WATER GLASS ACCELERATOR FOR HEAT TREATED PORTLAND CEMENT CONCRETE

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ABSTRACT
Concretes and manufacturing techniques to ensure compressive strengths of 25-45 MPa in 3 hours were developed. The basic mechanical and durability properties were examined, as well as the chemical and physical structure. The workability of the developed concretes is suitable for normal concreting practice.

Key words: concrete, water glass, rapid strength development, high early strength, mechanical properties, microstructure

1. INTRODUCTION

The aim of this work was to develop concrete and manufacturing technique to ensure a compressive strength of 25-45 MPa in 3 hours. In many manufacturing processes it is worthwhile to accelerate the strength development first and subsequently other phases. The greatest benefit can be derived from accelerated hardening by making the process so fast that casting could take place twice during an 8 hour workshift. It is also the goal of this study. With a stripping strength of 25-45 MPa at 3 hours, it should be possible to achieve this.

Three new concrete types were developed to achieve the strength development required /7/. The concretes were based on:

- Water glass as an accelerator for heat treated workable Portland cement concrete
- High alumina cement with blast furnace slag in heat treated concrete
- Alkali activated blast furnace slag in heat treated concrete

This paper deals with only the use of water glass as an accelerator for heat treated Portland cement concrete. Water glass used in this study was sodium silicate solution. In the tests presented in this paper the silicate modulus (molar ratio SiO_2/Na_2O) was 3.3 and solid content 37%.

When rapid strength development is needed, both the use of accelerators and heat treatment are possible approaches. Among others, calcium chloride, calcium formate and triethanolamine have been known to accelerate the setting and hardening of PC. They are efficient accelerators especially at low temperatures. However, in this work no accelerator was so effective that the target of this research could be achieved with PC without heat treatment. This is true especially when good workability is needed. Thus heat treatment is essential.

On the other hand, the practical heat treatment alone is not effective enough to accelerate strength development. Maximum temperatures are limited due to practical reasons and the possible instability of hydration products /4/.

The combined use of accelerator and heat treatment was chosen for closer examination. It is important to notice that both calcium chloride and many commercial chloride-free accelerators can actually retard strength development at elevated temperatures /1, 8/. So the efficiency of accelerators at elevated temperatures is important.

2. LITERATURE STUDY

Many salts precipitate additional phases when added to C_3S or cement pastes. If the hydroxide of the added cation is less soluble than calcium hydroxide salt is precipitated. The calcium salt of an added anion, if of sufficiently low solubility, is similarly precipitated. Examples of such anions are SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, F^-, borate, aluminate and silicate /14/. These salts have widely varying effects on setting and hardening. Silicates are accelerators. The chemistry underlying the accelerating effect of silicates is not fully understood, and probably more than one mechanism operates.

Possible mechanisms concerning sodium silicate are as follows:

- Precipitated calcium silicate hydrate increases the permeability of the protective layer around the cement grain, allowing ions and water to move more freely to and from the unhydrated grain /14/.
- Precipitating calcium ions lowers the concentration of Ca^{2+} close to the surface of the cement grain, causing new Ca^{2+} to dissolve from the unhydrated cement /9, 14/.
- As sodium hydroxide can be an accelerator /6, 11/, a Na^+-cation from sodium silicate and an OH^--anion from calcium hydroxide may act the same way.
- Precipitated C-S-H provides nuclei for hydration products /13/.

Water glass is used widely as a shotcrete accelerator and is known to shorten the open time of the mix to a few minutes /2/. Its purpose in shotcreting is to accelerate setting of the concrete mix allowing thicker chotcrete layers. Due to the very rapid setting of the mix, the water glass accelerator is added in the nozzle of the shotcreting equipment /10/.

In studies of the effects of water glass on the properties of concrete, water glass dosages have been very high. Setting times have been short and workability of the concrete low, making it unclear as to whether the water glass or poor compactability were to blame for the result. Thus the effect of water glass on the properties of workable concrete is unclear and requires further study.

