

Chloride-Free Accelerators for Concrete Setting and Hardening

by H. Justnes

Synopsis: Calcium chloride is an excellent accelerator for concrete, improving both setting time and hardening rate. However, it can not be used for reinforced concrete in efficient dosages because of initiation of rebar corrosion. In the search for other bulk chemicals working as accelerators, calcium nitrate has proven to be a good candidate as set accelerator; however it is not a hardening accelerator (e.g. improving 1 day strength). Efforts have been made to combine calcium nitrate with other admixtures in order to make the mix work as a combined chloride-free setting and hardening accelerator. This paper sums up research over the last 10 years regarding this matter and also compares performance with other chemicals.

Keywords: accelerator; chloride-free; hardening; setting; strength

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INTRODUCTION

In the past, a concrete accelerator was synonymous with an admixture increasing the 1 day compressive strength. It is only in the recent years, with the implementation of the European standards that the industry distinguishes between setting and hardening accelerators, realizing practical utilizations of both admixture effects independently.

According to the European admixture standard EN 934-2 of 2001¹, a setting accelerator must give at least 30 min initial setting time at 20°C, and maximum 60% of the initial setting time of the reference at 5°C measured on mortar with equal flow. A hardening accelerator should give minimum 120% compressive strength compared to the reference after 1 day at 20°C, and minimum 130% compressive strength compared to the reference after 2 days at 5°C, as measured on concrete of equal flow. Requirements are established for long term strength and air content also.

Note that the European standard¹ uses the practical approach of equal flow of mixes allowing variations in water-cementitious materials ratio (w/cm). However, variations in w/c may mask the chemical effects of admixtures, so more fundamental studies searching for active accelerators tend to use constant w/cm and cement content.

Concrete is a relatively low priced construction material, which means that any high-priced chemical admixture must enhance its performance at a relative small dosage, or alternatively a cheaper chemical can be allowed at moderate dosage. Hence, accelerators should be sought among industrial bulk chemicals.

Calcium chloride, CaCl_2 , was an ideal accelerator being both a setting and hardening accelerator in one compound, in addition to being an industrial bulk product. However, in 1960's awareness of corrosiveness of chlorides on embedded reinforcement arose and today chloride containing admixtures is limited for steel reinforced concrete ($< 0.4\% \text{ Cl}^-$ of cement mass for ordinary concrete, but $< 0.1\% \text{ Cl}^-$ for reinforced concrete serving in chloride containing environment, based on SR cement or with pre-stressed steel²).

Dodson³ has given a review of non-chloride, non-corrosive set accelerating salts; Dodson began research on such salts in 1962 and found calcium formate, $\text{Ca}(\text{CHO}_2)_2$, to meet all these requirements⁴. The second salt to fulfill the requirements was calcium nitrite, $\text{Ca}(\text{NO}_2)_2$, which was introduced in 1968 and patented in 1969⁵. Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, was proposed as a basic component of a set-accelerating admixture, in conjunction with

triethanolamine, by Tokar⁶. The most recent non-chloride, non-corrosive set accelerating salt to be introduced to the concrete market was thiocyanates (salts of SCN^-)⁷. Like the nitrate, the thiocyanates should be accompanied by an alkanolamine in order to attain the desired end results. Gerber⁸ patented the combination of thiocyanate salts with those of nitric acid and alkanolamine. Abdelrazig et al.⁹ compared the accelerators calcium chloride, calcium nitrate and sodium thiocyanate. Their laboratory results agreed with the known effects from site practice; calcium chloride is effective at all ages, calcium nitrate at early ages and sodium thiocyanate at later ages.

In the search for a relatively cheap chloride-free accelerator, calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, has arisen as an alternative setting accelerator, but it must be combined with other components to function as a hardening accelerator as shown in the proceeding sections. Unless otherwise stated the calcium nitrate referred to here is of granulated, technical quality with formula $x\text{NH}_4\text{NO}_3 \cdot y\text{Ca}(\text{NO}_3)_2 \cdot z\text{H}_2\text{O}$ where $x = 0.092$, $y = 0.500$ and $z = 0.826$, or in other words composed of 19.00 % Ca^{2+} , 1.57 % NH_4^+ , 64.68 % NO_3^- and 14.10 % H_2O .

SINGLE COMPOUND, CHLORIDE-FREE, SETTING ACCELERATORS

When testing accelerators, it is important to know that outcome may strongly depend on the composition of the portland cement used. Justnes and Nygaard¹⁰ published the set accelerating efficiency of calcium nitrate at 5-7°C on pastes ($w/cm = 0.40$) based on 5 different portland cements with a C_3A content ranging from 7.4 to 1.0 %. The accelerating efficiency ranged from very strong to slight and there was no correlation between set accelerating efficiency and C_3A as initially assumed, but rather surprisingly with the belite, C_2S , content as plotted in Fig. 1. The correlation between belite content and set accelerating efficiency of calcium nitrate was confirmed by Justnes and Nygaard¹¹ in a study of five other cement pastes at 5°C. According to Gebler¹², calcium formate, $\text{Ca}(\text{HCOO})_2$, is an efficient accelerator when the ratio C_3A to SO_3 of the cement is > 4 . Heikal¹³ recently confirmed the set accelerating effect of calcium formate at 20 °C with a 1 day compressive strength increase in the order of 120%. Smith¹⁴ compared the effect of the two non-chloride accelerators sodium thiocyanate and calcium nitrate on the setting characteristics of two different portland cement mortars with the accelerator calcium chloride, and found that any one of the three accelerators may be more effective with one cement than with another cement having similar setting characteristics without accelerators.

Justnes and Nygaard¹⁵ found the reason for acceleration efficiency differences among portland cements through analyses of the liquid of cement pastes prior to setting. The mechanism for accelerated setting might be caused by calcium suppressing gypsum solubility and precipitating sulfate from soluble alkali sulfates. A lower sulfate concentration will lead to slower or reduced formation of ettringite, which will shorten the onset of aluminate, C_3A , hydration. Interaction of anions (e.g. nitrate) with C_3A hydration products can not be ruled out. It was noted that a cement with very low response to $\text{Ca}(\text{NO}_3)_2$ contained much more of the mineral Aphthitalite, $\text{K}_3\text{Na}(\text{SO}_4)_2$, which leads to a

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high initial sulfate concentration in the fluid. When $\text{Ca}(\text{NO}_3)_2$ was added, much of the calcium precipitated as minimally soluble gypsum. The authors¹⁵ showed a linear correlation between the alkali content of the fluid of 9 cement pastes in the fresh state with the reduction in initial setting time when 1.55 % calcium nitrate was added, as reproduced in Fig. 2. The linear correlation between belite content and set accelerating efficiency in Fig. 1 is then understandable as an indirect effect since belite can incorporate a portion of the total alkalis in its structure and consequently prevent them from taking part in the early fluid chemistry since belite is a slow reacting mineral. Hence, for a series of cements with about equal total alkali content and increasing belite content, it is expected that the set accelerating efficiency of $\text{Ca}(\text{NO}_3)_2$ will increase.

In order to find out whether setting acceleration is dominated by the calcium cation or nitrate anion in $\text{Ca}(\text{NO}_3)_2$, Justnes (unpublished data) tested the efficiency of both calcium nitrate (65% NO_3^- due to some crystal water) and sodium nitrate (73 % NO_3^-) as set accelerators for 4 different portland cements (see Table 1 for compositions) pastes at 5 °C by Vicat needle. The dosages were 0.00, 0.25, 0.50, 0.75 and 1.00 % calcium nitrate of cement mass, while sodium nitrate was dosed to give correspondingly equimolar nitrate content. The influence on setting time is listed in Table 2. From this limited study, calcium nitrate seems in general to be a substantially better set accelerator than sodium nitrate for portland cements. Specifically, $\text{Ca}(\text{NO}_3)_2$ gave shorter setting time relative to reference than NaNO_3 in 10 out of 12 comparative tests and about twice or more reduction in setting time in 6 of the 12 cases. For portland cements with a rather high alkali content ($\geq 1\%$ $\text{Na}_2\text{O}_{\text{equiv}}$), calcium nitrate performs better than sodium nitrate for higher dosages only (about 1% of cement mass). This effect may be explained by alkali counter-ions (e.g. hydroxide or sulfate) precipitating calcium and forming alkali nitrate *in situ*. Thus, Ca^{2+} seems to dominate setting, while NO_3^- may have an effect as well, depending on cement type.

Temperature evolution profiles in insulated concrete (i.e. semi-adiabatic) and early compressive strengths for concrete cubes cured at 20°C have been measured¹⁶ for different additions of $\text{Ca}(\text{NO}_3)_2$. The concrete composition corresponded to w/cm = 0.45 and 4 % silica fume replacement of both CEM I 52,5R-LA and CEM I 42,5R cements¹⁷ (compositions as in Table 1). The accelerating effect of $\text{Ca}(\text{NO}_3)_2$ was also compared to additions of calcium acetate, $\text{Ca}(\text{CH}_3\text{COO})_2$, and formate, $\text{Ca}(\text{HCOO})_2$, at equimolar concentrations of Ca^{2+} for 3.5 % $\text{Ca}(\text{NO}_3)_2$ added to the CEM I 42,5R concrete. Calcium acetate and formate gave about the same acceleration according to the temperature profiles in Fig. 3, while $\text{Ca}(\text{NO}_3)_2$ showed greater accelerating effect in spite of soluble calcium ions dominating the set accelerating effect. The reason for the lesser efficiency of calcium salts of organic acids (i.e. formate, acetate etc) may be due to partial complex formation with one of the anions (e.g. CaOOCCH_3^+), meaning that the overall chemical equilibrium of the paste fluid does not experience the same effective concentration of Ca^{2+} ions as for $\text{Ca}(\text{NO}_3)_2$. In fact, the logarithm of the complex formation constant, $\log K_1$, is 0.60 and 0.28 for acetate and nitrate, respectively, which corresponds to 61 and 75 % "free" Ca^{2+} in 0.1 N solutions of these salts. The temperature profiles in Fig. 3 reveal that setting time is accelerated (criterion is 2°C above base line) and not the early strength development rate (i.e. temperature increase slope not steeper than reference).

Justnes et al.¹⁸ tested setting time of cement pastes (two different cements) where different calcium salts with equal amounts of Ca^{2+} ions were added. The order of effectiveness of anions as set accelerators was $\text{CH}_3\text{COO}^- \leq \text{NO}_2^- < \text{NO}_3^- \leq \text{HCOO}^- < \text{Cl}^-$ for CEM I 52,5R-LA cement¹⁷ (see Table 1) and as $\text{CH}_3\text{COO}^- < \text{HCOO}^- \leq \text{NO}_2^- < \text{NO}_3^- < \text{Cl}^-$ for a similar Swedish portland cement.

A neat concrete with CEMI 52,5R-LA (composition as in Table 1) and $w/cm = 0.62$ exhibited compressive cube strengths after 8 h and 48 h moist curing of 2.5 ± 0.0 and 23.1 ± 0.3 MPa, respectively, while the corresponding strengths when 2 % $\text{Ca}(\text{NO}_3)_2$ was added were 4.0 ± 0.1 (due to earlier setting) and 27.7 ± 0.2 MPa. However, 1 day strength for concrete accelerated by only calcium nitrate, is usual equal or slightly lower than reference. Further examples of concrete strength data with calcium nitrate are given by Justnes and Nygaard¹⁹.

Another important parameter to control when testing accelerators is the temperature. Justnes et al.¹⁸ measured reductions in initial and final set at 5 °C, 13 °C and 23 °C for cement pastes with 1.55% calcium nitrate and equimolar Ca dosage of calcium chloride hexahydrate, and compared them with neat cement pastes (two different portland cements). The results revealed that the efficiency of calcium nitrate as set accelerator is higher at lower temperatures. Assuming that the same amount of hydration product is necessary to obtain initial setting at all temperatures, and knowing that reaction rate simply is amount of hydration product divided by time, it is possible to make linear Arrhenius plots; $\ln(1/t) = a \cdot (1/T) + b$, where t is initial setting time (s) and T is absolute temperature (K). The slope of such a plot, $a = E_a/R$, where R is the universal gas constant and E_a is the overall activation energy for the hydration. The concept functions very well for neat cement paste and for cement paste with calcium chloride as shown in Fig. 5, but not with calcium nitrate. The reason is that calcium nitrate is much more effective at 5 °C than predicted by the slope, indicating a different mechanism at this temperature.

Practical utilizations of set accelerators are often to start concrete hardening earlier to avoid cooling of concrete in winter concreting or to counteract the retarding effect of plasticizers. Rettvin and Masdal²⁰ showed that additions of 50 % technical calcium nitrate solution (ammonium free) to concrete gave a set acceleration proportional with the dosage up to 0.50 % of the cement weight. They also described the utilization of calcium nitrate to secure the slip forming rate during the construction of the shafts for the Troll Gravity Base Structure (369 m height) in the North Sea, since calcium nitrate counteracted the retarding effect of the plasticizer and super-plasticizer used.

SINGLE COMPOUND, CHLORIDE-FREE, HARDENING ACCELERATORS

The perhaps most promising single compound, hardening accelerator is sodium thiocyanate. It can be seen from mortar strengths in Tables 3 and 4 that 0.25% NaSCN gives compressive strength increase of 121% after 1 day at 20 °C and 113% after 2 days

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at 5 °C. Although fulfilling the 20 °C criterion of the EN 934-2 standard¹, it fails on the 5 °C criterion (>130%). In fact, the present author is not aware of any single compound that fulfils these criteria, and blended accelerators seem to be required.

