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Conduction calorimetric investigation of the effect of retarders on the hydration of Portland cement

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Abstract

Eleven potential retarders, calcium gluconate, glucose, glycolic acid, molasses, sodium borate, sodium citrate, sodium heptonate, sodium hexametaphosphate, sodium pyrophosphate, sugar-free calcium lignosulfonate and sucrose, were added to Portland cement in dosages ranging from 0.025% to 1.2%, at a constant water:cement ratio of 0.5 and their conduction calorimetric behavior was investigated for periods up to 72 h. All retarders increased the induction period, from about 4 h to 55 h. Less than 0.15% of the most efficient retarders were needed to extend effectively the induction period to 40 h. They included Ca-gluconate, Na-heptonate and sucrose. The least effective retarders such as Ca-lignosulfonate (sugar-free), Na-pyrophosphate, Na-hexametaphosphate, Na-borate and glycolic acid had to be added at levels above 0.5% to attain an induction period of 40 h. Others such as glucose, molasses and Na-citrate were designated as moderately retarding admixtures. In most instances the degree of extension of the induction period was approximately linear with respect to the dosage of retarders, but the slopes were different.

INTRODUCTION

Most concrete used in North America contains at least one admixture as a constituent. An admixture is an ingredient added in small amounts to concrete to provide several beneficial effects such as enhanced frost and sulfate resistance, controlled setting and hardening, improved workability, increased strength, etc. Retarding admixtures are used in hot-weather concreting operations when delays in transport and handling between mixing and placing may result in early setting and loss of workability. In concreting of deep bore holes where the temperature is usually higher than 90 °C, retarders have to be used. In the construction of large structural units and dams and the manufacture of exposed aggregate panels, retarders are incorporated into concrete. Recently, retarders have also been used to maintain concrete returned from the ready-mix concrete trucks.

The action of retarders is related mainly to their influence on the tricalcium silicate and tricalcium aluminate components of cement. Retarders, by influencing the hydration and physical characteristics of these components extend the initial and final setting times of cement. Several techniques have been used to study the influence of retarders on the hydration of cements, in order to obtain a better understanding of the mechanisms of retardation, rate of hydration, setting phenomena, etc. The techniques include DTA, DSC, TG, chemical shrinkage measurements, XRD, loss on ignition, scanning electron microscopy and IR. Most of these techniques do not monitor the hydration processes continuously. The hydration is stopped at predetermined periods before they are subjected to examination by these methods. The conduction calorimetric technique estimates the instantaneous rate of heat liberation and amount of heat developed as a function of time and provides a rapid method of following hydration of cement. It is especially useful to investigate the effect of admixtures on the rate of hydration [1,2].

When developing an admixture formulation there is a need to test a number of potential candidates. For example, for developing a retarder there is a need to know the relative efficiencies of chemicals that retard the setting of cement. The setting times obtained from the normal standard techniques consume time and material. The relative setting times may be estimated by conduction calorimetry in which six samples may be studied simultaneously. The setting times occur after the end of the induction period but before the time corresponding to the maximum inflection in the conduction calorimetric curves [3,4]. The objective of this work was to determine the relative effects of various retarders on the hydration of cement in order to determine the type and dosage of admixture required for a particular degree of set retardation.

EXPERIMENTAL

Materials

Portland cement, Type I, was obtained from Lafarge Canada Inc. The analysis of the cement (oxide composition (%)) was: $SiO_2 = 20.05$; $Al_2O_3 = 4.60$; $CaO = 61.88$; $Fe_2O_3 = 2.47$; $MgO = 2.37$; $SO_3 = 3.79$. The phase composition was: $C_3S = 54.29\%$; $C_2S = 16.53\%$; $C_3A = 8.01\%$ and $C_4AF = 7.52\%$. In cement chemistry nomenclature, $C = CaO$; $A = Al_2O_3$; $S = SiO_2$; $F = Fe_2O_3$ and $H = H_2O$. The Blaine fineness was 3480 $cm^2\ g^{-1}$.

