

GUIDE TO COMPOUNDS OF INTEREST IN CEMENT AND CONCRETE RESEARCH

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1972

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Subject Area

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FOREWORD

In 1965 the Highway Research Board Committee on Basic Research Pertaining to Portland Cement and Concrete established a Subcommittee on Nomenclature. The mission of the subcommittee was the preparation of a set of rules, consistent with accepted practice in inorganic chemistry and mineralogy, to govern the preferred designation of the compounds of interest in the cement-chemistry field and to be used as a guide to the many compounds discussed in that field. It was felt that such a guide would help to remove the prevailing disorder and confusion relating to the nomenclature of those compounds. This report is the result of the subcommittee's work.

The subcommittee hopes that this compilation will be used by authors and researchers who work in the field of cement chemistry or in related fields and particularly hopes that it will be useful to students and others just entering those fields. The names selected or coined in this report have no official status, and individuals and organizations may prefer to use other designations. Nevertheless, the consistent use of the nomenclature provided should result in a considerable decrease in the confusion that now exists.

The subcommittee wishes to acknowledge the advice and assistance of several colleagues who provided helpful assistance and encouragement in the preparation of this report. These include W. L. Dolch, who was chairman of the Committee on Basic Research Pertaining to Cement and Concrete for most of the period during which the subcommittee worked; Katharine Mather, who is the present chairman; G. L. Kalousek; N. R. Greening; and Bryant Mather. Also acknowledged are the efforts of W. R. Gunderman of the Highway Research Board staff in furthering the publication of this report.

INTRODUCTION

This report contains a brief discussion of the names and pertinent characteristics of approximately 100 compounds and phases of interest in the chemistry of portland and related cements. It is obvious that such a list cannot be complete because of the multiplicity of phases, hydration states, and solid solution possibilities. In selecting phases, we have tried to include almost all of the compounds of interest without letting the compendium become overwhelmingly large.

The compounds are classified into 18 groups for ease of reference. The groups are generally arranged in increasing order of compositional complexity; e.g., unhydrated phases are listed at the beginning and complex hydrated phases are listed near the end. The groups are by no means uniform in terms of number of individual compounds contained in each; one group contains only one entry, whereas the largest group contains 20 individual compounds. The organization of the groups is apparent from the assigned group headings. Within groups, individual phases are listed in a logical order, and an attempt was made to keep related phases close together. The largest group, the well-crystallized calcium silicate hydrates other than tobermorites, is ordered in terms of decreasing calcium-to-silica ratio, with phases containing additional elements being placed at the end.

A number of compounds that are considered to be of special significance because of their occurrence in portland cement and portland cement concrete have been designated by an asterisk. A special effort has been made to provide structural information and other details for most of these compounds.

For each compound listed, the following information (in the following format) is provided when possible.

1. Preferred name—mineral, compositional, or special.
2. Synonym equally acceptable to the committee.
3. Compositional designation—conventional cement shorthand notation used by cement specialists.
4. Other names commonly used.
5. Chemical formula that may reflect the structure, if known.
6. Crystal system and unit cell parameters.
7. Refractive indexes.
8. X-ray powder diffraction file number assigned to the compound or phase by the Joint Committee on Powder Diffraction Standards, 1601 Park Lane, Swarthmore, Pennsylvania 19081. This file, formerly published by ASTM, provides a means whereby a full X-ray diffraction pattern and supplementary information can be obtained.
9. X-ray powder pattern information—consisting of the six strongest X-ray peaks and an indication of their relative intensities in parts per ten, listed in the order of decreasing intensity. The information is given in the following format: 2.11₁₀, 4.33₈, and so on, with 2.11 representing the d-spacing of the peak and the subscript representing the relative intensity. The data are usually provided from the powder diffraction file; if the compound is not listed or if the listing in the file is thought inadequate or incorrect, a pattern is provided from the literature.
10. Remarks—particularly those bearing on the nomenclature, stability, occurrence in concrete, and, in some cases, the structure of the compound in question.
11. References—citations of a major compendium or of very significant individual papers describing the compound. No attempt has been made to be exhaustive or even representative in listing the literature; the intent is to provide a set of easily obtainable and authoritative sources for further information.

All X-ray diffraction data and crystal unit cell sizes are given in angstrom units. (1 \AA is equal to 10^{-10} m.)

Many different nomenclature schemes and improvised compound designations exist side by side in the modern literature. Some compounds are designated by mineral names even though the precise identity of the synthetic compound and the natural mineral has not, in many cases, been established. Other compounds have no names at all and are referred to by standardized abbreviations of their compositions expressed in oxide form, e.g., C_4AH_{13} . (The standard abbreviations in common use are $\text{S} = \text{SiO}_2$, $\text{A} = \text{Al}_2\text{O}_3$, $\text{C} = \text{CaO}$, $\text{H} = \text{H}_2\text{O}$, $\text{C} = \text{CO}_2$, $\text{S} = \text{SO}_3$, $\text{N} = \text{Na}_2\text{O}$, $\text{K} = \text{K}_2\text{O}$, $\text{M} = \text{MgO}$, and so forth.) Some poorly crystallized phases, e.g., several of the calcium silicate hydrates, have been called by mineral names (e.g., tobermorite and tobermorite gel) that more properly apply to well-crystallized compounds that may or may not be the same kind of material. Some compounds have been designated very informally, e.g., Roy's phase X and Assarsson's phase Z; and some informal names have come to be widely used by cement specialists, e.g., alite and belite. The use of prefixes such as α - and β - has not been consistent.

Unfortunately, the subcommittee could not formulate one system of nomenclature that was acceptable even to the majority of its members. However, a series of principles was agreed on and serves as a basis for the preferred designations used in this report. These principles can be stated as follows:

1. So that further confusion is avoided, most long-accepted mineral names are retained, especially where a proposed chemical name would be long and unwieldy.
2. Where mineral names are not established or widely known, or where it is desired to emphasize the composition, compositional names are used.
3. Compositional names are formulated to express clearly the compound's composition and, insofar as is practicable, to meet the criteria of the International Union of Pure and Applied Chemistry's 1957 Report of the Commission on Nomenclature in Inorganic Chemistry (American version with comments). In particular, the conventions adopted include the following:
 - a. The composition is to be indicated with appropriate prefixes, e.g., tricalcium disilicate, except that "mono" is used only where the existence of several compounds with similar compositions might cause confusion. Thus, tricalcium aluminate is used rather than tricalcium monoaluminate.
 - b. For numbers larger than four, prefixes are not used. Instead, the composition is indicated by using the Arabic numeral with (or surrounded by) hyphens, e.g., 12-calcium-7-aluminate.
 - c. Where two compounds have the same composition but belong to different crystal systems, the differentiation is indicated by use of a standard abbreviation for the crystal system in parentheses, e.g., tricalcium disilicate (mon.) for rankinite and tricalcium disilicate (o.-rh.) for kilchoanite. The standard list of abbreviations taken from the IUPAC report mentioned previously is as follows: cub. = cubic; tetr. = tetragonal; o.-rh. = orthorhombic; hex. = hexagonal; trig. = trigonal; mon. = monoclinic; and tric. = triclinic.
4. Phases with a characteristic substitutional impurity have the name of the substituent element or group included in parentheses in the appropriate place, e.g., dicalcium (potassium) silicate.
5. In addition to the use of mineral names and of chemically descriptive names, a number of special terms that have been used extensively in the literature have been retained to avoid causing further confusion. For example, alite is retained as a name specifically referring to the substituted form of tricalcium silicate occurring in portland cement and belite for the corresponding dicalcium silicate. The designations for the poorly crystallized calcium silicate hydrates used currently in the literature are retained as calcium silicate hydrate gel, calcium silicate hydrate I, and calcium silicate hydrate II. These may be abbreviated as C-S-H gel, C-S-H I, and C-S-H II, but these abbreviations should not be used as formal names, especially in titles or indexes.

COMPOUNDS AND PHASES

I. OXIDES AND HYDRATED OXIDES

- I-A**
1. calcium oxide*
 - 2.
 3. C
 4. lime, quicklime
 5. CaO
 6. cubic: $a_o = 4.81$
 7. $n = 1.837$
 8. 4-0777
 9. $2.41_{10}, 1.70_4, 2.78_3, 1.45_1, 1.08_1, 1.09_1$
 10. Constituent of most fresh portland cement clinkers. Large quantities (e.g., greater than 2 percent) possibly indicate poor control in manufacture.
 11. 1, pp. 33-34; 2
- I-B**
1. magnesium oxide*
 - 2.
 3. M
 4. periclase
 5. MgO
 6. cubic: $a_o = 4.21$
 7. $n = 1.732$
 8. 4-0829
 9. $2.11_{10}, 1.49_5, 0.94_2, 0.86_2, 1.22_1, 2.43_1$
 10. Identifiable in some portland cement clinkers, and is possible cause of disruptive expansions of some portland cement concrete.
 11. 3, p. 58; 4, p. 403
- I-C**
1. α -quartz
 - 2.
 3. S
 4. silicon dioxide, silica
 5. SiO₂
 6. hexagonal (trig.): $a_o = 4.91, c_o = 5.41$
 7. $n_\omega = 1.545, n_\epsilon = 1.553$
 8. 5-0494
 9. $3.34_{10}, 4.26_3, 1.82_2, 1.54_2, 2.46_2, 2.28_1$
 10. Stable below 573 C at which temperature it inverts to β -quartz. Jasper, chert, and chalcedony are related forms with variant X-ray diffraction patterns due to inclusions and impurities. Cristobalite and tridymite are high-temperature forms of silicon dioxide with distinct crystal structures.
 11. 3, p. 246; 4, pp. 340-355
- I-D**
1. calcium hydroxide*
 - 2.
 3. CH

4. portlandite, hydrated lime
5. Ca(OH)_2
6. hexagonal (trig.): $a_o = 3.59$, $c_o = 4.91$
7. $n_\omega = 1.573$, $n_\epsilon = 1.545$
8. 4-0733
9. 2.63_{10} , 4.90_7 , 1.93_4 , 1.80_3 , 3.11_2 , 1.69_2
10. A major constituent of hydrated portland cement that is generated by reaction of alite and belite with water. The structure consists of layers containing rows of linked Ca(OH)_6 octahedra. There is no significant hydrogen bonding. Calcium hydroxide dehydrates to calcium oxide at about 400 C; in D.T.A. this gives rise to a strong endothermic peak at about 550 C.
11. 1, pp. 174-175, 280; 2; 5, pp. 173-174; 6, p. 352

I-E 1. magnesium hydroxide

- 2.
3. MH
4. brucite
5. Mg(OH)_2
6. hexagonal (trig.): $a_o = 3.15$, $c_o = 4.77$
7. $n_\omega = 1.57$, $n_\epsilon = 1.59$
8. 7-239
9. 2.37_{10} , 4.77_9 , 1.79_5 , 1.57_3 , 1.49_2 , 1.37_2
- 10.
11. 4, pp. 434-435

II. CARBONATES

II-A 1. calcite

- 2.
3. $\overline{\text{CC}}$
4. calcium carbonate (hex.)
5. CaCO_3
6. hexagonal (trig.): $a_o = 4.99$, $c_o = 17.06$ (hex.)
7. $n_\omega = 1.66$, $n_\epsilon = 1.49$
8. 5-0586
9. 3.04_{10} , 2.29_2 , 2.10_2 , 1.91_2 , 2.50_1
10. Chief constituent of limestone, the basic raw material in cement manufacture. Mg ions may substitute for Ca ions to about 9 mole percent, also Mn, Fe, and the like. Decomposes to calcium oxide at about 900 C, with strong endothermic peak on D.T.A. It may form as a result of reaction of atmospheric CO_2 with hydroxide and other components in concrete, resulting in "carbonation shrinkage."
11. 1, pp. 473-477; 4, pp. 476-483; 5, pp. 28-29

II-B 1. aragonite

- 2.
3. $\overline{\text{CC}}$
4. calcium carbonate (o.-rh.)
5. CaCO_3
6. orthorhombic: $a_o = 4.96$, $b_o = 7.97$, $c_o = 5.74$
7. $n_\alpha = 1.53$, $n_\beta = 1.68$, $n_\gamma = 1.69$
8. 5-0453
9. 3.40_{10} , 1.98_7 , 3.27_5 , 2.70_5 , 2.37_4 , 2.48_3
10. Specific gravity higher than calcite (2.94 versus 2.71). It may transform to calcite over long time periods.
11. 4, pp. 497-501