BLEND, CHLORIDE-FREE, SETTING AND HARDENING ACCELERATORS

Justnes²¹ tested calcium nitrate in combination with inorganic salts like sodium thiocyanate, NaSCN, and thiosulfate, Na₂S₂O₃, and with amines like triethanolamine (TEA) and triisopropanolamine (TIPA) at equal w/cm in a search for combined setting and hardening accelerators. The amines did not affect setting or contributed to 1 day strength, but they lead to enhanced 28 days strength. According to Gartner and Myers²² small amount of amines may have a catalytic effect on C₄AF that may explain the long term strength increase. Calcium nitrate in combination with sodium thiocyanate was the most promising combination as shown by the results reproduced in Table 3 for 20°C curing and Table 4 for 5 °C curing. The 24 h compressive strength is ≥ 120% of reference for all mixes with admixtures at 20°C, except 1 % Ca(NO₃)₂. The mixture 1.0 % Ca(NO₃)₂ with 0.25 % NaSCN seems to be a chloride free alternative to calcium chloride with an even better strength as early as 6 h. None of the admixtures fulfilled the compressive strength criterion of >130% compared with the reference after 2 days at 5 °C, not even 1 % calcium chloride hexahydrate (i.e. 0.32% Cl⁻ of cement mass). However, note that the comparisons in this study are done at constant w/cm, and not equal flow.

The objective of Justnes²³ was to compose a liquid accelerator blend from calcium nitrate and a plasticizer or super-plasticizer that fulfilled the criteria for both set and hardening accelerators according to the EN 934-2 standard¹ (i.e. equal flow). Earlier findings by Petersen and Justnes^{24, 25} showed that calcium nitrate was capable of at least partly counteracting the retardation of plasticizers while maintaining rheology.

Justnes²³ formulated a total of 5 accelerators before the preceding objective was reached. The composition of the 5 accelerator blends are listed in Table 5 as % active ingredient in components (i.e. water subtracted). The test results for 2 accelerators (no. 3 and 5) according to the EN 934-2¹ criteria for both set and hardening acceleration are given in Table 6. Accelerators 1 and 2 were skipped after failure in an initial cement paste test. Accelerator 1 was an effort to make an alkali-free blend, but it retarded too much at particular 5 °C. Accelerator 2 retarded also too much at 5 °C. Accelerator 3 nearly fulfilled the requirements (failed compressive strength after 2 days at 5°C only), while accelerator 5 passed the criteria with a good margin. Accelerator 4 was actually not tested since accelerator 5 had an excellent performance and a potential market advantage of being colorless and odorless compared to the dark brown smelly solution (due to SNF) of accelerator 4. Note that accelerator 5 consisting of about 30% calcium nitrate, 11% melamine based super-plasticizer and 6% sodium thiocyanate in water (53%) was not optimized in this limited study, but merely demonstrating a possibility. Furthermore, it was assumed that the strength improvement found for mortar will occur

in concrete as well, but this has to be documented prior to practical application. Combinations with the newer polyether grafted polyacrylate super-plasticizers were not tried out at this point.

CONCLUSIONS

Calcium nitrate is the most promising chloride-free set accelerator considering performance at low temperature, availability and industrial mass production. However, it is not a hardening accelerator with sufficient improvement in 1 day strength.

It has been demonstrated that ternary blends of calcium nitrate, sodium thiocyanate and sulphonated melamine-formaldehyde plasticizer have the potential of fulfilling the criteria of the European admixture standard EN 934-2 as both setting and hardening accelerator.

REFERENCES

1. *European Standard* EN 934-2: "Admixtures for Concrete, Mortar and Grout – Part 2: Concrete Admixtures – Definitions, Requirements, Conformity, Marking and Labelling", July 2001, European Committee for Standardization, Rue de Stassart 36, B-1050 Brussels, Belgium, pp. 10-11
2. *Norwegian - European Standard* NS-EN 206-1: "Concrete. Part 1: Specification, Performance, Production and Conformity (amendment prA1:2003 incorporated), Dec. 2000, European Committee for Standardization, Rue de Stassart 36, B-1050 Brussels, Belgium, Norwegian version with informative national amendment (NA), NA.5.2.7, p.84
3. Dodson, V.H., *Concrete Admixtures*, Structural Engineering Series, Van Nostrand Reinhold, New York, 1990, Chapter 4: "Set Accelerating Admixtures", pp. 73-102.
4. Dodson, V.H.; Farkas, E. and Rosenberg, A.M., "Non-Corrosive Accelerator for Setting of Cements", *U.S. Patent* No. 3,210,207, Oct. 5, 1965.
5. Angstadt, R.L. and Hurley, F.R., "Accelerator for Portland Cement", *U.S. patent* No. 3,427,175, Feb. 11, 1969.
6. Tokar, V., "Additive Composition for Portland Cement Materials", *U.S. Patent* No. 4,337,094, June 1982.
7. Rosskopf, P.A., "Additive for Hydraulic Concrete Mixes", *U.S. Patent* No. 4,373,956, Feb. 15, 1983.
8. Gerber, H.A., "Admixture for Hydraulic Cement", *U.S. Patent* No. 4,473,405, Sept. 25, 1984.
9. Abdelrazig, B.E.I.; Bonner, D.G.; Nowell, D.V.; Dransfield, J.M. and Egan, P.J., "Effects of Accelerating Admixtures on Cement Hydration", *Proceedings of the International RILEM Symposium Admixtures for Concrete - Improvement of Properties*, May 14-17 1990, Barcelona, Ed. E. Vázquez, Chapman and Hall, pp. 106-119.

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10. Justnes, H. and Nygaard, E.C., "Technical Nitrate as Set Accelerator for Cement at Low Temperatures", *Cement and Concrete Research*, V. 25, No. 8, 1995, pp. 1766-1774.
11. Justnes, H. and Nygaard, E.C., "Technical Nitrate as Set Accelerator for Cement at Low Temperatures", *Advances in Cement Research*, Vol. 8, No. 30, Apr. 1996, pp.1-9
12. Gebler, S., "Evaluation of Calcium Formate and Sodium Formate as Accelerating Admixtures for Portland Cement Concrete", *Journal of the American Concrete Institute*, Vol. 80, No. 5, September - October 1983, pp. 439-444.
13. Heikal, M.: "Effect of Calcium Formate as an Accelerator on the Physiochemical and Mechanical Properties of Pozzolanic Cement Pastes", *Cement and Concrete Research*, Vol. 34, 2004, pp. 1051-1056.
14. Smith, P., "Effect of Two Non-Chloride Accelerating Agents on Setting Characteristics of Portland Cement Mortars", SP 102-3, American Concrete Institute, Detroit, ACI SP 102 *Corrosion, Concrete and Chlorides. Steel Corrosion in Concrete: Causes and Restraints*, Ed. F.W. Gibson, 1987, pp. 25-34.
15. Justnes, H. and Nygaard, E.C.: "The Mechanism of Calcium Nitrate as Set Accelerator for Cement", *Proceedings of 10th International Congress on the Chemistry of Cement*, H. Justnes, ed., Gothenburg, Sweden, 2-6 June 1997, paper 3iii012, 8 pp.
16. Justnes, H. and Nygaard, E.C.: "Calcium Nitrate - A Multifunctional Concrete Admixture", *Proceedings of the International Conference on High-Performance Concrete, and Performance and Quality of Concrete Structures*, June 05-07 1996, Florianopolis, Brazil, pp. 514-525.
17. *European Standard EN 197-1*: "Cement – Part 1: Composition, Specification and Conformity Criteria of Common Cements", June 2000, European Committee for Standardization, Rue de Stassart 36, B-1050 Brussels, Belgium, pp. 14-15.
18. Justnes, H.; Clemmens, F.; Depuydt, P.; Van Gemert, D. and Sellevold, E.J.: "Setting Accelerators for Portland Cement", *the Sixth International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, Nice, France, 11-13 October 2000, CANMET/ACI SP-195, Supplementary papers, pp. 1- 16.
19. Justnes, H. and Nygaard, E.C.: "Performance of Concrete with Calcium Nitrate Admixtures", *4th CANMET/ACI International Conference on Durability of Concrete*, August 17-22, 1997, Sydney, Australia, Supplementary Papers, pp. 111-126.
20. Rettvin, Å. and Masdal, T., "Use of Calcium Nitrate Solution as Set-Accelerating Admixture in Slip forming of High Strength Concrete", *Proceedings of ERMCO'95*, Istanbul, Turkey, 1995.
21. Justnes, H.: "Accelerator Blends for Portland Cement", *Proceedings of Cement and Concrete Technology in the 2000s*, September 6-10, 2000, Istanbul, Turkey, Vol. 1, pp. 433-442.
22. Gartner, E. and Myers, D.: "Influence of Tertiary Alkanolamines on Portland Cement Hydration", *Journal of American Ceramic Society*, V.76, No.6, 1993, pp. 1521-1530.
23. Justnes, H.: "Development of Combined Set and Hardening Accelerators for Concrete", *SINTEF Report STF22 A03602*, 2003-02-27, 5 pp.
24. Justnes, H. and Petersen, B.G.: "Counteracting Retardation of Cement Setting by Other Admixtures with Calcium Nitrate", *Proceedings of 5th CANMET/ACI*

International Symposium on Advances in Concrete Technology, July 29 – August 1, 2001, Singapore, ACI SP 200-3, pp. 39-49.

25. Justnes, H.: "Counteracting Plasticizer Retardation of Cement Setting with Calcium Nitrate", *Proceedings of the International Conference Innovations and Developments in Concrete Materials and Construction*, Dundee, Scotland, 9-11 September, 2002, p. 259-267.

Table 1 Specifications of tested portland cements

CEMENT NAME	STANDARD	STANDARD FA	ANLEGG	SR
Cement type	CEM I 42,5R	CEM II A-V 42,5R	CEM I 52,5R-LA	CEM I 42,5R-LA
<u>Composition (%):</u>				
CaO	62.25	-	64.19	64.62
SiO ₂	19.69	-	21.27	21.98
Fe ₂ O ₃	3.41	-	3.41	4.88
Al ₂ O ₃	4.55	-	4.39	3.48
SO ₃	3.43	2.68	2.91	2.18
MgO	2.32	-	1.80	1.45
Na ₂ O	0.41	-	0.22	0.20
K ₂ O	1.15	-	0.47	0.56
Free lime	0.87	0.78	0.78	0.73
Carbon	0.55	-	0.56	-
Fly ash	-	16.30	-	-
Loss on ignition	2.93	1.82	2.42	-
<u>Bogue Minerals (%):</u>				
C ₃ S (Alite)	55.0	-	53.8	56.5
C ₂ S (Belite)	15.0	-	20.4	20.4
C ₄ AF (Ferrite)	10.4	-	10.4	14.8
C ₃ A (Aluminate)	6.3	-	5.9	1.0
C _S (Anhydrite)	7.4	-	6.3	4.7
<u>Properties :</u>				
Blaine (m ² /kg)	360	467	369	290
Water demand (%)	26.8	29.4	26.4	-
Le Chatelier (mm)	0.0	0.3	0.3	-
Initial set (min)	140	125	135	-
Final set (min)	165	150	160	-
1 day σ_c (MPa)	19.7	22.5	16.9	-
2 day σ_c (MPa)	32.7	32.1	29.2	-
7 day σ_c (MPa)	43.5	43.8	44.0	-
28 day σ_c (MPa)	51.2	57.1	56.2	-

σ_c (MPa) = compressive strength, SR = sulfate resistant cement.

Table 2 Initial setting time for different cement pastes ($w/cm = 0.40$) at 5°C with different dosages of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, and sodium nitrate, NaNO_3 . Setting times are listed in hours with relative setting time (%) to reference in brackets.

NAME	STANDARD	STANDARD FA	ANLEGG	SR
Cement type	CEM I 42,5R	CEM II A-V 42,5R	CEM I 52,5R-LA	CEM I 42,5R-LA
<u>$\text{Ca}(\text{NO}_3)_2$ (%)</u>				
0.00	8.10 (100)	6.75 (100)	7.40 (100)	12.25 (100)
0.25	5.50 (67.9)	5.41 (80.1)	5.80 (78.4)	4.7 (38.4)
0.50	5.25 (64.8)	4.41(65.3)	3.00 (40.5)	7.5 (61.2)
0.75	5.33 (65.8)	5.83 (86.4)	4.60 (62.2)	3.8 (31.0)
1.00	4.30 (53.1)	5.70 (84.4)	1.80 (24.3)	4.0 (32.7)
<u>NaNO_3 (%)</u>				
0.25	5.60 (69.1)	5.15 (76.3)	6.10 (82.4)	8.33 (68.0)
0.50	5.55 (68.5)	6.55 (97.0)	5.40 (73.0)	6.33 (51.7)
1.00	6.00 (74.1)	7.52 (111.4)	4.80 (64.9)	5.00 (40.8)

Table 3 Estimated setting times (min) from heat evolution curves (Fig. 4) for paste ($w/cm = 0.4$) and flexural (lower value) and compressive (upper value) strengths (MPa) of mortar ($w/cm = 0.5$) cured at 20°C with admixtures based on calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and sodium thiocyanate (NaSCN) versus calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Property	Ref. (0%)	1.0% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.0% $\text{Ca}(\text{NO}_3)_2$	0.25% NaSCN	1.0/0.25% $\text{Ca}(\text{NO}_3)_2/\text{NaSCN}$
Setting	190 min	-	130 min	190 min	120 min
6 h σ	0.85±0.06	1.7±0.1	2.0±0.1	1.4±0.1	2.2±0.1
	0.4±0	0.6±0.1	0.7±0.1	0.6±0.1	0.7±0.1
24 h σ	19.3±0.2	23.6±1.1	20.3±0.2	23.4±0.9	23.3±0.9
	4.3±0.1	4.4±0.2	4.3±0.1	4.7±0.2	5.0±0.1
28 d σ	61.3±1.4	71.9±1.6	66.2±1.0	65.7±1.2	68.9±2.8 (!)
	8.7±0.1	9.1±0.2	9.0±0.1	8.4±0	9.1±0.1

Table 4 Flexural (σ_f) and compressive (σ_c) strengths (MPa) of mortar ($w/cm = 0.50$) with different admixtures when mixed and cured at 5°C .

