
aphthitalite	$K_3 Na(SO_4)_2$	2703
syngenite	$K_2Ca(SO_4)_2 \cdot H_2O$	2575
'aluminosulfate'	$Ca_4(Al_2O_3)_3(SO_4)$	2607
'silicosulfate'	$Ca_5(SiO_2)_2(SO_4)$	2972
tricalcium aluminate (cubic)	$Ca_3Al_2O_6$	3030
tricalcium aluminate (orthorombic)	$Ca_3Al_2O_6$	3023
tetracalcium aluminoferrite	$Ca_2(Al,Fe)_2O_5$	3708
R-tricalcium silicate at 1200°C	R- Ca_3SiO_5	3025
R-tricalcium silicate- Sr stabilized	R- Ca_3SiO_5	3168
M3-tricalcium silicate- Mg stabilized	M3- Ca_3SiO_5	3182
M3-tricalcium silicate- less well ordered	M3- Ca_3SiO_5	3153
T1-tricalcium silicate	T1- Ca_3SiO_5	3120
α -dicalcium silicate- Ba stabilized	α - Ca_2SiO_4	2968
α'_H -dicalcium silicate- P_2O_5 stabilized	α'_H - Ca_2SiO_4	3148
α'_L -dicalcium silicate- Sr stabilized	α'_L - Ca_2SiO_4	3092
β -dicalcium silicate	β - Ca_2SiO_4	3326
γ -dicalcium silicate	γ - Ca_2SiO_4	2960
ettringite with low H ₂ O content (30 H ₂ O)	$[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot 24H_2O$	1768
Ettringite (32 H ₂ O)	$[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot (24+2)H_2O$	1778
ettringite with high H ₂ O content (36 H ₂ O)	$[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot (24+6)H_2O$	1863
carbonate ettringite	$[Ca_3Al(OH)_6]_2(CO_3)_3 \cdot (24+2)H_2O$	1760
iron ettringite	$[Ca_3Fe(OH)_6]_2(SO_4)_3 \cdot (24+2)H_2O$	1830
thaumasite	$Ca_3(SO_4)(CO_3)[Si(OH)_6] \cdot 12H_2O$	1882
hydroxy - AFm	$Ca_4Al_2(OH)_{14} \cdot 6H_2O$	2044
Fe-hydroxy AFm	$Ca_4Fe_2(OH)_{14} \cdot 6H_2O$	2162
α_1 -tetracalcium aluminate -19- hydrate	α_1 - $Ca_4Al_2(OH)_{14} \cdot 12H_2O$	1804
α_2 -tetracalcium aluminate -19- hydrate	α_2 - $Ca_4Al_2(OH)_{14} \cdot 12H_2O$	1802
monosulfoaluminate (12 H ₂ O)	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$	2015
monosulfoaluminate (14 H ₂ O)	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 8H_2O$	1998

Mineral or Chemical Name	Formula	Density [kg/m ³]
monosulfoaluminate (16 H ₂ O)	Ca ₄ Al ₂ (SO ₄)(OH) ₁₂ ·10H ₂ O	1983
Fe-monosulfoaluminate	Ca ₄ Fe ₂ (SO ₄)(OH) ₁₂ ·6H ₂ O	2117
strätlingite	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O	1937
monocarboaluminate	Ca ₄ Al ₂ (CO ₃)(OH) ₁₂ ·5H ₂ O	2175
Fe-monocarboaluminate	Ca ₄ Fe ₂ (CO ₃)(OH) ₁₂ ·6H ₂ O	2219
hemicarboaluminate	Ca ₄ Al ₂ (CO ₃) _{0.5} (OH) ₁₃ ·5.5H ₂ O	1985
dicalcium aluminate -8- hydrate	Ca ₂ Al ₂ (OH) ₁₀ ·3H ₂ O	1950
α-Friedel's salt	α-Ca ₄ Al ₂ (Cl) ₂ (OH) ₁₂ ·4H ₂ O	2064
β-Friedel's salt	β-Ca ₄ Al ₂ (Cl) ₂ (OH) ₁₂ ·4H ₂ O	2094
β-Fe-Friedel's salt	β-Ca ₄ Fe ₂ (Cl) ₂ (OH) ₁₂ ·4H ₂ O	2228
Kuzel's salt	Ca ₄ Al ₂ (SO ₄) _{0.5} (Cl) (OH) ₁₂ ·6H ₂ O	2114
Fe-Kuzel's salt	Ca ₄ Fe ₂ (SO ₄) _{0.5} (Cl) (OH) ₁₂ ·6H ₂ O	2222
hydrogarnet (katoite)	Ca ₃ Al ₂ (OH) ₁₂	2530
Fe-hydrogarnet	Ca ₃ Fe ₂ (OH) ₁₂	2809
siliceous hydrogarnet	Ca ₃ Al ₂ SiO ₄ (OH) ₈	2832
jennite	9CaO·6SiO ₂ ·11H ₂ O	2331
tobermorite 14 Å	5CaO·6SiO ₂ ·8H ₂ O	2228
afwillite	3CaO·2SiO ₂ ·3H ₂ O	2645
hydrotalcite	Mg ₄ Al ₂ (OH) ₁₂ CO ₃ ·3H ₂ O	2122
Fe-hydrotalcite	Mg ₄ Fe ₂ (OH) ₁₂ CO ₃ ·3H ₂ O	2269
meixnerite	Mg ₆ Al ₂ (OH) ₁₈ ·4H ₂ O	1945
OH-hydrotalcite	Mg ₄ Al ₂ (OH) ₁₄ ·3H ₂ O	2036

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