The effects of the following retarders were investigated by conduction calorimetry: sodium heptonate, glycolic acid, sucrose, sodium hexametaphosphate, calcium gluconate, sodium borate, sugar-free calcium lignosulfonate, sodium pyrophosphate, glucose, molasses and sodium citrate.

Calcium gluconate and glycolic acid were analytical grade chemicals. The molasses was supplied by Intaco, Costa Rica, and contained 0.9% chloride by weight. The sugar-free calcium lignosulfonate was obtained as follows. Normal calcium lignosulfonate was fractionated according to molecular weight size by continuous diffusion using a Dowex 50WX2 resin bed in a calcium salt form [5]. The high molecular weight fraction, analyzed by the chromatographic method, showed it to be sugar-free, with a molecular weight of 6500 (weight average) [6]. The remaining chemicals were of reagent grade.

Conduction calorimetry

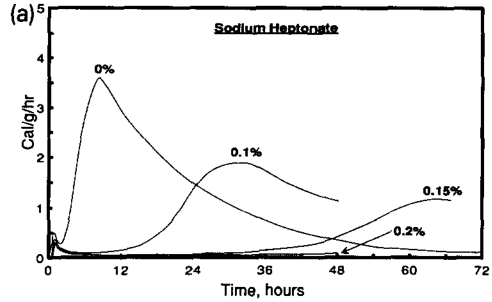
The rate and amount of heat development by cement with and without retarders was measured using a conduction calorimeter supplied by the Institute of Applied Physics, Delft, The Netherlands. The calorimeter was placed in a bath maintained at a constant temperature of $25 \pm 0.1\,^{\circ}$C. The calorimeter was interfaced with an NHC 286 AT computer using a DT100 Datataker datalogger. Data files from the Datataker were transferred via the Decipher, a software package supplied by Data Electronics, Australia. Voltage outputs were converted to calories using the spreadsheet software Excel, Microsoft, California. Graphical presentation of data plots was created using Charisma, Micrografx, Texas.

Sample preparation

In each of the experiments, 5 ml of the aqueous solutions containing the required amounts of the retarder (% by weight of the cement) was added to 10 g of cement, so that all the samples were hydrated at a water : cement ratio of 0.5. The amount of retarder added varied between 0.025% and 1.2%. At least three concentrations of each retarder were used. The samples were all pre-mixed with the aqueous solution for about 30 seconds and were placed in the calorimeter for a few minutes before collecting data.

RESULTS AND DISCUSSION

Figures 1–11 represent the conduction calorimetric curves for the hydrating cement containing various retarders at different dosages. In each of these figures the curve for the reference cement hydrated without any addition is also given. The rate as well as the amount of heat developed up to about 72 h are shown. Normal Portland cement exhibits an initial exotherm within the first 10 min of hydration and this is attributed to a combination of reactions such as the hydration of free lime, hydration of calcium sulfate hemihydrate, heat of wetting and the formation of ettringite



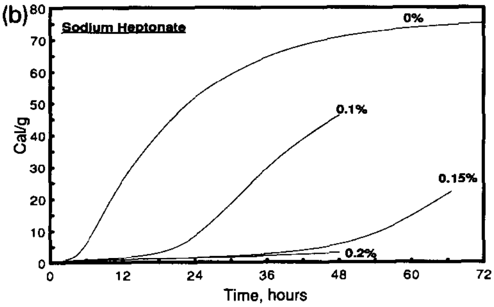
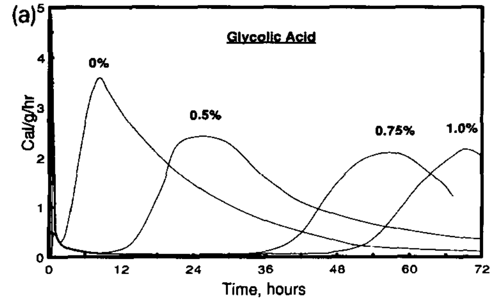


Fig. 1a. The effect of sodium heptonate on the hydration of Portland cement.

Fig. 1b. The effect of sodium heptonate on the heat of hydration Portland cement.