Admixture	2 d σ_c	2 d σ_f	28 d σ_c	28 d σ_f
None, Ref.	13.6±0.3	2.9±0.2	54.0±1.0	8.0±0.5
1% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	15.3±0.5	3.17±0.03	58.5±2.3	8.8±0.3
1% $\text{Ca}(\text{NO}_3)_2$	12.1±0.2	3.0±0.1	56.3±0.6	8.1±0.4
1% CN/0.1% NaSCN	13.2±0.3	3.22±0.03	55.0±1.5	8.2±0.4
1% CN/0.2% NaSCN	14.6±0.3	3.3±0.2	56.5±0.7	9.3±0.9
1% CN/0.3% NaSCN	14.2±0.4	3.4±0.2	55.9±2.5!	7.8±0.3
0.2% NaSCN	15.3±0.3	3.4±0.2	56.5±1.6	7.8±0.2
0.3% NaSCN	15.5±0.5	3.2±0.1	60.4±2.2	8.1±0.8

Table 5 Accelerator blend composition (% active ingredient)

Accelerator	1	2	3	4	5
AN-free $\text{Ca}(\text{NO}_3)_2$	42.8	32.3	37.1	37.1	30.3
Ca-LS	5.1	-	-	-	-
Na-LS	-	3.9	4.4	-	-
SNF	-	-	-	4.4	-
SMF	-	-	-	-	10.9
TEA	1.7	-	-	-	-
NaSCN	-	12.8	7.4	7.4	6.1
Water	50.4	51.0	51.1	51.1	52.7

Comments to Table 5:

AN-free $\text{Ca}(\text{NO}_3)_2$ = 50% ammonium-free calcium nitrate of industrial grade.

Ca-LS = 40% calcium lignosulphonate without defoamer of industrial grade.

Na-LS = 40% sodium lignosulphonate without defoamer of industrial grade.

SNF = 40% naphthalene sulphonate-formaldehyde condensate of industrial grade.

SMF = 40% sulphonated melamine – formaldehyde condensate of industrial grade.

TEA = tri-ethanol amine of analytical grade.

NaSCN = analytical grade sodium thiocyanate.

Accelerators 1, 2 and 3 were added 25 drops/liter of tri-butyl phosphate (TBP) as defoamer.

Table 6 Mortar composition and properties

Mix no.		11 (ref)	12	15	21 (ref)	22	25
at temperature, °C		+ 20			+ 5		
Accelerator (% of cement)	ACC 3	none	3	-	none	3	-
	ACC 5	none	-	3	none	-	3
w/cm		0.50	0.477	0.494	0.50	0.476	0.450
Water reduction (%)		-	4.6	1.2	-	4.8	11.1
flow (mm)		166	163	174	169	171	168
Time to setting (h-min)	initial ¹	4-00	3-25	3-05	10-10	6-00	5-40
	final	5-05	4-50	4-35	11-50	10-05	7-25
Flexural strength (MPa) at	1 day	3.7	4.6	4.8	-	-	-
	2 days	-	-	-	2.8	2.8	4.2
Compressive strength (MPa) at	1 day ²	17.7	21.6	23.0	-	-	-
	2 days ²	-	-	-	12.2	11.8	18.6

Comments to Table 6:

¹Requirements to a set accelerator for effect on initial setting time;

at 20°C minimum 30 min shorter than for reference (i.e. maximum 3-30 for Mix 12 and 15),

at 5°C maximum 60% of reference (i.e. maximum 6-06 for Mix 22 and 25).

²Requirements to a hardening accelerator for effect on compressive strength of concrete (initially measured on mortar for experimental simplicity);

after 1 day at 20°C minimum 120% of reference (i.e. minimum 21.2 MPa for Mix 12 and 15),

after 2 days at 5°C minimum 130% of reference (i.e. minimum 15.9 MPa for Mix 22 and 25).

³Bold numbers showing fulfillment of above requirements

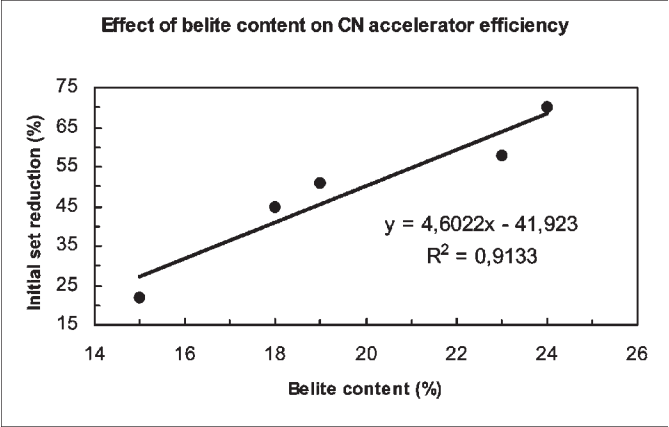


Fig. 1—The linear correlation between accelerating efficiency of 1.5% $\text{Ca}(\text{NO}_3)_2$ additions of different cements and their belite content.

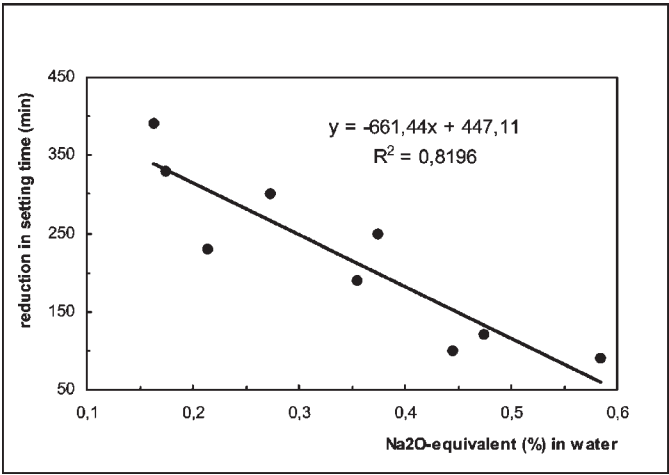


Fig. 2—The reduction in setting time for portland cement pastes when 1.55% calcium nitrate is added vs. the alkali content of the liquid phase 20 min after mixing.

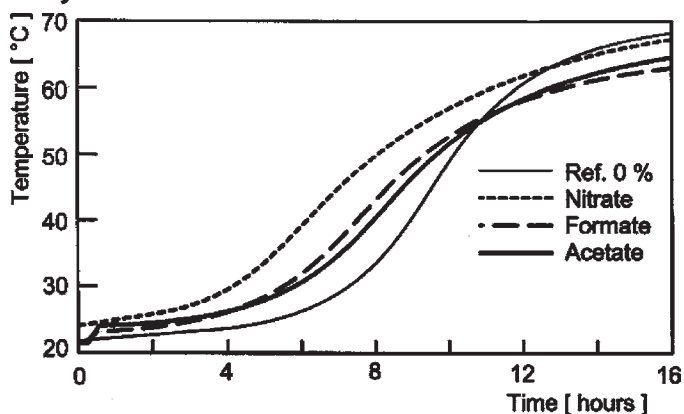


Fig. 3—Temperature vs. hardening time curves for OPC concrete with equivalent dosages of soluble calcium from nitrate, acetate and formate compared with reference concrete.

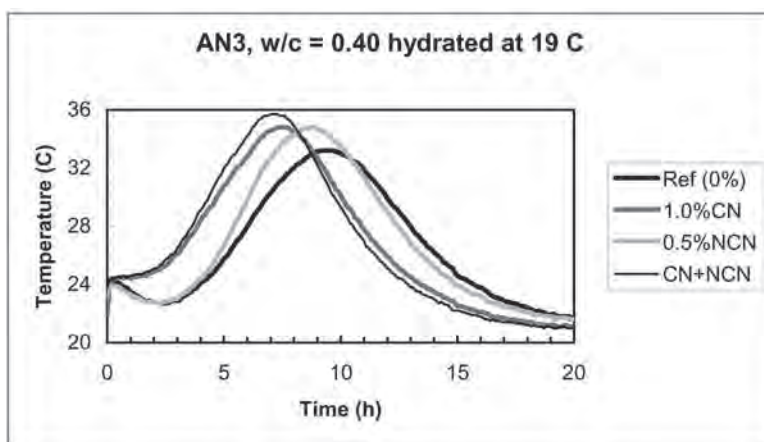


Fig. 4—Temperature evolution in CEM I 52,5R-LA paste ($w/cm = 0.40$) without admixture, with 1.0% calcium nitrate (CN), with 0.5% sodium thiocyanate (NCN) and a combination of the two (CN+NCN) at their individual dosages.

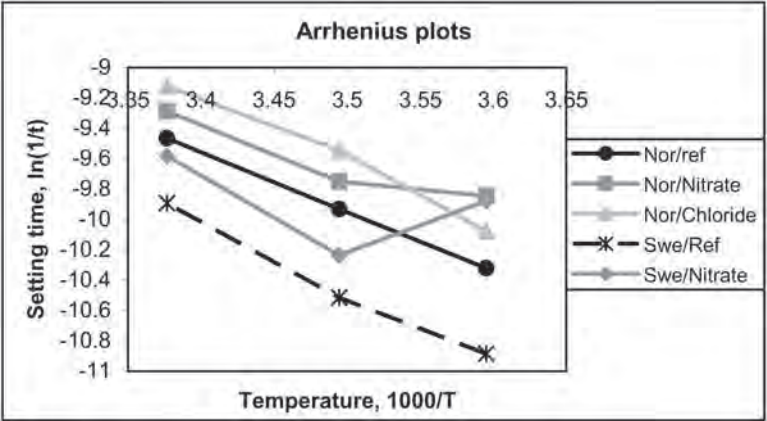


Fig. 5—Arrhenius plots revealing that reference pastes for two portland cements and a paste with calcium chloride accelerator has a linear relationship between the natural logarithm of the inverse of setting time and inverse absolute temperature (the 3 data points corresponds to 20, 13 and 5°C). This is an indication of unchanged setting mechanism within the temperature range. The break at the lower temperature towards shorter setting time for the two cements within calcium nitrate indicates that the mechanism of setting has changed between 13 and 5°C. Calcium nitrate is a more effective set accelerator at lower temperatures where it is needed in practice.

Realkalisation of the Carbonated Concrete using Alkaline Solutions

by F.W.C. Araújo and E.J. Pazini Figueiredo

Synopsis: Some protective techniques, such as anti-carbonation coating, provide the concrete a protection due to the creation of a surface barrier that prevents the penetration of CO₂ and moisture. However, these procedures are not always so effective when the carbonation process moves as a front through the concrete pores, reaching the reinforcement. In this case, the procedure often adopted is the repair technique, which can include the anchorage of the structure, the entire removal of the carbonated layer and localized or general repair.

The purpose of this research was to study the non-destructive repair technique referred as realkalisation by the absorption and diffusion of alkaline solutions. In order to provide evidence for further analyses of the technical viability, besides the main realkalisation testing, some additional tests such as compressive strength, capillary absorption, electrochemical techniques and mortar adherence on realkalised substrates, were performed.

The results obtained show that realkalisation through direct contact of the alkaline solution on the concrete surface is effective in re-establishing the high pH of the concrete, although it presented a slight decrease in the compressive strength. The realkalisation process does not interfere in the mortar adherence to realkalised substrates.

Keywords: carbonation; concrete; corrosion; realkalisation

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INTRODUCTION

The process of carbonation is irreversible. The realkalisation technique is not employed only to re-establish the passivation of the reinforced structure by increasing the pH of the carbonated concrete, but it can also be utilized to prevent the reinforcement from depassivating, as a technique to prevent carbonation. The fact that the carbonated concrete does not need to be removed is one of the advantages of this technique. Generally, only the concrete layer that is detached or deteriorated requires to be removed and repaired before beginning the treatment. The realkalisation technique side effects are another point that can be discussed, more specifically the alkali-aggregate reaction (AAR), once that technique rises the pH values. But this kind of repair will be employed after ten years or more, so the problem of AAR is not a problem for this kind of structure.

In general, there are three critical alternatives to re-establish the alkalinity in the surrounding environment, namely, the diffusion and absorption of an alkaline solution by capillary and hydrostatic forces; production of hydroxyl ions (OH^-) through a cathodic reaction in the reinforced steel; and the transportation of alkaline solution within the capillary pores of the concrete through an electro-osmotic flow. The mechanism of absorption/diffusion does not depend on the electrical field and the current flow applied, in contrast to the electro-osmotic flow that depends on the electrical field application. However, the formation and maintenance of the protective repassivating film of oxides and iron hydroxides on the reinforcing steel surface depend on the alkaline ions introduced to the concrete by the realkalisation process.

The benefits provided by the realkalisation technique are directly associated with the type of electrolyte used during the treatment. Several authors (1-5) have suggested sodium carbonate as the best electrolyte to repassivate the reinforcing steel, maintaining a constant pH around 10.5, i.e, a pH favorable to keep the film.

