

EFFECT OF SOME CHEMICALS ON ALKALI-SILICA REACTION

H. Wang and J.E. Gillott

Dept. of Civil Engineering, The University of Calgary,
Calgary, Alberta, Canada

Expansion of mortar bars containing 2% reactive opal was greatly reduced by small amounts of sucrose. Rate of setting of cement was accelerated and early rate of strength gain of mortars was retarded but 14 and 28 day mortar cube strengths exceeded those of controls. Thermogravimetric analysis of cement pastes showed that $\text{Ca}(\text{OH})_2$ content remained well below that of controls to an age of 28 days. CaCl_2 , a known accelerator, increased expansion of mortar bars containing opal and reduced strength. Lactic acid, EDTA and oxalic acid in the proportions used did not have significant effects on expansion due to alkali-silica reaction.

INTRODUCTION

Lignosulphonates, some hydroxycarboxylic acids, carbohydrates and calcium chloride are used to formulate commercial chemical admixtures used in Portland cement concrete. The effect of chemical admixtures on alkali-silica reaction (ASR) is generally unknown. The purpose of this research was to test the effect on ASR of some chemical admixtures selected on the basis of the mechanism of expansion proposed by Wang and Gillott (1).

MATERIALS

Aggregates consisted of a non-reactive limestone from Exshaw, Alberta, 2% of which was replaced by Nevada opal - a highly alkali-expansive mineral. A type 10 low alkali cement was used and the alkali content was boosted to 1.0% by adding NaOH to the mixing water. The chemicals used as admixtures included calcium chloride (CaCl_2), lactic acid, ethylenediaminetetraacetic acid (EDTA), oxalic acid and sucrose.

EXPERIMENTAL

The effect of the chemical admixtures on expansion due to ASR was assessed by ASTM C-227. Mortar bars were cast in triplicate and average values of length change are shown in Figs. 1 - 3. Effects of ASR on compressive strength in the presence of the chemical admixtures were estimated by ASTM C-109. Three cubes were tested at each age and average strengths are shown in Figs. 4 and 5. Mortar bars and cubes were cast from the same batch and mix designs are shown in Table 1.

All mortar bars and cubes, except those containing sucrose, were cured in a fog room ($21 \pm 2^\circ\text{C}$; 100% R.H.) for one day after casting and then demoulded. After recording the initial

lengths, the demoulded mortar bars were placed over water in perspex containers and stored in a temperature controlled oven at $38 \pm 1^\circ\text{C}$. The demoulded mortar cubes were stored over water at $38 \pm 1^\circ\text{C}$. Specimens containing sucrose were not strong enough to withstand demoulding after one day in the fog room so they were placed over water at $38 \pm 1^\circ\text{C}$ for further curing. At an age of 3 days, mortar cubes were demoulded and treated in the same way as cubes containing other admixtures. At an age of 5 days, mortar bars were demoulded and after recording initial lengths bars were conditioned in the same manner as all other bars.

TABLE 1 - Mix Design of Mortar Bars, Mortar Cubes and Cement Pastes

	Mortar bars and cubes						Cement pastes				
	cement	limestone	opal	NaOH	adm.	H ₂ O	H ₂ O	NaOH	adm.	H ₂ O	
control	1273	2808	57.3	9.5	/	611	650	5.0	/	185	
CaCl ₂ 0.5 (%)	1273	2808	57.3	9.5	6.4	611	650	5.0	3.25	185	
	1.0	1273	2808	57.3	9.5	12.7	611	650	5.0	6.50	185
lactic acid(%) 0.25	1273	2808	57.3	9.5	3.2	611	650	5.0	1.63	185	
	0.5	1273	2808	57.3	9.5	6.4	611	650	5.0	3.25	185
EDTA (%) 0.25	1273	2808	57.3	9.5	3.2	611	650	5.0	1.63	180	
	0.5	1273	2808	57.3	9.5	6.4	611	650	5.0	3.25	185
oxalic acid(%) 0.25	1273	2808	57.3	9.5	3.2	611	650	5.0	1.63	190	
	0.5	1273	2808	57.3	9.5	6.4	611	650	5.0	3.25	195
sucrose (%) 0.25	1273	2808	57.3	9.5	3.2	611	650	5.0	1.63	180	
	0.5	1273	2808	57.3	9.5	6.4	611	650	5.0	3.25	180

