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Lattice defects and the effect of Melment on the hydration of alite

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The hydration of alite has been studied in the presence of different concentrations of the superplasticizer Melment by using various experimental techniques. Heat of hydration and non-evaporable water content determinations show that Melment retards the hydration; pH measurements indicate that in presence of Melment, Ca^{2+} ion dissolution is reduced. Zeta potential measurements give definite proof that Melment molecules are adsorbed at alite surfaces and the retardation of hydration may be due to adsorption. Thermoelectric power measurements prove that the material is an n-type semiconductor, whereas electrical conductivity measurements of solid pellets of C_3S (C = CaO, S = SiO_2) show that the material is an intrinsic semiconductor above 746 K and an extrinsic semiconductor below 746 K. Extrinsic semiconductivity may be due to the presence of defects or impurities in the crystal lattice. The results also show that oxide ion vacancies are created in the crystal lattice and the reactivity of C_3S is related to the defects. Probably Melment molecules are adsorbed at the sites of defects and oxide ion vacancies and hence retard the hydration.

1. Introduction

Tricalcium silicate in the form of alite is the major constituent of Portland cement and its hydration has been studied extensively. In spite of a large number of studies [1–4], the mechanism of the early hydration reactions is still not well understood. Heat of hydration measurements show that upon mixing with water, C_3S undergoes a five-stage sequence of reactivity:

1. Immediate reaction with Ca^{2+} ions passing into solution.
2. A dormant or induction period in which a slow rise in Ca^{2+} ion concentration continues to take place.
3. An acceleration period in which solid $Ca(OH)_2$ crystallizes from solution and C–S–H deposits into the available water-filled space.
4. A deceleration period, i.e. a consequence of hydration products being formed, involving a decrease of the porosity of the system and the transportation of the ionic species on the liquid–solid interface.
5. A totally diffusion-controlled process due to decreased porosity and decreased transport of ionic species as a consequence of Stage 4.

All the above stages of hydration can be affected by the following factors:

(i) temperature of hydration,
(ii) water–solid ratio,
(iii) surface area,
(iv) admixtures,
(v) nature and quantity of dopant in the crystal lattice of C_3S,
(vi) nature and concentration of defects.

A number of retarding admixtures have been used to extend the workability of cement. Amongst the retarders, superplasticizing admixtures have gained considerable interest during the recent years [5–12]. Shestakov [13] has divided all known superplasticizers into four main categories and proposed that these are adsorbed at cement surfaces, change the surface charge and have a peptizing and stabilizing action with respect to the cement suspension. However, the mechanism of action of superplasticizers is still not clear.

Attempts have also been made to understand the role of lattice defects in the hydration of cement and its constituents [14, 15]. However, very little is known about this aspect.

In the present communication attempts have been made to understand the mechanism of hydration of alite in the presence of the superplasticizer Melment, with special reference to the nature of the defects present in the C_3S crystal lattice.

2. Experimental procedure

2.1. Preparation of alite

Silica (Aerosil) was mixed with CaO in the stoichiometric ratio of 1 : 3; CaO was taken slightly in excess. To this mixture known amounts of Al_2O_3, Fe_2O_3 and MgO were added. This mixture was ball-milled for 24 h in the presence of an excess of water in order to obtain a homogeneous mixture. The entire mass was dried over a gypsum plate and then granulated. The granules thus obtained were fired at 1310° C for 20 min. Alite with the composition in Table I, referred to as AFM (112), was obtained.

The alite formed was also characterized by X-ray diffraction. The free lime content and Blaine surface area were respectively 1.6 wt % and 3890 $cm^2 g^{-1}$. The particle size distribution as measured by a laser granulometer is shown in Fig. 1.

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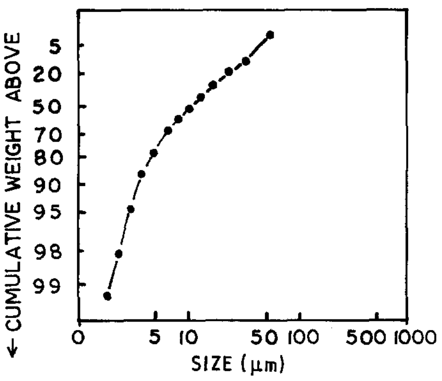

Figure 1 Particle size distribution for alite (RRSB diagram).

Melment (commercial resin) was used as an admixture.