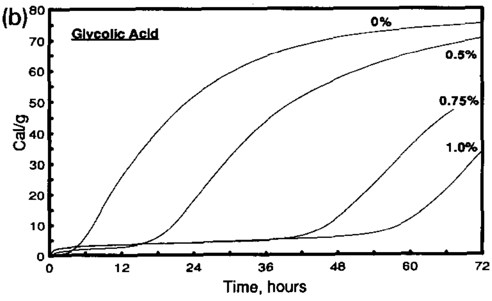
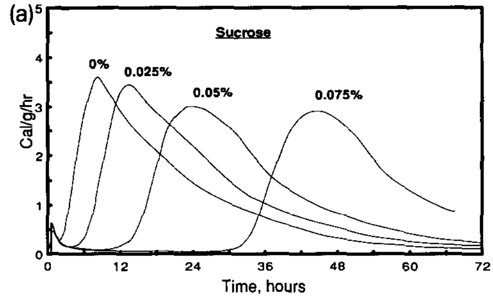


Fig. 2a. The effect of glycolic acid on the hydration of Portland cement.

Fig. 2b. The effect of glycolic acid on the heat of hydration of Portland cement.



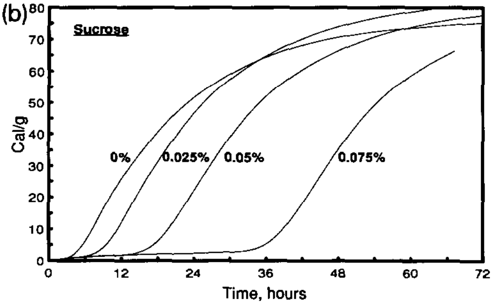
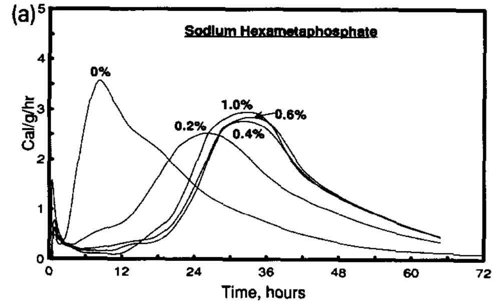


Fig. 3a. The effect of sucrose on the hydration of Portland cement.

Fig. 3b. The effect of sucrose on the heat of hydration of Portland cement.



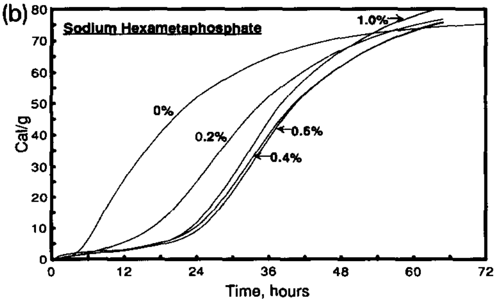
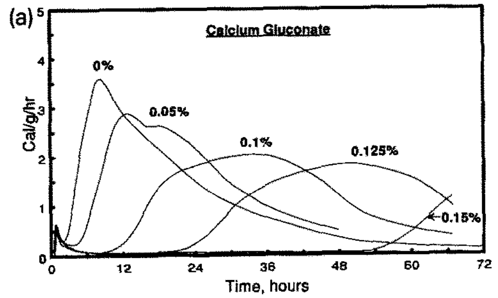


Fig. 4a. The effect of sodium hexametaphosphate on the hydration of Portland cement.

Fig. 4b. The effect of sodium hexametaphosphate on the heat of hydration of Portland cement.



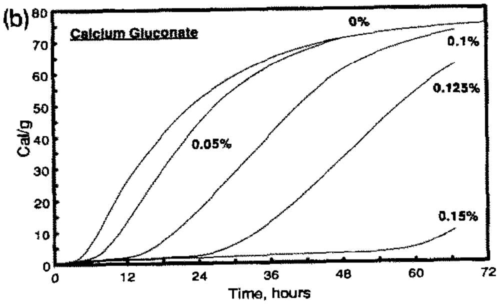
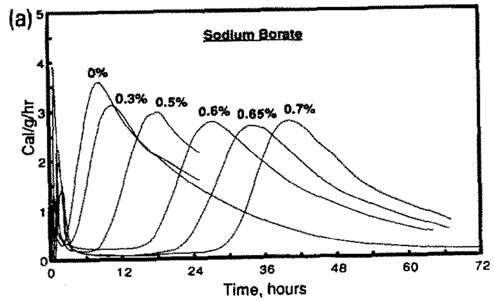


Fig. 5a. The effect of calcium gluconate on the hydration of Portland cement.

