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Identification of Chemical Agents for the Control of Alkali-Aggregate Reaction in Concrete

Kumar Natesaiyer
Kenneth C. Hover

Cornell University

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Program Manager: *K. Thirumalai*
Project Manager: *Inam Jawed*
Program Area Secretary: *Vondell Little*

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Strategic Highway Research Program
2101 Constitution Avenue N.W.
Washington, DC 20418

(202) 334-3774

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Contents

Abstract

A number of chemical compounds were evaluated for their effectiveness in inhibiting alkali-silica reaction in concrete, either as admixtures in the concrete mix or as penetrating agents to stop further progress of the reaction in already-affected or damaged concrete. Two compounds, zinc sulfate and aluminum sulfate, were found to be effective admixtures for fresh concrete. Zinc sulfate also appeared to significantly reduce the subsequent expansion of mortar bars, and could be a suitable penetrating agent for arresting alkali-silica reaction in hardened concrete.

Executive Summary

The project is complete and two chemical agents have been tentatively identified for the control of alkali-silica reaction (ASR) in concrete. In the first stage of the project three chemicals, aluminum sulfate, zinc sulfate, and pyrogallol, were identified to be effective retardants of silica dissolution in a model high alkali solution (1N sodium hydroxide). The same chemicals when tested as admixtures in portland cement mortar mixes did not seem to reduce the expansions due to alkali-silica reaction. Some possible reasons for this differing behavior in model high-alkali solution and portland-cement mortar mixes are given in the report. None of the three chemicals had any significant adverse effect on the compressive strength of mortar cubes. Zinc sulfate, when used as a penetrant, significantly reduced the expansions of mortar bars made with 3% opal replacement.

The primary goal of the short experimental research project conducted was the development of chemical agents to control alkali aggregate damage in concrete. It was proposed to develop chemicals to be used as traditional admixtures, and as aggregate pre-treatments, to control alkali aggregate reaction in fresh concrete. It was also proposed to develop chemicals to be used as penetrating agents to arrest the progress of alkali aggregate reaction in hardened concrete. The experimental program was conducted in three stages. The first stage was aimed at rapid evaluation of a number of chemical agents for their effectiveness in preventing dissolution of reactive silica in strong alkaline solutions. On the basis of the first stage, promising chemical agents were selected for use in Stages II and III.

In Stage I of the project ten chemicals were tested to determine their effectiveness in reducing the dissolution of silica in 1N sodium hydroxide solutions. Two types of reactive aggregates were used in the study: Opal and Spratts. Opal is a highly reactive form of amorphous silica and has been found in aggregates used for concrete. Spratts aggregate is a slowly reactive natural aggregate which has caused damage to concrete structures in Canada. Of the 10 chemicals tested, three chemicals - aluminum sulfate, zinc sulfate, and pyrogallol proved to be effective. Aluminum sulfate reduced the solubility of silica in 1N sodium hydroxide by more than 98%, zinc sulfate reduced the solubility of silica by about 75%, and pyrogallol reduced the solubility of silica by about 50%. The concentration of chemicals needed to reduce the dissolution of silica was found to be proportional to the reactivity of the aggregate.

The highly reactive opal, when compared with the slowly reactive Spratts, required a larger concentration of chemical to reduce its solubility in sodium hydroxide solutions.

The three chemicals selected from Stage I (aluminum sulfate, zinc sulfate, and pyrogallol) were tested as admixtures in Stage II to determine their effectiveness in reducing expansions of mortar bars made with reactive aggregates. Due to instability in high pH solutions, aluminum sulfate had to be used as an aggregate pre-treatment rather than as an admixture.

Aluminum sulfate pre-treatment and zinc sulfate admixture seemed to reduce the net expansions of mortar bars made with Spratts aggregate. Pyrogallol admixture did not significantly alter the expansions of mortar bars made with Spratts aggregate. All bars, including bars without admixtures, experienced a large shrinkage during the first week due to 60-70% relative humidity in the storage containers. The bars with admixtures, however, had shrinkage strains greater than the bars without admixtures. There was no significant difference in the post-shrinkage expansion of bars made with and without chemical admixtures.

For Spratts aggregate, the gel fluorescence test for the amount of reaction product revealed no significant difference between bars made with and without admixtures.

In experiments with opal as the reactive aggregate, the required concentration of all chemical agents was increased. At the high concentrations required, pyrogallol and zinc sulfate admixtures dramatically altered the setting properties of mortar mixes (pyrogallol was a strong retarder, zinc sulfate was a strong accelerator). Therefore, all three chemicals were used as aggregate pre-treatments for mortar mixes made with opal replacements. Zinc sulfate pre-treatment at 240 mM concentrations and aluminum sulfate pre-treatment decreased the expansions of mortar bars made with 3% opal replacement, while pyrogallol pre-treatments increased the expansion of mortar bars made with 3% opal replacement. For mortar bars made with 1% opal replacement, pyrogallol pre-treatment increased the expansions while zinc sulfate and aluminum sulfate pre-treatment did not decrease the expansions.

For bars made with 3% opal replacements, there was no significant differences in the amount of reaction product with and without admixtures. However, for bars made with 1% opal replacement, zinc sulfate and pyrogallol pre-treatments markedly reduced the gel product as observed using the ultra-violet test. Ultimate expansions, however, were not similarly affected.

The admixtures did not cause any significant reduction of the compressive strength of mortar cubes made with either Spratts aggregate or with opal replacements.

In Stage III zinc sulfate and pyrogallol were tested as penetrants to determine their effectiveness in reducing expansions due to ASR already in progress in hardened mortar. Initial tests with mortar cubes in pyrogallol solutions showed that the pyrogallol solutions coagulated and discolored the surface of the cubes. It was decided, therefore, that pyrogallol solutions would not be used for soaking mortar bars in Stage III.

Immersion in zinc sulfate solutions did not have any significant effect on the subsequent expansions of mortar bars made with Spratts aggregate. All mortar bars made with opal replacements expanded upon immersion, and the final expansions of bars made with 1% opal replacement were not significantly different from the expansions of bars immersed in water. At 3% replacement, however, immersion in zinc sulfate solutions significantly reduced the subsequent expansions. While none of the bars immersed in zinc sulfate solutions cracked, all the bars immersed in water cracked. Zinc sulfate immersion thus seemed to inhibit both expansion and cracking of bars made with 3% opal replacement.

There were no significant differences in the amount of reaction product between bars immersed in water and bars immersed in chemical solutions. This conclusion held true for bars made with Spratts aggregate and for bars made with opal replacements.

There was no significant difference in the compressive strength of mortar cubes immersed in chemical solutions when compared with the compressive strength of cubes immersed in water. This conclusion holds for both mortar cubes made with Spratts aggregate and mortar cubes made with opal replacements.

In summary, zinc sulfate and aluminum sulfate have been tentatively identified as promising chemical agents for the control of alkali-silica reaction in fresh concrete. Since pyrogallol did not have any significant effect on the expansion of mortar bars made with Spratts aggregate and seemed to increase the expansions of mortar bars made with opal replacements, it has not been recommended. Zinc sulfate is tentatively recommended for use as a penetrant to retard the progress of alkali-silica reaction in hardened concrete.

Overview of Project

This is the final report of the research project titled "Development of Chemical Agents for the control of Alkali Aggregate reaction in Concrete". The project was awarded to Cornell University by the Strategic Highway Research Program (SHRP) under the Innovation Deserving Exploratory Analysis (IDEA) program. The official start date of the project was April 1, 1989. The principal investigator of the project is Professor Kenneth C. Hover and the co-investigator is Dr. Kumar Natesaiyer.

The primary goal of the short experimental research project conducted was the identification of chemical agents to control alkali aggregate damage in concrete. It was proposed to identify chemicals that can be used as admixtures and as aggregate pre-treatments, to control ASR in concrete. It was also proposed to develop chemicals to be used as penetrating agents to arrest the progress of ASR in hardened concrete. Details on the project background and proposed workplan are available in the original proposal [1] and the addendum to the proposal [2]. Stage I was completed in six months and a technical report on stage I [3] was submitted in October 1989. Two brief progress reports [4,5] were also submitted during the course of this work.

This report summarizes the work done during the entire project period (April 1989 to October 1990). Brief summaries of the information presented in the proposal and the earlier reports are presented herein. Additional details can be found in references [1,2,3,4,5].

Stage I: Identification of potentially useful Chemical Agents (by modified Quick Chemical test)

Introduction

A modified version of the widely used Quick Chemical Test (ASTM C 289) was used to study the efficacy of chemical agents in reducing the dissolution of silica in high pH solutions. In the quick chemical test, 25g of crushed aggregate in 150-300 μm range is reacted with 1N sodium hydroxide at 80 degrees Celsius for 24 hours. After rapid cooling to below 30 degrees Celsius the mixture is filtered and the filtrate analyzed for dissolved silica using photometry, and alkalinity by titration. In the standard test the amount of dissolved silica and the reduction in alkalinity are correlated with the deleterious nature of the test aggregate.

An analysis of the chemistry of the quick chemical test was presented by Dentglasser and Kataoka [6] and enlarged upon in the first quarterly report [4]. Based on these studies it was decided that in this project the sodium and silicon concentration in the filtrate would be determined using atomic emission spectrophotometry (hence the name "modified" quick chemical test).

Materials and Methods

The stability of a candidate chemical in high pH (>12) solutions governed the mode of testing. If a chemical was soluble in sodium hydroxide, the crushed aggregate was reacted with solutions of sodium hydroxide containing the chemical in question. On the other hand, if the chemical was insoluble in sodium hydroxide or if it reacted with sodium hydroxide and precipitated out of solution, other steps were required. In this case the crushed aggregate was presoaked in aqueous solutions of the chemical agent being studied before the aggregate was reacted with sodium hydroxide. The decision tree used in Stage I of the project is shown in Table 1.

The chemicals tested were chosen on the basis of their reported ability to reduce the dissolution of silica in normal and high pH solutions. Some of the chemicals used had been reported to reduce the solubility of silica only in normal pH (7-8) solutions but were nevertheless tested to determine whether they would reduce the solubility in high pH solutions. Table 2 presents the list of chemicals tested in Stage I along with pertinent references where the efficacy of the chemical in reducing the solubility of silica has been reported.

The stability of the chosen chemicals in sodium hydroxide solutions was researched from chemistry literature. In cases where information was unavailable, the chemical was tested by adding small amounts of the chemical to 1N sodium hydroxide in a test tube. If a precipitate was observed the chemical was regarded as unstable in sodium hydroxide. If the chemical dissolved in sodium hydroxide, a small amount of calcium hydroxide was then added to test stability in an approximately simulated cement environment. The stability of the chosen chemicals and hence their mode of testing with 1N sodium hydroxide is given in Table 3.

The reactive aggregates used in the study were prepared and characterized as follows:

Opal was purchased from Geoscience Resources (a geological supply company), while Spratts aggregate was obtained from the Ontario Ministry of Transportation, Canada. Spratts aggregate is a slowly reactive natural aggregate from the Spratts quarry in Ontario, Canada. Spratts aggregate has a field record of causing damage due to alkali silica reaction.

The reactive aggregates were crushed using mechanical rotary and jaw crushers and sieved using a set of sieves (No.4, No.8, No.16, No.30, No.50, and No.100). The size fraction retained on No.100 sieve and passing the No.50 sieve was washed, dried, and stored in plastic containers for further testing in Stage I. All specimens incorporating Spratts aggregate consisted of 100% crushed, sieved Spratts as the aggregate phase. Specimens incorporating highly reactive opal contained 1% or 3% opal with the other 99% or 97% aggregate phase composed of natural sand, approved by the New York State Department of Transportation (NYSDOT).

The chemical composition of the aggregates was determined by X-ray diffraction (XRD) analysis. An XRD analysis produces a spectrum with peaks at various diffraction angles. A given crystalline phase of a mineral has a set of distinctive peaks which can be matched with the peaks obtained for the sample in question. (Amorphous phases do not have diffraction peaks.) The XRD spectra for opal and Spratts aggregate are included. It is seen that opal contains mostly amorphous phases with a small amount of cristobalite. Spratts aggregate, on the other hand, contains limestone, quartz of low crystallinity, and very small amounts of amorphous phases. Similar XRD spectra of Spratts aggregate are presented in Reference 10.

The specific gravity and water absorption of the aggregates were determined using standard ASTM methods. Further, since the solubility of silica in alkali solutions was expected to be dependent on the effective surface area

of the aggregates, surface area was determined using nitrogen adsorption. The physical properties of the aggregates are summarized in Table 4. Some more general information on properties of Spratts aggregate is available in Reference 15.

In order to avoid silica contamination from glass only plastic labware was used for the entire modified quick chemical test procedure. In cases where the chemical was stable in high pH solutions (See Table 3), 1N sodium hydroxide solutions with various concentrations of chemical were prepared. Twenty five mL portions of the solutions so prepared were reacted with 25g of crushed reactive aggregate in accordance with the procedures of ASTM C 289.

In cases where the candidate chemical was unstable in high pH solutions, an aggregate pre-treatment procedure was used. One hundred gram portions of crushed aggregate were soaked in 150 mL of aqueous solution containing the candidate chemical at various concentrations for 1 hour. The mixture was then filtered and the sand dried in an oven maintained at 105 degrees Celsius for 1 hour. The dried sand was cooled and split into 25g portions for further use in the quick chemical test.

The test was conducted according to standard ASTM C289 procedures except that the filtrate was analyzed for the sodium and silicon concentrations using atomic emission analysis (AES). An inductively-coupled plasma atomic emission spectrophotometer (ICP-AES) available in the Pomology department at Cornell University was used. The instrument is capable of measuring 15 metallic elements in the filtrate in one exposure and has a large dynamic range for each element. The silicon concentration in the diluted filtrate could thus vary by orders of magnitude without a loss in measurement accuracy. The instrument was controlled by software through a personal computer which continuously checked the precision of the measurements by performing 4 exposures for each sample.

Results

The effectiveness of three chemicals in reducing the dissolution of Spratts aggregate in 1N sodium hydroxide is shown in Figure 1. It is seen that aluminum sulfate, zinc sulfate, and pyrogallol reduced the solubility of silica by 95%, 75%, and 50% respectively.

The silicon concentration in blank solutions (without chemical addition) can be observed in Figure 1 to vary between 2000 to 3000 parts per million (approx mg/L). This corresponds to "S_C values" of 71 to 106 mM/L; such values are comparable to those reported for Spratts aggregate by other workers [15]. The sodium concentrations in blank

solutions (without chemical addition) varied between 22000 to 23000 mg/L. The "reduction in alkalinity" is thus approximately 0 to 1000 mg/L (or R_c ~ 0 to 43 mM/L) when measured in terms of sodium ion concentration. Again, the values of R_c are similar to values reported in Reference 15.

The decrease in silicon concentration for the other 7 chemicals tested was small when compared to the three chemicals shown in Figure 1. The ineffectiveness of some of the chemicals tested in reducing the solubility of silica is shown in Figure 2. Complete graphs for all the chemicals tested with Spratts aggregate can be found in the summary report on Stage I [3].

The effectiveness of aluminum sulfate, zinc sulfate, and pyrogallol in reducing the dissolution of opal, and when tested in the concentrations used for Spratts, is shown in Figure 3. It is seen that there is no significant decrease in the silicon concentration of the filtrate. It was hypothesized that the ineffectiveness of the chemicals in reducing the dissolution of opal may be related to the higher reactivity and larger surface area of opal when compared to Spratts aggregate. In order to test this hypothesis, opal was tested with higher chemical concentrations of 60 to 360 mM. The concentrations were arrived at by approximately scaling the concentration used for Spratts aggregate by the ratio of the blank silicon concentrations of opal and Spratts aggregate.

The effect of larger concentrations of chemicals on the solubility of opal is shown in Figure 4. It is observed that the chemicals have reduced the silicon concentration significantly indicating that the ineffectiveness observed earlier was due to the small concentrations of chemical used. The effect of aluminum sulfate and pyrogallol is similar to their effect on Spratts while zinc sulfate is seen to be not as effective.

The silicon concentrations in blank solutions (without chemical addition) can be seen in figures 3 and 4 to vary between 20000 and 40000 mg/L. These values correspond to S_c values of 700 to 1400 mM/L. It is also observed that the triplicate blank samples tested with any particular chemical showed very similar silicon concentrations. The sodium ion concentrations in blank solutions are observed to generally vary between 16000 and 21000 mg/L. These values correspond to R_c values of 300 to 90 mM/L.

Dr. Inam Jawed from SHRP visited the research team during the course of the project and, in discussions held with Dr. Jawed, it was suggested that the effectiveness of the chemicals tested could better be graphed in terms of the cation concentration and not in terms of the total chemical concentration. The effect of aluminum sulfate and zinc

sulfate on solubility of Spratts is re-graphed in terms of the cation concentration in Figure 5. The graphs in terms of chemical concentration are also shown for reference. It is seen that when plotted in terms of cation concentration, divalent Zn^{2+} is almost as effective as trivalent Al^{3+} in reducing the dissolution of Spratts in 1N sodium hydroxide. A similar re-graphing of the effectiveness of chemicals on opal dissolution is shown in Figure 6.

Conclusions of Stage I

1. Aluminum sulfate, zinc sulfate, and pyrogallol, in that order, were found to be effective retardants of silica dissolution (as measured by silicon concentration in the filtrate) in 1N sodium hydroxide solution.
2. The concentration of chemical agents necessary to reduce the dissolution of silica by comparable amounts depends on the surface area of the reactive aggregate and the inherent reactivity of the aggregate.

Stage II: Evaluation of promising Chemical Agents from Stage I as Admixtures or Aggregate pre-treatments

Introduction

The effectiveness of the chosen chemicals in preventing initiation of ASR distress in new concrete was tested in Stage II. In a short term study such as this one, it is impractical to conduct tests with concrete mixes containing coarse aggregates which contain reactive silica. The time required to obtain conclusive results with such mixes will be excessive. In order to accelerate the process, the reactive silica was proposed to be crushed to sand sizes and used in mortar specimens rather than concrete specimens. Thus, Stage II tests were conducted on mortar bars made with crushed aggregate instead of concrete. Since the ability of the chemical agents to reduce the solubility of silica is based on fundamental mechanisms, it was anticipated that this size substitution would not invalidate the work. Since both aggregate gradation and specimen geometry affect the observed expansion, the Cornell gel fluorescence test [16,17,18] was also conducted to compare the amount of reaction product in the specimens.

It was recognized that chemicals which may be effective in reducing distress due to ASR may have other undesirable effects on the setting and hardening properties of concrete. The scope of this project did not allow an extensive investigation of other effects of chemicals on concrete. Nevertheless, a limited study was conducted to determine the effect of the chemicals (if any) on the compressive strength of mortar cubes made from the same batches used to cast mortar bars.

Materials and Methods

General

The stability of the chemical agents in strong alkaline solutions was shown in Table 3. Of the three chemicals selected in Stage I, it is observed that aluminum sulfate is not stable at high pH while zinc sulfate and pyrogallol are stable at high pH. Since the final pH of the pore solution of concrete is highly alkaline, different mixing procedures were used for the three chemicals. The aggregates were **pre-soaked** in aluminum sulfate solutions before addition of cement, while zinc sulfate and pyrogallol solutions were introduced directly to cement and untreated aggregate. Variations to this general procedure were needed with opal replacements as explained in detail in the next section.

The grading and preparation of aggregates used in the study followed the requirements of ASTM C 227 [19]. Spratts aggregate was crushed and used alone in the mortar bars. Opal aggregate was crushed and 1% and 3% of the innocuous fine aggregate was replaced by opal in the case of mortar bars made with opal replacements. In general, mortar bars were proportioned and cast according to the procedures given in ASTM C 227 [19] while mortar cubes were proportioned and cast according to the procedures stipulated in ASTM C 109 [20]. A fixed water cement ratio of 0.5 was used for both mortar bars and cubes. Type I cement with an alkali content of 0.9% (Na_2O equivalent) was used. Analysis of the cement showed that the alkalies were composed of 99% potassium salts and 1% sodium salts. Some variations in the casting procedures were necessary and are described in detail in the following section.

The specimens were demolded at 24 hours and transferred to a moist cabinet maintained at room temperature and 95-100% relative humidity for the duration of the study. The length changes of the mortar bars was monitored periodically for six months.

At the end of the study, bars from each of the reactive aggregate-chemical combinations were selected for the determination of amount of reaction products. The bars were broken longitudinally and the gel fluorescence test was conducted on one of the interior surfaces of the broken mortar bar. In the gel fluorescence test, the suspect specimen, after proper conditioning, is treated with uranyl acetate. After further conditioning, the specimen is observed under short-wave ultraviolet light in a darkened room. The reaction products are identified by their characteristic greenish yellow fluorescence in the gel

fluorescence test. Details of the conduct and interpretation of the gel fluorescence test can be found elsewhere [16,17,18]. The presence or absence of reaction product was noted and photographs taken.

Specimens with Spratts Aggregate

As explained in detail earlier, aluminum sulfate, zinc sulfate, and pyrogallol in the concentration range of 12 - 24 mM had reduced the dissolution of Spratts aggregate in 1N sodium hydroxide. It was decided to use the chemicals at two concentrations (12 and 24 mM) in Stage II testing as admixtures. A total of 32 mortar bars (12" x 1" x 1") and 42, two-inch cubes were cast with Spratts aggregate. The detailed breakdown of the chemical/Spratts aggregate combinations is given below.