Cement pastes were cast using mix proportions shown in Table 1 and specimens were cured in the fog room. The progress of hydration was studied by x-ray diffraction and thermogravimetric analysis (TGA) using specimens removed from sample interiors. Samples for x-ray diffraction study were freeze-dried and samples for TG analysis were oven-dried; TG analysis was performed in duplicate. Non-evaporable water content (hydrate water) was calculated from the weight loss between 105 and 1000 °C and weight loss due to the dehydration of crystalline Ca(OH)₂, "CH water", was obtained according to the method described by Marsh and Day (2). Calcium hydroxide content was calculated from the "CH water". Both calcium hydroxide and non-evaporable water contents were expressed as a percentage based on the paste weight at 1000 °C.

RESULTS

Expansion of Mortar Bars

Results of the dimensional change tests show that the chemical admixtures divide the mortar bars into three groups as follows:

Group I: Expansion Increased. In this group, expansion of mortar bars was increased due to the presence of CaCl₂ (Fig.1).

Group II: Expansion Remained about the same as that of the Control Sample. This group includes mortar bars containing lactic acid, EDTA and oxalic acid at dosages of 0.25% and 0.5% (Fig.2). The expansion of mortar bars containing these chemicals did not differ very much from that of the control bars except for the bars containing lactic acid at a dosage of 0.5% which showed a somewhat lower average expansion than the control.

Group III: Expansion Decreased. In this group, expansion of mortar bars was greatly reduced due to the presence of sucrose (Fig.3).

Strength of Mortar Cubes

Mortar cubes may be divided into two groups on the basis of compressive strength development.

Group I: Strength Decrease after age 14 days. Mortars in this group contained either CaCl_2 or lactic acid. The trend of strength development was about the same as that of the control, i.e. strength increased from 3 days to 14 days, and decreased from 14 days to 28 days (Fig.4).

Group II: Continuous Increase in Strength from 3 days to 28 days. This group includes mortar cubes containing EDTA, oxalic acid and sucrose which showed a continuous increase in strength from 3 days to 28 days; in contrast the average strength of the control cubes increased only from 3 days to 14 days, but decreased from 14 days to 28 days (Fig. 5). A most interesting effect was that the mortar containing sucrose showed a much lower strength than the control at an age of 3 days, but at 14 and 28 days strengths were much higher than that of the control. In order to compare the effect of sucrose and sucrose plus opal on strength development, another set of mortar cubes was cast and compressive strength of the cubes was tested. The results are shown in Fig. 6. It can be seen that the cubes containing 0.25% of sucrose with no opal showed much lower strengths than the cubes containing sucrose plus opal. Furthermore cubes which contained sucrose plus opal were stronger than control cubes which contained neither opal nor sucrose. These results indicate that alkali-reactive silica in the presence of sucrose contributes to strength development.

Setting Time of Cement Pastes

The setting times of cement pastes containing different chemicals are shown in Table 2. CaCl_2 decreased setting time, lactic acid had no significant effect on setting time, EDTA and oxalic acid increased setting time. Sucrose had different effects on setting time which depended on the duration of mixing prior to addition of the sucrose and on the dosage. When sucrose was added after about 2 minutes premixing, initial and final setting times were greatly decreased with dosages of both 0.25% and 0.5%. When added after 3 minutes premixing an addition of 0.5% sucrose decreased both the initial and final setting times of the paste but in the paste containing 0.25% sucrose, the initial setting time was decreased, whilst the final setting time was considerably increased.

