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THE MICROSTRUCTURAL AND HARDENING BEHAVIOUR OF
TRICALCIUM SILICATE PASTES IN THE PRESENCE OF
CALCIUM CHLORIDE

BY

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LE COMPORTEMENT MICROSTRUCTURAL ET DE DURCISSEMENT DES PATES DE SILICATE TRICALCIQUE EN PRESENCE DE CaCl_2

SOMMAIRE

On a effectué un examen séquentiel du développement de la résistance en termes de microdureté au cours de l'hydratation de la pâte de C_3S en présence de 2 et de 5 pour cent de CaCl_2 à un rapport eau/solide de 0.3 ou de 0.5. On a tenté de relier la résistance aux aspects microstructuraux étudiés au moyen de microscope électronique à grille. En général, l'addition de 2 pour cent de CaCl_2 produit le matériau le plus résistant. L'échantillon de six mois de la série, avec un rapport eau/solide de 0.3, produit l'effet le plus prononcé. La résistance élevée de cet échantillon est peut-être liée à une phase C-S-H CaO/SiO_2 élevée, à une faible porosité et même à un complexe de chlorure en hydratation. On mesure également la répartition du diamètre des pores. Règle générale, plus la porosité est élevée, plus la résistance est faible, mais le rapport n'est pas parfaitement linéaire même pour le diagramme semi-logarithmique.

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The Microstructural and Hardening Behaviour of Tricalcium Silicate Pastes in the Presence of Calcium Chloride

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A sequential examination of strength development in terms of microhardness was studied during paste hydration of C_3S in the presence of 2 and 5% $CaCl_2$ and at w/s ratios of 0.3 or 0.5. An attempt has been made to relate strength with microstructural features studied by means of Scanning Electron Microscopy. Generally, at earlier periods it was found that the 2% addition of $CaCl_2$ gave the strongest material; the effect was most pronounced in the 6-month sample of the series with 0.3 w/s. The high strength for the sample prepared at a w/s ratio of 0.3 may be related to a high CaO/SiO_2 C-S-H-phase, low porosity, and possibly a hydrated calcium hydroxy chloride complex. The pore size distribution was also measured. In general, the higher the porosity the lower the strengths but the relationship was not perfectly linear even on the semi-logarithmic plot.

1. Introduction

The tricalcium silicate phase, constituting the major component in Portland cement, greatly influences its strength characteristics. The acceleration of hardening of Portland cement in the presence of admixtures such as $CaCl_2$ is mainly attributed to its action on the silicate phases. Most work on the influence of $CaCl_2$ on the hydration of C_3S ^b has been concerned with the determination of the degree of hydration and some morphological features,¹⁻¹⁰ and little attention has been directed to the study of the development of strength.¹¹⁻¹⁶ One reason for this is that it is costly to provide the amounts of C_3S normally considered necessary for strength determinations.

One of the most important questions in cement chemistry is that concerning the mechanism of strength development. Divergent views have been expressed and different factors have been considered viz., porosity, amount of the hydrated product, chemical composition, morphology, surface area, and degree of polymerisation, but no satisfactory method to predict the development of strength in cementitious materials with any accuracy has been offered.

It appears that a combination of methods should be used to follow the hydration behaviour sequentially for materials such as C_3S with and without $CaCl_2$. The significance of microhardness measurements for porous inorganic materials has been

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^b In cement literature C = CaO , S = SiO_2 , H = H_2O and w/s = water/solid ratio.

discussed by Sereda in a recent paper.¹⁷ In this present work an attempt has been made to correlate the microstructural development in the system $C_3S + CaCl_2 + H_2O$ with strength as indicated by microhardness indentation and cone penetration measurements. The strength has also been discussed in terms of microstructural development, porosity and hydration characteristics.

2. Experimental

2.1. Samples

The synthetic C_3S was supplied by Tetratich International, San Diego, and chemical analysis showed it to contain: 73.5% CaO , 26.0% SiO_2 , 0.5% MgO and 0.1% insolubles. The C_3S had a N_2 surface area of $0.45 \text{ m}^2/\text{g}$. The calcium chloride, $CaCl_2 \cdot 6H_2O$ was a Fisher certified reagent. The water used was decarbonated and de-ionized.