2.2. Preparation of hydrated samples

2 g of alite were mixed with 2 cm^3 of distilled water or Melment solution (0.5 or 1.0 wt %) in sealed polythene bags and were allowed to hydrate at 30° C. The hydration at different time intervals (1, 2, 4, 8, 10, 12, 15, 20 and 24 h) was stopped with isopropyl alcohol and ether. The samples were then dried at 105° C for one hour, cooled and stored in polythene bags in a desiccator.

2.3. Determination of non-evaporable water content (W_n)

Approximately 1 g of the hydrated samples was heated first at 105° C for one hour and then at 1000° C for another hour. From the loss in weight of the samples in this process, W_n and α (the degree of hydration) were calculated.

2.4. Determination of heat of hydration

The heat of hydration of the alite was measured with the help of a conduction calorimeter as described elsewhere [16]. 2 g of alite were weighed in the cylindrical cell of the calorimeter and the same amount of finely ground quartz was also weighed in another cylindrical cell. The two cells were then separately fitted with pipettes attached to syringes containing 2 ml distilled water in order to have a water/solid ratio of unity. The two cells were then placed in the calorimeter kept at a constant temperature. Upon thermal equilibriation, the water was injected into the cells containing alite and quartz and the calorimeter chamber was shaken for one minute for mixing. The experiments were performed at 20° C.

2.5. pH measurements

The change in pH of the pastes of alite (water/solid = 1) with 0.0, 0.5 and 1.0 wt % of Melment solutions were measured by a digital pH meter Model 335 (Systronics) at 30° C using glass and calomel (reference) electrodes.

2.6. Zeta potential measurements

Zeta potential measurements were made with the help of a zetameter; 0.02 g of alite was dispersed in 100 ml water or 0.25, 0.5, 0.75 and 1.0 wt % Melment solution and homogenized ultrasonically for 10 min. The suspension was then placed in the electrophoretic cell of the zetameter fitted with two electrodes. A molybdenum cylinder acted as an anode and a platinum–iridium strip as a cathode. First of all the specific conductivity of the suspension was determined and the corresponding voltage (given in the instrument manual) was applied for determining the electrophoretic mobility of the particles. The movement of each particle was observed under a microscope fitted with the zetameter. The time required for a particle to move a fixed distance (160 μm) in response to a specific field gradient was the usual measurement made. The time for migration of particles was noted at different intervals of hydration time. In the absence of Melment it was found that the particles moved from anode to cathode, indicating that the particles carry a positive charge, whereas in the presence of Melment, the particles moved from cathode to anode, indicating that they carry a negative charge. From these observations, the zeta potential was calculated with the help of a table supplied with the instrument and temperature correction was made. Each zeta potential value is an average of ten observations.

2.7. Electrical conductivity and dielectric constant measurements in the solid state

The measurement of a.c. electrical conductivity and dielectric constant was done by a two-electrode method using a platinum disc as a sample holder. A Wayne–Kerr universal bridge (Model 224 B) was used with an internal oscillator frequency of 1.592 kHz. The sample holder was made of stainless steel with a screw clamping system. The powdered C_3S sample was pelletized using a die of 1 cm diameter with a load of 3000 lb (1.361 tonne) and a thickness of about 0.6 cm. Silver was deposited on both the faces of the pellet to make a good electrical contact. The whole assembly was kept in a tube furnace, the temperature of which was monitored by a chromel–alumel thermocouple in a temperature range up to 1000° C. The activation energies for conduction for the higher and lower temperature ranges were calculated from the curve.

2.8. Thermoelectric power measurement in the solid state

Pressed pellets of C_3S were used for this measurement also. The pellets were made with the help of a hand-operated hydraulic press and a suitable die. The pellet on which final measurements were carried out was made at a load of 7 tons (7.11 tonne) and had a diameter of 1.54 cm and a thickness of 0.6 cm. Before

TABLE I Composition of alite

Oxide	CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	K_2O	Na_2O	MgO
Composition (wt %)	70.0	24.7	1.03	1.22	0.29	0.05	0.03	2.26

