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Influence of admixtures on strength development of Portland cement and on the microstructure of tricalcium silicate

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The influence of various inorganic salts, used as additives to Portland cement paste, on strength development was studied. The salts used were: $CaCl_2$, $CrCl_3$, CdI_2. It was found that $CaCl_2$ and $CrCl_3$ accelerate the rate of strength development, while CdI_2 retards it compared to Portland cement without admixtures. No influence by $CdCl_2$ was observed. The effect of the same admixtures on the microstructure of hydrated tricalcium silicate was examined by a scanning electron microscope, and correlation between the morphology of the simple system and the mechanical behaviour of the complex cement system is discussed.

1. Introduction

The present work is a part of a more extensive research, the purpose of which is to study the effect of various inorganic admixtures on the hydration of Portland cement and of tricalcium silicate (C_3S*), the latter being the main component of Portland cement.

In previous studies [1, 2] the authors reported the effect of $CaCl_2$, $CrCl_3$ and CdI_2 on hydration of C_3S obtained from thermal and infra-red data. It was found that all the salts affect the hydration to different extents. The estimation of the degree of hydration was based, in all cases, on the amount of $Ca(OH)_2$ formed as determined by thermogravimetry. The present work contains observations on development of compressive strength of Portland cement paste under the influence of the same admixtures for periods from one day to three months, and microscopic observations (using a scanning electron microscope) showing the microstructure development of the hydration products of C_3S in the presence of the same admixtures.

The first observations by a scanning electron microscope (SEM) on hydrated Portland cement, made by Chatterji and Jeffery [3, 4] showed that the hydration products consist of hexagonal crystals of $Ca(OH)_2$ and needles of C–S–H. Many recent investigations have been made since to study the detailed morphology and microstructure of C–S–H. The hydration products seem to appear as fibres of C–S–H covering semicrystalline unhydrated grains and plates [5, and references therein]. In 1974 Walsh *et al.* [6] reported an extensive high resolution SEM study of fracture surfaces of Portland cement paste. They show that fibres bond with one another to hold the C–S–H spherulites together and that the volume between these spherulites consists of $Ca(OH)_2$ hexagonal plates. The cleavage through the cement occurs mostly across the weakly bonded basal planes of the $Ca(OH)_2$ and secondly through the C–S–H/$Ca(OH)_2$ interface; the strongest bonding occurs between the C–S–H spherulites.

Microscopic observations [7–10] made on neat C_3S paste have shown a change in the morphology of the hydration products with age from a foil-type to a fibrous structure. Collepardi and Marchese [11] observed in the first stages of hydration that the particles change from a laminar into a curled cigar shape within some hours of paste hydration of C_3S. This morphological transformation is accompanied by a large reduction of the specific surface area. The influence of admixtures on the microstructure development of the hydration pro-

*C = CaO; S = SiO_2; H = H_2O; C_3S = $3CaO \cdot SiO_2$; C–S–H = calcium silicate hydrate.

ducts has not been fully studied, although it has been shown [11–15] that there are differences in structure and shape of the C–S–H formed mainly in the presence of $CaCl_2$.

Lawrence and Young [16] tried to find a correlation between the microstructure development and the degree of hydration of neat C_3S, while Chatterji [17] tried to explain the relationship between the microstructure of the cementic paste and various other physical properties including strength development. An assumption was made [18] that set Portland cement paste is a random packing of almost ideal needles of C–S–H in which larger particles are embedded. These needles are bonded together by forces arising from free surface energy. A method was also outlined for a possible quantitative relationship between the volume density of the C–S–H and the compressive strength of the paste.

The rate of development of compressive strength of Portland cement as described by Taylor [19] is influenced mainly by the composition of the cement (content of C_3S and C_2S), and also by the fineness of the clinker grains. Bajza [20] studied other factors such as type of cement, initial water:cement (w/c) ratio, initial porosity and curing time affecting the rate of strength development both for early ages and for longer periods. A significant correlation was found between the rate hydration and the development of compressive strength.

The presence of admixtures in the cementic paste has a great influence on strength development in that they accelerate or retard the hydration process. When accelerating effect is observed, higher values of strength can be achieved in shorter periods of hydration.

Young and co-workers [12, 21] have studied the tensile strength development of hydrated C_3S with calcium salts. It has been found that even though the admixtures modify the morphology of the hydration products, thus affecting the strength development, the dominant factor is the capillary porosity.