3 PRELIMINARY TESTS

3.1 Calorimeter tests

The test series examined the effects of water glass on heat evolution and workability of concrete mix. When the water glass dosage was increased (from 0 to 1.8%-solid), the heat evolution became faster, the workability poorer and the open time shorter. According to the test results, workability loss associated with sodium silicate can be compensated for with superplasticiser.

3.2 No-slump concrete

In the preliminary test series where the effect of water glass on the strength development of heat-treated no-slump concrete was investigated, the greatest strength increase at 2 hours was almost fourfold and at 3 hours 30%. From 4 hours onward, the effect was negligible or some strength reduction was observed.

The effect on pore size distribution was also measured with mercury intrusion porosimetry and it was found that the water glass evidently lowered the average size of capillary pores.

Changes in the chemical structure were measured with thermogravimetry. The amount of $Ca(OH)_2$ decreased with increasing water glass dosage. At the same time, total loss on ignition from 110 - 1100°C did not change when water glass was introduced. Because the amount of $Ca(OH)_2$ decreased, it is probable that sodium silicate reacted with it.

3.3 Plastic precast concrete

Dosage of water glass and plasticiser

Water glass and superplasticiser dosages had a considerable effect on strength development rate and workability. Raising the water glass dosage would also increase the strength development rate but reduce the workability. The workability loss must be compensated for with a plasticiser or water. If water is used, however, the strength of concrete will be lower. This test series sought to establish optimum dosages of plasticiser.

The effect of water glass dosage on strength development is presented in Figure 1. The superplasticiser dosage was such that the slump of the concrete was 6 - 8 cm. The dosages are indicated in Figure 1. The cement content was 520 kg/m^3 and the water-cement ratio 0.45. The superplasticiser dosage varied from 1 to 5%. The water glass dosage varied from 0 to 2% (solid). Admixtures were added 1 minute after water introduction. The heat treatment temperature in this test series was 50°C.

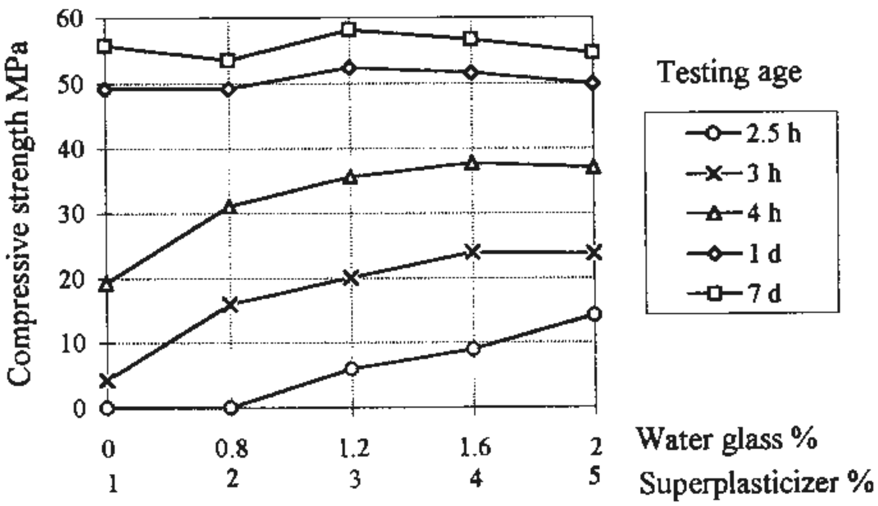

Figure 1. Effect of water glass dosage on strength development in heat treated (+50°C) concrete. Water glass dosage presented as solid-% and superplasticiser dosage as liquid-% of the cement weight.

According to the results the best water glass dosage seems to be 1.6% (solid) and superplasticiser dosage 4% to achieve good workability.

Delayed dosage

In the tests it was found that delayed dosage of water glass had a marked effect on the workability and strength development rate. The effect is presented in Figures 2 and 3. The cement content was 520 kg/m^3 and water-cement ratio 0.45. The water glass dosage was 1.6% (solid) and superplasticiser 4%. The heat treatment temperature in this test series was 50°C.