Fig. 5b. The effect of calcium gluconate on the heat of hydration of Portland cement.



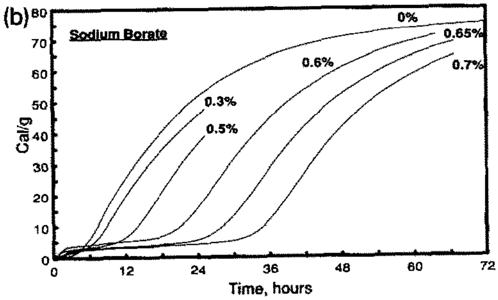
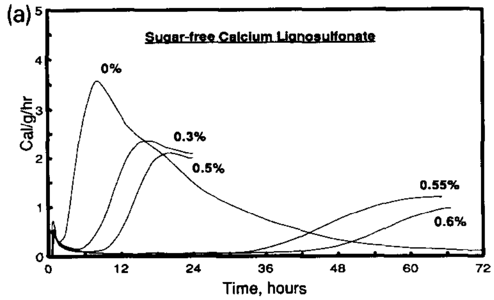


Fig. 6a. The effect of sodium borate on the hydration of Portland cement.

Fig. 6b. The effect of sodium borate on the heat of hydration of Portland cement.



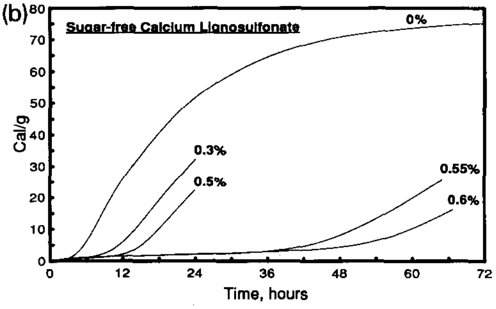
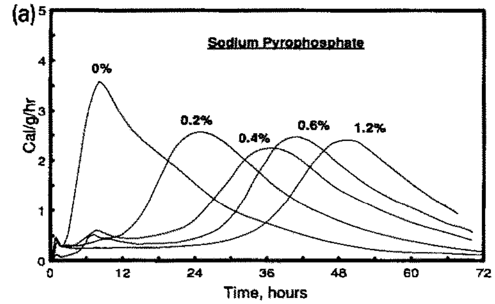


Fig. 7a. The effect of sugar-free calcium lignosulfonate on the hydration of Portland cement.

Fig. 7b. The effect of sugar-free calcium lignosulfonate on the heat of hydration of Portland cement.

of formula $3CaO(Al_2O_3,Fe_2O_3) \cdot 3CaSO_4 \cdot 31\text{–}32H_2O$. 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 relatively low chemical reactivity between about 30 min and 2.5 h; this period is known as the ‘induction’ or ‘dormant’ period. At the end of this period an increase in heat evolution occurs with a peak at about 8 h and this is due to the hydration of the tricalcium silicate component of the cement yielding 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 70 h.

