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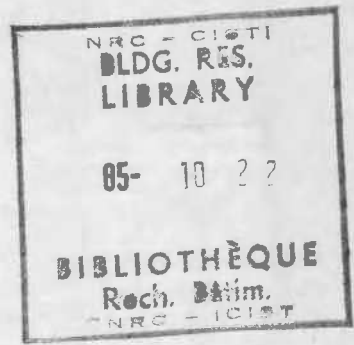
Evaluation of Concrete Admixtures Using Differential Thermal Technique

by V.S. Ramachandran

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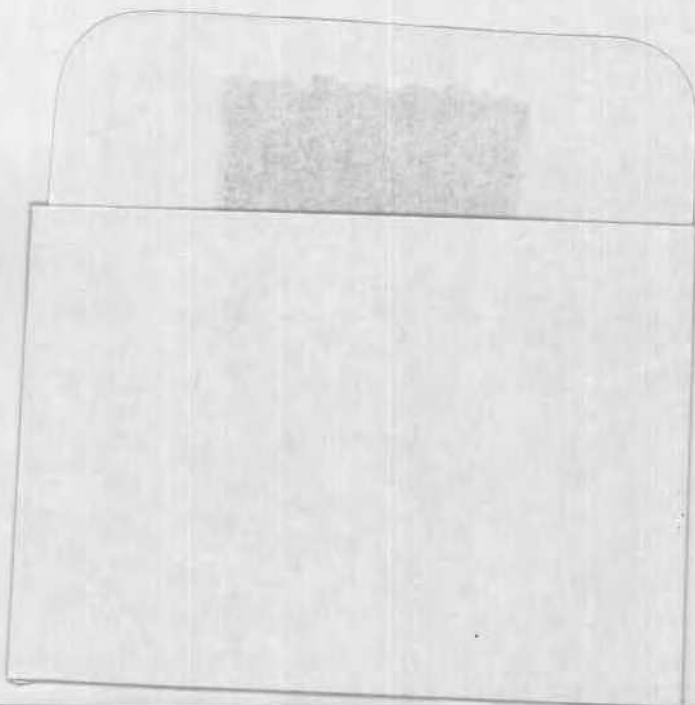
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"EVALUATION OF CONCRETE ADMIXTURES USING DIFFERENTIAL THERMAL TECHNIQUE"

By Dr. V.S. Ramachandran *

Reprint of the paper presented by Dr. V. S. Ramachandran in the ACI/RILEM Symposium on 'Technology of Concrete when Pozzolans, Slags and Chemical Admixtures are used', sponsored by the Autonomous University of Nuevo Leon, held in Monterrey, Mexico, March 10-15, 1985.

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Evaluation of Concrete Admixtures using Differential Thermal Technique

By Dr.V.S.Ramachandran

Synopsis: Thermoanalytical methods, especially the differential thermal technique, are used increasingly to evaluate concrete admixtures: for studying the kinetics of hydration, relative effects of different admixtures, effects of various factors on the influence of admixtures, identification, estimation and composition of products, mechanisms, crystallinity, etc. Examples illustrate how one may observe by means of the differential thermal method the effects of accelerators, retarders, water reducers, superplasticizers and mineral admixtures on hydrated pastes formed from cement and cement minerals.

Keywords: Accelerators, admixtures, fly-ash, hydration, retarders, - silica fume, slags, superplasticizers, thermal analysis, water reducers.

Evaluación de Aditivos para Concreto Utilizando la Técnica del Diferencial Térmico

Por: Dr. V.S. Ramachandran

RESUMEN: Se están utilizando en una forma incrementada los métodos - termoanalíticos, especialmente la técnica del diferencial térmico, para evaluar aditivos para concreto: para el estudio de la cinética de hidratación, efectos relativos de diferentes aditivos, efectos de varios factores en la influencia de aditivos, identificación, estimación y composición de productos, mecanismos, cristalinidad, etc. Los ejemplos ilustran cómo pueden observarse por medio del método del diferencial térmico, los efectos de acelerantes, retardantes, reductores de agua, superplastificantes y aditivos minerales en las pastas hidratadas formadas de cemento y minerales cementantes.

Palabras clave: Acelerantes, aditivos, ceniza volante, hidratación, - retardantes, humo de sílica, escorias, superplastificantes, análisis térmico, reductores de agua.