II-C 1. vaterite

- 2.
3. $\overline{C\overline{C}}$
4. μ -calcium carbonate
5. CaCO_3
6. hexagonal (trig.): $a_o = 7.14$, $c_o = 8.52$
7. $n_\omega = 1.55$, $n_\epsilon = 1.65$
8. 13-192
9. 3.58_{10} , 3.30_{10} , 2.73_{10} , 2.06_{10} , 1.83_{10} , 4.26_8
10. Metastable and has a low specific gravity (2.54). It is often formed along with calcite as carbonation products of calcium silicate and aluminate hydrates.
11. 3, p. 114; 4, p. 474; 7

II-D 1. dolomite

- 2.
3. $\text{CM}\overline{C}_2$
4. calcium magnesium carbonate
5. $\text{CaMg}(\text{CO}_3)_2$
6. hexagonal (trig.): $a_o = 4.81$, $c_o = 16.02$
7. $n_\omega = 1.68$, $n_\epsilon = 1.50$
8. 11-78
9. 2.89_{10} , 2.19_3 , 1.78_3 , 1.80_2 , 2.02_2 , 1.39_2
10. Usually contains small amounts of Fe replacing Mg. Structure is best considered as combining one layer of CaCO_3 from calcite and one layer of MgCO_3 from magnesite; it has a double high-temperature endotherm on D.T.A.
11. 3, p. 114; 4, pp. 489-493

II-E 1. magnesite

- 2.
3. $\overline{M\overline{C}}$
4. magnesium carbonate
5. MgCO_3
6. hexagonal (trig.): $a_o = 4.63$, $c_o = 15.01$
7. $n_\omega = 1.51$, $n_\epsilon = 1.70$
8. 8-479
9. 2.74_{10} , 2.10_5 , 1.70_4 , 2.50_2 , 1.94_1 , 1.35_1
10. Refractive indexes increase with Fe, Mn substitution.
11. 4, p. 484

III. SULFATES AND HYDRATED SULFATES

III-A 1. anhydrite

- 2.
3. $\overline{C\overline{S}}$
4. calcium sulfate
5. CaSO_4
6. orthorhombic: $a_o = 6.24$, $b_o = 6.99$, $c_o = 7.00$
7. $n_\alpha = 1.57$, $n_\beta = 1.58$, $n_\gamma = 1.61$
8. 6-226
9. 3.49_{10} , 2.85_4 , 2.33_2 , 2.21_2 , 1.87_2 , 1.65_1
10. Harder than gypsum (Mohs' hardness 3 versus 2) and more dense (2.93 versus 2.32). It is sometimes used in lieu of or as a blend with gypsum in cement to avoid false set.
11. 4, pp. 470, 472; 5, p. 323; 8

III-B 1. soluble anhydrite*

- 2.
3. \overline{CS}
4. calcium sulfate
5. $CaSO_4$
6. hexagonal (?)
7. $n_\omega = 1.51$, $n_\epsilon = 1.55$
8. 2-0134
9. 6.05₁₀, 3.01₉, 2.80₉, 3.48₆, 1.85₆, 1.69₄
10. Formed by low-temperature (< 400 C) dehydration of gypsum. It reacts rapidly with water to produce solutions highly supersaturated with respect to gypsum, whereas anhydrite reacts slowly and produces only slightly supersaturated solutions.
11. 8; 9

III-C 1. bassanite*

- 2.
3. $\overline{CSH}_{0.5}$
4. calcium sulfate hemihydrate, hemihydrate
5. $2CaSO_4 \cdot H_2O$
6. monoclinic: $a_0 = 6.85$, $b_0 = 11.88$, $c_0 = 12.60$, $\beta \approx 90$ deg
7. $n_\omega = 1.55$, $n_\epsilon = 1.57$
8. 14-453
9. 3.00₁₀, 6.01₉, 2.80₅, 3.46₅, 1.84₁, 2.14₁
10. Also called plaster of paris. It is a partial dehydration product of gypsum and is often produced in cement by heating during intergrinding of gypsum with clinker; presence may result in "false set." Two forms, γ (stable) and β (metastable), may be end members of a continuous series of decreasing lattice order ($\gamma \rightarrow \beta$), and increasing extent and time of supersaturation in solution.
11. 5, pp. 322-323; 8; 9; 10; 11; 136

III-D 1. gypsum*

- 2.
3. \overline{CSH}_2
4. calcium sulfate dihydrate
5. $CaSO_4 \cdot 2H_2O$
6. monoclinic: $a_0 = 5.68$, $b_0 = 15.18$, $c_0 = 6.51$, $\beta = 118$ deg 23 min
7. $n_\alpha = 1.52$, $n_\beta = 1.52$, $n_\gamma = 1.53$
8. 6-0046
9. 7.56₁₀, 3.06₆, 4.27₅, 2.68₃, 2.87₃, 3.79₂
10. Intergrind with portland cement clinker to retard set. Various unit cells are described in ref 4. The structure involves pairs of layers normal to the b-axis containing alternate Ca ions and SO_4 tetrahedra. Water molecules are located between successive pairs of layers and are H-bonded to oxygens of the SO_4 groups.
11. 4, pp. 466-469; 5, pp. 316-318, 329-333; 8; 9; 10; 11; 136

III-E 1. thenardite

- 2.
3. \overline{NS}
4. sodium sulfate
5. Na_2SO_4
6. orthorhombic: $a_0 = 5.86$, $b_0 = 12.30$, $c_0 = 9.82$
7. $n_\alpha = 1.47$, $n_\beta = 1.48$, $n_\gamma = 1.48$
8. 5-0631

9. 2.78₁₀, 4.66₇, 3.18₅, 2.65₅, 3.08₅, 1.86₃
- 10.
11. 3, p. 169; 14

III-F 1. metathenardite

- 2.
3. \overline{NS}
4. sodium sulfate form I
5. Na_2SO_4
6. hexagonal (?)
- 7.
8. 1-0990
9. 2.82₁₀, 2.66₁₀, 3.87₆, 3.56₄, 1.93₄, 4.60₂
10. High-temperature form stabilized by fusing with Na_2CO_3 .
11. 14

III-G 1. α -sodium sulfate

- 2.
3. \overline{NS}
- 4.
5. Na_2SO_4
6. hexagonal: $a_o = 5.38$, $c_o = 7.26$
7. $\overline{n} = 1.48$
8. 3-0280
9. 3.92₁₀, 2.86₉, 2.70₉, 1.96₇, 3.62₆, 1.50₄
10. One of five forms of sodium sulfate known.
11. 12; 13; 14

III-H 1. sodium sulfate, form III

- 2.
3. \overline{NS}
- 4.
5. Na_2SO_4
6. orthorhombic: $a_o = 5.59$, $b_o = 8.93$, $c_o = 6.95$
- 7.
8. 8-31
9. 2.80₁₀, 3.91₉, 3.76₉, 2.63₉, 3.48₈, 2.37₈
10. Metastable at room temperature.
11. 14; 15

III-I 1. arcanite

- 2.
3. \overline{KS}
4. potassium sulfate (o.-rh.)
5. K_2SO_4
6. orthorhombic: $a_o = 5.77$, $b_o = 10.07$, $c_o = 7.48$
7. $n_\alpha = 1.49$, $n_\beta = 1.49$, $n_\gamma = 1.50$
8. 5-0613
9. 2.90₁₀, 3.00₈, 2.89₅, 4.18₃, 2.42₃, 2.09₃
10. \overline{KS} has been detected in commercial clinker, and if sufficient SO_3 is available it is said to be the preferred form of alkali sulfate.
11. 3, p. 169; 16

- III-J
1. α -potassium sulfate
 - 2.
 3. $\overline{K\bar{S}}$
 4. potassium sulfate (hex.)
 5. K_2SO_4
 6. hexagonal: $a_o = 5.71$, $c_o = 7.85$
 - 7.
 8. 3-0565
 9. 3.09_{10} , 2.86_{10} , 2.10_8 , 1.98_6 , 1.69_6 , 4.19_4
 - 10.
 11. 17

- III-K
1. aphthitolite
 - 2.
 3. $(N,K)\bar{S}$
 4. sodium, potassium sulfate
 5. $(Na,K)_2SO_4$
 6. hexagonal: $a_o = 5.68$, $c_o = 7.33$
 7. $n_\omega = 1.49$, $n_\xi = 1.50$
 8. 1-0978, 6-429, 20-926, 20-928
 9. 2.84_{10} , 2.94_8 , 2.04_5 , 4.10_3 , 3.67_2 , 2.44_2
 10. A continuous series exists between 3:1 and 1:3 $K_2SO_4 \cdot Na_2SO_4$. It is found in flue dusts and kiln deposits and possibly in clinkers where sulfate is low.
 11. 16; 18

- III-L
1. sodium sulfate-10-hydrate
 - 2.
 3. $N\bar{S}H_{10}$
 4. sodium sulfate decahydrate, Glauber's salt
 5. $Na_2SO_4 \cdot 10H_2O$
 6. monoclinic: $a_o = 12.84$, $b_o = 10.37$, $c_o = 11.52$, $\beta = 107^\circ 77'$
 7. $n_\alpha = 1.394$, $n_\beta = 1.396$, $n_\gamma = 1.398$
 8. 11-647
 9. 5.49_{10} , 3.21_8 , 3.26_6 , 3.11_6 , 4.77_5 , 3.83_4
 - 10.
 - 11.

- III-M
1. potassium calcium sulfate
 - 2.
 3. $KC_2\bar{S}_3$
 - 4.
 5. $K_2Ca_2(SO_4)_3$
 - 6.
 - 7.
 8. 17-741
 9. 3.31_{10} , 3.38_8 , 3.27_6 , 2.78_5 , 2.75_5 , 2.79_4
 10. Double salt that appears to be formed preferentially in clinkers and flue deposits.
 11. 16; 18

- III-N
1. syngenite
 - 2.
 3. $KC\bar{S}_2H$
 4. potassium calcium sulfate hydrate
 5. $K_2Ca(SO_4)_2 \cdot H_2O$

6. monoclinic: $a_0 = 9.78$, $b_0 = 7.16$, $c_0 = 6.25$, $\beta = 103.97$ deg
7. $n_\alpha = 1.50$, $n_\gamma = 1.52$
8. 11-117
9. 2.86_{10} , 3.16_8 , 9.52_6 , 5.71_6 , 4.63_4 , 2.74_4
10. Said to form in cement during storage by reaction of potassium sulfate with gypsum. It has been found in secondary deposits in deteriorating portland cement concrete.
11. 16; 19; 107

III-O 1. hydroxyl ellestadite

- 2.
3. $C_{10}S_3\bar{S}_3H$
- 4.
5. $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$
6. hexagonal: $a_0 = 9.48$, $c_0 = 6.93$
7. $\bar{n} = 1.63$
8. 3.708
9. 2.83_{10} , 2.74_6 , 2.80_5 , 3.47_3 , 2.65_3 , 2.28_3 (see ref. 111)
10. Occurs in steam-cured and hydrothermally treated portland cement pastes where the sulfate content of the cement is high and also in pastes exposed to seawater at high temperatures.
11. 109; 110; 111; 112

IV. TRICALCIUM SILICATES

IV-A 1. tricalcium silicate

- 2.
3. C_3S
- 4.
5. Ca_3SiO_5
6. triclinic, monoclinic, and hexagonal (trig.) forms
triclinic III: $a_0 = 14.08$, $b_0 = 14.15$, $c_0 = 25.10$, $\alpha = 90.30$ deg, $\beta = 89.77$ deg, $\gamma = 119.53$ deg
7. $n_\alpha = 1.713$, $n_\gamma = 1.717$
8. 16-406, 16-407, 17-445
9. triclinic III: 2.79_{10} , 2.61_9 , 2.77_7 , 3.02_7 , 2.75_7 , 3.06_6
10. Distinguished from alite by lack of significant isomorphous substitution. Six polymorphic varieties are known: (a) trig., stable above 1,050 C; (b) mon. I, stable between 990 and 1,050 C; (c) mon. II, stable between 980 and 990 C; (d) tric. I, stable between 920 and 980 C; (e) tric. II, stable between 600 and 920 C; and (f) tric. III (above), stable below 600 C. This nomenclature differs from that of Guinier and Regourd. The variations represent only small differences in symmetry and in layer stacking.
11. 5, pp. 147-151; 20; 21