In the present work, the influence of the various admixtures on the strength development was studied under identical conditions in order to avoid side effects mentioned above.

2. Experimental procedure

2.1. Materials

A stoichiometric mixture of $CaCO_3$ (Analytical Reagent, Malinckrodt) and precipitated SiO_2 (BDH Laboratory Reagent) was repeatedly heated to 1550° C until C_3S containing practically no free CaO (by X-ray analysis) was obtained. The silicate was milled to pass a 200 mesh sieve and had a surface area of $1330\,cm^2\,g^{-1}$ (Blaine method).

Ordinary Portland cement ("Nesher" Israeli Cement Factory, Ltd) having a surface area of $3000\,cm^2\,g^{-1}$ (Blaine method) was used, and the admixtures used were: $CaCl_2$, $CrCl_3$, CdI_2, $CdCl_2$ (A.R. BDH Laboratory Reagents). Triple distilled water was used for preparing all solutions, which were all 0.36 M equivalent to 2% $CaCl_2$ by weight of cement.

2.2. Preparation of samples

The samples for compressive strength measurements were prepared by adding the appropriate salt solution to 3 kg Portland cement in a w/c ratio of 0.5. The pastes were mixed with a Hobart mixer for 10 min, poured into cubic casts of 4 cm × 4 cm × 4 cm, vibrated for 2 min and stored in a saturated-humidity room at a temperature of 22° C (± 0.5). After one day the bricks formed were taken out of the casts and stored in a water bath at a temperature of 22° C (± 0.5) until measurement.

The samples for microscopic studies were prepared by treating 5 g C_3S with the various solutions in a w/c ratio of 0.5 at a temperature of 22° C (± 1). The solutions used for hydration besides pure water were those of $CaCl_2$, CdI_2 and $CrCl_3$. The pastes were divided into different vials which were tightly stoppered and kept in an atmosphere free of CO_2, at a temperature of 22° C (± 1). At different "ages", the hydration process was interrupted by breaking the "stone", washing it several times with cold acetone and storing under vacuum.

2.3. Methods of investigation

Compressive strength measurements were carried out with Losenhausenwerk equipment on four identical bricks for every "age", and the average result was noted.

Scanning electron microscopy: a stereoscan S4 of Cambridge Scientific Instruments was used. The samples were coated with a conductive layer of gold before scanning.

3. Results and discussion

3.1. Compressive strength studies

Compressive strength development for the various pastes compared to Portland cement paste without

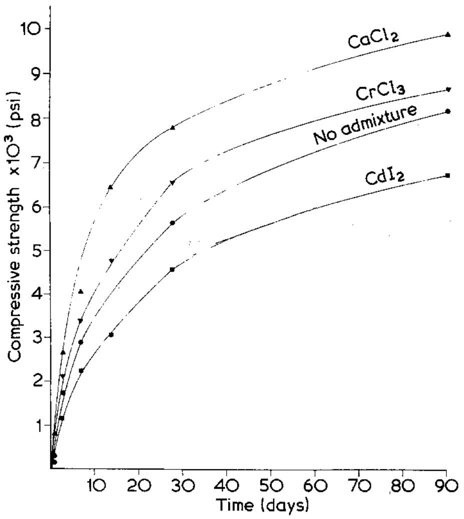


Figure 1 Compressive strength vs. time for Portland cement pastes

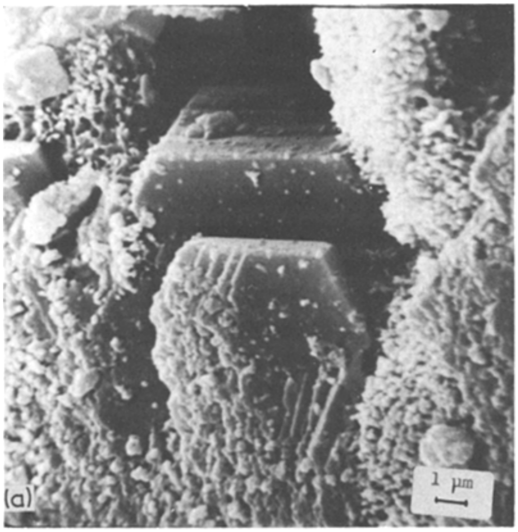
admixture, is shown in Fig. 1. The strong accelerating effect of $CaCl_2$ is immediately observed. An accelerating effect in strength development is also observed for $CrCl_3$, although it is less pronounced than that for $CaCl_2$, while CdI_2 seems to retard the hydration process.