Content of Crystalline Calcium Hydroxide in Cement Pastes

Cement pastes can be also divided into two groups on the basis of the calcium hydroxide content:

Group I: Higher Calcium Hydroxide Content than Control Paste. Pastes in this group contained CaCl_2 and lactic acid (Table 3). The pastes containing CaCl_2 showed considerably higher contents of crystalline calcium hydroxide than the control paste, while pastes containing lactic acid showed slightly higher calcium hydroxide contents than the control paste.

TABLE 2 - Setting Time of Cement Pastes

		Initial setting time (minutes)			Final setting time (minutes)		
Control		345			420		
CaCl_2	0.5%	285			375		
	1.0%	245			360		
Lactic acid	0.25%	300			390		
	0.5%	345			425		
EDTA	0.25%	435			585		
	0.5%	525			630		
Oxalic acid	0.25%	435			535		
	0.5%	495			645		
		Mix I ¹	Mix II ²	Mix III ²	Mix I	Mix II	Mix III
Sucrose	0.25%	25	50	74	40	1035	1525
	0.5%	40	20	21	60	30	30

¹ Mix I: Sucrose was added after about 2 minutes premixing;

² Mix II & III: Sucrose was added after about 3 minutes premixing.

Group II: Lower Calcium Hydroxide Content than Control Paste. Pastes in this group contained EDTA, oxalic acid and sucrose (Table 3). In this group, the content of crystalline calcium hydroxide in the cement pastes containing oxalic acid and EDTA was slightly lower than in the control paste, while pastes to which sucrose was added contained much less crystalline calcium hydroxide than the control paste.

Non-evaporable water content

Pastes containing CaCl_2 at both dosages and lactic acid at a dosage of 0.5% showed slightly higher non-evaporable water contents than the control, while pastes containing lactic acid at a dosage of 0.25% showed slightly lower non-evaporable water contents (Table 3).

The non-evaporable water content of the cement pastes containing EDTA and oxalic acid did not differ very much from that of the control paste whereas that of pastes containing sucrose were lower particularly at early ages or when 0.5% sucrose was used (Table 3).

Analyses by X-Ray Diffraction

X-ray diffractograms were recorded over an angular range from 2° to $75^\circ 2\theta$ using $\text{Co K}\alpha$ radiation and a Philips diffractometer; x-ray diffraction patterns of cement pastes are shown in Fig. 7. Results of peak intensity measurements for ettringite (9.7\AA ; 5.6\AA ; 4.7\AA) and gypsum (7.6\AA ; 4.3\AA) are shown in Table 4.

TABLE 3 - Content of Crystalline Calcium Hydroxide and Non-evaporable Water in Cement Pastes

		Calcium hydroxide content (%)					Non-evaporable water content (%)					
		30-min.	6-hr.	1-day	7-day	28-day	30-min.	6-hr.	1-day	7-day	28-day	
	control	0.8	2.6	6.2	7.5	9.5	1.6	3.0	10.0	11.5	12.7	
group I	CaCl ₂ 0.5	/	/	7.9	9.8	11.1	/	/	10.4	12.2	13.4	
	1.0	0.9	2.8	8.7	10.6	11.7	2.2	3.7	10.8	12.2	13.5	
	lactic acid (%)	0.25	/	/	7.5	8.5	9.7	/	/	10.0	11.2	12.2
	0.5	/	/	7.8	8.5	10.3	/	/	10.7	11.9	13.5	
group II	EDTA (%)	0.25	/	/	6.1	7.0	9.1	/	/	11.0	12.4	13.3
	0.5	/	/	5.4	7.0	9.0	/	/	10.7	12.4	13.3	
	oxalic (%)	0.25	/	/	5.4	6.9	8.6	/	/	9.6	11.2	12.7
	0.5	/	/	5.7	7.7	8.9	/	/	10.5	11.9	13.1	
	sucrose (%)	0.25	0.5	0.7	1.3	3.9	7.9	2.1	2.4	6.3	10.2	11.1
	0.5	/	/	0.3	0.3	0.5	/	/	5.8	6.4	5.3	