Powdered samples (2 g of each) were taken in small polypropylene vials and water or $CaCl_2$ solution was added. They were then rotated on rollers for the required length of time. Hydration was stopped at the necessary intervals of time (4 h to 6 months) by placing sample in cold acetone. Subsequently the sample was vacuum-dried for 24 h using liquid air trap. The samples were prepared at $70 \pm 1^\circ \text{F}$.

For strength tests, pastes of C_3S were prepared by rapidly mixing the solid with water or a $CaCl_2$ solution, then transferred to specially designed plexiglass cylinders 2.5 cm in diameter and 1.3 cm high. The pastes were kept under vapour-sealed conditions and rotated until set in order to prevent segregation. Two series of pastes with w/s ratios of 0.3 and 0.5 were made of three compositions, pure C_3S , $C_3S + 2\%$ $CaCl_2$ and $C_3S + 5\%$ $CaCl_2$ (anhydrous basis). The strength was tested at intervals from 4 h to 6 months. The shape of the samples was similar to that used for previous studies.¹⁸ The surface of the sample was large enough to permit both microhardness and cone penetration determinations.

2.2. Methods

2.2.1 Microhardness

A Leitz Miniload Hardness Tester was used; the test method employed the Vicker's pyramid indenter, which was placed in a conditioned box free of CO_2 . The hardness was calculated from the formula:

$$H_v (\text{kg/mm}^2) = \frac{1854.4 \times P}{d^2}$$

where P = load in grams

d = mean value of the indentation diagonals.

Microhardness indentations were done on 5 spots on the surface and 10 diagonals were averaged for calculation of the hardness according to the given formula.

2.2.2. Cone penetration

This method has been investigated for different kinds of materials by Sereda¹⁹ and results on the $C_3A + H_2O + CaSO_4 \cdot 2H_2O + CaCl_2$ system described in a previous

paper.¹⁸ It has been found especially useful for strength investigations of cement paste in the early setting period. However, in the present work, penetration measurements were taken to determine if this method gives reasonable values for strength development in the hardened state also in relation to the microhardness results.

The hardness is calculated on the basis of the applied load per unit area on the circumferential area of the 60° cone as follows:

$$H_c = \frac{\text{load}}{2.1 \times h^2}$$

where H_c = lbs/in.²

h = depth of penetration (inches).

load = lbs.

The load was supplied in steps of 3 lb and the penetration depth was measured at each level after reaching the equilibrium value. Hardness was obtained by averaging the values representing the deeper penetration that are believed to represent the hardness of the three-dimensional structure.¹⁸ The microhardness values were converted to kg/mm².

2.2.3 Scanning electron microscopy

The microstructure of the pastes was examined using a Cambridge Stereoscan Mark 2A. The examination was done on fractured pieces.

Surface area was obtained by means of a Numinco-Orr surface area-pore volume analyser with N₂ as the adsorbate. Powdered samples were dried for 3 h at 110 °C prior to the measurements.

Total porosity and pore size distribution were measured by an Aminco-Winslow Porosimeter. The fractured samples were initially dried for 3 h at 110 °C under vacuum.

3. Results and Discussion

3.1. Compressive strength-microhardness relationship

To assess the validity of using the microhardness as a measure of the strength of porous materials, a series of tests was run comparing microhardness with compressive strength. Because a large amount of material is required for these tests, Portland cement was used in place of pure C₃S. As Portland cement paste is composed predominantly of silicate hydrates, similar to those formed in C₃S paste, it is reasonable to conclude that the relation found between microhardness and compressive strength for Portland cement paste would also be applicable to the C₃S paste.

A paste of Portland cement was prepared according to ASTM C-305. Normal consistency cubes were made at a w/c ratio of 0.24. Discs 2.6 cm in diameter and 3 mm thick were prepared for the microhardness measurements, and 2-in. cube specimens were prepared for the compressive strength tests. During hydration the discs and cubes were stored in a conditioning room at 100% r.h. at 70 ± 2 °F. The tests were carried out after hydration times of 6 and 12 h, and 1, 3, 7, 17 and 28 days.

Five microindentation measurements were taken for each specimen. Each measurement yielded 2 values based on the two diagonals. Compressive strength represented an average of 3 values.

In Figure 1 the mean value of the compressive strength is plotted versus the mean value of microhardness for corresponding hydration times. The data resulted in a reasonably good linear relationship between microhardness and compressive strength when the 6-h value was omitted. The low strength at 6 h may have been due to the surface of the paste being somewhat soft at this age.

Figure 1. Compressive strength versus microhardness for hydrated Portland cement.