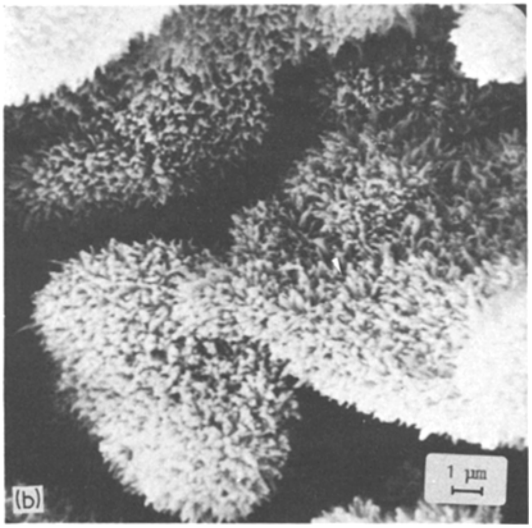
Addition of $CdCl_2$ to Portland cement paste (not shown in Fig. 1) does not show any influence on the rate of strength development and its curve virtually overlaps with that of neat Portland cement.

3.2. Scanning electron microscope

Young *et al.* [12] have found that the microstructural development of the hydration products of C_3S is modified by certain admixtures. The morphology of the outermost C–S–H gel surrounding the clinker is changed with time from a normal acicular appearance to a more lacey nature, described as "honeycomb" appearance. This phenomenon was also observed in this study by comparing hydrated C_3S without admixture (Fig. 2a to c) and that with $CaCl_2$ added admixture (Fig. 3a to d).

In hydrated neat C_3S, the hexagonal plates which appear after 3 days hydration (Fig. 2a) are surrounded by C–S–H gel. Traetteberg *et al.* [15] have also found such plates for hydration period of one day, and no significant changes in the morphology could be observed before that period. After 8 days hydration (Fig. 2b) there is more regularity in the structure of the developed C–S–H





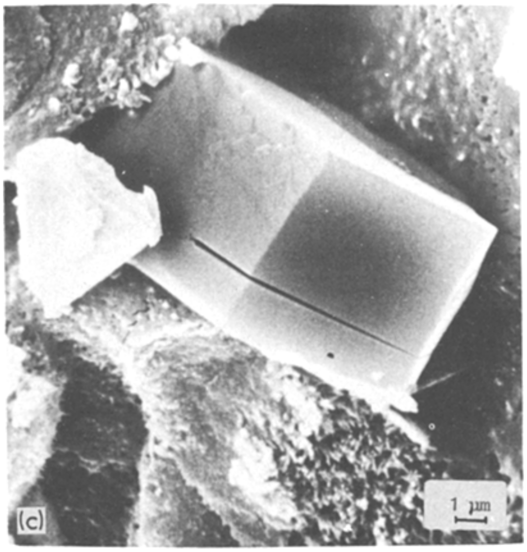


Figure 2 Neat C_3S hydrated (a) 3 days, (b) 8 days, (c) 28 days.

gel, showing a "sponge-like" shape consisting of needles. These "sponges" spread out with time and the thin hexagonal $Ca(OH)_2$ plates also grow and a rather large crystal is seen after 28 days (Fig. 2c). That is, the hydration process is associated, in the case of neat C_3S, with larger $Ca(OH)_2$ crystals and with larger islets of "sponges".

The effect of $CaCl_2$ on the morphology is shown in Fig. 3a to d. Although the overall morphological shape is unchanged, (cf. Berger *et al.* [22]), it is clear that there are no hexagonal plates. The morphology of the C–S–H gel is changed in a way that the needles are longer for an earlier "age" (cf. Figs. 2a and 3a).

After 1 day of hydration (Fig. 3a) intergranular fibres can be seen along with unhydrated grains. After 3 days hydration with $CaCl_2$ (Fig. 3b) the C–S–H gel contains longer needles as compared to the same age without $CaCl_2$ (Fig. 2a), and after 28 days there is a characteristic "honeycomb" morphology of the C–S–H in the presence of $CaCl_2$ (Fig. 3d) in contrast to the "sponge-like" appearance of the neat hydrated C_3S (Fig. 2c). That is, the honeycomb morphology present in the case of accelerating additives seems to lend more strength to the structure as compared to the "sponges" present in neat C_3S or C_3S with retarding or non-accelerating additives.