Although sodium carbonate is considered to be the most advantageous electrolyte to be employed in the realkalisation of the carbonated concrete (6), other investigators have suggested the use of alternative electrolytes that provide other advantages in relation to the sodium carbonate. For instance, because of the formation of

crystals that occur in the surface of the repaired structure when using sodium carbonate as an electrolyte, the replacement of this carbonate by potassium has shows satisfactory results (7). On the other hand, Sergi et al. (6) investigated the use of lithium hydroxide as electrolyte. These authors state that the LiOH, compared to the sodium carbonate, provides the same pH required to restore the passivation film, but has also the advantage of keeping the lithium ions for a longer period of time inside the structure than the sodium and potassium ions do.

The first model to perform the realkalisation was based on the diffusion principle (or passive realkalisation), where an external layer of the alkaline mortar was applied to the carbonated concrete, and through diffusion, the hydroxyl ions penetrated the concrete because of the concentration gradient. However, the practical results were not always successful as expected, mainly because of the slow rate of the diffusion process (Haardt and Hilsdorf, (6)).

The electrochemical realkalisation technique was developed in the mid 1980s, by the Norwegian company Norwegian Concrete Technologies. The technique consists in re-establishing the protection quality against the concrete corrosion by increasing the alkalinity through an electro-osmotic process, where the alkalis from the alkaline solution applied to the structure surface to be treated penetrate by applying an electrical current.

Another technique is the realkalisation performed through the absorption/diffusion of alkaline solutions inside the carbonated concrete, which, like the electrochemical treatment, raises the pH of the carbonated concrete, employing solutions rich in alkalis, but without using the electrical current.

Realkalisation by Absorption/Diffusion

The realkalisation made using a solution rich in alkalis consists in the absorption and diffusion of an alkaline solution, which by capillary action and hydraulic forces penetrate the carbonated concrete, without the application of an electrical field and a current flow, as in the electrochemical realkalisation. Fig. 1 illustrates the realkalisation process by absorption and diffusion. As for its application, the feasibility of this technique is not fully established, since it is a new procedure and therefore, not extensively studied.

The first study reported in Brazil (8), showed that this technique is as effective as the electrochemical realkalisation, with the advantage of not requiring the use of expensive monitoring machines as it occurs with the electrochemical realkalisation technique.

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The realkalisation technique by absorption and diffusion has been shown to be effective, mainly in terms of the time required to realkalise 2.5 cm of mortar (8). Even in the case of a difficult condition for realkalisation, as the one showed by cement portland type V – ARI (is the same cement as type III of ASTM: high early strength), with a w/c of 0.40, the time required to complete the realkalisation of the mortar was less than twenty days (Fig. 2), which confirms the applicability of this technique, although it has not been actively encouraged by the technical and scientific community.

Some aspects, not so well known to the scientific community, related to this technique are studied and discussed in the present work.

METHODOLOGY

The purpose of the methodology developed in the present investigation was to study some of the most important features of the realkalisation by absorption and diffusion of alkaline solutions, in order to make the technique technologically feasible for application to carbonated reinforced concrete structures.

Estimation of the Type, Concentration and pH of the Alkaline Solutions

In the preliminary stage of the study, the accumulation of crystals on the surface of the specimens immersed in the sodium hydroxide solution (NaOH) with a concentration of 21g/100ml was seen (Fig. 3). For this reason, there is a need to study and estimate the type, concentration and the pH of the best alkaline solution to be employed in the realkalisation by absorption and diffusion of the carbonated specimens, without using the electrical current.

Evaluation of the Influence of the Alkaline Solutions on Compressive Strength

In order to assess the influence of the realkalisation process on the compressive strength, thirty mortar specimens (5 x 10 cm) were made according to Brazilian Standards (9) in a mixture proportion of 1:5 (portland cement type II-Z¹ and washed sand) and w/c of 0.50, stripped after 24 hours and placed in a humid chamber for 7 days.

¹ Cement portland type II-Z is a kind of cement with 6-14% of pozzolanic material, 0-10% of carbonatic material and 76-94% of clinker and gypsum.

Before beginning the accelerated carbonation, the specimens were placed in a room for 19 days, at controlled room temperature ($25 \pm 5^\circ\text{C}$) and RH ($50 \pm 10\%$), until the specimens reached a balance with the controlled room RH. The stabilization control was made by successive measurements of mass.

The measurements of the carbonation and realkalisation progress were performed right after take away small specimen's fragments, with the use of an alcoholic solution of phenolphthalein diffused in the carbonated specimens and of thimolphthalein in non-realkalised specimens.

Once the carbonation and realkalisation of the mortar specimens were made in different alkaline solutions, three specimens were tested, in order to make a comparative study of the results obtained. When analyzing the results, it was possible to observe that the alkaline solutions had an influence on the compressive strength of the specimens. Table 1 shows the number of molded specimens to be investigated for compressive strength in the different situations studied.

Bond Strength Tests on the Realkalised Substrate

Six premolded boards provided by SENAI-SP were used in the adherence resistance to traction tests of coatings applied to realkalised substrates. The boards were molded according to Brazilian Standards (10). The specification requires that the concrete of the standard substrate is made with portland cement, sand and crushed stone, in a mixture proportion of 1:2.58:1.26, water/cement between 0.45 and 0.50 and a minimum amount of cement of 400 kg/m^3 .

The purpose of this study was to investigate the influence of the realkalisation on the bonding of industrial mortars (11,12) applied to realkalised substrates. In order to do so, premolded boards of standardized concrete were used as the reference substrate. Some of these boards were carbonated and others carbonated and realkalised. The realkalisation was made only with solutions selected from the results obtained in previous study.

The six boards were divided in two groups, in each group different industrial mortars was used (Table 2).

In each board, ten different results, corresponding to one system investigated, were obtained. Fig. 4 shows the coating scheme applied on the premolded board.

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The mean depth of the carbonation and realkalisation for this study was 5 mm, since the purpose of this study is only to evaluate the contact between the realkalised substrate surface and the coatings applied.

APPLICATION

Carbonation Test

The carbonated specimens that were further realkalised had their dimensions and mixture proportions established according to Table 3.

The equipment employed to the accelerated carbonation test was the carbonation chamber provided by the LMC-UFG (Figs. 5a and b). The carbonation was made with the carbonic gas with the concentration of 100%, with internal RH between 50 and 70% and internal temperature controlled at $25 \pm 5^\circ\text{C}$.

The progress of the carbonation depth was observed using phenolphthalein. The result shown in Fig. 6 indicates that the specimen used as parameter for other studies, was completely carbonated before the realkalisation. This way, it was possible to see that all specimens, before being realkalised, were fully carbonated.

Estimation of the Type, Concentration and pH of the Alkaline Solutions

The pH of the Na_2CO_3 , NaOH, KOH and TRIPLE solutions, as well as their solubility are listed in Table 4. Based on the preliminary evaluations, three solutions were selected to be employed in the research. The concentrations used are shown in Table 5.

Realkalisation Tests

The progression of the realkalisation front was investigated using a thimolphthalein solution, due to the more increased pH, between 9.3 and 10.5, providing a greater safety in the pH evaluations inside the concrete, after the realkalisation.

Fig. 7 shows the progression of the realkalisation front in carbonated specimens for the three solutions investigated. Solution 2 was the one which showed the best

performance in relation to the realkalisation time, followed by solution 3 and 1. While solution 1 took 840 hours (35 days) to be realkalised, solution 2 was realkalised in only 686 hours (nearly 28 days).

Evaluation of the Influence of the Alkaline Solutions on Compressive Strength

Some tests to assess the influence of the realkalisation on compressive strength show that the concrete compressive strength significantly increased (4). On the other hand, other test show a 10% decrease in compressive strength, compared to the reference specimens and those realkalised through the diffusion/absorption (8). The decrease in compressive strength is suggested to be caused by the formation of new compounds or by the non-stabilized microstructure within the realkalised concrete.

In this investigation, as shown in Fig. 8, an increase in compressive strength was seen, when comparing the results of the reference specimens and the realkalised specimens, except when using solution 2. This is contrary to some other results (8). This difference can be explained by the fact that the realkalised specimens were immersed in alkaline solutions, unlike the reference and the carbonated specimens, providing the specimens a better curing and consequently a better hydration of the cement. In this case, the best result was shown by solution 1, followed by solution 3 and 2.

Bond Strength Tests on the Realkalised Substrate

As solution 3 had an intermediate performance in terms of compressive strength and degree of realkalisation, the one selected to be employed in the bond strength test was the solution analyzed to realkalise the carbonated substrate.

Although some authors believe that the realkalisation damages the adherence of coatings of the realkalised substrates, the results achieved in this investigation show that the mortar adherence on the realkalised substrate, when compared to the reference substrate, showed a slight increase of 2% with the adhesive industrialized mortar type I (Fig. 9) and of 2.5% for type II (Fig. 10). These results are higher than the minimum value required, which is about 0.50 Mpa (11).

CONCLUSIONS

The realkalisation by diffusion/absorption showed to be an effective technique in order to prevent corrosion of the reinforced concrete, and for the rehabilitation of structures where the carbonation front has already reached the reinforced steel.

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The investigation shows that inside the structure, the realkalisation does not only produce a physical phenomenon, but it may also yield chemical reactions. The results presented in this paper show an increase in compressive strength. However, it is well known that this only occurs because the specimens were immersed in solutions with water during the realkalisation, providing a greater hydration of their compounds inside the structure.

The results obtained demonstrate that solution 3 presented the best performance. In terms of time of realkalisation and compressive strength, solution 2 caused a decrease in compressive strength and solution 1, when compared to solution 3, needed a shorter period of time to be realkalised, that is, 336 hours (14 days).

Solution 3 showed that it does not interfere with the results obtained in the bond strength test. On the contrary, it presented a bonding strength higher than the values found for the reference substrate.

REFERENCES

1. EGGERS, M.; OLIVEIRA, P. S. F. Realcalinização e dessalinização: novas técnicas eletroquímicas de recuperação de estruturas de concreto. *Téchne*, n. 30, p. 41-45, set./out. 1997.
2. ODDEN, L. The repassivating effect of electro-chemical realkalisation and chloride extraction. In: *International Conference on Corrosion and Corrosion Protection of Steel in Concrete*. Anais. University of Sheffield, 1994, p. 1473-1488.
3. KENNEDY, D.; MILLER, J. B.; NUSTAD, G. E. Review of chloride extraction and re-alkalisation of reinforced concrete. *NTC*, Paper n. 53, 1995.
4. BANFILL, P. F. G. Re-Alkalization of carbonated concrete – effect on concrete properties. *Construction and Building Materials*, nº 11, p. 255 – 258, Elsevier, 1997.
5. MILLER, J. B. The perception of the ASR problem with particular reference to electrochemical treatments of reinforced concrete. In: *EUROCORR 97 – Corrosion of reinforcement in concrete: monitoring, prevention and rehabilitation*. Anais. Trondheim, Norway, 1998, p. 141-149.
6. MIETZ, J.; Electrochemical rehabilitation methods for reinforced concrete structures, *European Federation of Corrosion Publications*, n. 24, 1998.
7. FOSROC. Compatibility of coatings applied over realkalised and desalinated concrete. *Fosroc International Limited*, sd. 12p.
8. TEIXEIRA, F. A. Realcalinização do concreto carbonatado empregando solução rica em álcalis. Goiânia, 2002. 150p. Dissertação (Mestrado) – Curso de Mestrado em Engenharia Civil, Universidade Federal de Goiás.

9. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 7215. Cimento Portland – Determinação da resistência à compressão. Método de Ensaio. Rio de Janeiro, 1996.
10. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 14082. Argamassa colante industrializada para assentamento de placas cerâmicas – Execução do substrato padrão e aplicação de argamassa para ensaios. Método de Ensaio. Rio de Janeiro, 1998.
11. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 14081. Argamassa colante industrializada para assentamento de placas cerâmicas – Especificação. Rio de Janeiro, 1998.
12. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 14084. Argamassa colante industrializada para assentamento de placas cerâmicas – Determinação da resistência de aderência. Método de Ensaio. Rio de Janeiro, 1998.
13. WEAST, R. C.; SELBY, S. M.; HODGMAN, C. D. Handbook of Chemistry and Physics. 46TH Edition, Cleveland, The Chemical Rubber CO, 1964.

Table 1 – Number of molded specimens to be investigated for compressive strength, in different situations.

Situation		Specimen number	
		For control	For study
Reference		–	03
Carbonation		03	03
Realkalisation	Na ₂ CO ₃ (Solution 1)	04	03
	KOH (Solution 2)	04	03
	TRIPLE - Na ₂ CO ₃ + KOH+NaOH (Solution 3)	04	03

Table 2 – Adherence strength system used for each board situation.

System	Situation	Number of board
Internal industrial mortar (AC-I)	Reference	1
	Carbonation	1
	Realkalisation	1
External industrial mortar (AC-II)	Reference	1
	Carbonation	1
	Realkalisation	1

Table 3 – Format, dimensions and mixture proportions of the body-of-test for each study

Material	Specimens	Essay		Mixture proportions
Mortar	Cylinder (5 x 10 cm)	Compressive strength		1:3:0.5
Concrete	Prismatic (25 x 50 x 2 cm)	Adherence strength	Internal industrial mortar	Premolded
			External industrial mortar	Premolded

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Table 4 – Compounds solubility in grams/ml (13) and the solutions pH obtained in laboratory.

Compounds	Cold water	Hot water	pH
KOH	107 ^{13*}	178 ^{100*}	13
NaOH	42 ^{0*}	347 ^{100*}	14
Na ₂ CO ₃	7.10 ^{0*}	45.5 ^{100*}	12
TRIPLE (Na ₂ CO ₃ , NaOH, KOH)	–	–	13

*Water temperature (°C)

Table 5 – Concentration of the alkaline solutions used in the realkalised mortar specimens.