Spratts aggregate:

3 chemicals x 2 concentrations x 4 bars/combination

= 24 bars

Control bars = 8 bars

Total = 32 bars

3 chemicals x 2 concentrations x 2 test periods x

3 cubes/combination = 36 cubes

Control = 6 cubes

Total = 42 cubes

The following pre-soak procedure was used with aluminum sulfate/Spratts aggregate combinations. The required weight of Spratts aggregate for a batch was soaked in aluminum sulfate solutions for an hour. The amount of solution was equal to the amount of mixing water that was required for the batch. After an hour of soaking, the solution/fine aggregate mixture was filtered to remove any non-adsorbed aluminum sulfate. The wet aggregate was weighed and the amount of solution held in the wet aggregate was calculated. Water was added to the mix to replace the filtrate and bring the total solution and water weight to the required weight of mixing water for the batch. In general, however, less than 1% of the solution could be filtered from the wet aggregate, and thus the final mix contained approximately 99% of the aluminum sulfate originally introduced to the solution.

Zinc sulfate and pyrogallol solutions were introduced directly to cement and untreated aggregate for all specimens. For the concentrations used with Spratts aggregate, no problems were encountered in the mixing or casting procedures even though at higher concentrations pyrogallol had been shown to be a retarder [21].

Specimens with Opal replacements

As explained earlier, aluminum sulfate, pyrogallol, and zinc sulfate in the concentration range of 60-360 mM reduced the dissolution of opal in 1N sodium hydroxide. It was decided to use the chemicals at 240 and 360 mM in Stage II testing as admixtures. A total of 56 mortar bars (12" x 1" x 1") and 24, two-inch cubes were cast with two (1% and 3%) opal replacement levels. The 3% opal replacement is expected to be close to the pessimum level for this combination of materials. The detailed breakdown of the chemical/opal replacement combinations is given below.

Opal aggregate:

3 chemicals x 2 concentrations x 2 proportions x

4 bars/combination = 48 bars

2 proportions x 4 bars/proportion (Control) = 8 bars

Total = 56 bars

3 chemicals x 1 concentration x 2 proportions x

1 test period x 3 cubes/combination = 18 cubes

2 proportions x 1 test period x 3 cubes = 6 cubes

Total = 24 cubes

The pre-soak procedure used for aluminum sulfate solutions was similar to that used for Spratts aggregate except that only the opal portion of the aggregate was soaked in aluminum sulfate solutions. The limestone fraction was not pre-conditioned. Hence, more than 95% by weight of the aluminum sulfate solution could be filtered after the soaking period and only a small amount of aluminum sulfate was present in the final mix.

Initial attempts were made to directly use zinc sulfate and pyrogallol solutions during mixing. The mixes attempted with zinc sulfate solutions of 240 mM concentration stiffened and set even while in the mixing bowl. The mixes attempted with pyrogallol solutions of 240 mM concentration were excessively fluid and did not set for 24 hours. Based on these observations it was decided that zinc sulfate and

pyrogallol should not be added directly to the mix. Instead, the opal portion of the aggregate was pre-soaked in zinc sulfate and pyrogallol solutions. As before, 95% of the solutions could be filtered and thus only a small amount of the chemicals were present in the final mix.

The difficulty encountered in adding zinc sulfate and pyrogallol solutions at the required concentrations affected the expansions of the mortar bars made with opal. The effects will be discussed in detail in the next section.

Results

Effect of Chemicals on Mortar Bar Expansions

Bars made with Spratts Aggregate

The effect of the three admixtures on expansions of mortar bars made with Spratts aggregate is shown in Figure 7. Each point plotted in the graph is the average of at least four mortar bar expansions. The uncertainty band (one standard deviation about the mean) around each point, though not shown, is approximately half a division on the vertical scale. It is noted that the mortar bars were stored at room temperature (21-23 degrees Celsius) and thus the observed expansions will be smaller than those observed at ASTM C 227 storage temperatures (40 degrees Celsius).

After an initial period of shrinkage in the first week, the mortar bars with no chemical treatments (controls) had an expansion of 0.025% after eight months. The bars made with pyrogallol admixture can be observed to have expanded after some initial shrinkage and had a net expansion after eight months in storage. The bars made with aluminum sulfate presoak and zinc sulfate admixture can be seen to have a net shrinkage even after eight months of storage. From Figure 7 a tentative conclusion might be reached that zinc sulfate admixture and aluminum sulfate pre-treatment reduced the expansions of mortar bars made with Spratts aggregate.

However, it is seen that the bars with chemical treatments experienced a large initial shrinkage during the first week. In order to prevent leaching of alkalies none of the containers used were equipped with blotting paper wicks. A review of the relative humidity measurements of the storage containers during the first week revealed that the relative humidity in all the containers, including the containers holding the control bars, was 60-70%. Normal drying shrinkage can occur at these humidities. Thus, the observed initial shrinkage may be due to the effect of the chemicals in conjunction with the environmental conditions present during the first week of storage. Since all bars were subjected to the same conditions, it can be concluded

that the presence of chemicals has enhanced the shrinkage propensities of the mortar bars. It is noted that all the storage containers reached relative humidity levels of 90-98% after the first week.

In order to determine the importance of the initial shrinkage on the observed final expansions, the data in Figure 7 have been re-graphed in Figure 7a with the initial shrinkage subtracted from all subsequent readings. It is seen that if the initial shrinkage is not considered, there is no significant difference in the expansions of mortar bars made with and without admixtures.

The results of Stage II (admixture) tests on mortar bars made with Spratts aggregate indicate that zinc sulfate admixture and pre-treatment of aggregates with aluminum sulfate might reduce the expansions due to alkali-silica reaction in concrete structures. The increased shrinkage of cement mortar observed with these admixtures, however, clouds this conclusion and makes it less definite.

Bars made with Opal Replacements

The effect of the three chemicals on mortar bars made with 1% opal replacement is shown in Figure 8. The bars with no chemical treatment (control) started shrinking and had a net shrinkage after eight months. Pyrogallol treatments increased the expansions of mortar bars. Aluminum sulfate and zinc sulfate treatments have expanded less than bars treated with pyrogallol. The shrinkage of control bars in this case, however, makes suspect the results obtained with chemical additions.

The expansions of bars made with 1% opal replacement without the initial shrinkage is shown in Figure 8a. If the initial shrinkage is neglected, it is seen that the bars with no chemical treatment have expanded 0.02% in 8 months, a level of expansion which is considerably lower than normal. This trend was very surprising. Previous experiments with 1% opal replacement have shown that the mortar bars expanded considerably. Attempts were made to determine the cause of this anomalous behavior. X-ray diffraction studies of the opal, re-analysis of the cement, and a review of the mix designs for the mortar batches was performed to determine the cause of the low expansions. None of these investigations revealed the reasons for the observed low expansions.

The effect of the three chemicals on mortar bars made with 3% opal replacement is shown in Figure 9. The bars with no chemical treatments (control) had expanded about 0.08% after eight months. It is observed that pyrogallol pre-treatments have <u>increased</u> the expansions while aluminum sulfate pre-treatments have decreased the expansions of the

mortar bars. Zinc sulfate pre-treatment seems to have decreased the expansion when used at 240 mM concentration while it seems to have made no significant difference at 360 mM. It is reiterated here that zinc sulfate and pyrogallol could not be added to the mix directly because of the effect of the high concentrations on the setting properties of the mix. The expansions of the bars without the initial shrinkage is shown in Figure 9a. The expansion plots have shifted upward but the conclusions remain the same.

It was observed during the measurement of mortar bars that a number of them were cracked. The expansion of mortar bars made with 3% opal replacement is plotted against the presence or absence of cracking in Figure 10. It is seen that, with a few exceptions, bars which had expanded more than 0.10% had cracked while bars which had expanded less than 0.10% had not cracked.

Effect of Chemicals on Amount of Reaction Products

Bars made with Spratts Aggregate

A total of four sets of bars made with Spratts aggregate were broken and tested for the amount of reaction products. A set consisted of four mortar bars - a control bar and three bars with the three admixtures at one of the two concentrations used. Though all the 16 bars showed alkali-silica reaction products, there was no significant difference in the amount of reaction products between the bars made with admixtures and the control mortar bar. Photograph 1 shows the mortar bars in natural light while Photograph 2 shows the fluorescence of reaction products (under ultra-violet light) in a typical set of four bars. The areas of greenish-yellow fluorescence are the locations of the reaction products.

Bars made with Opal Replacements

Two sets of mortar bars were broken for each of the two opal replacement percentages used. Photographs 3 and 4 show the mortar bars and the reaction products in a set made with 1% opal replacement while Photographs 5 and 6 show the mortar bars and the amount of reaction products in a set made with 3% opal replacement. It is observed that the amount of reaction product in mortar bars made with 3% opal replacement is considerably higher than the amount found in those made with 1% opal replacement. In the bars made with 1% opal replacement (Photograph 4), the bars made with pyrogallol and zinc sulfate pre-treatment have a lesser amount of reaction products when compared with the control bar and the bar made with aluminum sulfate pre-treatment. In the case of mortar bars made with 3% opal replacement (Photograph 6), it is seen that there is no significant difference in the amount of reaction product among the bars.

Effect of Chemicals on Compressive Strength

Cubes made with Spratts Aggregate

As discussed earlier, a limited number of 2-inch mortar cubes were cast from the same batches used to cast mortar bars. A total of 42 cubes were made and tested for compressive strength at two periods. The results of the tests are shown in Figure 11. It is observed that the chemical admixtures had no deleterious effect on the compressive strength of mortar cubes made with Spratts aggregate. On the contrary, zinc sulfate additions seem to have increased the compressive strength of mortar cubes. Aluminum sulfate pre-treatment and pyrogallol additions did not significantly change the compressive strength of mortar cubes made with Spratts aggregate.

Cubes made with Opal Replacements

A total of 24 cubes were made with two opal replacements (1% and 3%) and were tested for compressive strength 60 days after casting. The cubes were stored at 90-95% relative humidity and room temperature after demolding at 24 hours. The results of the tests are shown in Figure 12. It is seen that the chemical treatments did not significantly alter the compressive strength of the mortar cubes. It is emphasized that in the case of mortar bars made with opal replacements, the chemicals were used as pre-treatments and not as admixtures.

Conclusions from Stage II

The following conclusions can be made from the chemical admixture tests conducted on mortar bars made with Spratts aggregate and mortar bars made with 1% and 3% opal replacements:

1. Aluminum sulfate pre-treatments and zinc sulfate admixture appeared to slightly reduce the net expansions of mortar bars made with reactive Spratts aggregate when the extreme shrinkage is included.

2. Aluminum sulfate pre-treatment and zinc sulfate admixture seem to have increased the shrinkage of mortar bars made with Spratts aggregate.

3. When the initial shrinkage of the bars was neglected, there was no significant difference in the post-shrinkage expansions of bars with and without chemical treatments.

4. Chemical additions at the required concentration levels could not be added to the mortar mixes with opal replacements due to the undesirable effects on the setting

properties of the mixes. Thus, aluminum sulfate, zinc sulfate, and pyrogallol were used as pre-treatment for the opal portion of the aggregate in these tests.

5. For mortar bars made with 1% opal replacement, pyrogallol pre-treatment increased the expansions while zinc sulfate and aluminum sulfate pre-treatment did not decrease the expansions.

6. Zinc sulfate pre-treatment at 240 mM concentrations and aluminum sulfate pre-treatment decreased the expansions of mortar bars made with 3% opal replacement.

7. Pyrogallol pre-treatments increased the expansions of mortar bars made with 3% opal replacements.

8. There was no significant difference in the amount of reaction products observed in mortar bars made with Spratts aggregate with and without chemical admixtures.

9. For mortar bars made with 1% opal replacements, there was a marked reduction in the amount of reaction product observed in mortar bars made with pyrogallol and zinc sulfate pre-treatments.

10. For mortar bars made with 3% opal replacements, there was no significant difference in the amount of reaction product observed in mortar bars made with and without admixtures.

11. There was no significant reduction in compressive strength of mortar cubes made with admixtures when compared to cubes made without chemical admixtures.

Stage III: Evaluation of promising Chemical Agents from Stage I as Penetrants to Retard ASR in Progress

Introduction

The effectiveness of chemicals in arresting or retarding distress to existing concrete was studied in Stage III. For the reasons discussed in the introduction to Stage II, this study was also conducted with mortar bars made with crushed reactive aggregate instead of concrete mixes. Bars made without chemical treatments (control bars) in Stage II remained in storage until they had sufficiently expanded due to alkali-silica reaction. The bars were then soaked in chemical solutions and the subsequent expansions monitored over a period of time.

Since the pH of pore solution of hardened concrete is high (12-14), only chemicals that are stable at high pH could be used in Stage III. Of the three chemicals selected

in Stage I, zinc sulfate and pyrogallol are stable at high pH and were therefore considered as penetrants in Stage III.

As discussed earlier, the concentration of chemicals needed for bars made with opal replacements was about 15-20 times greater than the concentrations required for mortar bars made with Spratts aggregate. Mortar cubes made with opal replacements were immersed in zinc sulfate and pyrogallol solutions of 360 mM concentration. Freshly prepared pyrogallol solutions were transparent to light and had a light color. In a few weeks the color of the pyrogallol solutions turned very dark and surface discolorations of the immersed mortar cubes could be observed. The immersion solutions also seemed to coagulate and had a thick consistency. Though the mortar cubes were tested for compressive strength, it was decided that mortar bars made with opal replacements would not be immersed in pyrogallol solutions as originally planned. Since pyrogallol solutions of 12 and 24 mM concentrations, in which mortar cubes made with Spratts aggregate were immersed, also showed similar behavior after 45 days it was decided that mortar bars made with Spratts aggregate would not be immersed in pyrogallol solutions.

Experimental Procedure

Mortar bars and mortar cubes made with Spratts aggregate and opal replacements cast in Stage II were immersed in chemical solutions. The expansions of mortar bars were monitored approximately once a week after immersion. Mortar cubes were similarly immersed in chemical solutions and tested for compressive strength after two to three months of immersion. A detailed break-down of the type and number of specimens tested in Stage III is given below:

Spratts aggregate:

1 chemicals x 2 concentrations x 4 bars/combination = 8 bars

Control = 4 bars

Total = 12 bars

5 immersion conditions x 2 time periods x 3 cubes/combination = 30 cubes

Opal aggregate:

1 chemicals x 2 concentrations x 2 proportions x

4 bars/combination = 16 bars

Control = 4 bars

Total = 20 bars

3 immersion conditions x 2 proportions x 1 test period

x 3 cubes/combination = 18 cubes

Results

The effect of zinc sulfate immersions on mortar bars made with Spratts aggregate is shown in Figure 13. It is seen that there is no significant difference in the subsequent expansion of bars immersed in water and bars immersed in zinc sulfate solutions up to 125 days. Three bars were broken to determine the differences in the amount of reaction products (if any) due to the penetrant. Photograph 7 shows the three bars in natural light while Photograph 8 shows the three bars under short wave ultraviolet light. It is observed that there is no significant difference in the amount of reaction product between the bars immersed in zinc sulfate and the bar immersed in water.

The effect of zinc sulfate immersions on mortar bars made with 1% opal replacement is shown in Figure 14. The bars immersed in 360 mM zinc sulfate solution expanded considerably upon immersion but the final expansion of bars immersed in water and bars immersed in zinc sulfate solutions are not significantly different. As discussed earlier, the bars made with 1% opal replacement are considered to be suspect because of the abnormally low expansions of the control bars. Three bars were broken to determine the amount of reaction products and Photograph 9 shows the three bars in natural light while Photograph 10 shows the same bars under ultraviolet light. It is seen from Photograph 10 that there is no significant difference in the amount of reaction product among the three bars.

The effect of zinc sulfate immersions on mortar bars made with 3% opal replacement is shown in Figure 15. It is observed that on immersion all bars experienced a large expansion after which the expansions seem to have proceeded at a very slow rate. Zinc sulfate immersions in this case, however, have reduced the subsequent expansions of mortar bars significantly. The expansions plotted in Figure 15 are the average of 4 mortar bars. Visual observation showed

that while all four bars immersed in water had cracked extensively, none of the eight bars immersed in zinc sulfate showed cracking. The results of the gel fluorescence test (Photographs 11 and 12), however, showed no significant difference in the amount of reaction product between the bars immersed in water and bars immersed in zinc sulfate solutions.

The results of immersion tests on mortar cubes made with Spratts aggregate is shown in Figure 16. There is considerable scatter in the compressive strengths obtained and it is observed that there are no significant reductions in the compressive strengths of cubes immersed in zinc sulfate and pyrogallol solutions.

The effect of immersion on the compressive strengths of mortar cubes made with opal replacements is shown in Figure 17. Immersion in pyrogallol (360 mM) has decreased the compressive strength of the mortar cubes while immersion in zinc sulfate has not significantly changed the compressive strength values.

In all cases above, in which mortar specimens were soaked in a variety of solutions, the effect of leaching, if any, was not specifically addressed.

Conclusions from Stage III

The following conclusions can be made from the abbreviated study conducted on bars which had been preconditioned as described herein:

1. For mortar bars made with Spratts aggregate there was no significant difference in the expansion of bars immersed in water and the expansion of bars immersed in zinc sulfate solutions (12 mM and 24 mM) up to a period of 125 days after immersion.

2. For mortar bars made with Spratts aggregate there was no significant difference in the amount of reaction product between bars immersed in water and bars immersed in 12 mM and 24 mM zinc sulfate solutions.

3. For mortar bars made with 1% opal replacement there was no significant difference in the expansion of bars immersed in water and the expansion of bars immersed in zinc sulfate solutions (240 mM and 360 mM) up to a period of 180 days after immersion.

4. Immersion in zinc sulfate solutions (240 mM and 360 mM) significantly reduced the subsequent expansion of mortar bars made with 3% opal replacement.

5. Immersion in zinc sulfate solutions (240 mM and 360 mM) also seemed to inhibit cracking of mortar bars made with 3% opal replacement.

6. There were no significant differences in the amount of reaction products in mortar bars made with opal replacements and immersed in water or zinc sulfate solutions.

7. There is no significant compressive strength reductions of mortar cubes due to the zinc sulfate immersions.

Discussion

Deterioration of concrete due to alkali-silica reaction is generally believed to proceed as follows: The hydroxyl ions present in cement pore solution react with amorphous or strained silica (SiO_2) and cause the silica to go into solution. In the presence of calcium hydroxide, which is plentiful in concrete, the silica immediately precipitates to ultimately form a reaction product known generally as "alkali-silica gel". If moisture is available, the gel imbibes the moisture, swells, and exerts pressure on the surrounding matrix. When the stress on the matrix exceeds the strength of the matrix, cracks form and the concrete is gradually deteriorated.

The fundamental hypothesis of this short project was to test whether retardants of silica dissolution will prevent the initiation of alkali-silica reaction in fresh concrete and to test whether the same retardants could be used as penetrants to stop the progress of ASR in hardened concrete. It is seen from the description of the reaction mechanism described above that silica dissolution in highly alkaline solutions is the first step in the onset of ASR damage.

The intent of Stage I was to quickly evaluate the efficacy of 10 chemicals in retarding the dissolution of silica in a model high-alkali solution, namely 1N sodium hydroxide. The results obtained in Stage I show that pyrogallol, zinc sulfate, and aluminum sulfate dramatically reduced the dissolution of silica in 1N sodium hydroxide. It was also found that Spratts aggregate (a natural reactive aggregate from Ontario) required chemical concentrations of less than 24 mM, while highly reactive opal required a much larger concentration (360 mM) of chemicals for similar reductions in solubility. This result suggests that to obtain similar reductions in silica dissolution in concrete, the concentration of chemical agents in the final pore solution in concrete must be similar to the concentrations proven effective with 1N sodium hydroxide.

While the initial chemical concentration represented by the admixture dosage in Stage II matched those determined in Stage I, the fraction of dissolved species which may have been incorporated into the products of hydration or otherwise reacted with the portland cement is not known. As a result the final or "effective" concentration of the chemical agents at the aggregate surface is not known. One can only estimate that the final concentration of the chemical agents in the pore solution would probably have been lower than the initial concentration.

The results of admixtures on expansions of mortar bars made with Spratts aggregate may be interpreted to suggest that zinc sulfate additions and aluminum sulfate pre-treatments reduce the expansions due to alkali-silica reactions. However, it may be that the differences observed in the final expansions of the mortar bars is simply due to the large initial shrinkage strains experienced by the bars with chemical additions. The effectiveness of the chemicals in reducing silica dissolution in Stage I and their ineffectiveness in reducing expansions in Stages II and III raises questions about the mechanism of alkali-silica reaction and expansion. This is discussed further under "Potential Applications".

The negligible effects of chemicals at low concentrations on the compressive strength of mortars is encouraging and suggests that if the chemicals do prevent or retard alkali-silica reaction, they will not have to be discarded because of undesirable side effects on other properties of concrete. It is cautioned that such a suggestion is supportable at this point only for low concentrations of the chemicals, and only for compressive strength of mortars.

The significant reduction in the subsequent expansion of mortar bars made with 3% opal replacements and immersed in zinc sulfate can be interpreted to mean that if the chemical concentration in the pore solution is similar to that used in Stage I, zinc sulfate may retard the expansions due to alkali-silica reaction. The delivery of the desired chemical agent to the reaction site may be the most significant practical problem in the use of penetrants to retard the progress of ASR. Attempts to conduct further studies of forced injection should await conclusive evidence from admixture studies using the same chemical.

Overall Conclusions

1. Aluminum sulfate, zinc sulfate, and pyrogallol were found to be effective retardants of silica dissolution in 1N sodium hydroxide.

2. The concentration of chemicals needed to reduce the solubility of opal was found to be about 15 times the concentration of chemicals needed for Spratts aggregate.

3. When the chemicals were used as admixtures, zinc sulfate and aluminum sulfate seemed to reduce the net expansions of mortar bars made with Spratts aggregate while pyrogallol did not significantly reduce the expansions. All bars experienced a large initial shrinkage. When the initial shrinkage was neglected, there was no significant difference in the post-shrinkage expansions of mortar bars with and without chemicals.

4. Chemical admixtures at the required concentration levels could not be added to the mortar mixes with opal replacements due to the undesirable effects on the setting properties of the mixes. Therefore, the results of admixture tests on mortar bars made with opal replacements were ambiguous.

