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The role of phosphonates on the hydration of Portland cement

V. S. Ramachandran, M. S. Lowery, T. Wise, G. M. Polomark

Six phosphonates including three acids Aminotri(methylenephosphonic acid) (ATMP); 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP) and Diethylenetriaminepenta (methylenephosphonic acid) (DTPMP) and their corresponding Na-salts Na_5ATMP ; Na_4HEDP and Na_6DTPMP were added to Portland cement in dosages ranging from 0.03% to 0.09%, at a constant water:cement ratio of 0.35 and their conduction calorimetric behaviour was investigated up to 72 hrs. The induction period, the time to attain the maximum heat effect and the integral heat developed at different times were determined. All phosphonates increased the induction period, from about 3 hrs to greater than 72 hrs with respect to the reference cement, with an induction period of 2 hrs. The acid phosphonates were more effective retarders than their corresponding salts. At a concentration of 0.05% the induction period extended from 10.1 to 21.1 hrs with the acids and only from 4.1 to 16.2 hrs with the salts. DTPMP was the most effective retarder among all the phosphonates, a concentration of 0.05% produced an induction period of 21.1 hrs and an exothermic inflection at 42.4 hrs compared to values of 2.2 hrs and 7.9 hrs respectively for the reference. The corresponding salt (Na_6DTPMP) was the most efficient of all the salt retarders. At a concentration of 0.05%, the induction period was extended to 16.2 hrs and the exothermal inflection to 31.4 hrs. In most instances the degree of extension of the induction period increased with the dosage of retarders. Phosphonates appear to be much more efficient retarders than many other retarders used in concrete practice.

1. INTRODUCTION

An admixture is an ingredient that is added in small amounts to concrete to obtain several beneficial effects such as controlled setting and hardening, improved workability and strength, and increased frost and sulfate resistance. Most concrete placed in North America contains one or more admixtures. A patent literature survey on admixtures indicates that in the years 1976-1989, on an average, more than 90 patents were taken annually, suggesting that there has been a sustained interest in the development of novel admixtures.

Retarding admixtures in small amounts are used in concrete practice to delay the setting times of cement paste, mortar and concrete. In hot weather concreting, delays in transport and handling between mixing and placing may result in early setting and loss of workability and in such instances incorporation of retarders becomes necessary. Retarders may be used in steam curing of concrete, to offset the long term lower strengths developed by the silicate phase and in the construction of large structural units, dams and the fabrication of exposed aggregate panels. Another important application of retarders is to maintain returned concrete from ready-mixed trucks in a workable condition overnight by completely freezing the hydration. Special types of retarders are capable of controlling the slump loss in superplasticized concrete. In oil well cementing operations where a temperature in the order of 90°C or more is encountered, retarders are invariably added (1).

Many organic and inorganic compounds, including those derived as by-products from industries are capable of acting as retarders in concrete. The retarders are based on unrefined Na, Ca or NH_4 salts of lignosulfonic acids, hydroxycarboxylic acids and their salts, phosphates, fluorates, carbohydrates, lead and zinc oxides, borates and magnesium salts (2-6). Some of them may entrain air and the action of some of them is determined by the composition of the cement.

The action of many of the admixtures is related to their ability to form complexes with the hydrating compounds in the cement-water system (7-11). Phosphonic acid-based chemicals are known to form complexes with the inorganic species. Thus if present in small amounts in the cement-water systems, they should be able to form complexes and influence the hydration reactions. Phosphonates are suggested for use in high temperature oil and gas plugging operations, soil-cement mixtures, gypsum plasters and as set time extenders for cements. Most work related to phosphonates is to be found only in patents and their role in the hydration of Portland cement at normal temperatures is not well established. There is thus a need for an understanding of the effect of phosphonate-based compounds on the physico-chemical characteristics of the cement paste. The objective of this investigation was to evaluate the following: 1) The role of phosphonic acids and their salts in the cement-water system; 2) The applicability of conduction calorimetry as a quick method to follow the effect of phosphonates on the hydration of cement.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Normal Type 10 Portland cement was obtained from Lafarge Canada Inc. for this work. The Blaine fineness was $3480 \text{ cm}^2 \text{ g}^{-1}$. Analysis of the cement provided the following oxide and phase compositions*:

Oxide Composition (%):

SiO_2	20.05%
Al_2O_3	4.60%
TiO_2	0.20%
P_2O_5	0.19%
Fe_2O_3	2.47%
CaO	61.88%
SrO	0.14%
MgO	2.37%
Na_2O	0.19%
K_2O	0.94%
SO_3	3.79%
LOI	2.44%
Total	99.26%

Phase Composition (%):

Tricalcium Silicate (C ₃ S)	54.29%
Dicalcium Silicate (C ₂ S)	16.53%
Tricalcium Aluminate (C ₃ A)	8.01%
Tetracalcium Aluminoferrite (C ₄ AF)	7.52%
Gypsum	6.44%
Total	<hr/> 92.79%

* Cement nomenclature: C = CaO; S = SiO₂; A = Al₂O₃; F = Fe₂O₃

The phosphonate compounds used were manufactured and supplied by Monsanto Chemical Company, St. Louis, MO., U.S.A. Three families of phosphonate compounds were studied, thus three acids and their corresponding sodium salts were used. Figure 1 summarizes the chemical names, abbreviations and molecular structures of the phosphonic acid compounds.

2.2 Techniques

Isothermal conduction calorimetry was used to measure the heat evolved during cement hydration as a function of time with and without phosphonate compounds added. Most of the heat was released during the first 72 hours of hydration.

The calorimeter contained six cells mounted on a metal base plate surrounded by foam insulation. A thermopile located under each cell measures the heat production. Each cell contains a Teflon-coated aluminum specimen holder into which a polyurethane insert was placed holding the sample. An aluminum cover, surrounded by a rubber O-ring, was securely fastened to the base plate to keep the vessel watertight. The calorimetry unit was manufactured by the Institute of Applied Physics, TNO-TU Delft, Netherlands.

The calorimeter was placed in an isothermal water bath. The voltage signals from each thermopile were recorded by a Datataker DT100 Data Logger manufactured by Data Electronics Ltd., Australia. The logged data was retrieved by a software program Decipher, also distributed by Data Electronics, onto a NHC 386 AT microcomputer. The voltages were converted to calories using a formula that considered sample weights and cell sensitivities with the spreadsheet software Excel, Microsoft, Calif. Data was calculated as rate of hydration (cal/g/hr) and integral heat (cal/g). Graphical plots were created using Charisma, Micrografx, Texas.