These results suggest that a linear relationship exists between compressive strength and microhardness in Portland cement, thus it is reasonable to assume that such a relationship also exists for cement components such as C_3S .

3.2. Microhardness

The results for the two w/s ratio series are recorded in Table 1. Some minor scattering in the values does occur, but the general trend is evident. The three pastes, pure C_3S , $C_3S+2\%$ $CaCl_2$ and $C_3S+5\%$ $CaCl_2$ generally exhibited a steady increase in strength with hydration time. With a w/s ratio of 0.5, the 2% addition of $CaCl_2$ resulted in the strongest paste up to 3 months. This result is in agreement with that of Kurczyk and Schwiete¹⁶ who examined the compressive strength of 28-day-old pastes in the shape of cylinders containing different amounts of $CaCl_2$ up to 3%.

Figures 2 to 4 and 5 to 7 show representative morphologies of the pastes (w/s = 0.5) at 30 days and 3 months respectively. Surface areas for these samples are given in Table 2. The loose morphology and the relatively lower content of the C-S-H phase in the pure C_3S paste, as well as the lower surface area of this paste, correspond to the lower strengths compared with $C_3S+2\%$ $CaCl_2$ paste.²⁰ The DTA and TGA analysis showed that in the $C_3S+5\%$ $CaCl_2$ paste less $Ca(OH)_2$ is formed compared

TABLE 1. Microhardness (kg/mm^2) for pastes of C_3S , $\text{C}_3\text{S}+2\% \text{CaCl}_2$ and $\text{C}_3\text{S}+5\% \text{CaCl}_2$

Hydration time	Water/solid = 0.5			Water/solid = 0.3		
	C_3S	$\text{C}_3\text{S}+2\% \text{CaCl}_2$	$\text{C}_3\text{S}+5\% \text{CaCl}_2$	C_3S	$\text{C}_3\text{S}+2\% \text{CaCl}_2$	$\text{C}_3\text{S}+5\% \text{CaCl}_2$
4 h						2.7
6 h					3.7	4.3
8 h					4.5	5.8
12 h				2.7	—	—
16 h	0.6	2.9	1.2	—	—	—
1 day	0.9	11.6	1.3	5.3	13.5	10.0
2 days	1.5	8.5	2.3	7.4	22.5	15.8
3 days	1.5	10.0	2.8	8.7	27.7	23.0
7 days	2.3	12.0	4.2	11.9	29.8	29.0
10 days	1.3	15.3	5.8	14.1	36.5	35.3
15 days	3.1	19.0	9.4	17.2	31.7	36.0
30 days	5.6	33.2	20.5	20.9	34.6	50.5
3 months	7.0	36.5	15.8	22.0	47.8	60.4
6 months	8.4	23.8	22.8	32.2	66.0	41.7
(cut sample)

Figure 2 (a). Paste of $C_3S + H_2O$ hydrated 30 days ($w/s = 0.5$); (b) Paste of C_3S hydrated 30 days ($w/s = 0.5$) at higher magnification.

Figure 3. Paste of $C_3S + 2\% CaCl_2$, hydrated 30 days ($w/s = 0.5$).

Figure 4. Paste of $C_3S + 5\% CaCl_2$, hydrated 30 days ($w/s = 0.5$).

with the 2% $CaCl_2$ paste. A different structural arrangement might possibly be the reason for the much higher surface area in this paste. This cannot be adequately demonstrated from the morphology of the 30-day sample because the surface area is influenced at a more micro level. However, the sample seems to consist of agglomerates of more separate particles that might cause the weaker structure (Figure 4). The surface areas for the pastes containing 2% $CaCl_2$ are about the same at 1 month and 3 months. There is a decrease however, for $C_3S + 5\% CaCl_2$ and it is assumed that some coalescence of the individual microunits has taken place in this paste

Figure 5. Paste of C₃S+H₂O hydrated 3 months (w/s = 0.5).

Figure 6. Paste of C₃S+2% CaCl₂ hydrated 3 months (w/s = 0.5).

Figure 7. Paste of C₃S+5% CaCl₂ hydrated 3 months (w/s = 0.5).