IV-B 1. alite*

- 2.
3. C_3S (subst.)
4. substituted tricalcium silicate
5. Ca_3SiO_5 (subst.)
6. triclinic, monoclinic, and hexagonal (trig.) forms
mon.: $a_0 = 12.25$, $b_0 = 7.05$, $c_0 = 24.9$, $\beta = 90.04$ deg
7. $n_\alpha = 1.71$, $n_\gamma = 1.72$
8. 11-593, 13-272

9. mon.: 2.78₁₀, 2.61₈, 2.74₆, 3.04₅, 2.18₄, 1.76₄
10. Major constituent of portland cement. True solid solutions with substituents are limited to a few percent of elements such as Fe, Al, Mg, Cr, and Zn. X-ray pattern is somewhat variable with substitution. Structure consists of independent SiO₄ tetrahedral linked by Ca ions; these ions are octahedrally coordinated to additional oxygens not linked to silicon. There are holes adjacent to each calcium ion.
11. 5, pp. 90-92, 147-151; 20

V. DICALCIUM SILICATES

V-A 1. α -dicalcium silicate

- 2.
3. α -C₂S
- 4.
5. Ca₂SiO₄
6. hexagonal (trig.): $a_0 = 5.53$, $c_0 = 7.31$ (at 1,500 C)
7. $n_\omega = 1.66$, $n_\epsilon = 1.67$
8. 20-236
9. 2.71₁₀, 2.81₈, 1.95₅, 2.22₃, 1.58₃, 3.90₁
10. In pure form, stable only above 1,425 C. It may be stabilized at room temperature by comparatively large substitutions of various oxides.
11. 6, p. 359; 20; 22; 23

V-B 1. α' -dicalcium silicate

- 2.
3. α' -C₂S
4. bredigite
5. Ca₂SiO₄
6. orthorhombic: $a_0 = 6.88$, $b_0 = 5.60$, $c_0 = 9.54$ (α'_H form, 1,300 C)
7. $n_\alpha = 1.71$, $n_\beta = 1.71$, $n_\gamma = 1.74$
8. 20-237
9. 2.75₁₀, 2.69₈, 2.19₅, 4.65₃, 3.81₃, 3.37₃
10. Two distinct forms are known, a high-temperature form, α'_H , (stable from 1,420 to 1,165 C) and a lower-temperature form, α'_L , (stable from 1,165 to 650 C in the pure state). Both may be stabilized at room temperature by the presence of various oxides in solid solution.
11. 20; 22; 23; 24

V-C 1. β -dicalcium silicate

- 2.
3. β -C₂S
4. larnite
5. Ca₂SiO₄
6. monoclinic: $a_0 = 5.51$, $b_0 = 6.75$, $c_0 = 9.32$, $\beta = 94^\circ 38'$
7. $n_\alpha = 1.71$, $n_\beta = 1.71$, $n_\gamma = 1.73$
8. 9-351
9. 2.80₁₀, 2.74₈, 2.78₆, 2.61₇, 2.19₇, 2.73₄
10. Pure compound stable only below 650 C but transforms to γ -dicalcium silicate incompletely and sluggishly between 525 and 300 C. The transformation involves a considerable increase in volume, which causes disintegration (dusting) of the crystals.
11. 4, p. 58; 5, p. 144; 20; 23

V-D 1. γ -dicalcium silicate

- 2.
3. γ -C₂S
- 4.
5. Ca₂SiO₄
6. orthorhombic: $a_o = 5.08$, $b_o = 6.76$, $c_o = 11.23$
7. $n_\alpha = 1.64$, $n_\beta = 1.65$, $n_\gamma = 1.65$
8. 9-369
9. 2.73₁₀, 1.91₈, 3.01₇, 1.80₇, 4.32₆, 3.82₆
10. Stable at room temperature. Inadequately stabilized calcium silicate may spontaneously transform to this phase on cooling. This phase has little or no hydraulic cementing ability.
11. 5, pp. 145-147; 20; 25

V-E 1. belite*

2. substituted dicalcium silicate
3. C₂S (subst.)
- 4.
5. Ca₂SiO₄ (subst.)
6. usually monoclinic: $a_o = 5.50$, $b_o = 6.75$, $c_o = 9.30$ to 9.34 , $\beta = 94.2$ to 94.6 deg
7. $n_\alpha = 1.72$, $n_\beta = 1.73$, $n_\gamma = 1.74$
- 8.
9. 2.74₁₀, 2.79₉, 2.21₄, 2.25₃, 3.07₁, 2.42₁ (ref. 115)
10. Major constituent of portland cement. X-ray diffraction patterns vary with substitution and clinking conditions but are generally similar to that of β -dicalcium silicate with some peaks broadened and others slightly displaced. Sometimes α - or α' -dicalcium silicate is also present in clinker. Ca can be substituted by Mg, K, Na, Ba, Cr, and Mn; silica tetrahedra by phosphate or sulfate tetrahedra. Belite occurs in portland cement clinkers as rounded striated grains with layered structures. The basic structure is composed of strings of isolated silica tetrahedra and alternating Ca ions, with the remaining Ca ions in holes between the tetrahedra. In portland cement, belite hydrates slowly but has significant hydraulic cementing ability.
11. 5, pp. 107-108; 20; 23; 114; 115

V-F 1. dicalcium (potassium) silicate

- 2.
3. KC₂₃Si₁₂
- 4.
5. K₂Ca₂₃Si₁₂O₄₈
6. orthorhombic: $a_o = 5.18$, $b_o = 9.52$, $c_o = 6.77$
- 7.
8. 7-348
9. 2.75₁₀, 1.96₈, 2.19₄, 2.03₄, 2.29₂, 2.24₂
10. Apparently a solid solution whose optical properties resemble those of β -dicalcium silicate but whose structure is similar to α' -dicalcium silicate; probably not a distinct compound. Potassium does not seem to enter into this phase in cement clinker if sulfate is present because alkalis react with any sulfate present.
11. 5, pp. 92, 98; 16

VI. TRICALCIUM DISILICATES AND COMPOUNDS OF SIMILAR COMPOSITION

VI-A 1. tricalcium disilicate (mon.)

2. rankinite

3. C_3S_2
- 4.
5. $Ca_3Si_2O_7$
6. monoclinic: $a_o = 10.55$, $b_o = 8.88$, $c_o = 7.85$, $\beta = 120.10$ deg
7. $n_\alpha = 1.64$, $n_\beta = 1.64$, $n_\gamma = 1.65$
8. 9-327, 11-317
9. 3.14_{10} , 2.69_{10} , 3.77_8 , 2.56_8 , 1.80_8 , 4.43_6
10. Natural mineral that also occurs in slags; has been called α -tricalcium disilicate.
11. 4, p. 77; 26; 27

VI-B 1. tricalcium disilicate (o.-rh.)

2. kilchoanite
3. C_3S_2
- 4.
5. $Ca_6(SiO_4)(Si_3O_{10})$
6. orthorhombic: $a_o = 11.42$, $b_o = 5.09$, $c_o = 21.95$
7. $n_\alpha = 1.65$, $n_\gamma = 1.65$
8. 14-77
9. 2.89_{10} , 2.68_9 , 3.07_9 , 3.56_8 , 2.36_8 , 1.96_8
10. Natural mineral that may be prepared hydrothermally at 700 C or in a slightly hydrous form down to 180 C. Its structure is closely related to γ -dicalcium silicate. It converts to tricalcium disilicate (mon.) on heating to about 1,100 C. It was originally called Roy's phase Z.
11. 5, pp. 209-210; 26; 27; 28; 29; 113

VI-C 1. 8-calcium-5-silicate

- 2.
3. C_8S_5
- 4.
5. $Ca_8(SiO_4)_2(Si_3O_{10})$
6. orthorhombic: $a_o = 11.45$, $b_o = 5.09$, $c_o = 28.70$
- 7.
- 8.
9. 3.05_{10} , 2.84_8 , 2.69_8 , 3.60_6 , 1.95_6 , 1.90_6
10. Prepared hydrothermally at 180 to 600 C. In a Ca-rich, disordered form, it is the main constituent of so-called γ -dicalcium silicate hydrate or $C_2SH(C)$, which also contains 5-calcium disilicate monohydrate (XIV-B).
11. 113; 133

VII. CALCIUM MONOSILICATES

VII-A 1. pseudowollastonite

2. calcium monosilicate (tric.-I)
3. α -CS
- 4.
5. $CaSiO_3$ or $Ca_3Si_3O_9$
6. triclinic (usually): $a_o = 6.82$, $b_o = 6.82$, $c_o = 19.65$, $\alpha = 90$ deg 24 min, $\beta = 90$ deg 24 min, $\gamma = 119$ deg 18 min
7. $n_\alpha = 1.61$, $n_\beta = 1.61$, $n_\gamma = 1.65$
8. 10-486
9. 3.20_{10} , 2.79_8 , 1.96_8 , 2.46_6 , 1.49_6 , 5.73_4
10. High-temperature stable form of calcium monosilicate. Several different stacking modifications are known.
11. 5, pp. 138-139; 30

- VII-B**
1. wollastonite
 2. calcium monosilicate
 3. β -CS
 - 4.
 5. β -CaSiO₃
 6. triclinic or monoclinic:
Mon: $a_0 = 15.33$, $b_0 = 7.28$, $c_0 = 7.07$, $\beta = 95$ deg 24 min
 7. $n_\alpha = 1.62$, $n_\beta = 1.63$, $n_\gamma = 1.63$
 8. tric.: 10-487; mon.: 10-489
 9. 2.97₁₀, 3.83₈, 3.52₈, 3.31₈, 2.47₆, 2.18₆ (both forms)
 10. Naturally occurring mineral. The monoclinic form was previously called para-wollastonite. Differences between the two forms are very slight. These are low-temperature stable calcium monosilicates, inverting to pseudowollastonite above 1,125 C.
 11. 4, pp. 140-143; 5, pp. 139-142; 31

VIII. CALCIUM SILICATES BEARING ADDITIONAL ANIONIC GROUPS

- VIII-A**
1. spurrite
 - 2.
 3. $C_5S_2\overline{C}$
 4. 5-calcium disilicate monocarbonate
 5. $Ca_5(SiO_4)_2CO_3$
 6. monoclinic: $a_0 = 10.49$, $b_0 = 6.71$, $c_0 = 14.15$, $\beta = 101$ deg 19 min
 7. $n_\alpha = 1.64$, $n_\beta = 1.67$, $n_\gamma = 1.68$
 8. 13-496
 9. 2.70₁₀, 2.64₇, 3.02₇, 2.66₅, 2.17₄, 3.81₃
 10. Natural mineral that can be hydrothermally synthesized over a wide range of temperature.
 11. 4, p. 59; 5

- VIII-B**
1. tilleyite
 - 2.
 3. $C_5S_2\overline{C}_2$
 4. 5-calcium disilicate dicarbonate
 5. $Ca_5(Si_2O_7)(CO_3)_2$
 6. monoclinic: $a_0 = 15.03$, $b_0 = 10.27$, $c_0 = 7.63$, $\beta = 105$ deg 50 min
 7. $n_\alpha = 1.61$, $n_\beta = 1.63$, $n_\gamma = 1.65$
 8. 13-416
 9. 3.01₁₀, 3.10₆, 1.90₅, 2.98₄, 2.80₄, 2.10₄
 10. Natural mineral that can be hydrothermally synthesized over a wide range of temperatures.
 11. 4, p. 77; 5, pp. 226-227

- VIII-C**
1. 5-calcium disilicate monosulfate
 - 2.
 3. $C_5S_2\overline{S}$
 4. calcium silicosulfate
 5. $Ca_5(SiO_4)_2SO_4$
 6. orthorhombic: $a = 15.41$, $b = 10.18$, $c = 6.84$
 7. $\overline{n} = 1.635$ with some grains below; very low birefringence
 8. 18-307
 9. 2.82₁₀, 2.84₁₀, 3.19₉, 2.56₉, 4.57₈, 2.61₈

