LA QUIMICA DE LOS SUPERFLUIDIFICANTES DEL CONCRETO: REOLOGIA Y CINETICA DE LA HIDRATACION DE LAS PASTAS DE CEMENTO PORTLAND CONTENIENDO MEZCLAS DE SUPERFLUIDIFICANTES A BASE DE NAFTALINA Y MELAMINA

por

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Sinopsis: Se midieron las áreas fluidas utilizando un mini cono de revenimientos y el calor de hidratación de las pastas de cemento conteniendo una relación agua/cemento de 0.35, en presencia de diversos superfluidificantes comerciales disponibles usándolos, ya sea en forma pura o en mezclas binarias de 50:50. Se ha estado investigando la influencia de los parámetros siguientes: variación en los compuestos del cemento, tipo de superfluidificante: sulfonato de polinaftalina de sodio y calcio (NaPNS y CaPNS) y sulfonato de polimelamina de sodio (NaPMS); y la concentración total de superfluidificante.

Los resultados de los experimentos reológicos (mini revenimiento) muestran que la fluidez de las pastas de cemento depende de las características de los superfluidificantes y del cemento usados. Se observó el efecto de saturación con diversas combinaciones de cemento-superfluidificante; por ejemplo: arriba de una concentración dada, un aumento de la concentración de superfluidificante tiene poco efecto sobre la fluidez. A bajas concentraciones de superfluidificante, las pastas de cemento fluidificado con mezclas binarias de 50:50 (o 1:1) de superfluidificantes, con frecuencia tenían fluideces intermedias de aquéllas conteniendo compuestos puros. A mayores concentraciones de superfluidificante, el efecto de saturación a menudo evita la diferenciación entre el efecto de los diferentes aditivos o mezclas de ellos. Los resultados de los experimentos calorimétricos muestran que la magnitud del efecto retardante depende del tipo de superfluidificante usado y que las propiedades medidas varían en forma lineal con la composición de la mezcla binaria de superfluidificante.

Palabras clave: Cemento, superfluidificante, sulfonato de naftalina, sulfonato de melamina, reología, calorimetría.

THE CHEMISTRY OF CONCRETE SUPERPLASTICIZERS: RHEOLOGY AND HYDRATION KINETICS OF PORTLAND CEMENT PASTES CONTAINING MIXTURES OF NAPHTHALENE- AND MELAMINE-BASED SUPERPLASTICIZERS

by

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Synopsis: The minislump spread areas and the heat of hydration of cement pastes having a water/ cement ratio of 0.35 were measured in the presence of several commercially available superplasticizers used, either in pure form, or in 50:50 binary mixtures. The influence of the following parameters have been investigated: variation in cement composition; type of superplasticizer: sodium and calcium polynaphthalene sulfonate (NaPNS and CaPNS) and sodium polymelamine sulfonate (NaPMS); and total superplasticizer concentration.

The results of rheological (minislump) experiments show that the fluidity of cement pastes depends on the characteristics of the superplasticizer and of the cement used. With various cement-superplasticizer combinations, a saturation effect is observed, i.e., above a given concentration, an increase of the superplasticizer concentration has little effect on the fluidity. At low superplasticizer concentrations, the cement pastes fluidified with 50:50 (or 1:1) binary mixtures of superplasticizers usually have intermediate fluidities between those of cement pastes containing the pure compounds. At higher superplasticizer concentrations, the saturation effect often precludes differentiation between the effects of the different additives or mixtures of these. The results of calorimetric experiments show that the magnitude of the retardation effect depends on the type of superplasticizer used and that the measured properties vary linearly with the composition of binary superplasticizer mixtures.

Keywords: Cement, superplasticizer, naphthalene sulfonate, melamine sulfonate, rheology, calorimetry.

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INTRODUCTION

The use of superplasticizers in the production of concrete leads to a major increase i the workability, and enables a reduction in either the water, or both the water and th cement quantities used depending on the application (1). In addition to their influence o rheological properties, the superplasticizer may affect other properties of fresh concrete which are related to the kinetics of hydration, such as the lag period, early strength, etc In practice, these properties are not severely altered by high range water reducers, sinc standard specifications define limiting acceptable values (2).

