different: cement B has a longer lag period and lower maximum heat flux than cement A. Cement C, which is very low in C_3A, shows an extended lag phase and a heat flux curve with only one main peak. However, the hydration reactions beyond this peak are more exothermic than for the other cements, giving a higher temperature increase after 24 hours.

The times evolved to reached the maximum heat flux values are plotted in Figure 7 for the various cement-superplasticizer systems investigated. The shifts in the heat flux peak due to the change in superplasticizer type are of comparable magnitude for cements A and B, but appear more important for cement C. A comparison of the results for the three cements shows that the time to reach maximum heat flux is longest with CaPNS and shortest with NaPNS. For cements A and B, the shift in the heat flux peak with these two superplasticizers is about one hundred minutes, while for cement C, it is about two hundred minutes. With NaPMS, the shifts are approximately half-way between those with CaPNS and NaPNS.

For the 1:1 binary mixtures of superplasticizers, the times to reach maximum heat flux are generally intermediate between those for the pure superplasticizers. One exception to this behavior is the 1:1 mixture of NaPNS and NaPMS with cement B for which the time is much higher than for the two pure compounds.

CONCLUSIONS

The results of this exploratory investigation on the influence of several pure and mixed superplasticizers on the rheological properties and hydration behavior of different cements enable the following conclusions.

As frequently observed, each cement-superplasticizer combination exhibit some peculiarities in the rheological properties and hydration kinetics. With the types of systems (pastes at W/C = 0.35) and measurement techniques investigated here, the peculiarities due to the superplasticizer (for a given cement) are best evidenced at relative superplasticizer contents of approximately 0.7 wt %.

Mixture of superplasticizers (1:1) were generally found to exhibit behaviors intermediate (average) between those observed with the pure superplasticizers at the same total concentration. At a concentration of 0.7 wt %, significant deviations from average behavior were found, in the rheology of pastes with one cement (A) in the presence of NaPNS/NaPMS mixtures. In another case, a positive synergy is found in the fluidification of cement C (low C_3A) with mixtures of NaPMS and CaPNS (i.e., fluidity higher with the 1:1 mix than with the pure compounds).

The influence of superplasticizers on the hydration kinetics of cement pastes, as measured by their hydration thermograms, also reflect peculiarities of cements and cement-superplasticizer combinations. In this case, changes induced by the

superplasticizers in the measurable parameters (lag time, time to maximum heat flux) are relatively smaller than those observed in the paste rheology; with superplasticizer mixtures, however, the proportionality rule is generally observed (i.e., the influence of a 1:1 superplasticizer mixture is intermediate between those of the pure superplasticizer, except in one case, where a synergistic effect was apparent (cement B) with a NaPNS/NaPMS mixture).

It is noteworthy that superplasticizer mixtures which lead to deviations from the simple proportionality rule, involve both the melamine- and naphthalene-based superplasticizers; mixtures of Na and Ca naphthalene sulfonates were found to behave predictably in all cases.

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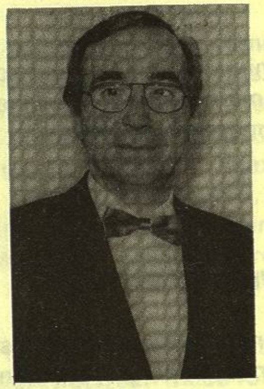

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Table 1: Main Characteristics of the Superplasticizers

	NaPNS	CaPNS	NaPMS
Base	Naphthalene	Naphthalene	Melamine
Na (%)'	11.7	0.8	10.0
SO_4 (%)	0.3	7.8	0.0
Ca (%)	2.9	0.0	2.0
HMM (%)	61.0	50.0	-----

All results are expressed on a dry weight basis.

Table 2: Cement Composition and Physical Properties

	Cement		
	A	B	C
C_3S (% (wt))	55.24	49.40	72.73
C_2S	18.01	21.85	11.10
C_3A	5.71	6.30	3.60
C_4AF	8.89	8.64	6.48
SO_3	3.45	2.95	2.37
Na_2O	0.16	0.48	0.18
K_2O	0.53	0.63	0.36
LOI	2.21	3.52	0.49
Blaine area (m^2/g)	362.00	389.00	300.00