5. There were no significant differences in the amounts of reaction product between bars that were immersed in water and bars that were immersed in chemical solutions.

6. There was no significant reductions in compressive strength of mortar cubes due to the admixtures.

7. When used as penetrants the chemicals did not have any significant effect on the subsequent expansions of mortar bars made with Spratts aggregate and 1% opal replacement.

8. Zinc sulfate immersions, however, significantly reduced the subsequent expansion of mortar bars made with 3% opal replacement. Zinc sulfate also appeared to inhibit cracking of the mortar bars.

9. There was no significant reduction in the compressive strength of mortar cubes immersed in chemical solutions when compared with the compressive strength of cubes immersed in water.

Suggestions for Further Study

The results of Stage I have clearly demonstrated that there are at least three chemicals, namely aluminum sulfate, zinc sulfate, and pyrogallol, which can reduce the solubility of silica in highly alkaline solutions. When the chemicals were added directly to mortar mixes and used as aggregate pre-treatments, there seemed to be no significant difference between the expansions of mortar bars with and without the chemical treatments. It is likely, however, that the final concentration of these chemicals in the pore solution was less than the initial concentration used. It would be of value to use pore solution extraction techniques

Problems encountered

The two-month delay between Stage I and the following stages were caused by two reasons: a) delay in the delivery of Spratts aggregate from Canada and b) the unanticipated delay in the formal approval of Stage II and Stage III.

The mortar bars made with Spratts aggregates did not expand as rapidly as expected in Stage II testing. Since Stage III testing could commence only after the control bars in Stage II had expanded sufficiently, the initiation of Stage III was delayed by a few months. This proved to be useful for Stage II testing since the additional time allowed more reliable conclusions to be drawn from Stage II results.

References

[1] K.C. Hover and K. Natesaiyer, "Development of chemical agents for the control of alkali aggregate reaction in concrete", proposal submitted to Strategic Highway Research Program, April 1988.

[2] K.C. Hover and K. Natesaiyer, "Development of chemical agents for the control of alkali aggregate reaction in concrete", addendum to proposal submitted to Strategic Highway Research Program, October 1988.

[3] K.C. Hover and K. Natesaiyer, "Development of chemical agents for the control of alkali aggregate reaction in concrete", Second quarterly report and summary report of Stage I, submitted to Strategic Highway Research Program, October 1989.

[4] K.C. Hover and K. Natesaiyer, "Development of chemical agents for the control of alkali aggregate reaction in concrete", First quarterly report, submitted to Strategic Highway Research Program, July 1989.

[5] K.C. Hover and K. Natesaiyer, "Development of chemical agents for the control of alkali aggregate reaction in concrete", Third quarterly report, submitted to Strategic Highway Research Program, February 1990.

[6] DentGlasser and Kataoka, Cement and Concrete Research, Vol.11, No.2, 1981, pp 191.

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to determine the concentration of the chemicals in the pore solution, or tests to determine the concentration of species adsorbed to the aggregate surface. Such studies would provide information on the initial dosage of chemicals necessary to provide the required final concentration in the pore solution or at the aggregate surface. Subsequent tests with the correct dosage should then provide conclusive evidence on the efficacy of the chemicals in preventing the dissolution of reactive aggregates and thus prevent damage due to alkali-silica reaction in concrete.

An alternative approach to determine the effectiveness of the chemicals in cement-water systems would be to conduct a modified Quick chemical test with cement-water-crushed aggregate systems and added alkalies. Since the mixture has to be filtered to determine the silica concentration in solution, a high water to cement ratio (2 to 3) should be used.

A number of research workers around the world are attempting various approaches to develop admixtures to prevent alkali-silica reaction in concrete. One of the themes of the research has been to attempt to immobilize the alkalies in the pore solution by means of compounds such as phosphates, crown ethers, or mercaptans. To date, only limited success has been derived from this approach. Other workers are attempting to change the characteristics of the reaction product from a gel with swelling tendencies to a gel with non-swelling properties. Lithium salts seem to be effective in this respect though conclusive results are not available. A mixture of chemicals which reduce the dissolution of silica and chemicals which alter the swelling characteristics of the reaction product may be a fruitful avenue for further work in this area.

Potential Applications

As mentioned earlier, the results of Stage I have demonstrated that aluminum sulfate, zinc sulfate, and pyrogallol are effective retardants of silica dissolution in high alkali solutions. The ineffectiveness of the same chemicals in reducing the expansions of mortar bars in Stages II and III raises a number of questions about the widely believed mechanism of alkali-silica reaction and expansion. There is currently a concerted effort to elucidate the mechanism of alkali-silica damage by Construction Technology Laboratories, the prime contractor for SHRP C-202. It would be of great value to transmit the results of this study to SHRP C-202 workers since it might aid them in refining their model of damage due to alkali-silica reaction. The authors would be willing to discuss this in greater detail with SHRP and C-202 personnel.

One of the reasons for the ineffectiveness of the chemicals when used with portland cement mortar may be related to the final concentration of the chemical in the pore solution of the mortar mixes. If the correct initial dosage of the chemical to provide the desired final dosage in the pore solution can be found, the chemicals can then be used with concrete mixes to prevent alkali-silica damage.

The effectiveness of the chemicals in reducing dissolution of silica in high alkali solutions will be useful in the formulation of an ASR reducing admixture. As mentioned earlier, a mixture of chemicals which reduce the dissolution of silica and chemicals which alter the swelling characteristics of the reaction product may be an effective approach to the development of an ASR reducing admixture.

The effectiveness of the chemicals in reducing the solubility of silica in high alkali solutions will also be useful in the development of stable glass fibers for use in fiber-reinforced concrete. The chemicals may also be applicable to other areas of glass chemistry.

The negligible effect of pyrogallol and zinc sulfate additions on the compressive strength of mortar mixes may be useful in formulating new retarders and accelerators for concrete mixes. Singh et al. [21] have reported that pyrogallol, though a good retarder, severely reduces the compressive strength of cement paste cubes. The initial concentration of pyrogallol used, however, was 130 mM. The results of this study suggests that when used at 12-24 mM concentrations pyrogallol has no significant effect on the compressive strength. Similarly, zinc sulfate or other zinc salts may be useful as set accelerators which do not have other undesirable effects on concrete. {The Zn^{++} cation was used to advantage here. The impact of $(SO_4)^{--}$ anion would have to be carefully assessed.}

Variance from plan

There were a few variations in Stage II and Stage III due to information generated during the project. Originally it was proposed to test two chemicals as admixtures in Stage II and two chemicals as penetrants in Stage III. Due to the undesirable properties of pyrogallol, only one chemical (zinc sulfate) was tested as a penetrant in Stage III. However, three chemicals were tested in Stage II as admixtures.

The project was delayed by about two months after Stage I and by another four months in the following two stages. There were no other significant variance from the project plan.

[12] Y. Sakaguchi et.al., Proc. of the 8th Intnl. Conf. on AAR, Kyoto, Japan, 1989, pp 229.

[13] Y. Ohama et.al., Proc. of the 8th Intnl. Conf. on AAR, Kyoto, Japan, 1989, pp 253.

[14] P.P. Hudec and E.Y. Larbi, Proc. of the 8th Intnl Conf. on AAR, Kyoto, Japan, 1989, pp 193.

[15] C.A. Rogers, "General information on standard alkali reactive aggregates from Ontario, Canada", Engineering Materials Office, Ministry of Transportation, Ontario, Canada, pp. 40-59.

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[18] K. Natesaiyer and K.C. Hover, "Some field studies of the new insitu technique for the identification of ASR products", Proc. of the 8th Intnl. Conf. on AAR, Kyoto, Japan, 1989, pp. 555-560.

[19] C 277-81, "Standard test method for potential alkali reactivity of cement-aggregate combinations (mortar bar method)", Annual Book of ASTM Standards, Volume 4.02, American Society for Testing and Materials, Philadelphia, PA, 1990.

[20] C 109-84, "Standard test Method for compressive strength of hydraulic cement mortars", Annual Book Of ASTM Standards, Volume 4.01, American Society for Testing and Materials, Philadelphia, PA, 1990.

[21] N.B. Singh, S.P. Singh, and R. Sarvehi, "Effect of phenols on the hydration of portland cement", Advances in Cement Research, Vol. 2, No. 6, April 1989, pp. 43-48.

Table 1: Decision Tree for Stage 1

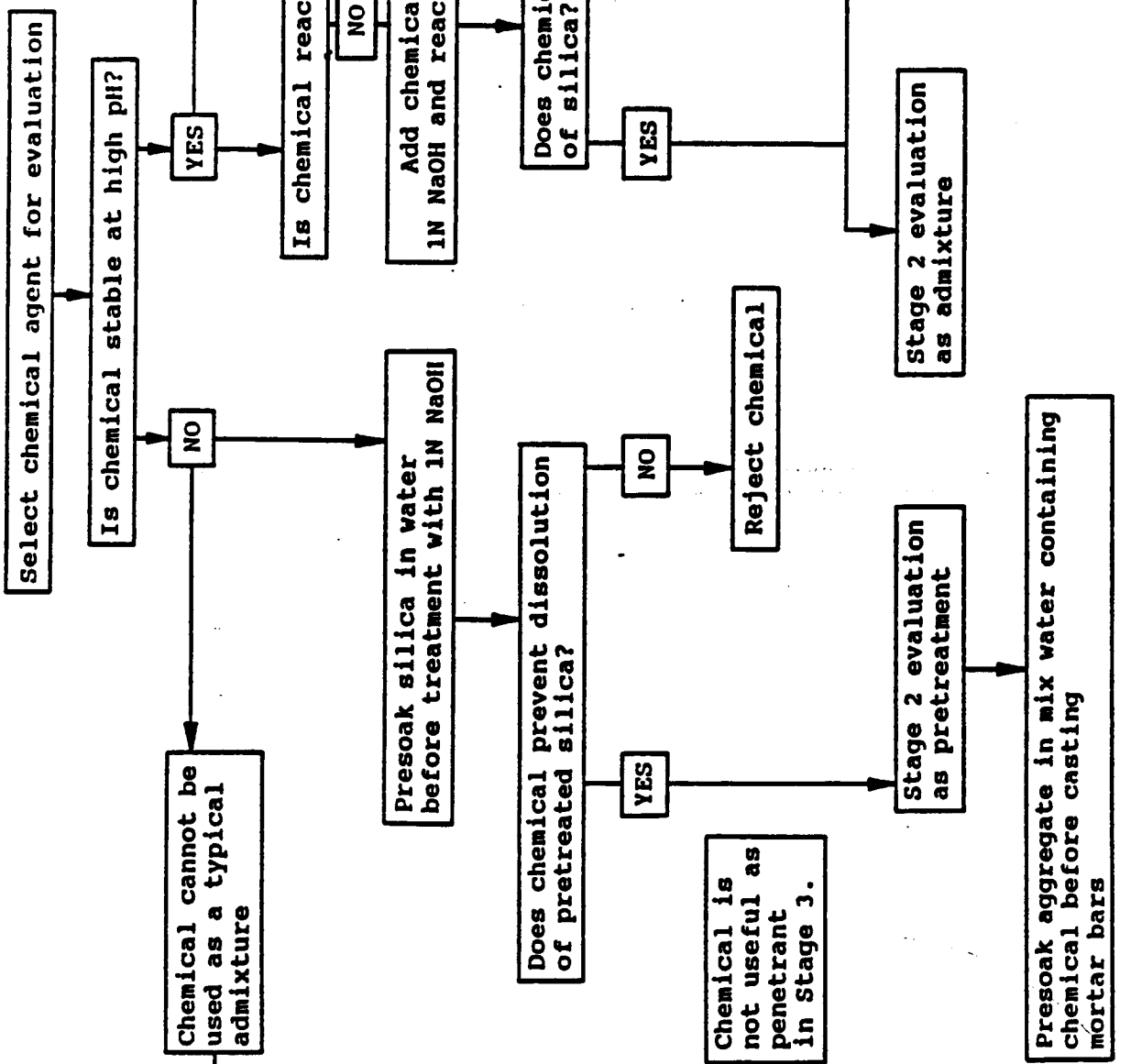


Table 2: Chemical agents tested in Stage I

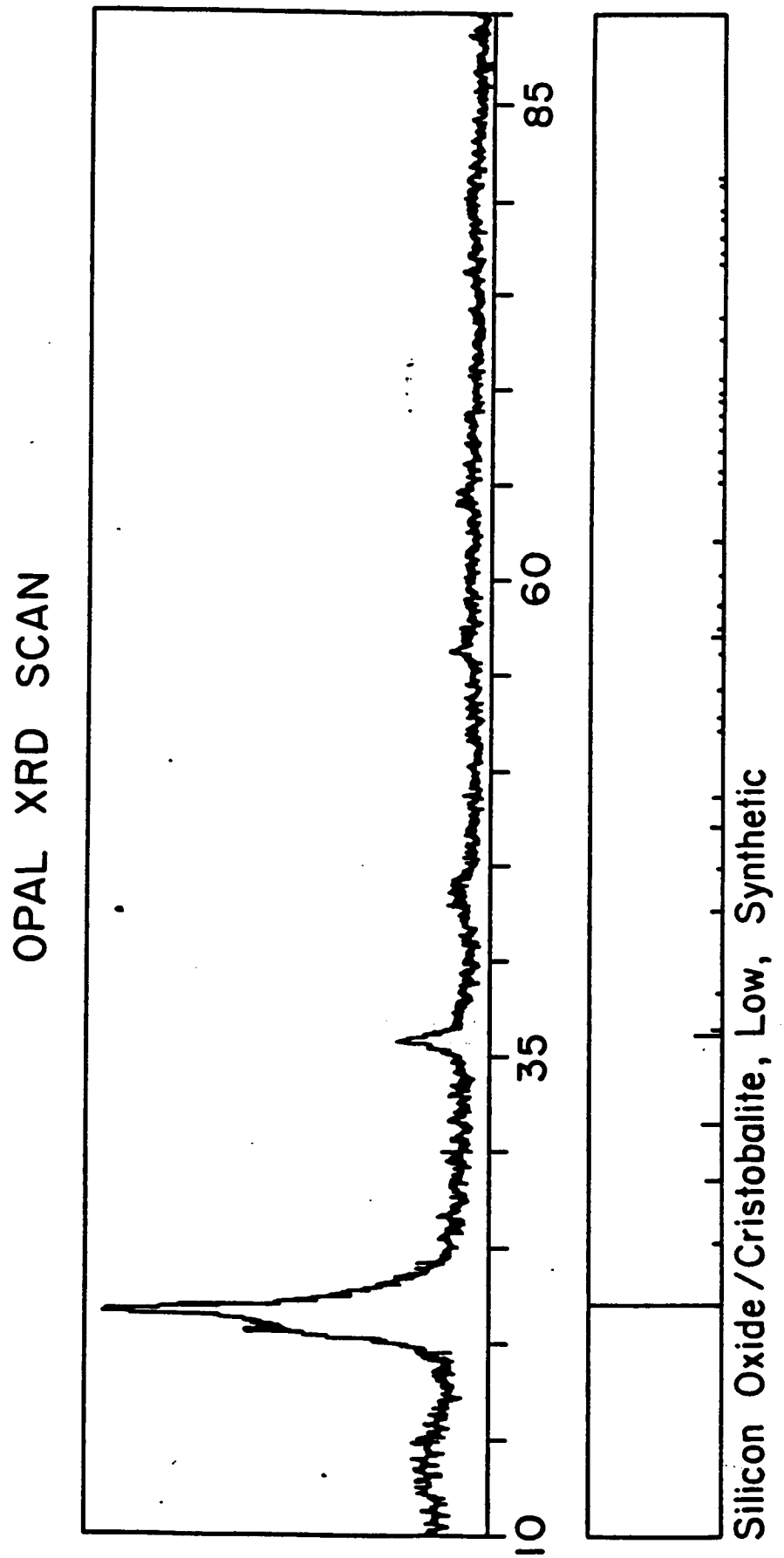
Chemical	References
Aluminum sulfate	[7], [8], [9], [10]
Zinc sulfate	[7], [8]
Pyrogallol	[7], [8]
Zirconium sulfate	[7], [8]
Catechol	[7]
Gadolinium nitrate	[7]
Uranyl acetate	[7]
Sodium fluosilicate	[13]
Lithium chloride	[11], [12]
Sodium orthophosphate (NaH_2PO_4)	[14]

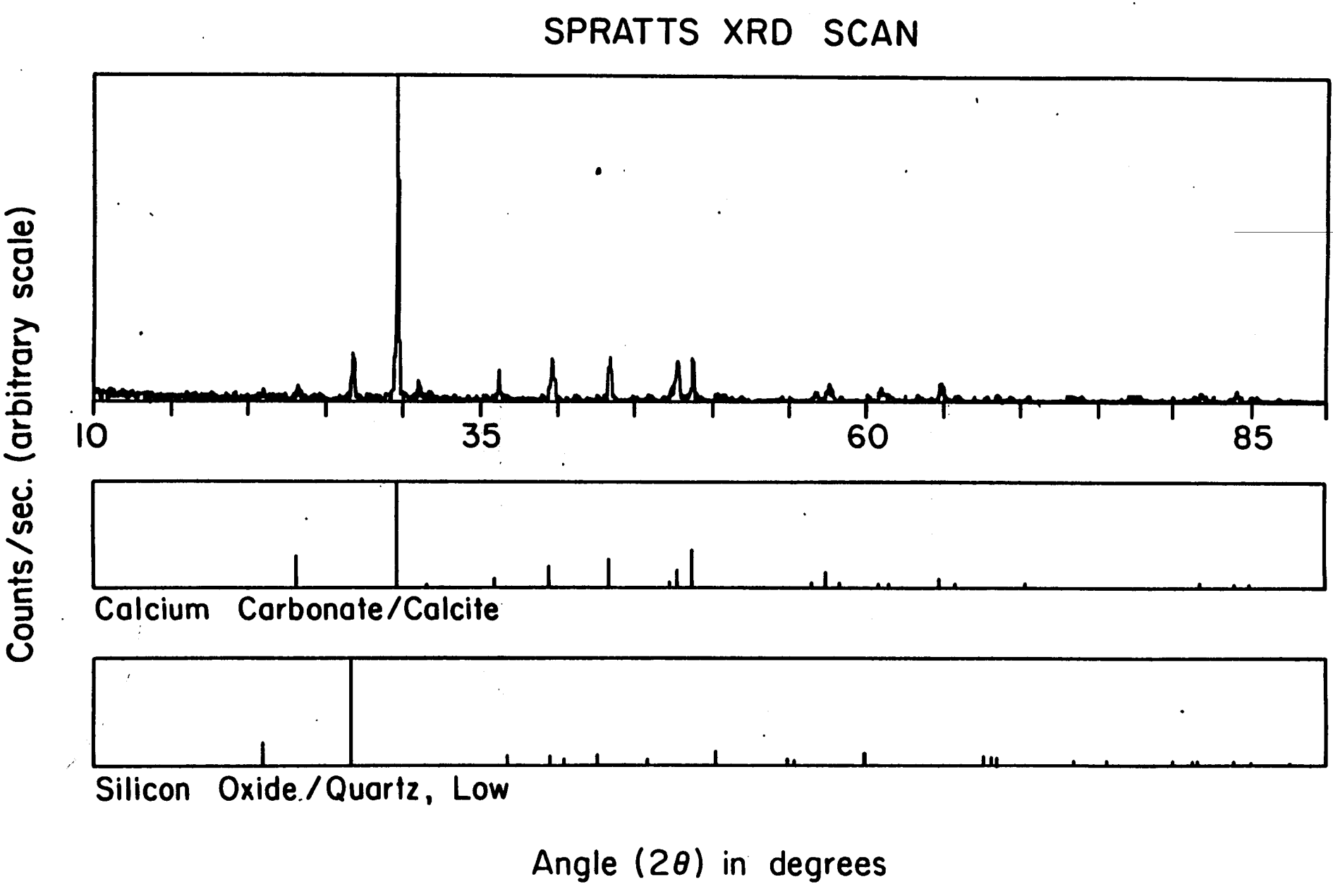
Table 3: Stability of chemicals in high pH solutions

Chemical	Stable (Yes/No)		Test Method
	$NaOH$	$Ca(OH)_2$	
Aluminum sulfate	no		Aggregate pre-treatment
Zinc sulfate	yes	yes	Direct addition to NaOH
Pyrogallol	yes	yes	Direct addition to NaOH
Zirconium sulfate	no		Aggregate pre-treatment
Catechol	yes	yes	Direct addition to NaOH
Gadolinium nitrate	no		Aggregate pre-treatment
Uranyl acetate	no		Aggregate pre-treatment
Sodium fluosilicate	no		Aggregate pre-treatment
Lithium chloride	yes	yes	Direct addition to NaOH
Sodium orthophosphate	yes	yes	Direct addition to NaOH

Table 4: Physical properties of reactive aggregates

Property	Aggregate Type	
	Opal	Spratts
Specific gravity	2.12	2.63
Water absorption (%)	-	0.67
Surface area (m^2/gm)	10.26	2.42


OPAL XRD SCAN
Counts/sec. (arbitrary scale)
10
35
60
85
Silicon Oxide/Cristobalite, Low, Synthetic
Angle (2θ) in degrees


SPRATTS XRD SCAN
Counts/sec. (arbitrary scale)
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35
60
85
Calcium Carbonate/Calcite
Silicon Oxide/Quartz, Low
Angle (2θ) in degrees

