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Review
The chemistry of dicalcium silicate mineral

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Dicalcium silicate is of vital importance in several fields of silicate science. It exists in several polymorphic forms, of which one (the γ-form) is stable at room temperature without any stabilizer. The β-form is commonly found in ordinary portland cement (OPC) in association with stabilizing ions. Stabilization of other forms, α, α'_L, α'_H and α'_m for structural and other studies have been reported. Theoretical structural analysis using topology has been reported to be of value in understanding the stabilization process of the polymorphs. The conversion of $\beta \rightarrow \gamma$ form is at times a problem in the cement industry, in addition to the formation of unwanted compounds, such as spurrite. The γ-form is low in hydraulic properties but in the presence of impurities such as excess CaO over the stoichiometric ratio, shows fairly high hydraulic properties. Of the other phases, the hydraulic properties of the α forms are quite encouraging but the choice of stabilizers etc. plays a dominant role. Correlation of hydraulicity with structural properties such as crystal defects, etc., has been reported but satisfactory explanation is yet to come. The hydration products of β-C_2S are quite similar to those of C_3S but the kinetics are fairly slow. In the presence of active silica, and at elevated temperatures, even the γ-form hydrates at a faster rate. The influence of chemical accelerators on the hydration of C_2S at room temperature is well studied and NaF is found to be one of the best accelerators. The formation of "reactive" β-C_2S by different preparative methods shows a quite interesting trend for potential manufacture of low-temperature inorganic cement or OPC with low C_3S; even utilization of low-grade limestone could be possible. The role of C_2S in the hydration of aluminous cements is being increasingly recognized and, in fact, a newer class of cements called alumina-belite cement, etc., are being developed in which C_2S is purposely maintained as a major phase.

1. Introduction

The solid state behaviour of dicalcium silicate is extremely complex and has, therefore, attracted great interest in both basic and applied material science. A subject of considerable discussion and research, this compound is vital to several fields of silicate science – cements, refractories and slags. Since the excellent review presented by Nurse [1] at the London symposium in 1952, a vast fund of knowledge has accumulated on the subject which calls for another critical review; hence this attempt. The present review covers the increased activity in the field of building materials especially with respect to (i) obtaining an inorganic cement produced at lower temperatures competitive with ordinary portland cement, (ii) utilization of low-grade limestones, industrial wastes and slags for the manufacture of cement, and (iii) manufacture of a new cement combining the beneficial features of both portland and high alumina cements. Dicalcium silicate, C_2S*, is a major component in almost all these cements. Yet, owing to the slow hydrating nature of the common polymorphs, i.e.

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* Cement chemists' shorthand notation: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $M = MgO$, $N = Na_2O$, $K = K_2O$, $F = Fe_2O_3$, $H = H_2O$, $P = PO_3$.

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TABLE I Crystallographic data on the polymorphs of C_2S

Polymorphs	a(Å)	b(Å)	c(Å)	Probable symmetry	Reference
α-C_2S	5.526	–	7.307	at 1500° C, $P\bar{3}ml$	[4]
	5.527	–	7.311	–	[9]
α_H-C_2S	5.593	9.535	6.860	at 1250° C, $Pmcn$ orthorhombic	[4]
	6.883	5.606	9.543	at 1300° C, $Pnma$	[9]
α'_L-C_2S	11.184	18.952	6.837	at 1000° C, $Pmcn$ orthorhombic	[4]
α'_m-C_2S	5.42	6.85	9.50	at 900° C, P_1, P_{21}	[5]
	5.504	6.831	9.318	or Pm; monoclinic	
β-C_2S	5.506	6.749	$\beta = 94.62°$	pure, $P_{21/n}$, monoclinic	[4]
γ-C_2S	5.06	11.28	6.78	pure, $pbnm$, orthorhombic	[9, 10]
	5.083	11.232	6.773		

γ, β or α, of this mineral the early strength of these cements/cementitious materials is mostly dependent on other minerals. The need to obtain a "reactive" form of this mineral is obviously based on these considerations, and the present review attempts to the extent possible, to cover the studies on such reactive forms of C_2S. The literature survey is by no means exhaustive and is limited mainly to publications over the last ten years, besides the contributions made to the international symposia on the chemistry of cement from time to time at London, Washington (1960), Tokyo (1968) and Moscow (1974).

2. Polymorphism of dicalcium silicate

Dicalcium silicate occurs in several polymorphic forms. Most of them are stable in the pure state only at elevated temperatures and it is only the γ-form which is stable at room temperature. The most widely known polymorphs α, α', β and γ were reported first by Bredig [2]. Later, the existence of two other polymorphs, α'_H and α'_L closely related to the already known α'-form, was reported by Niesel and Thorman [3] and Regourd *et al.* [4]. Later, Midgley reported another monoclinic form [5] called α'_m. Besides these well characterized polymorphs, the existence of a cubic β'-phase (1600° C) [6], a metastable β-phase [7] and a C_2S phase stabilized at 600° C with SiO_2 [8] are also recently reported. The α-form has the stability range 1425–2130° C while the α'_L and α'_H forms are stable in the ranges 675–1160° C and 1160–1420° C, respectively [9]. The α'_m form is reported to be stable in the range 711–979° C. The revised stability diagram given by Niesel and the phase transitions reported by Midgley based on thermal studies are shown in Fig. 1. An interesting feature of the phase transition studies is the hysterisis of 11° C observed between the heating and cooling curves of the 920° C DTA peak. The crystallographic data [4, 5, 7, 10] of the polymorphs are given in Table I.

The conversion of $\alpha \rightarrow \alpha'_H$ takes place without hysterisis while the $\alpha' \rightarrow \beta$ transition is associated with a hysterisis [11, 12]. The $\alpha \rightarrow \alpha'_H$ conversion is associated with half of the SiO_4 tetrahedra

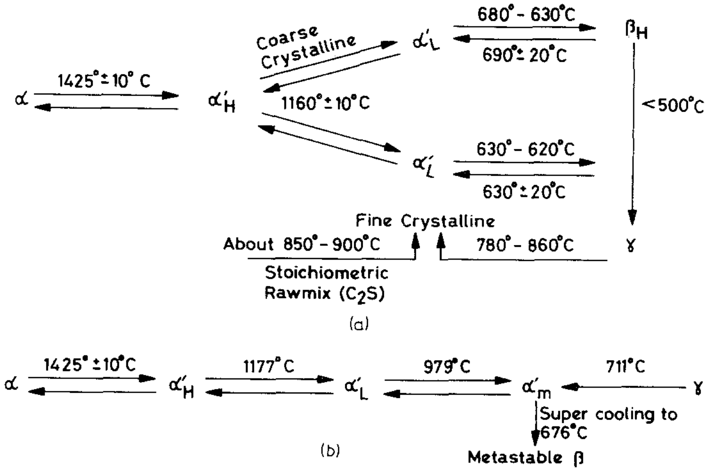

Figure 1 Stability diagram of C_2S polymorphs, (a) as reported [9]; (b) as indicated [5].

rotating so that their apices point in opposite directions at the phase transition. The $\alpha' \rightarrow \beta$ conversion at 650° C involves a rotation of the SiO_4 tetrahedra and also a change in the co-ordination of the Ca^{2+} ion [7]. The well-known $\beta \rightarrow \gamma$ transition responsible for the dusting of an odd sample of portland cement clinker, involves a rotation of the SiO_4 tetrahedra and large movements of calcium atoms. The other transformations, $\gamma \rightarrow \alpha'_L$ and $\beta \rightarrow \alpha'_L$ explained by Smith *et al.* [7], need to be updated in order to account for the newly discovered α'_m-phase. The crystallographic data on α'_m, α'_L and α'_H are presented by Midgley [5] while those of the α, β and γ forms are already known [1, 7].