Evaluation des Adjuvants du Béton

par une Technique Thermique

Différentielle

Par: Dr. V.S. Ramachandran

Résumé: On a utilisé des méthodes thermoanalytiques et principalement de la technique thermique différentielle pour étudier la cinétique de l'hydratation, les effets relatifs des différents adjuvants et les effets de facteurs variés sur l'influence des adjuvants ainsi que l'identification, l'estimation et la composition des produits, les mécanismes, la cristallinité, etc. On s'est servi d'exemples pour - - illustrer comment on peut observer les effets des accélérateurs, des retardateurs de prise, des réducteurs d'eau, des superplastifiants et des adjuvants minéraux sur des pâtes hydratées formées de ciment et de minéraux de ciment grâce à la méthode thermique différentielle.

Mots clés: Accélérateurs, adjuvants, cendre volante hydratation, retardateurs, fumée de silice, laitier, superplastifiants, analyse thermique, réducteurs d'eau.

BIOGRAPHY

Dr. V.S. Ramachandran is the Head of the Materials Section, Division of Building Research, National Research Council of Canada. His main research interests are in the fields of concrete science and technology. He has published five books, 13 chapters and about 120 research papers.

INTRODUCTION

It is estimated that 80% of the concrete produced in North America contains one or more admixtures, and they are being used increasingly in many other countries. That there is intense activity in this field is evident from the number of patents, publications and conferences devoted to them. In spite of extensive investigation, however, the use of admixtures is based more on art than on science.

Several physical, chemical and mechanical techniques have been applied in studying the role of admixtures in concrete. One that has attained wide recognition in recent years is related to thermal analysis: Differential Thermal Analysis (DTA) has been used with considerable success to study the mechanisms, kinetics and composition involved, and for identification and estimation of the products of hydration. It is simple, reliable, and yields quick results. This paper describes several applications of DTA in the investigation of the role of admixtures such as accelerators, retarders, water reducers, superplasticizers and mineral admixtures on the hydration of cement and cement minerals.

EXPERIMENTAL

Differential Thermal Technique

When a substance is gradually heated at a predetermined rate, it may at a particular temperature undergo a thermal change that manifests itself as an endothermal or exothermal effect. The temperature at which this occurs, the intensity of the effect and its endo- or exothermal nature are characteristics of the particular substance under study. These thermal changes are caused by reactions such as crystal inversion, dehydration, decomposition, oxidation, reduction, chemical reaction between two or more components, and destruction of lattice. In DTA the temperature difference (termed differential temperature) between the sample and a reference material (such as $\alpha\text{-Al}_2\text{O}_3$, which does not show any thermal change) is continuously recorded as a function of temperature of the furnace, reference material, or time. The exothermal peaks are shown as upward peaks and the endothermal peaks as downward ones with respect to the base line. In the differential scanning calorimeter, which yields curves similar to those of DTA, the sample is maintained isothermal to an inert material by a supply of heat to the sample or reference material. The heat energy required to maintain the isothermal condition is recorded as a function of time or temperature. For most cases reported in this paper a constant amount of sample was used and the rate of heating was maintained at $10^\circ\text{C}/\text{min}$.

Samples

Tricalcium silicate (C_3S),* dicalcium silicate (C_2S), and tricalcium aluminate (C_3A) were synthesized from pure compounds. Portland cement type I was commercially obtained and the admixtures were either pure chemicals or commercial samples. The pastes were prepared by mixing the constituents on specially made rollers, care being taken to prevent contamination by CO_2 in the atmosphere.

RESULTS AND DISCUSSION

Accelerators

Many substances act as accelerators for concrete: alkali hydroxides, silicates, fluorosilicates, formates, nitrates, thioculfates, carbonates, chlorides and amines. Of these, $CaCl_2$ appears to be the most efficient.

Kinetics--The kinetics of hydration of cement or silicates requires an estimate of the $Ca(OH)_2$ formed at different times. Although chemical extraction methods can be used, they are known to be time-consuming and to yield slightly higher values. The decomposition of $Ca(OH)_2$ results in an endothermal effect in the temperature range 450-550°C; its intensity can be used to determine quantitatively the amount of $Ca(OH)_2$ present in a paste. Figure 1 shows that $Ca(OH)_2$ estimated in C_3S pastes by the thermal method is comparable to that obtained from chemical analysis (1).