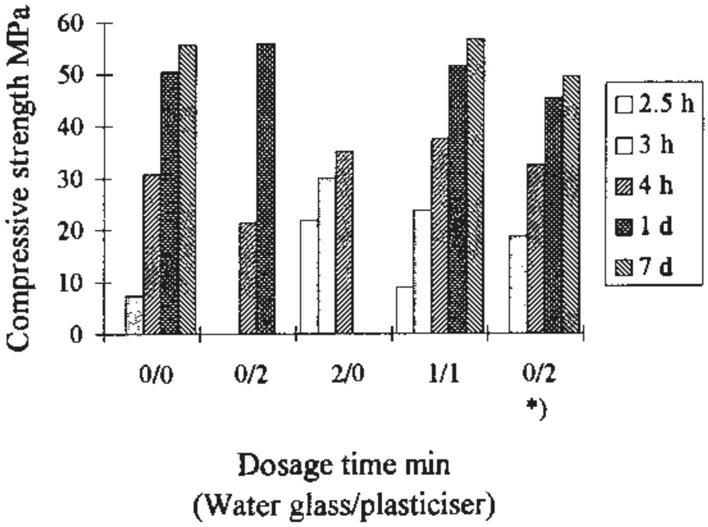

Figure 2. Effect of dosage time on compressive strength. Mix marked *) has less plasticiser than the other mixes.

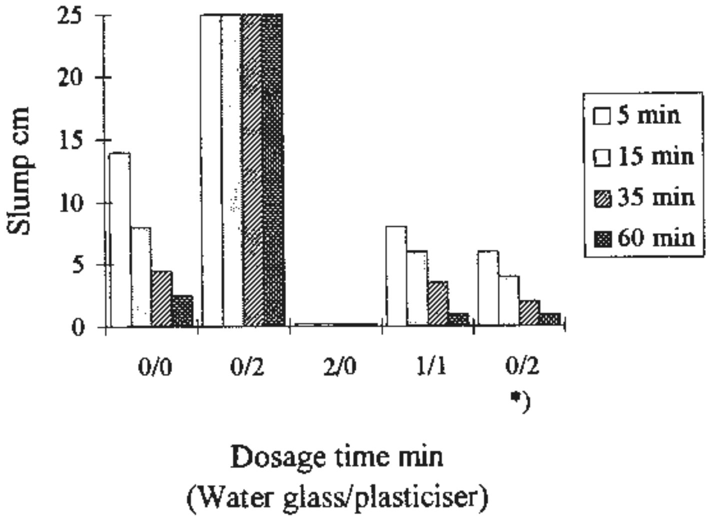

Figure 3. Effect of dosage time on workability. Mix marked *) has less plasticiser than the other mixes.

The effect of delayed dosage is very significant. Delayed dosage can give dramatically different results depending on which admixture is added first. With the same admixture dosages but different dosage sequence the workability can be very poor or very good. Unfortunately the rate of strength development is inversely proportional to the workability. The best compromise for early strength and workability was achieved when both admixtures were added simultaneously 1 minute after water introduction.

The effect of delayed dosage of superplasticiser is well known in the literature. The delayed dosage of both water glass and superplasticiser has a far more intense effect than the delayed dosage of superplasticiser only. Proper dosage sequence is essential when using a water glass accelerator in plastic concrete.

One possible explanation for this very remarkable effect on workability and strength development rate may lie in the hydration model presented by Gartner & Gaidis /3/. They suggested that the C_3S grains are covered by a metastable hydration product (C-S-H) immediately after coming into contact with water (less than 30 sec). This hydration is a topochemical process. Further hydration is prevented/inhibited by this protective layer. Once the through-solution hydration product is precipitated, it catalyses its own formation, eventually leading to the setting and hardening process.