Due to the wide range of cement and admixture types available, and to the inheren variability in their industrial production, compatibility problems may sometime arise wi particular cement-admixture combinations. For example, a superplasticizer may affect th rheological properties of various cements in different ways depending on the chemica composition of the cements, or on their physico-chemical characteristics (3,4). On th other hand, a cement may behave differently with various superplasticizers; this ma depend on factors such as their chemical type (naphthalene- or melamine-based (5)), the molar mass (6), their counterion (sodium or calcium), or the presence of by-products.

Blends of different superplasticizers may also be used for the production of concrete For example, lignosulfonates are frequently mixed with synthetic superplasticizers fo economical or technological reasons. Blends of naphthalene- and melamine-base superplasticizers have also been used occasionally as reported in the literature (4 However, systematic comparisons of the behavior of superplasticizer mixtures with th of pure components are not available.

In this paper, we initiated an investigation to determine how the rheological propertie and the hydration kinetics of cement pastes are altered by binary mixtures o superplasticizer, as compared to the influence of the pure admixtures. In particular, w

aim to establish if there are any synergetic or antagonistic effects when superplasticizer blends are used.

EXPERIMENTAL

Materials

Three commercially available superplasticizers have been selected for this study: sodium poly-β-naphthalene sulfonate (NaPNS), calcium poly-β-naphthalene sulfonate (CaPNS), and sodium polymelamine sulfonate (NaPMS). The poly-β-naphthalene sulfonates were supplied by Handy Chemicals as concentrated solutions, and the polymelamine sulfonate was obtained from SKW in a solid form. The superplasticizers were characterized by ionic chromatography (sulfate analysis), by ICP spectrometry (sodium and calcium analysis) and by ion pairing HPLC (molar mass distribution). Typical chromatograms are shown in Figure 1, for NaPNS and NaPMS. The percentage of high molar mass (HMM) chains in the polymers can be calculated from the area under the large peaks eluted at the longer retention times. This HMM fraction, together with other relevant superplasticizer features are summarized in Table 1. The results of ultrafiltration experiments on Na- or CaPNS have shown that the peak at $\approx$ 35 min (Fig. 1a) represents the polymers with molar mass ranging from 5 kD (Dalton = g/mol) to more than 100 kD (7). For PMS, ultrafiltration data showed that the peak at $\approx$ 30 min (Fig. 1b) represents mainly the 5-30 kD polymers, while that at 55 min is due to polymer with still higher molar mass (8).

Three Portland cements of different origin were used in this study. Their phase compositions, SO_3 and alkali contents, losses on ignition, and Blaine surface areas are presented in Table 2.

Methods

Mixing procedure -- The cement pastes were prepared at a water/cement ratio (W/C) of 0.35. The superplasticizer was first mixed with water and the cement was added to the solution. The paste was mixed manually for one minute and then with a high speed mixer for two minutes in order to obtain a well dispersed slurry. The mixing procedure was made under controlled temperature conditions to obtain a final temperature of 25 $\pm$1°C. The superplasticizer concentration in the mix is expressed on a dry weight basis (weight of superplasticizer relative to the weight of cement). For binary mixtures of superplasticizers, the total concentration and the mass ratio of the superplasticizers are indicated.

Rheology -- The paste fluidity was determined as function of time following a method described by Kantro (9). In the latter, the cement paste is poured into a plexiglass cone having the same geometry as the Abraham cone for regular slump tests, but with reduced dimensions (height of 6 cm). The minicone is raised and the area of the spread area of the cement paste is measured.

Calorimetry -- Hydration thermograms of cement pastes have been recorded for a period of 24 hours with an isoperibol calorimeter coupled with a data acquisition system. The experimental procedure used in the present work is similar to that described by Simard *et al.* (10).

RESULTS AND DISCUSSION

Rheological studies

Minislump areas of cement pastes prepared with pure superplasticizers and with their 1:1 binary mixtures have been measured as function of time (10, 60 and 120 minutes) at four total superplasticizer concentrations (0.3, 0.5, 0.7 and 1 wt %).