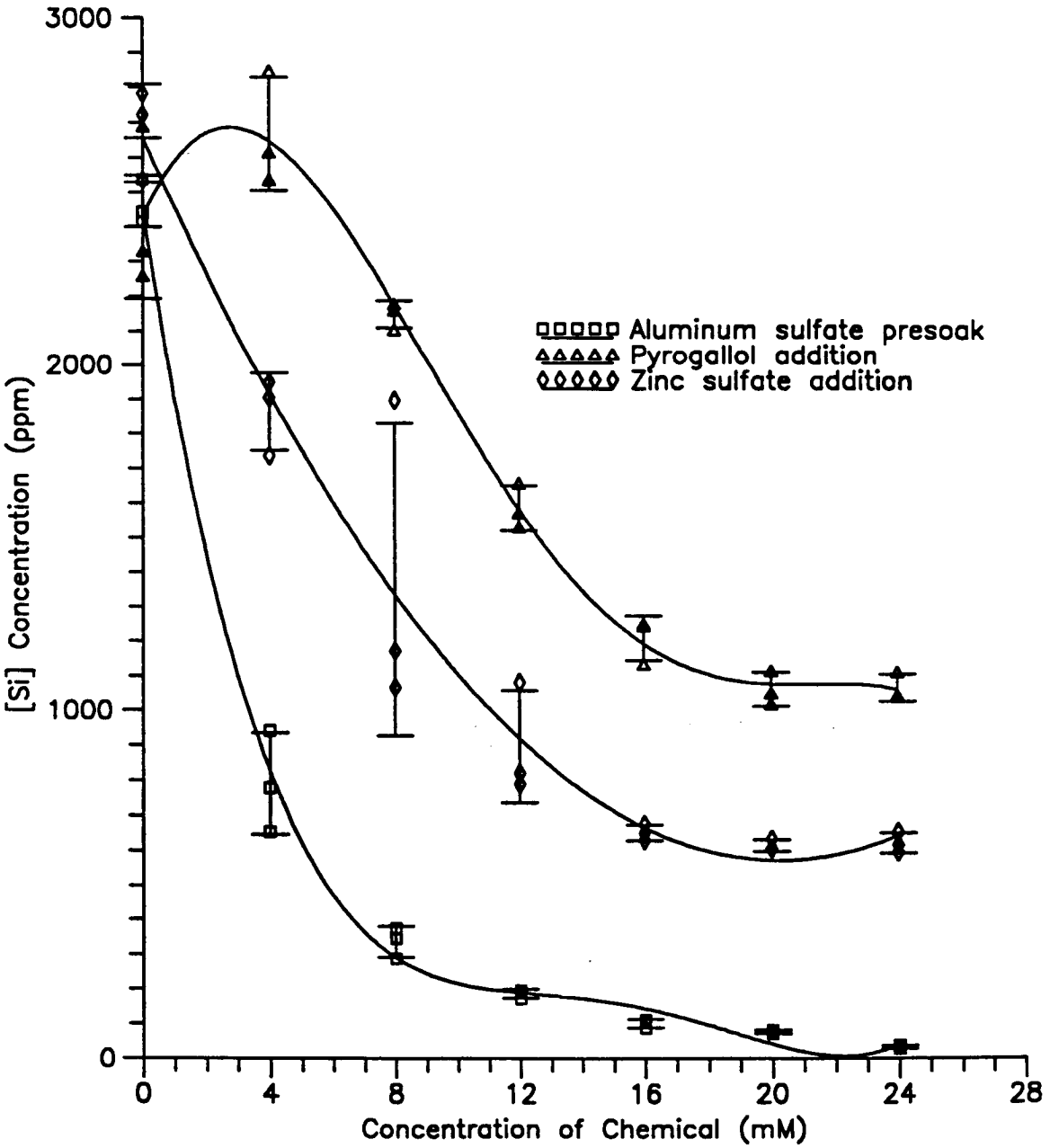


Figure 1: Effect of chemicals on solubility of spratts aggregate (ASTM C289)

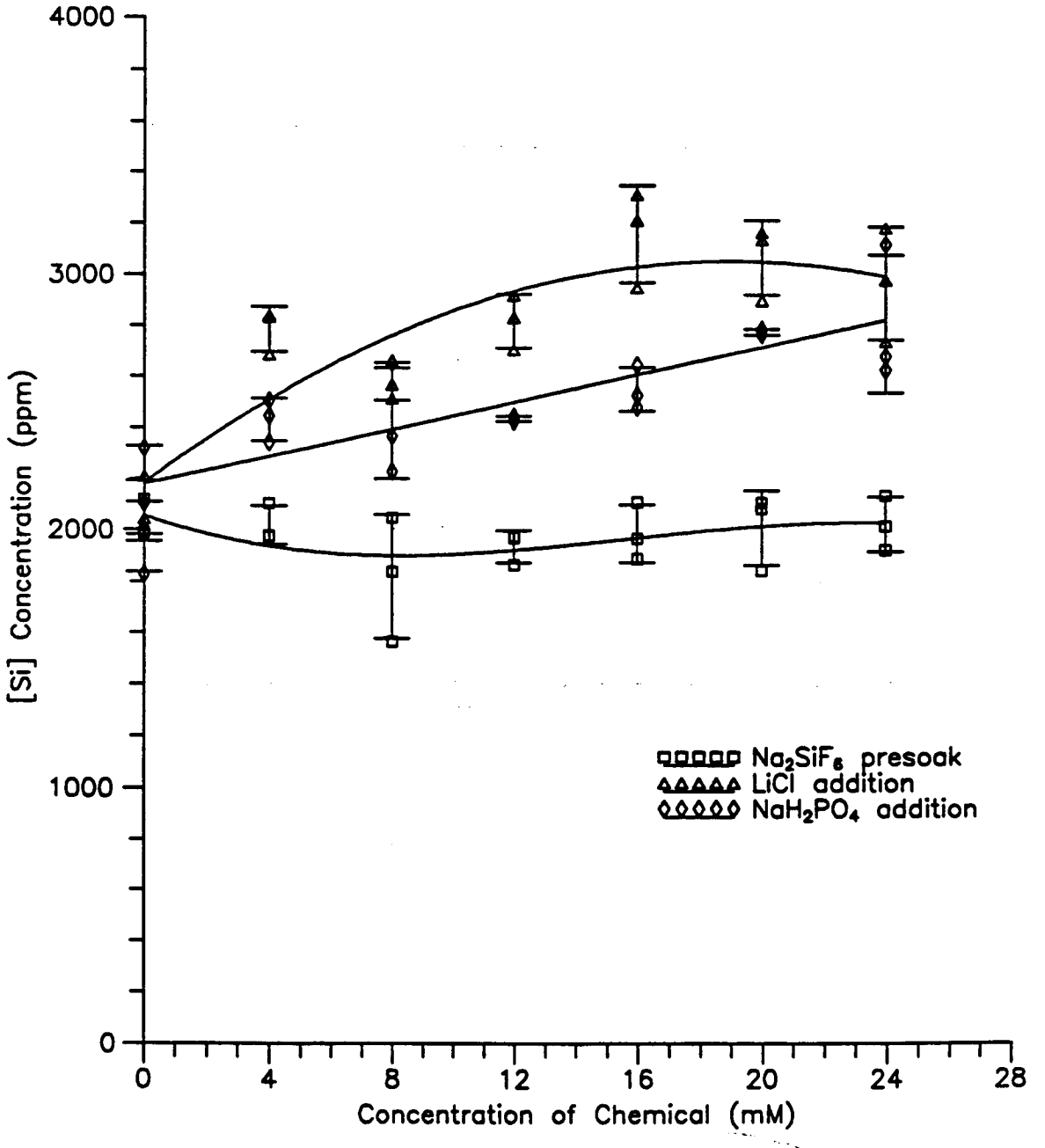


Figure 2: Effect of chemicals on solubility of spratts aggregate (ASTM C289)

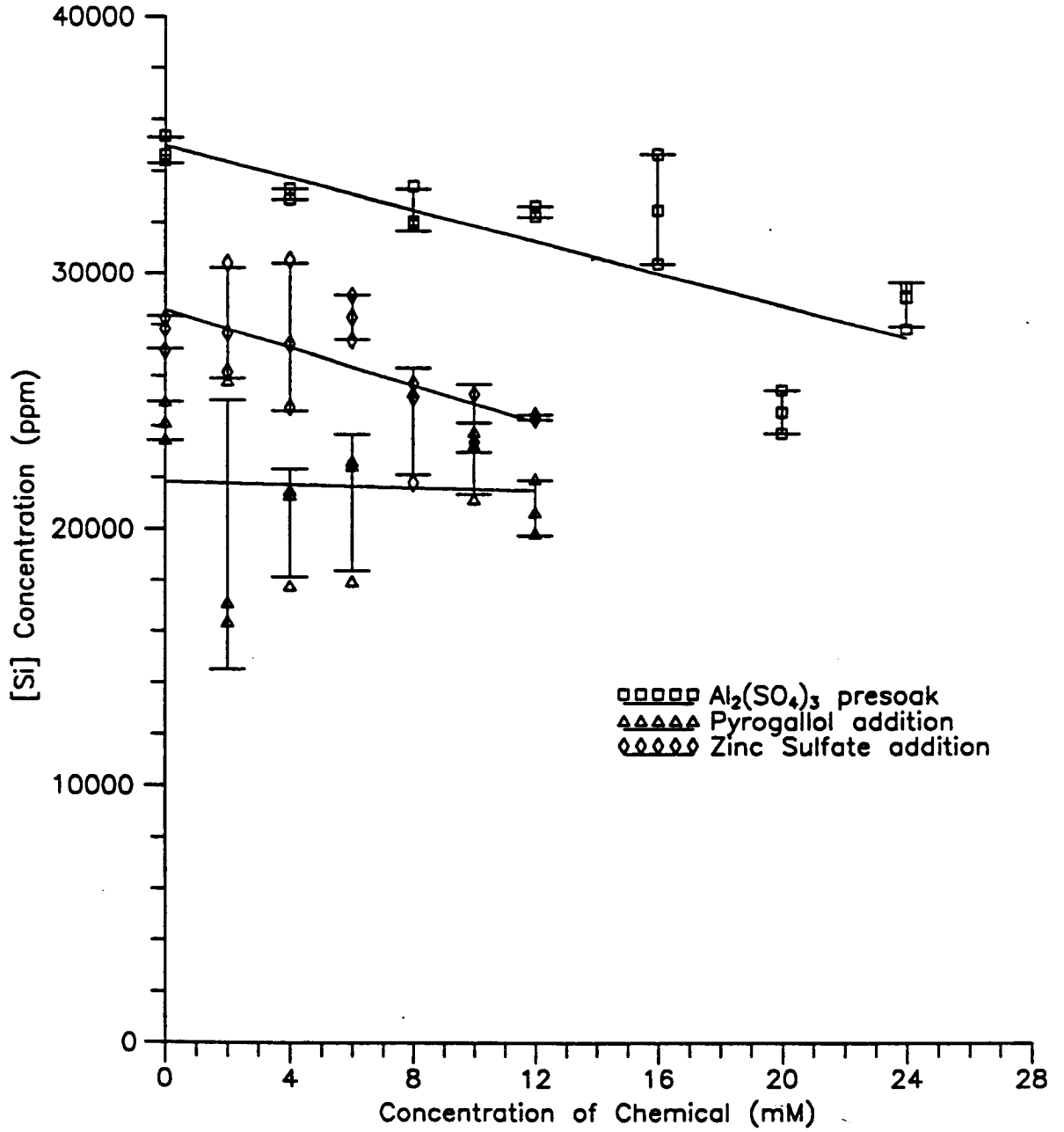


Figure 3: Effect of chemicals on solubility of opal (ASTM C289); Low concns

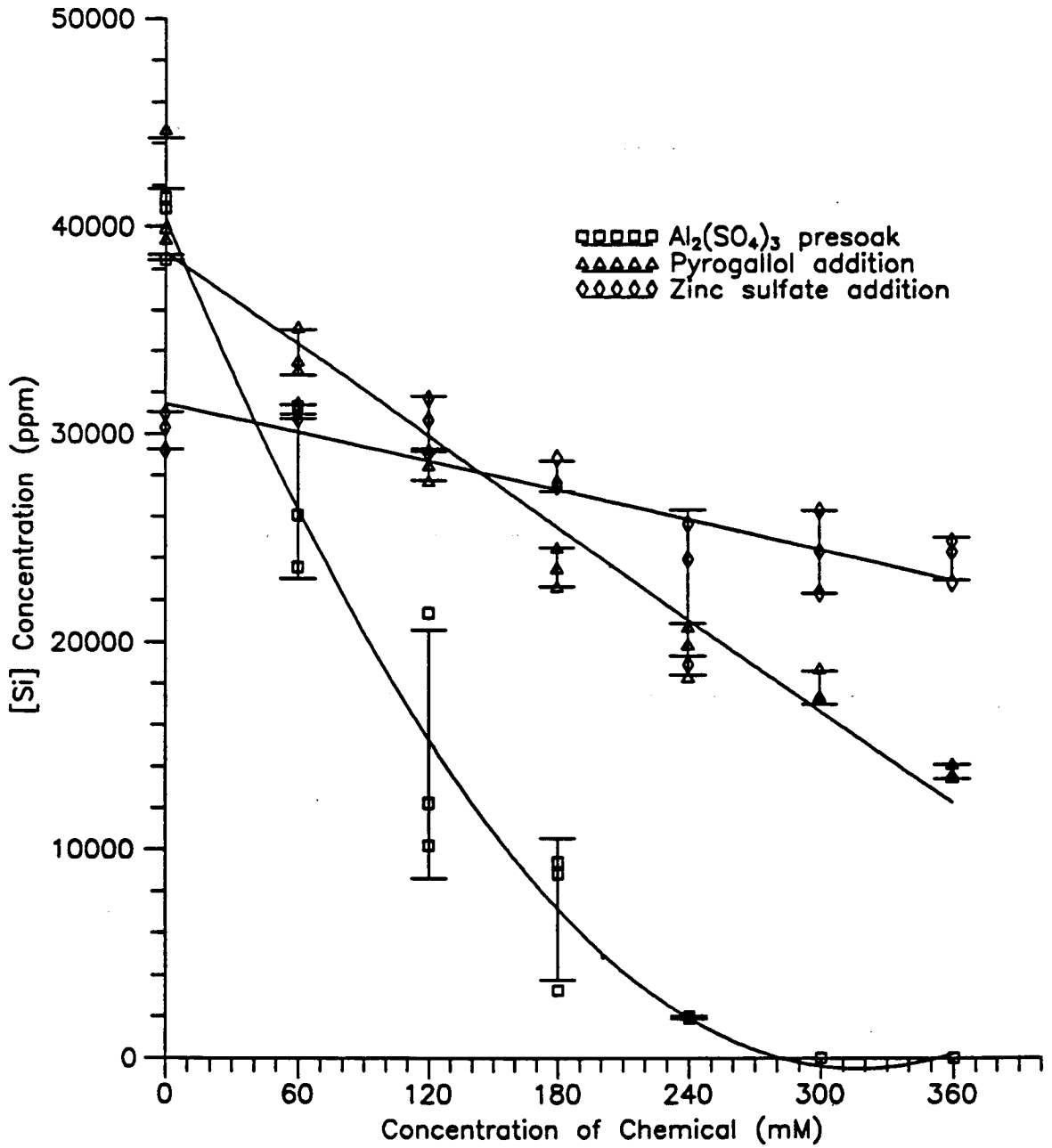
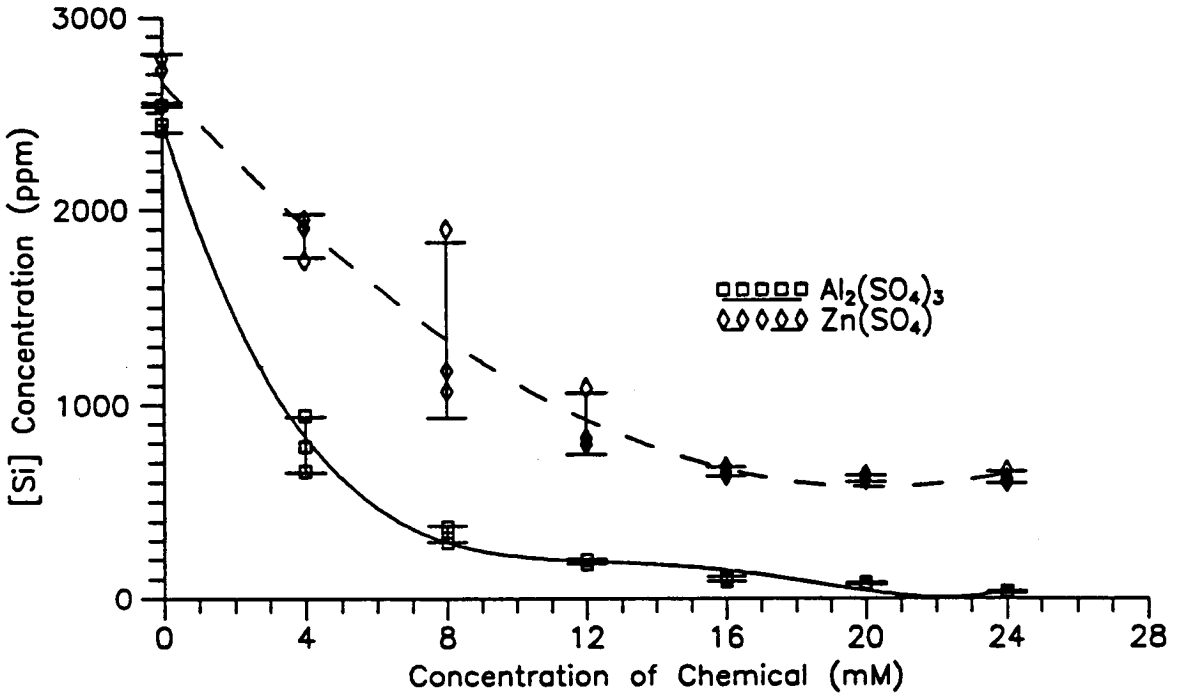


Figure 4: Effect of chemicals on solubility of opal (ASTM C289)



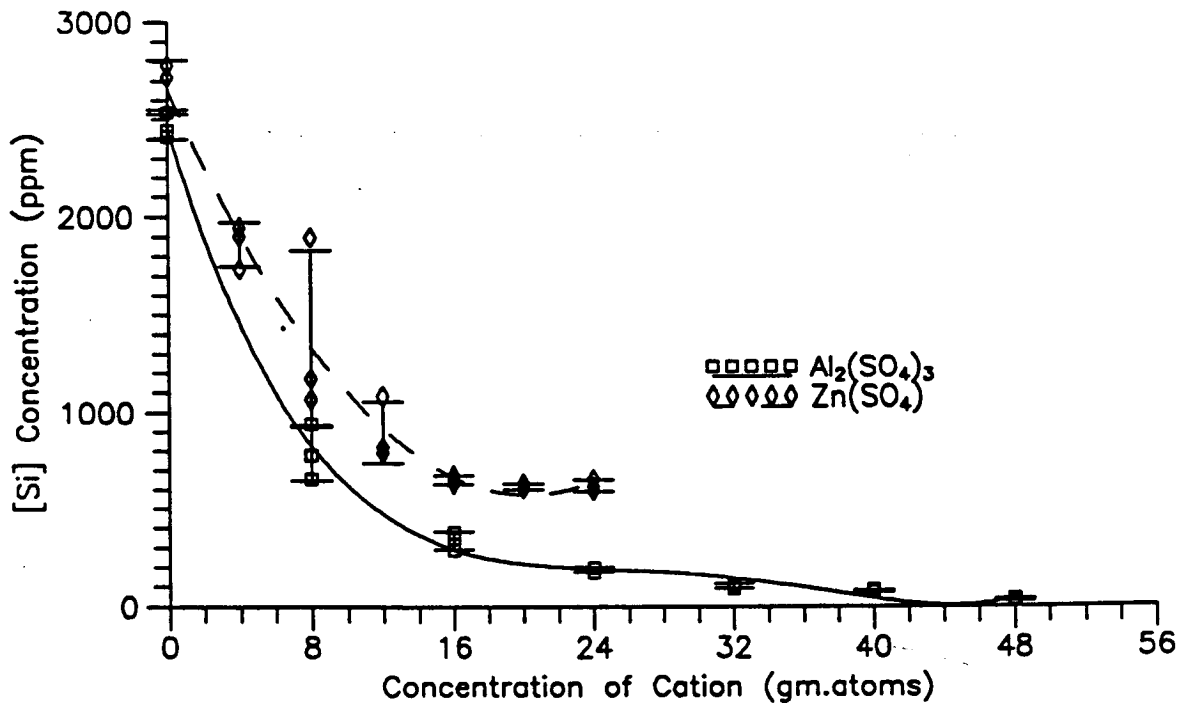


Figure 5: Effect of cations on solubility of Spratts aggregate (ASTM C289)