Consideration of the intensities of three strong ettringite diffraction peaks showed that after as little as 30 minutes hydration ettringite had developed in the paste containing sucrose but peaks were weak or absent on diffractograms both of the control paste and of the paste containing CaCl₂. After 6 hours hydration ettringite peaks were much stronger on diffractograms of the paste containing sucrose than on diffractograms of either of the other samples. By 24 hours however the situation had reversed and ettringite peaks were strong on the diffractograms of the control paste and paste containing CaCl₂, but were much weaker on the diffraction pattern of the paste made with sucrose. Decline in intensity and disappearance of peaks attributed to ettringite suggests conversion to monosulphate but no diffraction peaks due to this phase were detected.

TABLE 4 - Relative Intensity of Ettringite and Gypsum Peaks on Diffractograms of Cement Pastes

Diffraction peak Å		Hydration time 30 min.			Hydration time 6 h.			Hydration time 24 h.		
		control	CaCl ₂	sucrose	control	CaCl ₂	sucrose	control	CaCl ₂	sucrose
ettringite	9.7	0	4	11	10	4	22	22	18	10
	5.6	0	2	6	5	4	14	12	10	4
	4.7	0	3	2	3	4	8	8	7	4
	Average	0	3	6.3	6	4	14.7	14	11.7	6
gypsum	7.6	26	19	4	0	8	0	0	0	0
	4.3	7	11	0	0	4	0	0	0	?
	Average	16.5	15	2	0	6	0	0	0	/

Peaks attributed to gypsum were very weak on the diffractogram of paste containing

sucrose which had been hydrated for 30 minutes whereas those peaks were strong on the patterns of the control paste and paste containing CaCl_2 . After 6 hours hydration gypsum peak intensities declined in all cases and by 24 hours gypsum peaks were absent from the patterns of the control and paste containing CaCl_2 . Hence the rate of ettringite formation and gypsum consumption was faster in the paste containing sucrose than in either of the other pastes.

DISCUSSION

The mechanism of alkali-aggregate reactions and the part played by Ca(OH)_2 has been discussed for over 40 years (3, 4, 5, 6, 7, 8, 9, 10, 11, 12). Magnitude of expansion has been shown to increase with increase in amount of Ca(OH)_2 (1, 7) so admixtures were selected which are thought to have a significant effect on that compound. This required consideration of the mechanism of admixture interaction with Ca(OH)_2 itself and with the cement minerals. Admixtures which react mainly with the calcium silicates will have most effect since the Ca(OH)_2 in Portland cement paste is a hydration product of those phases. On the other hand some workers believe that the aluminates have an important influence on microstructural development particularly during setting. Strength and porosity at early ages may affect the ability of the cement paste to resist expansive stress and to accommodate gel interstitially particularly if gel formation is accelerated. So admixture effect on the aluminates may not be ignored.

The only inorganic compound used in this work (CaCl_2) is a well known accelerator. It increases the rate of setting and hardening of Portland cement concrete and has also been shown to increase expansion due to ASR (13). An increase in rate of hydration of the calcium silicates will lead to an increase in the amount and rate of formation of Ca(OH)_2 and reaction between the added CaCl_2 and NaOH in the pore solutions may precipitate further amounts of Ca(OH)_2 . Also the increased rate of setting and hardening implies a more rapid development of microstructure in the cement paste. This may be unable to accommodate swelling alkali-silica gel produced after formation of a relatively impermeable and rigid structure so the potential for expansion and damage is increased by the accelerator.

The other four admixtures used in this work are organic compounds of which three are known to be retarders (EDTA, oxalic acid, sucrose) and one (lactic acid) is reported to be an accelerator (14). Organic retarders often contain hydroxycarboxylic acids and Taplin (15) noted that the best retarders are often compounds in which adjacent carbon atoms in the molecule are linked to oxygen atoms or hydroxyl groups so the accelerating effect of lactic acid is unexpected.