In addition to the thermal transitions described above, some $\beta \rightleftharpoons \alpha'_L$ transitions induced by pressure (~ 7 kbar) are also reported [13]. Certain environmental effects on the kinetics are also known, such as the influence of hydrogen atmosphere on hastening the $\alpha' \rightarrow \alpha$ transformation [14]. Some of the polymorphs have been studied by infra-red spectroscopy [15, 16]. In contrast to dicalcium silicate, only two γ and α modifications of dicalcium germanate are known to date [17].

3. Stabilization of polymorphs

The stabilization of the polymorphs of C_2S is important for structural studies and more so for industrial applications. Most of the investigations are based on X-ray diffraction and lately the high-temperature X-ray technique is frequently in use.

3.1. Mechanism of stabilization

Niesel [9] summarized the mechanisms of stabilisation of polymorphs on the basis of earlier observations by Nurse [1].

(i) Crystal chemical stabilization is obtained by the addition of suitable "stabilizers" forming solid solutions with C_2S. Nurse [1] described the details of a substitutional mechanism, for example, replacement of SiO_4^{4-} by BO_4^{5-}, PO_4^{3-}, VO_4^{3-} and SO_4^{2-}, etc., with suitable charge compensation by bringing in additional positive charge by trapping extra Ca^{2+} ions interstitially or by the removal of some SiO_4^{4-} ions from the lattice [18]. The substitution process is more or less dependent on the size of the RO_4 group which is, in turn, controlled by the O–O bond distances.

(ii) Physical stabilization is obtained by external influence on the crystallite, e.g. by solidifying a fused mass under rapid cooling. The fused mass surrounding the crystallite may have little or no reactivity towards the crystallite or sometimes it may even aid the crystal growth.

Some of the broad generalizations arrived at are:

(a) the replacement of SiO_4^{4-} by smaller ions of higher negative charge is effective in stabilizing β-C_2S;

(b) certain substitutions in C_2S lattice produce an extension of the hexagonal c-axis and tend to perpetuate the α-form;

(c) in any realistic situation, the physical or crystal chemical mechanisms cannot be isolated and, therefore, the effects of pressure and rate of nucleation must be simultaneously considered along with any crystal chemical mechanisms.

Based on their studies on the electrical conductivity of C_2S, Maycock and McCarty [18] observed that (i) C_2S is an ionic conductor rather than an electronic conductor, and (ii) the dependance of conductivity on reciprocal temperature is not significantly affected by the "purity" of the sample. It was very difficult for these authors to prepare "solid state" pure C_2S and thus they concluded that the addition of any more impurities over and above those already existing, did not cause any more point defects; instead the added impurities would be precipitated as a separate phase rather than form a solid solution.

3.2. Stabilization of the β-phase

This is probably the most widely studied problem because of its direct bearing on cement manufacture and the stability of certain blastfurnace slags. A conversion of $\beta \rightarrow \gamma$ leads to dusting in cement manufacture. Incorporation of small amounts of certain impurities even at levels as low as 0.1% stabilize the β-phase at room temperature. There is, however, no fully accepted model for the stabilization of the β-phase over the γ-phase by impurities. Suzukawa and Sasaki [19] reported the influence of FeO on the $\beta \rightarrow \gamma$ inversion of C_2S stabilized with various kinds and amounts of agents and on the dusting of synthetic clinkers. It was found that the $\beta \rightarrow \gamma$ inversion due to the presence of FeO is related to the ionic radius of a stabilizer and that the amount of FeO required for dusting cement clinkers decreases with increase in the content of Na_2O. β-C_2S can be stabilized by the addition of B_2O_3, Na_2O, K_2O, BaO, MnO_2, Cr_2O_3 or their combinations [19–23]. The conditions of transformation of γ-C_2S into the β-form by heat-treatment has also been reported [24]. β-C_2S synthesized below 1160° C does not change to the γ-phase unlike those above 1160° C [25]. However, β-C_2S thus produced, preserves the shape of the grain, the cleavage, the extinction and elongation (crystal) which is typical of the γ-form. The addition of silica modifies the distribution growth rate in C_2S crystal and favours the transformation $\beta \rightarrow \gamma$ [22]. Percussion of pellets of β-C_2S is known to induce transformation [23, 26]. The KBr-pellet infra-red spectrum of β-C_2S differs in band positions with that of β-C_2S taken in nujol [17]. Addition of a small amount of Fe (II) oxide was found to give very pure γ-phase (free from β-phase) [27].

Belite (a term used for β-C_2S phase as found in portland cement) similar to that found in cement has been synthesized [28]. This is an oxygen-defective solid solution with Si-subsitution. Belite produced by using $Ca(OH)_2$ and silicic acid in the low-temperature range 700 to 1300° C showed a higher rate of formation up to 1000° C and the grain size increases with increasing temperature [24]. The stabilization of the belite phase in cement clinker was reported. The addition of 0.5% to 2% SO_3 to cement clinker raw mixes leads to stabilization of the β-phase while at 3%, the α'-phase is formed; 0.5% P_2O_5 stabilizes β-phase, but 1.2% stabilizes α'-phase; 5% of Cr_2O_3 or SO_3 produces a certain amount of γ-phase in clinker [29].

3.3. α and α' phases

The higher temperature polymorphs have attracted much attention recently. Several oxides such as MgO, Al_2O_3, Fe_2O_3, BaO, K_2O, P_2O_5 and Cr_2O_3 stabilize these phases [5, 30–35]. α-C_2S phase can be stabilized with 20% $6CaO.Al_2O_3.2Fe_2O_3$ and 0.2% K_2O [36]. It can also be stabilized in C_2S–C_3P [37]. Table II gives some of the stabilizing agents of these phases.