	Na ₂ CO ₃	NaOH	KOH	pH
Solution 1	10 g/100 ml	–	–	12
Solution 2	–	–	15 g/100 ml	13
Solution 3	3 g/100 ml	1.5 g/100 ml	5 g/100 ml	13

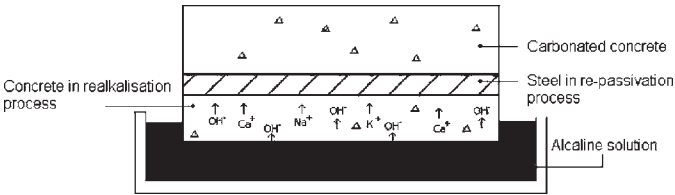


Fig. 1 Realkalisation process by absorption and diffusion.

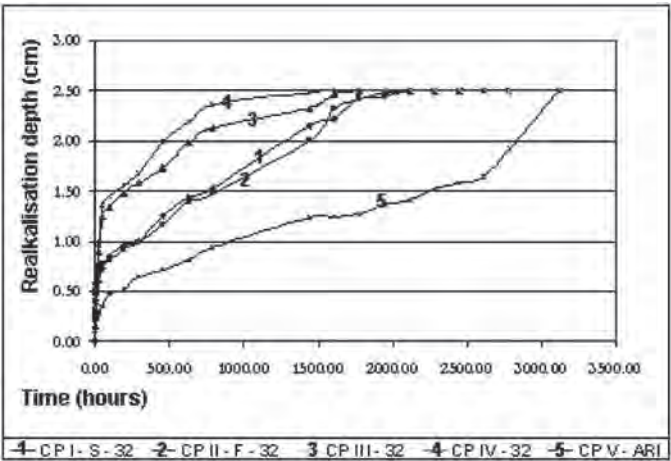


Fig. 2 Realkalisation with a w/c of 0.40 (Texeira (8)).



Fig. 3 NaOH crystals in the surface of the realkalised specimens.



Fig. 4 Coating scheme applied on the premold board.

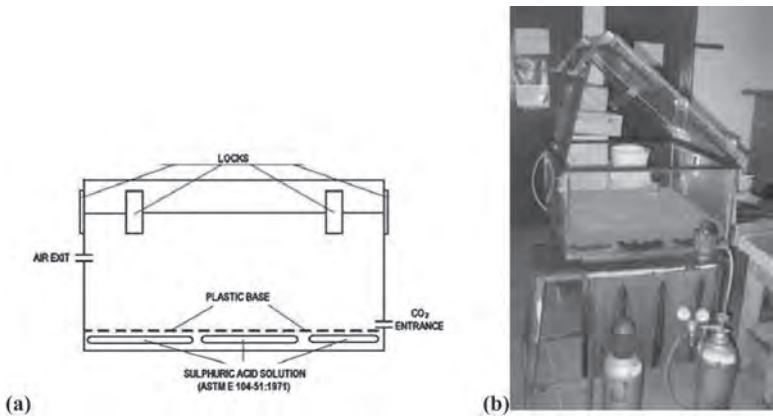


Fig. 5 Carbonation chamber scheme (a). Carbonation chamber used (b).

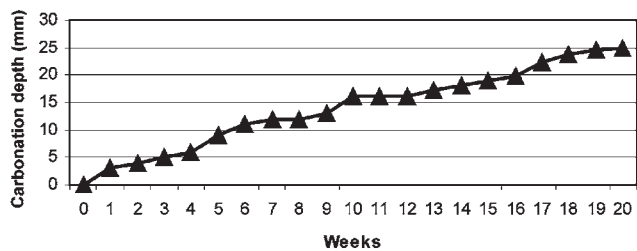


Fig. 6 Advance of the depth carbonation in specimens.

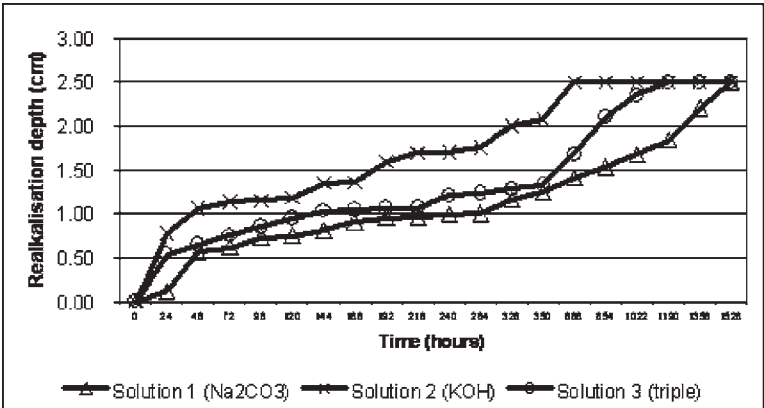


Fig. 7 Realkalisation progress in carbonate specimens.

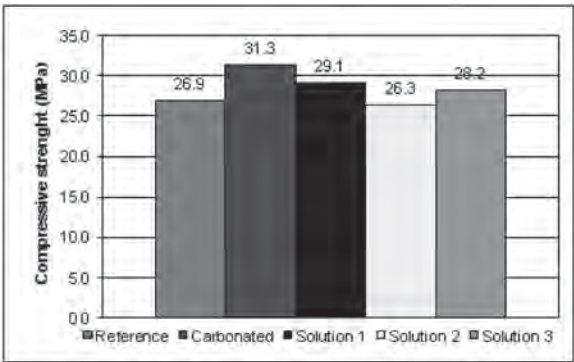


Fig. 8 Compressive strength in referenced carbonated and realkalised specimens with three different alkaline solutions.

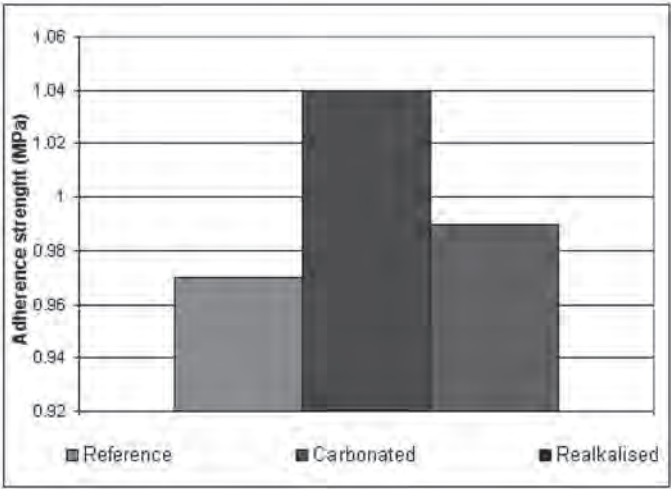


Fig. 9 Adherence strength of mortar coatings type AC-I in different substrates.

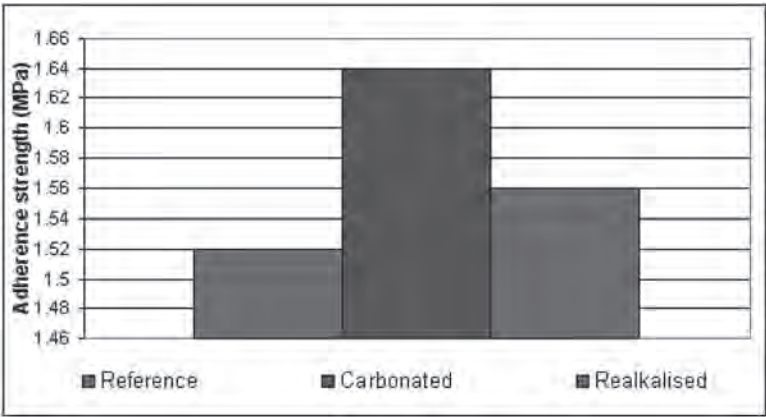


Fig. 10 Adherence strength of mortar coatings type AC-II in different substrates.

Effects of Binder Materials on the Properties of Polystyrene Aggregate Concrete

by R. Sri Ravindrarajah, V. DiFalco, and S. Surian

Synopsis: Lightweight concrete could be producing by incorporating expanded polystyrene in the conventional concrete. This paper discusses the results of an experimental investigation into the effects of binder materials on the engineering properties of polystyrene aggregate concrete (PAC), having the nominal density of 1800 kg/m^3 . Four types of binders, namely, general purpose cement, shrinkage limited cement, a combination of 60% general purpose cement and 40% low calcium fly ash, and blended cement with 62% granulated blast-furnace slag, were used. The results showed that as expected, the use of supplementary cementitious materials such as fly ash and slag reduced the early-age strength of the polystyrene aggregate concrete. The strength development of PAC was also affected by the curing condition. Although the use of shrinkage limited cement reduced the shrinkage of PAC by 12%, it increased the creep potential by 76%. The paper also discusses the relationships between: shrinkage and moisture loss; strength and rebound number; and strength and pulse velocity.

Keywords: blast-furnace slag; cement; creep; curing; fly ash; modulus; polystyrene beads; shrinkage; strength

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INTRODUCTION

Polystyrene aggregate concrete (PAC) consists of conventional concrete-making materials and lightweight expanded polystyrene beads. By varying the content of the polystyrene beads, the density of concrete can be adjusted to obtain lightweight concrete with the density ranging from 1200 to 2000 kg/m³. A chemical coating on the beads helps to avoid segregation through its bonding characteristics with the surrounding cement paste. A significant research program on the development and properties of PAC has been conducted for over 10 years at the University of Technology, Sydney and the findings were reported elsewhere (1-7).

Supplementary cementitious materials, namely fly ash and ground granulated blast furnace slag, are commonly used with ordinary portland cement to produce structural concrete mixtures, which exhibit distinctive characteristics such as low heat of hydration, low permeability, and improved chemical resistance.

This paper reports the results of an investigation into the effects of the binder material on the engineering properties of PAC, having a nominal density of 1800 kg/m³. Four types of binder combinations were used. The same concrete mixture composition was used and the concrete mixtures were tested for their fresh and hardened properties. Workability, compressive strength development under moist-curing and air-drying conditions, tensile strength, flexural strength, modulus of elasticity, drying shrinkage and compressive creep are reported. The relationship between moisture loss and drying shrinkage as affected by the binder type is discussed. Non destructive testing methods, such as rebound number and ultrasonic pulse velocity, were used to establish the appropriate relationships of these with compressive strength.

RESEARCH SIGNIFICANCE

Lightweight polystyrene aggregate concrete (PAC) is a suitable material for structural, semi-structural and non-structural applications. Fly ash and ground granulated blast-furnace slag could be used in PAC as partially replacement to environmentally unfriendly portland cement. The research significance of this study is to evaluate the engineering properties of PAC containing fly ash and slag. The effects of using of shrinkage-limited cement on the properties of PAC are also studied.

EXPERIMENTAL DETAILS

Materials and compositions for concrete mixes

The binder materials used are general purpose (GP) cement, shrinkage limited (SL) cement, general blended (GB) cement with 62% blast-furnace slag content, and a combination of 60% GP cement and 40% low calcium fly ash. Commercially available Types GP, SL and GB cements are produced in accordance with the Australian Standard AS3972 (8). Low calcium fine grade (over 75% passing 45 micron sieve) fly ash, complying with the Australian Standard AS3582.1 (9), from NSW, Australia was used. Crushed basalt (10 mm maximum size) and river sand were used as coarse and fine aggregates, respectively. Commercially available, chemically-coated expanded polystyrene beads (3 mm mean diameter) were used. The chemical coating initiates bonding with cement paste and to achieve uniform dispersion within the concrete mixture without segregation. The particle density of the beads is 55 kg/m^3 .

Following a number of trial mixtures, a mixture composition for PAC was developed to obtain a wet density of 1800 kg/m^3 having adequate workability and strength. The mixture composition was as follows: 545 kg/m^3 of binder; 750 kg/m^3 of river sand; 415 kg/m^3 of basalt coarse aggregate; 230 kg/m^3 of free water; and 9 kg/m^3 of polystyrene beads. Since it is possible for the admixtures to have varying influences with different binder types, no chemical admixture was used.

Batching and Mixing of Polystyrene Aggregate Concrete

The mixing procedure outlined by Sri Ravindrarajah and Tuck (1) was used to produce the PAC mixtures. Aggregates were pre-dried in the laboratory environment. Basalt coarse aggregate and river sand were first placed into a pan-type mixer with a fine sprinkle of water. They were mixed for 1.5 minutes. The binder materials were then added and the mixing was carried out for an additional 1.5 minutes. A fine sprinkle of water was added again prior to mixing. Then, a quarter of the mixing water was added and the mixing was started again. During the final mixing, the remaining water and polystyrene beads were added gradually and mixing was continued for about 3 minutes. This mixing method for PAC was found to be successful in that all aggregate particles

were coated with the binder paste. In addition, the polystyrene beads were uniformly distributed throughout the concrete mixture.

Testing of fresh polystyrene aggregate concrete

Workability of polystyrene aggregate concrete was assessed using the standard tests, such as slump test (AS1012.3) (10) and the compaction index test (DIN1048: Part 1) (11). The compaction index is defined as the volume ratio of the uncompacted concrete without vibration to compacted concrete with vibration. Therefore, the compaction index, which is always equal to or more than 1, measures the degree of compaction without vibration and increases with the decrease in the workability of concrete.

Casting and curing of the test specimens

For each concrete mixture, thirty 100 by 200 mm high cylinders, twelve 150 by 300 mm cylinders, and three 100 by 100 by 500 mm prisms were cast in steel molds for tests of hardened concrete. The specimens were compacted on a vibrating table and demolded 24 hours after casting. Table 1 gives the details of the tests performed and conditions of curing used. Six large cylinders (150 mm diameter by 300 mm high) for creep, shrinkage and strength testing were water cured for 7 days and stored in the uncontrolled laboratory environment, having the mean temperature and humidity of 20°C and 65% R.H thereafter.