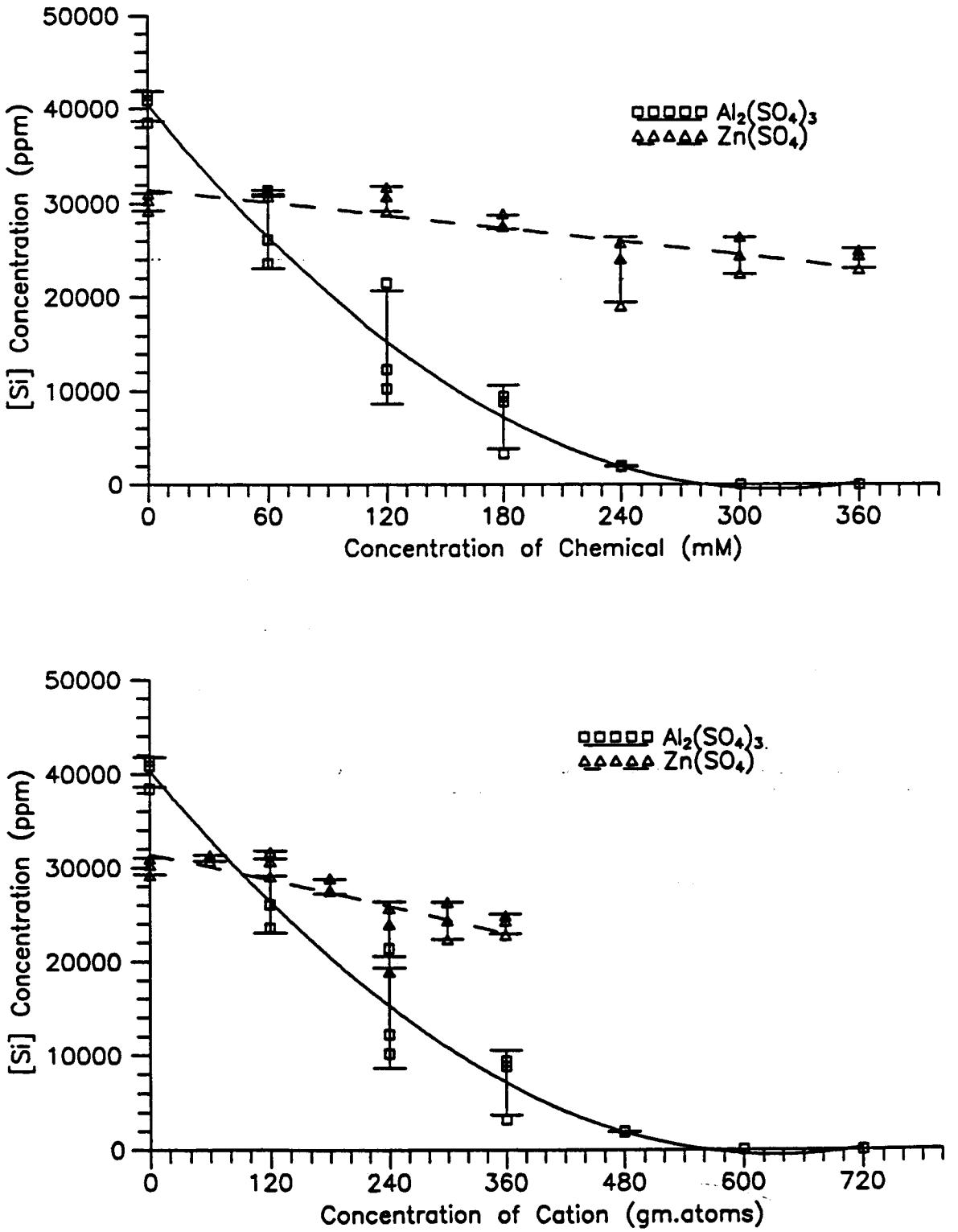


Figure 6: Effect of cations on solubility of Opal (ASTM C289)