The effect of $CrCl_3$ and CdI_2 on the morphology of hydrated C_3S is shown in Figs. 4a and b, and 6a

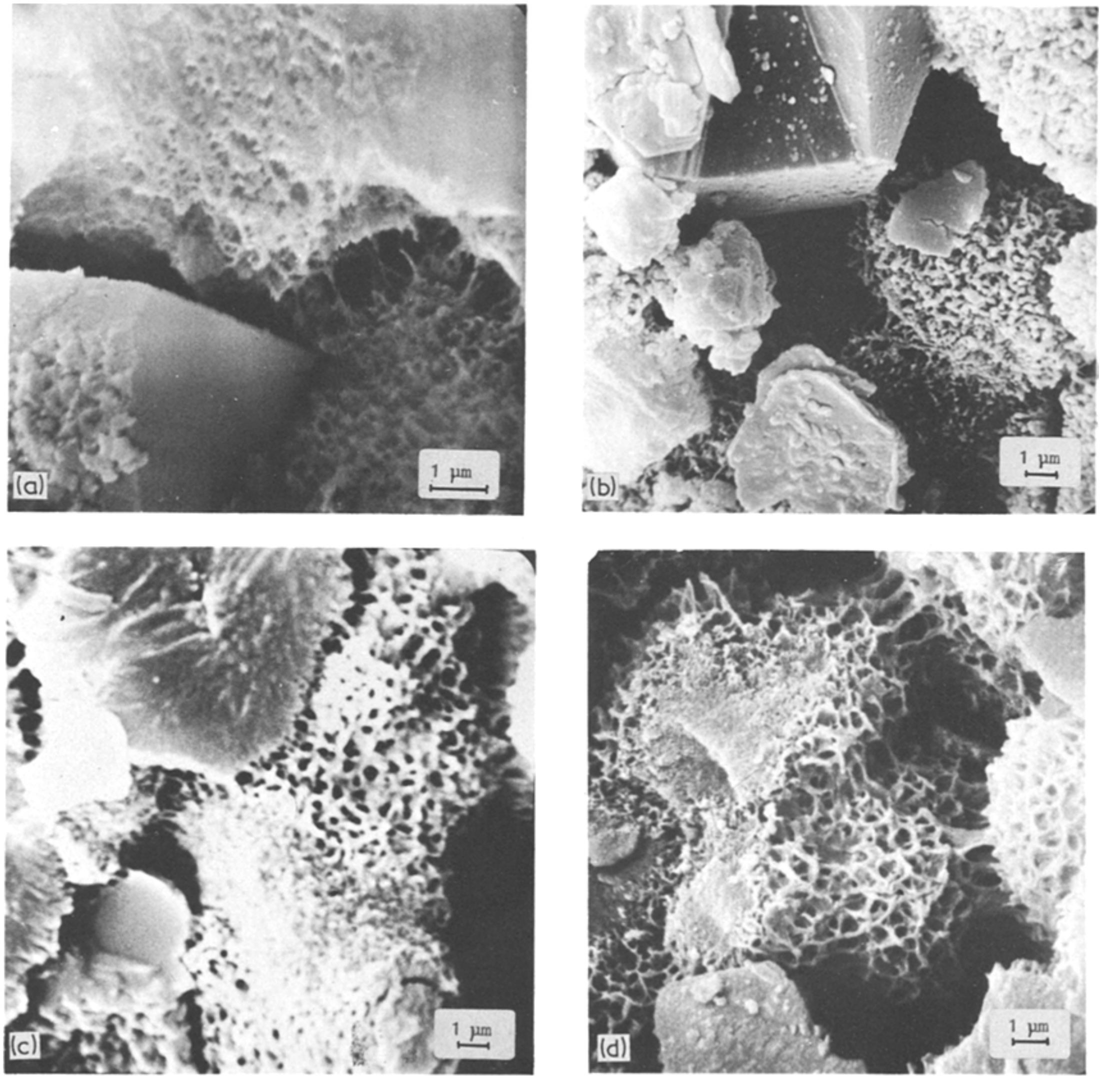


Figure 3 C_3S with $CaCl_2$ hydrated (a) 1 day, (b) 3 days, (c) 21 days, (d) 28 days.