Testing of Hardened Concrete

Testing of hardened concrete specimens for its compressive, tensile and flexural strengths, and modulus of elasticity were carried out in accordance with AS 1012 (12-15) at the appropriate ages as shown in Table 1.

At the age of 28 days, two 150 mm by 300 mm cylinders were loaded in a specially designed creep rig. Four companion cylinders were stored under the same conditions. Three of them were tested for the compressive strength at 28 days and the fourth was used to determine the drying shrinkage from the start of drying (7 days). The shrinkage measurements were made using a demountable mechanical strain gauge over two 150mm gauge lengths at the diagonally opposite locations at the middle part of the specimen.

The creep cylinders were loaded to 30% of the compressive strength, obtained with the three companion cylinders. The applied load was sustained for 90 days in the creep rig. The longitudinal strain variation with time after loading was measured over 200 mm gauge length on the diagonally opposite sides of each cylinder. The reported results are the mean of four readings taken on two identical cylinders. From the total time dependent strain, the shrinkage strain from the time of loading was deducted to obtain the creep strain.

Non-destructive testing methods such as rebound number and pulse velocity were conducted in accordance the relevant ASTM Standards procedures (16).

RESULTS AND DISCUSSION

Properties of fresh polystyrene aggregate concrete

Table 2 summarises the properties of fresh concrete mixtures. The density of the fresh PAC ranged from 1800 to 1855 kg/m³. Hence, the change of binder material had a marginal effect on the density. Ease of placing, compacting and finishing of polystyrene aggregate concrete showed a good correlation with the measured slump of concrete.

PAC with fly ash showed improved workability compared with the control concrete with Type GP cement. Since the high density cement (3150kg/m³) was partially replaced on equal mass basis with a lower density fly ash (2400kg/m³), the binder paste volume in fly ash concrete increased. In addition, the fly ash particles are spherical in shape compared with angular cement particles. These two factors contributed to the observed improvement in the workability of concrete. Furthermore, the increased surface area of the binder materials (fly ash and cement) may have reduced the bleeding tendency of the concrete with fly ash. The slump and compaction index values clearly identified the increased workability of PAC with fly ash. Although the ground granulated blast furnace slag particles (2900 kg/m³) have a lower density than the cement particles (3150 kg/m³), both of them are angular in shape due to the grinding process used in producing them.

Based on the compaction index, three ranges of apparent workability for normal weight concrete have been recognized, as shown in Table 3. Bartos (17) stated that the main advantage of the compaction index test over the slump test is that it provides a useful test of compactability of concrete through normal means of vibration. Sabaa and Sri Ravindrarajah (3) reported the correlation between slump and compaction index for polystyrene aggregate concrete.

Placability and finishability of polystyrene aggregate concrete

Over vibration of the PAC mixtures was found cause the beads to rise to the surface, which could significantly affect the uniformity of strength. In addition, finishing the cast concrete surface was at times found to be difficult as the beads tended to stick to the trowel. This problem was solved by delaying finishing until 20 to 30 minutes after casting. Hence, strict adherence to the correct construction practices is needed to ensure that the placement of PAC does not influence adversely the desired concrete properties.

Effect of binder material on compressive strengths development

Figure 1 shows the development of the compressive strength of water-cured PAC with age. PAC with Type GP cement showed highest strength at all ages and the use of blended cement and fly ash reduced the early-age and long-term strength. Figure 2 shows the strengths of the PAC with other binders relative to the strength of PAC with Type GP cement at the same age.

Although the density of concrete was maintained around 1800 kg/m^3 , both the early-age and later-age compressive strength of PAC are affected by the binder material used (Figure 2). The compressive strength of the mixture with Type SL cement is lower than with Type GP cement at all ages. For water-curing condition, the relative strength fluctuated from 0.85 to 0.96 and no clear trend with the age was noted. For air-storage condition, the same ratio varied from 0.82 to 0.94. Differences in chemical composition and fineness for Types GP and SL cements may have contributed to the strength difference. Manufacturer's information revealed that the tricalcium silicate content of Type SL cement is 65% compared with 66% for Type GP cement. Magnesium oxide contents of Types GP and SL cements are 0.1% and 1.1%, respectively. Manufacturer's data indicated that the Blaine's values for the specific surface area for Types GP and SL cements are 385 and $360 \text{ m}^2/\text{kg}$, respectively.

When portland cement is partially replaced with fly ash or slag, more significant strength reductions were observed. The compressive strength of water-cured PAC with 40% fly ash at 3 days and 91 days were 0.59 and 0.77 of the concrete with Type GP cement at the same respective ages. PAC with 62% slag showed relative strength values of 0.52 and 0.76 at the ages of 3 and 91 days, respectively. The slow hydration reactions of fly ash and slag contributed to the improvement in the relative strength with age.

Figure 3 shows the influence of the binder material on the strength development in relation to the 28-day strength. Similar to normal weight concrete, the slow hydration reactions of fly ash and slag contribute to the later age strengths of PAC.

Moisture loss in PAC test cylinders due to drying in air

Moisture in concrete is essential for the hydration reactions to continue and hence development of strength. According to Powers (18), for cement hydration to continue the relative humidity inside the concrete has to be maintained above 80%. Below this humidity, the capillary pores will have insufficient moisture to sustain hydration. Hydration products require water-filled voids in order to precipitate.

Figure 4 shows the mean mass loss with time for PAC cylinders. PAC with 40% fly ash showed 4.2% weight loss over 91 days compared with the loss of 2.65% for PAC with Type GP cement. Any difference in the rate of drying is due to the existing differences in the internal pore structure of the hardened paste related to hydration of fly ash and cement. In addition, the concrete with cement and fly ash may contain more unbound free water than that in the concrete with cement alone.

Effect of curing condition on the compressive strength of PAC

Figure 5 shows the development of compressive strength of PAC specimen stored in air. Although strength increased with age, it has stabilised at 28 days. This effect is clearly seen from Figure 6, which shows the strength up to 91 days relative to the corresponding strength for PAC with Type GP cement. The strength of PAC with 62% slag is 45% and 66% of the corresponding strengths of PAC with Type GP cement, at 3 and 91 days, respectively. The corresponding values for water cured PAC are 52% and 76%, at the

respective ages. Thus, the absence of water curing slowed the hydration reactions of the granulated slag component in the Type GB cement.

Figure 7 shows the influence of improper curing on the compressive strength of PAC as affected by the binder material type. When the specimens were allowed to dry in air, they lost significant amounts of their potential strengths, and the strength losses increased with increasing age. At 91 days, strength losses of 28% and 43% occurred for PAC with Types GP and SL, respectively. The corresponding strength losses for the PAC with 40% fly ash and 62% slag were 28% and 47%, respectively. Beyond the age of 28 days, the strength reduction is mainly due to the increasing strength of PAC under water-cured condition, since the PAC stored in air had marginal strength increase beyond the age of 28 days (Figure 6). The water-cured PAC with 40% fly ash increased 33% in strength from 28 to 91 days compared to only 6% during the same period under air-drying condition.

Figure 8 shows the age factor of PAC allowed to dry in air. The results show marginal strength improvement beyond 28 days. PAC with Type SL cement showed the highest rate of relative strength development at the early ages, whereas the PAC with 40% fly ash showed the lowest strength development rate at these early ages. Therefore, it can be said that the binder type has a significant influence on the early age strength of PAC allowed to dry.

Non-destructive testing of PAC

Two non-destructive test methods, namely rebound number and ultrasonic pulse velocity, could be used to estimate the compressive strength of concrete. Figure 9 correlates the rebound number to the compressive strength of concrete. Although significant scatter is noted, cylinder strength is generally linearly proportional to the rebound number and affected by the curing condition. Drying causes the surface hardness of the concrete to increase, thus affecting the strength-surface hardness relationship. Figure 10 shows that the compressive strength increases exponentially with the increase of the pulse velocity, independent of the binder material used. A value of 0.94 was obtained as the correlation coefficient for this relationship.

Tensile and Flexural strengths and Elastic Modulus of PAC

Table 4 summarises the compressive, tensile and flexural strengths and the modulus of elasticity of water-cured PAC at 28 days. The tensile strength of PAC varied between 11.2% and 12.9% (mean value of 12.1%) of the compressive strength, whereas the flexural strength varied from 19.2% to 20.8% (mean value of 20.2%) of the compressive strength. The modulus of elasticity of PAC varied from 15.3 to 18.9 GPa, and PAC with 40% fly ash showed the lowest value for the elastic modulus.

Influence of binder material on drying shrinkage of PAC

Figure 11 shows the free drying shrinkage with time for four PAC mixtures. PAC with 62% slag showed the highest shrinkage, and the lowest shrinkage occurred with Type SL

cement. Table 5 summarises the measured drying shrinkage after 28 and 110 days. The ultimate shrinkage was estimated using the Ross equation (19).

PAC with Type SL cement showed 10% reduction in the 110-day shrinkage compared with PAC with Type GP cement. In contrast, PAC with 40% fly ash and 62% slag showed 9% and 12% more shrinkage, respectively, than PAC with Type GP cement. Considering ultimate shrinkage, PAC with Type SL cement had 12% lower shrinkage, whereas PAC with fly ash and slag had 14% and 7% greater shrinkage when compared with PAC with Type GP cement.

Drying shrinkage and Moisture Loss Relationship

Figure 12 shows that the relationship between drying shrinkage and water loss is influenced by the type of binder. Shrinkage of PAC with 40% fly ash is less sensitive to water loss compared with the other mixtures. Figure 4 shows that PAC with fly ash dried at a faster rate than the other mixtures. Since free water lost from air voids and large capillary pores produces little shrinkage, it is possible that majority of water lost from PAC with fly ash is of this type. On the other hand, water lost from fine capillary and gel pores is responsible for the majority of observed shrinkage (20).

Influence of binder material on compression creep

Table 6 summarizes the creep data under sustained compressive loading. The creep coefficient, which is defined as the ratio of the creep strain to the instantaneous strain, was calculated at all ages. Figure 13 shows the development of creep coefficient for the four mixtures. Table 7 shows the specific creep (creep per unit stress) and creep coefficient at 90 days. Relative specific creep and creep coefficient are shown relative to the values with Type GP cement. PAC with Type SL cement showed the highest creep coefficient, this is opposite to drying shrinkage. PAC with fly ash and slag showed significantly reduced creep compared with PAC with Type GP cement.

CONCLUSIONS

From the results obtained, the following conclusions are made about the effects of binder type on the properties of polystyrene aggregate concrete:

1. Cement replacement with 40% fly ash and 62% ground granulated blast-furnace slag reduced the early-age strength of concrete compared with the control concrete with Type GP cement.
2. The compressive strength of PAC specimens allowed to air dry was stabilized at 28 days, independent of the binder type. The ratios of tensile and flexural strengths to compressive strength were not affected by binder type.
3. Drying shrinkage after 110 days of PAC mixtures with fly ash or slag were slightly higher (by 9 to 12%) than the PAC mixture with Type GP cement.

4. Compressive creep coefficients after 90 days for mixtures with fly ash or slag were 21% and 48% lower than for the control PAC with Type GP cement.
5. The use of shrinkage limited cement (Type SL) reduced the 110-day drying shrinkage by 12% but caused a 78% increase in the 90-day compressive creep coefficient compared with the control mixture.
6. The relationship between drying shrinkage and moisture loss depends on the binder type.
7. Compressive strength of PAC independently correlates with rebound number and ultrasonic pulse velocity.

REFERENCES

1. Sri Ravindrarajah, R. and Tuck, A.J., Properties of polystyrene aggregate concrete, Proceedings of the 13th Australasian Conference on the Mechanics of Structures & Materials, July 5-7, 1993, Wollongong, Australia.
2. Sri Ravindrarajah, R. and Naji, B. T., Internal sulphate attack on polystyrene concrete, Proceedings of the 6th International Conference on Durability of Building Materials and Components, October 26-29, 1993, Omiya, Japan.
3. Sabaa, B.A., and Sri Ravindrarajah, R. , Workability assessment for polystyrene aggregate concrete, Proceedings of the CONPAT 99: V IBEROAMERICAN Congress of Building Pathologies, VII Quality Control Congress, 18-21 October 1999, Montevideo, Uruguay.
4. Sri Ravindrarajah, R., Bearing strength of concrete containing polystyrene aggregate, Proceedings of the 8th RILEM Conference on the Durability of Building Materials & Components, Vancouver, Canada, 1999, pp. 505-514.
5. Sabaa, B.A., and Sri Ravindrarajah, R., Investigation of pull-out strength between polystyrene aggregate concrete and reinforcing steel, Proceedings of the Second International Symposium on Structural Lightweight Aggregate Concrete, 18-22 June 2000, Kristiansand, Norway, pp. 729-736.
6. Sri Ravindrarajah, R. and Sivakumar, R., Effect of polystyrene particle shape on the properties of lightweight concrete, Proceedings of the South African Conference on Polymers in Concrete, July 2000, Kruger National Park, South Africa.
7. Sri Ravindrarajah, R. and Jones, W., Engineering properties of adjusted density high-performance concrete using expanded polystyrene aggregate, Proceedings of Conference in Advances in Structures: Steel, Concrete, Composites and Aluminium, 23-25, June 2003, Sydney, Australia.
8. Standards Australia, AS3972: Portland and blended cements, 1997.
9. Standards Australia, AS3852: Part 1, Supplementary cementitious materials for use with portland and blended cement - Fly ash, 1998.
10. Standards Australia, AS1012.3: Methods of testing concrete: Methods for determination of properties related to the consistence of concrete, 1983.
11. DIN1048.1: Part 1, Chapter 3.1.1, Concrete according to German standards (Edited by B. Dartsch), Dusseldorf: Beton-Verlag, 1977, pp. 50-52.