3.4. Solid solutions and compound formation

The solubility of Al_2O_3 is between 2 and 3% by weight in the α-form (1400 to 1500° C) and less than 1% in the α'-form (1300 to 1350° C); the solubility of Fe_2O_3 is 1.5% in the α-form at 1400° C; 2.5% in the α-form at 1500° C and less than 1% in the α'-form at 1300 to 1350° C [37]. The solubility of MgO is 1.5% in α-C_2S at 1600° C while at 1400° C, it is either 1% [38] or 2% [39]. Some solubility of merwinite in α-C_2S has also been noted [39]. In the system 2 CaO–SiO_2–2 MnO.SiO_2, maximum solid solubilities of 19 and 31.5% $MnSiO_4$ in the α- and α'-C_2S have been reported [40]. At 1300° C, followed by air-quenching, β-C_2S is stable up to 5% KCS: at 10% α'-C_2S is stabilized while at 25% α-C_2S is stabilized [41].

A recent study [42] in the C_2S–C_2NP system indicates that in the range 15 to 32.5 mol % C_2NP, the α'_L-C_2S phase exists along with a new compound $Ca_4Na_2(PO_4)_2.(SiO_4)$. In the range 35 to 50 mol % C_2NP, α'-C_2S and α-C_2S phases co-exist. The transition temperature α'_H-$C_2S \rightarrow \alpha$-C_2S is lowered to 820° C (with 35% $CaNaPO_4$) from 1425° C. An interesting phenomenon was also noted, that on heating β-C_2S at 600° C for 24 h no γ-C_2S was formed.

The maximum limit of solid solution of phosphate with C_2S was reported as 34 wt % C_3P in the C_2S–C_3P system [37]. At 1500° C, the following two limiting solid solutions were reported [43].

PSS′ (87.5% 2CaO–SiO_2, 12.5% 3CaO.P_2O_5)

PSS″ (62.4% 2CaO.SiO_2, 37.6% 3CaO.P_2O_5)

Considerable variations have been observed in the cell parameters of the α'-phase when stabilized by various ions at different temperatures [44]. Considerable change in the X-ray diffraction pattern (Figs. 2 and 3) with increasing amount of C_3P (especially of the two strong reflection lines in the range $2\theta = 32$ to 33.5) was observed. Some weak superstructural lines can be seen on the fragment of X-ray pattern of the α'_L-phase. Another recent study [45] on the above system

TABLE II Stabilizing agents of α- and α'-C_2S

α-C_2S	α'_m-C_2S	α'_L-C_2S	α'_H-C_2S
(1) $3CaO.P_2O_5$ (2) $CaNaPO_4$ (3) Mg_2SiO_4 and Fe_2SiO_4 (4) Al_2O_3 + Fe_2O_3 (5) CaO + Na_2O + Al_2O_3 [1]	(1) 15–25% $CaNaPO_4$ (2) 3.6% K_2O (3) Na_2O and PO_4 [5]	(1) Na_2O + PO_4 (2) PO_4 (3) MgO and other ions [5]	(1) 10% $CaMgSiO_4$ + K_2O [11]

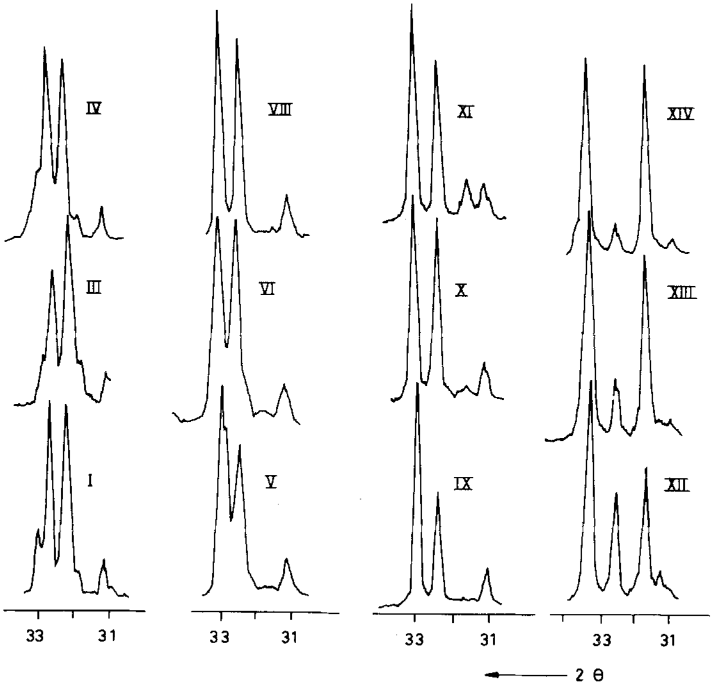

Figure 2 Portions of X-ray patterns of solid solutions in the C_2S–C_3P system. I up to 96% C_2S: III up to 94% C_2S; IV up to 92% C_2S; V up to 90% C_2S; VI up to 86 to 88% C_2S; VIII up to 82% C_2S; IX 80% C_2S; X 75% C_2S; XI 70% C_2S; XII 65% C_2S; XIII 60% C_2S. XIV 55% C_2S.

using electron microscopy to correlate the defects in the crystal with reactivity of the polymorphic phases, is interesting. The addition of C_3P from 2 to 45 wt% stabilizes the β-, α'- and α-phases (Table III).

Various minor constituents have been detected in the belite phase using electron microprobe [46]. They are Na_2O (0.008%), K_2O (0.008%), MgO (0.010%), TiO_2 (0.002%) and $Al_2O_3 + Fe_2O_3$ (0.026%) (average molar composition). It was found that the concentrations of minor constituents in host crystals may differ by a factor of 4 within the same sample indicating the heterogeniety of the system. The limiting values of Na_2O (0.2 to 1.0%) and K_2O (0.3 to 1.0%) in the C_2S phase have also been given [47]. The solid solution of Al, Fe and B in C_2S was determined by DTA through the decrease of $\alpha'_H \rightarrow \alpha$ transition temperature [4]. In belite containing Al, synthesized at 1550° C, a very rapid quenching from 1550° C, stabilizes a large part of the α'-phase; quenching from 1450° C gives a mixture of α'- and β-forms, and 1000° C gives rise to a β-modification and C_3A. Yamaguchi and Takagi [48] proposed a formula for belite in portland cement; Ca_{87} MgAlFe $(Na_{\frac{1}{2}}\ K_{\frac{1}{2}})$ $(AlSi_{42}O_{180})$, while Midgley and Bennett [49] proposed a formula for larnite (β-C_2S) as $(Ca_{2.01}Na_{0.01})(Si_{0.97}\ S_{0.03}\ P_{0.01})O_4$.