TABLE 2. Surface area of C₃S pastes with 2% and 5% CaCl₂ and w/s ratios 0.5 and 0.3. Age 30 days and 3 months

Paste	w/s	Surface area (m ² /g)	
		30 days	3 months
C ₃ S	0.5	11.2	9.9
C ₃ S+2% CaCl ₂	0.5	24.1	25.1
C ₃ S+5% CaCl ₂	0.5	57.7	31.9
C ₃ S	0.3	10.7	2.6
C ₃ S+2% CaCl ₂	0.3	15.2	3.0
C ₃ S+5% CaCl ₂	0.3	22.8	2.6

between 1 and 3 months. The micrograph of the 3-month sample containing 2% CaCl_2 shows a more dense microstructure than that of the paste with 5% CaCl_2 (Figures 6 and 7), and this may lead to higher strength.

The micrographs of the series with w/s ratio 0.3 (Figures 8 to 10) indicate a denser morphology of the 30-day pastes compared with the 0.5 w/s series (Figures 2 to 4). Surface areas of the 0.3 w/s series are less than the corresponding pastes of the 0.5 w/s series (Table 2). The strength at 30 days is also higher for all three mixtures.

The amount of hydration is estimated to be about the same in all three pastes²⁰ at 3 months at a w/s ratio 0.3. It is generally believed,¹⁶ that the C-S-H phase with a

Figure 8. Paste of $\text{C}_3\text{S} + \text{H}_2\text{O}$ hydrated 30 days (w/s = 0.3).

Figure 9. Paste of $\text{C}_3\text{S} + 2\% \text{CaCl}_2$ hydrated 30 days (w/s = 0.3).

Figure 10. Paste of $\text{C}_3\text{S} + 5\% \text{CaCl}_2$ hydrated 30 days (w/s = 0.3).

higher CaO/SiO_2 ratio yields a weaker material than that containing lower C/S ratios. This is probably true for pastes prepared at higher w/s ratios. However, in the paste containing 5% CaCl_2 with a w/s ratio of 0.3, DTA results indicate that a higher C/S product is formed and higher strengths have been obtained. It appears that if conditions are adjusted so that C-S-H forms in a confined space the high C/S product has a better opportunity to form good bonds. Similar behaviour has been observed in other systems.^{21,22} In the system $\text{CaO}-\text{CaCl}_2-\text{H}_2\text{O}$ two oxychlorides of composition $3\text{CaO}.\text{CaCl}_2.16\text{H}_2\text{O}$ and $\text{CaO}.\text{CaCl}_2.2\text{H}_2\text{O}$ exist. The former is stable at CaCl_2 concentrations of 18% or more and the latter at 34% or more. At a w/s ratio of 0.3 and with 5% CaCl_2 , the concentration of CaCl_2 may possibly be sufficiently high, especially at later periods, to encourage formation of calcium hydroxy chloride²³ which may impart some strength to the paste. However, no definite evidence was obtained for the presence of this complex in the X-ray diffraction pattern.

The surface area of the 3-month samples in this series had diminished considerably from 1 month (Table 2), probably due to the polycondensation of SiOH units with ageing. The micrographs gave some evidence for a coalescence of the grains and denser matrix (Figures 11 to 13). This is in accordance with the relatively high strength of the pastes in the 0.3 w/s series.

Measurement of microhardness requires that the hydrated phase is not carbonated. This becomes a more serious problem in the measurement of microhardness of samples hydrated over a longer period. In the samples of C_3S hydrated for 6 months the average amount was 3.7% CO_2 and, therefore, the microhardness measurements were carried out on samples cut 2 mm from the surface. The results (Table 1) show that samples containing 2% CaCl_2 showed highest strengths at a w/s of 0.3. A higher value for the 6-month sample at w/s ratio of 0.3 from 47.8 at 3 months was unexpected. The immediate reason is not obvious but there is a possibility that ageing

Figure 11. Paste of $\text{C}_3\text{S}+\text{H}_2\text{O}$ hydrated 3 months (w/s = 0.3).

Figure 12. Paste of $\text{C}_3\text{S}+2\%\text{CaCl}_2$ hydrated 3 months (w/s = 0.3).

Figure 13. Paste of C_3S + 5% $CaCl_2$ hydrated 3 months ($w/s = 0.3$).

and polycondensation has proceeded more in this sample or carbonation has proceeded farther into this sample than in the others, in this series. This is known to increase strengths of C_3S pastes.²⁴ It is thus possible that the values of 3-months-old samples are lower than those reported in Table 1 as these values were obtained from uncut samples.