42 Sri Ravindrarajah et al.

12. Standards Australia, AS1012.9 – Methods of testing concrete – methods for determination of compressive strength of concrete specimens, 1986.
13. Standards Australia, AS1012.10 – Methods of testing concrete – methods for determination of indirect tensile strength of concrete cylinders, 1985.
14. Standards Australia, AS1012.11: Methods of testing concrete – Methods for determination of flexural strength of concrete specimens, 1985.
15. Standards Australia, AS1012.17: Methods of testing concrete – Methods for determination of the static chord modulus of elasticity Poisson's ratio of concrete specimens, 1997.
16. American Society for Testing Materials – C 805-85: Test for rebound number for concrete; C 597-83: Test for pulse velocity through concrete.
17. Bartos, P., Fresh concrete: Properties and Tests, Elsevier, Amsterdam, 1992.
18. Powers, T.C., A discussion of cement hydration in relation to the curing of concrete, Proc. Highway Research Board, Vol. 27, 1947, pp. 178-188.
19. Ross, A. D., Concrete creep data, The Structural Engineer, Vol. 15, London, 1937, pp. 314-326.
20. Powers, T. C., Causes and control of volume changes, Journal of Portland Cement Association Research and Development Laboratories, Vol. 1, No. 1, Jan. 1959, pp. 29-39.

Table 1: Tests details for the hardened polystyrene aggregate concrete

Test	Specimen size	Curing	Test ages (days)	Nos.
Compressive strength	100 mm dia. x 200 mm	Water at 20°C	3, 7, 14, 28 & 90	15
Compressive strength	100 mm dia. x 200 mm	Laboratory (70% RH & 22°C)	3, 7, 14, 28 & 90	15
Splitting tensile strength	150 mm dia. x 300 mm	Water at 20°C	28	2
Flexural strength	100 x 100 x 500 mm	Water at 20°C	28	3
Pulse velocity	100 x 100 x 500 mm	Water at 20°C	1, 3, 7, 14 & 28	1
Dynamic modulus	100 x 100 x 500 mm	Water at 20°C	1, 3, 7, 14 & 28	1
Static modulus	150 mm dia. x 300 mm	Water at 20°C	28	2
Drying shrinkage	150 mm dia. x 300 mm	7 days in Water + Lab.	7 to 120 days	1
Compressive strength	150 mm dia. x 300 mm	7 days in Water + Lab.	28	3
Compression creep	150 mm dia. x 300 mm	7 days in Water + Lab.	28 to 120 days	2

Table 2: Properties of fresh polystyrene aggregate concrete

Binder	Slump (mm)	Compaction Index	Wet Density (kg/m ³)
GP	20	1.116	1840
60% GP + 40% F	50	1.083	1800
GB (62% S)	40	1.093	1845
SL	35	1.103	1855

Note: GP - General purpose cement; GB - General blended cement;
SL - Shrinkage limited cement; F - Fly ash; S - Ground granulated blast-furnace slag

Table 3: Correlation between compaction index and workability (18)

Compaction Index	Apparent Workability
1.26 to 1.40	Low
1.11 to 1.25	Medium
1.04 to 1.10	High

Table 4: Summary of the properties of PAC at the age of 28 days

Binder	Compressive strength (MPa)	Tensile strength (MPa)	Flexural strength (MPa)	Elastic Modulus (GPa)
GP	22.9	2.88	4.40	18.5
60% GP + 40% F	15.9	1.83	3.28	15.3
GB (62% S)	18.6	2.09	3.87	16.8
SL	20.8	2.68	4.18	18.9

Table 5: Summary of the drying shrinkage (microstrain) of PAC

Binder	28-day shrinkage	110-day shrinkage	Ultimate shrinkage
GP	348 (100%)	636 (100%)	707 (100%)
60% GP + 40% F	369 (106%)	692 (109%)	804 (114%)
GB (62% S)	485 (139%)	712 (112%)	755 (107%)
SL	283 (81%)	571 (90%)	619 (88%)

Table 6: Summary of the compressive creep (microstrain)

Binder	Sustained stress (MPa)	Instantaneous strain ($\times 10^{-6}$)	90-day Creep strain ($\times 10^{-6}$)
GP	7.25	421	587
60% GP + 40% F	5.53	475	527
GB (62% S)	5.43	454	330
SL	6.22	259	641

Table 7: Summary of the specific creep and creep coefficient of PAC at 90 days

Binder	Specific creep 10 ⁻⁶ /MPa	Creep coefficient	Relative Spec. creep	Relative Creep coefficient
GP	81.0	1.39	1.00	1.00
60% GP + 40% F	95.3	1.10	1.18	0.79
GB (62% S)	60.8	0.73	0.75	0.52
SL	103.1	2.47	1.27	1.78

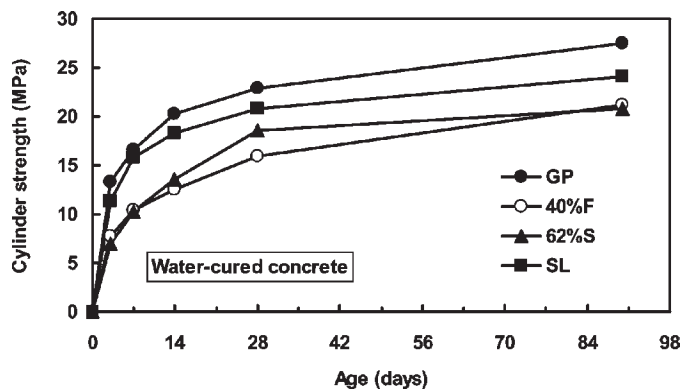


Figure 1—Compressive strength development with age for water-cured PAC.

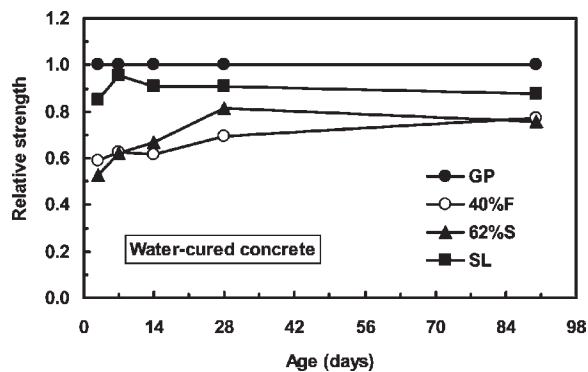


Figure 2—Relative compressive strength development with age for water-cured PAC.

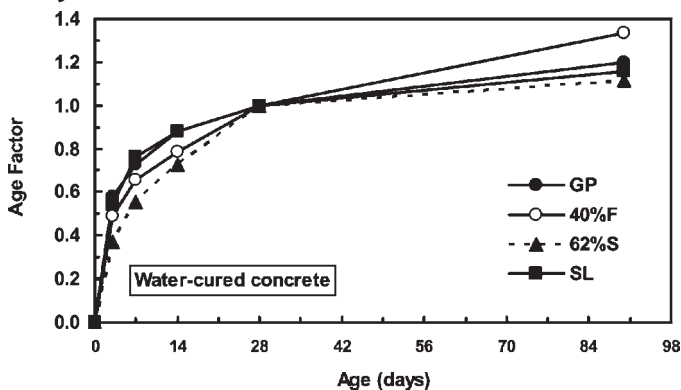


Figure 3—Development of age factor with age for water-cured PAC.

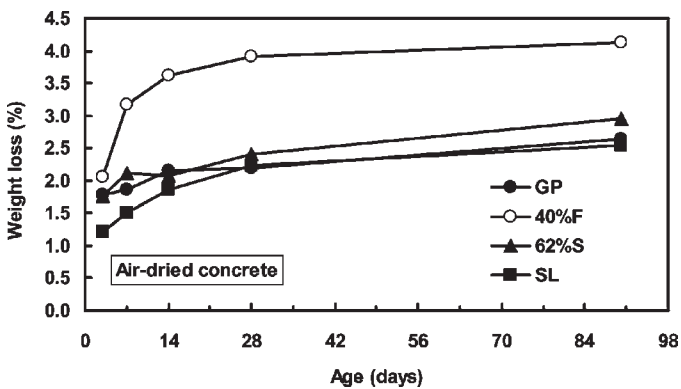


Figure 4—Mass loss in PAC test cylinders (100 by 200 mm) stored in air.

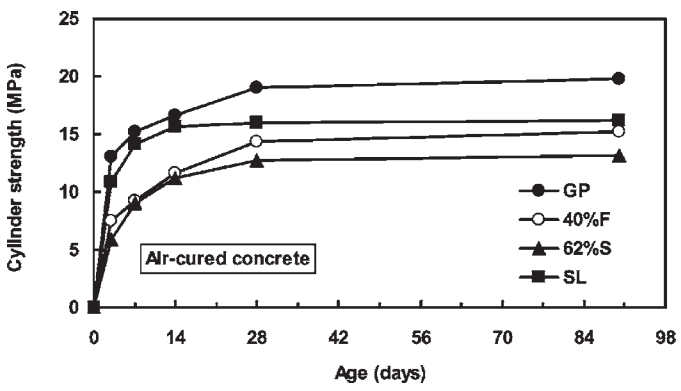


Figure 5—Compressive strength development with age for PAC stored in air.

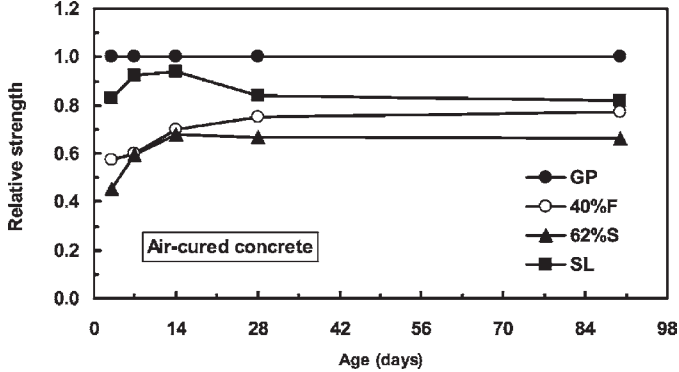


Figure 6—Relative strength development with age for PAC allowed to air dry.

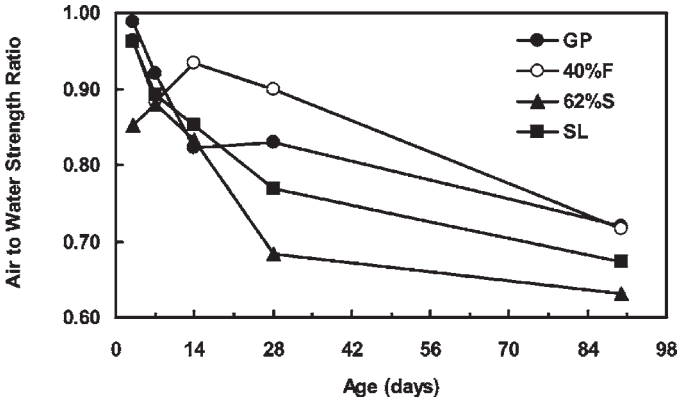


Figure 7—Effect of curing condition on the compressive strength of PAC.

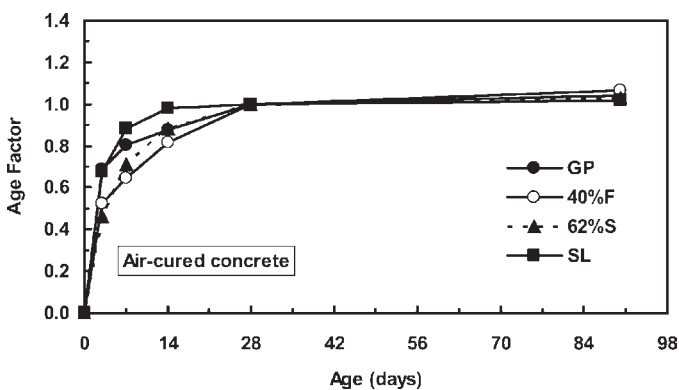


Figure 8—Development of age factor with age for PAC stored in air.

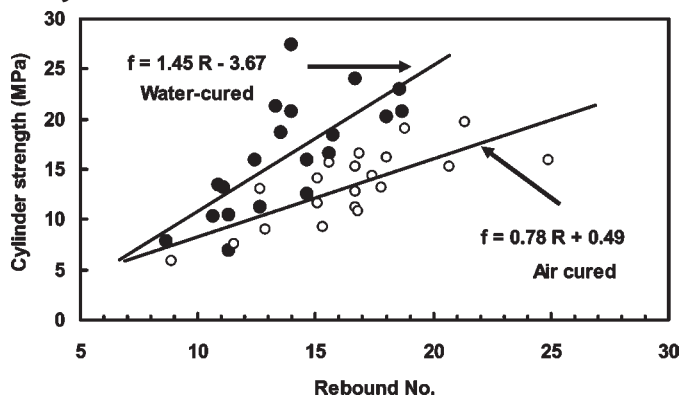


Figure 9—Correlation between compressive strength and rebound number for PAC.

