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LOST CIRCULATION CONTROL MATERIALS

PROGRESS REPORT

1994

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SUMMARY

Work in FY 94 continued to investigate the use of calcium phosphate cements as lost circulation control materials for geothermal wells. The calcium phosphate cements were produced by reacting calcium aluminate cement with sodium phosphate compounds. Pumpable formulations with thickening times up to two hours at temperatures between 25 to 90°C were developed and characterized. The materials showed rapid set behaviour, early strength development, low permeability and acceptable durability in hydrothermal environments. Strengths up to 4 MPa were achieved four hours after mixing and water permeabilities were of the order of 10^{-9} to 10^{-7} cm/s at 24 hours. Partial replacement of calcium aluminate cement with ground granulated blast furnace slag was found to reduce the amount of borax retarder required to maintain pumpability at elevated temperatures and pressures.

1.0 INTRODUCTION

The ongoing objective of this work is to develop cementitious slurries with superior properties for plugging loss zones in rock formations encountered during drilling of geothermal wells. Loss zones result in excessive consumption of drilling fluids and add a significant cost to geothermal exploration and development. Information on lost circulation control methods and materials is given by Messenger (1981), Smith (1990), Glowka (1990) and Loeppke et al. (1990). When loss zones consist of major fractures, as is common in geothermal drilling, rapid setting cements are required. Conventional oil well cements have excessive set up times (around 8 to 24 hours) and may not withstand harsh geothermal environments. In order to decrease the time period between placement of a lost circulation control cement and resumption of drilling it is necessary to decrease the set time of the cement and increase the rate of strength development after setting.

The lost circulation control materials (LCCMs) under investigation are designed to have reduced set up times and improved durability and to be compatible with the LCCM placement techniques being developed at Sandia National Laboratories. For the drillable straddle packer placement hardware under development at Sandia the desired pumpability time is 1-2 hours during which the LCCM must have a consistency less than approximately 70 Beardon units (Bc) (~ 700 cP) and preferably less than 30 Bc. The setting time desired is 2-4 hours at the downhole temperature (16-300°C), although 4-6 hours would represent an

improvement over conventional cements.

In addition to the pumpability and setting time requirements, it is necessary that the LCCMs have compressive strength greater than ~ 2-3 MPa 2 hours after setting and permeability less than ~ 10^{-2} Darcy ($\sim 10^{-5}$ cm/s). Strength and permeability must be maintained throughout the exposure period of up to approximately 30 days. An increase in volume is desirable to ensure adequate sealing of the loss zone. Conventional oil well cements have excessive set up times and may not withstand high temperature conditions of a geothermal well. The lost circulation control materials (LCCMs) under investigation are designed to have reduced set up times and improved durability and to be compatible with the LCCM placement techniques being developed at Sandia.

Phosphate cements typically have rapid set times, high strength and good durability for above ground applications and are often used as rapid repair materials. The properties of calcium phosphate cements prepared by reacting calcium aluminate (high alumina) cements with sodium phosphate solutions have been investigated by Ma and Brown (1992, 1994). Research conducted in FY 92 and 93 demonstrated that calcium phosphate cements had desirable properties of rapid set, adequate early strength and durability for geothermal applications. Calcium aluminate cement was used as the basis for production of calcium phosphate cement. The phosphate reactants selected were $\text{Na}_5\text{P}_3\text{O}_{10}$ (sodium tripolyphosphate), $(\text{NaPO}_3)_n$ (sodium polyphosphate) and $(\text{NaPO}_3)_3$ (sodium trimetaphosphate). Addition of retarders was necessary to extend the pumpability time of calcium phosphate cements, otherwise setting occurred within a few minutes. Work in FY 93 identified $\text{Na}_5\text{P}_3\text{O}_{10}$ to be a suitable reactant at low temperatures, but at 90°C the amount of retarder necessary to maintain pumpability was excessive. $(\text{NaPO}_3)_n$ and $(\text{NaPO}_3)_3$ were found to give greater pumping times for a given retarder concentration at a given temperature than $\text{Na}_5\text{P}_3\text{O}_{10}$.

In FY 94 the specific objective was to optimize the properties of calcium phosphate cements for lost circulation control. The roles of mix proportions and additives in controlling pumpability and thickening time were investigated. Ground granulated blast furnace slag was used to control set and to modify the hardened properties of the calcium phosphate cement. Filler materials were added to the calcium phosphate cements to test for compatibility.

Mixes were tested in a high temperature-high pressure consistometer and the relationship between retarder concentration, slag replacement and thickening time determined. Compressive strength-time relationships were studied at elevated temperatures and atmospheric pressure, as well as under autoclave conditions at 150°C and 380 kPa. Permeability measurements were also conducted since impermeability is a critical requirement of an effective lost

circulation control material.

2.0 MATERIALS

The calcium aluminate cement used in this work was Secar 80 (Lafarge Corporation) and is comprised mainly of calcium aluminate and calcium dialuminate. The typical composition of Secar 80 is 79.5-81.5 wt.% Al_2O_3 , 17.5-19.5 wt.% CaO , <0.7 wt.% $\text{K}_2\text{O}+\text{Na}_2\text{O}$, <0.4 wt.% SiO_2 , <0.25 wt.% Fe_2O_3 , <0.2 wt.% MgO and <0.2 wt.% SO_3 . The cement used in the studies by Ma and Brown (1992, 1994) was Secar 71, with the major compositional differences from Secar 80 being lower Al_2O_3 content and higher CaO content. The phosphate reagents were $(\text{NaPO}_3)_3$ and $(\text{NaPO}_3)_n$. Borax (sodium tetraborate decahydrate) was used as a retarder. The ground granulated blast furnace slag was ASTM C 989 Grade 100 (Koch Minerals). Wyoming bentonite was added to some mixes primarily to aid dispersion of filler material and reduce bleeding. The filler materials used were medium grade ground walnut shells and ground recycled rubber tyres.

3.0 EXPERIMENTAL PROCEDURE

3.1 Sample Preparation

The calcium phosphate cements were mixed in a Waring blender. The order of charge was water, bentonite (if added), borax, calcium aluminate cement, slag (if added), phosphate and filler (if added). Bentonite and borax were mixed with the water for one minute, prior to addition of the aluminate cement and any slag and further mixed for another minute. Mixing continued for one more minute when the phosphate was added.

In this work the phosphates were added as solids rather than solutions. The reasons for this include reduced reaction rate and greater practicality for field use. For example, concentrated solutions of $\text{Na}_5\text{P}_3\text{O}_{10}$ are highly alkaline and corrosive and, therefore, difficult to handle. Polyphosphate solutions can hydrolyze to orthophosphates and this may affect the reaction kinetics and properties of the final product. Trials performed at room temperature to compare the addition of $(\text{NaPO}_3)_n$ (polyphosphate) with Na_2HPO_4 (orthophosphate) showed that the reaction is slower and the final calcium phosphate cement weaker for the Na_2HPO_4 reactant. Hence, use of polyphosphate that had been stored for a long period and hydrolyzed could cause unexpected slow setting and reduced strength.

3.2 Viscosity

Apparent viscosity of the neat calcium phosphate slurries was measured using a Fann 35A direct indicating coaxial viscometer.

Neat slurries refer to those which do not contain any filler materials (walnut shells or rubber). It was not possible to measure the viscosity of slurries containing filler materials due to inadequate clearance between the viscometer bob and rotor. Measurements were taken at 300 rpm (511 s^{-1}).