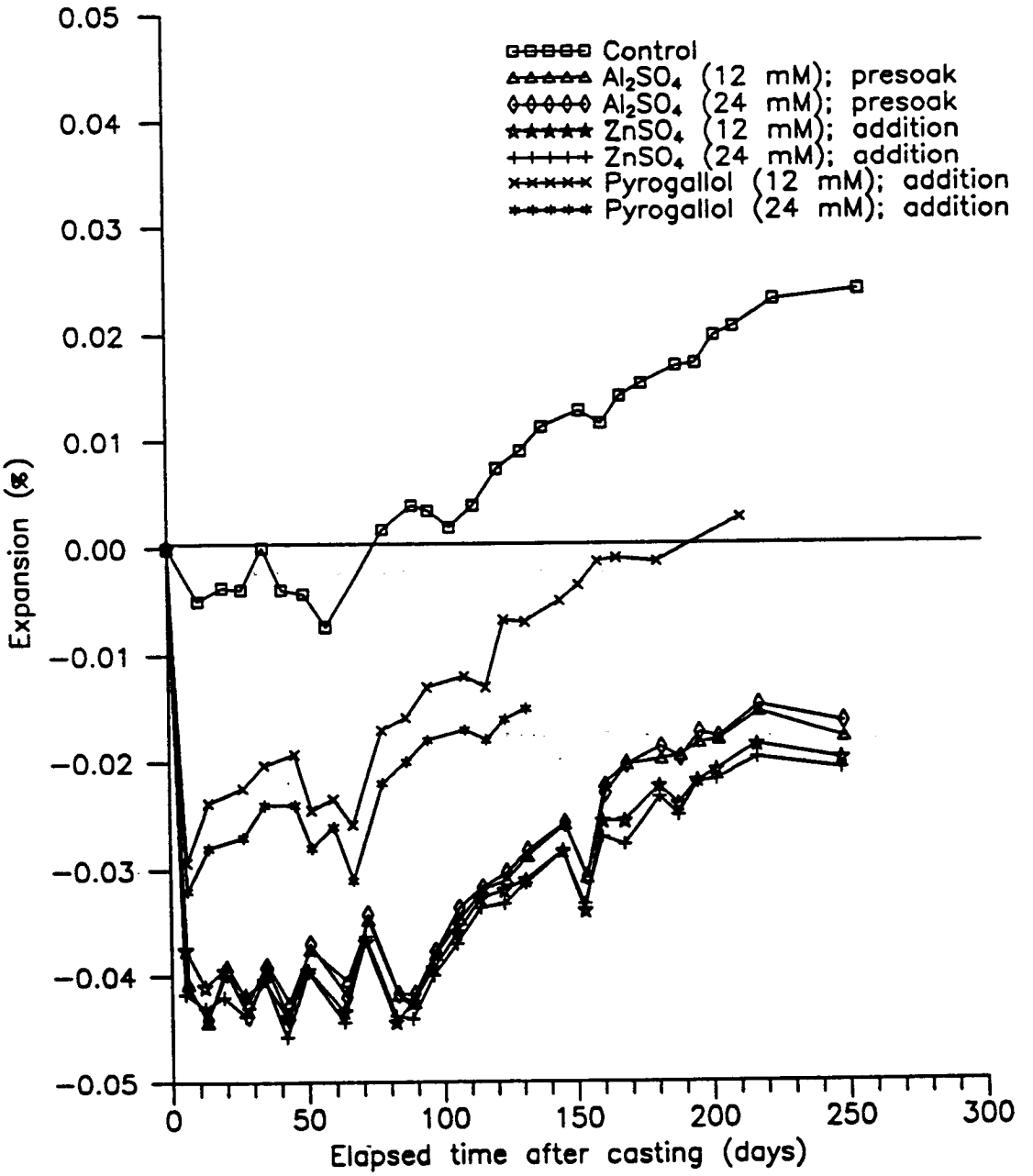


Figure 7: Expansion of mortar bars made with Spratts aggregate; Admixture tests

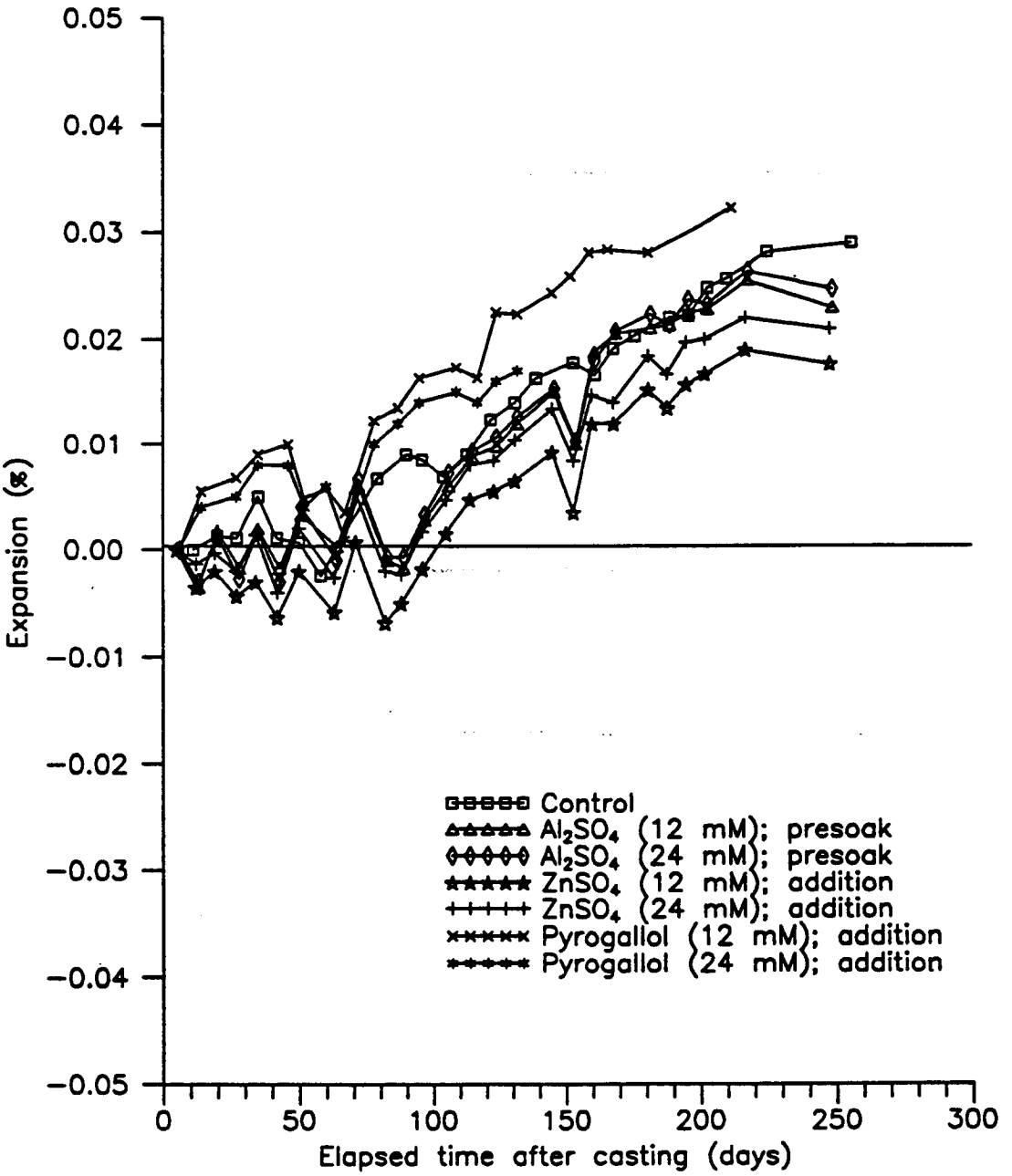


Figure 7a: Shrinkage compensated expansion of bars shown in Figure 7

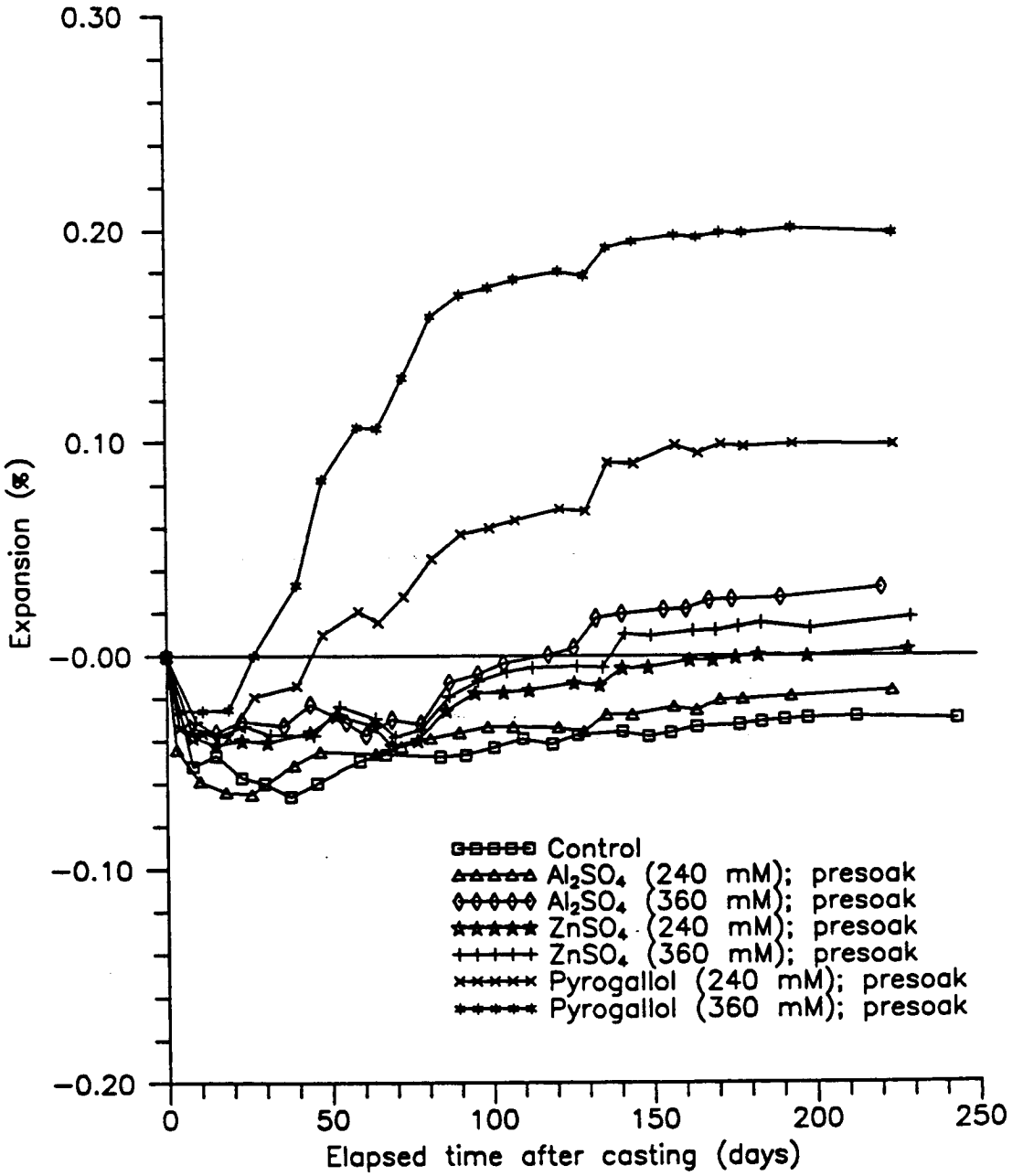


Figure 8: Expansion of bars made with 1% Opal replacement; Admixture tests

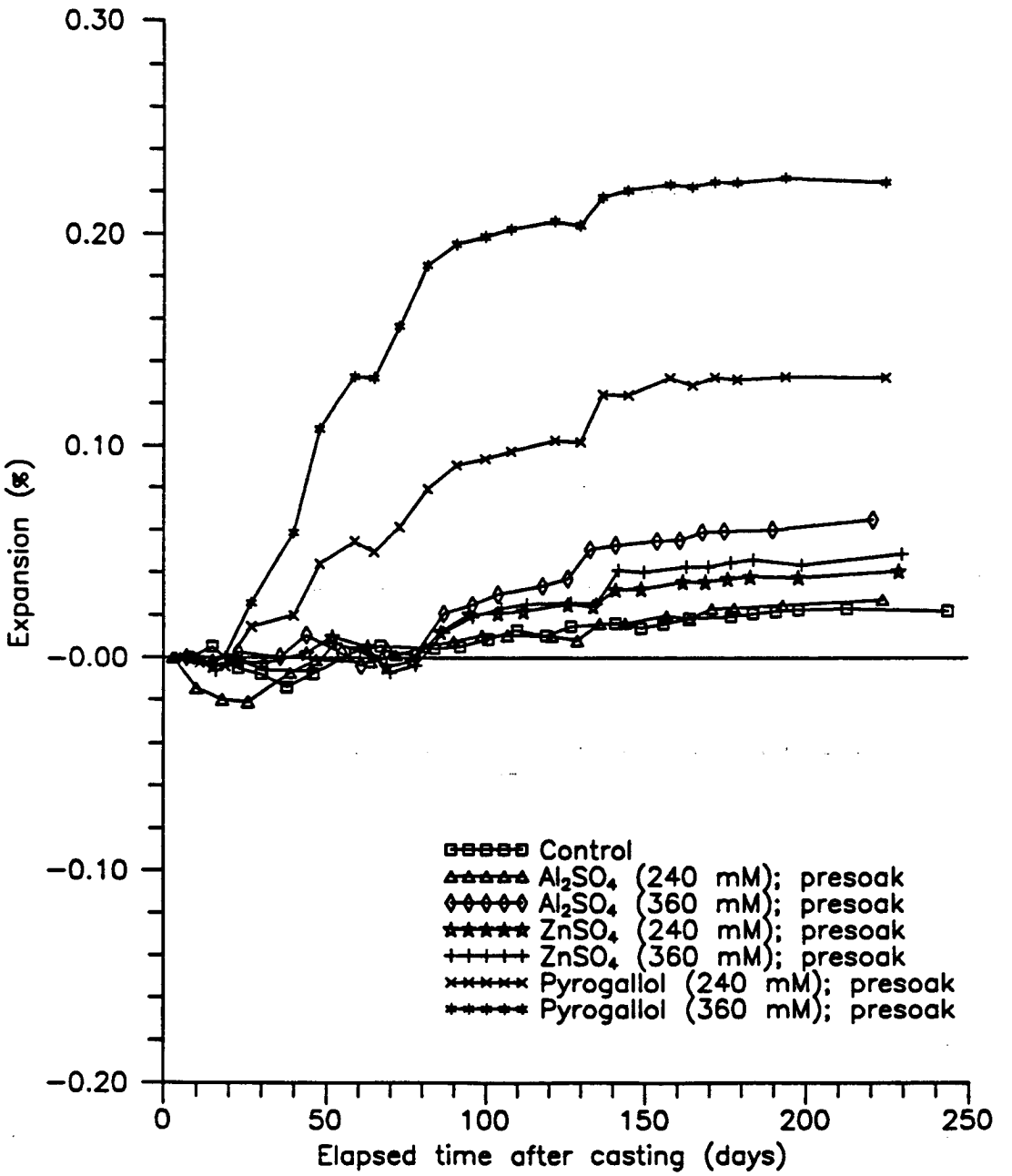


Figure 8a: Shrinkage compensated expansion of bars shown in Figure 8

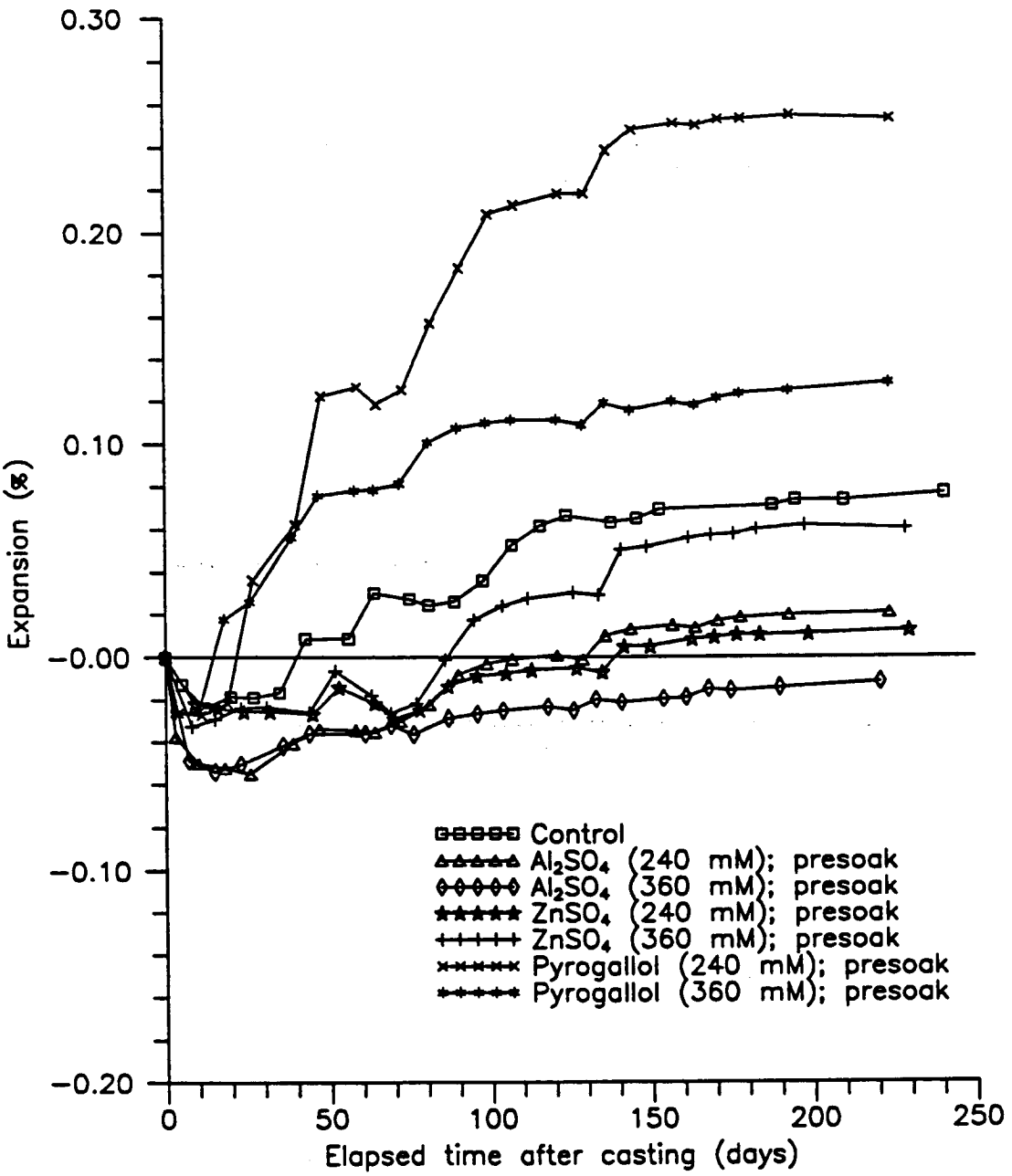


Figure 9: Expansion of bars made with 3% Opal replacement; Admixture tests

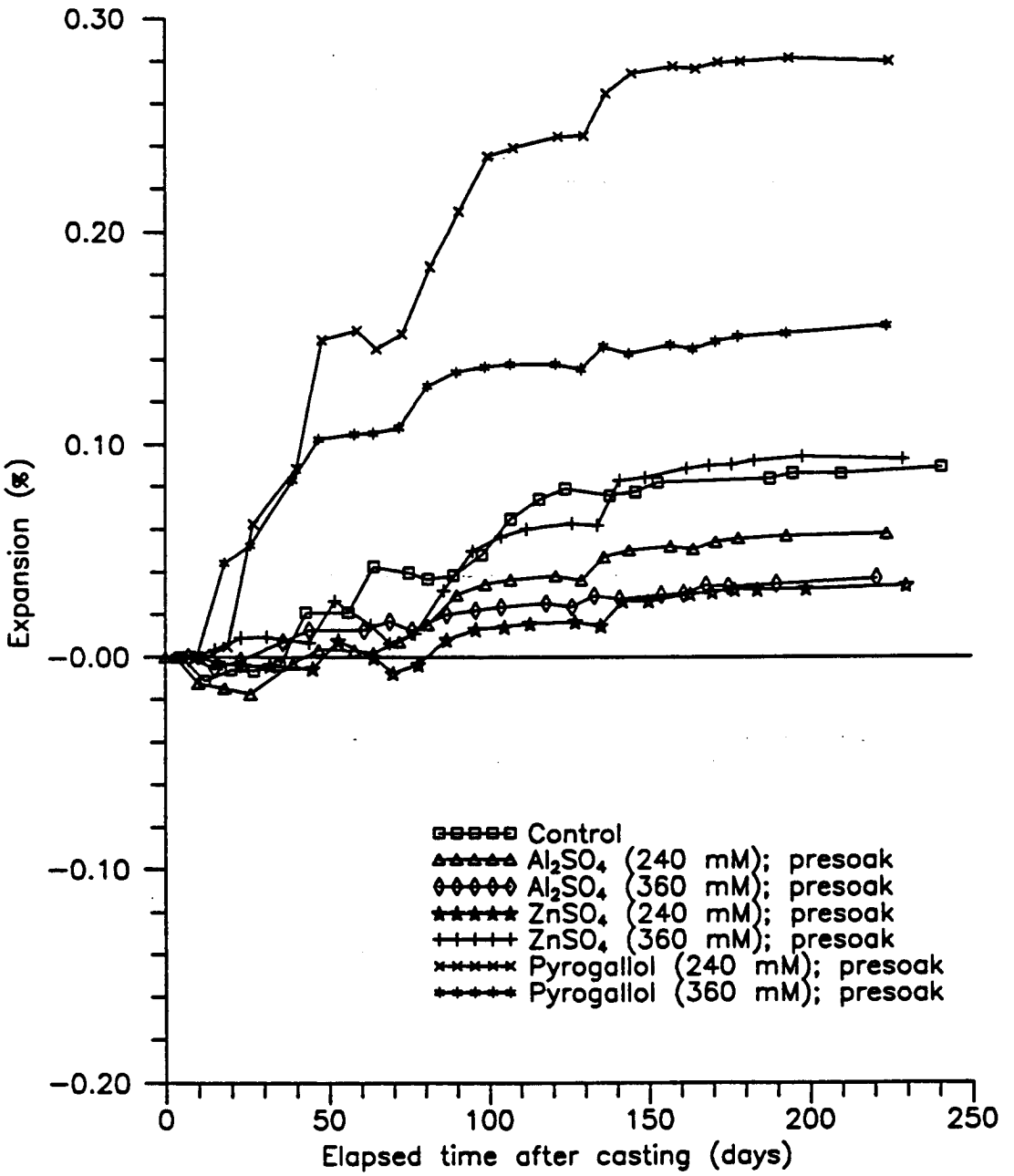


Figure 9a: Shrinkage compensated expansion of bars shown in Figure 9

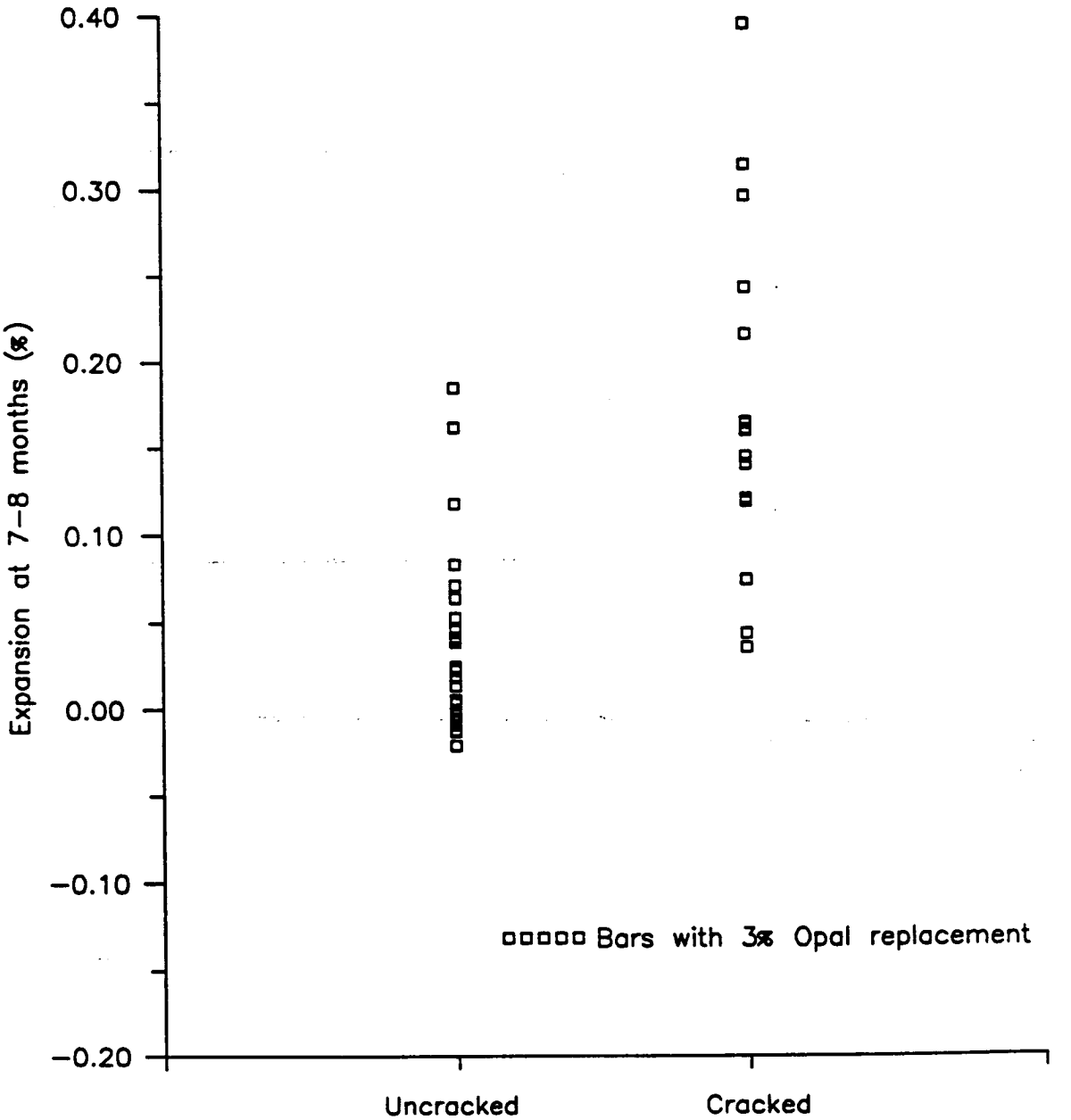


Figure 10: Correlation between expansion at 7−8 months and cracking of bars

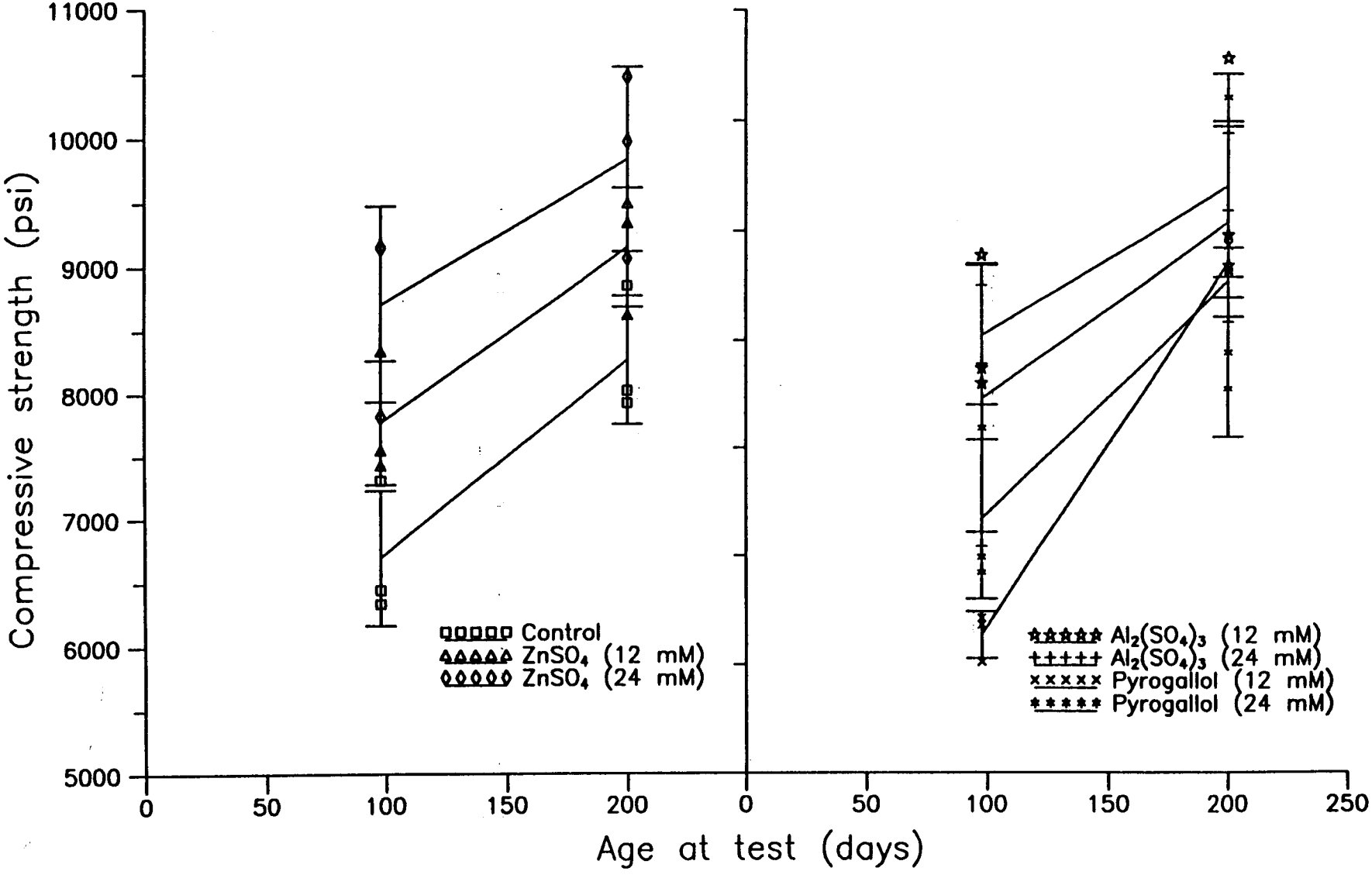


Figure 11: Compressive strengths of cubes made with spratts aggregate; Admixture tests

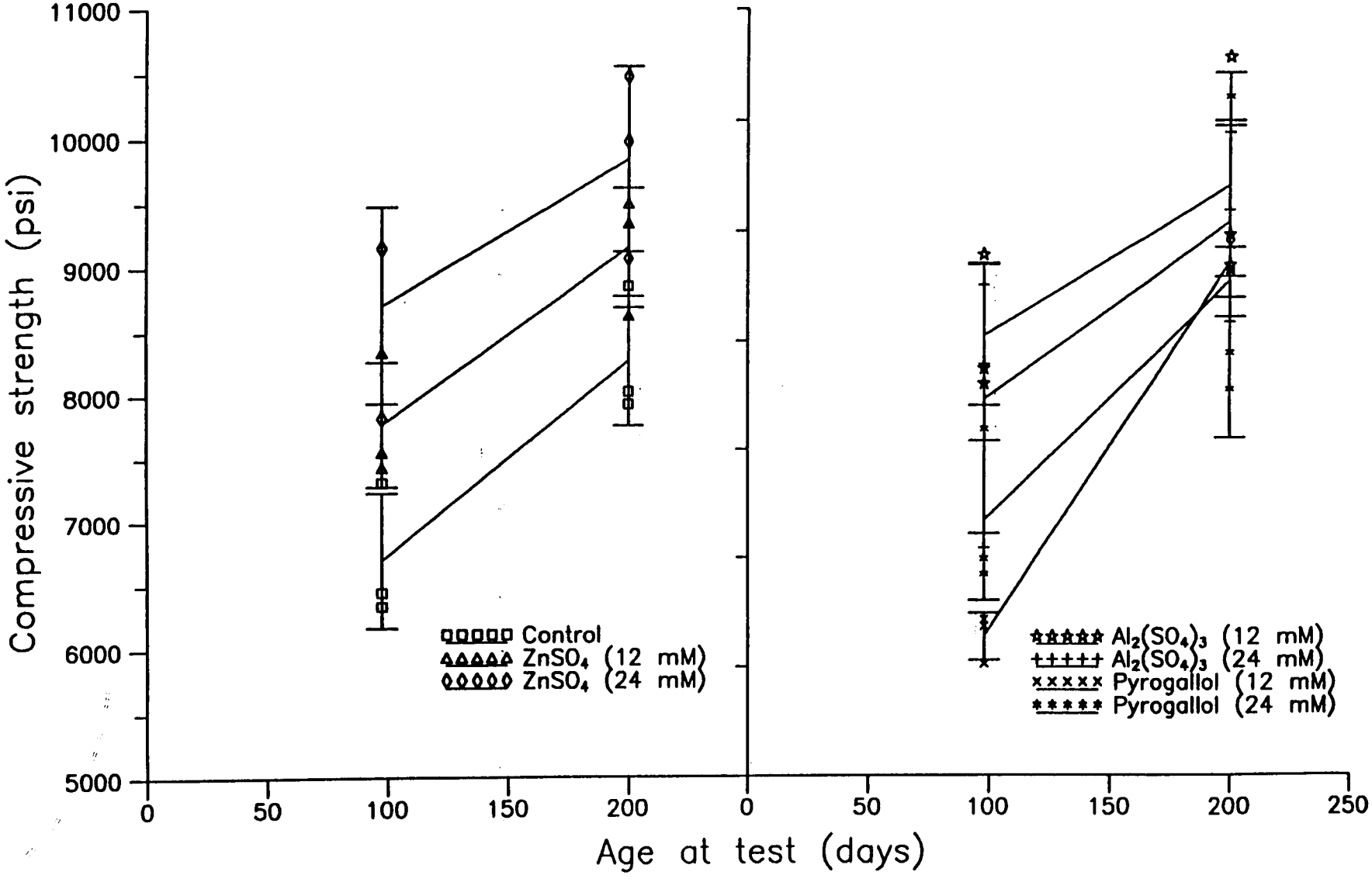


Figure 11: Compressive strengths of cubes made with spratts aggregate; Admixture tests

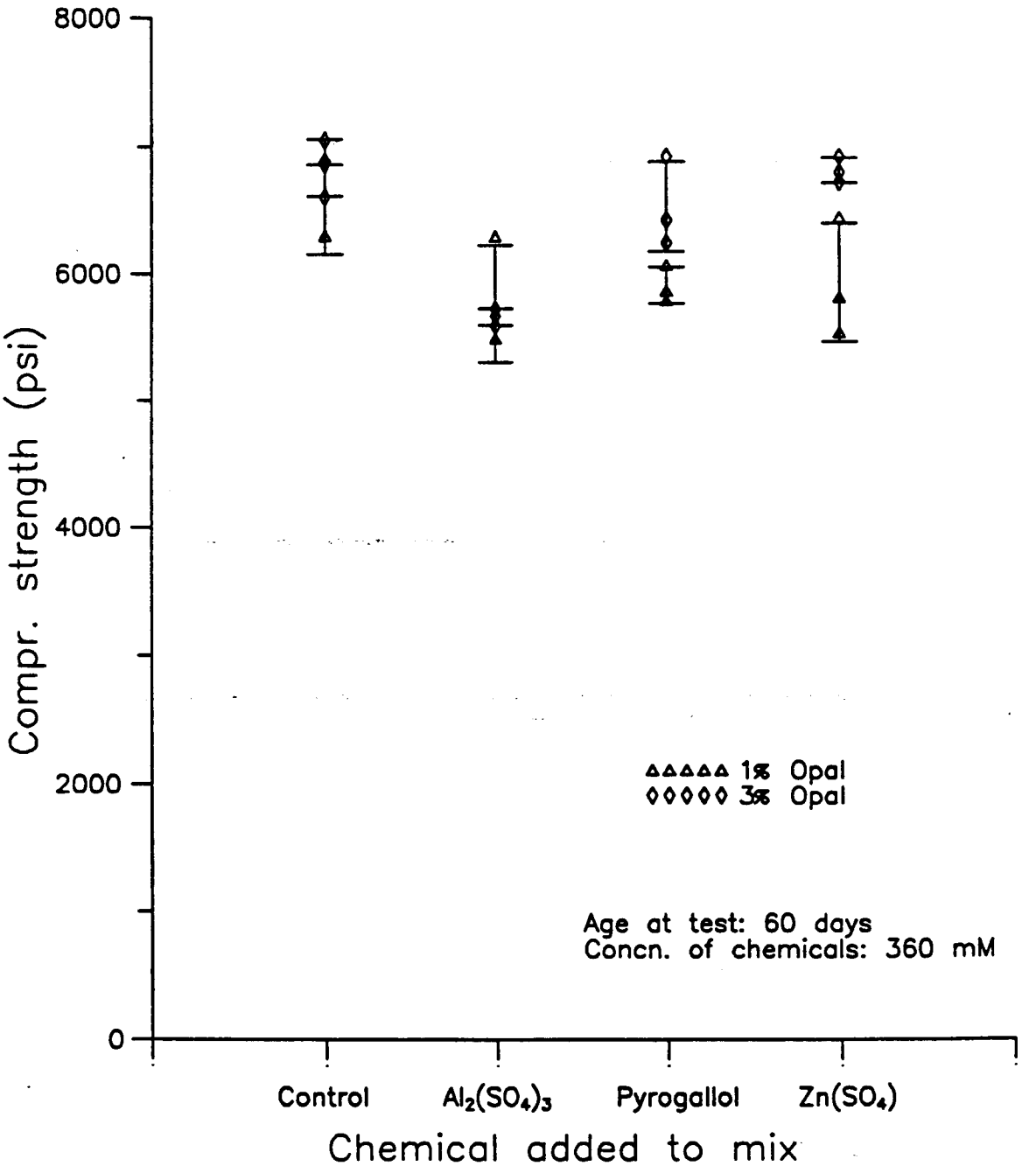


Figure 12: Compressive strengths of cubes made with opal replacements; Admixture tests