Figure 1 gives the conduction calorimetric curves for the reference cement containing no retarder, and for cement containing 0.1%, 0.15% and 0.2% sodium heptonate. Although the induction period for the reference cement can be determined to be about 2.5 h, it is not easy to determine this period for some of the samples containing retarders. The reference cement exhibits an intense thermal peak at about 8 h and thereafter there is a gradual decrease in the rate of heat development, the rate being only about 0.1 cal g^{-1} h^{-1} at 72 h. The addition of sodium heptonate alters the curve significantly. The induction period is extended to 12.5 and 37 h with 0.1% and 0.15% heptonate respectively. The hydration of the C_3S phase virtually



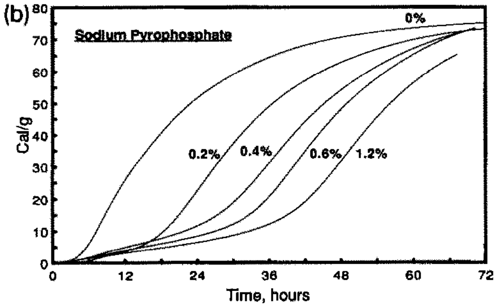
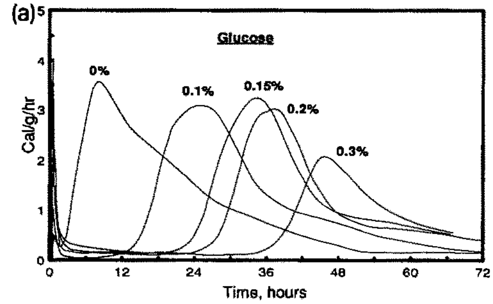


Fig. 8a. The effect of sodium pyrophosphate on the hydration of Portland cement.

Fig. 8b. The effect of sodium pyrophosphate on the heat of hydration of Portland cement.



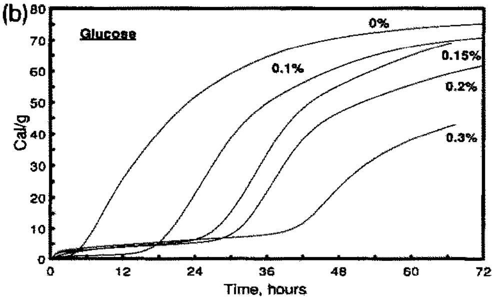
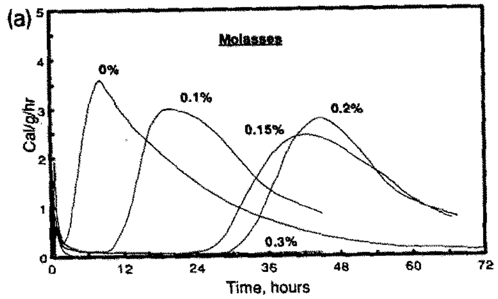


Fig. 9a. The effect of glucose on the hydration of Portland cement.

Fig. 9b. The effect of glucose on the heat of hydration of Portland cement.



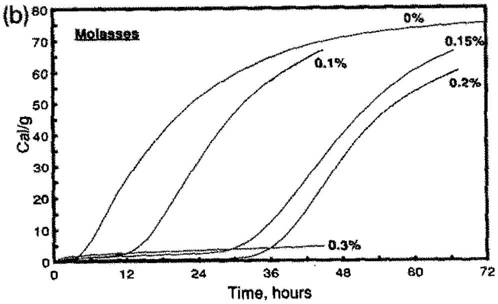
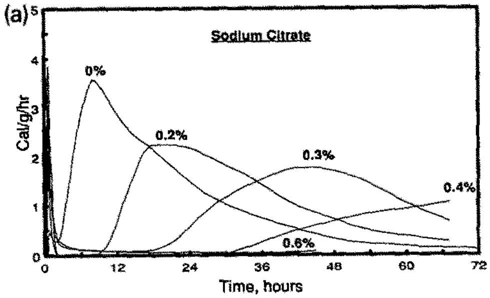


Fig. 10a. The effect of molasses on the hydration of Portland cement.

Fig. 10b. The effect of molasses on the heat of hydration of Portland cement.



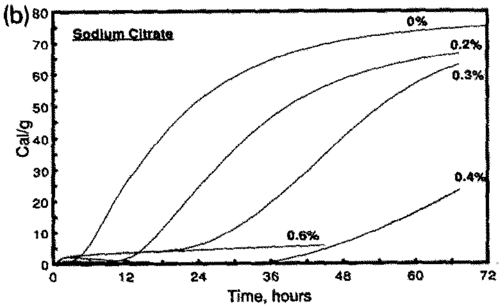


Fig. 11a. The effect of sodium citrate on the hydration of Portland cement.