2.3 Procedure

A 3.5 ml aqueous solution containing the required amount of phosphonate was added to 10.000 g of cement at a water-cement ratio of 0.35. Concentrations (percentage phosphonate by weight of cement) ranging from 0.03% to 0.05% and 0.03% to 0.09% were used for the acid and salt phosphonates respectively. The samples were mixed and placed in the calorimeter. The apparatus was sealed and then submerged in a water bath maintained at $25 \pm 0.01^\circ\text{C}$. Averaged millivolt signals for each thermopile were collected every ten minutes for up to 72 hours by the Datataker.

3. RESULTS AND DISCUSSION

Figures 2 to 7 represent the conduction calorimetric curves for the hydrating cement containing phosphonates at different dosages. In each of these figures the curve for the reference cement hydrated without any addition is also given. The rate (A) as well as the amount of heat (B) developed up to 72 hrs are shown. Normal Portland cement (Fig. 2A) exhibits an initial exotherm within the first 10 mins of hydration and this is attributed to a combination of reactions such as the hydration of free lime, heat of wetting and the formation of ettringite of formula $3\text{CaO}(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3) \cdot 3\text{CaSO}_4 \cdot 31-32\text{H}_2\text{O}$. Only a small inflection is registered in the figures because the cement was placed in the calorimeter a few minutes after it had been pre-mixed with water outside the calorimeter. This effect is followed by a period of relatively low chemical reactivity between about 30 mins and 2.2 hrs and this period is known as 'induction' or 'dormant' period. An expanded view for both the rate (C) and integral heat (D) curves for the first 8 hrs of hydration are shown in Figures 2 to 7. At the end of this period an increase in heat evolution occurs with a peak at about 8.0 hrs and this is due to the hydration of tricalcium silicate component of cement that yields calcium silicate hydrate and calcium hydroxide. After this peak, there is a gradual diminution in the evolution of heat, and attainment of a steady state after about 50 hrs.

Fig 2 also gives the conduction calorimetric curve for the cement containing 0.03, 0.04 and 0.05% ATMP. Although the induction period for the reference cement can be determined at about 2.2 hrs, it is not easy to determine this period for the sample containing 0.05% phosphonate. The reference cement exhibits an intense thermal peak at about 8.0 hrs and thereafter there is a gradual decrease in the rate of heat development, the rate being only about 0.2 cal/g/hr at 72 hrs. The addition of ATMP alters the curve (Fig. 2A). The induction period is extended from 3.8 to 13.2 hrs with 0.03 and 0.05% ATMP respectively. The peak corresponding to the maximum rate of heat for the sample containing the ATMP is less sharp than that for the reference and appears in the form of a hump when concentration is increased. This hump for the phosphonate-treated sample appears at about 12.7 hrs at a dosage of 0.03%. The hump appears beyond 20hrs for other dosages. The curve in the acceleration mode after the first few hours seems to have two slopes for the cement containing 0.05% ATMP. This has been observed in cement containing sodium hexametaphosphate (12). It is possible this may represent delayed reactions of the aluminate phase; some chemicals are known to complex with aluminate species, especially at higher concentrations and extend their hydration effects (13).

Fig 2B was obtained by integrating, at different times, the curves in Fig 2A. The total amount of heat developed at different times may be used to estimate the degree of hydration of the C_3S phase in cement. At about 48 hrs, addition of 0.05% ATMP reduces the amount of heat by about 25% with respect to the reference. The setting time normally occurs below the exothermic peak for C_3S , but above the induction period (14). The conduction calorimetric curves indicate that it is possible to retard the setting times of cement from a few hrs to a day using ATMP in the range of 0.03 to 0.05%. At all concentrations, even up to 72 hrs the cement containing ATMP has hydrated to a lesser extent than the reference (Fig.2B).

The addition of the Na-salt of the phosphonic acid ATMP (Na_5ATMP) also results in the retardation of cement hydration in terms of the extension of the induction period and the appearance of the exothermic peak (Fig 3A). Generally the exothermal peak is sharper in the presence of Na_5ATMP . The induction period at a dosage of 0.03, 0.04 and

0.05% Na₅ATMP is 3.8, 4.1 and 4.7 hrs respectively. The corresponding values for the acid are 3.2, 6.6, and 13.2 hrs. Thus Na₅ATMP is a less efficient retarder than ATMP. At 72 hrs the addition of 0.05% Na₅ATMP increases the amount of heat by 3.7% with respect to the reference, compared to a 10.5% reduction achieved with 0.05% ATMP (Fig 3B). It appears that the hydration is accelerated at dosages of 0.03-0.05% at about 30 hrs. At 0.09% Na₅ATMP, the percentage hydration at 72 hrs equals that of the reference.

HEDP is a less efficient retarder than ATMP. The induction periods are 3.4, 3.6 and 10.1 hrs for dosages of 0.03, 0.04 and 0.05% HEDP respectively (Fig 4A & C). The corresponding values with the addition of ATMP are 3.2, 6.6, and 13.2 hrs. HEDP at a concentration of 0.05% exhibited a low hump effect prior to the main C₃S hydration peak noted previously with ATMP. The amount of heat produced by the addition of 0.05% HEDP (73.6 cal/g) is much greater than that produced by the addition of 0.05% ATMP (58.3 cal/g) at 48 hrs (Fig 2B and 4B).

The effect of Na₄HEDP on the hydration characteristics of cement is shown in Fig 5. This phosphonate salt is also not as effective as the acid from which it is derived (HEDP). At a concentration of 0.09% (nearly twice that of 0.05% HEDP), Na₄HEDP produces a total heat of 56.3 cal/g compared to 73.6 cal/g by addition of HEDP. In other words with Na₄HEDP to attain the value of 73.6 cal/g the cement has to hydrate for a further period of 12 hrs. Therefore HEDP is a better retarder than its sodium salt.

Conduction calorimetric curves of cement with DTPMP show large humps for the hydration of the silicate phase (Fig 6). The apex of the maximum inflection peak is greatly reduced in magnitude and is also broadened as the concentration of DTPMP is increased. At both concentrations of 0.04 and 0.05%, DTPMP induces distinct double humps. The induction period varies between about 3.5 and 21.1 hrs with 0.03-0.05% of DTPMP.