3.3 Thickening Time

Thickening, or pumping, time of the neat slurries was measured using a Halliburton consistometer. The thickening time refers to the time that the cement slurry remains in a fluid and pumpable state under high temperature-high pressure conditions. The procedure for measuring thickening time of oil well cements is given in API Specification 10 (1988) and was used in this study. Viscosity was measured prior to commencing the consistometer tests. The slurry was added to a cylindrical cup that rotates around a stationary paddle and the assembly was placed in a chamber to which heat and pressure were applied. Consistency, in Beardon units (Bc), was monitored with time. A slurry is regarded to be pumpable up to consistencies of 70 to 100 Bc.

The test temperatures were 50, 70, and 90°C. The test pressures were 35900 kPa at 50 and 70°C, and 51700 kPa at 90°C. Heating rates were 1.67, 2.93 and 3.47 °C/minute for 50, 70, and 90°C, respectively. Heating and pressurization rates followed API Specification 10, Schedules 26, and 27. The target thickening time was 2 hours, and mixes were formulated to reach that objective.

The API definition of thickening time is the elapsed time between application of heat and pressure and the achievement of a consistency of 100 Bc. With the calcium phosphate cements, consistency often increased rapidly at the initiation of setting as shown in Fig. 1. The rate of thickening depended on retarder concentration and temperature. To prevent equipment damage and to facilitate easier removal of the setting cement, the test was stopped once a consistency of approximately 40 to 50 Bc was reached and the chamber was cooled and depressurized. Extrapolation between the initiation of thickening to 100 Bc was performed to estimate the 100 Bc thickening time.

3.4 Compressive Strength

Slurries to be tested for compressive strength were cast into cylindrical moulds with inner diameter of 30 mm and length of 62 mm. Both neat and filled cements were tested. Three to six specimens per batch were cast. For early strength measurements the specimens were maintained in a water bath at the temperature of interest until testing. Specimens used for measuring strength after autoclaving were demoulded after either four or twenty four

hours and placed in the autoclave. The autoclave conditions were 150°C and 380 kPa. Tests were performed in tap water. Some tests were performed in 0.01M NaHCO₃ solution to simulate a geothermal fluid in FY 93. At the conclusion of the desired time period, the autoclave was allowed to cool and strength tests on the autoclaved specimens were performed at room temperature.

3.5 Permeability

The water permeability of neat and filled cements was measured using a Ruska Model 1013 rigid-wall permeameter. The specimen dimensions were 26 mm diameter and 36 mm long. The applied pressure gradient over the length of the specimen was 2 atm. The specimens were tested at different ages and after autoclaving to determine the effectiveness of the calcium phosphate materials as loss zone sealants. Specimens were cooled to room temperature and saturated with water prior to testing.

3.6 Specific Gravity

The specific gravity of the slurries was measured using a Baroid mud balance.

4.0 RESULTS AND DISCUSSION

The Results and Discussion are divided into two sections: calcium phosphate cements and slag-modified calcium phosphate cements.

4.1 Calcium Phosphate Cements

4.1.1 Viscosity and Thickening Time

In continuation of work initiated in FY 93, calcium phosphate cements prepared from either (NaPO₃)₃ or (NaPO₃)_n were tested at 70°C in the consistometer. All of the slurries were prepared with 2.5% phosphate by weight of calcium aluminate cement and a water/cement ratio by weight (w/c) of 0.55. The results for initial apparent viscosity, initial thickening time and extrapolated 100 Bc thickening time are presented in Table 1. The borax/cement ratio by weight (b/c) is indicated. Initial viscosity was measured at room temperature and 300 rpm (511 s⁻¹) before commencing the consistometer test. The relationship between initial thickening time and borax concentration is shown in Figure 2. The results obtained for 2.5% (NaPO₃)_n at 50°C are also indicated for comparison.

Table 1. Viscosity and Thickening Time Results for Calcium

Phosphate Cements tested at 70°C.

Phosphate	b/c	Initial Viscosity (cP)	Initial Thickening Time (min)	100 Bc Thickening Time (min)
(NaPO ₃) ₃	0.25	116	87	105
(NaPO ₃) _n	0.25	100	75	96
(NaPO ₃) _n	0.30	105	87	120
(NaPO ₃) _n	0.40	185	123	162

The data in Table 1 indicates that (NaPO₃)₃ had a slightly greater thickening time for the same borax concentration as for (NaPO₃)_n. The difference between the initial and the extrapolated 100 Bc thickening times depends on borax concentration. The consistency versus time curves showed a decrease in thickening rate with increase in borax. Figure 2 shows that there is an approximately linear relationship between thickening time and borax concentration for a given temperature. This could be used to estimate the borax concentration required for a desired thickening time. The figure also shows the relative sensitivity to borax concentration, and that the sensitivity decreases with increasing temperature.

Initial consistencies were in the range of 19 to 30 Bc. Once constant temperature and pressure were achieved, consistencies decreased to 13 to 15 Bc, depending on the mix. If desired, the consistency could be reduced by increasing the water content of the slurry. However, this will reduce strength, increase permeability and may increase thickening time.

At temperatures above 50°C and at elevated pressures the amount of borax that must be added to the slurry to maintain pumpability for two hours becomes excessive. This necessitates additional mixing water, and the high water and borax contents would probably be detrimental to the strength and permeability of the final product. Also, since the solubility limit of borax in water is exceeded at these levels, particles of undissolved borax will exist in the set cement and give rise to localized weakness. At the high retarder concentrations used the borax is probably acting as a filler.

The effect of using simulated drilling fluid as an alternative to water was investigated. The fluid was prepared with 94% water and 6% bentonite by weight. The addition of bentonite caused the calcium phosphate cement slurry to have increased viscosity and

consistency and exhibit thixotropic behaviour. Reduction of initial consistency to a value less than 20 Bc required additional mixing water. Hence, if drilling fluid is used as the liquid for slurry preparation, higher water/cement ratios will be necessary to retain pumpability, and this will result in reduced strength and durability.

4.1.2 Compressive Strength

Compressive strength tests were performed on neat calcium phosphate cements (i.e. no filler) with 2.5% $\text{Na}_5\text{P}_3\text{O}_{10}$ by weight of calcium aluminate cement were conducted in FY 93. The borax concentrations ranged from 5 to 40% by weight of calcium aluminate cement for temperatures from 25 to 90°C. The early strengths (4-6 hours) were 0.2 to 4.0 MPa, depending on cure temperature and retarder concentration. Different strength development and final strengths will be achieved in the field under higher pressure conditions, or if mix proportions change.

The effect of phosphate type on early strength of filled calcium phosphate cements was investigated at room temperature. The phosphates added were $\text{Na}_5\text{P}_3\text{O}_{10}$, $(\text{NaPO}_3)_3$ and $(\text{NaPO}_3)_n$. The mix proportions were 1 part calcium aluminate cement:0.5 parts water:0.5 parts walnut shells:0.025 parts phosphate by weight. The compressive strengths at 6 and 24 hours are compared in Figure 3. At 6 hours the mix produced with $(\text{NaPO}_3)_n$ has the greatest strength, whereas at 24 hours the greatest strength is achieved using $(\text{NaPO}_3)_3$. This suggests a delayed exothermic reaction with $(\text{NaPO}_3)_3$.