Figure 2 indicates the amount of $Ca(OH)_2$ formed at different times in the hydration of C_3S (2). The relative degrees of hydration of C_3S in terms of $Ca(OH)_2$ formation are as follows: at 6 h the relative rates are $C_3S + 4\% CaCl_2 > C_3S + 1\% CaCl_2 > C_3S + 0\% CaCl_2$; at 24 h the order is $C_3S + 1\% CaCl_2 > C_3S + 4\% CaCl_2 > C_3S + 0\% CaCl_2$; and at 30 days, $C_3S + 1\% CaCl_2 > C_3S + 0\% CaCl_2 > C_3S + 4\% CaCl_2$.

Relative accelerating effects--If a new material has to be assessed for its accelerating action, thermal analysis may be used to compare its action with respect to other accelerators (3). Figure 3 compares the relative amounts of $Ca(OH)_2$ formed when C_3S is hydrated in the presence of 2% $CaCl_2$ or Ca-formate. Although Ca-formate is an accelerator, it is not so effective as $CaCl_2$.

Factors influencing acceleration--The rate of hydration depends on the crystal nature, particle size, surface area, water/solid ratio, temperature, etc., and the influence of these factors on hydration of cement and cement minerals may be studied by thermal analysis. In an investigation of the hydration of cement paste containing 3½% $CaCl_2$, it was found that at 24 h less $Ca(OH)_2$ was formed at a water/solid ratio of 0.25 than at one of 0.4 (4).

States of chloride--A knowledge of the state of chloride in cement paste is important in studying the mechanism of hydration and the corrosion potential. In the C_3S - $CaCl_2$ - H_2O system thermal analysis in conjunction with leaching experiments with alcohol and water indicate that calcium chloride exists in different forms: free state, adsorbed on the C_3S surface, chemisorbed on the C-S-H

*Cement nomenclature: C = CaO , S = SiO_2 , A = Al_2O_3 , H = H_2O

surface or in the interlayers and strongly incorporated into the lattice of C-S-H. Figure 4 shows the possible states of chloride in C_3S hydrated for different periods (5).

Composition of C-S-H--Admixtures may alter the composition of C-S-H formed during the hydration of C_3S or cement. At any stage in the hydration of C_3S , a lower amount of $Ca(OH)_2$ is formed in the presence of triethanolamine than is normally formed. But although lower amounts are formed, larger amounts of C_3S are consumed in the presence of triethanolamine (6). It may be concluded that triethanolamine promotes the formation of C-S-H with a higher CaO/SiO_2 ratio; larger endothermal peaks below 300°C and between 720° and 760°C are indicative of the existence of a higher CaO/SiO_2 ratio.

Crystallinity of $Ca(OH)_2$ --In hydrating C_3S and cements, there is a possibility that under certain conditions non-crystalline $Ca(OH)_2$ will form. In the hydration of C_3S with triethanolamine, the endothermal effect at 500°C, representing decomposition of $Ca(OH)_2$, is of a lower intensity, indicating that the amine is a retarder of hydration of C_3S (Fig. 5) (7). In the presence of triethanolamine, dual peaks appearing in the temperature range 450-500°C indicate the possibility of formation of both crystalline and non-crystalline forms of $Ca(OH)_2$.

Retarders

Many organic and inorganic compounds, including those derived as by-products, can be used as retarders. Unrefined Na, Ca or NH_3 salts of lignosulfonic acid, their modifications and derivatives, hydroxycarboxylic acids and their salts, carbohydrates, and inorganic compounds based on phosphates, fluorates, oxides, borax and magnesium salts act as retarders.

Hydration--The rate of hydration of cement or cement components is retarded by the incorporation of retarders. The relative retarding action of various admixtures may be followed by determining the type and amount of the hydrated products. All saccharides, with the exception of trehalose, strongly retard the set of cement. In the hydration of C_3A , a strong endothermal effect observed at 550°C at 3 h is indicative of the stable cubic aluminate hydrate (5). In the presence of 1% sucrose, endothermal effects indicative of hexagonal phases are present. These results show that sucrose retards the conversion of the hexagonal phase to the cubic phase. That trehalose is a weaker retarder is evident from the presence of both hexagonal and cubic phases when it is used.