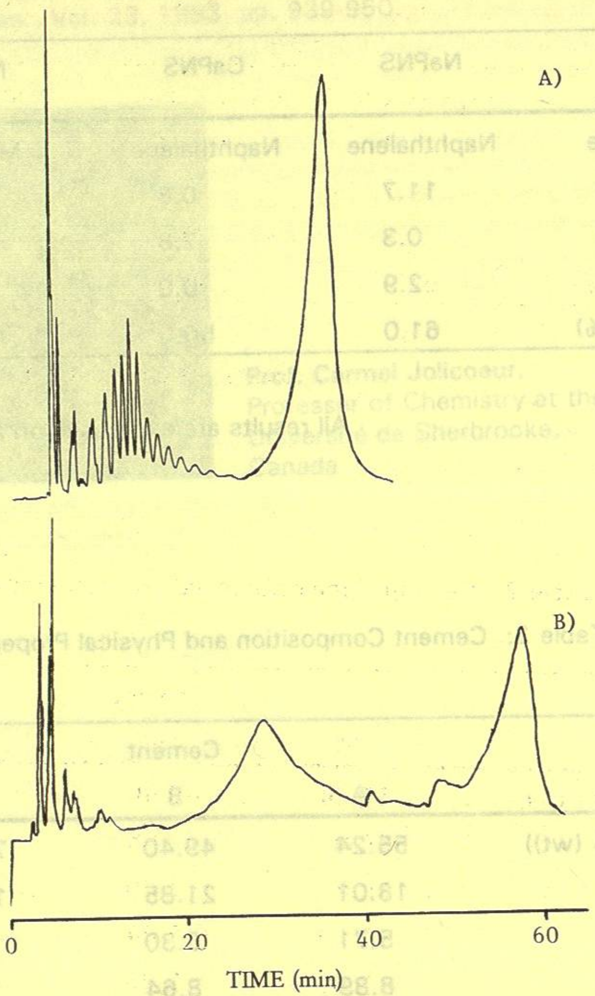

Fig. 1: HPLC chromatograms of the superplasticizers. a) NaPNS; b) NaPMS.

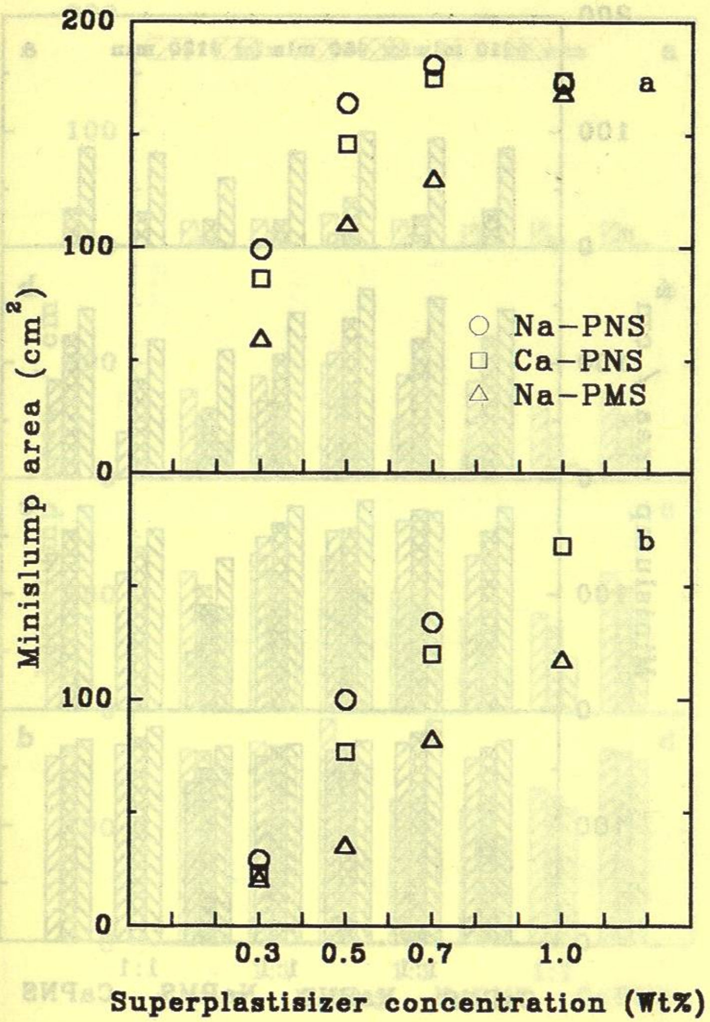

Fig. 2: Minislump area of cement pastes, W/C = 0.35 as function of superplasticizer concentration. a) cement A; b) cement B. ○: NaPNS; □: CaPNS; △: NaPMS.