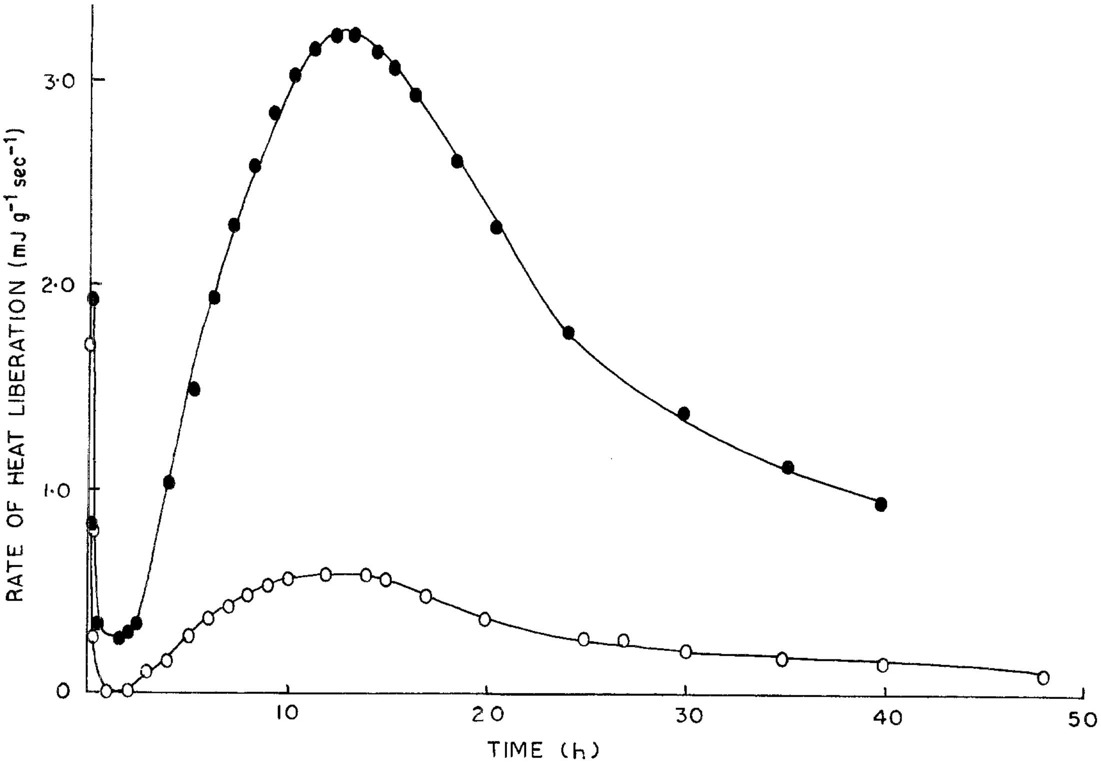

Figure 2 Effect of 1% Melment on the rate of heat evolution of hydrating alite (AFM (112)). (○) 1% Melment, (●) control.

measurements were made, the pellet was annealed at a temperature of 700° C for 20 h in a platinum crucible. The annealing of material is very necessary to obtain good and reliable results. True thermoelectric data are almost impossible to obtain with an unannealed sample. In order to ensure better electrical contact, both surfaces of the pellet, which were in contact with the platinum electrodes were painted with silver paint. The thermoelectric power was measured with a digital-multimeter PM 2522/90 (Philips, India) with an accuracy better than $\pm 0.20\%$. A temperature difference of $\Delta T = 20°$ C was produced across the pellet with the help of a microfurnace fitted with the sample holder assembly, and the temperatures of both the surfaces of the pellet were recorded by chromel–alumel thermocouples attached to the platinum electrodes. Each reading was taken after attaining thermal equilibrium (about 2.5 h). In all the measurements, the two-electrode method was employed and mica sheets were used for insulation.

3. Results and discussion

The rate of heat evolution in the presence of 1% Melment is given in Fig. 2. The curve indicates that the rate of alite hydration is reduced considerably in the presence of 1% Melment. It appears that Melment surrounds the C_3S surfaces and hinders the approach of water molecules, which in turn decreases the rate of reaction.

The variation of non-evaporable water content in the presence of 0.0, 0.5 and 1.0 wt % Melment is given in Fig. 3. Without Melment the percentage of non-evaporable water content increases continuously, whereas in the presence of 0.5 wt % Melment there is practically no reaction up to 15 h of hydration and after this the reaction accelerates with time. However, in the presence of 1.0 wt % Melment very little reaction occurred up to 24 h of reaction. The results show that as the concentration of Melment is increased, the induction period is also increased and the overall rate of hydration is decreased.