Oxalic acid was found to have relatively little effect on expansion due to ASR and this agrees with its relatively small effect as a retarder. Hydroxycarboxylic acids of low molecular weight such as oxalic acid and formic acid have been found to be inferior as retarders to related compounds of higher molecular weight such as citric acid and tartaric acid (16). EDTA also had a relatively small effect on ASR. Oxalic acid removes Ca from solution by precipitation and EDTA is an excellent complexing agent for Ca. Both work on a 1:1 basis at the molecular level so relatively large amounts will be required to remove significant quantities of Ca from the system. It seems probable that the amounts used in this work were too small to have a significant effect on Ca(OH)_2 , so effect on expansion due to ASR was also small.

Sucrose was the most effective admixture in reducing the expansion of mortar bars containing reactive opal. The expansion was reduced by about 68% in the bars containing 0.25% sucrose, and reduced by 76% in the bars containing 0.5% sucrose. Sucrose also reduced the

amount of calcium hydroxide formed and the amount of non-evaporable water. The delay in hydration of the paste containing 0.5% sucrose remained quite significant even at an age of 28 days. The compressive strengths of mortar cubes were however significantly greater than those of controls at ages of 14 days and 28 days although the strength at an age of 3 days was greatly reduced.

The mechanism by which retarders affect the rate of hydration has received considerable attention. One early suggestion was that retarders are strongly adsorbed by cement minerals and inhibit hydration by interfering with the access of water. Banfill and Saunders (17) showed that there is very poor correlation between sorption on unhydrated cement and the effectiveness of admixtures as retarders. They found better correlation between reaction rate and sorption on hydrated cement and Ca(OH)_2 and concluded that retarders limit the rate of hydration by poisoning nucleation sites and hindering growth of Ca(OH)_2 and C-S-H.

Similar conclusions regarding the action of sugars were reached by Thomas and Birchall (18). They found that the ion concentration of Si, Fe, Al, OH and Ca increased significantly in the pore solution of Portland cement containing 15 mM sucrose but the Ca/Si ratio was considerably decreased. This may well have decreased the rate of formation of swelling alkali-silica gel and be partly responsible for the decrease in expansion. Also the low early age strengths due to decreased rate of cement hydration imply that formation of a dense microstructure was also delayed. Swelling gel which did form early may have been accommodated within available pore space so that expansion and damage was much reduced. Absorption of the swelling alkali-silica gel followed by ion exchange and conversion into non-expansive calcium-alkali-silica gel may have helped to densify the structure of the paste and contributed to the increase in strength.

Sucrose also had a significant effect on the setting time of cement pastes. The effect was found to be very sensitive to the duration of mixing prior to addition of sucrose probably reflecting the amount of prior hydration particularly of the C_3A component. There is general agreement that sucrose retards the hydration of C_3S and decreases rate of Ca(OH)_2 production. Conflicting results have been obtained however concerning its effect on C_3A but accelerated gypsum consumption and ettringite formation have been reported (19). In this work time to initial set was found to be greatly reduced in all sucrose-containing samples and time to final setting was greatly increased only when 0.25% sucrose was added after 3 minutes premixing. Ettringite has been considered important in early age stiffening (20) and here the effect of sucrose on rate of ettringite formation may be the significant factor. Some support for this suggestion is provided by x-ray diffraction analyses (Table 4). Rate of gypsum consumption and ettringite formation appeared to be fastest in the paste containing sucrose and slowest in the paste containing CaCl_2 . The very rapid initial set of the sucrose-containing paste (Table 2) suggests correlation with the more rapid formation of ettringite. Possibly the long delay in final setting time, of some sucrose-containing pastes, reflects delayed hydration of the C_3S but results were inconsistent.

CONCLUSIONS

- (1). CaCl_2 increased expansion of mortar bars due to ASR. This may be attributed to increase in the rate of hydration of cement, more rapid formation of paste structure and production of more Ca(OH)_2 . More swelling alkali-silica gel may have been produced and less absorbed during the plastic stage so expansion was increased.