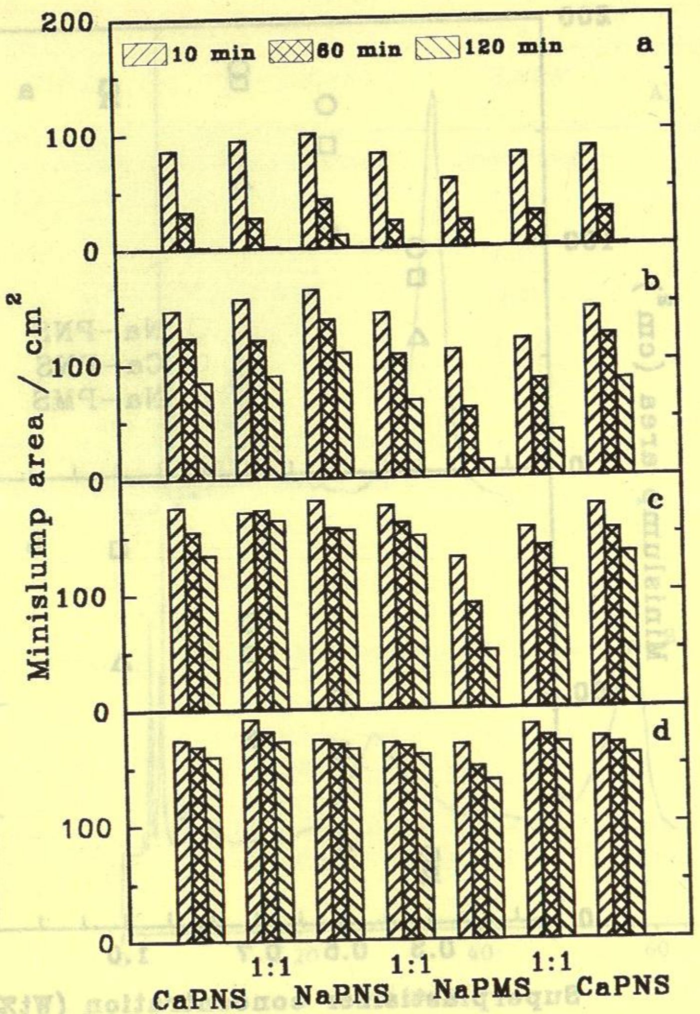

Fig. 3: Minislump areas of pastes of cement A, W/C = 0.35, with the various superplasticizers or their 1:1 binary mixtures. a) 0.3%; b) 0.5%; c): 0.7%; d) 1%.

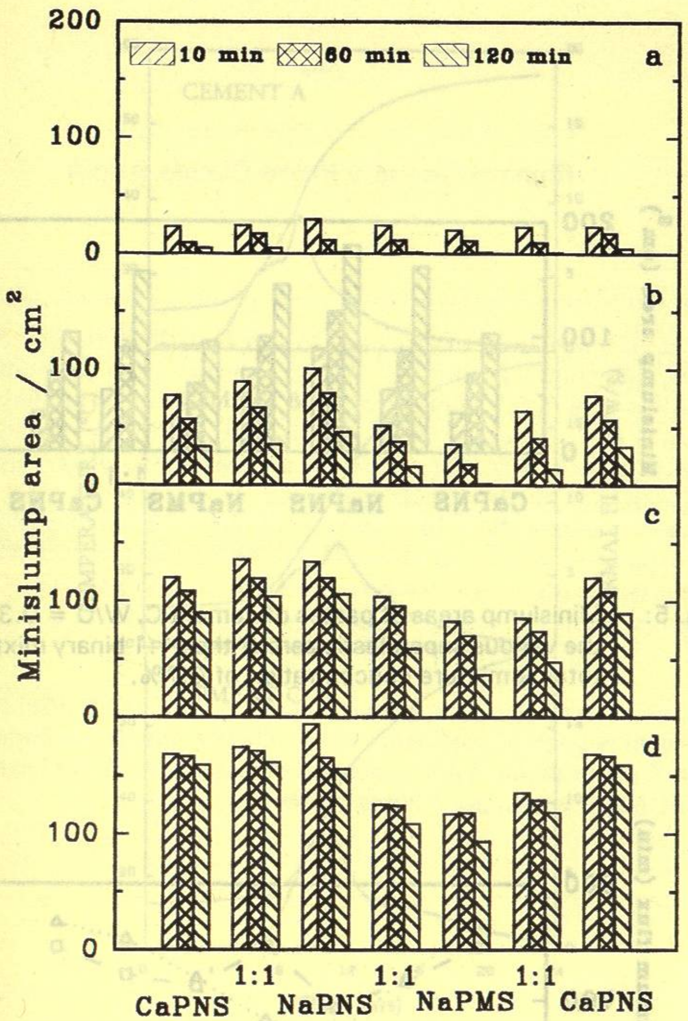

Fig. 4: Minislump areas of pastes of cement B, W/C = 0.35, with the various superplasticizers or their 1:1 binary mixtures. a) 0.3%; b) 0.5%; c): 0.7%; d) 1%.