3.4.1. Compound formation

The compound silico-sulphate $2(2CaO.SiO_2)$ $CaSO_4$ decomposes at 1298° C into α'-C_2S and $CaSO_4$ [50]. The maximum content of SO_3 in α'-C_2S at 1200° C is 0.4%. In the case of the

TABLE III Experimental findings of electron microscopic analysis of etched surface of solid solution in C_2S–C_3P system

Range of composition	Polymorphic form	Density of pits	Orientation of etch pits
98% C_2S + 2% C_3P ↕ 94% C_2S + 6% C_3P	β	43–62	Linear
92% C_2S + 8% C_3P	β	42	Linear and chaotic
90% C_2S + 10% C_3P ↕ 75% C_2S + 25% C_3P	α'	38–22	Linear, chaotic
70% C_2S + 30% C_3P ↕ 60% C_2S + 40% C_3P	$\alpha + \alpha'$	30–26	Chaotic
55% C_2S + 45% C_3P	α	18	Chaotic

$CaO{-}CaF_2{-}CaO.SiO_2$ system, an intermediate compound is formed with the composition 2 $(2CaO.SiO_2)CaF_2$ [51]. This compound decomposes at 1040° C into α'-C_2S and CaF_2. In the $CaO{-}NaF{-}2CaO.SiO_2$ system, formation of β- and α'-phases below 1000° C was observed [52] and the α'-phase disappears on adding a small quantity of $CaSO_4$ or CaS [53]. Studies on the system $2BaO.SiO_2{-}2CaO.SiO_2$ similar to $2CaO.SiO_2{-}2Nd_2O_3.2SiO_2$ [54], and several new compounds in the system $2BaO.SiO_2{-}2MgO.SiO_2$ have also been reported [55]. The formation of spurrite $2(2CaO.SiO_2){\cdot}CaCO_3$ is a problem in cement manufacture [56].

3.5. Polyhedral approach to the polymorphism

Moore [57] described a polyhedral approach to the understanding of the structures of calcium orthosilicates in relation to the other isotypes, e.g. glaserite $(K_3Na(SO_4)_2)$ and potassium sulphate. The glaserite structure consists of a large alkali cation at the centre, ideally co-ordinated by 12 oxygen atoms, six of which define the vertices of an elongated trigonal antiprism while the other six form a hexagonal ring in the plane of the central alkali atom. The arrangement of the tetrahedral groups around the antiprism is defined by Moore as a "pin wheel" where the apical oxygens point either up or down. The concept of a bracelet structure, a topological concept described earlier by Gardener [58], is also brought in. A bracelet structure is a loop with n nodes and m symbols where $m < n$. For any bracelet there is a pin wheel which, when idealized, defines the maximum co-ordination number of the central atom. The maximum co-ordination number is $12 - p$ where p is the number of tetrahedra apical oxygens co-ordinated to the central atom with $0 \leqq p \leqq 6$.

Using these concepts of the condensation of polyhedra, Moore worked out the requirements satisfied by the real, and even some of the hypothetical, atomic arrangements in calcium orthosilicates. Based on these methods it was concluded that larnite (β-Ca_2SiO_4) is topologically equivalent to β-K_2SO_4 but with some geometrical distortion.

Application of the concept of the bracelet structure to bredigite (α'-Ca_2SiO_4) led to the conclusion that the possible co-ordination numbers are 6, 8, 9, 10 and 12. This gives rise to a generalized bredigite-type composition $Ca_{28}M_2M_2^1(TO_4)_{16}$ where M and M^1 are "small impurity" cations of 6 and 8 co-ordination numbers, respectively. Accordingly, Moore arrived at the solid solution range of Mg^{2+} in bredigite, $Ca_{1.75}Mg_{0.25}$ to $Ca_{1.88}Mg_{0.12}$ which is in good agreement with the results reported by Bigger [59] on synthetic bredigite.

A self-consistent relationship, as Moore puts it, is also evident between the structures of calcium orthosilicates and alkali sulphates. Calcium orthosilicates have an olivine-type structure at low temperature, a geometrically distorted β-K_2SO_4 structure at intermediate temperatures, and a glaserite-type structure at high temperature.

Moore has extended the application of the concepts of pin wheel and bracelet structures to arrive at generalizations on the distribution of

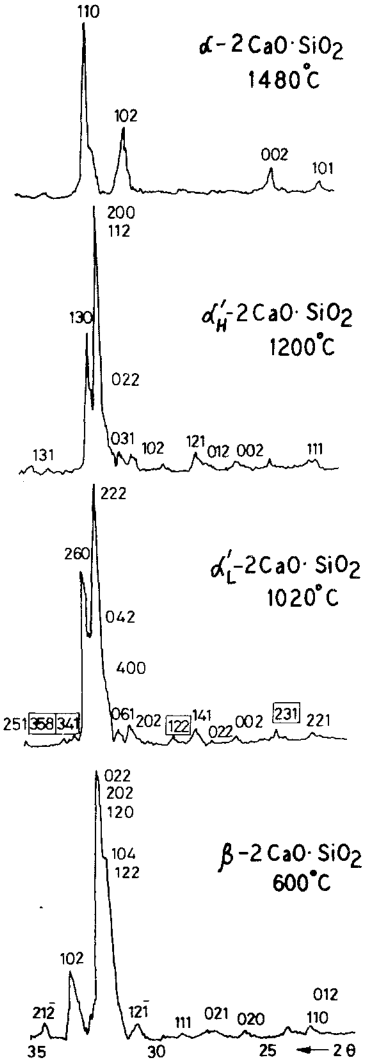

Figure 3 Fragments of high-temperature X-ray pattern of C_2S. Symbol □ designates super structural lines.

TABLE IV Compressive strengths of β-C_2S (1:3 mortar) using different stabilizers

Stabilizers	Gypsum addition	Compressive strength (psi)*		
		7 days	28 days	6 months
$Fe_2O_3 + Na_2O$	None	295	436	–
	3%	212	350	1544
$\frac{1}{2}\%$ B_2O_3	None	350	763	1869
	3%	401	726	2417
5% $Ca_3(PO_4)_2$	None	485	1837	4380
	3%	553	1402	3607

* 10^3 psi = 6.89 N mm^{-2}.

impurity cations, taking into consideration the ionic charges and ionic radii. In particular, this approach appears to explain the stabilization of polymorphs of dicalcium silicate by Na^+, Mg^{2+}, Sr^{2+} and Ba^{2+} ions. However, more accurate results on the refinement of the crystal structure of polymorphs with special emphasis on the site preferences of the impurity cations is needed, before any serious attempt may be made to verify the theoretical approach proposed by Moore.

4. Hydration of polymorphs

The hydration of polymorphs is very important so far as cement chemistry is concerned. The development of strength by the hydration of polymorphs depends on several factors, most important being the kinetics of reaction since the products of hydration are more or less similar to those of C_3S phase.