Role of lignosulfonate--The retarding action of commercial lignosulfonates (CLS) is attributed to the presence of sugars. Adsorption-desorption studies of lignosulfonates indicate, however, that they are irreversibly adsorbed by the hydrating cement components (Fig. 6) (8), suggesting that pure lignosulfonate could act as a retarder. To verify this, cements hydrated with and without sugar-free lignosulfonates were compared. Samples hydrated in the presence of sugar-free lignosulfonate showed peaks of lower intensity for C-S-H (below 200°C) and $Ca(OH)_2$ (400-500°C) (Fig. 7) (3).

Normal Water Reducers

A water reducer is usually a water-soluble organic compound

that reduces the water requirement of concrete for a given consistency. It is effective with portland cement, portland blast furnace slag cement, and portland-pozzolan cement. Normal water reducers consist of Ca, Na or NH_4 salts of lignosulfonic acids, hydroxycarboxylic acids and their salts or hydroxylated polymer.

Interaction--Ca-lignosulfonate, in addition to acting as a water reducing agent, retards the hydration of C_3S and C_3A components. The mechanism by which the hexagonal phase in the hydration of C_3A is stabilized by Ca-lignosulfonate was studied by subjecting the lignosulfonate-treated hexagonal phase to thermal analysis. The thermogram exhibits an intense exothermic peak at 790°C and an endothermic peak at 825°C (Fig. 8) (5). The higher-temperature exothermic peak at 790°C (in the complex), absent in Ca-lignosulfonate, indicates that in the hexagonal phase the lignosulfonate existing in the interlayer positions is more resistant to oxidation. In the XRD studies of the hexagonal phase containing 10% lignosulfonate, an increase in the C-axis spacing could be explained by the existence of lignosulfonate in the interlayer positions.

Delayed addition--The addition of lignosulfonate a few minutes after water comes into contact with cement results in a better retarding/fluidizing effect than if it is added along with the mixing water. Thermal analysis shows that the hydration of C_3S is completely inhibited in the presence of 0.5% lignosulfonate. Addition of 5% C_3A is sufficient to promote the hydration of C_3S . The inhibitive action on C_3S hydration is more pronounced when lignosulfonate is added to a mixture of $\text{C}_3\text{S} + \text{C}_3\text{A}$ prehydrated for a few minutes. These results show that when lignosulfonate is added a few minutes after water comes into contact with cement, the hydrated products adsorb lower amounts of admixture and release more admixture for retarding and fluidizing of the C_3S phase.

Superplasticizers

Superplasticizers are chemically different from normal water reducers and are capable of reducing water requirements by about 30%. They are classified in four groups, viz., sulfonated melamine formaldehyde (SMF), sulfonated naphthalene formaldehyde, modified lignosulfonate, and others including sulfonic acid esters, carbohydrates, etc.

Hydration rate--The influence of superplasticizers on the hydration of cement and its components has been studied by thermal analysis. Superplasticizer (SMF) retards the hydration of C_3A , C_3S and cement but accelerates the formation of ettringite from $\text{C}_3\text{A} + \text{gypsum}$. These effects are related to the rate and amount of adsorption of SMF on cement and cement components (Fig. 9) (9).

Initial setting--The products formed at the time of initial setting of cements containing various admixtures in combination with an SMF superplasticizer were examined by thermal analysis. The results show that both the reference mortar and that containing the admixture exhibit endothermal effects in the region of 500°C (Fig. 10) (10). This indicates that at the time of initial setting some hydration of C_3S in the cement has occurred.

Other Admixtures

Fly ash, slags, silica and other types of admixture are added

to concrete for economy and to provide desirable properties. Thermal methods are used to study the reactions in cements containing these additions alone and in combination with other admixtures.

Fly ash--DTA can be used to determine the amount of Ca(OH)_2 that has reacted with fly ash in fly ash-cement mixtures. Table 1 compares the amount of Ca(OH)_2 formed in two blended cements containing 35% fly ash and 70% slag (7). In the fly ash blend, lime decreases from 14.1% at 14 days to 9.9% at 28 days. A significant reaction occurs between Ca(OH)_2 and fly ash during this period. In the slag blends formation of lower amounts of lime is due to the presence of only 30% cement in the blend. The decrease in Ca(OH)_2 from 3.3 to 2.6% indicates that some lime reacts with the slag.