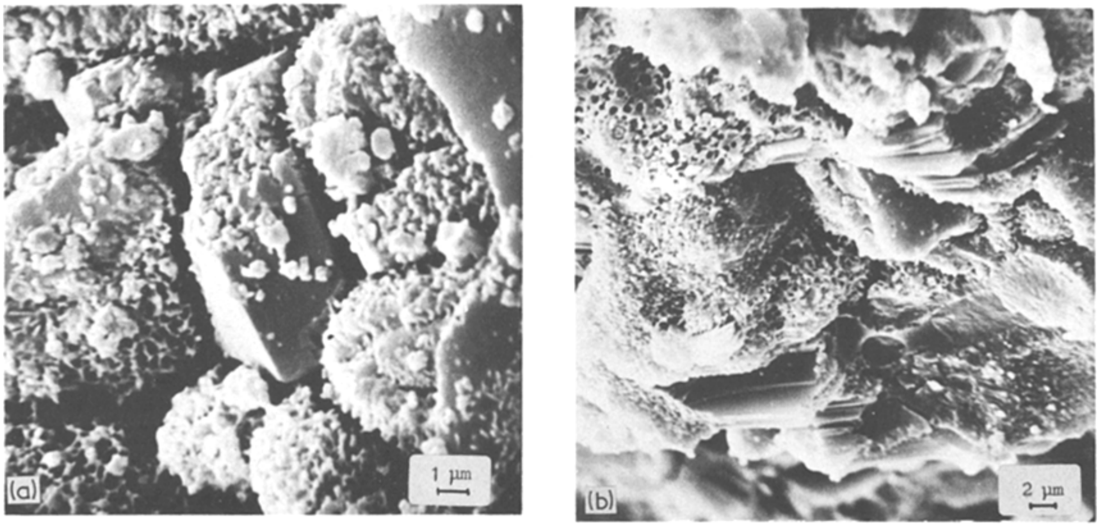


Figure 4 C_3S with $CrCl_3$ hydrated (a) 4 days, (b) 14 days.

to d. Again, no hexagonal plates appear in both admixtures, a fact that substantiates the assumption that these plates appear only when no accelerating admixture is present in the hydration process. In the presence of $CrCl_3$ the acicular morphology together with some honeycomb morphology develops, associated indeed to strength development somewhat higher than that shown by neat cement but lower than that obtained from $CaCl_2$ as additive. In the hydrated product in the presence of $CrCl_3$, fewer C–S–H gel fibres from adjacent grains are in contact as compared to the case of $CaCl_2$ (cf. Figs. 3b and 4a). In the presence of CdI_2 the development of the C–S–H gel is slower, and the typical acicular morphology apears after longer periods of hydration. It is interesting to compare the morphology of the unhydrated cement (Fig. 5) with that of 1 day's hydration of C_3S with CdI_2 (Fig. 6a). Although the overall morphology seems identical, a definite growth on the surface of the grains can be observed in the case of the CdI_2 already after 1 day of hydration. Further hydration to 7 days (Fig. 6b) and up to 21 days showed little hydration products and only after that period (Fig. 6c and d) some honeycomb morphology begins to be observed in some cases. This behaviour is associated with the lowering of strength development as compared to the other additives. In the presence of lower concentrations of CdI_2 (~ 0.1 M solution) the behaviour is virtually that of neat C_3S containing no admixture (Fig. 7a to c), i.e. there appear again hexagonal plates of $Ca(OH)_2$. The presence of these plates is striking, for they are never found in the case of admixtures which accelerate the hydration of the neat mineral. Thus, the retarding effect of CdI_2 as gathered from mechanical behaviour of cement paste, is associated with the slower formation of hydration products in C_3S and the appearance of $Ca(OH)_2$ hexagonal plates. The $CaCl_2$ is a parent material both to the $Ca(OH)_2$ formed and to the mineral itself, and accelerates the hydration reaction; $CrCl_3$ is not a parent material, but its soluble hydroxide (being

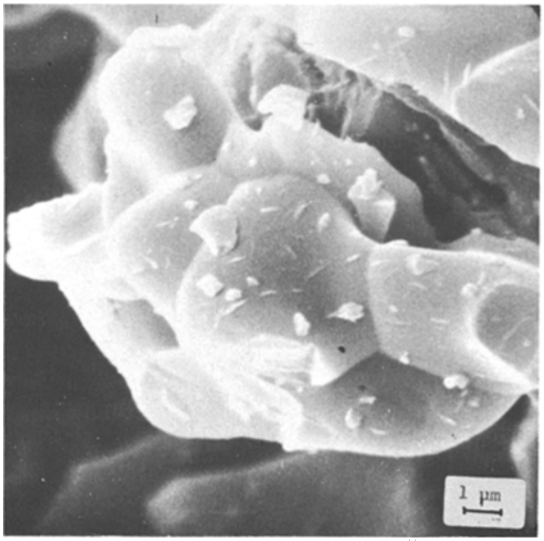


Figure 5 Unhydrated C_3S.