4.1. Reactivity due to foreign ions and structures

The kinetics of the hydration of pure γ-C_2S are very slow [27] but in the presence of excess Ca (more than the stoichiometric ratio), the reactivity of the γ-form is somewhat noticeable [24]. The reactivity of the β-form is quite variable [1] depending on the impurities present in the system, as shown in Table IV. In the C_2S–C_3P system, the α'- and α-forms have considerably less activity compared to the β-form. The α-form is inactive [34, 60] while the α and α' phases stabilized by Al_2O_3, Na_2O, MgO and K_2O showed considerable high reactivity with water [61] as is evident from the compressive strength data shown in Table V. The reactivity of the C_2S polymorphs in the C_2S–C_3P system has recently been correlated to the number of defects as determined from etch points with the help of electron microscopy [45]. β-C_2S crystals contained more defects compared to α'-C_2S, and α-C_2S had the lowest number of defects (Table III) inspite of the fact that the defects in α' and α forms were more random in nature. On the other hand, Maycock and McCarty's findings do not support this view (Section 3.1). Furthermore, these authors did not find much change in the X-ray pattern in contrast to Boikova *et al.* [45].

The irregular and high co-ordination of Ca ions in all the high-temperature stable polymorphs (for example, β-C_2S has two types of Ca ions – six and eight co-ordinated; α' and α-C_2S have 8 or 10 co-ordination numbers) may lead to vacancies or holes to which the high reactivity of the polymorphs compared to the γ-form (which has regular six co-ordinated Ca-ions but open structure) has been attributed [47, 62]. Lea [47] argued that the "hole" formation and higher co-ordination are not very convincing to correlate the reactivity of these polymorphs in the light of the reactivities of C_3S (which has six co-ordinated Ca-ions) and also the easy dissolution of NaCl (which has no holes in the structure) in water.

The high-temperature polymorphs of C_2S are, after all, stabilized by impurities for studying their reactivity with water and, therefore, the high co-ordination of Ca or the presence of holes, etc., appear to be not straightforward as such, because the effects of these impurities, whether in the structure or as a separate phase, should also be considered.

4.2. Kinetics and mechanism of hydration

Detailed studies on the kinetics of hydration of dicalcium silicate were reported by Funk [63], Kantro *et al.* [64, 65] and Brunauer *et al.* [66], wherein the degreee of hydration was determined as a function of time, and the effect of temperature was also brought out. The latter authors refer

TABLE V Compressive strength of the polymorphs of C_2S (kg cm^{-2})

Polymorphs	Chemical composition							7 days	28 days	91 days
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O			
α	30.4	2.4	2.5	59.1	–	–	5.8	47	80	169
α'	33.8	–	–	60.0	2.3	3.8	–	11	41	86
β	31.4	2.5	2.5	63.1	–	–	0.5	11	38	51

to a stoichiometric equation representing the hydration of β-C_2S.

$$2Ca_2SiO_4 + 4H_2O = Ca_3Si_2O_7.3H_2O + Ca(OH)_2.$$

However, Lea [47] presents another equation reportedly valid for any water–cement ratio and for any age of hydration:

$$C_2S + (1.5 + n)H = C_{1.5+m}SH_{1+m+n} + (0.5 - m)CH.$$

The initial hydration product is formed only as a surface coating and has a C/S ratio close to 2. Within 12 h this converts into a low-lime calcium silicate hydrate related to CSH(I) and the molar ratio drops to a minimum, somewhere in the range 1.1 and 1.2. A stable lime-rich hydration product related to CSH(II) is finally formed and the molar ratio rises to 1.65 to 1.8 in about a year [47].

A direct relationship has been observed between the structure and crystallographic orientation and the hydration of larnite and bredigite [67]. Taplin [68] studied the kinetics of hydration of β-C_2S and reported an apparent activation energy of 18 kcal mol^{-1}. Lehmann and Dutz [69] studied the hydration product of β-C_2S by infra-red spectroscopy, while Yamaguchi *et al.* [70] employed the X-ray diffraction technique for the study of hydration of cement minerals and portland cement. The rates of strength development of all the individual minerals of portland cement [47] are shown in Fig. 4, which shows that belite is the slowest to undergo hydration. A mechanistic explanation of the relative rates of hydration of cement minerals was offered by Danilov [71] in terms of the electronegativities and ionic/covalent character of Ca–O–X bonds where X is any element including calcium. Among the known stable polymorphs of C_2S, the γ-form has the slowest rate of hydration and this is attributed to its orthrhombic structure of the olivine type [72] wherein there is a regular co-ordination of calcium ions with respect to oxygens. Another special feature reported of γ-dicalcium silicate is that its hydration proceeds by a "through solution" mechanism [73] unlike the β-form which follows a topochemical mechanism. Although γ-C_2S hydrates very slowly at room temperature, the rate of hydration is very significant at elevated temperatures in the presence of saturated steam. α-C_2SH is obtained when γ-C_2S is hydrated alone [74, 75], but in the presence of quartz sand the products have lower C/S ratios and the specimens attain high compressive strength [75]. This hydraulic activity of γ-C_2S at elevated temperatures is put to advantage in the utilization of industrial wastes, such as ferrochrome slag containing γ-C_2S as the major component, for the production of autoclaved building materials, without the use of any other conventional binders such as cement, lime or

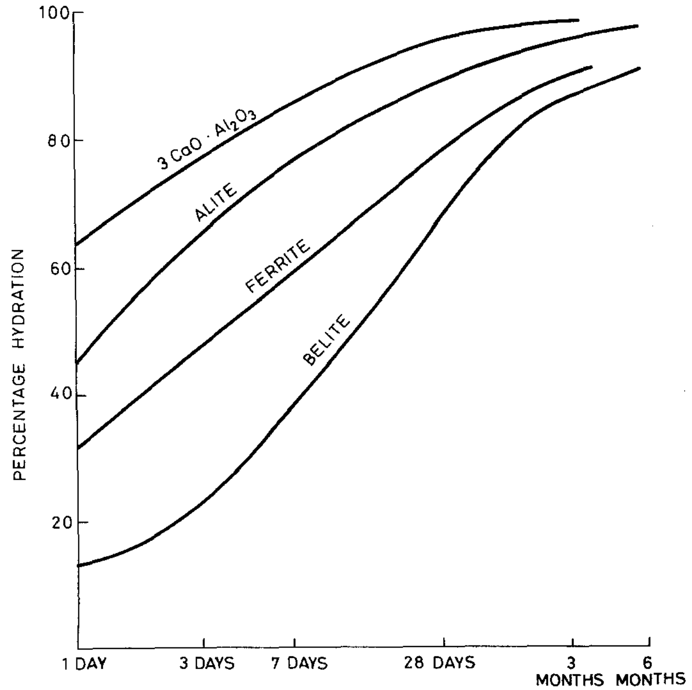

Figure 4 Rates of hydration of compounds in a portland cement.

gypsum [76]. The hydraulic behaviour of α-dicalcium silicate [36, 77] and α'-C_2S [78] was reported by Bensted and others.