The salt (Na₆DTPMP) appears to be a less effective retarder than its acidic component (Fig 7). It appears that the Na-salts of all acids are less efficient retarders than the acids from which they are derived. By using dosages between 0.03 and 0.05%, the induction period can be increased from 4.3 hrs to 16.2 hrs. Induction periods of greater than 72 hrs can be achieved with Na₆DTPMP at a concentration of 0.09%.

At low concentrations, each pair of acid and salt compounds behaved similarly. Induction periods with salt compounds at 0.03% were slightly greater than those of the corresponding acids. However, at higher concentrations the acids were much more effective retarders (Table 1). This could be related to the lower pH of the acids.

The relative retarding effects of phosphonates can be evaluated by comparing the induction periods attained at different dosages of retarders (Fig 8). In Fig 8 the time of termination of the induction periods is plotted as a function of dosage. Some of the figures are approximate values because of the difficulty in determining the termination of the induction period.

Generally the curves with steeper slopes pertain to the acid-containing pastes. Among the acids the most efficient retarder is DTPMP which requires 0.05% for an induction period of 21 hrs compared to 13 and 10 hrs respectively for acids ATMP and HEDP. It has been established that of all the phosphonates DTPMP has the best sequestration ability (15). From the curves in Fig 8, Na₆DTPMP should be construed as the most effective retarder of all the salts. At a concentration of 0.05%, cement with

Na₆DTPMP exhibited a similar induction period to that provided by the other two salts at a concentration of 0.09%. Phosphonates appear to be much more efficient retarders than many other retarders studied previously (12).

The examination of the conduction calorimetric curves suggested that generally at higher dosages of phosphonates humps rather than peaks appeared. In Figure 9 the slopes of the curve during the acceleratory period are plotted as a function of concentration of phosphonates. The acids which are better retarders than the salts showed generally lower slopes. This would indicate that at higher concentrations, it takes longer for the inhibited hydration (caused by complexation effects) to proceed normally.

The retarding effect of many chemicals in the hydration of cements is attributed to the difference in the solubilization of Ca, OH, and Si ions, complexation of the cations with the retarders, and poisoning of the nuclei of Ca(OH)₂ and C-S-H phases (8). Phosphonates are known to be effective in preventing scaling and corrosion. One molecule of phosphonate can inhibit 5000-10,000 molecules of scalant. This has been explained by the ability of phosphonates to get absorbed on growth sites. Phosphonates can sequester and chelate with metallic species. In the hydration of cement the retarding effect of phosphonates is related to the complex formation of phosphonates with Ca and Si, both on the surface of the silicates and in the solution phase. The pH determines the degree of complexation. The acid phosphonates, having much lower pH than their sodium salts will be able to chelate Ca ions more efficiently and hence are better retarders.

4. CONCLUSIONS

Conduction calorimetry was found to be a quick method of assessing the relative effects of phosphonate compounds on the hydration of cements. The time of termination of the induction period and also the rate of hydration of the calcium silicate phase may be determined by this technique.

Phosphonates appear to be much more efficient retarders than many other retarders normally used in concrete practice. It appears that the Na-salts of all the phosphonic acids are less efficient retarders than the acids from which they are derived. The lower pH of aqueous acids improves their chelating or complexing ability resulting in poisoning and stabilization of the calcium silicate hydrate on the hydrating C₃S phase.

The most effective retarder amongst all phosphonate compounds studied is DTPMP which at a concentration of 0.05% extended the induction period to 21.1. hrs. DTPMP is also the best sequestering compound of the phosphonates studied.

Phosphonates may be classified as superretarders and may find application in the recycling of concrete in ready-mix concrete operations, controlling of slump in superplasticized concrete and steam-curing of concrete.

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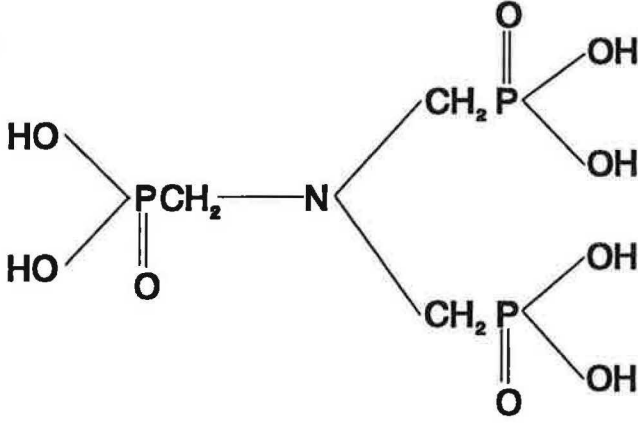
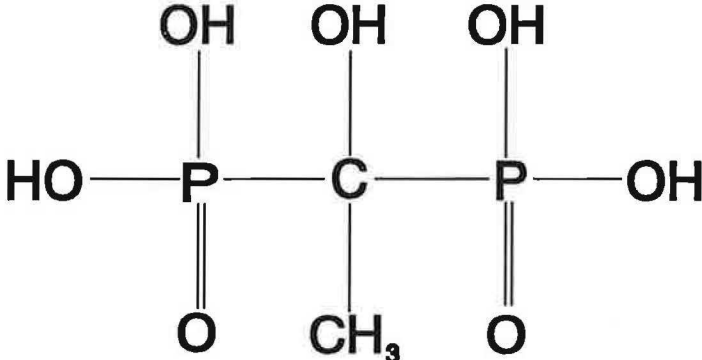
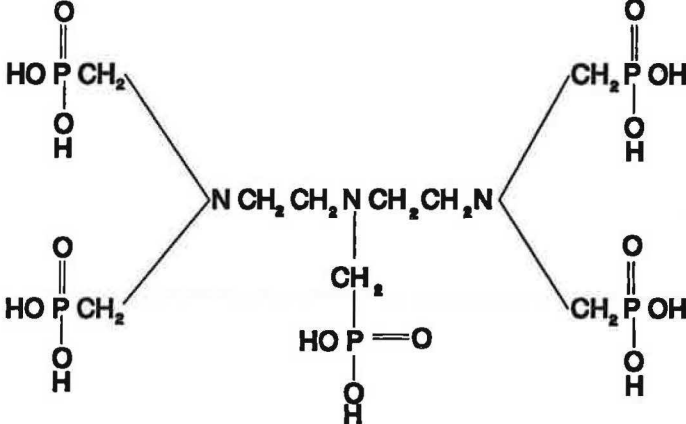
<p>ATMP</p>	 <p>Aminotri(methylenephosphonic acid)</p>
<p>HEDP</p>	 <p>1-Hydroxyethylidene-1,1-diphosphonic acid</p>
<p>DTPMP</p>	 <p>Diethylenetriaminepenta(methylenephosphonic acid)</p>

Figure 1: The molecular structures, chemical names and abbreviations of the phosphonic acid compounds.