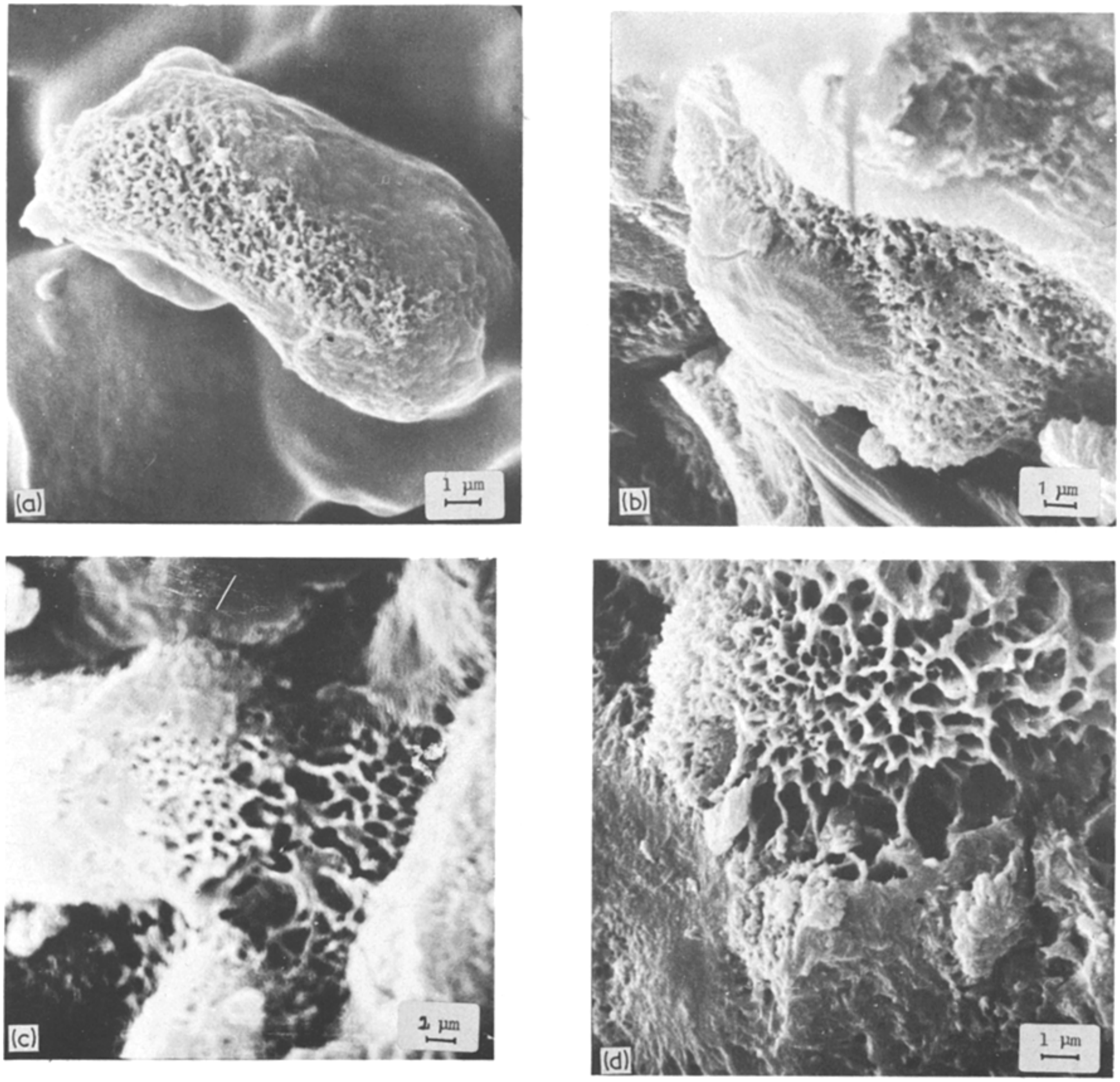
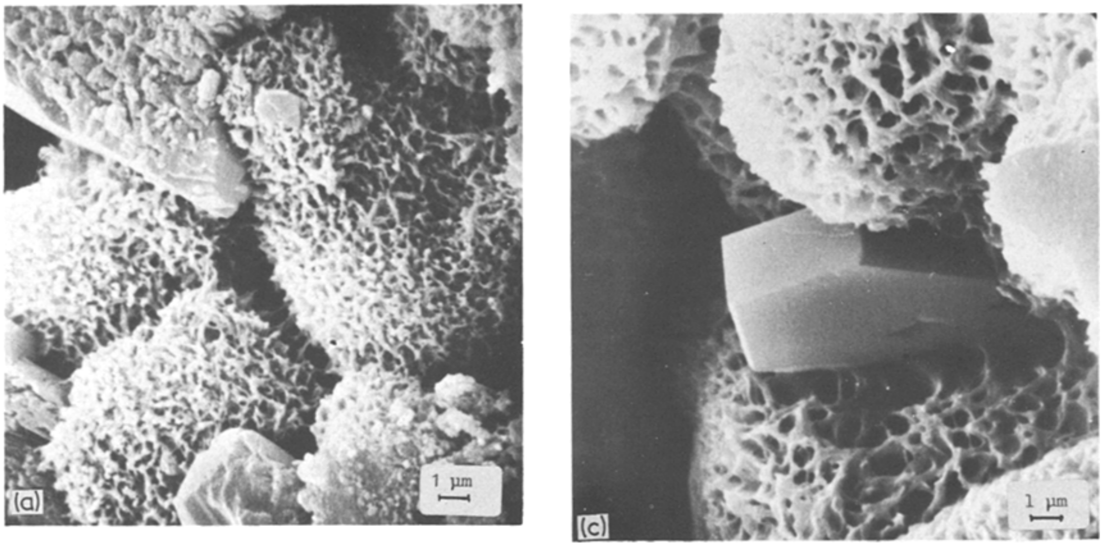