4.1.3 Permeability

The results of the permeability tests on neat calcium phosphate cements conducted at room temperature were reported in the FY 93 Progress Report. The permeability at 24 hours age for curing temperatures of 25 to 70°C was of the order of 10^{-9} cm/s.

4.1.4 Specific Gravity

The specific gravity of the neat calcium phosphate cements ranged from 1.70 to 1.80, depending on mix proportions.

4.2 Slag-Modified Calcium Phosphate Cements

Alternative means of extending thickening time were sought since the amount of borax necessary to achieve an initial thickening time more than two hours remained excessive at elevated temperatures with different phosphate reactants. Ground granulated blast furnace slag was investigated as a partial replacement for calcium aluminate cement. Slag is a byproduct of the steel making

industry and consists mainly of silica, alumina and calcium oxide and is used as a supplementary cementing material for Portland cement. In this work slag was used primarily to reduce the heat of hydration of the calcium phosphate cement. Use of slag also reduces the material and energy costs of the lost circulation control material.

Preliminary experiments at room temperature showed that partial replacement with slag did increase the thickening time and set time of calcium phosphate cements. The increase in set time depended on the proportion of slag. The greatest extension of set times was achieved with 60 and 80% slag. Rate of strength development was also affected by slag proportions and this is discussed further in the section on compressive strength of the slag-modified mixes.

4.2.1 Viscosity and Thickening Time

Calcium aluminate cement replacement levels of 40 and 80% was chosen for the thickening time tests. $(\text{NaPO}_3)_n$ was used as the phosphate reactant at a concentration of 2.5% by weight of calcium aluminate cement plus blast furnace slag. The results are tabulated in Table 2 and 3 and presented in Figs. 6 and 7. The water/(cement plus slag) ($w/(c+s)$) and borax/(cement plus slag) ($b/(c+s)$) ratios are given in the tables. The percentage of borax by weight of calcium aluminate cement plus slag is indicated by the X axis.

Table 2. Viscosity and Thickening Time Results for 80% Slag-Modified Calcium Phosphate Cements

T (°C)	w/ (c+s)	b/ (c+s)	Viscosity (cP)	Initial Thickening Time (min)	100 Bc Thickening Time (min)
50	0.40	0	131	16	23
50	0.45	0.018	92	126	141
50	0.45	0.020	110	136	146
70	0.50	0.040	63	76	110
70	0.50	0.050	69	90	140
70	0.50	0.060	71	110	166
90	0.50	0.080	78	85	96
90	0.50	0.100	82	100	104
90	0.50	0.120	92	123	131

Table 3. Viscosity and Thickening Time Results for 40% Slag-Modified Calcium Phosphate Cements

T (°C)	w/(c+s)	b/(c+s)	Viscosity (cP)	Initial Thickening Time (min)	100 Bc Thickening Time (min)
50	0.45	0.025	98	99	105
50	0.45	0.030	91	123	136
50	0.45	0.035	96	147	165
70	0.50	0.100	81	91	104
70	0.50	0.130	95	117	133
70	0.50	0.150	105	133	160

Blast furnace slag increased viscosity of slurries due to its fine particle size. However, since borax concentration could be reduced, water/cement plus slag ratios ($w/(c+s)$) of 0.4 to 0.58 could be used. The initial apparent viscosities ranged from 61 cP for $w/(c+s) = 0.58$ and borax/cement plus slag ratio ($b/(c+s)$) = 0.12 to 110 cP for $w/(c+s) = 0.45$, and $b/(c+s) = 0.02$. Initial consistencies ranged from 15 to 25 Bc. Once constant temperature and pressure conditions were achieved, the consistencies of the different mixes were 12 to 19 Bc.

The required retarder concentration for a thickening time of two hours was substantially reduced by partial replacement of calcium aluminate cement by slag. Higher amounts of slag were required at high temperatures. Based on the consistometer tests, the slag-modified calcium phosphate cements were candidates for lost circulation control and were tested for strength and permeability.

4.2.2 Compressive Strength

The effect of slag content on early strength development was studied at room temperature. All mixes had $w/(c+s) = 0.5$, walnut shells/(c+s) = 0.5, and $(\text{NaPO}_3)_n/(c+s) = 0.025$. Bentonite was added at a level of 10% by weight of water to reduce bleeding, and no borax was added. The relationship between strength and time for varying slag replacement levels is illustrated in Fig. 8.

The results showed that the rate of strength development and the strength at a given time varied with slag level in a non-linear manner. While high strengths are preferable, the lower levels of slag did not sufficiently increase thickening time and retard set for the application of interest. The mix with 40% slag/60% calcium aluminate cement showed the best rate of early strength development, and was better than the calcium phosphate without any slag.

Slag replacement levels of 40, 60 and 80% were selected for further study at elevated temperatures. The mix proportions were the same as those used for the room temperature tests described above. Figs. 9 to 11 show the relationship between strength and time at cure temperatures of 50, 70 and 90°C, respectively. The strength is inversely proportional to the slag content at all temperatures. Lowest strengths were obtained at 70°C. At 50°C the 6 hour strengths were lower than those measured at 4 hours for all mixes. The results suggest formation of different phases at different temperatures and cure times. Greatest strength gain over 24 hours occurred with the lowest slag content and at 90°C. Since rapid strength development is required, a compromise must be reached between extended pumpability with high slag contents and improved strength gain after setting with low slag contents. Higher strengths can be expected in loss zones with higher temperatures and pressures. Water and retarder concentrations will also affect strength and rate of strength development.

Slurries containing filler materials and 60 and 80% slag by weight of calcium aluminate cement plus slag were cured at room temperature for 24 hours and then maintained in an autoclave at 150°C for 7 days. The mix proportions were the same as those described above. Both walnut shells and ground rubber tyres were used as fillers. The mixes with rubber filler underwent expansion, cracking and severe deterioration in the autoclave. Thus, ground rubber was eliminated from further studies. The 7-day mean strengths for the walnut shell mixes were 7.32 ± 0.29 and 2.10 ± 0.20 MPa for 60 and 80% slag levels, respectively. Hence, greater autoclaved strength is achieved with lower slag levels.

Experiments conducted on slag-modified calcium phosphates prepared with $(\text{NaPO}_3)_3$ showed that set was severely retarded. Mixes with 80% slag replacement level did not set after 24 hours at 50°C. The mean compressive strength of 24-hour old mixes with 60% slag, filled with walnut shells and cured at 50°C was 0.18 ± 0.02 MPa compared with 1.72 ± 0.12 MPa for the same material prepared with $(\text{NaPO}_3)_n$. Mixes with 60 and 80% slag prepared with $(\text{NaPO}_3)_3$ underwent severe deterioration in the autoclave at 150°C. Hence, $(\text{NaPO}_3)_3$ appears to be an unsuitable reactant when the formulation contains slag.

The strength of mixes with and without walnut shells was compared for slag levels of 60 and 80% when cured in water at 50 and 70°C for 4, 6 and 24 hours. The strength of the neat (no walnut shells) mixes was approximately half of that for the filled cements at any given time. The improvement in strength is probably due to reduced shrinkage and reduced microcracking which occurs when the cements are reinforced with particulates.