Fig. 11b. The effect of sodium citrate on the heat of hydration of Portland cement.

stops for 2 days with addition of 0.2% heptonate. The peak corresponding to the maximum rate of heat for the sample containing the heptonate is less sharp than that for the reference and appears in the form of a hump. This hump for the retarder-treated sample appears at about 30–33 h at a dosage of 0.1%. The hump appears beyond 60 h for other dosages. Figure 1b was obtained by integrating, at different times, the curves in Fig. 1a. 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 h addition of 0.15–0.2% heptonate reduces the amount of heat by about 90% with respect to the reference. These results indicate that it is possible to retard the setting times of cement from a few hours to several days using sodium heptonate in the range 0.1–0.2%.

The addition of glycolic acid also results in the retardation of cement hydration in terms of the extension of the induction period as well as the appearance of the exothermic peak (Fig. 2). Similar to heptonate, glycolic acid addition also produces an exothermal hump effect. The induction period at a dosage of 0.5, 0.75 and 1.0% glycolic acid is 12, 37 and 50 h respectively. Glycolic acid is a less efficient retarder than sodium heptonate. At 72 h the addition of 0.5% glycolic acid reduces the amount of heat by only 7% with respect to the reference, compared to 90% achieved with 0.15% sodium heptonate (Fig. 2b).

Sucrose is a very efficient retarder. Even a small amount, of the order of 0.025%, is sufficient to extend the induction period to 6 h. The induction periods are about 6, 12 and 31 h for dosages of 0.025%, 0.05% and 0.075% respectively (Fig. 3a). The retarding effect of sucrose does not appear to be proportional to the amount added. For example, an increase of dosage by 0.025% (from 0.025% to 0.05%) extends the induction period by about 6 h whereas the same increment of dosage from 0.05% to 0.075% results in the increase of induction period by nearly 19 h. It is possible that part of the sucrose is absorbed by the aluminate phases and only that which is in the free form retards the hydration of the C_3S phase. Thus the retardation at lower dosages will not be as efficient as at higher dosages because of the preferential absorption of sucrose by the aluminate phases [7]. Once a particular amount is exceeded, substantial amounts will be available for the retardation of the silicate phase. The heat produced by the addition of 0.075% sucrose (37 cals) is much less than that produced by the addition of 0.1% sodium heptonate (47 cals) at 48 h (Fig. 1b and 3b).

The effect of sodium hexametaphosphate on the hydration characteristics of cement is shown in Fig. 4. Phosphates are known to be good retarders [8]. The calorimetric curves for cements containing hexametaphosphate are somewhat different from other admixtures mentioned above as the induction period is not well defined. The curve in the acceleration mode after the first few hours seems to have two slopes. This is especially evident with 0.2% hexametaphosphate. It is possible this may represent delayed reactions of the aluminate phase. The phosphate reacts with lime and the hydrated calcium silicate to retard hydration of C_3S. In the range 0.4–1.0% hexametaphosphate, the maximum peak occurs at about the same time and the induction period is in the range 12–18 h. From a practical consideration a dosage in the range 0.4–1.0% may be used to achieve an induction period of about 12–20 h. The enhancement in the intensity of the first peak within the first half hour in the presence of hexametaphosphate is possibly due to the acceleration of the hydration of the aluminate phase.

Gluconate is a good retarder and also a water-reducing agent. Its retarding action is possibly related to the poisoning effect on the hydration products of cement [9]. It has been advocated for use with superplasticizing admixtures to control the slump loss [4]. Conduction calorimetric curves of cement with calcium gluconate show large hump effects for the hydration of the silicate phase (Fig. 5). The retarding effect of gluconate is broadly similar to that of sodium heptonate (Fig. 1). The induction period can be controlled between about 4.5 and 55 h with 0.05–0.15% of gluconate.