Figure 6 C_3S with 0.36 M CdI_2 hydrated (a) 1 day, (b) 7 days, (c) 21 days, (d) 28 days.

amphoteric) might be the reason for the positive effect of this additive. The hydroxide obtained from the cadmium salts is basic and rather insoluble, possibly being the cause for hindering the hydration. The less CdI_2 added the less is the retardation and in practice the behaviour of CdI_2 in the low concentration is virtually that of the neat C_3S.

4. Conclusions

A comparative deduction may be drawn on the influence of admixtures on both the mechanical behaviour of hydrated Portland cement and the morphological changes on the hydration products of C_3S. Although the two systems are not identical, the former being more complex, a correlation could be carried out between the two sets of data and seems justified. When a certain additive improved only slightly or even reduced the compressive strength of Portland cement, the morphology of the hydrated products of C_3S were identical with those obtained in the absence of accelerating additives. Thus, $Ca(OH)_2$ hexagonal plates appear in the case of hydration of neat C_3S or when CdI_2 is added to it and the C–S–H gel is "sponge-like". No hexagonal plates appear in the case of the accelerators $CaCl_2$ and $CrCl_3$ and the gel is "honeycomb".



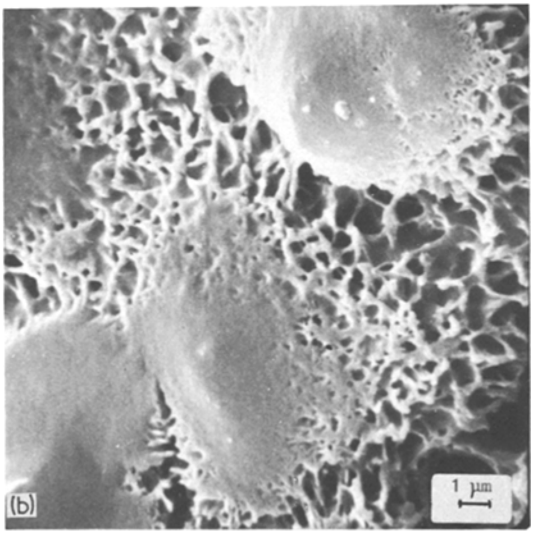


Figure 7 C_3S with 0.1 M CdI_2 hydrated (a) 3 days, (b) 21 days, (c) 28 days.

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