10. An intermediate product in the cement-sulfuric acid process; found in kiln rings in portland cement kilns; found in some type K expansive cements. The structure is believed to resemble that of silicocarnotite, a silica-substituted apatite.
11. 137, 138; 139

IX. CALCIUM ALUMINATES AND RELATED COMPOUNDS

IX-A 1. tricalcium aluminate*

- 2.
3. C_3A
- 4.
5. $Ca_3Al_2O_6$
6. cubic: $a_0 = 15.26$
7. $n = 1.70$
8. 8-5
9. $2.70_{10}, 1.91_4, 1.56_3, 4.08_2, 2.79_1, 2.20_1$
10. Major constituent of portland cement, hydrating more rapidly than other components but developing less strength than the calcium silicates. Its hydration is retarded somewhat by calcium sulfate. It appears as equant grains in the dark interstitial phase in reflected light. A number of possible structures have been proposed but not proved. The aluminum is tetrahedrally coordinated.
11. 5, pp. 55-56; 20; 32

IX-B 1. tricalcium (sodium) aluminate

- 2.
3. NC_3A_3
4. sodium calcium aluminate
5. $NaCa_4Al_3O_9$
6. orthorhombic
7. $n_\alpha = 1.70, n_\gamma = 1.71$
8. 2-0929
9. $2.67_{10}, 1.55_{10}, 2.19_8, 1.91_8, 1.88_8, 1.34_6$ (but see ref. 34)
10. Found as prismatic crystals constituting a minor constituent in the interstitial phase of some clinkers. The potassium analogue, KC_3A_3 , is not definitely established. A second sodium-bearing orthorhombic structure exists at lower sodium contents, and a high-temperature tetragonal phase has recently been shown to be formed in clinkers and may be stabilized at room temperature.
11. 5, pp. 97-99; 16; 20; 33; 34; 140; 141; 142

IX-C 1. 12-calcium-7-aluminate

- 2.
3. $C_{12}A_7$
4. mayenite
5. $Ca_{12}Al_{14}O_{33}$
6. cubic: $a_0 = 11.98$
7. $n = 1.61$
8. 9-413
9. $2.68_{10}, 4.89_9, 2.45_5, 3.00_5, 2.19_4, 1.95_3$
10. Usually found in small proportions in calcium aluminate cements. This compound hydrates rapidly but contributes little to strength. It was originally thought to have the composition C_5A_3 . It is relatively stable compared to the metastable 5-calcium-3-aluminate. It is known to absorb atmospheric water at high temperatures to approach the composition $C_{12}A_7H$, with 4 OH ions in the structure apparently replacing 2 oxygen ions.
11. 5, pp. 103, 157-158; 32; 130

IX-D 1. 5-calcium-3-aluminate

- 2.
3. C_5A_3
- 4.
5. $Ca_5Al_3O_{14}$
6. orthorhombic: $a_o = 10.98$, $b_o = 11.25$, $c_o = 10.28$
7. $n_\alpha = 1.68$, $n_\beta = 1.68$, $n_\gamma = 1.69$
8. 11-357
9. 2.93₁₀, 2.89₉, 2.47₆, 1.59₆, 3.37₅, 2.34₅
10. Synthetic metastable compound.
11. 32; 35

IX-E 1. calcium monoaluminate

- 2.
3. CA
- 4.
5. $CaAl_2O_4$
6. monoclinic: $a_o = 8.70$, $b_o = 8.10$, $c_o = 15.21$, $\beta = 90.1$ deg
7. $n_\alpha = 1.64$, $n_\beta = 1.66$, $n_\gamma = 1.66$
8. 1-0888
9. 2.97₁₀, 2.52₄, 2.41₃, 1.92₂, 1.53₂, 4.69₁
10. Major constituent of calcium aluminate cements. It is strongly hydraulic.
11. 5, pp. 153-154; 6, pp. 12-13; 32; 36, pp. 34-47

IX-F 1. calcium dialuminate

- 2.
3. CA_2
- 4.
5. $CaAl_4O_7$
6. monoclinic: $a_o = 12.90$, $b_o = 8.88$, $c_o = 5.45$, $\beta = 107.0$ deg
7. $n_\alpha = 1.62$, $n_\beta = 1.62$, $n_\gamma = 1.65$
8. 7-82
9. 3.52₁₀, 2.61₉, 4.44₈, 2.76₆, 3.08₆, 2.72₆
10. Constituent of some commercial calcium aluminate cements. It reacts slowly at first, but the rate increases with growing concentration of hydration products.
11. 5, p. 152; 32; 36, pp. 34-47

IX-G 1. calcium-6-aluminate

- 2.
3. CA_6
- 4.
5. $CaAl_{12}O_{19}$
6. hexagonal: $a_o = 5.57$, $c_o = 22.01$
7. $n_\omega = 1.75$, $n_\epsilon = 1.75$
8. 7-85
9. 1.39₁₀, 2.48₉, 2.11₈, 1.53₉, 2.01₈, 2.62₈
10. Harder than other calcium aluminates and nonhydraulic. It may occur in high-temperature castable refractories.
11. 5, pp. 151-152; 32

IX-H 1. calcium aluminate fluoride

- 2.
3. $C_{11}A_7 \cdot CaF_2$
- 4.

5. $\text{Ca}_{11}\text{Al}_{14}\text{O}_{32} \cdot \text{CaF}_2$
6. cubic: $a_o = 11.97$
7. $n = 1.60$
- 8.
- 9.
10. May be prepared by heating anhydrous 12-calcium-7-aluminate or $\text{C}_{12}\text{A}_7\text{H}$ with CaF_2 . Its structure is similar to that of 12-calcium-7-aluminate with the fluoride occupying holes in the structure.
11. 32; 37; 38

IX-I 1. calcium aluminate chloride

- 2.
3. $\text{C}_{11}\text{A}_7 \cdot \text{CaCl}_2$
- 4.
5. $\text{Ca}_{11}\text{Al}_{14}\text{O}_{32} \cdot \text{CaCl}_2$
6. cubic: $a_o = 12.00$
7. $= 1.626$
- 8.
- 9.
10. Structure presumably analogous to that of calcium aluminate fluoride.
11. 32; 37; 38

IX-J 1. tetracalcium trialuminate sulfate

- 2.
3. $\text{C}_4\text{A}_3\bar{\text{S}}$
- 4.
5. $\text{Ca}_4(\text{Al}_6\text{O}_{12})\text{SO}_4$
6. cubic: $a_o = 18.39$
7. $n = 1.57$
- 8.
9. 3.76₁₀, 2.65₃, 2.17₂, 3.25₁, 1.62₁, 2.46₁ (ref. 127)
10. Synthetic compound that is an essential constituent of type K expansive cement. It is prepared by firing mixtures of calcite, gypsum, and bauxite and is apparently the only stable compound in the ternary system. In expansive cement it hydrates to produce ettringite if the system is sufficiently rich in available sulfate, or tetracalcium aluminate monosulfate hydrate if it is not. A calcium aluminate monosulfate-18-hydrate has been reported to be a product of hydration under certain circumstances.
11. 125; 126; 127; 128; 129

X. CALCIUM FERRITES AND ALUMINOFERRITES

X-A 1. calcium aluminoferrite solid solution series*

- 2.
3. $\text{C}_2(\text{F}_{1-p})\text{A}_p$ where $p = \text{A}/\text{A} + \text{F}$, $0 < p < 0.7$
- 4.
5. $\text{Ca}_4\text{Fe}_4\text{O}_{10}$ to $\text{Ca}_4\text{FeAl}_3\text{O}_{10}$
6. orthorhombic: lattice shifts are as follows (ref. 39):

$p = 0.3$	0.5	0.7
$a_o = 5.35$	5.35	5.31
$b_o = 14.61$	14.51	14.46
$c_o = 5.59$	5.56	5.51

7. $p = 0$: $n_\alpha = 2.20$, $n_\beta = 2.22$, $n_\gamma = 2.29$
 $p = 0.5$: $n_\alpha = 1.96$, $n_\beta = 2.01$, $n_\gamma = 2.04$
8. $p = 0.5$: 11-124; $p = 0.7$: 16-410
9. $p = 0.5$: 2.63₁₀, 2.77₈, 1.92₈, 2.67₇, 2.04₆, 7.24₅
 $p = 0.7$: 2.62₁₀, 2.76₈, 1.91₈, 2.65₈, 2.04₇, 1.53₇
10. Continuous solid solution series, with a small structural discontinuity at $p = 0.3$. In cements it is frequently called the ferrite phase. The composition at $p = 0.5$ (C_4AF) has been considered a separate compound (brownmillerite) in the past. It appears as light interstitial material in reflected light, and it is a minor constituent in portland cement clinker. In clinker it ranges in composition probably from $p \approx 0.33$ to $p \approx 0.67$, with some substitution of other ions. It hydrates slowly but has some hydraulic qualities. The structure consists of layers of FeO_6 octahedra joined to layers of FeO_4 tetrahedra with Ca ions in holes between the layers; Al substitutes in tetrahedral layers (up to $p = 0.33$) then in both tetrahedral and octahedral layers.
11. 5, pp. 77, 93, 113-116, 158-161; 20; 39

X-B 1. dicalcium ferrite

- 2.
3. C_2F
- 4.
5. $Ca_2Fe_2O_5$
6. orthorhombic: $a_o = 5.42$, $b_o = 14.76$, $c_o = 5.60$
7. $n_\alpha = 2.20$, $n_\beta = 2.22$, $n_\gamma = 2.29$
8. 11-675
9. 2.67₁₀, 2.78₇, 1.94₇, 2.71₆, 2.07₅, 7.36₄
10. End member of calcium aluminoferrite solid solution series.
11. 5, pp. 77, 93, 113-116; 20; 39

XI. CALCIUM ALUMINATE FERRITE SILICATES

XI-A 1. garnet-hydrogarnet solid solution series

- 2.
3. $C_3(F_{1-p}A_p)(Si_{1-q}H_{2q})_3$ where $p = A/A + F$ and $q = 2H/2H + S$
- 4.
5. $3CaO \cdot (Fe_2O_3)_{1-p} \cdot (Al_2O_3)_p \cdot [(SiO_2)_{1-q} \cdot (H_2O)_{2q}]_3$
 where p varies from 0 to 1 and q varies from 0 to 1, except that some doubts exist for compositions of $p = 1$ and $q > 0.84$.
6. cubic: a_o varies with composition from about 11.85 to about 12.75
7. n varies from about 1.60 to about 1.90
8. C_3AH_6 : 3-0125, 2-1124; C_3FH_6 : 3-1126; C_3AS_3 : 3-0826; C_3FS_3 : 10-288; $C_3AS_2H_4$: 4-0723
9. C_3AS_3 : 2.65₁₀, 1.58₉, 2.96₈, 1.65₈, 1.92₇, 2.44₆
 C_3FS_3 : 2.70₁₀, 3.02₆, 1.61₆, 2.46₅, 1.96₃, 1.67₃
10. A complete 4-way solid solution series seems to exist, although compositions approaching C_3FH_6 have been questioned. Previous nomenclature and some composition-dependent parameters for the end members are as follows:
 $p = 1$ $q = 1$ (C_3AH_6); called C_3AH_6 , $a_o = 12.56$, $n = 1.60$
 $p = 0$ $q = 1$ (C_3FH_6); called C_3FH_6 , $a_o = 12.74$, $n = 1.72$
 $p = 1$ $q = 0$ (C_3AS_3); called grossular, $a_o = 11.85$, $n = 1.74$
 $p = 0$ $q = 0$ (C_3FS_3); called andradite, $a_o = 12.06$, $n = 1.89$

The intermediate member having the composition corresponding to $p = 1$, $q = 0.67$ ($C_3AS_2H_4$) is called hibsichte. Members of composition intermediate between grossular and hibsichte are called hydrogrossular. Garnet is a general name for cubic

calcium, magnesium, iron, or manganese aluminum silicates having structures similar to those of the present compounds, and hydrogarnet is often used for members of the series containing appreciable crystalline water. Members of the garnet-hydrogarnet solid solution series as defined here occur sporadically and to a limited extent in portland cement concrete. Occurrence is favored by low sulfate content and high temperatures. They appear to confer some sulfate resistance to the concrete. They occur more frequently in lime-pozzolan systems. C_3AH_6 is a major component of aluminous cement concrete after exposure to high temperatures and moist environmental conditions.