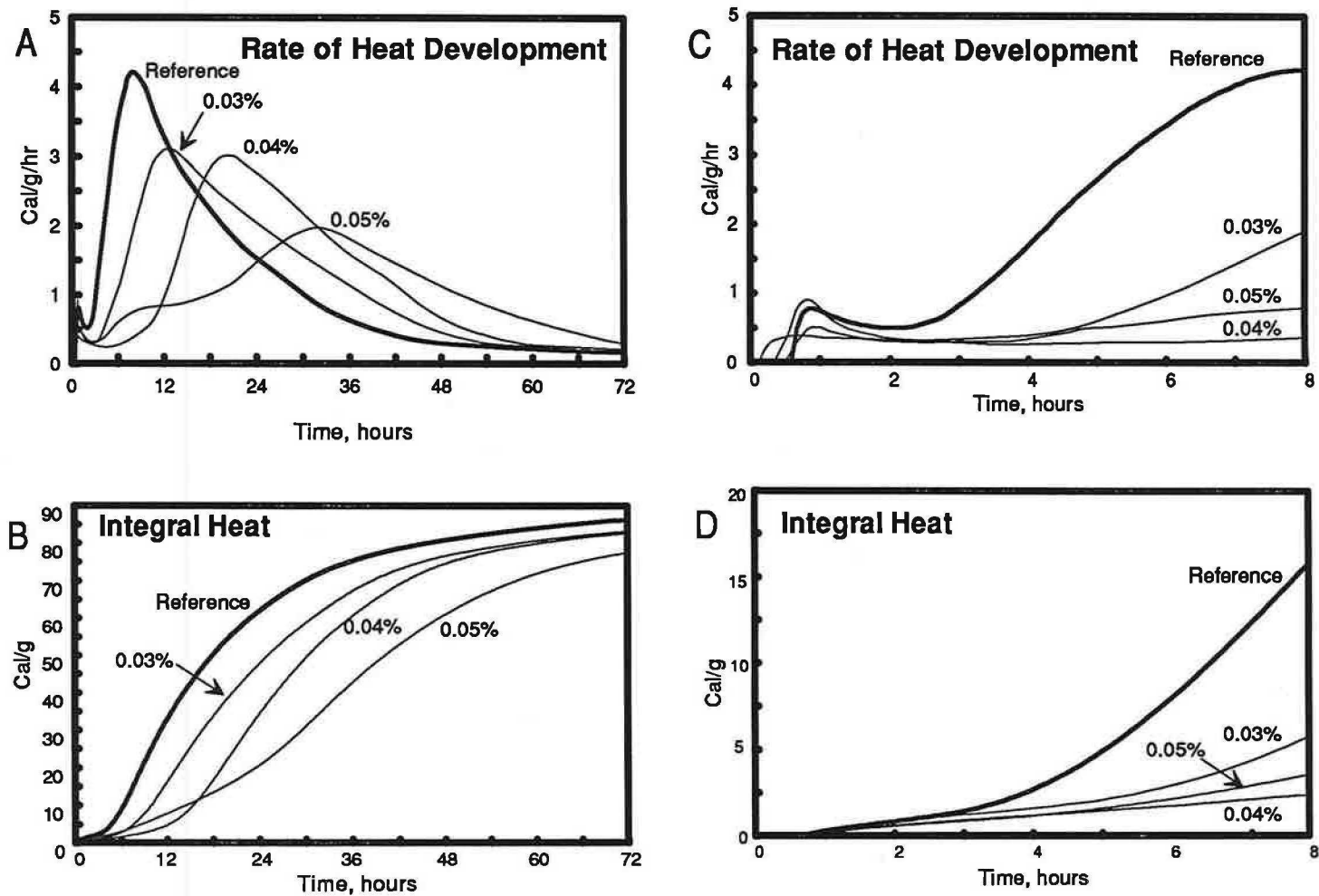


Figure 2: Conduction calorimetric curves of Portland cement in the presence of Phosphonate systems: ATMP.