Slags--Hydration sequence in slag cements and the mechanism of activation of slags has been investigated by DTA. The reactivity of slag is related to the amount and nature of the glassy phase. The DTA thermograms show an exothermal effect beyond 800°C. The area of the peaks is indicative of the amount of glass in slags.

Silica fume--The influence of silica fume on the hydration of cement and cement minerals may be followed by differential scanning calorimetry (11). Silica fume accelerates the hydration of both C_2S and C_3A phases in the first few hours. Figure 11 shows the amount of Ca(OH)_2 formed at different times in cement blends containing 30% silica fume or 30% ground silica sand. At about 8 h the amounts of Ca(OH)_2 formed in the three samples are about the same, although blends contain only 70% cement. This indicates that both ground sand and silica fume accelerate the hydration of cement.

Carbonates--Some cements contain small amounts of carbonate, and there is controversy as to their effect on cement properties. Thermal examination of the effect of CaCO_3 on C_2S and cement hydration has shown that the carbonate has an accelerating effect. For example, at 7 h the degree of hydration of C_2S containing 0 and 15% CaCO_3 was 5 and 17%, respectively, and the corresponding values at 1 day were 35 and 45%.

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Dr. V.S. Ramachandran

Table 1: Amount of Ca(OH)_2 Formed in Blended Cements

Hydration, days	Cement	Cement + Fly Ash % Ca(OH)_2	Cement + Slag
2	16.8	10.9	3.3
7	18.6	12.3	2.8
14	19.7	14.1	3.1
28	19.6	9.9	2.6

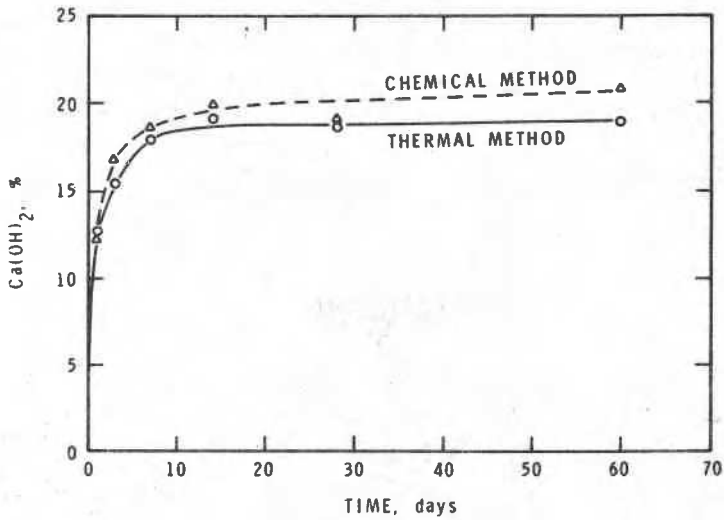


Fig. 1 -- Amounts of Ca(OH)_2 formed in the hydration of C_3S

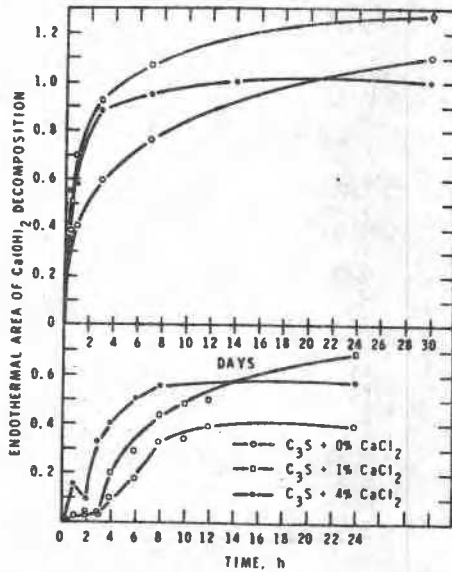


Fig. 2 — Estimation of Ca(OH)_2 at different periods of hydration of $3 \text{CaO} \cdot \text{SiO}_2$ by DTA.