Saturation point -- The minislump areas recorded at 10 minutes for pastes of cements A and B fluidified with the pure superplasticizers at different concentrations are shown in Figure 2. For the two cements, the efficiency of the superplasticizers to increase the paste fluidity varies in the order NaPNS > CaPNS > NaPMS. The behavior of each cement upon addition of superplasticizer is otherwise quite different: Cement A is easier to fluidify than cement B (i.e., at the same superplasticizer concentration, the minislump areas are much greater for cement A). Pastes of the latter cement also show a saturation effect at a superplasticizer concentration between 0.5 and 0.7% for NaPNS and CaPNS; beyond the saturation point, an increase in superplasticizer concentration has little effect on the fluidity. For cement A containing NaPMS, and for cement B with all superplasticizers, the saturation point would be at 1% or more. Similar results were also found for the other measurement times investigated (60, 120 min).

Superplasticizer mixtures -- As noted above, different superplasticizers can exhibit important differences in their effectiveness to fluidify cement pastes. In this section, we present the results of cement paste fluidification obtained with binary mixtures of superplasticizers.

Minislump areas at 10, 60 and 120 min after mixing are shown in Figure 3 for pastes of cement A containing, either pure, or 1:1 binary mixtures, of superplasticizers at four total concentrations (W/C = 0.35). At admixture concentrations of 0.3%, the initial fluidity is low and the loss of fluidity as function of time is important. For most pastes, measurements cannot be made at 120 minutes. However, at other measurement times, differences in efficiency can be observed between the three pure superplasticizers; the efficiency varies in the order NaPNS > CaPNS > NaPMS. The difference between NaPNS and CaPNS may be attributed mainly to their relative content in high molar mass polymers. For the 1:1 binary mixtures, the fluidities appear intermediate between those obtained with the pure superplasticizers.

At admixture concentrations of 0.5%, cement paste fluidities increase and the relative loss in fluidity as function of time is greatly reduced. Binary mixtures of superplasticizers again show fluidity results intermediate between those of the pure admixtures, and this is observed at the three measuring times.

For admixture concentrations of 0.7 and 1%, a saturation point is reached with NaPNS and CaPNS as noted previously for pastes containing either pure superplasticizer or their mixture. At a total concentration of 0.7%, the NaPMS-NaPNS mixture yields fluidities similar to those obtained with pure NaPNS, while the 1:1 binary mixture of NaPMS and CaPNS, which has not yet reached the saturation point, gives fluidities intermediate between those of the pure admixtures at the three times of measurement. The behavior of the NaPMS/NaPNS mixture (0.7%) is a first indication of deviations from a simple proportionality mixing rule.

Similar results of minislump experiments with cement B containing pure or binary mixtures of superplasticizers are shown in Figure 4. As noted earlier, at the same admixture concentration, cement B is much less fluid than cement A. This is due in part to the higher Blaine area of cement B and, possibly, to differences in the chemical composition of the two cements. Despite the lower paste fluidities, the general trend of results as function of superplasticizer concentration or as function of admixture types, is similar to that observed for cement A. All 1:1 binary mixtures show results intermediate between those of the pure admixtures, except for the mixture CaPNS-NaPNS at a concentration of 0.7%, where the results are closer to those with NaPNS, and at 1%, where there is no variation of fluidity between NaPNS or CaPNS or their mixture. Again, slight deviation from a simple proportionality rule in the mixed superplasticizer are only evidenced at a concentration ≈ 0.7 wt %.

For cement C, minislump areas have only been measured at a superplasticizer concentration of 0.7%, the results are presented in Figure 5. With the 1:1 binary mixtures, CaPNS-NaPNS and NaPNS-NaPMS, fluidities are intermediate between those of the pure components. However, with the NaPMS-CaPNS mixture, a synergistic effect can be observed, the fluidities being higher than those with the pure components. This behavior is rather unique and would appear related to the particular composition of cement C (Table 2).

Calorimetric Studies

The hydration thermograms were recorded over a period of 24 hours for pastes of each of the three cements containing pure or binary mixture of superplasticizers at a total concentration of 0.7%. The temperature-versus-time curves (integral heat) and their derivatives (heat flux) are illustrated in Figure 6 for cements A, B, and C containing 0.7% of NaPNS.

As evidenced by these curves, the hydration kinetics of the three cements show significant differences. For cements A and B, which have comparable chemical compositions, the shape of the heat flux curves is similar, showing a two steps reaction. The lag period and the maximum heat flux found with these cements are however quite