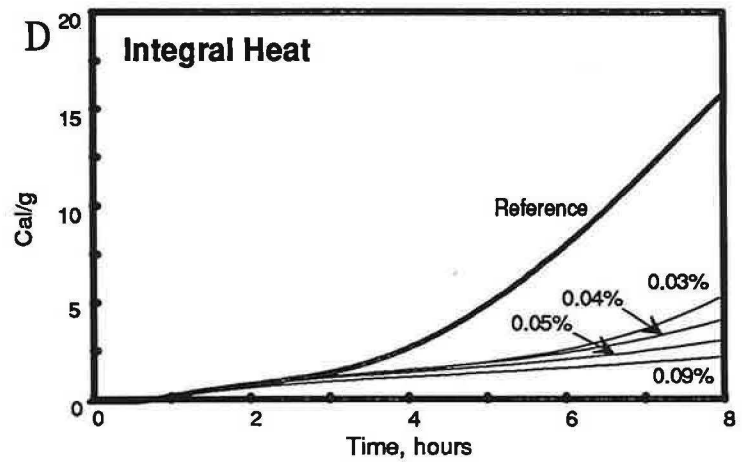
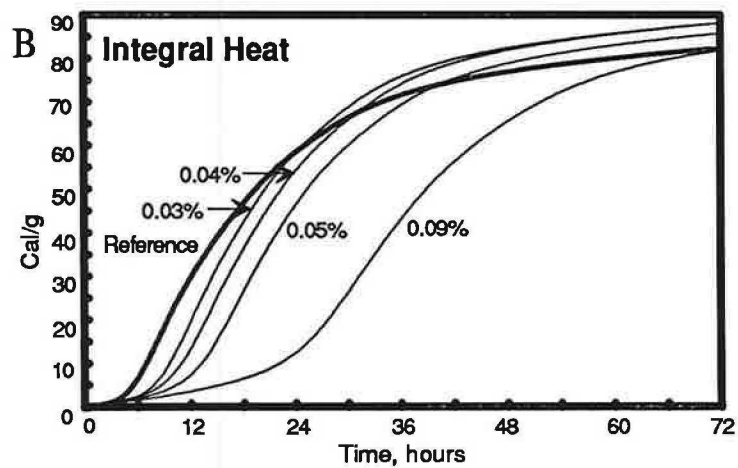
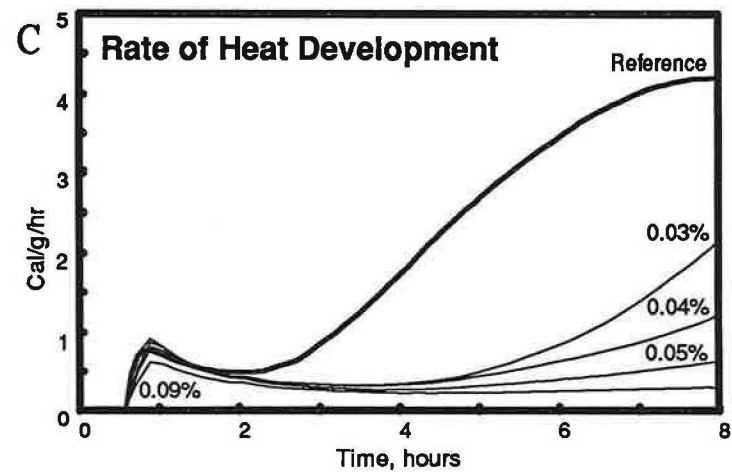
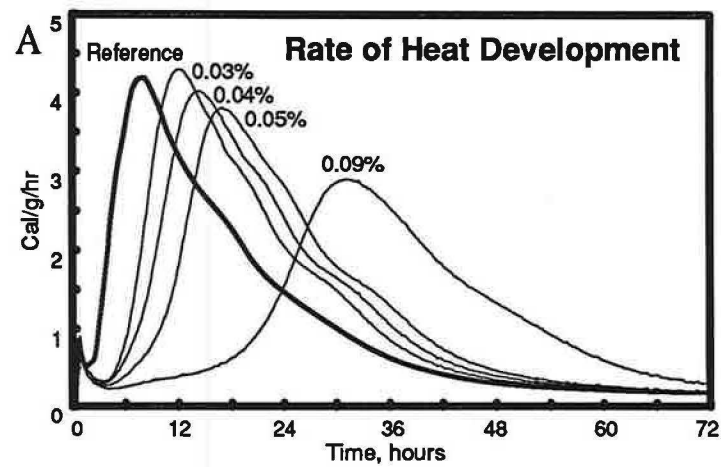


Figure 3: Conduction calorimetric curves of Portland cement in the presence of Phosphonate systems: Na_5ATMP .

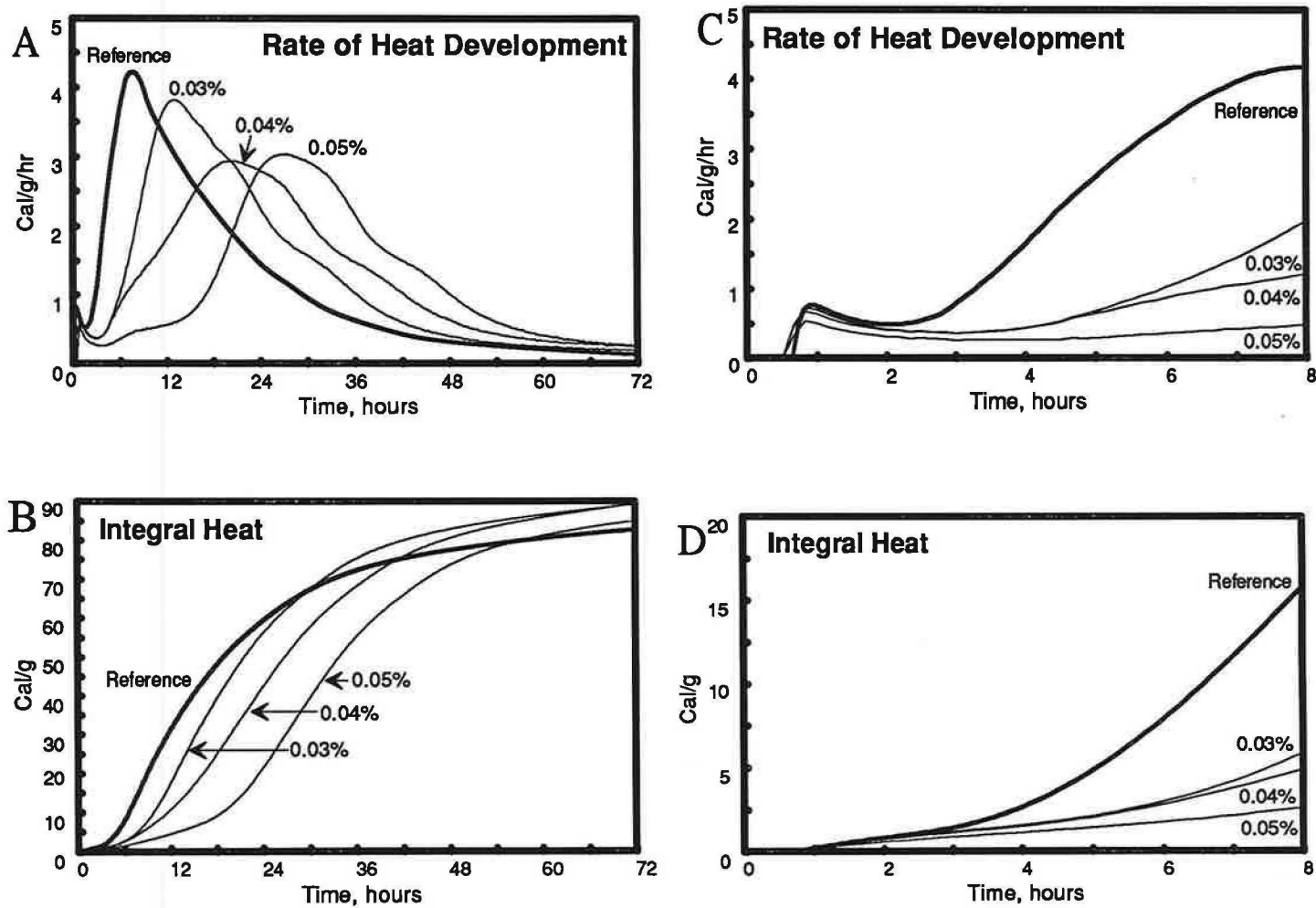


Figure 4: Conduction calorimetric curves of Portland cement in the presence of Phosphonate systems: HEDP.