This model may well explain the effect of using plasticiser and water glass together. If the plasticiser is added first, it will act as a retarder and stabilise the initial hydration product. Introducing water glass will precipitate C-S-H from the solution and new, stable and self-catalysed hydration products will be formed. Workability is lost and hardening starts vigorously. When water glass is introduced first, a metastable inhibiting hydration layer forms around the cement grains as usual. In addition to this, C-S-H from the solution is also precipitated, which should accelerate hardening as is the case when no plasticiser is added. When plasticiser is added, it will stabilise both the initial hydration products and the precipitated products. Workability is then good but the plasticiser retards hardening considerably. In the test where less plasticiser was used, reducing the dosage was not found to compensate for the retarding effect.

4. EXPERIMENTS

The aim of these tests was to develop concretes for precast structural frame units ("precast concrete"), hollow-core slab production ("no-slump concrete"), and for cast-in-place production ("cast-in-place concrete"). The concretes were designed to meet the requirements for early age strength and workability for each of the three types of applications. The basic mechanical and durability properties of these concretes were examined. The effects of heat treatment and water glass on the chemical and physical structure of concrete and cement paste were investigated. A special feature of water glass is its chemical reaction with calcium hydroxide ($Ca(OH)_2$). The reaction is expected to have implications for carbonation rate and pore structure.

4.1 Materials

The cement used was ultra rapid hardening PC. The chemical composition and properties of the cement are presented in Table 1. The aggregate was rounded normal granite-based natural aggregate, except for fraction 8 - 16 #mm which was partly crushed. The aggregate was combined from seven fractions. The combined grading is presented in Table 2. Tap water was used. The water glass was Zeopol 33 (manufactured by Zeofin Ltd), with solid content 37%, density 1.38 kg/dm^3 and molar ratio (SiO_2/Na_2O) 3.3. The superplasticiser used was Scancem

SP 62 (Mighty 150), a sulphonated naphthalene formaldehyde condensate with specific gravity 1.21 kg/dm^3 and solid content 42%.

Table 1. Chemical composition and properties of the cement used in the experiments with water glass and PC.

Composition			
SiO_2	19.5%	Specific surface area	868 m^2/kg Blaine
Al_2O_3	4.7%	Setting time:	
Fe_2O_3	2.3%	- start	1.25 h.min
MgO	2.8%	- end	2.15 h.min
CaO	61.7%	Mortar strength *)	
Na_2O	0.78%	- 1 d	43.6 MPa
K_2O	0.94%	- 3 d	49.9 MPa
SO_3	4.5%	- 7 d	53.4 MPa

*) According to Standard EN 196

Table 2. Grading of aggregate used in the experiments with water glass and PC.

#mm	0.125	0.25	0.5	1	2	4	8	16	32
%	0.6	2.8	8.5	15	26	42	63	99	100

4.2 Mix design

Plastic concrete for precast structural frame units must have reasonable workability (slump 5 - 10 cm). The open time must be about 15 minutes. Trowelling must be possible at age 30 minutes. The strength target was 30 MPa at 3 hours.

No-slump concrete for hollow-core slabs must be stiff but still compactable. The open time of the concrete must be at least 40 minutes, as in the laboratory the manufacturing of test specimens takes at least that time. In real manufacturing a shorter open time might be adequate. The strength target was 45 MPa at 3 hours.

Concrete for cast-in-place production must have good workability (slump ~10 cm), be able to withstand transportation, and have a sligtly longer open time after transportation than for precast concrete. In this study the transportation time was assumed to be 30 minutes. The strength target was 25 MPa.

Concretes are marked in this Section as follows: A is concrete accelerated with water glass, H is heat treated concrete and Ref is reference concrete (no heat treatment, no accelerator).

Table 3. Mix design of concretes. The reference concrete has no water glass accelerator.

	Precast concrete		No-slump concrete		Cast-in-place concrete	
	A	Ref	A	Ref	A	Ref
Cement kg/m3	480	480	560	560	520	520
Water kg/m3	193	220	198	193	206	228
Aggregate kg/m3	1631	1630	1590	1645	1575	1574
Superplasticiser SP 62 kg/m3	19.2	5.3			15.6 + 2.1 **)	5.2 + 1.0**)
Water glass *) kg/m3	20.7	-	24.2	-	16.8	-
w/c	0.47	0.47	0.38	0.345	0.45	0.45

**) Superplasticiser dosage at 2 minutes + repeated dosage at 30 minutes after water introduction

*) Solid content 37%

4.3 Testing procedures

Workability and air content were measured for the fresh concrete. For the hardened concrete, the mechanical and durability properties as well as the chemical and physical structure of the concrete were studied.