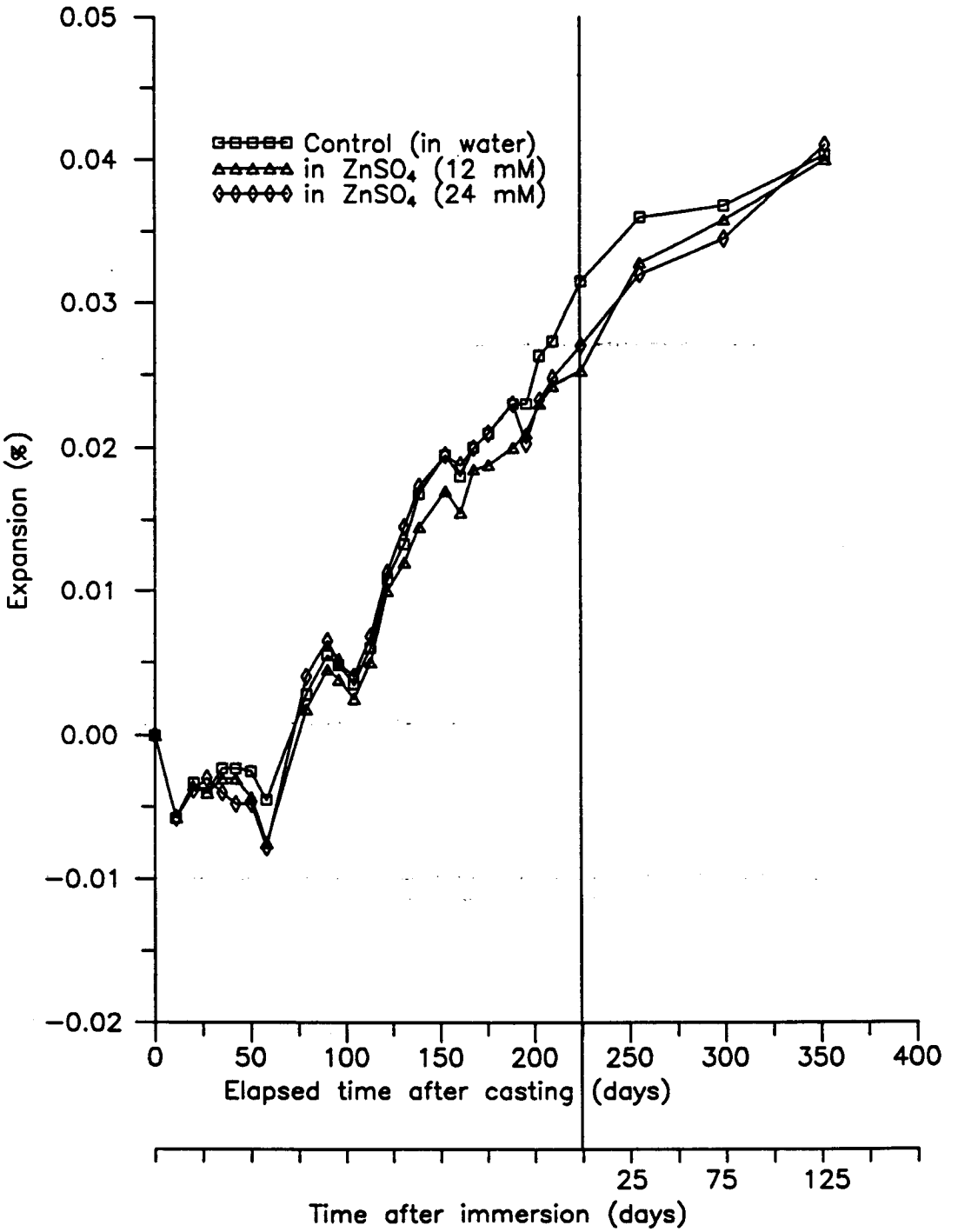


Figure 13: Expansion of mortar bars made with Spratts aggregate; Penetrant tests

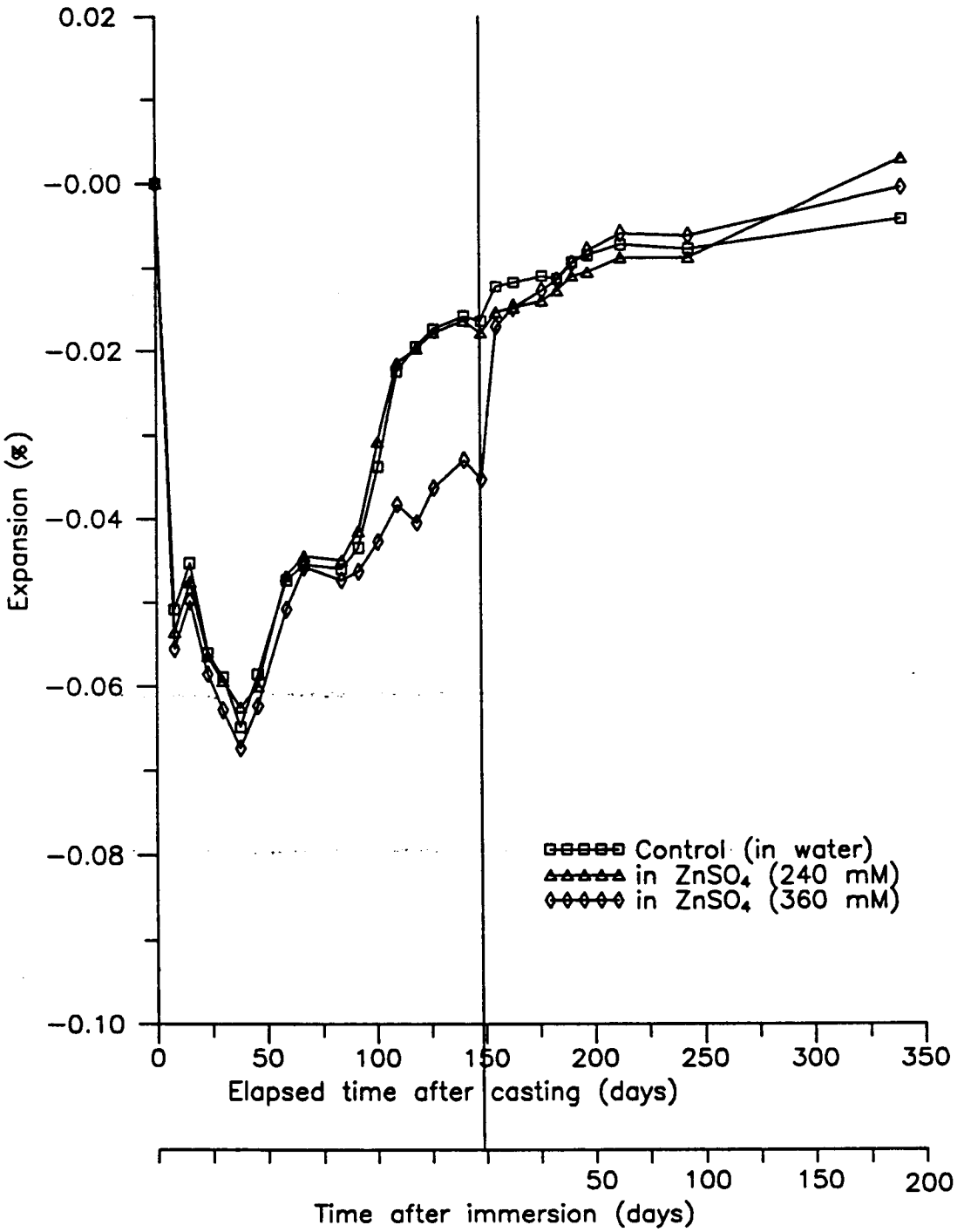


Figure 14: Expansion of mortar bars made with 1% Opal replacement; Penetrant tests

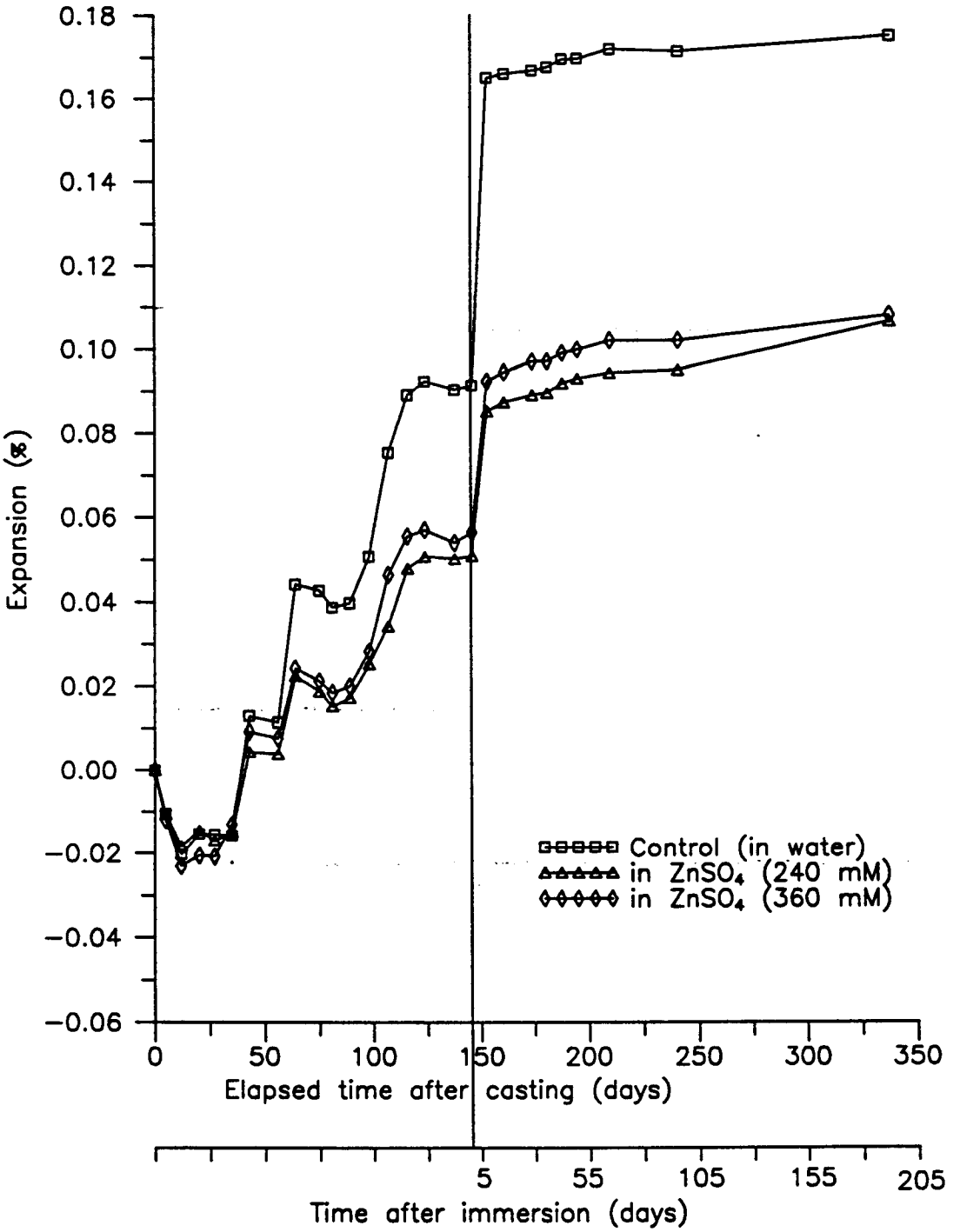


Figure 15: Expansion of mortar bars made with 3% Opal replacement; Penetrant tests

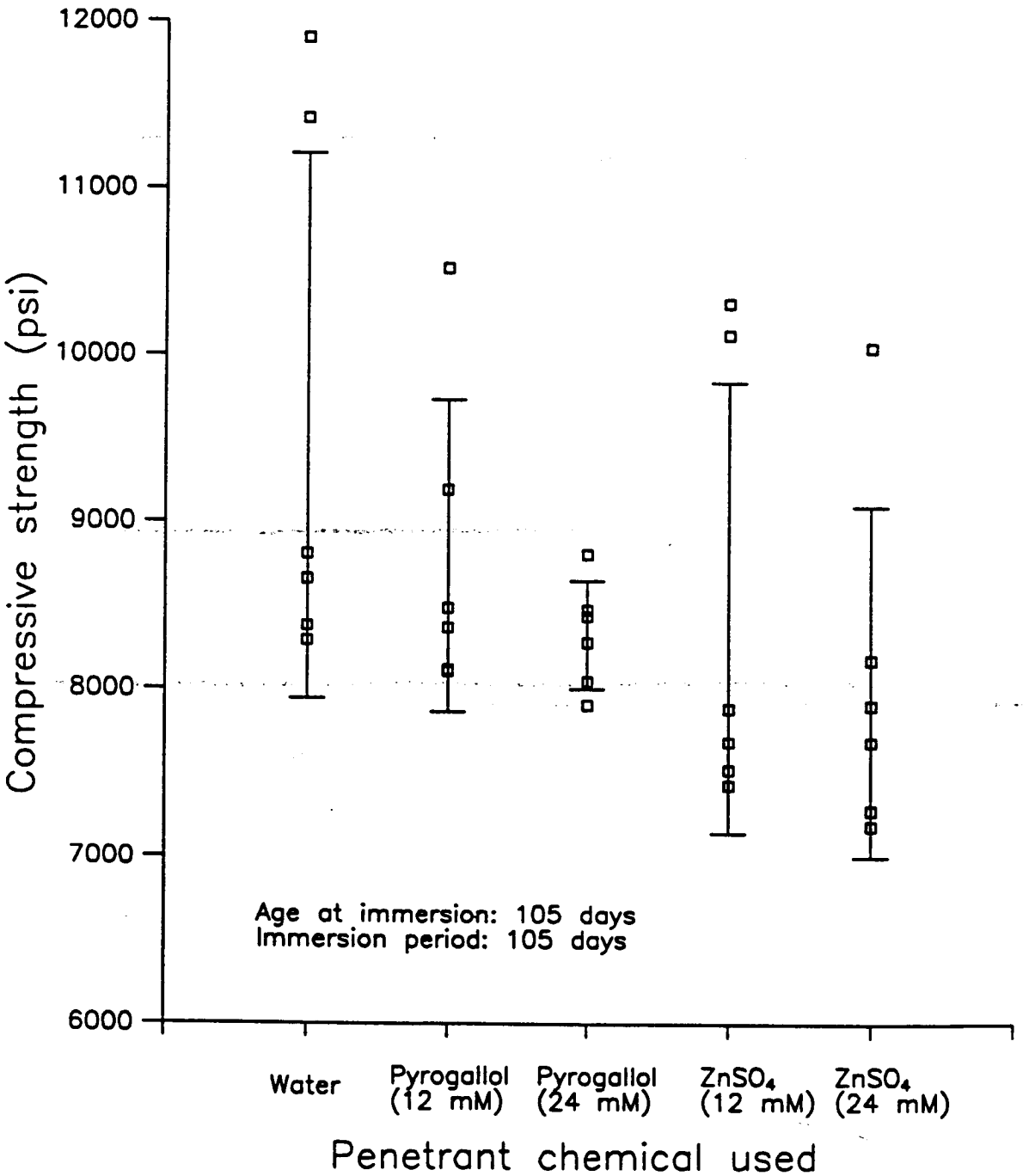


Figure 16: Compressive strengths of cubes made with spratts aggregate; Penetrant tests

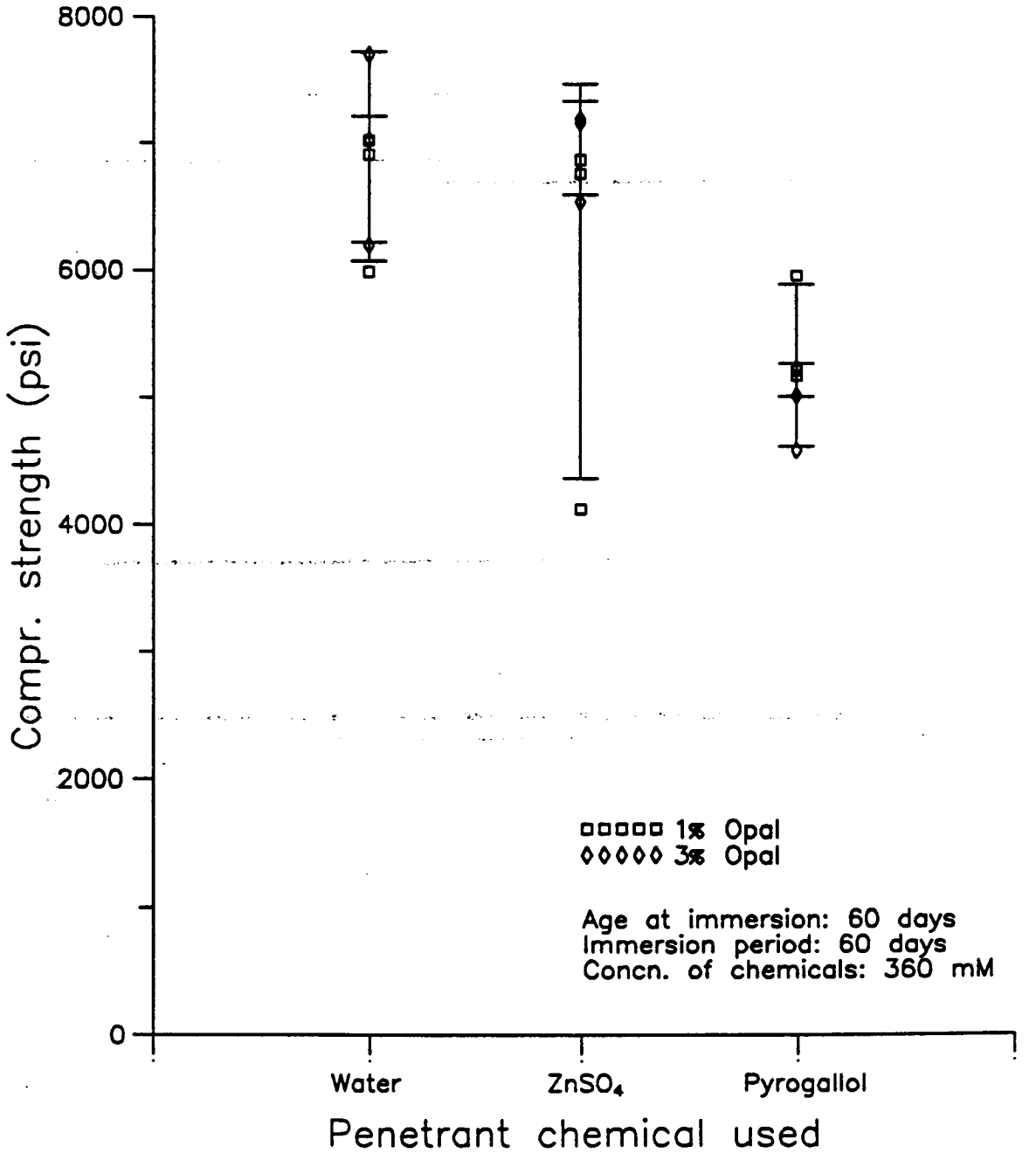
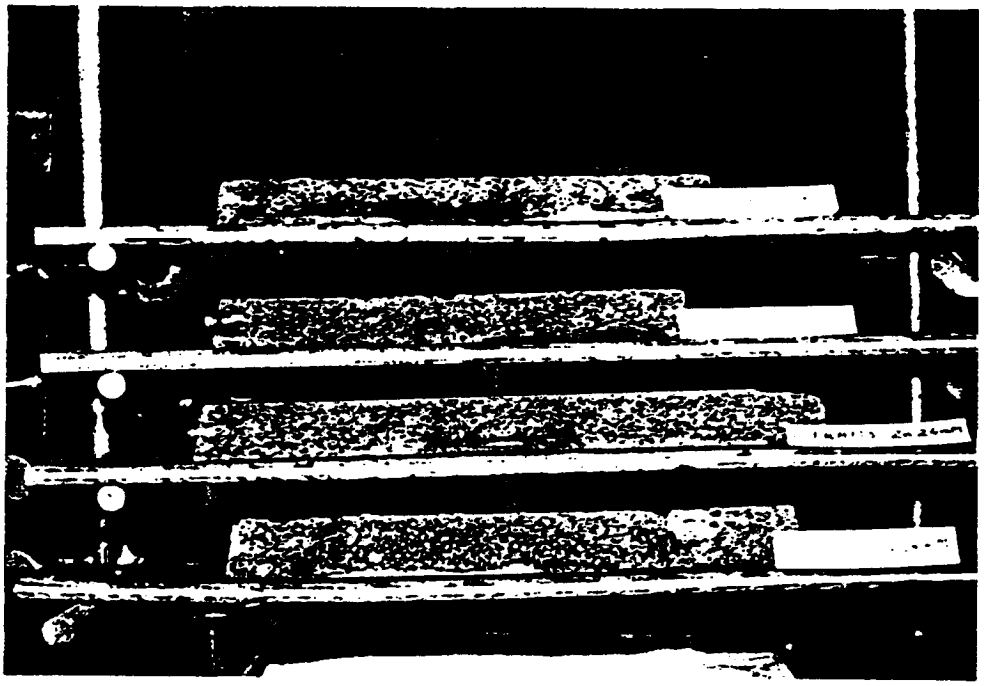
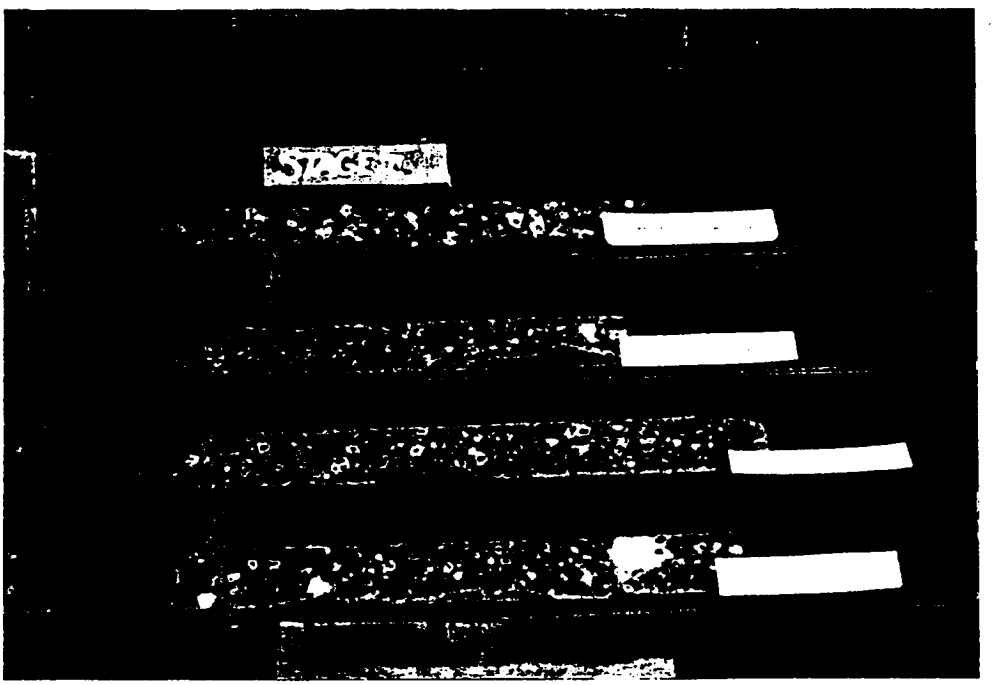