4.2.3 Permeability

Slag-modified calcium phosphate cements containing walnut shells were cured in water at temperatures of 50, 70 and 90°C for 24 hours and tested for permeability at room temperature. The results are shown in Fig. 12. The mix proportions were the same as those used for the compressive strength tests. The mean permeability of a mix with 80% slag/20% calcium aluminate cement autoclaved for 7 days in tap water at 150°C was $5.2 \times 10^{-7} \pm 8 \times 10^{-8}$ cm/s. The permeabilities were acceptable for lost circulation control and increased with slag replacement level and cure temperature.

4.2.4 Specific Gravity

The specific gravities of neat (unfilled) slurries with 60 and 80% slag were 1.84 and 1.78, respectively. Mixes containing walnut shells and 40 to 80% slag had a specific gravity of 1.65.

4.2.5 Costs

The cost of calcium phosphate loss circulation control materials will depend on slag replacement levels, retarder concentrations and shipping expenses. The calcium phosphates are more expensive than conventional cements. However, other factors to consider are the savings in drilling rig time and the savings in material volumes associated with alternative placement methods. The latter has been discussed by Glowka (1990).

5.0 FUTURE WORK

Slag-modified calcium phosphate cements will be tested in a high-temperature, high-pressure rig that simulates the downhole nozzle shear environment. In conjunction with Sandia National Laboratories, it is planned to evaluate the cements in a test facility that simulates lost circulation zones and permits post-placement evaluation of the performance of the cements for sealing loss zones. The facility will be used to demonstrate a drillable straddle packer assembly that is designed to direct flow of the lost circulation control material to the loss zone of interest (Glowka et al., 1992; 1993). Alternating layers of gravel and clay and a simulated wellbore will be placed in a three-sided concrete structure. Cement will be pumped to the gravel layer "loss zones".

Excavation after cement placement will permit determination packer and cement performance. Ultimately, it is planned to test the cements in the field.

Since the slag modified calcium phosphate cements are new for lost circulation control, characterization of the reaction mechanisms and kinetics under hydrothermal conditions is necessary for optimum understanding and advantage. Modelling of the time and temperature-dependent flow behaviour of the cements would also be beneficial for effective application.

6.0 CONCLUSIONS

Calcium phosphate cements produced by reacting calcium aluminate cement with sodium phosphates exhibit potential as lost circulation control materials for geothermal drilling. Rapid set and strength development can be achieved. The calcium phosphates show low permeability and good durability under hydrothermal conditions. Thickening time can be controlled by addition of borax. The type of phosphate used also controls thickening time and compressive strength. Use of ground granulated blast furnace slag as a partial replacement for calcium aluminate cement can be used to extend thickening time, particularly at elevated temperatures, and has the added benefit of cost reduction.

7.0 ACKNOWLEDGMENT

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Figure Captions

Fig. 1. Typical thickening time curve, 50°C. Borax/cement = 0.05, (NaPO₃)_n/cement = 0.025, water/cement = 0.4.

Fig. 2. Viscosity versus time for calcium phosphate cements prepared with Na₅P₃O₁₀. Water/cement and borax/cement ratios indicated.

Fig. 3. Thickening time versus borax concentration for calcium phosphate cements prepared with Na₅P₃O₁₀.

Fig. 4. Thickening time versus borax concentration for calcium phosphate cements prepared with (NaPO₃)_n.

Fig. 5. Effect of phosphate type on compressive strengths at 6 and 24 hours for curing in water at 25°C. Error bars represent one standard deviation.

Fig. 6. Thickening time versus borax concentration for slurry with 80% slag/20% calcium aluminate cement prepared with (NaPO₃)_n.

Fig. 7. Thickening time versus borax concentration for slurry with 40% slag/60% calcium aluminate cement prepared with (NaPO₃)_n.

Fig. 8. Effect of slag replacement on early strength for cements prepared with (NaPO₃)_n and cured in water at 25°C. Error bars represent one standard deviation.

Fig. 9. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 50°C . Error bars represent one standard deviation.

Fig. 10. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 70°C . Error bars represent one standard deviation.

Fig. 11. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 90°C . Error bars represent one standard deviation.

Fig. 12. Effect of slag replacement and cure temperature on 24 hour permeability for cements prepared with $(\text{NaPO}_3)_n$. Error bars represent one standard deviation.

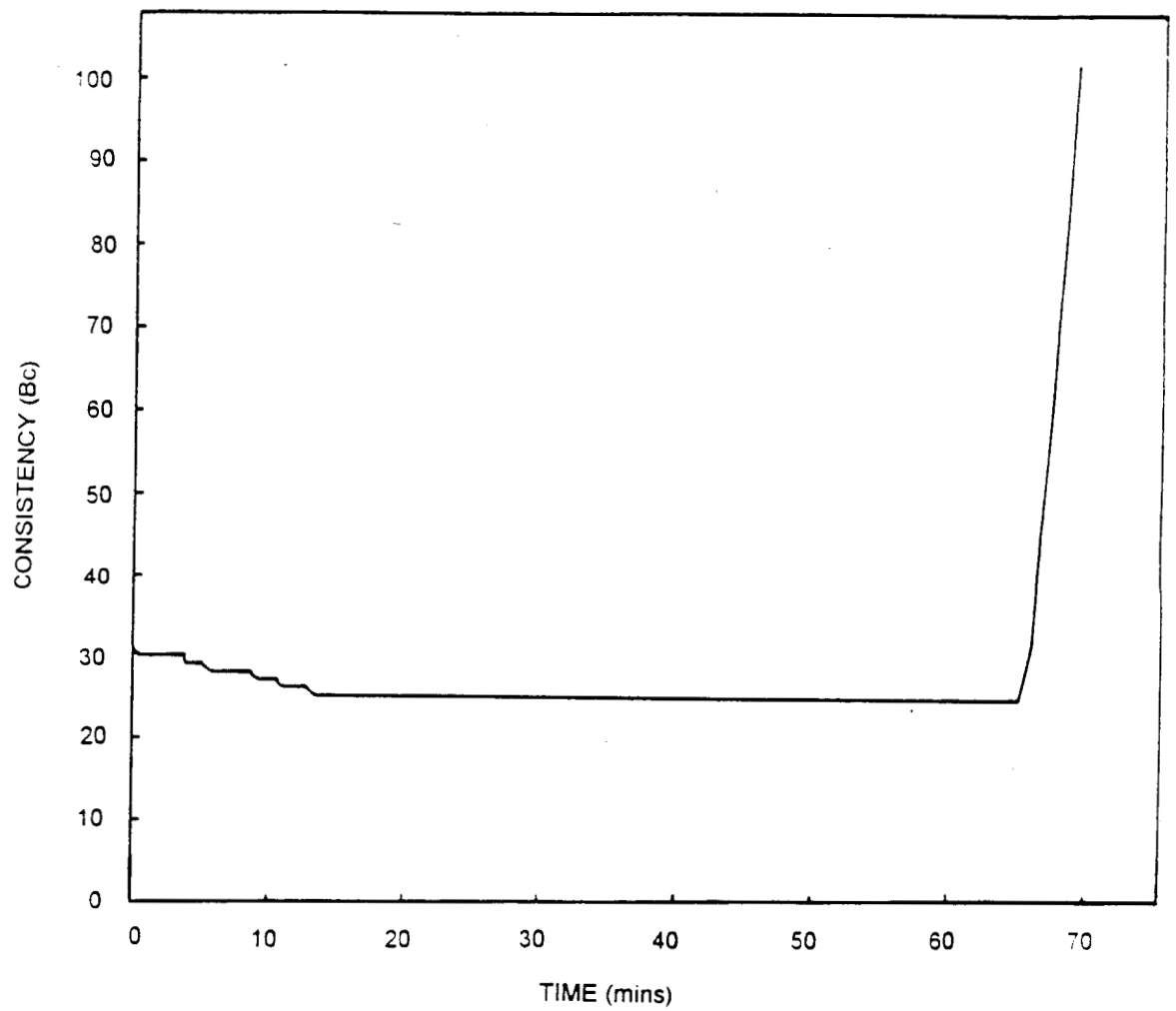


Fig. 1. Typical thickening time curve, 50°C. Borax/cement = 0.05, $(\text{NaPO}_3)_n$ /cement = 0.025, water/cement = 0.4.