Sodium borate retards the hydration of the silicate phase (Fig. 6). The increased intensity of the peak in the first few hours may be attributed to increased hydration of the calcium aluminate phase. Sodium borate in excess of 1% is reported to result in quick setting [10]. It is possible that higher amounts of borate increase the rate of hydration of the aluminate phase and cause unduly short setting times. By using dosages between 0.3% and 0.7%, the induction period can be increased from 4 to 28 h. Retardation, as well as the heat development effects with this retarder, are not as sensitive to dosage as with calcium gluconate.

The sugar-free lignosulfonate acts as a retarder by extending the induction period from 6 to 43 h when used in the range 0.3–0.6% (Fig. 7). The retardation effect of commercial lignosulfonates is mainly attributed to the action of sugars contained in them [11]. The results in Fig. 7 indicate that pure lignosulfonate has the ability to retard hydration of cement to a significant extent. Earlier studies have shown that lignosulfonate forms complexes with hydrating C_3S and aluminates to retard their hydration [12,13]. What is significant about sugar-free lignosulfonate is that an additional dosage of only 0.05% (from 0.5% to 0.55%) will increase the induction period from 9 to 34 h.

The effect of sodium pyrophosphate at earlier times is similar to that of hexametaphosphate; exothermal humps occur in the first few hours before the onset of the hydration of the silicate phase (Fig. 8). In the sample treated with hexametaphosphate the temperature of the maximum inflection occurs at about the same time at dosages from 0.4 to 1.0%. However, with pyrophosphate the peaks occur at later times as the dosage is increased; the induction periods are 12, 21, 25 and 32 h for dosages of 0.2%, 0.4%, 0.6% and 1.2% respectively. It is not easy to determine the induction periods because of the interference of the hump at earlier times.

Several types of sugars are known to act as good retarders. All sugars however, are not equally good retarders. Sucrose and raffinose are termed retarders par excellence whereas glucose, maltose, lactose and cellobiose are considered good retarders. Trehalose and alpha-methyl glucoside are non-retarding sugars. The effect of sucrose has already been discussed (Fig. 3). The conduction calorimetric curves for cement containing 0.1–0.3% glucose are shown in Fig. 9. Compared with sucrose, glucose is only a moderate retarder. To achieve an induction period of about 12 h, 0.1% glucose is needed compared with a dosage requirement of only 0.05% for sucrose. The variation in the retarding efficiency is attributed to the differences in the solubilization of Ca, OH and Si ions and the poisoning effects of retarders on the hydration surface [14]. Addition of glucose intensifies the exothermal effect within the first hour and this may be ascribed to its accelerating effect on the hydration of the C_3A–gypsum reaction to form ettringite [15].

Molasses is a by-product of the sugar industry. It is the mother liquor remaining after crystallization and removal of sucrose from juices of sugarcane or sugar beet. The composition of molasses is variable, containing 30–40% sucrose and 15–20% reducing sugars. In economic terms, molasses is a good candidate for consideration as a potential retarder. The retarding action of molasses is significant because it contains sugars (Fig. 10). At a dosage of 0.1% the induction period is as high as 10 h, and at 0.3% it is higher than 40 h. Molasses, although containing sugars, is not as efficient as sucrose as a retarder because it contains chloride (0.9%) which has an accelerating effect. The reducing sugars that are contained in molasses are not as efficient retarders as sucrose (Fig. 3).

Most aliphatic acids are known to retard the setting of cements. Amongst aliphatic acids, citric acid seems to be one of the best retarders [2]. The action of sodium citrate in dosages from 0.2 to 0.4% establishes it as a good retarder (Fig. 11). The induction period is as high as 31 h at 0.4% and at 0.6%, it exceeds 40 h. Also, as the dosage is increased, the exothermal effect within the first hour is intensified, suggesting the possibility of an early stiffening effect at higher dosages. Although not completely understood, the retarding mechanism of the citrate seems to be related to the chemistry of precipitation of the C–S–H phase, the complexation of Ca and Si ions either in solution or by incorporation into the precipitated gel. As a consequence, this may result in the formation of a less permeable and more adhesive gel coating around the cement grains [2].