The total porosity and the pore size distribution were examined for the 6-month samples by means of mercury porosimetry (Figures 14 and 15). Generally, the highest strength corresponded to the lowest porosity and the lowest strength to the highest porosity. A plot of porosity against log microhardness yielded a linear type of relationship with some scatter (Figure 16). Some scatter in the results was expected

Figure 14. Pore size distribution in C_3S paste hydrated for 6 months ($w/s = 0.5$). C_3S + 0% $CaCl_2$ (---); C_3S + 2% $CaCl_2$ (—); C_3S + 5% $CaCl_2$ (-.-.-).

Figure 15. Pore size distribution in C_3S paste hydrated for 6 months ($w/s = 0.3$). $C_3S+0\% \text{ CaCl}_2$ (---); $C_3S+2\% \text{ CaCl}_2$ (—); $C_3S+5\% \text{ CaCl}_2$ (- - -).

Figure 16. Microhardness versus porosity relationship for C_3S paste. $w/s = 0.5$ (Δ); $w/s = 0.3$ ($\circ$)

TABLE 3. Hardness values (kg/mm^2) obtained by cone penetration measurements for paste of C_3S with the addition of CaCl_2

Hydration time	Water/solid = 0.5			Water/solid = 0.3		
	C_3S	$\text{C}_3\text{S}+2\% \text{CaCl}_2$	$\text{C}_3\text{S}+5\% \text{CaCl}_2$	C_3S	$\text{C}_3\text{S}+2\% \text{CaCl}_2$	$\text{C}_3\text{S}+5\% \text{CaCl}_2$
4 h						2.7
6 h					9.3	2.8
8 h				0.2	14.0	17.5
12 h				2.5	—	—
16 h	0.7	9.7	1.5	—	—	—
1 day	0.8	3.7	2.0	6.8	28.6	29.1
2 days	0.9	4.7	1.3	13.3	78.8	47.6
3 days	1.8	7.0	2.3	23.4	115.0	43.7
7 days	2.2	13.2	2.8	11.4	203.0	125.0
10 days	2.5	14.3	3.4	26.9	228.0	122.0
15 days	3.0	29.7	5.0	25.8	220.0	175.0
30 days	6.6	82.3	10.4	85.6	338.0	297.0
3 months	14.9	97.3	12.8	196.0	790.0	1070.0

since the points referred to may have different structuration. Earlier work by Sereda indicated that in the gypsum system small amounts of admixtures were sufficient to change the structure of the product to yield individual straight-line relationship for any particular method of preparation.¹⁷ In addition to this the mercury porosimetry may yield slightly lower porosity values than the theoretical values.

Assuming that the density of the hydrated products is the same, porosity: surface area is an increasing function of the so-called hydraulic radius, and it was found that for a particular w/s ratio the larger the porosity: surface area ratio the lower was the microhardness value. For example for samples prepared at w/s ratio of 0.5 the microhardness values were 8.4, 23.8, and 22.8 kg/mm² and the porosity: surface area values were 3.2, 0.9 and 0.9 respectively. For samples prepared at a w/s ratio of 0.3 the hardness values were 32.2, 66.0 and 41.7 kg/mm² and the corresponding porosity:surface area ratios were 8.6, 3.4 and 4.9 kg/mm². It appears that the strength for a particular w/s ratio increases as the average pore radius decreases.

In a previous report¹⁸ it was found that above a certain hardness level the cone penetration measurements give too high a hardness value. Despite this fact the method was employed for strength examination of C₃S pastes for two reasons: other workers have applied the cone penetration in pastes;¹⁵ and, it was of interest to determine if the method would show the same pattern in hardness values as the microhardness indentations.

The penetrations were carried out for all the pastes up to 3 months and the calculated hardness values are recorded in Table 3. Only a fair agreement between the methods was obtained for the pure C₃S paste and the C₃S + 5% CaCl₂ paste (w/s = 0.5), which had the lowest hardness level. In the other pastes the hardness values showed some agreement at early hydration stages, but as the materials became harder the cone penetration method gave increasingly higher values than the microhardness measurements. The difference in cone penetration and microhardness values may be due to the former being done at a deeper location than the latter. Within each of the two w/s series the pattern in strength development seemed to follow similar trends for both methods. It might, therefore, be seen that cone penetration is convenient and useful in the early setting period, and may give relative estimates of strength at later stages.