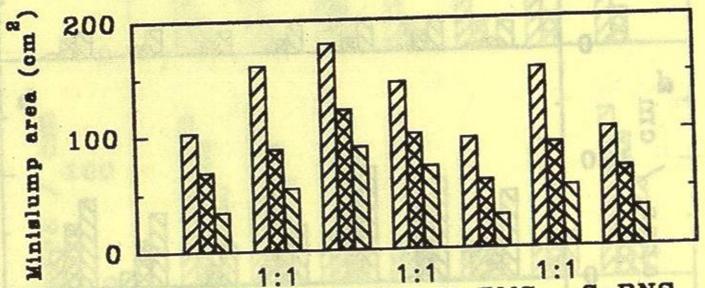

Fig. 5: Minislump areas of pastes of cement C, W/C = 0.35, with the various superplasticizers or their 1:1 binary mixtures at total admixture concentration of 0.7%.

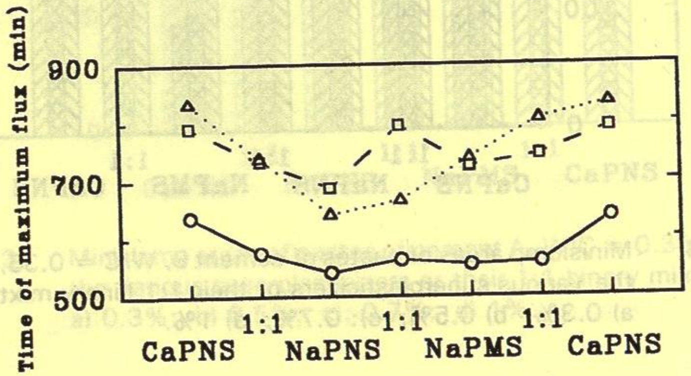

Fig. 7: Time elapsed to maximum heat flux of cement pastes, W/C = 0.35 containing 0.7% of the various superplasticizers or their 1:1 binary mixtures. ○: cement A; □: cement B; △: cement C.

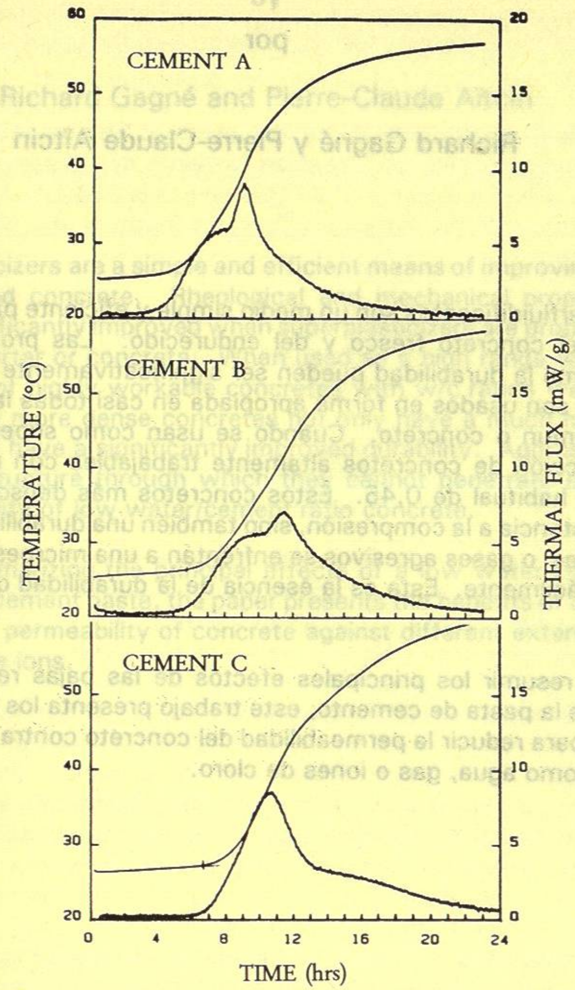

Fig. 6: Thermograms of the cement pastes, W/C = 0.35, containing 0.7% of NaPNS; both the temperature vs time curve and its time derivative (heat flux) are illustrated for each cement.