The practical considerations that determine the usefulness of a retarder depend on several factors such as: its efficiency (in terms of the minimum dosage that would yield the required retardation), a dosage range that could be used without adversely affecting the retardation, physical and

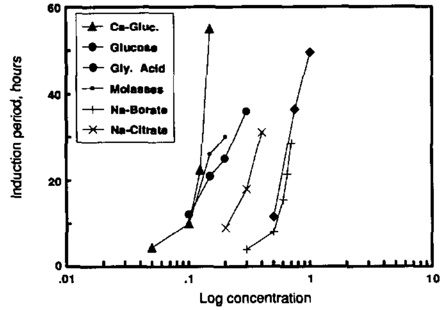


Fig. 12. The effect of retarder concentration on the induction period of Portland cement.

durability characteristics, easy dispensing and economy. Some of these aspects can be addressed by comparing the induction periods attained at different dosages of retarders (Figs. 12 and 13 and Table 1). In Figs. 12 and 13 the time of termination of the induction periods is plotted as a function of dosage and in Table 1, the dosages required for induction periods of 10, 20, 30 and 40 h are indicated. Some of the figures are approximate values because of the difficulty in determining the termination of the induction period.

The curves in Figs. 12. and 13 show an approximately linear relationship if the lowest dosage is not considered for some of the retarders. They can be used to discern the dosage ranges required for attaining a particular induction period. Data in Table 1 may be divided broadly into three categories to evaluate the efficiency of the retarders. The most efficient retarders are calcium gluconate, sodium heptonate and sucrose which need about 0.15% or less to extend the induction period to 40 h. The least efficient retarders that require more than 0.5% for an induction period of 40 h are sugar-free lignosulfonate, sodium pyrophosphate, sodium hexametaphosphate, sodium borate and glycolic acid. The moderately effective retarders are glucose, molasses and sodium citrate, requiring a dosage in the range 0.15–0.5%. The slopes in Figs. 12 and 13 indicate that with some

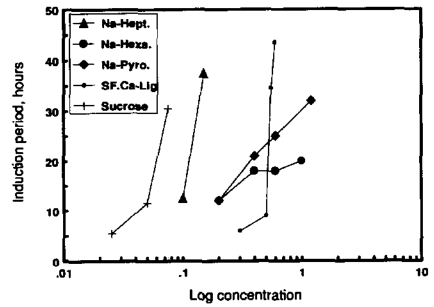


Fig. 13. The effect of retarder concentration on the induction period of Portland cement.

TABLE 1

Minimum concentration of various retarders (%) required to achieve desired induction periods

Retarding agent	Induction periods (h)			
	10	20	30	40
Ca gluconate	0.10	0.12	0.13	0.14
Glucose	< 0.10	0.15	0.23	> 0.30
Glycolic acid	< 0.50	0.55	0.64	0.79
Molasses	0.10	0.13	0.20	> 0.20
Na borate	0.51	0.63	> 0.70	< 1.00
Na citrate	0.21	0.32	0.39	< 0.50
Na heptonate	< 0.10	0.12	0.14	⩾ 0.15
Na hexametaphosphate	< 0.20	1.00	> 1.00	–
Na pyrophosphate	< 0.20	0.38	1.00	> 1.20
S.F. Ca lignosulfonate	0.51	0.52	0.54	0.58
Sucrose	0.04	0.06	0.073	> 0.075

retarders even small differences in dosages would result in substantial variations in induction periods. Examples are calcium gluconate, sodium heptonate and sucrose.

CONCLUSIONS

Conduction calorimetry is a quick method of assessing the relative effects of retarders 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. In some instances, the possibility of quick setting may be predicted from the initial exothermal effect caused by the hydration of the aluminate phase. The most efficient retarders that need dosages of about 0.15% or less to achieve an induction period of 40 h include calcium gluconate, sodium heptonate and sucrose. The least effective retarders that require a dosage of more than 0.5% for extension of the induction period by 40 h are sugar-free calcium lignosulfonate, sodium pyrophosphate, sodium hexametaphosphate, sodium borate and glycolic acid. Glucose, molasses and sodium citrate are termed moderate retarders requiring a dosage between 0.15% and 0.5%.

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