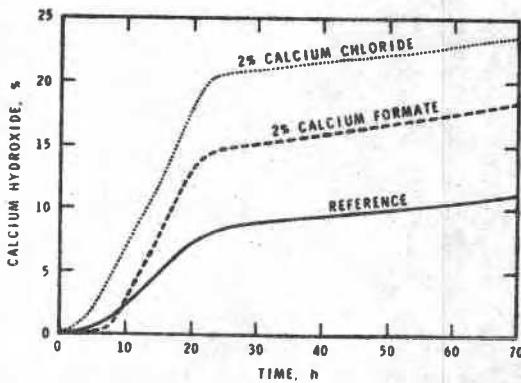


Fig. 3 — Effect of accelerators on the formation of calcium hydroxide in hydrated $3 \text{CaO} \cdot \text{SiO}_2$.

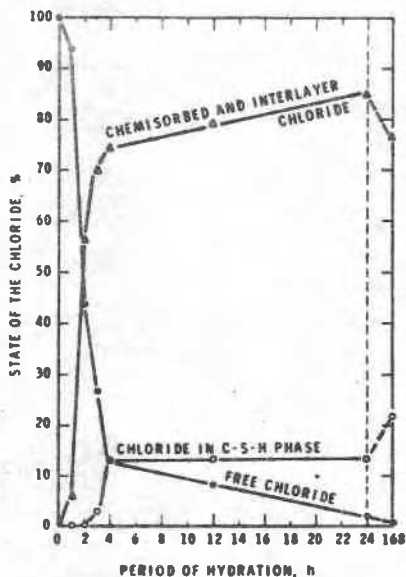


Fig. 4 -- Different states of chloride in hydrating tricalcium silicate.

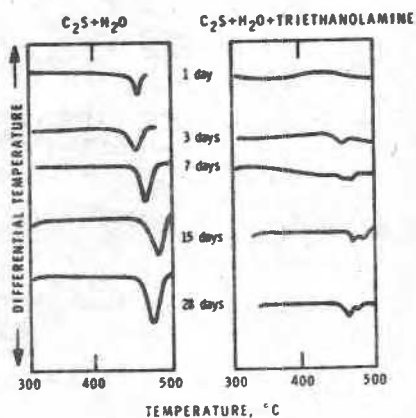


Fig. 5 -- Thermograms of $2 \text{CaO} \cdot \text{SiO}_2$ hydrated in the presence of triethanolamine (obtained in an N_2 atmosphere).

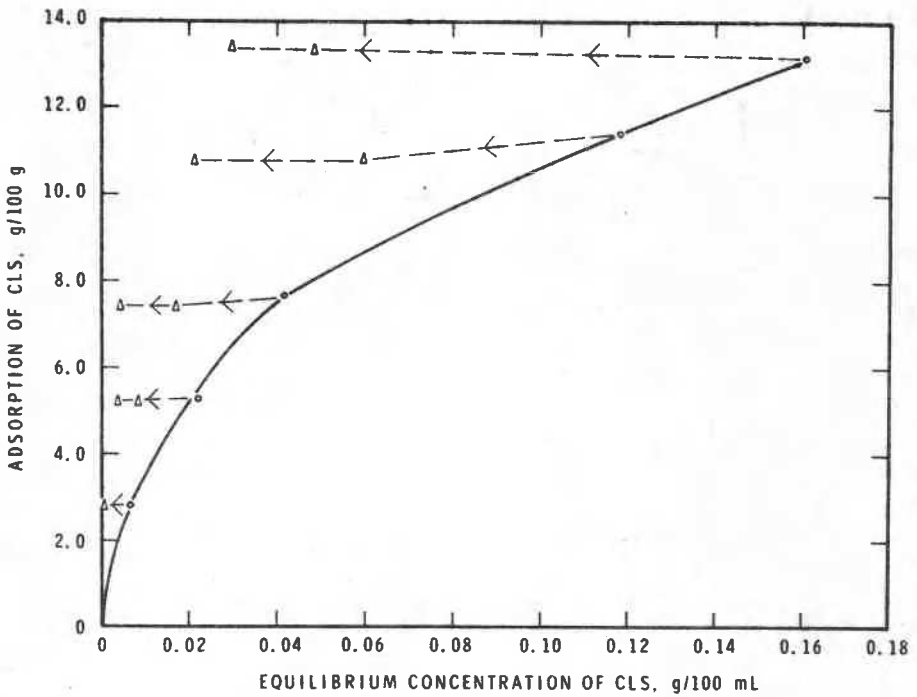


Fig. 6 -- Adsorption-desorption isotherms of CLS on hydrated C_3S in the aqueous medium.