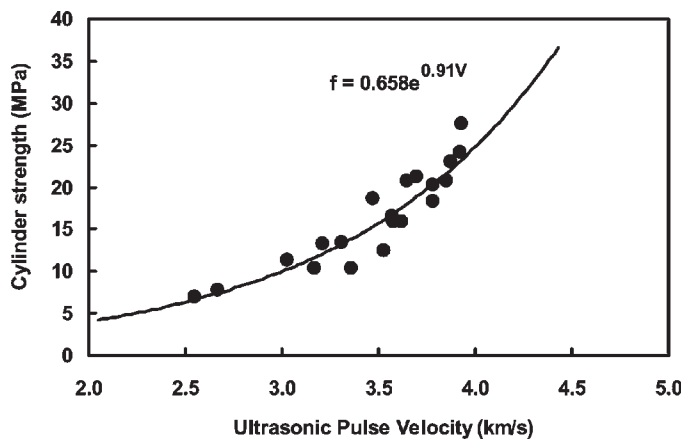


Figure 10—Correlation between compressive strength and pulse velocity for PAC.

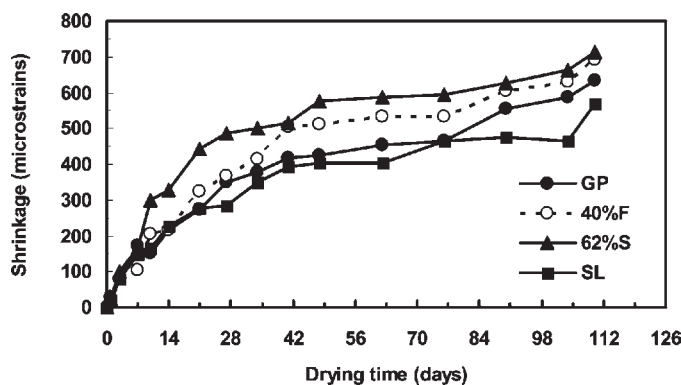


Figure 11—Development of free drying shrinkage with time.

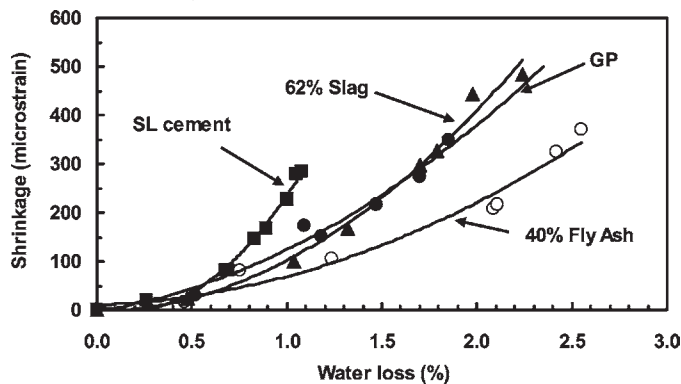


Figure 12—Relationship between drying shrinkage and moisture loss.

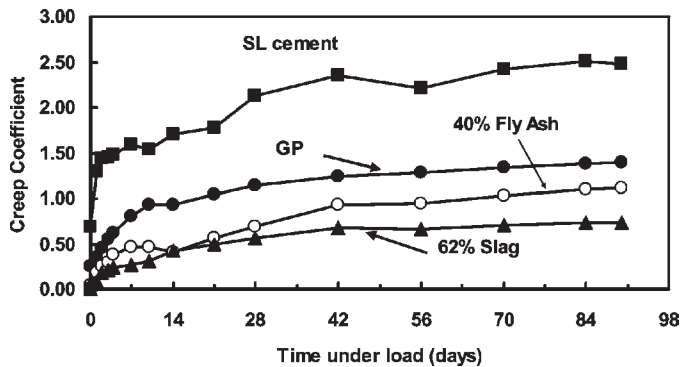


Figure 13—Development of creep coefficient with time for PAC.

Predicting Long-Term Creep from Short-Term Creep Test

by V. Sirivivatnanon

Synopsis: In the design and construction of modern structures such as high-rise buildings and long-span bridges, it is extremely important that realistic creep behaviour of concrete is known and used. In the 2003-2004 revision of the Australian Standard for concrete structures AS 3600, a new set of 'basic creep factors' or 'basic creep coefficients' are given to cover a wide range of concrete with characteristic strengths up to 100 MPa. This paper presents the background work undertaken to determine the basic creep factors. As part of this research, the suitability of various methods of extrapolating long-term creep from short-term creep tests were evaluated. The creep characteristics of a range of concretes were measured under sustained load in accordance with AS 1012.16. The concrete mixtures cover a range of constituent materials including a general purpose (GP) cement, an Australian version of an ordinary portland cement, binary and tertiary blends of GP with ground granulated blast furnace slag (slag), fly ash and silica fume. The coarse aggregates were either basalt from New South Wales and Victoria, or river gravel or air-cooled blast furnace slag from New South Wales. The mixtures cover a wide range of characteristic compressive strengths from 15 to 90 MPa. Of the three methods commonly used to extrapolate the long-term creep strain, the power model was found to be the most suitable method with good accuracy and a conservative overestimation of the creep strain. Two practical periods of measurement of short-term creep strain, 2-month and one-year, were examined from the 17 sets of medium-term (3-5 years) creep data. Based on the power model, the predicted ultimate creep strain from 2-month creep data tends to overestimate the basic creep factor by an average of 22% compared with measured values at the end of the 3-5 years of testing. Extending the measurement to one-year improves the accuracy with the average overestimation reduced to an average of 15%.

Keywords: basic creep factor; creep; creep coefficient; high-strength concrete

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INTRODUCTION

In designing reinforced and prestressed concrete structures, the strain in concrete due to creep is critical for serviceability and stress relaxation consideration. Creep strain is usually estimated from a basic creep factor (to be renamed basic creep coefficient in the revised Australian Standard for concrete structures AS 3600(1)). A basic creep factor can be obtained in a number of ways including tests in accordance with AS 1012.16 (2). More often, the basic creep factor is taken from a range of values given in Table 6.1.8.1 of AS 3600.

Table 6.1.8.1 BASIC CREEP FACTORS (AS 3600).

Characteristic Strength (f'c), MPa	20	25	32	40	≥50
Creep factor $\phi_{cc,b}$	5.2	4.2	3.4	2.5	2.0

There have been two practical problems associated with the use of Table 6.1.8.1. Firstly, the basic creep factor values, for the higher grades 40 and 50 concrete, tend to be lower than those found for local concrete. Secondly, no basic creep factor value is given beyond grade 50. High strength concretes with strength in excess of 50 MPa are commonly used in Australia. Extrapolation of existing creep factors to higher grades of concrete on the basis of the values given in Table 6.1.8.1 resulted in unrealistically low values as demonstrated in Fig. 5. As a consequence, basic creep factor specifications were not met causing undue problems to the concrete industry.

With the 2003-2004 revision of AS 3600, there is a great opportunity for adoption of more realistic basic creep factors. Some limits have already been proposed. Credible long-term test results are required to support the revision of the standard.

OBJECTIVE AND SCOPE

This study was undertaken to determine basic creep factors from long-term creep tests for a range of commonly used concretes in Australia. It also compared the method and accuracy of estimating basic creep factor from short-term tests.

The available creep data were confined to concrete manufactured from both GP (general purpose portland cement) and GB (general purpose blended cement) concretes with aggregates from New South Wales and Victoria. Medium-term measured creep data, taken over a 3 to 5 year period, were used and supplemented by other short-term test data.

RESEARCH TOOLS

Creep tests are conducted in accordance with AS 1012.16. The 3-5 year creep characteristics are used to determine the basic creep factors for concrete of various grades. Basic creep factors are evaluated from the experimental results.

With 3-5 year available data, creep factors are estimated from extrapolation of the initial 2-month or 1-year data. A number of extrapolation techniques will be used and compared to determine their relative accuracy in estimating at the 3-5 year creep factors. The reliability of each technique will be quantified and hence used in future with greater confidence.

DEFINITIONS

Creep strain: Strain under sustained compressive load less drying shrinkage strain measured after the same period of exposure of companion stress-free specimens.

Medium-term creep data: Creep strain data measured up to a period of three to five years.

Short-term creep data: Creep strain data measured up to a period of two to 12 months.

Specific creep: Creep strain per unit compressive stress.

Creep factor: The ratio of creep strain to elastic strain (instantaneous strain on loading).

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Basic creep factor or basic creep coefficient: A long-term creep factor. A period of 30 years is used in AS 3600.

PREDICTIVE MODELS FOR LONG-TERM CREEP STRAIN

Creep of plain and structural concrete has been comprehensively discussed by Neville et al. (3). Three models namely logarithmic, power and hyperbolic expressions have been used to represent the development of creep strain of concrete. These models can also be used to estimate long-term creep strain from short-term data. They are as follows:

Logarithmic Model

A logarithmic creep expression was first developed by the U.S. Bureau of Reclamation (4) in 1956. The logarithmic equation is simple and easily applied. The form of the equation is:

$$\Phi(t-t_0) = a + b \log(t-t_0)$$

Where $\Phi(t-t_0)$ is the creep strain at time $(t-t_0)$, t is the age of concrete, t_0 is the age of concrete when loaded, and a and b are constants. This form of the equation can also be used for modelling the creep factor or the specific creep (as the values for both are taken from the creep strain readings). When compared with the data from many creep tests, this method resulted in very accurate results; however, for some of the data this model may not be the most appropriate, as can be seen in an example of modelling the creep strain for a Mix 40 shown in Fig. 1. (Note that for a logarithmic scale of the time axis this model plots as a straight line)

Power Model

The power model was first suggested by Straub (5) and later by Shank (6), and it has the form of:

$$\Phi(t-t_0) = a + b(t-t_0)^c$$

Where $\Phi(t-t_0)$ is the creep strain at time $(t-t_0)$, t is the age of concrete, t_0 is the age of concrete when loaded, and a , b and c are constants. As with the logarithmic model, this equation can also be used for the modelling of specific creep and the creep coefficient. The advantage of this model is that it can follow a trend similar to the logarithmic model, but can also match the data where the logarithmic model fails to do so. As can be seen from Fig. 2, the power model matches the data well for both sample mixtures. Note that Mix 40 is the same mixture for which the logarithmic model could not match the non-linear trend in Fig. 1.

Power-Hyperbolic Model

The hyperbolic relationship between creep and time was proposed by Ross (7) and Lorman (8). The equation is used by ACI Committee 209 (9), as part of a “general theoretical procedure for determining creep and shrinkage in concrete”, and it has the following form:

$$\Phi(t-t_0) = \frac{a(t-t_0)^b}{c+(t-t_0)^b}$$

Where $\Phi(t-t_0)$ is the creep strain at time $(t-t_0)$, t is the age of concrete, t_0 is the age of concrete when loaded, and a , b and c are constants. This produces a versatile curve – which fits well to all medium-term creep data. However, this model may not result in a good curve for extrapolating short-term data as shown in Fig. 3.

Best Model for Extrapolation from 2-Month Data

In order to establish the most accurate model to predict medium-term creep stain from short-term data, only those data sets that had data for 1460 days or more (approximately 4 years) were used. There were 17 Australian data sets of varying strength and mixture proportions that satisfied this criterion. The creep strain data for the first 2-month were taken from each data set and used to extrapolate the creep stain at 1460 days using each of the above models. These predicted strains were then compared to the actual creep strains. Table 1 shows the results of the comparisons.

Table 2 shows the percentage difference of predicted 4-year creep strains from the measured creep strains of each method. Fig. 4 shows the same results plotted.

- The power-hyperbolic model is the least accurate – tending to underestimate the medium-term 4-year creep strain significantly.
- The power model has reasonable accuracy for the mixtures considered with a tendency to overestimate the creep strain.
- The logarithmic model is the most accurate but tends to consistently underestimate the creep strain.

Based on this analysis, the power model is considered the most suitable for predicting the long-term creep strain from short-term data, because it has reasonable accuracy. It overestimates creep strain and hence provides more conservative results. The logarithmic model gave on average the best accuracy. However, it tends to underestimate the long-term creep strain. Hence it is not a suitable technique to derive long-term creep limits for a design standard.

BASIC CREEP FACTOR FOR DIFFERENT GRADES OF CONCRETE

Using the power model, basic creep factors (or basic creep coefficients, BCC) are estimated from 38 sets of creep data. Out of these, 17 sets include medium-term creep data, 16 sets include 2 to 3 years data and five sets are one-year creep data. The compositions of these mixtures cover a range of characteristic compressive strengths (grades), binders and aggregates. The mixture constituents for Mixture No. 1 to 17 are given in Table 1.

Strength grades:	15 to 90 (using a nominal margin of 7 MPa)
Binders:	GP, blends of GP and slag or fly ash or silica fume, and triple blends of GP, slag, fly ash and silica fume.
Coarse aggregates:	basalt from New South Wales and Victoria, river gravel from New South Wales, and slag aggregates.

The basic creep factors are shown in Fig. 5 as a function of strength grade, with the best-fit curve and the upper and lower bounds (a range of $\pm 30\%$ as given in AS 3600) shown. Basic creep factors given in Table 6.1.8.1, of AS 3600, are also shown in the figure.

It can be seen that basic creep factors are similar to those given in AS 3600-2001 for grade 20 and 25, but gradually exceed the AS 3600 values in higher grades. For example, grade 50 has a basic creep factor of 2.7 compared with 2.0 in AS 3600.

There are seven points that lie beyond the upper bound. They do not represent any particular group of concrete, except that two of the seven are manufactured from air-cooled blast-furnace slag aggregate.

Basic creep factors that have been recommended for various grades of concrete are given in Table 3. It is clear that data found in this CSIRO work exceed values recommended in the current standard and those found by Setunge and Padovan (10). However, they generally agree well with factors suggested by Gilbert (11).

ACCURACY OF EXTRAPOLATION FROM 2 MONTH VERSUS 1 YEAR DATA

The accuracy of creep-strain extrapolation tends to improve as the testing period increases. However, practical considerations may prohibit longer-term testing. In an attempt to quantify the improvement in accuracy of