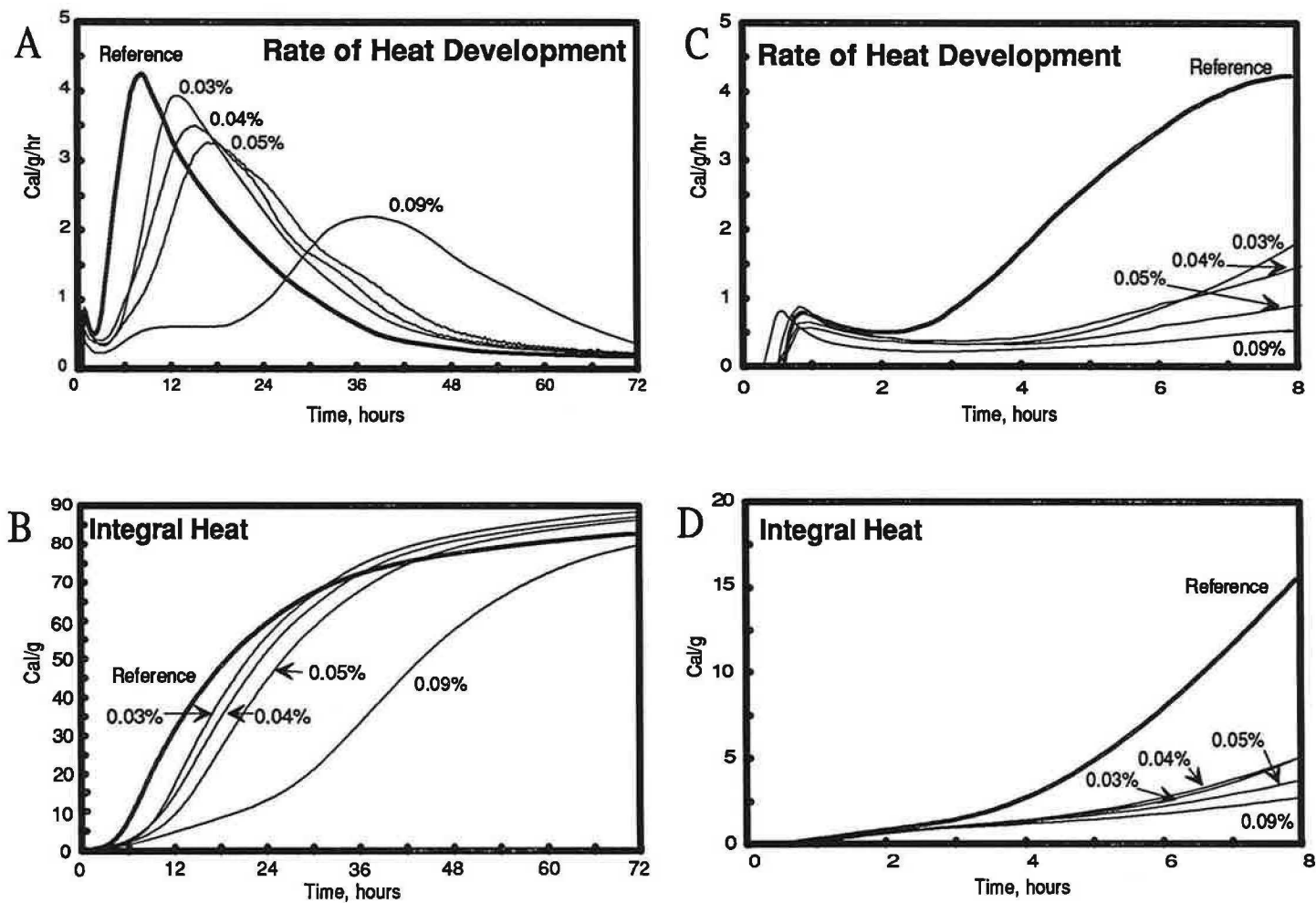


Figure 5: Conduction calorimetric curves of Portland cement in the presence of Phosphonate systems: Na_4HEDP .

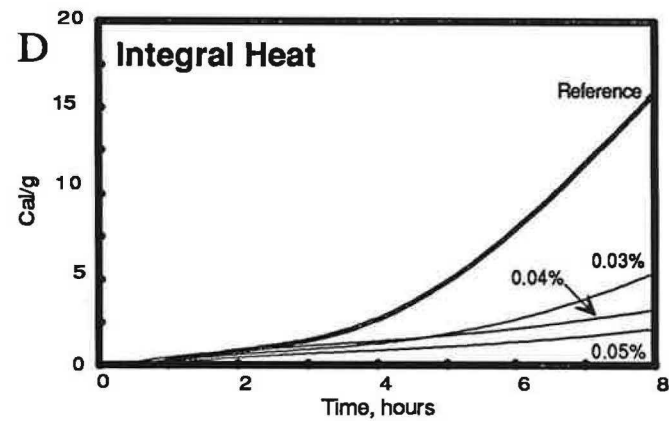
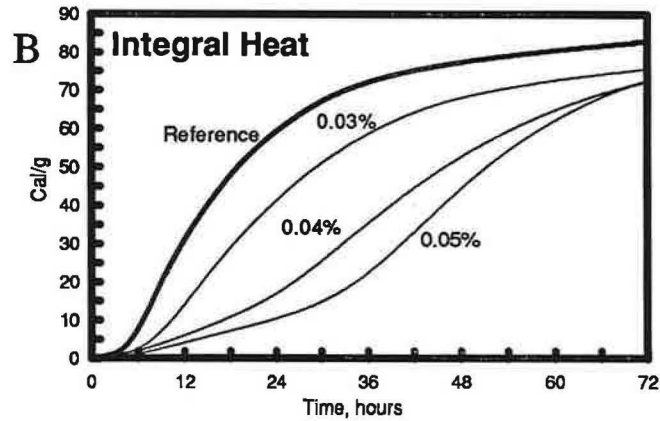
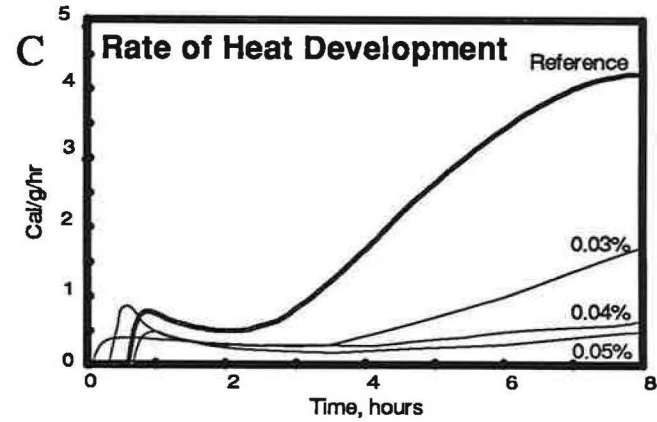
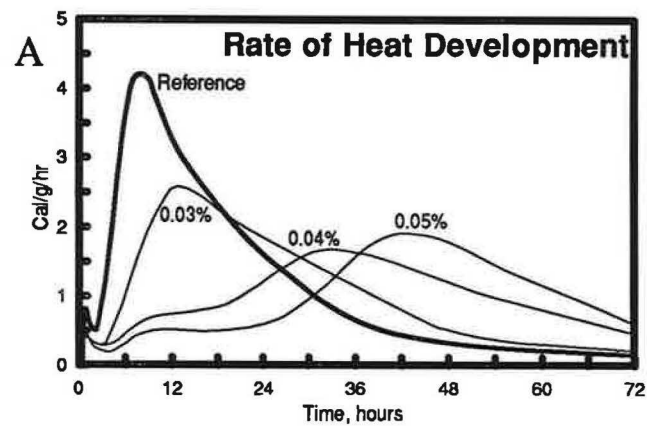