11. 4, pp. 21-31; 5, pp. 281-282, 344-386; 40; 41; 42; 43; 44; 45

XII. POORLY CRYSTALLIZED CALCIUM SILICATE HYDRATES

- XII-A
1. calcium silicate hydrate gel
 - 2.
 3. C-S-H gel (abbreviation)
 - 4.
 5. Composition variable: Two groups thought to be distinguishable are $x \text{ CaO} \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O}$ with x between 0.83 and 1.33, and x between 1.5 and 2, although the calcium-to-silica ratio is probably not restricted to these ranges, especially the upper limit.
 6. So badly organized as to be indefinite
 7. About 1.50
 - 8.
 9. Up to three weak and diffuse X-ray peaks observed usually at about 3.04, 2.80, and 1.80 Å
 10. Has been called C-S-H, tobermorite gel, or even tobermorite, although substantially different from the mineral of that name. The main X-ray peak (3.02 to 3.05 Å) is so broad that the peak usually cannot be resolved from a second peak near 2.80 Å with normal technique; this feature separates material of this somewhat indefinite category from the better crystallized calcium silicate hydrate I and calcium silicate hydrate II. Within this group, material of the lower Ca:Si ratio range converts readily to tobermorite on hydrothermal treatment and that of the higher Ca:Si ratio range converts to dicalcium silicate monohydrate (o.-rh.). The structure has long been thought to resemble tobermorite in disordered form, but possible resemblances between a lime-rich form of it and jennite have been mentioned. It undoubtedly consists of silica tetrahedra (either individual or linked in short chain segments) coupled to a disordered or at best locally ordered calcium-oxygen layer, with additional interlayer material. In substituted form it is the major constituent of the cementitious matrix of portland cement concrete. Kalousek has reported the preparation of phases that he designates as $C_{5-6}S_6H$ and $C_5S_4H_n$ in high-pressure steam-cured preparations. These resemble C-S-H gel in most particulars and are within the compositional range designated for C-S-H gel; however, their exact relationships to phases designated as C-S-H I by other workers is not yet clear.
 11. 5, pp. 199-203, 288-298, 378-379; 46; 47; 48; 49; 50; 63; 111

- XII-B
1. substituted calcium silicate hydrate gel*
 - 2.
 3. substituted C-S-H gel (abbreviation)
 - 4.
 5. Composition variable: Resembles C-S-H gel with additional anions and cations incorporated into the crystal structure
 - 6.
 - 7.

- 8.
9. Up to three weak and diffuse peaks observed at 3.04, 2.80, and 1.80 Å
10. Major constituent of the cementitious binder of portland cement concrete, responsible for much of the strength and hydraulic quality of this material. It almost always contains some sulfate substitution and usually contains incorporated alumina, iron, or other ions. It has been referred to as tobermorite gel and Kalousek's phase X and is the main component of so-called cement gel.
11. 5, pp. 336-337, 383-385; 46; 51; 52; 116

XII-C 1. calcium silicate hydrate I

- 2.
3. $C_{0.8-1.5}SH_x$; C-S-H I (abbreviation)
4. plombierite
5. $(CaO)_{0.8-1.5}SiO_2(H_2O)_x$
6. orthorhombic (?): $a_0 = 5.6$, $b_0 = 3.6$, c_0 variable
7. About 1.50
8. 10-416
9. 3.07_{10} , 2.81_{10} , 1.83_{10} , 5.48_6 , 2.07_6 , 1.67_6
10. Better crystallized than C-S-H gel. Its X-ray diffraction pattern typically shows up to 14 reflections, most of which approximate the $hk0$ reflections of tobermorite, usually with a basal peak at 10 to 12 Å. It has been called tobermorite and CSH(B) in some early papers. It is probably a degenerate form of tobermorite with partly condensed silicate chains and can be distinguished from C-S-H gel by the comparative narrowness of the strongest peak at 3.04 Å, which can be readily resolved from the adjacent peak at about 2.80 Å. It does not occur in ordinary portland cement concrete but may occur sporadically in laboratory autoclaved preparations.
11. 5, pp. 192-196, 378-379; 6, pp. 113-120, 130-131; 46; 53; 54; 63; 111

XII-D 1. calcium silicate hydrate II

- 2.
3. $C_{1.5-2.0}SH_x$; C-S-H II (abbreviation)
- 4.
5. $(CaO)_{1.5-2.0}SiO_2(H_2O)_x$
6. variable
- 7.
- 8.
9. X-ray pattern relates to fiber bundles: 3.07_{vs} , 9.8_{vs} , 2.80_{vs} , 1.83_{vs} , 2.00_{ss} , 1.56_s (ref. 6)
10. Name used to denote material of comparable or somewhat lower crystallinity than C-S-H I but with a composition in the range given, and may cover any of several perhaps different structural types. All forms are distinguished from calcium silicate hydrate gel by narrowness of strong X-ray peak at 3.07 Å, which can readily be resolved from the peak at about 2.8 Å with normal techniques, and from calcium silicate hydrate I by differences in the X-ray pattern, which generally include a basal peak at 10.4 to 10.7 Å for calcium silicate hydrate II. The morphology usually (but not always) is characterized by bundles of fibers. This material forms from C_3S or β - C_2S hydrating in excess water at room temperature.
11. 5, pp. 192-196; 6, p. 373; 46

XIII. WELL-CRYSTALLIZED CALCIUM SILICATE HYDRATES: TOBERMORITES

XIII-A 1. tobermorite (11 Å)

- 2.
3. $C_5S_6H_5$

- 4.
5. $\text{Ca}_5\text{Si}_6\text{O}_{22}\text{H}_{10}$
6. orthorhombic (geometrically; true cell is triclinic): $a_0 = 11.2$, $b_0 = 7.3$, $c_0 = 22.6$
7. $n_\alpha = 1.57$, $n_\beta = 1.57$, $n_\gamma = 1.58$
8. 19-1364
9. 3.08_{10} , 11.3_8 , 2.98_7 , 2.82_4 , 1.84_4 , 5.48_3
10. Has been misidentified with calcium silicate hydrate I. It occurs as a natural mineral and in autoclaved cement-silica or lime-silica building materials but does not form in cement systems hydrated at ordinary temperatures. This material is distinguished from calcium silicate hydrate I by being fully crystalline ~ 35 X-ray peaks by normal methods) and from other varieties of tobermorite by position of the basal peak. The structure can accommodate some Al with a resulting small increase in the (001) X-ray spacing.
11. 5, pp. 184-190; 46; 55; 63

XIII-B 1. tobermorite (14 Å)

- 2.
3. $\text{C}_5\text{S}_6\text{H}_9$
- 4.
5. $\text{Ca}_5\text{Si}_6\text{O}_{26}\text{H}_{18}$
6. orthorhombic: $a_0 = 11.2$, $b_0 = 7.3$, $c_0 = 28.0$
7. $\bar{n} = 1.54$
8. 6-0005
9. 14.0_{10} , 3.07_9 , 5.53_9 , 2.98_8 , 2.81_8 , 1.83_8
10. Occurs rarely as a natural mineral and may be synthesized hydrothermally. It dehydrates to tobermorite (11 Å) on heating to 55 C in air.
11. 5, pp. 181-185, 190-191; 46; 54; 57

XIII-C 1. tobermorite (9.3 Å)

- 2.
3. $\text{C}_5\text{S}_6\text{H}$
4. riversideite
5. $\text{Ca}_5\text{Si}_6\text{O}_{18}\text{H}_2$
6. orthorhombic: $a_0 = 11.2$, $b_0 = 7.3$, $c_0 = 18$
7. $n_\alpha = 1.60$, $n_\beta = 1.60$, $n_\gamma = 1.61$
8. 10-374
9. 2.99_{vs} , 9.4_s , 2.76_{ms} , 1.84_m , 4.80_{nw} , 3.58_{nw} (ref. 55)
10. Can be prepared by heating tobermorite (11 Å) 250 to 450 C. Its basic structure is thought to be similar to tobermorite (11 Å) except that the interlayer water has been removed. A natural mineral, riversideite, is similar but has a higher basal spacing.
11. 5, p. 191; 46; 55; 56; 57

XIII-D 1. tobermorite (9.7 Å)

- 2.
3. C_5S_6
- 4.
5. $\text{Ca}_5\text{Si}_6\text{O}_{17}$
6. orthorhombic: $a_0 = 11.2$, $b_0 = 7.3$, $c_0 = 19.4$
- 7.
- 8.
- 9.
10. May be produced by heating tobermorite (14 Å) from Crestmore, California, to 730 C. On slow heating the tobermorite (11 Å) phase forms first, followed by tobermorite (9.3 Å), and then, at 450 to 650 C, by the present phase, which is fully dehydrated.

In addition to water content and basal spacing differences between tobermorite (9.3 Å) and tobermorite (9.7 Å), structural differences within the layers are indicated by differences in the infrared absorption spectrum.

11. 46; 56; 57

XIII-E 1. tobermorite (12 Å)

- 2.
- 3.
- 4.
5. Chemical formula not definitely established
6. Presumably orthorhombic—similar to tobermorite (11 Å)
- 7.
- 8.
- 9.
10. Component of mixed crystal intergrowths found at Crestmore, California. Basal spacing is 12.5 Å; it may possibly be the same as tacharanite, a rare mineral with a 12.6 Å spacing, a composition about $\text{C}_{0.6}\text{SH}_{1.2}$, and a powder pattern showing some similarity to calcium silicate hydrate I.
11. 5, p. 191; 46; 58

XIII-F 1. tobermorite (10 Å)

- 2.
- 3.
- 4.
5. Chemical formula not definitely established
6. orthorhombic: $a_0 = 7.3$, $b_0 = 11.2$, $c_0 = 20.5$
- 7.
8. 6-0020
9. 10.0₁₀, 3.05₁₀, 2.93₈, 2.80₈, 1.83₇, 4.92₅
10. Found, usually as an intergrowth, at Crestmore, California. It partially dehydrates to tobermorite (9.3 Å) on heating and is thought to be richer in calcium and deficient in silicon compared to tobermorite (11 Å).
11. 5, p. 191; 46

XIV. WELL-CRYSTALLIZED CALCIUM SILICATE HYDRATES: OTHER THAN TOBERMORITE

XIV-A 1. 6-calcium disilicate trihydrate

- 2.
3. $\text{C}_6\text{S}_2\text{H}_3$
4. tricalcium silicate hydrate
5. $\text{Ca}_6(\text{Si}_2\text{O}_7)(\text{OH})_6$ (?)
6. hexagonal: $a_0 = 10.00$, $c_0 = 7.48$
7. $n_\omega = 1.59$, $n_\epsilon = 1.60$
8. 12-109 (also 3-0669, 11-502)
9. 8.6₁₀, 3.28₈, 3.03₈, 2.89₈, 2.08₈, 1.87₈
10. Not known to occur as a natural mineral. This compound may be prepared synthetically from C_3S or other calcium silicate materials at 180 to 350 C under saturated steam pressure.
11. 5, pp. 213-214; 46; 63

XIV-B 1. 5-calcium disilicate monohydrate

- 2.
3. $\text{C}_5\text{S}_2\text{H}$

4. calciochondrodite
5. $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$
6. monoclinic: $a_0 = 11.4$, $b_0 = 5.05$, $c_0 = 8.94$, $\beta = 109.3^\circ$
7. $\bar{n} = 1.63$
8. 11-300
9. 3.02_{10} , 1.90_{10} , 5.42_8 , 3.31_8 , 2.92_8 , 2.89_8
10. This compound has been called Roy's phase X. It has not been reported as a natural mineral but is formed hydrothermally at 400 to 800 C at pressures above 300 kg/cm^2 or at lower temperatures under saturated steam pressure. Material called γ -dicalcium silicate hydrate in the literature is a mixture of 5-calcium disilicate monohydrate and another compound.
11. 5, pp. 208-209; 46; 27; 117

XIV-C 1. dicalcium silicate monohydrate (mon.)