Test cubes were made from the plastic concretes (precast and cast-in-situ) using the vibrating table. No-slump concrete was compacted with the pressure/vibrating apparatus. The test concretes were heat treated in a Controls moist oven, in which the heating elements are at the bottom of the oven in water. The test specimens were placed about 10 cm above the water surface and heated by steam emission. A schematic representation of the treatments is given in Figure 4. Unless otherwise stated, the moulds were removed at age 1 d and the specimens cured at +20°C and >95% RH.

```
                   +60°C
      *---¤----------------#-------------  Plastic precast concrete
                   +50°C
      *-----¤--------------#-------------  No-slump concrete
                   +50°C
*---@---¤----------------#-------------  Cast-in-place concrete

      0---½---1-----------3-------------  Age (h)
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Figure 4. Treatment of test specimens.
* water addition ¤ start of heat treatment
@ remixing # end of heat treatment.

4.4 Test results

Properties of fresh concrete

The workability target was met in all concretes. The requirement for plastic concrete was a slump value of about 10 cm and the results were 8 - 11 cm (precast and cast-in-place plastic concretes). The concretes with accelerator stiffened faster than the reference concretes, but the difference was small. Open times with all of these plastic concretes were adequate (slump >5 cm).

No-slump concrete was stiff but still compactable. The open time with the compacting method used was at least 40 minutes, the time required for laboratory preparation of the test specimens. In real hollow core production a shorter open time is adequate. Because of the low efficiency of laboratory compacting apparatus, the cement content was greater than in normal hollow-core production. A much smaller cement content and shorter open time would be adequate in real manufacturing.

Loss of workability from adding water glass was compensated for by increasing the plasticiser dosage (as in this investigation with plastic concretes) or by increasing the water content. When increasing the water content, it is possible to keep the cement content or water-cement ratio constant. In no-slump concrete the cement content was kept constant and the water-cement ratio increased. This must be constantly borne in mind when dealing with the results.