From the non-evaporable water content, the degree of hydration (α) was calculated by assuming that 23% water is required for complete hydration. The kinetic data on the degree of hydration obeys Jander's equation [17]

$$[1 - (1 - \alpha)^{1/3}]^2 = kt \qquad (1)$$

where α is the degree of hydration at any time t and k is the apparent rate constant. The constant k includes

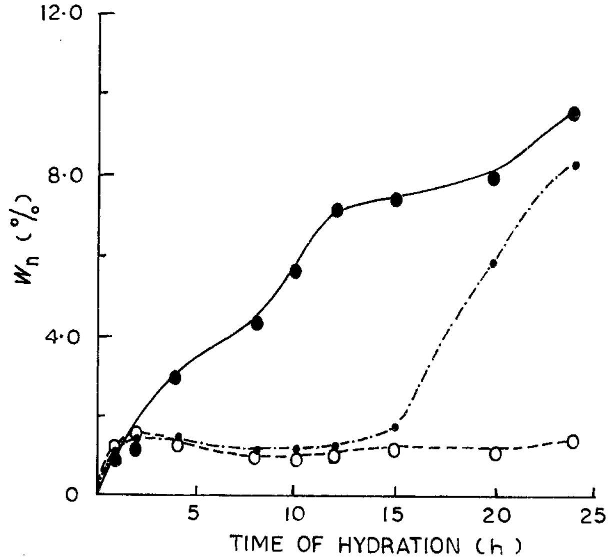

Figure 3 Variation of non-evaporable water content of alite (AFM (112)) with hydration time in the presence and absence of Melment. (——) Control, (–·–) 0.5% Melment, (– – –) 1% Melment.

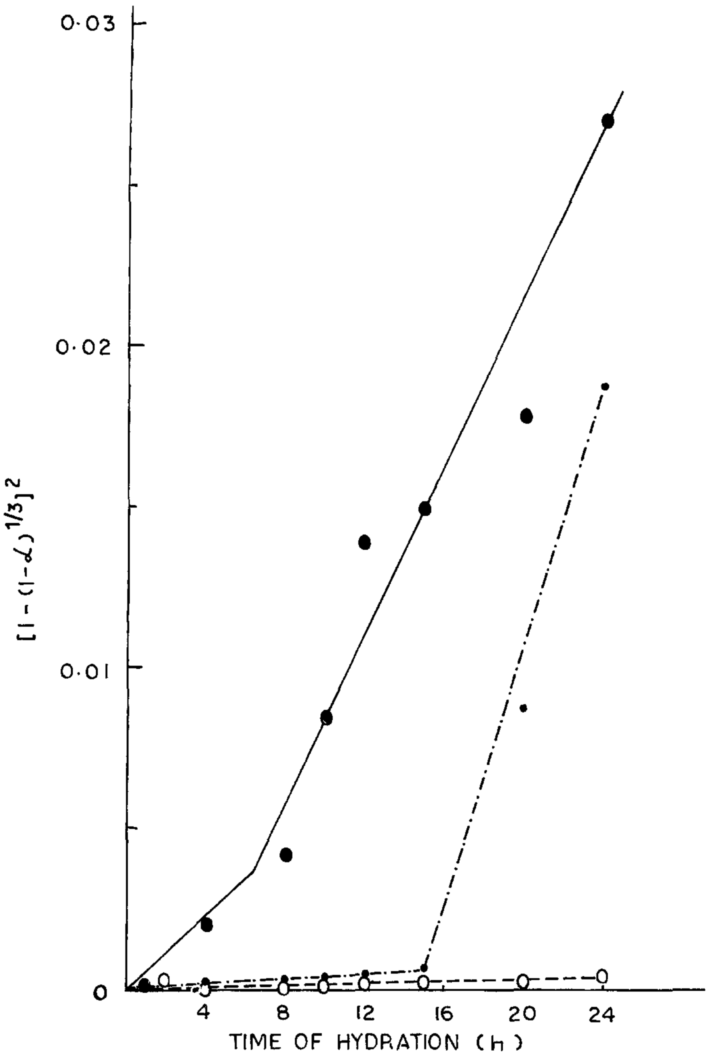

Figure 4 Test of Jander's equation. (——) Control, (–·–) 0.5% Melment, (– – –) 1% Melment.

the diffusion coefficient. A plot of $[1 - (1 - \alpha)^{1/3}]^2$ against t gave two lines (Fig. 4). The intersection of the two lines shows the end of the induction period. In the case of 1.0 wt % of Melment there is only one straight line, indicating that the reaction is very slow. Since Equation 1 is diffusion-controlled, it can be said that the hydration of C_3S may also be a diffusion-controlled process.