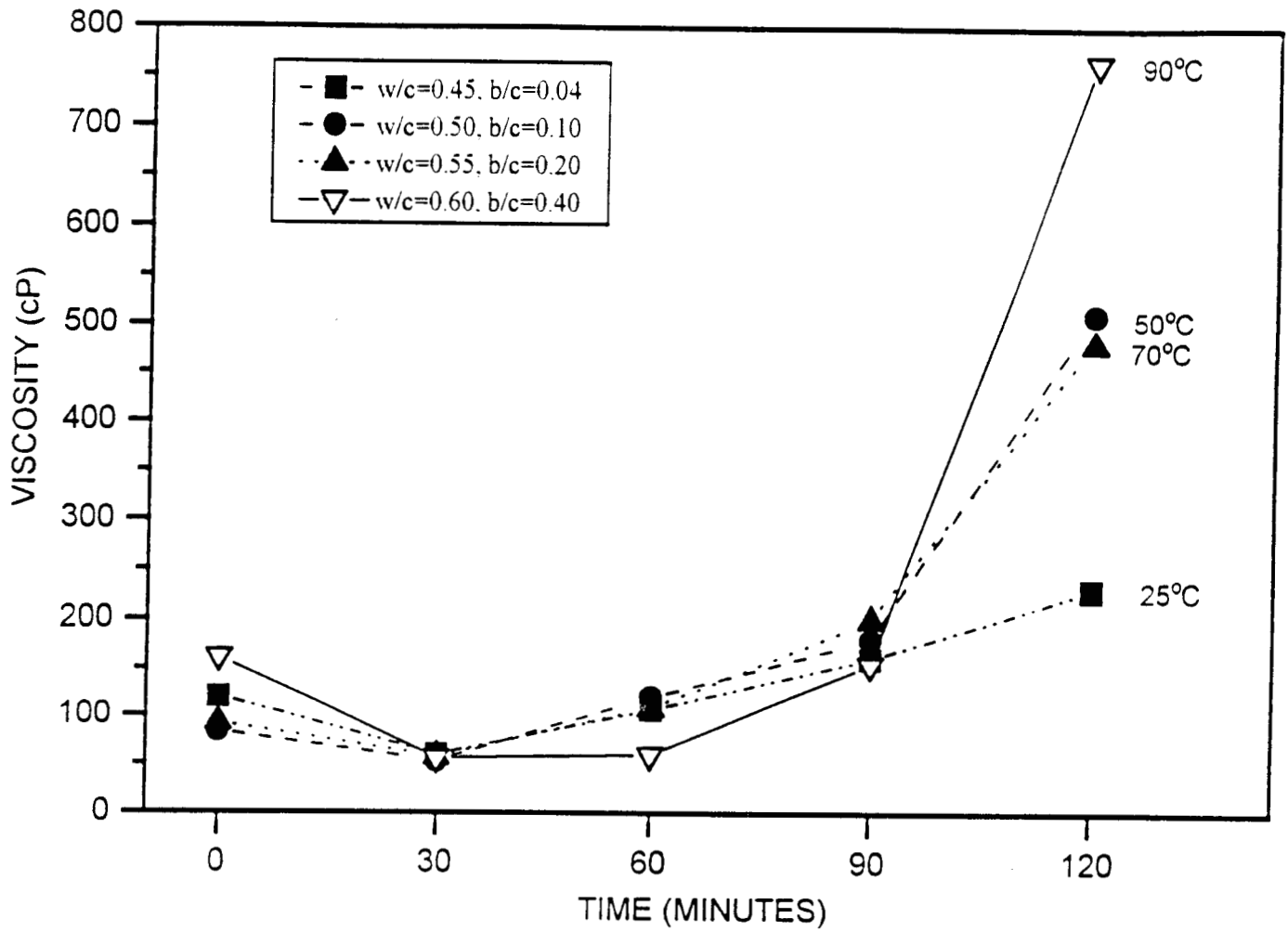


Fig. 2. Viscosity versus time for calcium phosphate cements prepared with $\text{Na}_5\text{P}_3\text{O}_{10}$. Water/cement and borax/cement ratios indicated.

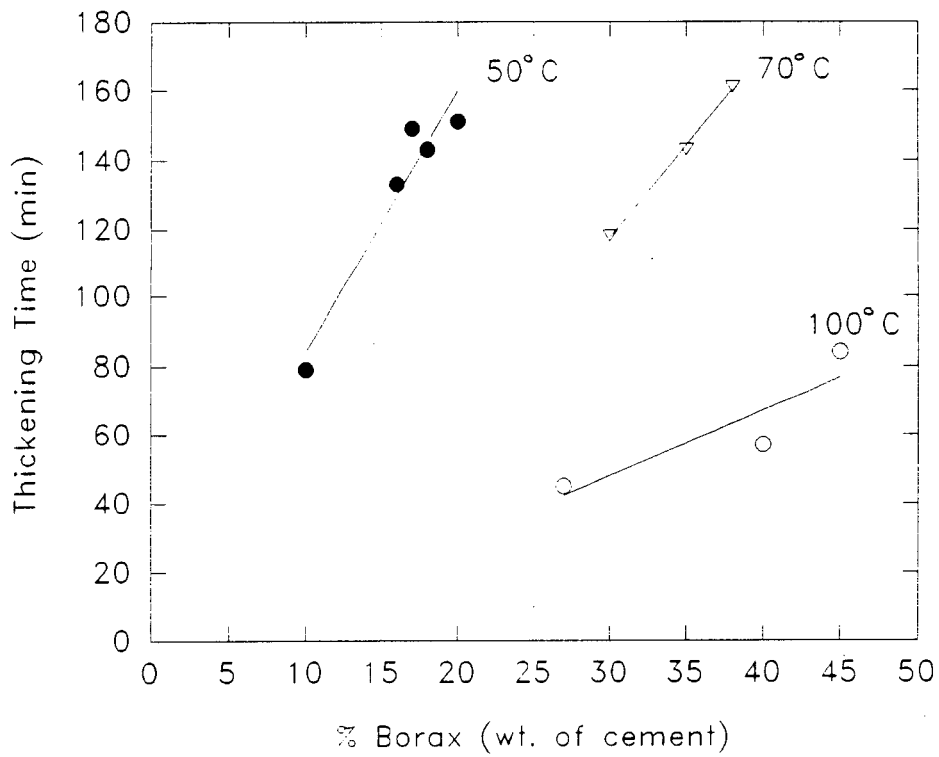


Fig. 3. Thickening time versus borax concentration for calcium phosphate cements prepared with $\text{Na}_5\text{P}_3\text{O}_{10}$.