4. Conclusions

A linear relation was obtained between microhardness and compressive strength for pastes of Portland cement. The method of microhardness indentation has been found useful as a tool for strength measurements with the added advantage that a small sample is required and because the samples are not broken the same specimen can be used for examination by other techniques.

The strength development during hydration of C₃S pastes has been found to be related to morphological features, the relative amounts and type of reaction products, and the porosity. The total porosity gives an approximate linear relationship with logarithm of strength. Lack of perfect linearity may be attributed to the samples being different in composition and morphology.

The porosity:surface area ratio at a particular w/s ratio gives a good indication of strength development in C_3S pastes. The addition of 2% $CaCl_2$ resulted in the strongest paste at earlier periods; the effect was most significant in the series with the 0.3 w/s ratio at 6 months. A decrease in the w/s ratio for a paste generally led to improved strength. In this case the higher strengths are ascribed to a C-S-H product with a higher CaO/SiO_2 ratio because at longer periods of curing, less $Ca(OH)_2$ is formed in these pastes compared to those prepared at a w/s ratio of 0.5. The two methods, microhardness indentation and cone penetration showed some agreement at early hydration stages; measurements of microhardness by indentation, however, are considered to give a better measure of strength at later stages of hydration.

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References

1. Collepardi, M.; Rossi, G.; Spiga, M. C. *Ann. di Chim.* 1971, **61**, 137.
2. Collepardi, M.; Marchese, B. *Cem. Concr. Res.* 1972, **2**, 57.
3. Collepardi, M.; Rossi, G.; Usai, G. *Ind. Ital. Chem.* 1968, **10**, 657.
4. Skalny, J.; Odler, I.; Hagymassy, J. *J. Colloid Sci.* 1971, **35**, 434.
5. Celani, A.; Collepardi, M.; Rio, A. *Ind. Ital. Cem.* 1966, **36**, 669.
6. Ramachandran, V. S. *Mat. Constr.* 1971, **4**, 3.
7. Ramachandran, V. S. *Thermochim. Acta*, 1971, **2**, 41.
8. Tenoutasse, N. V. *Intern. Symp. Chem. Cement Tokyo*, 1968, **2**, 372.
9. Rio, A.; Celani, A.; Saini, A. *Estr. U Cem.* 1970, **67**, 17.
10. Odler, I.; Skalny, J. *J. Am. Ceram. Soc.* 1971, **54**, 362.
11. Andreeva, E. P.; Segalova, E. E. *Dokl. Akad. Nauk SSSR* 1964, **158**, 1352.
12. P'ing-i, Chou; Segalova, E. E.; Luk'yanova, O. J. *Kolloidnyi zhurnal*, 1964, **26**, 373.
13. Andreeva, E. P.; Keshelava, B. F.; Rebinder, P. A. *Dokl. Akad. Nauk SSSR* 1969, **184**, 1144.
14. Luk'yanova, O. J.; Rebinder, P. A. *Dokl. Akad. Nauk SSSR* 1969, **184**, 1144.
15. Andreeva, E. P.; Segalova, E. E. *Kolloidnyi zhurnal* 1960, **22**, 503.
16. Kurczyk, H. G.; Schwiete, H. E. *Tonind.-Ztg. Keram. Rdsh* 1960, **84**, 585.
17. Sereda, P. J. *Cem. Concr. Res.* 1972, **2**, 717.
18. Traetteberg, A.; Sereda, P. J. *Strength of C_3A paste containing gypsum and $CaCl_2$* . (Submitted to the VI International Symposium on the Chemistry of Cement to be held in Sept. 1974, Moscow.)
19. Sereda, P. J. *Significance of Cone Penetration Test for Setting of Cements*. (To be published).
20. Traetteberg, A.; Ramachandran, V. S.; Grattan-Below, P. E. *A Study of the Microstructure and Hydration Characteristics of Tricalcium Silicate in the Presence of Calcium Chloride*. *Cem. Concr. Res.* 1974, **4**, 203.
21. Ramachandran, V. S.; Feldman, R. F. *Hydration Characteristics of Monocalcium Aluminate at a Low Water/Solid Ratio*. *Cem. Concr. Res.* 1973, **3**, 729.
22. Ramachandran, V. S.; Feldman, R. F. *J. App. chem. Biotechnol* 1973, **23**, 625.
23. Skalny, J.; Odler, I. *Mag. Concr. Res.* 1967, **19**, 203.
24. Berger, R. L.; Young, J. F.; Leung, K. *Nature*, 1972, **240**, 16.

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