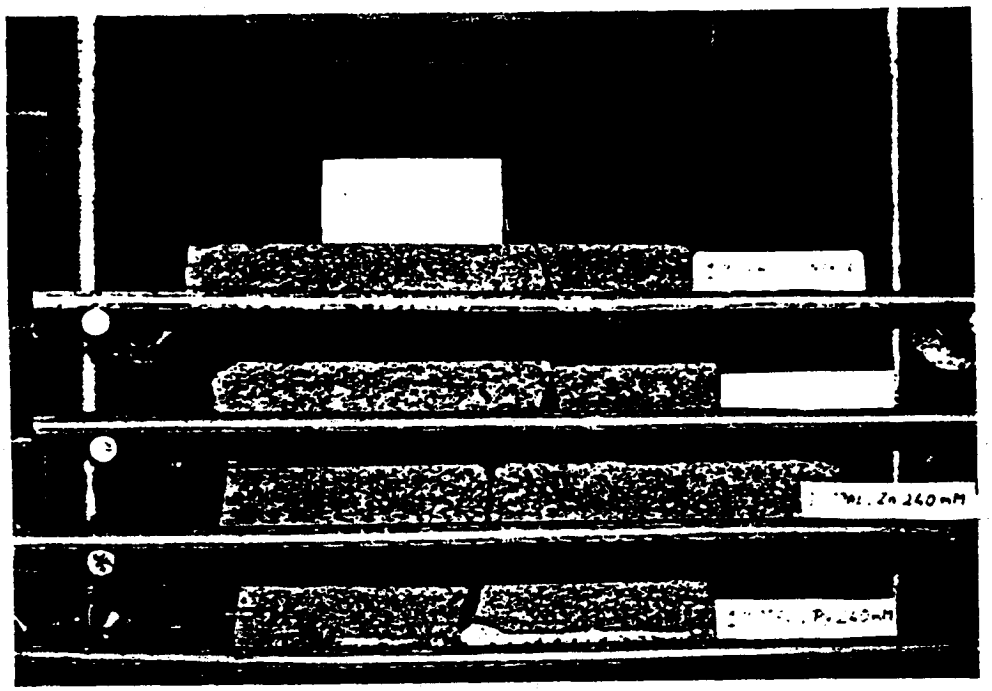
Figure 17: Compressive strengths of cubes made with opal replacements; Penetrant tests



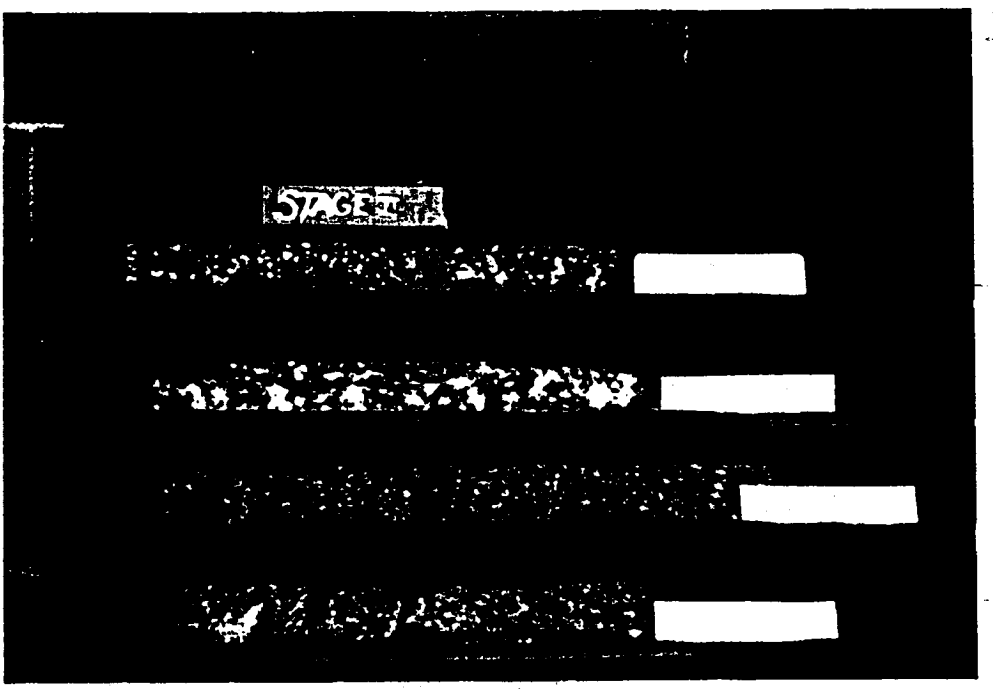
Photograph 1



Photograph 2



Photograph 3



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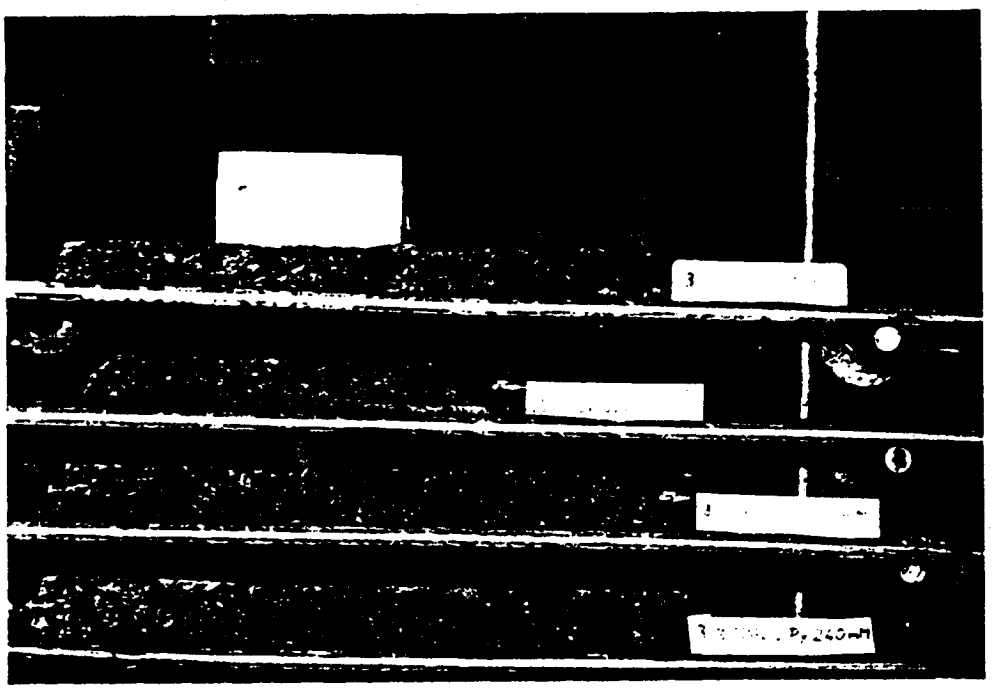
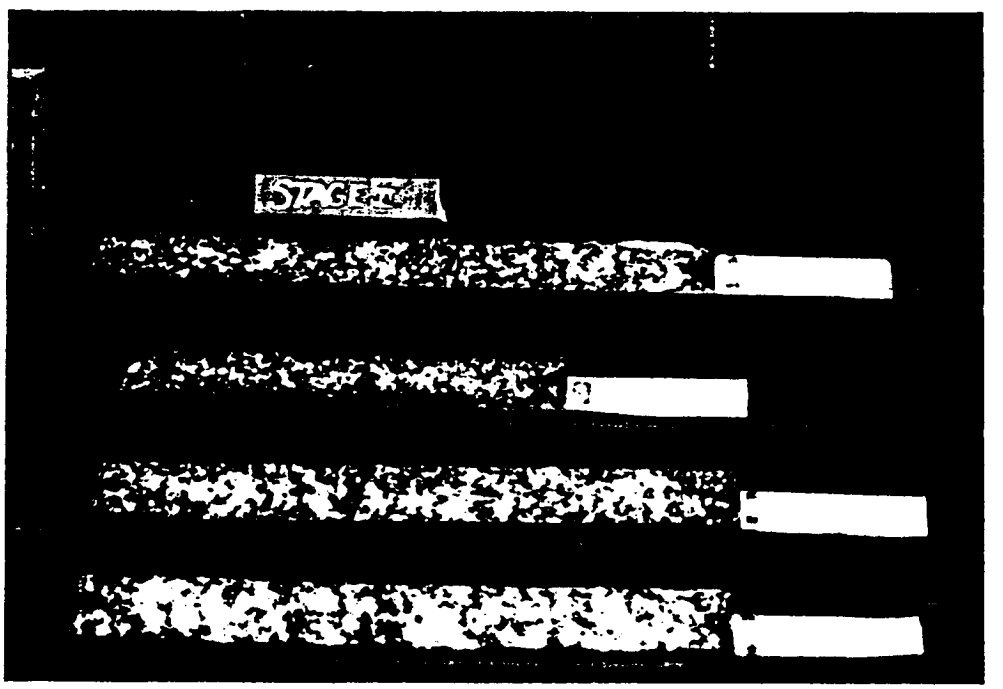


Photograph 5



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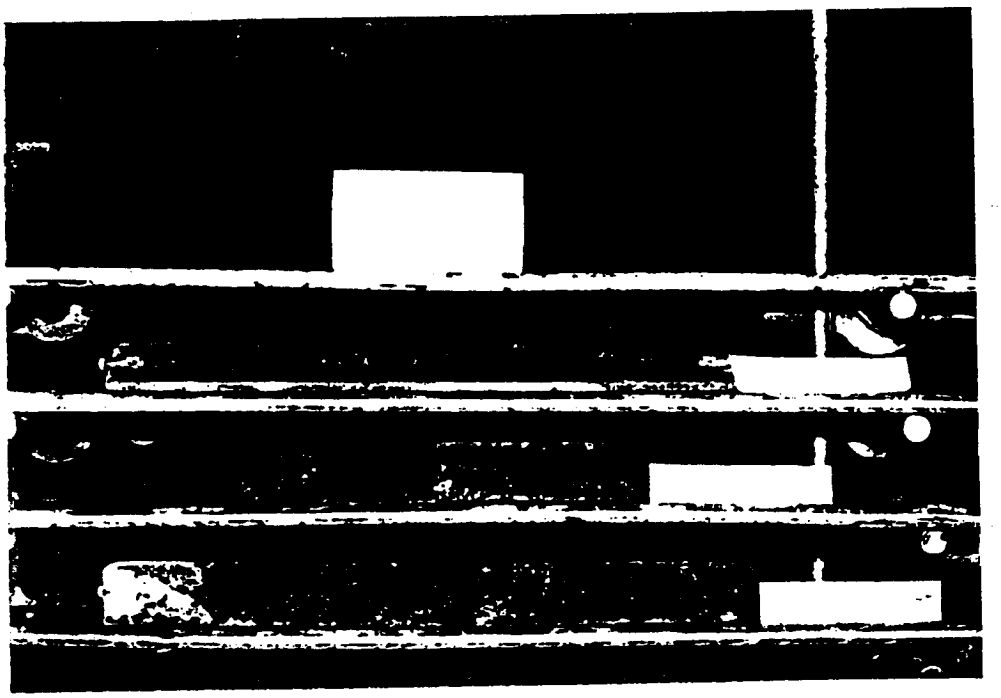
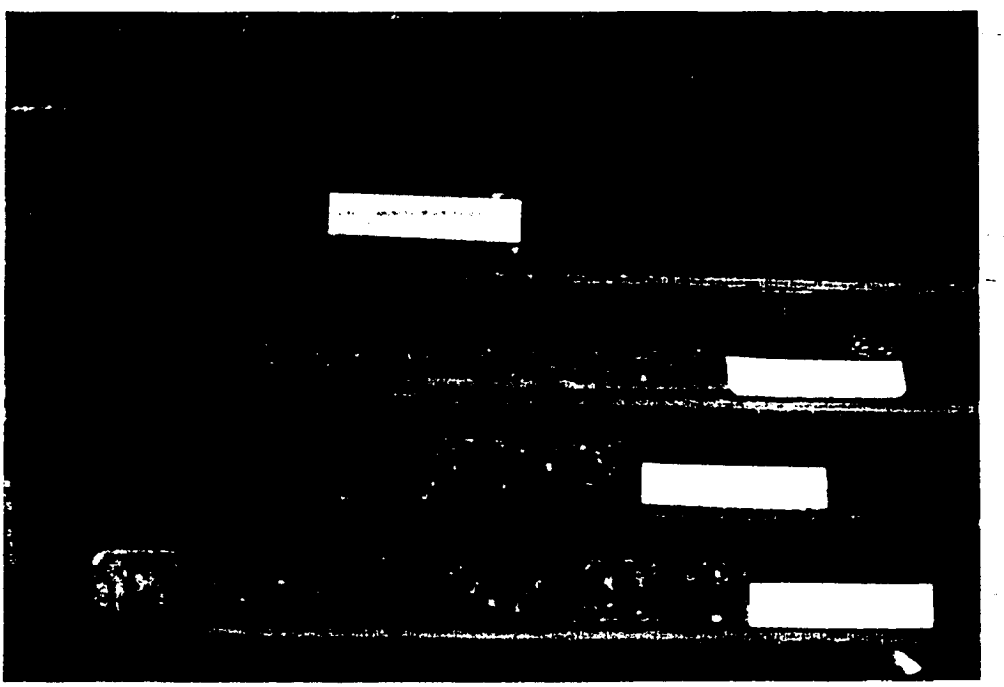
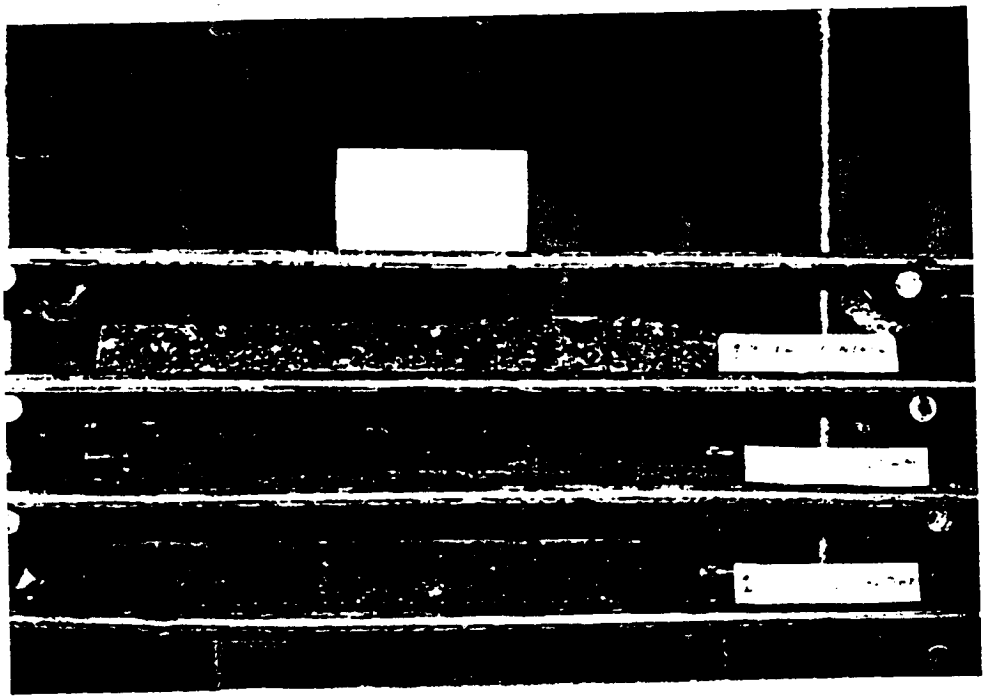


Photograph 7



Photograph 8



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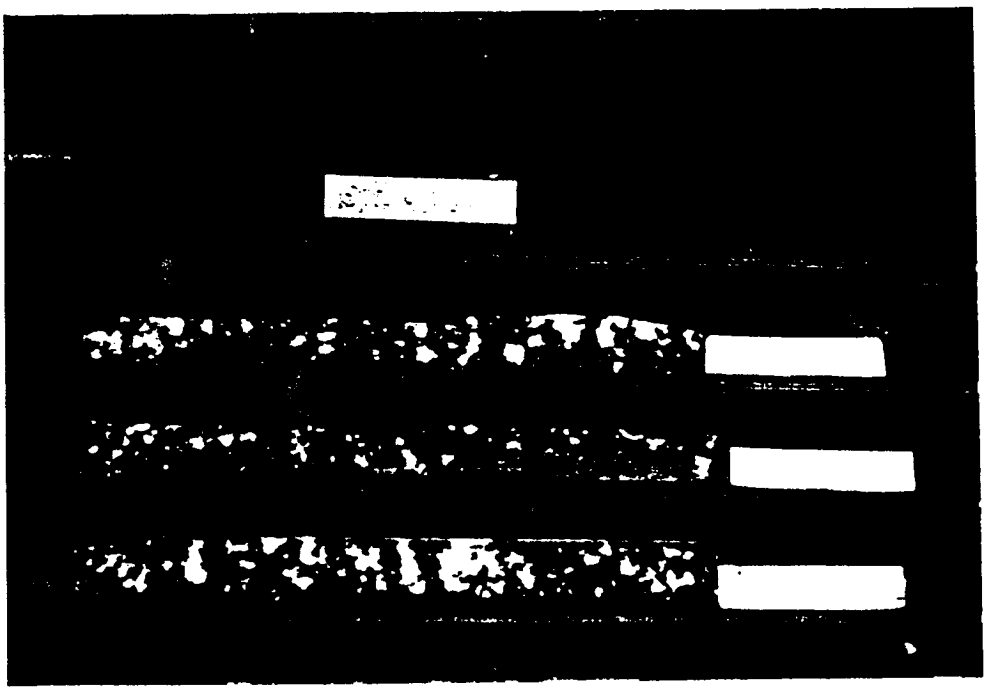
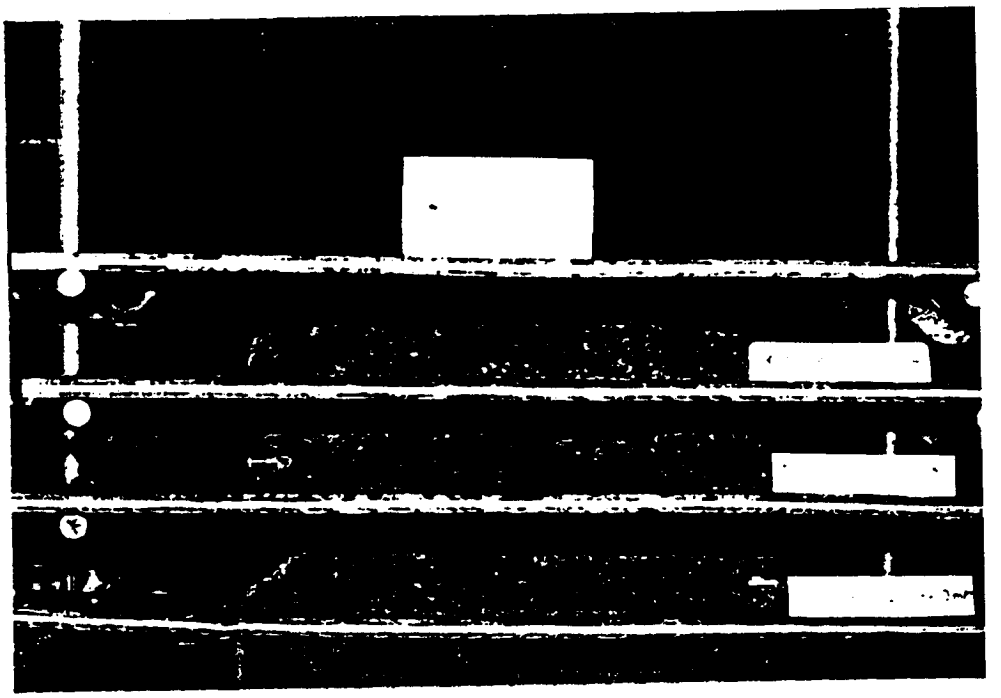
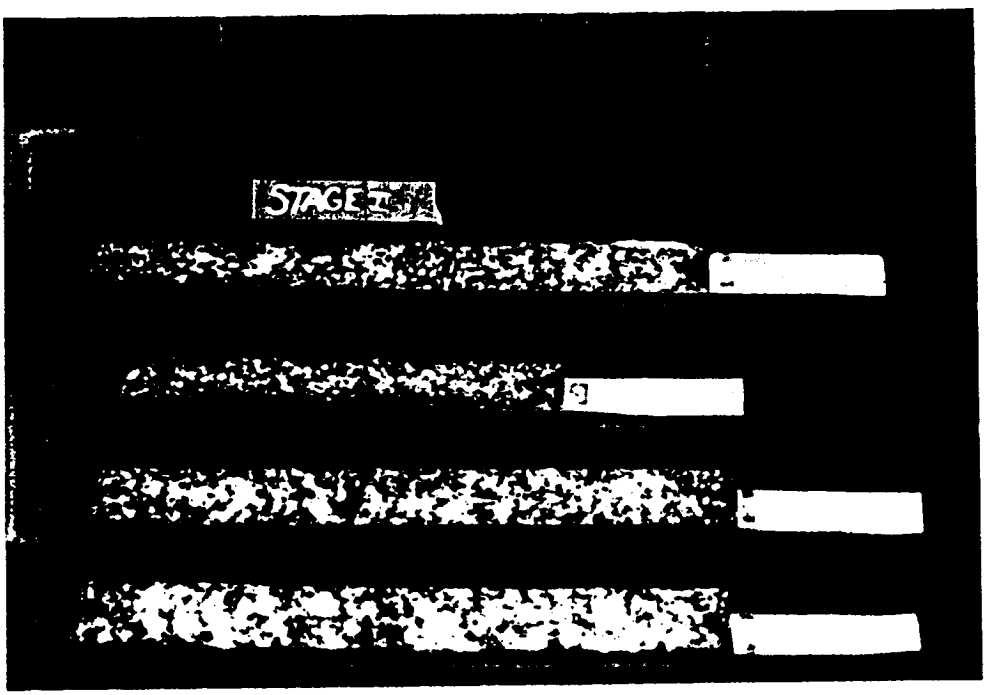


Photograph 10



Photograph 11



Photograph 12