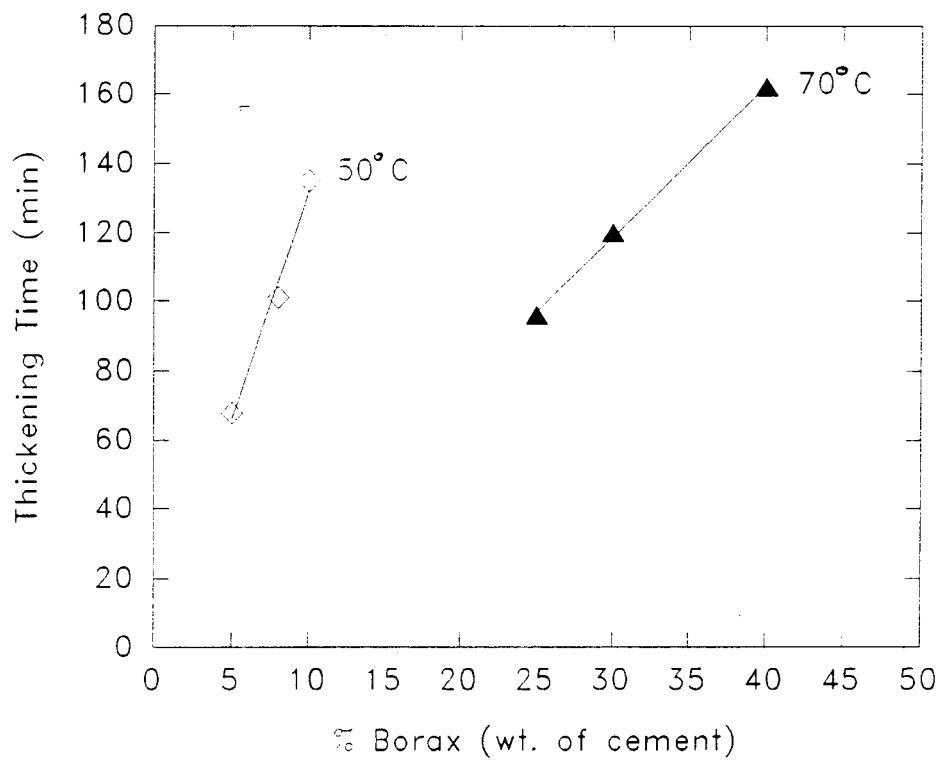


Fig. 4. Thickening time versus borax concentration for calcium phosphate cements prepared with $(\text{NaPO}_3)_n$.

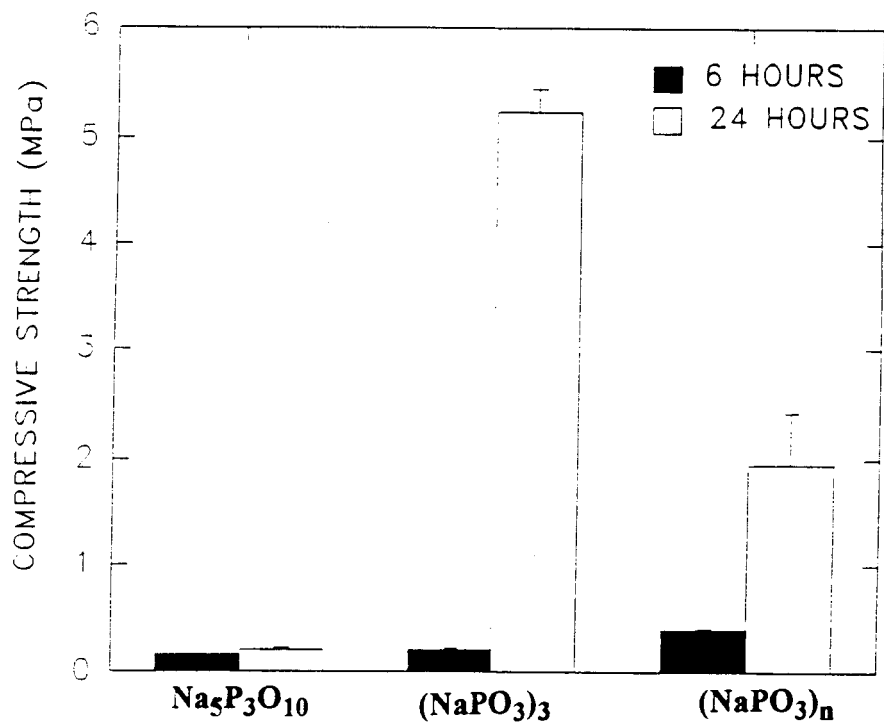


Fig. 5. Effect of phosphate type on compressive strengths at 6 and 24 hours for curing in water at 25°C. Error bars represent one standard deviation.

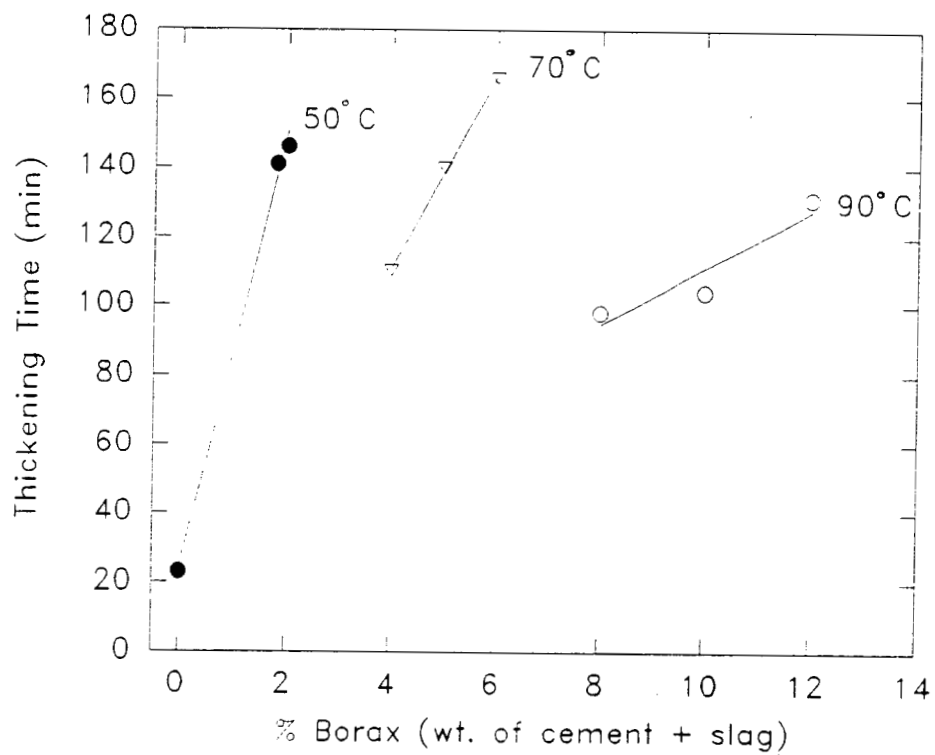


Fig. 6. Thickening time versus borax concentration for slurry with 80% slag/20% calcium aluminate cement prepared with $(\text{NaPO}_3)_n$.