4.3. Influence of admixtures on hydration

Bozhenov *et al.* [79] studied the hydration of synthetic β-C_2S and the liberation of calcium hydroxide under saturated steam at elevated temperatures. It was found that an admixture of SiO_2 enhanced the kinetics while addition of CaO retarded it. Teoraneau and Muntean [80] concluded that electrolytes such as $CaCl_2$ do not have as great an influence on the hydration kinetics of C_2S as observed in the case of C_3S. The composition of gel, pore structure, surface area and morphology were also influenced to a lesser degree by $CaCl_2$ than in the case of C_3S hydration. Young and Tang [81] report that compounds which accelerate the hydration of C_3S do not have the same effect on β-C_2S except at later stages of hydration. The best accelerator was NaF while the hydration was slowest with the addition of $NaHCO_3$. A significant increase in the hydration of β-C_2S by the addition of SiO_2 with Na_2O and K_2O has also been reported by Kuatbacv *et al.* [82]. Danilov *et al.* [83] studied the hydration of β-C_2S at constant pH in the range 3 to 10 and $CaCl_2$ concentrations of 0 to 40 wt% in the original solution. Equations of steady state and non-steady state diffusion were applied and a mechanism of the process involving the formation of a layer of silica gel around the C_2S grains was given.

4.4. Morphology and microstructure of hydration products

With the help of electron microscopic (EM) studies, Kurezyk and Schwiete [84] showed that the hydration products of C_2S were, in fact, tiny needle-shaped crystals as against "gel" or "gel-phase" considered up till then. It was also shown that the needles had an average length of 5000 Å. The hydration products were morphologically and structurally similar to tobermorite with the only difference that between pockets of tobermorite are included some Ca^{2+} and OH^- ions. Ciach and Swenson [85] studied with the help of EM techniques the hydration of calcium silicates with and without admixtures such as triethanolamine and calcium lignosulphonate and found that the microstructures of hydration products obtained with both C_2S and C_2S are similar. Scanning electron microscopic results on the morphology of hydrated pastes reported first by Williamson [86] were corroborated by Young and Tang [81] and the broad conclusions arrived at by the latter authors are reported in Table VI. Young and Tang also concluded that β-C_2S pastes also obey the Power's gel-space relationship obtained for C_3S pastes [87] at the same w/c ratio.

Further studies by Lawrence *et al.* [88] with the help of scanning electron microscopy showed that in the hydration product of C_2S, the crystals of calcium hydroxide are less abundant. but larger as compared to the case of C_3S.

5. Dicalcium silicate in slags and non-portland cements

5.1. Slags

Some of the air-cooled blast furnace slags and steel slags of European slags, contain β-dicalcium silicate as one of the mineral constituents. The $\beta \rightarrow \gamma$ transition of dicalcium silicate of air-cooled blast furnace slag is quite unpredictable [89] and for this reason the quality of air-cooled blast furnace slag for use as a coarse aggregate is controlled by BS:1047. Steel slags obtained as a by-product in the conversion of pig iron into steel, also contain metastable β-dicalcium silicate and are, therefore, used only for road aggregate after being allowed to weather for a year.

5.2. Alumina cement

β-dicalcium silicate is a minor phase in conventional high-alumina cements (HAC) used for structural concrete. According to the mineral analysis of several high-alumina cements reported [90] the mineral percentage of β-C_2S varied in the range 1 to 10 wt%. The role of β-dicalcium silicate in the hydration of HAC received little or no attention until Midgley [91] indicated the presence of Strätling's compound C_2ASH_8 in hydrated cement. It was shown later [92] that the reaction of the hydration products of C_2S with CAH_{10} results in the formation of Sträling's compound.

Dicalcium silicate is a major constituent (40 to 60%) in alumina–belite cement [93, 94]. It is stated that the loss in compressive strength, if any, due to the conversion of calcium aluminate hydrates is counter-balanced by the build up of strength from the hydration of β-C_2S [94]. However, it is likely that this arrest of strength drop is due to the formation of C_2ASH_8 in the matrix, because it has been claimed that C_2ASH_8 makes a

TABLE VI Morphology and microstructure of β-C_2S pastes

Time	% hydration	Features observed
7–14 h		C–S–H grows into water-filled capillaries. No definitive acicular morphology
3 days	25–32	Evidence of hydration products. Some kind of foil-like structure is obtained, unlike C_3S pastes
28 days	40	Acicular type I C–S–H is well developed and the "contact areas" appear to be better developed than in C_3S pastes. Clustering of acicular into fibrous bundles is also seen. Porosity of C–S–H adjacent to the unhydrated core is significant. The outer most acicular morphology extends right up to the core, unlike in C_3S paste
28–60 days	40–55	Development of a denser underlying C–S–H is observed (55% hydration) but no uniformity similar to C_3S is observed.
After 60 days	–	The features of fracture surface do not change very much except that the inner C–S–H product dominates the fracture surface. The fractured material showed irregular features and fine structure more than those observed in corresponding C_3S pastes
After 70 days	–	Type I C–S–H can be observed in remnants In matured paste (188 day hydration) pockets of partially hydrated C_2S grains and irregular fracture of calcium hydroxide crystals was observed

high contribution to the compressive strength of the matrix [92]. C_2ASH_8 was found in high concentrations in the hydrated pastes of a "porsal cement" [95] made up essentially of β-C_2S and calcium aluminates.

5.3. Reactive belite cements

Reactive belite cements are a newer class of cements in the developmental stage wherein the objective is to enhance the hydraulicity of C_2S so that the conventional requirement of C_3S content in portland cement can be minimized if not eliminated. The reactivity of C_2S towards water, as described in earlier sections, is dependent upon crystal imperfections and crystal size as well as polymorphic form. The variation in the reactivity of β-C_2S with a change in the stabilizer was appreciated [96] as early as 1960 and it was even hoped that a suitable stabilizer or a combination of them could possibly make β-C_2S as reactive as C_3S [97]. While among the α, α', β, γ forms, the α-form was found to be most hydraulic [61, 98], Bensted [36] found that β-C_2S stabilised with C_6AF_2 was less hydraulic than the α' and β forms. Inclusion of CaO as a solid solution in γ-C_2S (overall $CaO/SiO_2 = 2.2$) improved the hydraulic activity [24,99]. Gharpurey and Pai [100] studied the effect of substituting some of the Si^{4+} ions in β-C_2S with Al^{3+} ions, on the hydraulic activity.