The variation of the pH of the hydrating paste in the presence and absence of Melment is given in Fig. 5. As soon as C_3S comes in contact with water, the pH of the solution increases immediately due to the dissolution of Ca^{2+} ions in the solution, but as soon as the $Ca(OH)_2$ starts precipitating the pH decreases. Melment, which is probably adsorbed at the C_3S surface, reduces the dissolution of Ca^{2+} ions and hence the pH is lowered. Since the Ca^{2+} ion concentration in solution is low, Melment also hinders the precipitation of $Ca(OH)_2$ from the solution. So, after the initial rapid increase, the pH remains constant up to 90 min of hydration. As the concentration of Melment is increased, the initial rapid increase in pH is decreased. These results show that in the presence of higher concentrations of Melment, lesser amounts of Ca^{2+} ions go into solution. This may be due to an increased adsorption of Melment.

In order to understand the mechanism of hydration it is essential to have an idea about the nature of the charge species at the surface of alite at the beginning of hydration. For this purpose, the zeta potential is measured. The variation of zeta potential with Melment concentration is given in Fig. 6. In the absence of Melment, the zeta potential is positive. It has already been suggested [18] that as soon as C_3S comes in contact with water, hydrolysis starts and Ca^{2+} ions go into solution leaving silicon tetrahedra. The positive ions in the solution are then adsorbed at the surface, giving a positive zeta potential. From Fig. 6 it is clear that in the presence of Melment the zeta potential becomes negative and decreases with the increase of Melment concentration. The change of sign clearly indicates that Melment is adsorbed at the alite surface, giving a negative zeta potential. X-ray photoelectron spectrophotometric analysis [19] has shown that the surface of hydrating C_3S between 5 sec and 1 min is a site of continuous exchange and is not in a state of equilibrium. This is probably the period in which Melment is adsorbed at the C_3S surface.

The high reactivity of C_3S towards water may be due to defects in the C_3S crystal lattice. Many reports in the cement chemistry literature deal with electrical conductance studies of hydrating pure mineral calcium silicate. These data cannot be analysed in terms of defects in the C_3S crystal lattice. However, Singh [20] reported that electrical conductivity measurements of powdered C_3S pellets in the temperature range 1073 to 1273° C show that it is a semiconductor and the conduction is electronic in nature. Since the data are