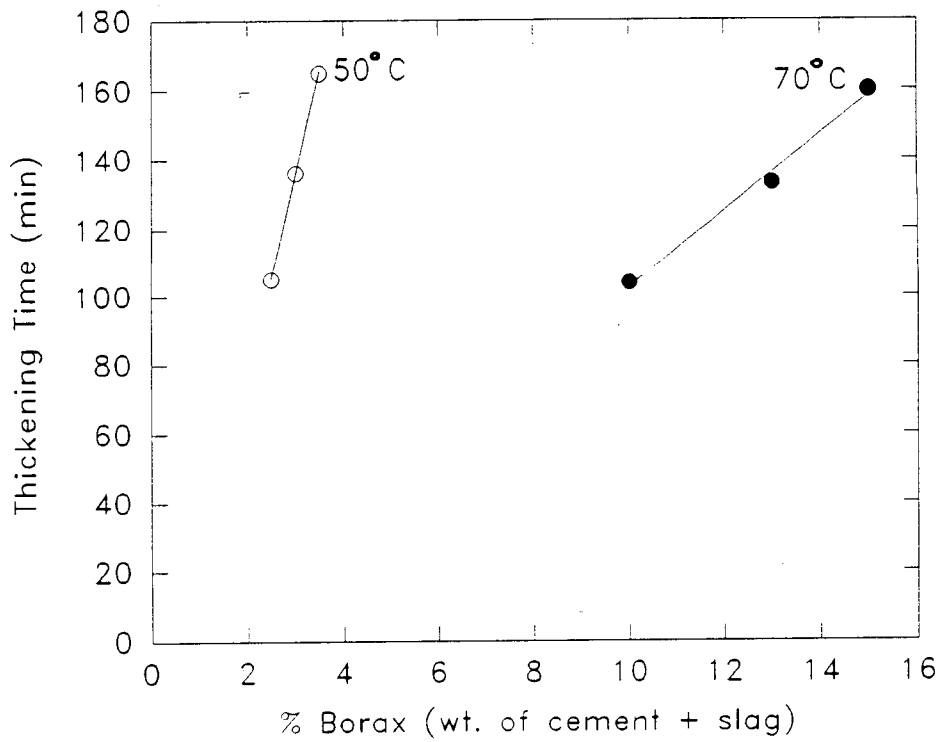


Fig. 7. Thickening time versus borax concentration for slurry with 40% slag/60% calcium aluminate cement prepared with $(\text{NaPO}_3)_n$.

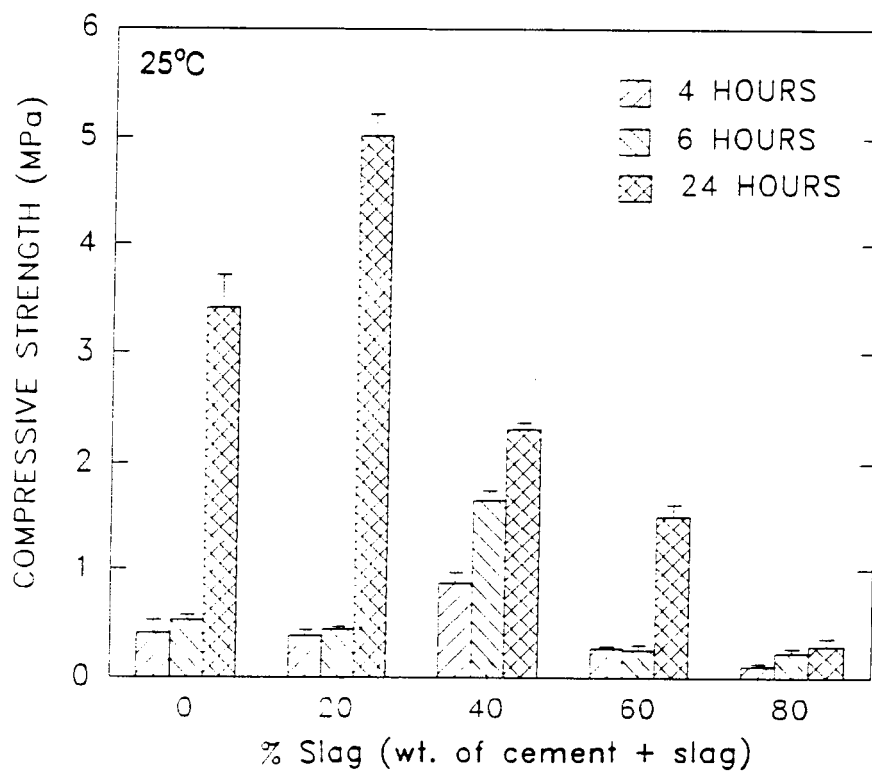


Fig. 8. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 25°C. Error bars represent one standard deviation.

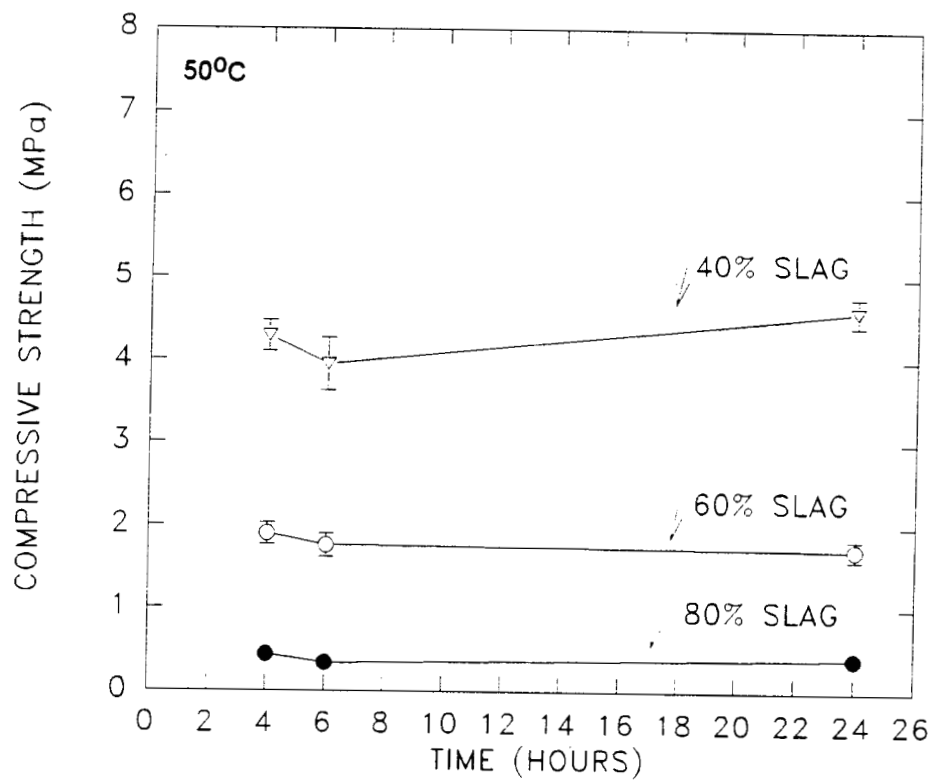


Fig. 9. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 50°C. Error bars represent one standard deviation.