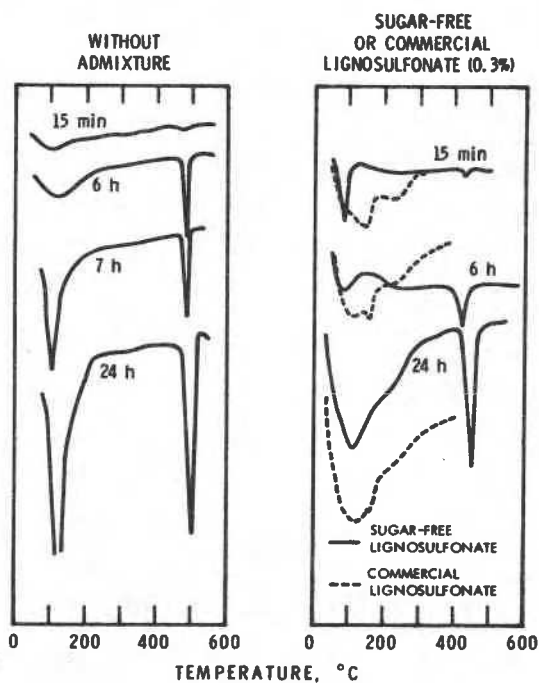


Fig. 7 — DTA of cement hydrated in the presence of lignosulfonates.

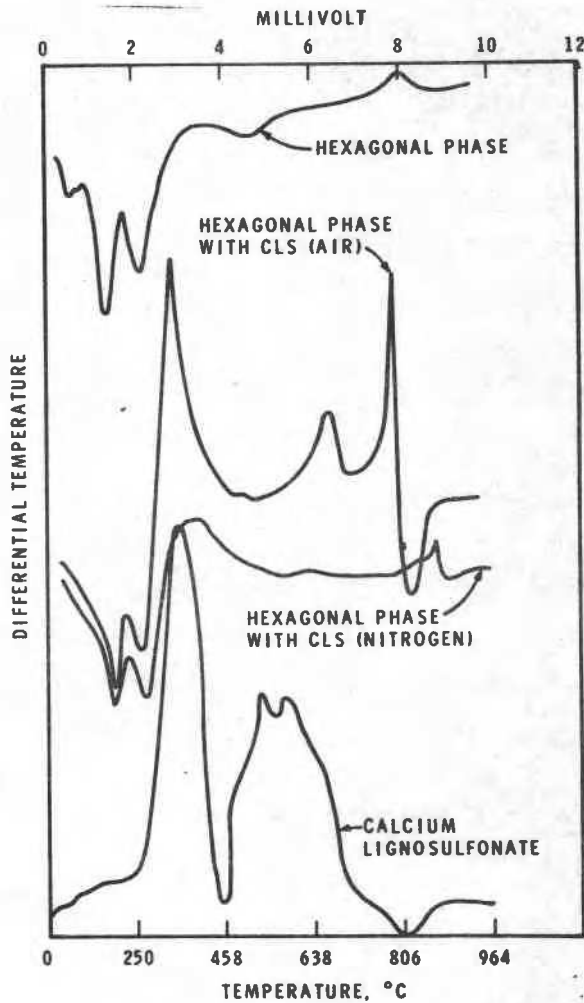


Fig. 8 -- Thermograms of hexagonal aluminate phase containing calcium lignosulfonate.

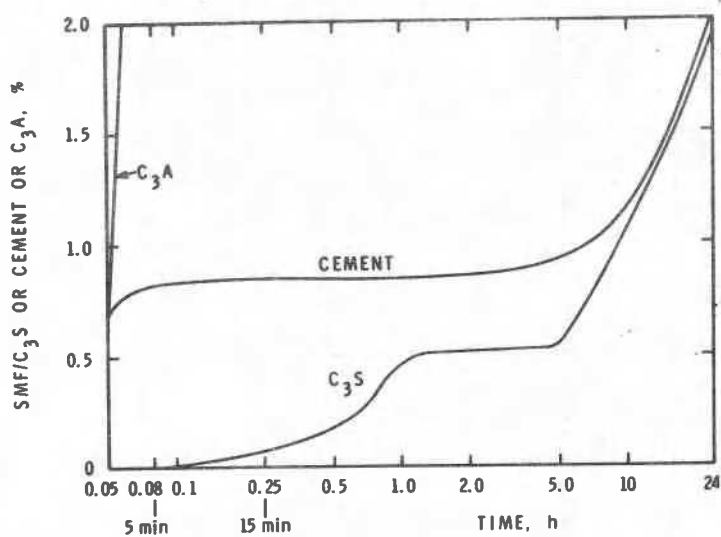


Fig. 9 — SMF adsorption on cement compounds during hydration.