Figure 6: Conduction calorimetric curves of Portland cement in the presence of Phosphonate systems: DTPMP.

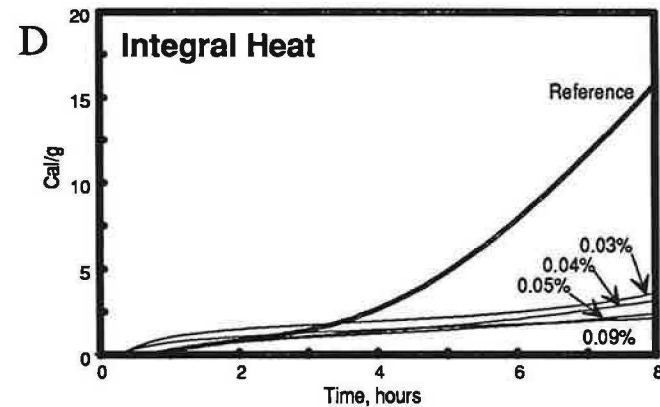
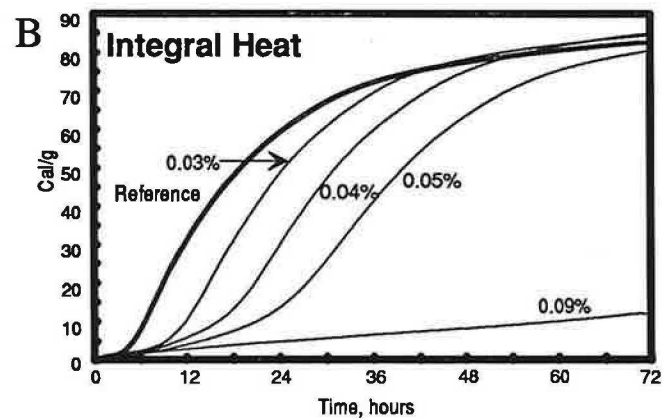
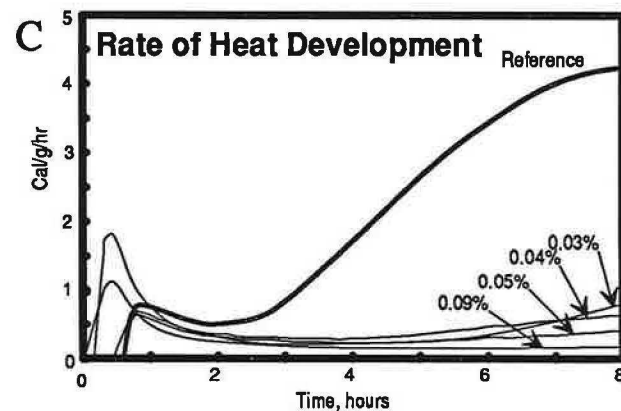
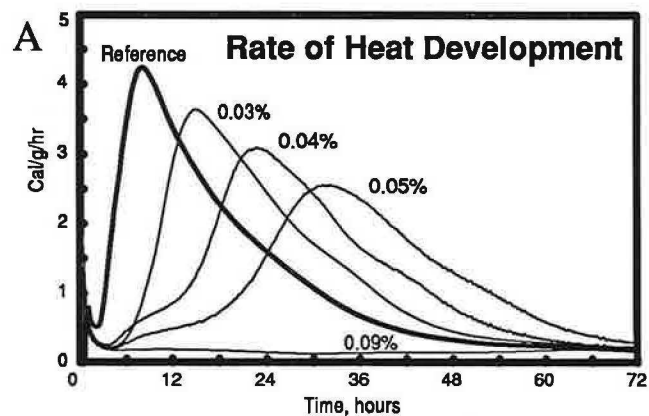


Figure 7: Conduction calorimetric curves of Portland cement in the presence of Phosphonate systems: Na_6DTPMP .

Table 1: The effects of phosphonate compounds on hydration parameters for Portland cement.

Phosphonate		End of Induction Period (hrs)	Time of Maximum Inflection (hrs)
ATMP	0%	2.2	7.9
	0.03%	3.2	12.7
	0.04%	6.6	20.6
	0.05%	13.2	32.0
Na5ATMP	0%	2.2	7.9
	0.03%	3.8	12.4
	0.04%	4.1	14.4
	0.05%	4.7	16.9
	0.09%	16.3	31.3
HEDP	0%	2.2	7.9
	0.03%	3.4	13.1
	0.04%	3.6	20.2
	0.05%	10.1	27.5
Na4HEDP	0%	2.2	7.9
	0.03%	3.8	12.8
	0.04%	3.2	15.3
	0.05%	4.1	17.0
	0.09%	18.0	37.7
DTPMP	0%	2.2	7.9
	0.03%	3.5	12.9
	0.04%	9.9	32.7
	0.05%	21.1	42.4
Na6DTPMP	0%	2.2	7.9
	0.03%	4.3	15.1
	0.04%	6.3	22.8
	0.05%	16.2	31.4
	0.09%	>72	>72