- 2.
3. C_2SH
4. hillebrandite, $\beta\text{-C}_2\text{SH}$
5. $\text{Ca}_2(\text{SiO}_3)(\text{OH})_2(?)$
6. monoclinic: $a_0 = 16.6$, $b_0 = 7.26$, $c_0 = 11.85$, $\beta \approx 90^\circ$
7. $n_\alpha = 1.60$, $n_\gamma = 1.61$
8. 9-51, 11-594
9. 2.92_{10} , 4.76_9 , 3.33_9 , 3.02_8 , 2.82_8 , 2.76_8
10. Occurs naturally and can be prepared hydrothermally at saturated steam pressure or above. The crystal habit is fibrous. It can be distinguished from 4-calcium trisilicate monohydrate (foshagite) by infrared spectrum and X-ray powder pattern.
11. 5, pp. 180-181; 46; 118

XIV-D 1. dicalcium silicate monohydrate (o.-rh.)

- 2.
3. C_2SH
4. $\alpha\text{-C}_2\text{S}$ hydrate, dicalcium silicate hydrate I; dicalcium silicate hydrate (A)
5. $\text{Ca}_2(\text{HSiO}_4)(\text{OH})$
6. orthorhombic: $a_0 = 9.34$, $b_0 = 9.22$, $c_0 = 10.61$
7. $n_\alpha = 1.61$, $n_\beta = 1.62$, $n_\gamma = 1.63$
8. 9-325
9. 3.27_{10} , 4.22_9 , 2.41_9 , 3.90_8 , 3.54_8 , 2.87_8
10. Synthetic hydrothermal product that is also formed by autoclaving $\beta\text{-C}_2\text{S}$ and C_3S pastes. It is a constituent found in sand-lime bricks (conferring relatively low strength), autoclaved slag cement concretes, and similar technical products with relatively high lime-to-silica ratios.
11. 5, pp. 212-213; 46; 63

XIV-E 1. 4-calcium disilicate monohydrate

2. rustumite
3. $\text{C}_4\text{S}_2\text{H}$
- 4.
5. $\text{Ca}_4\text{Si}_2\text{O}_7(\text{OH})_2$
6. monoclinic: $a_0 = 7.62$, $b_0 = 18.55$, $c_0 = 15.51$, $\beta = 104^\circ 20'$
7. $n_\alpha = 1.64$, $n_\gamma = 1.65$
8. 18-305
9. 3.03_{10} , 2.89_9 , 3.19_8 , 2.52_7 , 1.91_7 , 1.75_7
10. Formed as a natural mineral, and not yet synthesized. This compound appears to be related to tilleyite, a carbonate-bearing mineral, and to cuspidine, a fluoride-bearing mineral.
11. 46; 27

- XIV-F**
1. 6-calcium trisilicate hydrate
 2. dellaite
 3. C_6S_3H
 - 4.
 5. $Ca_6Si_3O_{13}H_2$
 6. triclinic: $a_o = 6.84$, $b_o = 6.94$, $c_o = 12.89$, $\alpha = 90$ deg 45 min, $\beta = 97$ deg 22 min, $\gamma = 98$ deg 16 min
 7. $n_\alpha = 1.65$, $n_\beta = 1.66$, $n_\gamma = 1.66$
 - 8.
 9. 2.82_{10} , 3.06_8 ; 2.89_8 , 2.86_8 , 2.29_8 , 2.98_6 (ref. 135)
 10. A natural mineral; synthesized hydrothermally at pressures over the temperature range 350 to 810 C, on decomposition of dicalcium silicate monohydrate (mon.) (hillebrandite).
 11. 28; 59; 121; 134

- XIV-G**
1. tricalcium disilicate trihydrate
 2. afwillite
 3. $C_3S_2H_3$
 - 4.
 5. $Ca_3(SiO_3OH)_2 \cdot 2H_2O$
 6. monoclinic: $a_o = 16.27$, $b_o = 5.63$, $c_o = 13.23$, $\beta = 134$ deg 48 min
 7. $n_\alpha = 1.62$, $n_\beta = 1.62$, $n_\gamma = 1.63$
 8. 9-454
 9. 3.19_{10} , 2.84_{10} , 2.74_{10} , 6.46_8 , 5.74_8 , 4.73_8
 10. A well-crystallized natural mineral of relatively constant composition and large crystal size; synthesized hydrothermally at low temperatures (100 to 160 C) or by prolonged ball-milling of C_3S in water.
 11. 5, pp. 211-212; 60

- XIV-H**
1. 4-calcium trisilicate monohydrate
 2. foshagite
 3. C_4S_3H
 - 4.
 5. $Ca_4(Si_3O_9)(OH)_2$
 6. monoclinic: $a_o = 10.32$, $b_o = 7.36$, $c_o = 14.07$, $\beta = 106$ deg
 7. $n_\alpha = 1.59$, $n_\beta = 1.59$, $n_\gamma = 1.60$
 8. 11-94
 9. 2.92_{10} , 1.74_9 , 6.80_7 , 4.95_7 , 3.37_7 , 2.30_7
 10. A natural mineral; also synthesized hydrothermally between 220 and 650 C. The composition was formerly thought to be nearer $C_5S_3H_3$. The mineral has been confused with dicalcium silicate monohydrate (mon.) (hillebrandite). The structure is related to that of calcium monosilicate (wollastonite).
 11. 5, pp. 179-180; 46; 61; 118

- XIV-I**
1. 5-calcium-5-silicate monohydrate
 2. xonotlite
 3. C_5S_5H
 - 4.
 5. $Ca_5(Si_5O_{17})(OH)_2 \cdot 0.2H_2O$
 6. monoclinic: $a_o = 16.53$, $b_o = 7.33$, $c_o = 7.04$, $\beta \approx 90$ deg.
 7. $n_\alpha = 1.58$, $n_\beta = 1.58$, $n_\gamma = 1.60$
 8. 10-488
 9. 3.07_{10} , 2.04_9 , 1.95_9 , 3.65_7 , 3.23_7 , 2.83_5

10. A natural mineral that is readily synthesized at 150 to 350 C under saturated steam pressure. It is a constituent of some sand-lime blocks and related products; satisfactory strength is attained with xonotlite present.
11. 5, pp. 177-179; 6, 116-120; 46; 62; 63

- XIV-J**
1. tricalcium trisilicate monohydrate
 2. rosenhahnite
 3. $\text{C}_3\text{S}_3\text{H}$
 - 4.
 5. $\text{Ca}_3\text{Si}_3\text{O}_{10}\text{H}_2$
 6. triclinic: $a_o = 6.95$, $b_o = 9.47$, $c_o = 6.81$, $\alpha = 108^\circ 39'$, $\beta = 94^\circ 49'$, $\gamma = 95^\circ 43'$
 7. $n_\alpha = 1.62$, $n_\beta = 1.64$, $n_\gamma = 1.65$
 8. 19-250, 15-313
 9. 3.20₁₀, 2.96₉, 3.04₆, 2.78₄, 3.36₃, 2.66₃
 10. A natural mineral that has been synthesized at 400 C under high pressure (25 to 50 kilobars). Rosenhahnite converts to calcium monosilicate (wollastonite) on heating to 400 to 500 C.
 11. 46; 64; 65

- XIV-K**
1. suolunite
 2. calcium monosilicate monohydrate
 3. CSH
 - 4.
 5. CaSiO_4H_2
 6. orthorhombic: $a_o = 11.15$, $b_o = 19.67$, $c_o = 6.08$
 7. $n_\alpha = 1.61$, $n_\beta = 1.62$, $n_\gamma = 1.62$
 - 8.
 9. Strong X-ray peaks at 4.03, 3.11, and 2.80
 10. A new mineral reported from Inner Mongolia.
 11. 46

- XIV-L**
1. gyrolite
 2. dicalcium trisilicate hydrate
 3. $\text{C}_2\text{S}_3\text{H}_2$
 - 4.
 5. $\text{Ca}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
 6. hexagonal: $a_o = 9.72$, $c_o = 132.8$ (6-layer thicknesses)
 7. $n_\omega = 1.55$, $n_\epsilon = 1.54$
 8. 9-449
 9. 22₁₀, 3.12₁₀, 11.0₈, 4.20₈, 1.82₈, 3.65₆
 10. A naturally occurring mineral that may be synthesized at temperatures between 120 and about 200 C under saturated steam pressure. The formula has been disputed.
 11. 5, pp. 204-205; 46; 66; 67; 68

- XIV-M**
1. calcium disilicate trihydrate
 - 2.
 3. CS_2H_3 (approximately)
 - 4.
 5. Exact composition not established
 6. hexagonal: $a_o = 9.73$, $c_o = 15.3$
 - 7.
 - 8.

9. 15.3 Å X-ray peak is considered diagnostic
10. Has been called Assarsson's Z-phase. This is a relatively unstable phase that can be synthesized at temperatures of the autoclave of 140 to 200 C. It seems to be related to gyrolite, truscottite, and reyerite.
11. 5, pp. 207-208; 46; 66; 67; 68

XIV-N 1. tricalcium-6-silicate-8-hydrate

2. nekoite
3. $C_3S_6H_8$
- 4.
5. $Ca_3Si_6O_{15} \cdot 8H_2O$
6. triclinic: $a_o = 7.60$, $b_o = 7.32$, $c_o = 9.86$, $\alpha = 111$ deg 48 min, $\beta = 86$ deg 12 min, $\gamma = 103$ deg 54 min
7. $\bar{n} = 1.54$
8. 11-595
9. 9.25₁₀, 3.36₁₀, 2.82₁₀, 2.47₇, 1.83₇, 1.90₅
10. Natural mineral that is not yet synthesized. Its crystal structure is unknown, and it may be more closely similar to calcium disilicate dihydrate (okenite) in composition than indicated.
11. 131

XIV-O 1. calcium disilicate dihydrate

2. okenite
3. CS_2H_2
- 4.
5. $CaSi_2O_5 \cdot 2H_2O$
6. triclinic: $a_o = 9.84$, $b_o = 7.20$, $c_o = 21.33$, $\alpha = 90$ deg, $\beta = 103.9$ deg, $\gamma = 111.5$ deg
7. $n_\alpha = 1.53$, $n_\gamma = 1.54$
8. 9-469
9. 21₁₀, 8.8₈, 2.93₈, 3.56₈, 3.07₆, 3.05₆
10. Natural mineral that is similar to nekoite and, like it, not yet synthesized and of unknown crystal structure.
11. 5, pp. 176-177; 46

XIV-P 1. truscottite

- 2.
3. C_2S_4H varying to $C_6S_{10}H_3$
- 4.
5. composition uncertain
6. hexagonal (trig.): $a_o = 9.72$, $c_o = 18.71$
7. $\bar{n} = 1.55$
8. 7-302, 17-761
9. 3.12₁₀, 19₈, 4.23₈, 2.82₆, 1.83₆, 9.40₅
10. Naturally occurring mineral that has been synthesized at temperatures from 200 to 300 C and varying pressures. The composition is uncertain. The mineral closely resembles reyerite, with which it has been confused, and to a lesser extent gyrolite.
11. 5, pp. 205-207; 46

XIV-Q 1. reyerite

- 2.
3. $KC_{28}S_{48}H_{15}$
- 4.
5. $KCa_{14}Si_{24}O_{60}(OH)_5 \cdot 5H_2O$

6. hexagonal (trig.): $a_o = 9.74$, $c_o = 19.04$
7. $n_\omega = 1.56$, $n_\epsilon = 1.56$
8. 17-760
9. 3.17_{10} , 2.85_8 , 2.66_8 , 1.85_8 , 4.23_6 , 3.52_5
10. Naturally occurring mineral closely resembling truscottite and to a lesser degree gyrolite. Reyerite has a somewhat different infrared absorption spectrum than truscottite, and the potassium is probably essential to the structure, which is unknown.
11. 5, pp. 205-207; 46