When the plasticiser dosage was increased to compensate the workability loss, the water-cement ratio was kept constant. Increased superplasticiser dosage has a retarding tendency, so the open time was increased. The dosage sequence of water glass and superplasticiser had a considerable effect on workability. If water glass is introduced first and plasticiser later, workability is high but the strength development rate low. If the plasticiser is introduced first and water glass later, workability is low and the strength development rate high. The best compromise is to introduce both admixtures simultaneously 1 to 2 minutes after water introduction.

Compressive strength

Compressive strength development is presented in Figures 5 - 7.

<u>Precast concrete</u>
The strength target for precast concrete was 30 MPa in 3 hours, and it was achieved. For higher strength development rates, the heat treatment temperature should have been higher or the temperature rise steeper. With the constituents in use, it seems that changing the composition of the concrete would not have any beneficial effect on the strength development rate.

The strength loss associated with heat treatment was 13% with the accelerator and 10% in the reference concrete at age 180 d. Although both concretes, with accelerator and the reference concrete, had the same water-cement ratio, long-term strengths with the accelerator were 5 - 10% higher than reference.

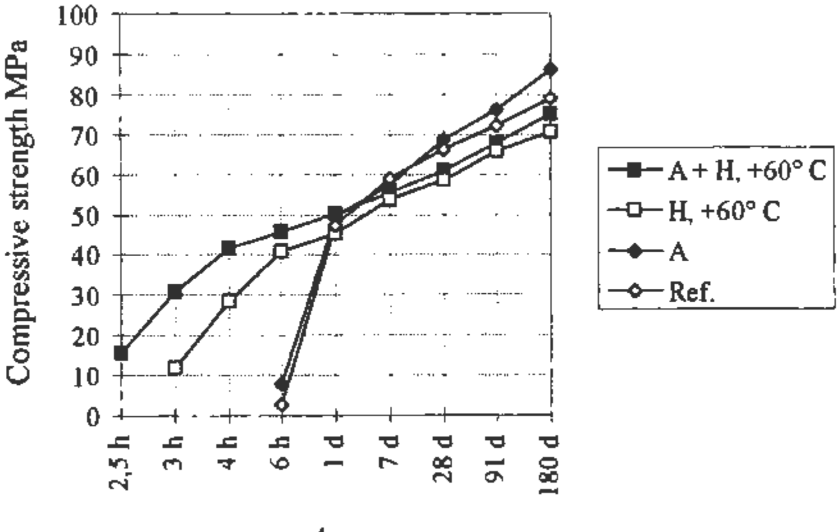

Figure 5. Compressive strength development of precast concrete. A is concrete accelerated with water glass, H is heat treated concrete and Ref is reference concrete (no heat treatment, no accelerator).

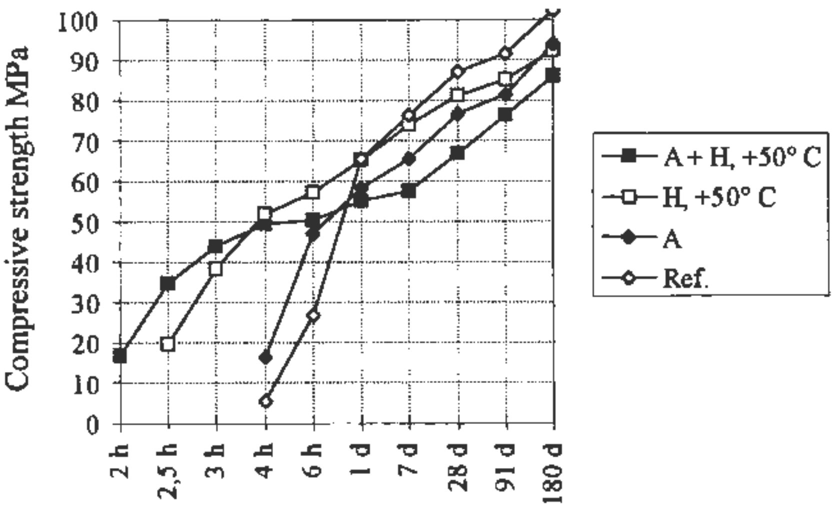

Figure 6. Compressive strength development of no-slump concrete. Notation as in Figure 5.

No-slump concrete

The strength target for no-slump concrete was 45 MPa at 3 hours, which was achieved with heat treatment at +60°C. With treatment at +50°C as used in the tests, 44 MPa was achieved at 3 hours. (With the same composition, 48 MPa was achieved during mix design testing. With fewer specimens in the oven, the temperature rose a little faster and treatment was more efficient.)

The strength loss associated with heat treatment was 9% with the accelerator and 10% in the reference concrete at age 180 d. The long-term strengths of the concretes with accelerator were lower than in the reference concretes (7 - 9%). The reference concretes had a water-cement ratio of 0.345 and the concretes with accelerator a ratio of 0.38. According to Penttala et al. /12/, such a difference in water-cement ratio would correspond to a strength difference of about 7% at age 91 d. Thus the difference in long-term strength is associated entirely with the water-cement ratio. If the ratio had been constant and the stiffening effect of water glass compensated for, for instance by raising the cement content, no difference would have occured in the long-term strength.