The influence of crystal defects generated by the incorporation of Mg^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, etc., in the C_2S lattice, on the hydraulic behaviour was reported by Regourd and Guinier [101]. The effect of all these minor oxides on the free energy of the host lattice and, therefore, on its hydraulicity is considered to be of two types [18]. In the first place these minor oxides are precipitated out as microscopic but discrete phases, thereby producing stress conditions in the lattice. Secondly, the SiO_4^{4-} ions in the lattice may be replaced by other ions and depending on the requirements of electrical neutrality, anionic or cationic vacancies are created [18, 99]. The importance of stress conditions is very much appreciated in the preparation of "an early hardening C_2S phase" by Rangnekar *et al.* [102] who had tried to impart the stress conditions to the lattice by means of a thermal shock to the raw meal, in the heating schedule. This thermal shock can be classified into a general class of non-equilibrium conditions affecting the balance between the nucleation and growth of crystals. The size of crystallites of the active phases was also dealt by Vlasova [103]. Two other techniques of preparing reactive C_2S, i.e. gel technique and spray-drying technique, were also recently reported [104]. The raw material consisted of calcium nitrate solution mixed in predetermined proportions with a 1 M solution of a stabilized aqueous sol of silica. The spray-drying technique involved spraying droplets of solution into a vertical furnace preheated to temperature between 750 and 940° C. In the gel technique, the mixed solution was dehydrated at 70° C followed by heating at 760° C for 1 h. The new preparations of β-C_2S showed a strength of 690 kg cm^{-2} as against 420 kg cm^{-2} of commercial β-C_2S. This clearly indicates the beginning of a trend to develop a low-temperature inorganic cement, using relatively lower grade (silicious) limestones.

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References

1. R. W. NURSE, Proceedings of the 3rd International Symposium on the Chemistry of Cement, London (Cement and Concrete Association, Slough, 1952) p. 56.
2. M. A. BREDIG, *J. Amer. Ceram. Soc.* **33** (1950) 188.
3. K. NIESEL and P. THORMAN, *Tonind. Zeitung* **91** (1967) 362.
4. M. REGOURD, M. BIGARE, J. FOREST and A. GUINIER, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968). p. 44.
5. H. G. MIDGLEY, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. Paper, Section 1.
6. H. SAALFELD, *Bert. Deut. Keram. Ges.* **30** (1953) 185.
7. D. K. SMITH, A. J. MAJUMDAR and F. ORDWAY, *Acta Cryst.* **18** (1965) 787.
8. W. KURDOWSKI, Proceedings of the 6th conference on the silicate Industry, Budapest (Hungarian Academy of Sciences, Budapest, 1961) 263.
9. K. NIESEL, *Silicates Industriels* **37** (1972) 136.
10. G. YAMAGUCHI, Y. ONO, S. KAWAMURA and Y. SODA, *J. Ceram. Assoc. Japan* **71** (1963) 9.
11. A. GUINIER and M. REGOURD, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 787.
12. R. ROY, Proceedings of the 4th International Symposium on the Chemistry of Cement, Washington Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 29.
13. W. KLEMENT Jr. and L. H. COHEN, *Cem. Concr. Res.* **4** (1974) 939.
14. E. WAGNER, *Zement – Kalk – Gips* **27** (1974) 773.
15. J. BENSTED and S. P. VARMA, *Cement Technol.* **5** (1974) 256.
16. S. N. GHOSH and A. K. CHATTERJEE, *J. Mater. Sci.* **9** (1974) 1577.
17. A. I. BOIKOVA and A. I. DOMANSKY, *Cem. Concr. Res.* **4** (1974) 773.
18. J. N. MAYCOCK and M. McCARTY Jr., *ibid.* **3** (1973) 701.
19. Y. SUZUKAWA and T. SASAKI, Proceeding of the 4th International Symposium on the Chemistry of Cement, Washington, Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 83.
20. C. M. MIDGLEY, *Acta Cryst.* **5** (1952) 307; *Brit. J. Appl. Phys.* **3** (1951) 277.
21. H. F. W. TAYLOR, ED., "The Chemistry of Cements", Vol. 2 (Academic Press, London, 1964).
22. N. YANNAQUIS and A. GUINIER, *Bull. Soc. Mineral Christ.* **82** (1959) 126.
23. *Idem*, Proceedings of the 4th International Symposium on the Chemistry of Cement, Washington, Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 21.
24. V. I. KORNEV and E. B. BYGALINA, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 285.
25. A. A. PASHOHENKO, E. A. STARCHEVSKAYA and V. P. SERBIN, Proceedings of the 6th International Congress on the Chemistry of Cement Moscow (Stroiizdat, Moscow, 1974), Suppl. Paper, Section 1.
26. P. BHASKARA RAO and S. N. GHOSH, Unpublished work.
27. J. BENSTED, *Cem. Concr. Res.* **8** (1978) 73.
28. J. FOREST, *Silicates Industrials* **32** (1967) 373,427.
29. Y. M. BUTT, V. V. TIMASHEV and L. I. MALOZOHN, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 340 and the references therein.
30. G. YAMAGUCHI, Y. ONO, S. KAWAMURA and Y. KANAI, *Semento Gijustu Nempo* **XVII** (1963) 37.
31. G. YAMAGUCHI, Y. ONO, S. KAWAMURA and Y. SODA, *ibid.* **XVII** (1963) 39.
32. N. F. FEDOROV and E. R. BRODKINA, *Izvest. Akad. Nauk. SSSR, Neorgan Materialy* **2** (1966) 745.
33. C. BRISI and P. APPENDINO, *Ann. di chim.* **55** (1965) 461.
34. R. W. NURSE, J. H. WELCH and W. GUTT, *J. Chem. Soc.* **220** (1952) 1077.
35. R. KONDO and S. GOTO, *Semento Gijutsu Nempo* **XIX** (1965) 42.
36. J. BENSTED, *Chem. Ind.* (1975) 885.