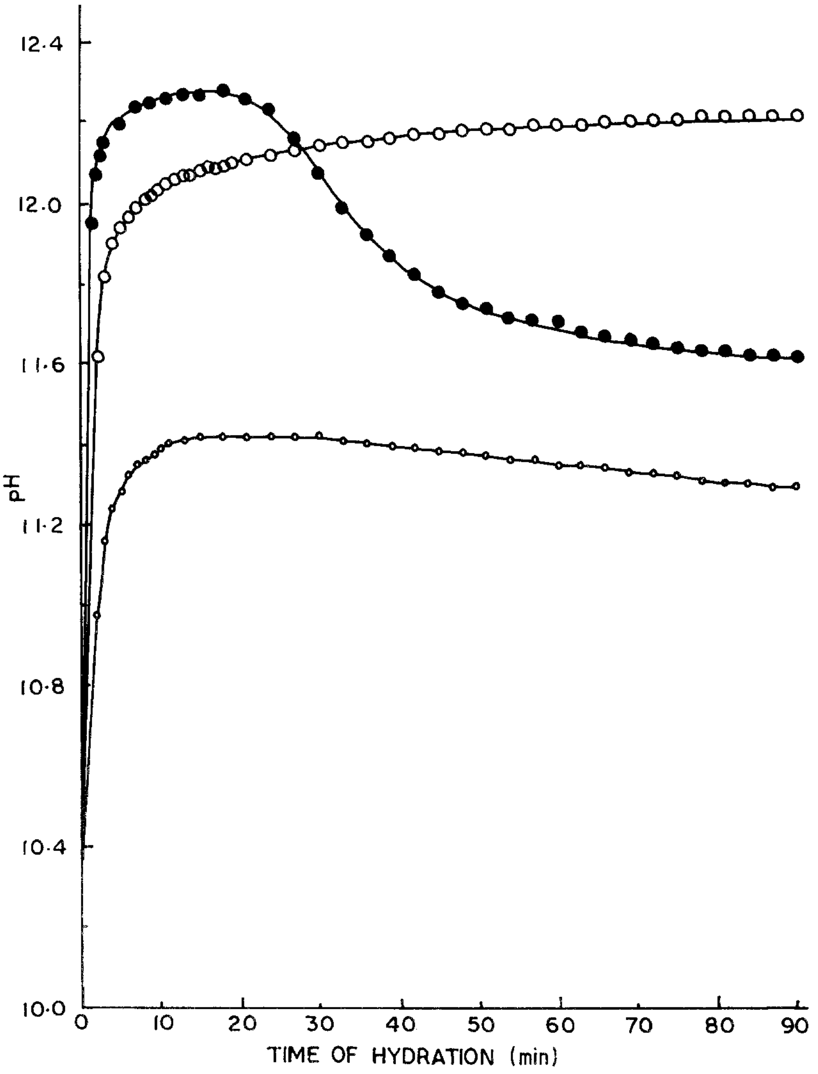

Figure 5 Variation of pH of the hydrating alite paste (AFM (112)) with time at 30°C in the presence and absence of Melment; water/cement ratio = 1.0 (●) Control, (○) 0.5% Melment, (○) 1% Melment.

available only in a limited temperature range and also no data are available at lower temperatures, it is difficult to say anything about the nature of the defects from these results and also to correlate hydration with defects. However, in the present communication we have measured the electrical conductivity σ in the temperature range 373 to 1273 K. When log σ is plotted against $1/T$, the curve shown in Fig. 7 is obtained. This curve can roughly be divided into two straight lines for which the following equation can be given:

$$\sigma = C \exp(-W/kT) \qquad (2)$$

where C is a constant, W is the energy of activation for conduction, T is the absolute temperature and k is Boltzmann's constant. It can be seen from the figure that there exists a discontinuity in the region of around 746 K. This discontinuity may be due to a phase transformation; however, it is not sharp. The data can be expressed by two straight lines, one below 746 K and the other above 746 K, as follows:

$$\sigma_1 = 21.13 \exp\left(-\frac{0.17\,\text{eV}}{kT}\right) \Omega^{-1}\,\text{cm}^{-1}$$

below 746 K

$$\sigma_2 = 4.46 \times 10^6 \exp\left(-\frac{1.05\,\text{eV}}{kT}\right) \Omega^{-1}\,\text{cm}^{-1}$$

above 746 K

The activation energies for conduction below and above 746 K are 0.17 and 1.05 eV, respectively. These values indicate that the material is an intrinsic semiconductor above 746 K and an extrinsic semiconductor below 746 K. In the lower temperature range (below 746 K), the extrinsic semiconductivity may be due to the presence of impurities, point defects or interstitials which are often present in the forbidden energy gap of

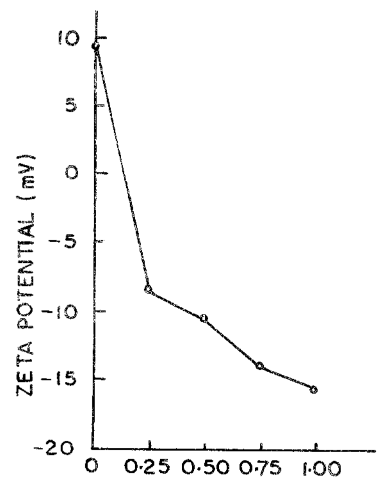

Figure 6 Variation of zeta potential with Melment concentration for alite (AFM (112)).