(2). Sucrose had a dramatic effect on alkali-silica reaction. It greatly reduced the amount of expansion of mortar bars containing 2% opal. This may be associated with delay in hydration of the Portland cement which delayed the formation of a rigid structure of low porosity. Also decrease in rate of C_3S hydration means that less $Ca(OH)_2$ was formed so less swelling alkali-silica gel was produced. Swelling gel which did form may have been accommodated within the pores of the immature plastic paste so that expansion and damage to the hardened material was reduced.

(3). Sucrose decreased the rate of strength gain and in the absence of reactive silica strength of mortar cubes remained low to 28 days. In mortars which contained opal however low strengths lasted only for a few days and by 14 and 28 days compressive strengths exceeded those of the control samples and of mortars containing all other admixtures including the accelerators. This suggests that gel formed by ASR actually contributed to strength probably by infilling pores in the paste.

ACKNOWLEDGEMENT

The authors express sincere thanks to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work.

REFERENCES

- (1) Wang, H. and Gillott, J.E., 1991, Cement and Concrete Research 21, 647.
- (2) Marsh, B.K. and Day, R.L., 1988, Cement and Concrete Research 18, 301.
- (3) Hansen, W. C., 1944, Jour. Am. Conc. Inst. 15, 213.
- (4) Vivian, H. E., 1950, CSIRO, Bull. 259, 60.
- (5) Powers, T. C. and Steinour, H. H., 1955, Jour. Am. Concr. Inst. 26, 497, 785.
- (6) Hadley, D. W., 1964, Highway Res. Rec. 45, 1.
- (7) Tang, M. S. and Han, S. F., 1981, Jour. Chinese Silicate Soci. 9, 160.
- (8) Dent Glasser, L.S. and Kataoka, N., 1982, Cement and Concrete Research 12, 321.
- (9) Chatterji, S., et al., 1986, Cement and Concrete Research 16, 246.
- (10) Davies, G. and Oberholster, R. E., 1988, Cement and Concrete Research 18, 621.
- (11) Diamond, S., 1989, Proc. 8th Int. Conf. AAR. 83.
- (12) Taylor, H. F. W., 1990, Cement Chem. Acad. Press. 392.
- (13) Wang, H. and Gillott, J.E., 1990, Cement and Concrete Research 20, 369.
- (14) Singh, N.B., et al., 1986, Cement and Concrete Research 16, 545.
- (15) Taplin, J.E., 1962, Proc. 4th Int. Symp. Cement Chem., Nat. Bur. St. (U.S.) Monog. 43, 924.
- (16) Wilding, C.R., et al., 1984, Cement and Concrete Research 14, 185.
- (17) Banfill, P.F.G. and Saunders, R.D.C., 1986, Cement and Concrete Research 16, 399.
- (18) Thomas, N.L. and Birchall, J.D., 1983, Cement and Concrete Research 13, 830.
- (19) Odler, I. and Abdul-Maula, S., 1987, Cement, Concrete and Aggregates 9, 38.
- (20) Seligmann, P. and Greening, N.R., 1964, Highway Research Record 62, 80.