37. R. W. NURSE, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 77.
38. C. M. SCHLAUDT and D. M. ROY, *J. Amer. Ceram. Soc.* **49** (1966) 430.
39. W. GUTT, Ph. D. Thesis, London University (1966).
40. F. P. GLASSER, *Amer. J. Sci.* **259** (1961) 46.
41. N. F. FEDEROV and E. R. BRODKINA, *Izvest. Akad. Nauk. SSSR, Neorgan Materialy* **2** (1966), 1458.
42. I. KAPRA'LIK and F. HANIC, *Trans. J. Brit. Ceram. Soc.* **76** (1977) 126.
43. W. GUTT, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 93.
44. F. K. F. LIEBAU, *ibid*, p. 74.
45. A. I. BOIKOVA, M. G. DEGEN and V. A. PARAMONOVA, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974), Suppl. paper, Section 1.
46. H. G. MIDGLEY, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 74.
47. F. M. LEA, "The Chemistry of Cement and Concrete" (Edward Arnold, 1970).
48. G. YAMAGUCHI and S. TAKAGI, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 181.
49. H. G. MIDGLEY and M. BENNETT, *Cem. Concr. Res.* **1** (1971) 413.
50. W. GUTT and M. A. SMITH, *Trans. J. Brit. Ceram. Soc.* **66** (1967) 337.
51. W. GUTT and G. S. OSBORN, *ibid* **65** (1966) 521.
52. S. N. GHOSH, A. K. PAUL and A. THAKUR, *J. Mater. Sci.* **13** (1978) 1602.
53. S. N. GHOSH and A. K. PAUL, unpublished work.
54. N. A. TOROPOV and N. F. FEDOROV, *Zh. Neorg. Khim.* **9** (1964) 1939.
55. F. NADACHOWSKI and M. GRYLICKI, *Silikat Technik* **10** (1959) 77.
56. B. COURTALT, Centre d'Etudes et de Recherches de L'Industries des Liants Hydraliques Pub. Tech. 140 (1963).
57. P. B. MOORE, *Amer. Mineral.* 58 (1973) 32.
58. M. GARDENER, *Sci. Amer.* **220** (1969) 113.
59. G. M. BIGGER, *Cem. Concr. Res.* **1** (1971) 493.
60. N. A. TOROPOV, N. F. FEDOROV and V. I. HENTOV, *Rep. Acad. Sci. USSR* **2** (1966) 550.
61. Y. ONO, S. KAWAMURA, and Y. SODA, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 275.
62. D. K. SMITH, A. J. MAJUMDAR and F. ORDWAY, *J. Amer. Ceram. Soc.* **44** (1961) 405.
63. H. FUNCK, *Z. Anorg. Allegem. Chem.* **291** (1957) 276.
64. D. L. KANTRO, S. BRUNAUER and C. H. WEISE, *Adv. Chem. Ser.* **33** (1962) 199.
65. *Idem, J. Phys. Chem.* **66** (1962) 1804.
66. S. BRUNAUER, D. L. KANTRO and L. E. COPELAND, *J. Amer. Chem. Soc.* **80** (1958) 761.
67. S. A. GREENBERG and T. N. CHANG, *J. Phys. Chem.* **69** (1965) 553, 2489.
68. J. H. TAPLIN, Proceedings of the 4th International Symposium on the Chemistry of Cement, Washington, Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 263.
69. H. LEHMANN and H. DUTZ, *ibid*, p. 513.
70. G. YAMAGUCHI, K. TAKEMOTO, H. UCHIKAWA and S. TAKAGI, *ibid*, p. 495.
71. V. V. DANILOV, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. paper, Section II.
72. R. W. G. WYCKOFF, "Crystal Structures", Vol. 4, 3nd Ed. (Interscience, New York, 1968) p. 162.
73. M. M. SYCHEV, V. I. KORNEEV, E. N. KAZANSKAYA and I. N. MEDVADAVA *J. Appl. Chem. USSR (English translation)* **46** (1973) 530.
74. H. FUNK, Proceedings of the 4th International Symposium on the Chemistry of Cement, Washington, Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 291.
75. J. JERNEJCIC and I. JELENIC, *Cem. Concr. Res.* **4** (1974) 123.
76. S. K. CHOPRA, P. BHASKARA RAO and K. C. NARANG, *Res. Ind. CSIR (India).*
77. P. BHASKARA RAO and S. N. GHOSH, unpublished work.
78. J. BENSTED, *Cim Betons Plastres Chaux* **703** (1976) 335.
79. P. I. BOZHENOV, V. I. KOVALEROVA, V. S. SALNIKOVA and G. F. SUVOROVA Proceedings of the 4th International Symposium on the Chemistry of Cement, Washington, Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 327.
80. I. TEORANEAU and M. MUNTEAN, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. Paper.
81. J. F. YOUNG and H. S. TANG. *Cem. Concr. Res.* **7** (1977) 627.
82. K. K. KUATBAEV, V. V. NI and G. T. PUZHANOV, *Chem. Abstr.* 77 (1972) 168086 W.
83. V. V. DANILOV, M. M. SYCHEV and V. I. KORNEEV, *Izv. Akad. Nauk. SSSR Neorg. Mater.* **12** (1976) 664.
84. H. G. KUREZYK and H. E. SCHWIETE, Proceedings of the 4th International Symposium on the Chemistry of Cement, Washington, Vol. 1 (U.S. Department of Commerce, Washington D.C., 1960) p. 349.
85. T. D. CIACH and E. G. SWENSON, *Cem. Concr. Res.* **1** (1971) 159.
86. R. B. WILLIAMSON, *Prog. Mater. Sci.* **15** (1972) 189.
87. R. L. BERGER, F. V. LAWRENCE and J. F. YOUNG, *Cem. Concr. Res.* **3** (1973) 497.
88. F. V. LAWRENCE, J. F. YOUNG and R. L. BERGER, Proceedings of the 6th International

Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. paper.

89. W. GUTT, *Chem. Ind.* (1972) 439.
90. H. G. MIDGLEY, *Cem. Concr. Res.* **6** (1976) 217.
91. *Idem, Trans. Brit. Ceram. Soc.* **66** (1967) 161.
92. H. G. MIDGLEY and P. BHASKARA RAO, *Cem. Concr. Res.* **8** (1978) 169.
93. L. A. ZAKHAROV, Proceedings of the 9th Conference on Silicate Industry, Budapest (Hungarian Academy of Sciences, Budapest, 1969). p. 303.
94. *Idem,* Proceedings of the 6th International Congress on Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. Paper.
95. S. J. RAINA, V. N. VISWANATHAN and A. K. CHATTERJEE, *Zement – Kalk – Gips,* **31** (1978) 516.
96. G. V. KUKOLEV and M. T. MEL'NIK, *Doklady Acad. Nauk. SSSR* **132** (1960) 168.
97. R. W. NURSE, Proceedings of the 7th Conference on Silicate Industry, Budapest (Hungarian Academy of Sciences, Budapest, 1965) p. 179.
98. M. Y. BIKBAU, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. Paper.
99. V. I. KORNEYEV, *ibid,* Suppl. paper.
100. M. K. GHARPUREY and V. N. PAI, Proceedings of the 5th International Symposium on the Chemistry of Cement, Tokyo, Vol. 1 (Cement Association of Japan, Tokyo, 1968) p. 289.
101. M. REGOURD and A. GUINIER, Proceedings of the 6th International Congress on the Chemistry of Cement, Moscow (Stroiizdat, Moscow, 1974) Suppl. Paper.
102. B. S. RANGNEKAR, V. R. G. SRINIVASAN and V. N. PAI, *ibid,* Suppl. paper.
103. M. T. VLASOVA, *ibid,* Suppl. Paper.
104. D. M. ROY and S. O. OYEFESOBI, *J. Amer. Ceram. Soc.* **60** (1977) 178.

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