XIV-R

1. scawtite
- 2.
3. $C_7S_6\overline{CH}_3$
- 4.
5. $Ca_7Si_6O_{21}H_6 \cdot CO_3$
6. monoclinic: $a_o = 10.22$, $b_o = 15.42$, $c_o = 6.70$, $\beta = 100$ deg 29 min
7. $n_\alpha = 1.60$, $n_\beta = 1.61$, $n_\gamma = 1.62$
8. 10-400, 12-777
9. 3.04_{10} , 1.90_6 , 3.02_5 , 2.50_5 , 2.24_5 , 4.56_4
10. Has been called CSH(A)-Bogue. It is a naturally occurring mineral that has been synthesized at 150 C under saturated steam pressure. The carbonate is probably essential to the structure; if carbon dioxide is rigorously excluded it does not form.
11. 5, p. 226; 46

XIV-S

1. jennite
- 2.
3. $NC_8S_5H_{11}(?)$
- 4.
5. $Na_2Ca_8Si_5O_{30}H_{22}(?)$
6. triclinic: $a_o = 10.56$, $b_o = 7.25$, $c_o = 10.81$, $\alpha = 99$ deg 42 min, $\beta = 97$ deg 40 min, $\gamma = 110$ deg 04 min
7. $n_\alpha = 1.55$, $n_\beta = 1.56$, $n_\gamma = 1.57$
8. 18-1206
9. 10.5_{10} , 2.92_8 , 3.04_6 , 2.83_6 , 2.66_6 , 6.46_5
10. Naturally occurring mineral found at Crestmore, California, and in Israel. It may resemble substituted calcium silicate hydrate gel occurring in cement paste. Work subsequent to the original investigation does not confirm the presence of Na. Heating at about 80 C removes 4 molecules of water and causes the basal spacing to shrink from 10.6 to 8.7 Å; the partly dehydrated phase is called meta-jennite. A tentative structure has been suggested that is different from that of tobermorite in the Ca-O sheets, which in jennite contain hydroxyl ions and water molecules.
11. 46; 70

XIV-T

1. thaumasite
- 2.
3. $C_3SCS\overline{SH}_{27}$
- 4.
5. $[Ca_3 \cdot Si(OH)_6 \cdot 24H_2O] (CO_3)(SO_4)$
6. hexagonal: $a_o = 10.99$, $c_o = 10.31$
7. $n_\epsilon = 1.47$, $n_\omega = 1.51$
8. 13-156
9. 9.66_{10} , 3.79_8 , 4.58_7 , 5.54_5 , 2.60_4 , 2.15_4
10. Structure closely resembles that of ettringite with $Si(OH)_6^{2-}$ for $Al(OH)_6^{3+}$ and $(CO_3)_2 + (SO_4)_2$ for $(SO_4)_3 + (H_2O)_{1.5}$. It has been reported in normally cured con-

crete and is known as a natural mineral, but it does not seem to have been synthesized under controlled laboratory conditions.

11. 120; 121; 124

XV. HYDRATED CALCIUM ALUMINATES AND RELATED COMPOUNDS

XV-A 1. tricalcium aluminate-6-hydrate*

- 2.
3. C_3AH_6
- 4.
5. $Ca_3Al_2(OH)_{12}$
6. cubic: $a_o = 12.56$
7. $n = 1.60$
8. 3-0125
9. 5.16₁₀, 2.30₁₀, 2.04₈, 4.47₆, 3.37₆, 3.15₆
10. End member of garnet-hydrogarnet solid solution series $C_3(F_{1-p}A_p)(S_{1-q}H_{2q})_3$ where $p = 1$ and $q = 1$. This compound is the stable calcium aluminate hydrate at room temperature, the hexagonal phases tending to convert to it at slightly elevated temperatures. It occurs sporadically and to a limited extent in portland cement concrete, is more commonly found in lime-pozzolan systems, and is a major constituent of hydrated aluminous cements that have been exposed to high temperature and moist weathering conditions.
11. 5, pp. 233-286; 40; 44; 45; 71

XV-B 1. tetracalcium trialuminate trihydrate

- 2.
3. $C_4A_3H_3$
- 4.
5. $Ca_2[Al_3O_5(OH)_2]OH$
6. orthorhombic: $a_o = 12.78$, $b_o = 12.42$, $c_o = 8.90$
7. $\bar{n} = 1.63$
8. 14-464
9. 3.60₁₀, 3.27₆, 2.80₅, 3.03₃, 2.84₃, 2.07₃
10. Synthesized at 350 C at saturated steam pressure or at temperatures above 260 C at 0.7 kilobars. It is also formed as a dehydration product of tricalcium aluminate-6-hydrate. On further dehydration tetracalcium trialuminate is formed.
11. 5, pp. 239-240; 72; 122; 135

XV-C 1. tetracalcium aluminate-19-hydrate

- 2.
3. C_4AH_{19}
- 4.
5. $[Ca_2Al(OH)_6][OH \cdot 6H_2O]$
6. hexagonal (trig.):
 α_1 : $a_o = 5.77$, $c_o = 64.08$
 α_2 : $a_o = 5.77$, $c_o = 21.37$
7. $n_\omega = 1.50$, $n_\epsilon = 1.49$
8. α_1 : 14-631; α_2 : 14-628
9. α_1 : 10.8₁₀, 2.79₁₀, 2.49₁₀, 2.88₇, 2.53₇, 3.94₄
 α_2 : 2.88₁₀, 2.79₁₀, 10.8₈, 4.10₈, 2.67₈, 2.50₈
10. Two closely similar forms, α_1 and α_2 , are described in the literature, and a β - C_4AH_{19} with a basal spacing at 10.42 Å has been reported to exist at temperatures below 15 C. This compound is the prototype AFm (aluminate-ferrite-monosubstituent) phase, implying hexagonal sheet morphology. It decomposes to lower hydration

states at relative humidity of 85 percent or less at room temperature. It is occasionally found in portland cement concrete, especially if the ratio of sulfate to tricalcium aluminate is low.

11. 5, pp. 240-242, 343; 44; 73; 74; 75

XV-D 1. tetracalcium aluminate-13-hydrate*

- 2.
3. C_4AH_{13}
- 4.
5. $[Ca_2Al(OH)_6][OH \cdot 3H_2O]$ or $[Ca_2Al(OH)_6][OH \cdot 2\frac{1}{2}H_2O]$
6. hexagonal (trig.): $a_o = 5.73$, $c_o = 47.16$
7. $n_\omega = 1.53$, $n_\epsilon = 1.52$
8. 16-339
9. 7.9₁₀, 3.99₈, 2.87₆, 2.46₆, 1.66₅, 2.70₄
10. Lower hydration state corresponding to tetracalcium aluminate-19-hydrate. The X-ray basal spacing is 7.9 Å. There is an unsettled dispute as to whether the composition of this phase is really C_4AH_{13} or C_4AH_{12} . Confusion also exists as to the possible occurrence of a C_4AH_{13} phase with a basal spacing of 8.2 Å in addition to the carbonate-bearing solid solution series $C_3AC_{0.25}H_{12}$ - $C_3AC_{0.5}H_{12}$, which shows the 8.2 Å spacing. A natural mineral, hydrocalumite, is similar in layer thickness and approximate composition to tetracalcium aluminate-13-hydrate but contains a little CO_3 ; it is, however, a 2-layer rather than a 6-layer polytype. Lower hydration states of tetracalcium aluminate occur, with 11 and 7 water molecules per formula unit. Solid solution with corresponding iron-bearing phases is known to occur. The basic structure consists of layers of $Ca_2Al(OH)_6$ units, with inter-layer composition consisting of $OH + H_2O$. The compound may be formed in hydrated portland cements high in alumina and low in sulfate.
11. 5, pp. 240-243; 44; 74; 75; 76

XV-E 1. tetracalcium aluminate-7-hydrate

- 2.
3. C_4AH_7
- 4.
5. $[Ca_2Al(OH)_6][OH]$
6. hexagonal: $a_o = 5.74$, $c_o = 5.4$ (structural element but not necessarily the unit cell)
- 7.
- 8.
- 9.
10. Reported basal spacings have been given as either 7.2 to 7.4 Å or 5.4 Å, apparently depending on the conditions of dehydration. There is also a tetracalcium aluminate-11-hydrate with a basal spacing of 7.4 Å.
11. 44; 74; 77; 80

XV-F 1. tetracalcium aluminate hemicarboxylate-12-hydrate

- 2.
3. $C_4AC_{0.5}H_{12}$
- 4.
5. $[Ca_2Al(OH)_6][0.50H_2O \cdot 0.25CO_3 \cdot aq]$
6. hexagonal: $a_o = 5.74$, $c_o \cong 8.2$ (structural element but not necessarily the unit cell)
7. $n_\omega = 1.54$, $n_\epsilon = 1.52$
- 8.
9. 8.2₁₀, 2.88₉, 2.45₉, 3.88₇, 2.72₆, 2.55₆ (ref. 6, p. 396)
10. Also informally called hemicarboxylaluminate and quarter-carbonate. This compound has been frequently misidentified as α - C_4AH_{13} , the existence of which is still in dispute. This phase has an X-ray basal spacing of 8.2 Å. The present phase has

recently been shown to be a solid solution series between the compositions $C_4\overline{AC}_{0.25}H_{11-12}$ and $C_4\overline{AC}_{0.5}H_{11-12}$. It is an AFm phase with a structure very closely related to that of tetracalcium aluminate-13-hydrate. It forms readily when solutions saturated in alumina and lime precipitate solids in the presence of atmospheric carbon dioxide.

11. 6; 75; 76; 78

XV-G 1. tetracalcium aluminate hemicarboxate-7-hydrate

- 2.
3. $C_4\overline{AC}_{0.5}H_7$
4. $[Ca_2Al(OH)_6][0.5OH \cdot 0.25 CO_3 \cdot \frac{1}{4}H_2O]$
5. hexagonal: $a_o = 5.74$, $c_o \approx 7.3$ (structural element but not necessarily the unit cell)
- 6.
- 7.
- 8.
- 9.
10. Dehydration product of the tetracalcium aluminate hemicarboxate-12-hydrate series, nominally corresponding to tetracalcium aluminate-7-hydrate. The actual compositions reported vary from 6 to 9 molecules of water per formula unit. The basal spacing is probably close to 7.3 \AA .
11. 44; 74; 77

XV-H 1. tetracalcium aluminate carbonate-11-hydrate

- 2.
3. $C_4\overline{ACH}_{11}$
- 4.
5. $[Ca_2Al(OH)_6][0.5CO_3 \cdot 2.5H_2O]$
6. hexagonal: $a_o = 5.7$, $c_o = 7.6$ (structural element but not necessarily the unit cell)
7. $n_\omega = 1.55$, $n_\epsilon = 1.53$
8. 14-83
9. 7.57_{10} , 3.78_5 , 2.86_3 , 2.42_3 , 2.52_2 , 2.49_2
10. An apparently constant-composition phase with a gap separating it from the high carbonate end of the tetracalcium aluminate hemicarboxate-12-hydrate series. However, a complete solid solution series has been reported with Mg replacing Ca.
11. 6; 44; 75; 81

XV-I 1. dicalcium aluminate-8-hydrate

- 2.
3. C_2AH_8
- 4.
5. $[Ca_2Al(OH)_6][Al(OH)_4 + 3H_2O]$
6. hexagonal: $a_o = 5.7$, $c_o = 10.7$ (structural element but not necessarily the unit cell)
7. $n_\omega = 1.52$, $n_\epsilon = 1.50$
8. 11-205
9. 10.7_{10} , 5.36_8 , 2.86_7 , 2.54_7 , 2.39_6 , 1.67_6
10. An AFm phase (see XV-C, tetracalcium aluminate-19-hydrate) said to have a layer structure in common with various members of this group but to differ by the presence of hydroxylaluminum ions in interlayer positions. Two slightly different α -polytypes are known with X-ray basal spacings of $\sim 10.7 \text{ \AA}$, and also a β -polytype with a 10.4 \AA spacing. A number of progressively more dehydrated forms can be prepared, and analogous iron compounds are known.
11. 44; 83; 84; 85