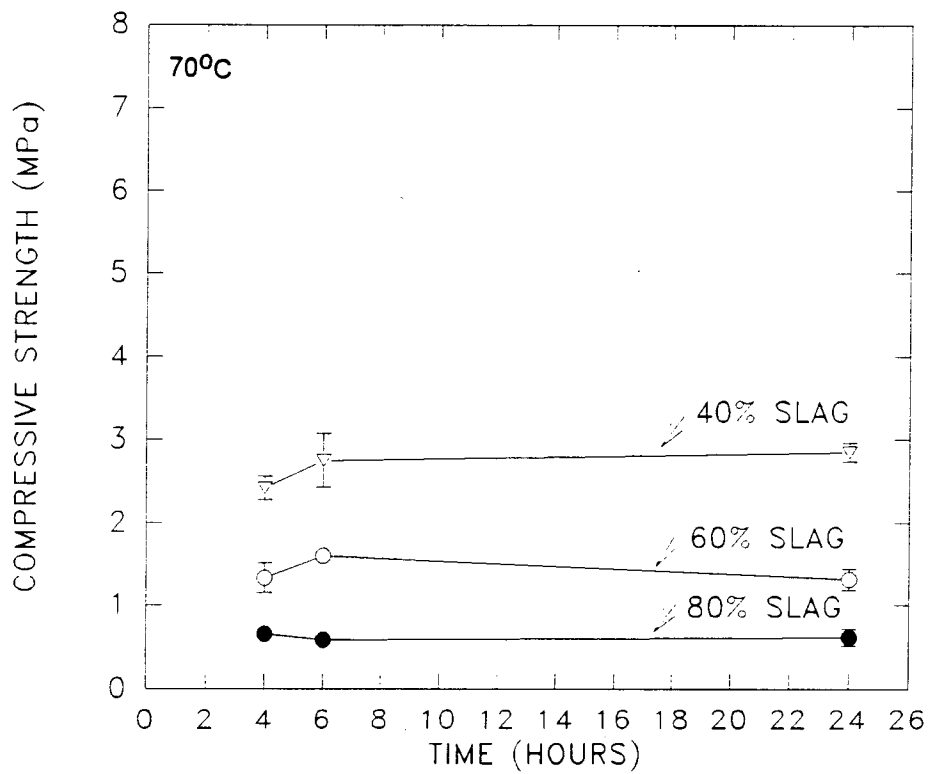


Fig. 10. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 70°C. Error bars represent one standard deviation.

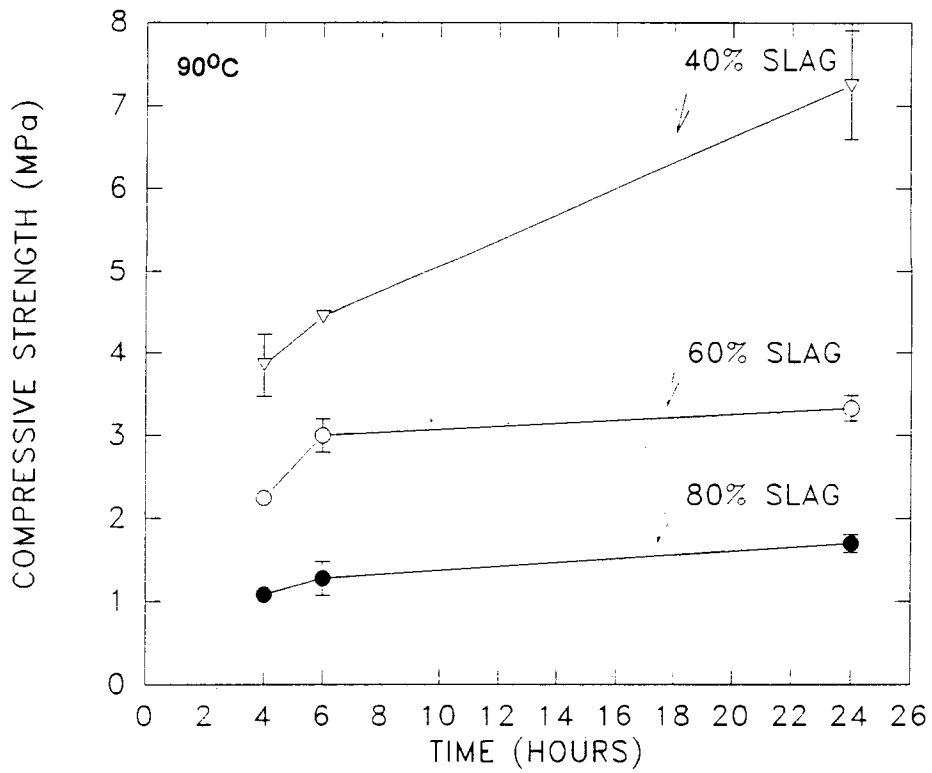


Fig. 11. Effect of slag replacement on early strength for cements prepared with $(\text{NaPO}_3)_n$ and cured in water at 90°C. Error bars represent one standard deviation.

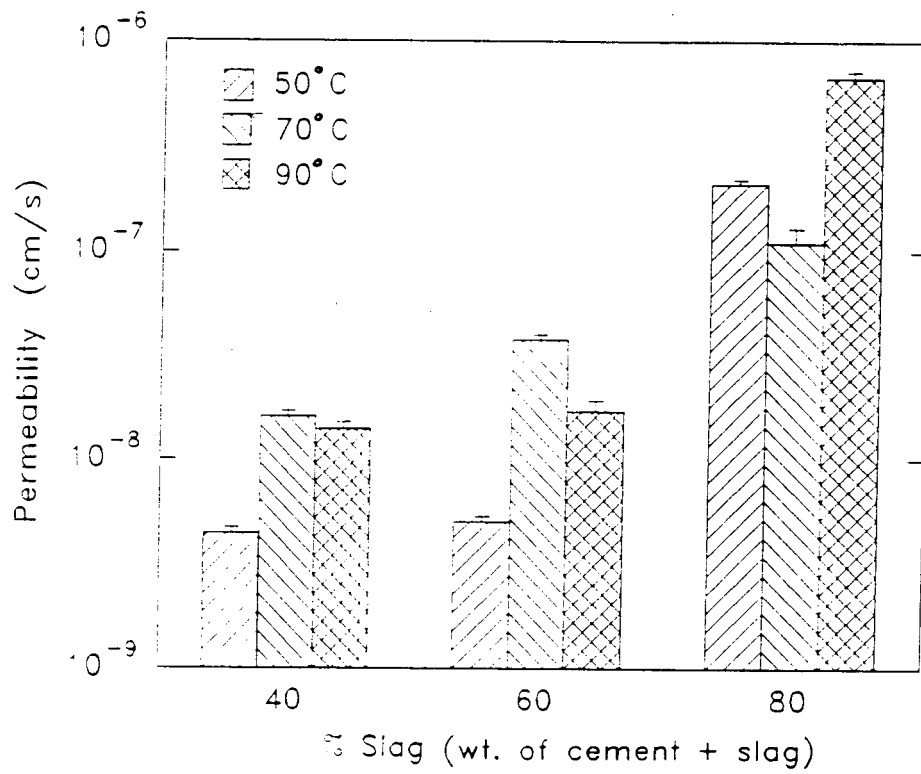


Fig. 12. Effect of slag replacement and cure temperature on 24 hour permeability for cements prepared with $(\text{NaPO}_3)_n$. Error bars represent one standard deviation.