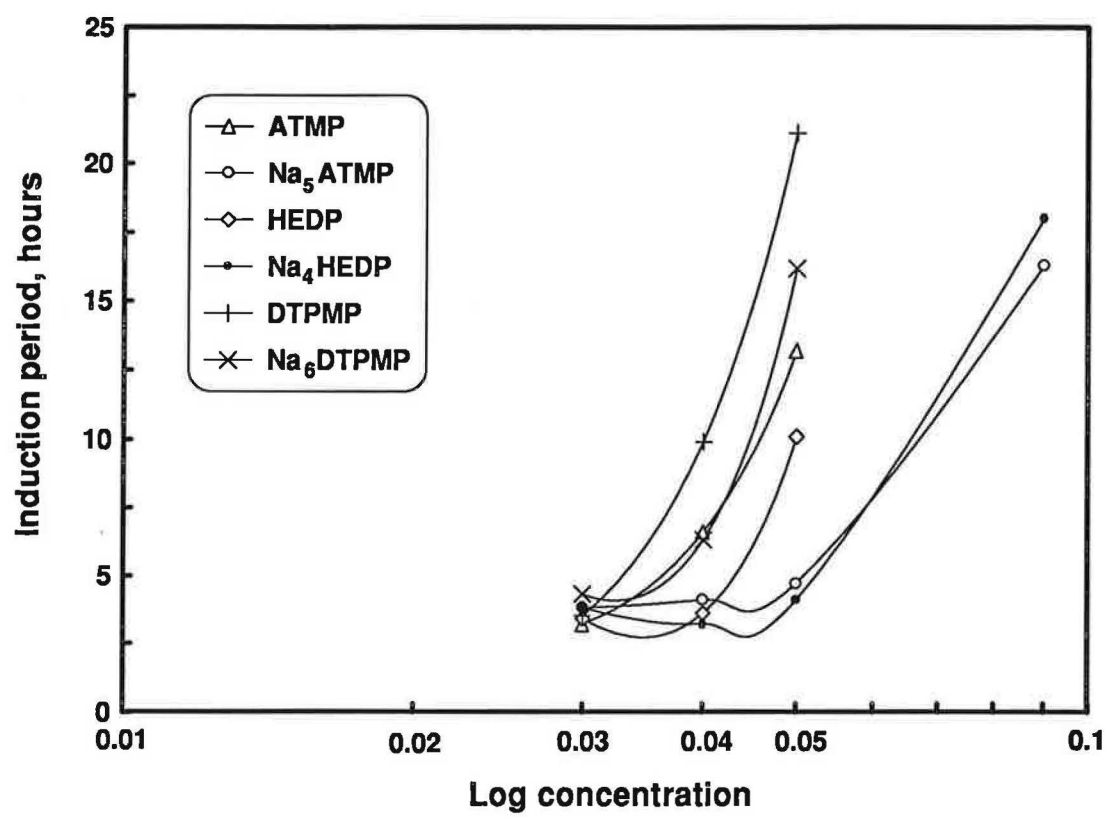


Figure 8: The effect of varied concentrations of phosphonate compounds on the induction period of Portland cement.

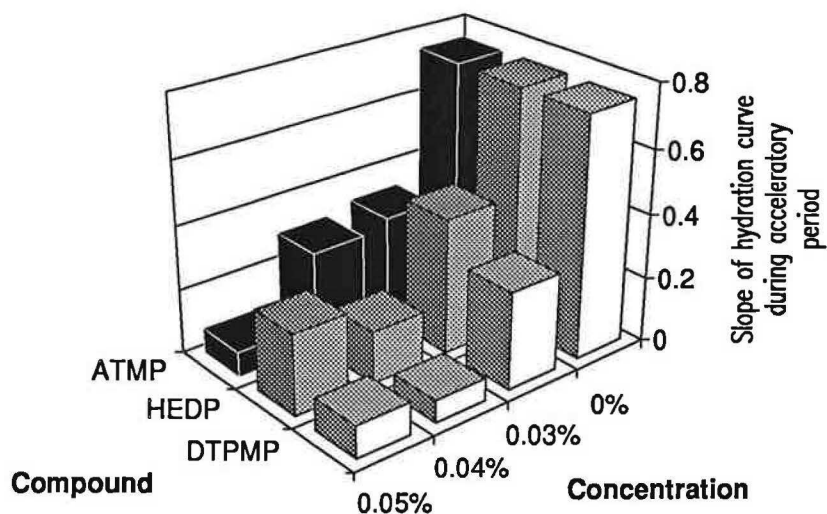
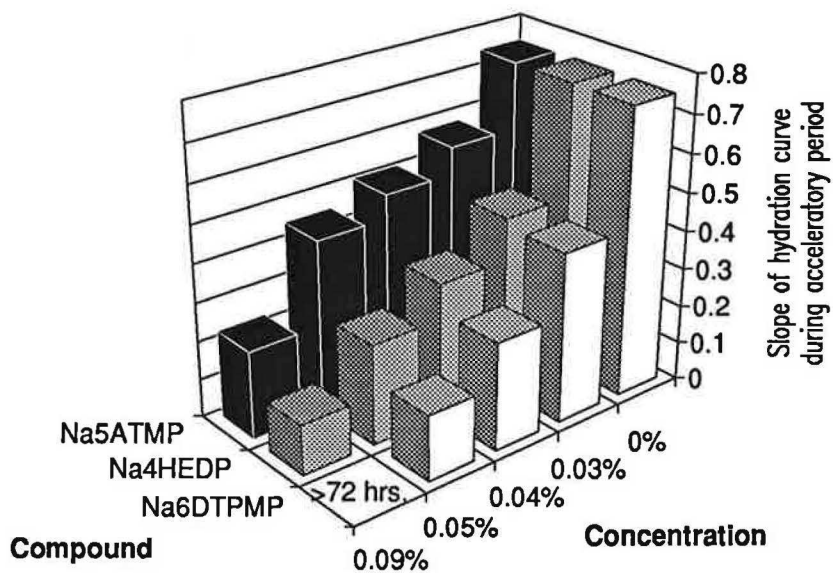
A**Slope of Hydration Curve During Acceleratory Period for Phosphonate Acid Compounds****B****Slope of Hydration Curve During Acceleratory Period for Phosphonate Salt Compounds**

Figure 9: The effect of varied concentrations of phosphonate compounds on the slope of the hydration curve of Portland cement during the acceleratory period.