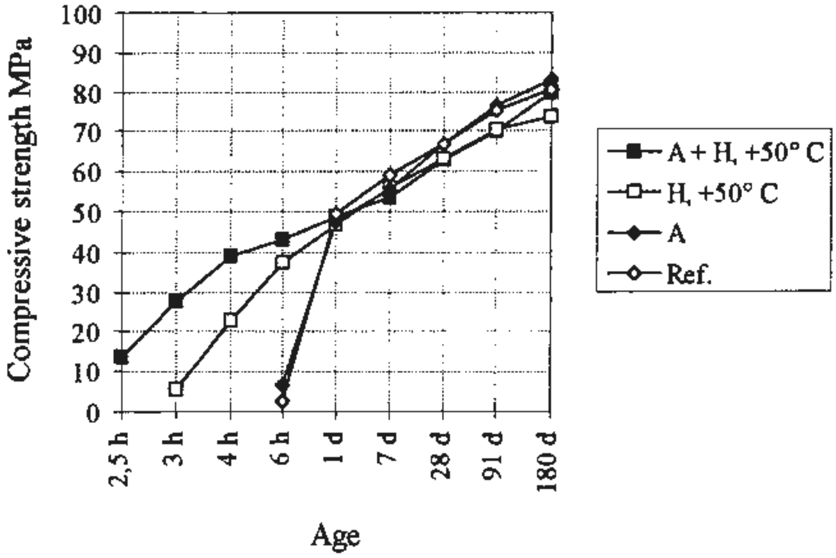

Figure 7. Compressive strength development of cast-in-place concrete. Notation as in Figure 5.

Cast-in-place concrete

The target strength for cast-in-place concrete was 25 MPa at 3 hours, which was achieved with heat treatment at +50°C. A high cement content was used to avoid a curing temperature exceeding +50°C. Strength loss and long-term strengths were as in precast concrete.

Chemical structure

During hydration the overall porosity, capillary porosity and the average pore radius of capillary pores all diminished. The effect of the accelerator and heat treatment on the overall porosity and capillary porosity measured with mercury intrusion porosimetry is small. On the other hand, the effect on the average pore radius of capillary pores is considerable. Both heat treatment and the use of water-glass-based accelerator decreases the average capillary pore radius. Some of the mercury intrusion porosinetry results are presented in Figure 8. A similar effect of heat treatment has been reported elsewhere /5/. The effect of water glass is a result of the reaction with $Ca(OH)_2$. The amount of coarse grained $Ca(OH)_2$ is decreased and the amount of finely grained C-S-H increased.

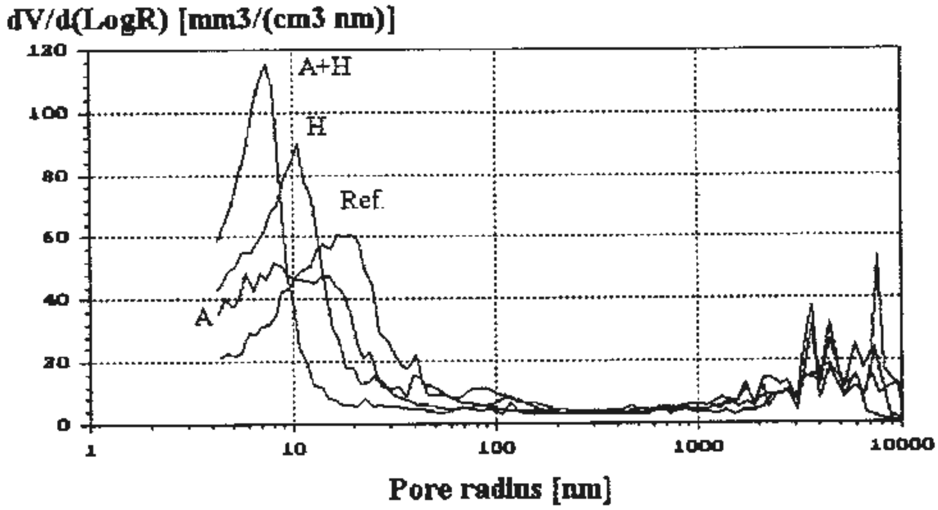

Figure 8. Mercury intrusion porosimetry results. Precast concrete 180 d. Notation as in Figure 5.

The $Ca(OH)_2$ content dimishes upon introduction of a water glass accelerator (see Figure 9). This phenomenon, which was also observed in the preliminary tests, makes it reasonable to assume that the water glass reacts as presented in Equation 1:

$$2\ C_3S + 8\ H_2O + 2\ Na_2SiO_3 \dashrightarrow 2\ C_3S_2H_3 + 4\ Na^+ + 4\ OH^- \qquad (1)$$

C-S-H formed will harden the concrete somewhat, but the actual accelerating mechanism of water glass is probably based on the mechanisms given in Section 2.

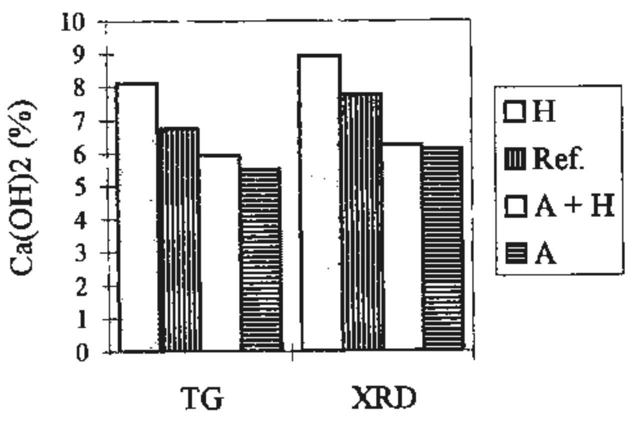

Figure 9. Amount of $Ca(OH)_2$. No-slump concrete 28 d. Notation as in Figure 5.

5. SUMMARY AND CONCLUSIONS

Water glass (sodium silicate) is used widely as a shotcrete accelerator and is known to cut the open time of the mix to a few minutes. Its purpose in shotcreting is to accelerate setting of the concrete mix so that thicker layers can be sprayed at one time. The use of water glass in plastic concretes is not dealt with in the literature.