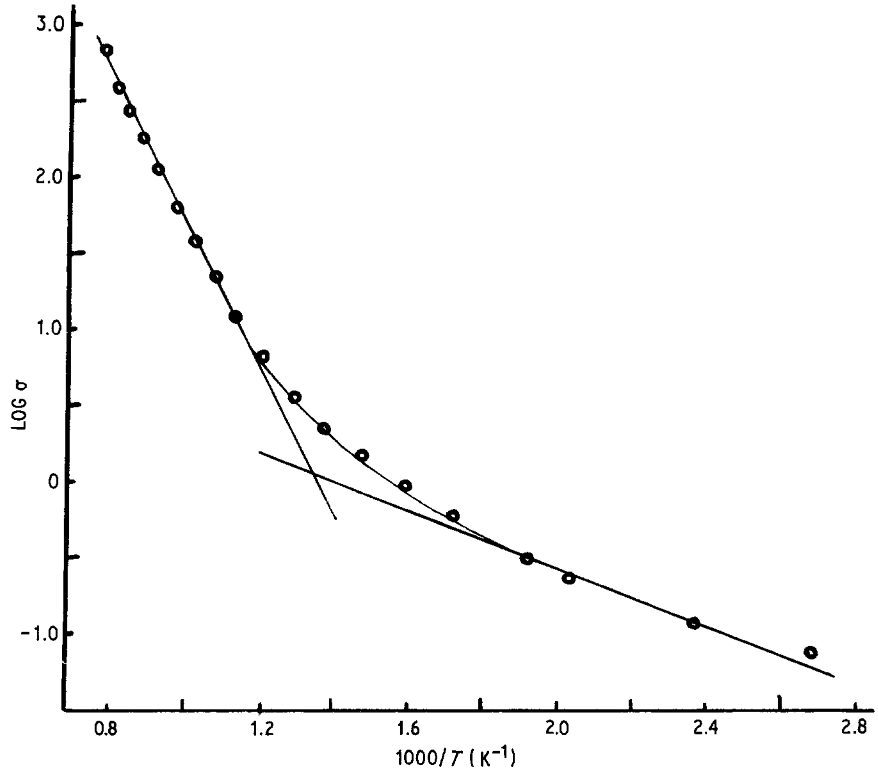

Figure 7 Variation of log of electrical conductivity with inverse of temperature for alite (AFM (112)).

the crystal. The contributions of defects and impurities towards conduction in a solid can be explained in terms of donors and acceptors and is represented by the expression [21]

$$\sigma = \sigma_0 \exp(-E_i/2kT) \qquad (3)$$

E_i is the ionisation energy of donors or acceptors and usually $E_i \approx 0.1$ eV. The activation energy calculated in this temperature range is 0.17 eV, which is comparable to the ionization energy of 0.1 eV. It therefore seems reasonable to conclude that electrical conduction in C_3S below 746 K is due to impurity charge carriers, point defects or interstitials present in the forbidden energy gap of the crystal.

In the case of the intrinsic semiconductor (above 746 K) the energy of activation is high (1.05 eV) and the band gap is 2.10 eV. It appears that the conduction is due to band theory and both the valence and the conduction bands are wide.

The variation of thermoelectric power (S) as a function of temperature is given in Fig. 8. S is found to be negative over the entire range of temperature studied and hence the compound is an n-type semiconductor and the majority charge carriers are negative electrons. S decreases with temperature up to around 600 K and then increases. Here the break in temperature is different from those found in Fig. 7. This break is also due to a phase transformation, and the difference may be due to a difference in the accuracies of the measurements or due to different phase transformations.

The n-type semi-conductivity may be due to the escape of oxygen from the crystal lattice. When oxygen leaves the crystal lattice, vacancies are created and the electrons are trapped in these vacancies which move under the influence of the applied potential; the charge carriers are negatively charged electrons. The escape of oxygen from the lattice sites may create oxide ion vacancies as represented below:

$$O^{2-}(\text{lattice sites}) \rightarrow \begin{cases} \frac{1}{2}O_2 + \square + 2e^- \\ \text{or} \\ \frac{1}{2}O_2 + \square^- + e^- \\ \text{or} \\ \frac{1}{2}O_2 + \square^{2-} \end{cases}$$

where $\square$ = oxide ion vacancy and $\square^-$, $\square^{2-}$ = oxide ion vacancies with one and two trapped electrons, respectively. The electrons trapped in the oxide ion

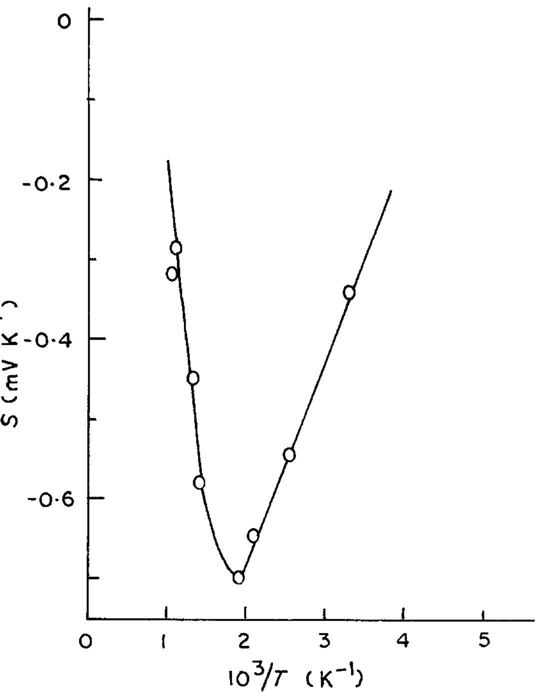

Figure 8 Variation of thermoelectric power as a function of temperature for alite (AFM (112)).