- XV-J**
1. monocalcium aluminate-10-hydrate
 - 2.
 3. CAH_{10}
 - 4.
 5. $\text{CaAl}_2(\text{OH})_8 \cdot 6\text{H}_2\text{O}$
 6. hexagonal: $a_o = 9.45$, $c_o = 14.60$ (?)
 7. $\bar{n} = 1.47$
 8. 12-408
 9. 7.16_{10} , 14.2_9 , 5.37_1 , 4.73_1 , 3.70_1 , 3.56_1
 10. Phase principally responsible for the hydraulic hardening and strength of aluminous cements. It is stable at low temperatures, but if relative humidity is high it may convert to tricalcium aluminate hexahydrate at moderately high ambient temperatures, with loss of strength. A number of dehydration states have been reported.
 11. 5, pp. 243-244; 6, pp. 17-22, 385; 44

XVI. HYDRATED CALCIUM ALUMINATES BEARING ADDITIONAL ANIONIC GROUPS

- XVI-A**
1. tetracalcium aluminate monosulfate-12-hydrate
 - 2.
 3. $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$
 4. monsulfoaluminate
 5. $[\text{Ca}_2\text{Al}(\text{OH})_6][0.5(\text{SO}_4) \cdot 3\text{H}_2\text{O}]$
 6. hexagonal (trig.): $a_o = 5.76$, $c_o = 26.79$
 7. $n_\omega = 1.50$, $n_\epsilon = 1.49$
 8. 18-275
 9. 8.90_{10} , 4.45_9 , 2.23_3 , 3.99_2 , 2.42_2 , 2.19_2
 10. Occurs as one of two major aluminum-bearing phases in ordinary hydrated portland cement concrete. This is an AFm phase with a layer structure similar to that of many others. A higher hydration stage (tetracalcium aluminate monosulfate-14-hydrate) can be prepared, and a number of lower hydration stages are known, containing variously 10, 8, 7, and possibly lower numbers of water molecules per formula unit. The 12-hydrate is stable down to 12 percent relative humidity at room temperature. An incomplete solid solution series is formed with tetracalcium aluminate-13-hydrate.
 11. 5, pp. 262, 341-343; 44; 75; 76; 87; 104; 107

- XVI-B**
1. tetracalcium aluminate monosulfate-14-hydrate
 - 2.
 3. $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{14}$
 - 4.
 5. $[\text{Ca}_2\text{Al}(\text{OH})_6][0.5(\text{SO}_4) \cdot 4\text{H}_2\text{O}]$
 6. hexagonal (trig.): $a_o = 5.76$, $c_o = 28.5$
 - 7.
 - 8.
 - 9.
 10. Higher hydration state of tetracalcium aluminate monosulfate-12-hydrate, stable only above 95 percent relative humidity at room temperature. The X-ray basal spacing is 9.5 \AA . A still higher hydration form ($16\text{H}_2\text{O}$, with a basal spacing 10.3 \AA) is formed in aqueous suspension at temperature less than 8°C .
 11. 75

- XVI-C**
1. ettringite*
 - 2.

3. $C_6\overline{A}S_3H_{32}$
4. 6-calcium aluminate trisulfate-32-hydrate
5. $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}[(SO_4)_3 \cdot 1\frac{1}{2}H_2O]$
6. hexagonal (trig.): $a_o = 11.23$, $c_o = 24.48$
7. $n_\omega = 1.46$, $n_\epsilon = 1.46$
8. 9-414
9. 9.73₁₀, 5.61₈, 3.88₅, 2.56₅, 2.21₅, 2.77₄
10. Type Aft (aluminate-ferrite-trisubstituted) compound and is typically needle-shaped. It is stable at room temperature down to 4 percent relative humidity. This compound is probably the first alumina-bearing hydration product formed in ordinary portland cement concrete and may persist indefinitely or else convert to tetracalcium aluminate monosulfate-12-hydrate. It is common in secondary deposits in concrete and mortar. The water content of ettringite is somewhat variable. The compound is stable to vapor pressures down to 0.7 mm Hg at 20 C; it can be dried to a water content of 8H₂O per formula unit without complete structural change. A complete solid solution exists with the iron analogue. A chloride-bearing analogue and a carbonate-bearing analogue are known. The structure consists of columns of $[Ca_3Al(OH)_6 \cdot 12H_2O]^{+3}$ parallel to the c or needle axis with sulfate anions and water molecules in the channels between adjacent columns.
11. 5, pp. 260-262, 337-343; 43; 88; 100; 143

XVI-D

1. 6-calcium aluminate tricarbonat-30-hydrate
- 2.
3. $C_6\overline{A}C_3H_{30}$
- 4.
5. $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}[(CO_3)_3]$
6. hexagonal (trig.)
- 7.
8. 18-277
9. 9.41₁₀, 2.51₇, 3.80₄, 2.70₄, 2.16₄, 5.43₃
10. Aft phase that is analogous to ettringite and shows the same needle-shaped morphology and probably has analogous structure.
11. 5, pp. 274-275; 44; 81; 87; 104

XVI-E

1. tetracalcium aluminate dichloride-10-hydrate
- 2.
3. $C_3A(CaCl_2)H_{10}$
4. Friedel's salt
5. $[Ca_2Al(OH)_6][Cl \cdot 2H_2O]$
6. monoclinic or hexagonal (trig.):
 α (mon.): $a_o = 9.96$, $b_o = 5.73$, $c_o = 16.84$, $\beta = 110.5$ deg
 β (hex.): $a_o = 5.74$, $c_o = 46.87$
7. $n_\omega = 1.55$, $n_\epsilon = 1.53$
8. 19-201, 19-202
9. α : 7.89₁₀, 3.94₈, 3.85₅, 2.87₅, 2.16₃, 2.63₂
 β : 7.81₁₀, 3.90₈, 2.87₈, 2.31₅, 2.20₅, 3.79₃
10. AFm phase related to tetracalcium aluminate-12-hydrate, with which limited solid solution may occur. A great many related quaternary salts may be prepared.
11. 5, p. 277; 44; 105; 106

XVI-F

1. 6-calcium aluminate-6-chloride-30-hydrate
- 2.
3. $C_3A \cdot 3(CaCl_2) \cdot 30H_2O$
- 4.
5. $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}[Cl_6]$

6. hexagonal: $a_0 = 11.74$, $c_0 = 20.71$
- 7.
- 8.
9. 10.15_{10} , 3.66_3 , 2.57_2 , 5.06_1 , 4.69_1 , 2.29_1 (ref. 44)
10. AFt compound analogous to ettringite. The needle-shaped morphology is similar, but the needles are much smaller.
11. 44; 90; 91; 105; 123; 143

XVI-G 1. tetracalcium aluminate sulfate sodium-16-hydrate

- 2.
3. $C_4A_{0.9}\bar{S}_{1.1}N_{0.5}H_{16}$
- 4.
5. $Ca_4Al_{1.8}Si_{1.1}NaO_{26.5}H_{32}$
6. hexagonal: $a_0 = 5.75$, $c_0 = 16$
- 7.
- 8.
9. 10_{10} , 5.0_{10} , 2.41_4 , 3.56_3 , 2.24_3 , 2.88_3 (ref. 96)
10. New alkali-bearing compound that appears to be a modified AFm phase with some or all of the alkali exchangeable. Two lower dehydration states are reported: a 12-hydrate with a basal spacing of 9.3 \AA and an 8-hydrate with a basal spacing of 8.1 \AA .
11. 44; 96

XVII. HYDRATED CALCIUM ALUMINATE SILICATES

XVII-A 1. dicalcium aluminate monosilicate-8-hydrate

- 2.
3. C_2ASH_8
4. Stratling's compound
5. $[Ca_2Al(OH)_6][SiAlO_2(OH)_4 \cdot 3H_2O]$
6. hexagonal: $a_0 = 5.75$, $c_0 = 12.6$ (structural element but not necessarily unit cell)
7. $\bar{n} = 1.51$
8. 19-210
9. 12.54_{10} , 4.17_{10} , 2.87_6 , 6.24_4 , 2.62_4 , 2.38_4
10. Has been called gehlenite hydrate, although another hydrate of different crystal structure is now known to occur. It is probably an AFm phase with silicate as the interlayer ion. Replacement of aluminum by iron in amounts up to 0.3 formula unit has been reported. It has been found to occur in reacted lime-pozzolan and cement-pozzolan mixtures.
11. 5, pp. 275-277; 92; 93; 94; 134

XVII-B 1. dicalcium aluminate monosilicate monohydrate

- 2.
3. C_2ASH
- 4.
5. $Ca_2Al_2SiO_8 \cdot H_2$
6. cubic: $a_0 = 8.83$
7. $n = 1.63$
8. 16-388
9. 2.79_{10} , 3.61_9 , 2.08_4 , 1.56_4 , 2.55_3 , 2.36_3
10. The ASTM file entry is misleadingly labeled "gehlenite hydrate." This cubic compound is formed from dicalcium aluminate monosilicate-8-hydrate at 350°C and has some similarity to tetracalcium trialuminate trihydrate.
11. 95

XVIII. HYDRATED CALCIUM FERRITES AND RELATED COMPOUNDS

XVIII-A 1. tricalcium ferrite-6-hydrate

- 2.
3. C_3FH_6
- 4.
5. $Ca_3Fe_2(OH)_{12}$
6. cubic: $a_o = 12.7$
- 7.
8. 3-1121
9. 1.70_{10} , 4.54_8 , 3.19_8 , 2.85_8 , 5.20_6 , 2.60_6
10. This compound, if it exists, would be an end member of the garnet-hydrogarnet solid solution series with $p = 0$ and $q = 1$. Some workers doubt its existence, suggesting that a minimum of about 0.16 molecule of alumina must be present in the highest iron structure that can be prepared.
11. 40; 42; 44; 97; 98

XVIII-B 1. tetracalcium ferrite-13-hydrate

- 2.
3. C_4FH_{13}
- 4.
5. $[Ca_2Fe(OH)_6][OH \cdot 3H_2O]$
6. hexagonal: $a_o = 5.90$, $c_o = 7.70$ (structural element but not necessarily true unit cell)
- 7.
- 8.
9. 7.80, 3.91, 2.94, 2.77, 2.63, 2.52 (ref. 43, relative intensities not given)
10. AFm product analogous to and forming a complete solid solution series with tetracalcium aluminate-13-hydrate.
11. 5, pp. 278-280; 43; 44; 97

XVIII-C 1. 6-calcium ferrite trisulfate-32-hydrate

- 2.
3. $C_6F\bar{S}_3H_{32}$
4. iron-ettringite
5. $\{Ca_6[Fe(OH)_6]_2 \cdot 24H_2O\}[(SO_4)_3 \cdot 1\frac{1}{2}H_2O]$
6. hexagonal (trig.): $a_o = 11.23$, $c_o = 22.14$
7. $n_\omega = 1.49$, $n_\epsilon = 1.49$
8. 19-223
9. 9.8_{10} , 3.95_8 , 5.60_7 , 2.80_7 , 2.60_7
10. Iron analogue of ettringite, thus an AFt phase. Solid solution occurs between the two, but apparently only to a maximum F:A ratio of 3. This phase does not appear to be formed in hydrated cements.
11. 5, pp. 280-281; 44; 99; 100; 101

XVIII-D 1. tetracalcium ferrite monosulfate-14-hydrate

- 2.
3. $C_4F\bar{S}H_{14}$
- 4.
5. $[Ca_2Fe(OH)_6][0.5(SO_4) \cdot 4H_2O]$
6. hexagonal: $a_o = 8.80$, $c_o = 10.40$
- 7.
- 8.
- 9.

10. Iron analogue of tetracalcium aluminate monosulfate-14H₂O, and forms solid solutions with the aluminum-bearing compound. A 12-hydrate state with a basal spacing of 9.0 Å is known, along with further dehydration states.
11. 44; 102; 103

XVIII-E

1. tetracalcium ferrite monosulfate-12-hydrate
- 2.
3. $C_4F\bar{S}H_{12}$
- 4.
5. $[Ca_2Fe(OH)_6][0.5(SO_4) \cdot 3H_2O]$
6. hexagonal: $a_o = 8.80$, $c_o = 8.98$
- 7.
- 8.
- 9.
10. A lower dehydration stage of tetracalcium ferrite monosulfate-14-hydrate, analogous to tetracalcium aluminate monosulfate-12-hydrate.
11. 44; 102; 103

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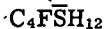
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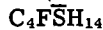
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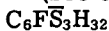
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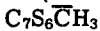
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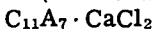
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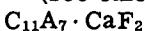
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