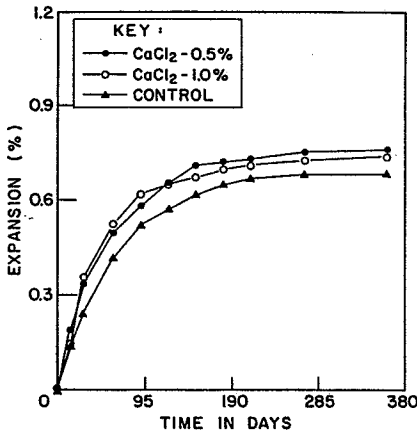


Figure 1 Expansion of mortar bars containing CaCl_2

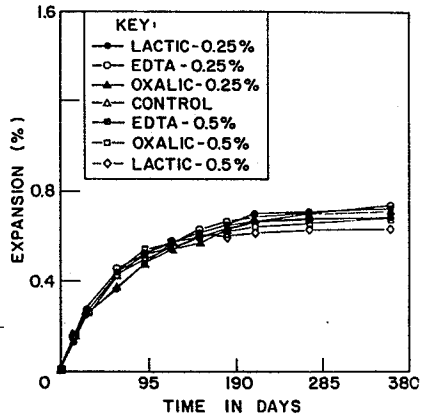


Figure 2 Expansion of mortar bars containing lactic acid, EDTA or oxalic acid

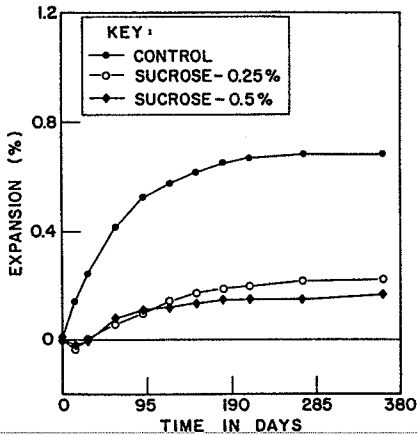


Figure 3 Expansion of mortar bars containing sucrose

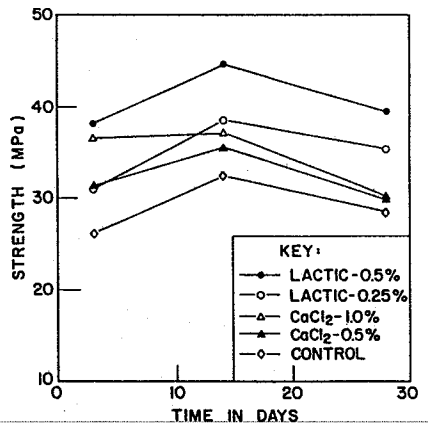


Figure 4 Compressive strength of mortar cubes containing opal and CaCl_2 or lactic acid

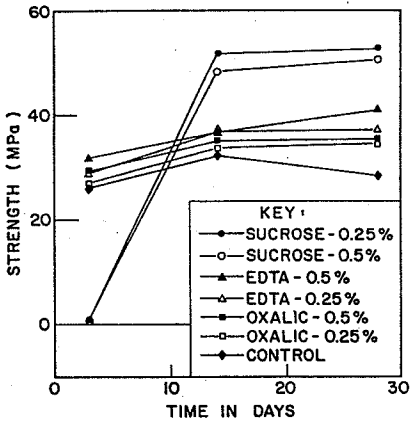


Figure 5 Compressive strength of mortar cubes containing opal & oxalic acid, EDTA or sucrose

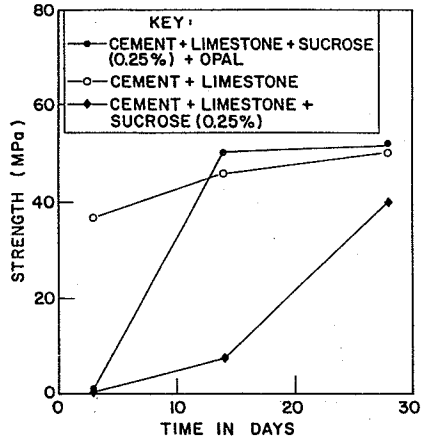


Figure 6 Comparison of compressive strength of mortar cubes

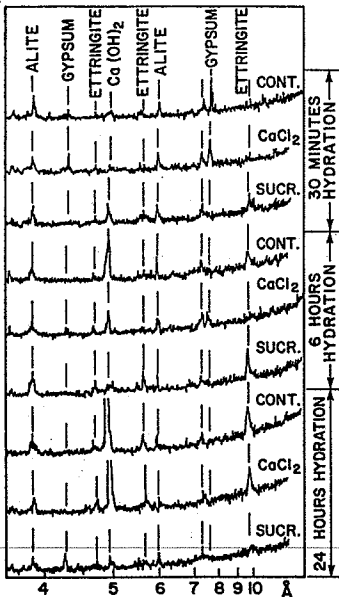


Figure 7 X-ray diffraction patterns of cement pastes