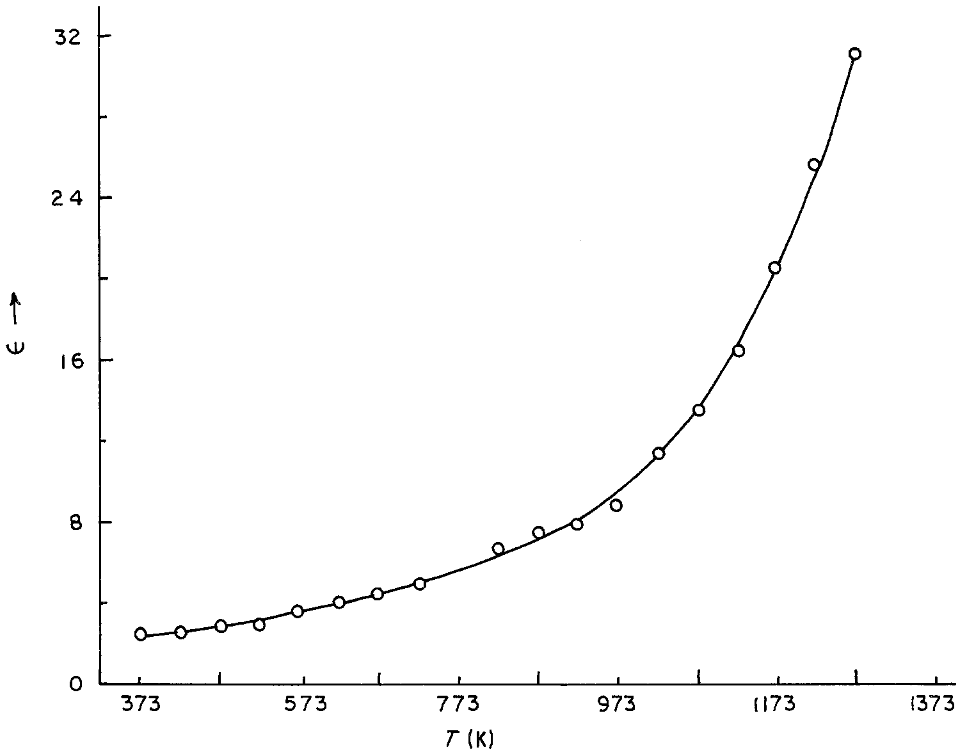

Figure 9 Variation of dielectric constant with temperature for alite (AFM (112)).

vacancies may impart interesting properties such as electrical conductivity to the crystal.

The variation of dielectric constant (ε) with temperature is given in Fig. 9. The increase of ε with temperature is very slow up to nearly 850 K, and above 850 K the dielectric constant increases rapidly with temperature. The slow variation of ε with increase of temperature is a characteristic of ionic solids [22]. Due to the increase in temperature, the lattice of the crystals expand with a consequent increase in polarizability of the ions. This increase in polarizability increases the dielectric constant of the material.

From the above results, one can visualize the overall hydration in the following way: C_3S crystals contain impurities, defects and oxide ion vacancies and also have an ionic character. When water molecules come into contact with C_3S crystals, dipolar attraction starts and the interaction is more pronounced in the region of defects because at those points a lower energy is needed. As a result of this, Ca^{2+} ions go into solution, increase the pH and get adsorbed at the negatively charged silica tetrahedra, giving a positive zeta potential. Melment, when present, is adsorbed at the C_3S surface, especially at those points where defects or impurities are present. Due to this, the interaction of water molecules is hindered and the dissolution of ions is reduced, which in effect retards the hydration.

4. Conclusions

1. Heat of hydration and non-evaporable water content measurements show that Melment retards the hydration of alite.
2. pH measurements of the hydrating paste indicate that Ca^{2+} ion dissolution is reduced in the presence of Melment, which in turn decreases the $Ca(OH)_2$ concentration in the solution and lowers the pH of the paste.
3. Zeta potential measurements give definite proof that the Melment is adsorbed at the alite surface and hence the retardation of hydration is due to adsorption.
4. Thermoelectric power measurements prove that the alite is an n-type semiconductor and the charge carriers are negatively charged electrons.
5. Electrical conductivity measurements of the solid pellet show that the material is an extrinsic semiconductor below 746 K and an intrinsic semiconductor above 746 K. The change in conductivity with temperature is due to changes in defect concentration, oxygen ion vacancies and impurities present in the crystal lattice.
6. Dielectric constant measurements indicate that the material behaves like an ionic compound.
7. It is possible than when water comes into contact with alite, dipolar interaction occurs and the hydration reaction starts. However, Melment is adsorbed over the alite surface mainly at the points of defects, vacancies and impurities and thus lowers the reactivity.

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