In this study concretes were developed for hollow-core slab production (no-slump concrete), precast structural frame units and cast-in-place production. The concretes were designed to meet the requirements for early age strength and the distinct workability requirements for each of the three types of applications. The basic mechanical and durability properties of these concretes were examined. The effects of heat treatment and water glass on the chemical and physical structure of the concrete and cement paste were investigated. A special feature of water glass is its chemical reaction with $Ca(OH)_2$. Because the reaction is expected to have implications for carbonation rate and pore structure, attention was paid to studying the reaction and pore size distribution.

From the results the following conclusions can be drawn:

- Water glass accelerated strength development, both in normal-cured (+20°C) and especially in heat treated concrete. With it stripping times could be reduced by 20 - 40%.
- Water glass with the highest tested SiO_2/Na_2O molar ratio had the greatest effect on concrete properties. The effect was positive on early age strength and negative on workability, but the latter could be compensated for by mix design. The workability of the developed concretes was good, plastic concretes having a slump of about 100 mm.
- When superplasticiser was used together with the water glass accelerator, delayed dosage could give dramatically different results depending on which admixture was added first. With the same admixture dosages but a different dosage sequence, workability could be nil or very high (slump >250 mm). Unfortunately, however, the strength development rate is inversely proportional to workability. The best compromise for early strength and workability was achieved when both admixtures were added simultaneously 1 - 2 minutes after introduction of water.
- When a water glass accelerator was used alone, the best dosage time was 2 minutes after introduction of water.
- SiO_2 from water glass reacts with $Ca(OH)_2$ according to Equation 1. When reacting with $Ca(OH)_2$, Si forms C-S-H, which is mechanically stronger than portlandite (reactant). When the water glass dosage was 1.6% as dry substance of PC, the reaction consumed roughly 25% of the $Ca(OH)_2$ delivered from the PC.
- The pore structure becomes denser when water glass accelerator is added.
- Due to the decreased amount of $Ca(OH)_2$ and microcracking, carbonation proceeded slightly faster than in the reference concrete. This difference was not compensated for by the denser pore structure.
- As with Si rich binders (BFS, PFA and silica fume), the rate of strength development was more temperature dependent than in pure PC systems. The difference was clearly demonstrated and partly explains the efficiency of water glass as an accelerator in heat treated concrete.

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