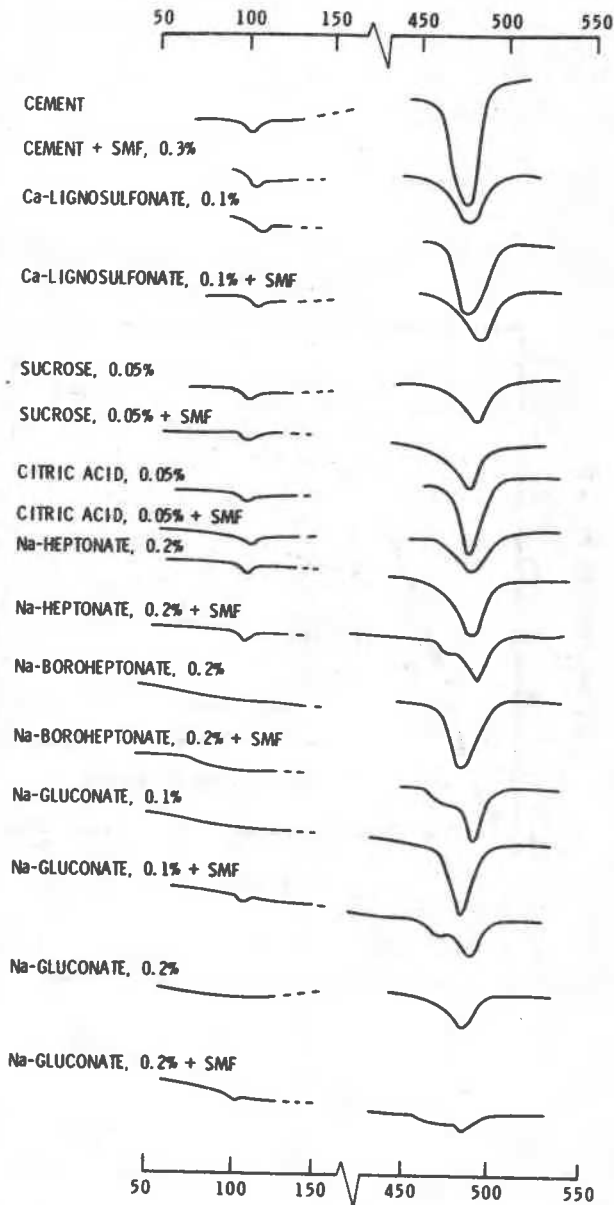


Fig. 10 -- Differential scanning calorimetric curves (at time of set) of cement mortars containing various admixtures.

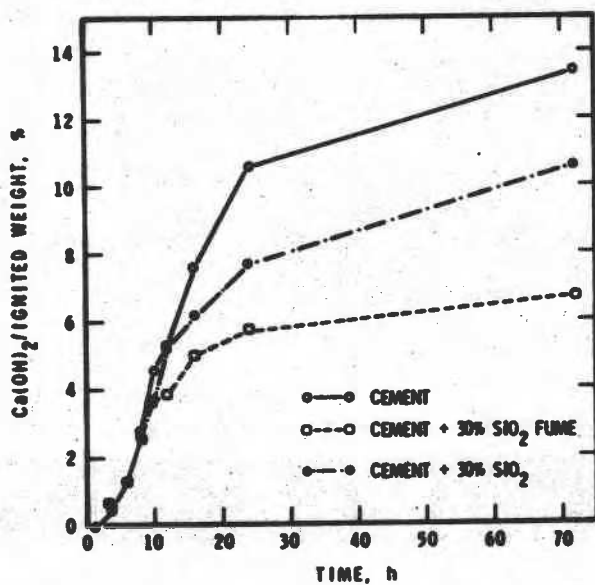


Fig. 11 — Influence of SiO₂ on the hydration of cement