Available online at www.sciencedirect.com

Cement and Concrete Research 38 (2008) 907 – 919

Influence of superplasticizers on the rheology and stability of limestone and cement pastes

Nikola Mikanovic *, Carmel Jolicoeur

Department of Chemistry, Université de Sherbrooke, QC, Canada J1K 2R1

Received 29 September 2006; accepted 22 January 2008

Abstract

The influence of superplasticizers on the rheological properties and dynamic stability of cement and reference limestone pastes were examined at room temperature. The pastes were initially formulated to exhibit nearly identical rheological parameters and bleeding–segregation characteristics, with w/c = 0.50 for the limestone and 0.55 for the cement. The former was examined at equilibrium pH ~ 10 and at pH 12.5 following addition of $Ca(OH)_2$ to allow distinction of effects related to high pH and Ca^{+2} from those related to cement hydration reactions. Both polynaphthalene- (PNS) and polyacrylate-type (PC) superplasticizers were investigated, adjusting the dosages to cover the same range of paste fluidity. Superplasticizer–particle interactions were monitored through binding isotherms and zeta potential measurements. The rheology of the pastes was evaluated through the mini-slump test and dynamic viscosity measurements which yielded key rheological parameters: yield stress, elastic and loss moduli (G' and G'') and zero-shear viscosity (η_0). The paste stability was monitored as function of time, i.e. migration of solids and liquid phase measured *in-situ* and in "real time", through surface bleeding measurements and from a multipoint conductivity method. The results provide new insight on the relative modes of action of PNS- and PC-type superplasticizers as dispersants. Also, the combined rheology and stability data allow an improved description of the processes responsible for bleeding and segregation in cementitious and reference systems.

Keywords: Limestone; Cement; Superplasticizers; Stability; Rheology

1. Introduction

Recent developments in concrete technologies have often aimed to achieve 'self-levelling' and 'self-consolidating' materials [1]. In this context, there appears an obvious need for understanding the conditions under which highly fluid concrete is stable enough to prevent phase separation, i.e., bleeding, sedimentation and segregation. While the properties of a fresh concrete are known to depend on many parameters (water content, binder fineness and reactivity, aggregate grading, chemical or mineral admixtures, etc.), one may generally expect a qualitative relationship between its rheological properties and its stability. There is, however, little quantitative basis for such relationships and practice often show that concrete stability towards phase separation cannot be predicted from rheological properties. The latter situation is particularly true in cementitious systems containing chemical admixtures.

It is widely accepted that bleeding in cement-based systems can be due to sedimentation (hindered sedimentation and sedimentation *en masse*), consolidation and segregation [2]. The segregation represents settling of the coarsest particles in cement pastes or mortar that depends on the yield stress of the cement paste and on the diameter of the coarsest particles [3]. However, the stability of cement paste itself is poorly understood; this paper deals only with the stability of mineral (cement) suspensions.

The interfacial and colloidal phenomena, which control the migration of water and solids in a dense mineral suspension, are complex kinetic processes, particularly in cementitious systems where hydration reactions alter the phase-separation processes. The presence of chemical admixtures, which also impact on various properties and processes, adds further complexity to the system. In order to distinguish the "physical" effects, which

---

* Corresponding author.
E-mail address: Nikola.Mikanovic@USherbrooke.ca (N. Mikanovic).

0008-8846/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2008.01.015

contribute to solid and liquid migration, from "chemical" effects, which depend on the reactive nature of cement, one may investigate the behaviour of dense colloidal slurries of an inert mineral. If the latter exhibits surface and colloidal properties similar to those of "un-hydrating" cement particles, the specific influence of hydration effects on the properties of the system can be clearly established. This approach should be particularly rewarding in studies of the mode of action of chemical admixtures; in such cases, the function of admixtures may be determined in a relevant controlled environment, but in the absence of hydration effects. This approach has indeed shown substantial benefits in previous investigations [4–9].

Recently, the authors have shown that calcium carbonate exhibits colloidal properties very similar to those of portland cement [10]. In the latter study, it was demonstrated that a $CaCO_3$ paste can duplicate many properties of a cement paste at early ages (i.e., <1 h), including the bleeding–sedimentation and rheological behaviours. At longer times, the properties of the cement paste depart from those of the limestone paste, as expected, reflecting the consequences of hydration reactions [11]. The potential of limestone pastes as a model system to elucidate the effect of chemical admixtures on the stability and rheology of cement-based systems has been further demonstrated in a recent study on surface-active admixtures [12]. The work described below was undertaken to further investigate the influence of superplasticizers on the stability and rheology of limestone and cement pastes, and the rheology–stability relationship referred to above.

2. Materials and methods

2.1. Materials

A common GU (ASTM Type I) portland cement was used, the composition of which is reported in Table 1. A calcium carbonate in the form of calcite provided by a local supplier was also used. The specific surface area and mean particle diameter (weight average) of the calcium carbonate and cement used are presented in the Table 2. The surfaces of both materials are comparable, although the particles of the limestone mineral are somewhat finer.

Table 1
Properties of the portland cement

	Composition
Chemical analysis	
CaO	62.9
SiO_2	21.0
Al_2O_3	4.2
Fe_2O_3	3.1
MgO	2.3
SO_3	2.7
Na_2O eq.	0.76
Mineralogy	
C_3S (%)	52
C_2S (%)	21.5
C_3A (%)	5.7
C_4AF (%)	9.5
Physical properties	
% passing 45 μm	96
Specific surface BET m^2/kg	1200
Specific surface Blaine m^2/kg	345

Table 2
Physical properties of selected $CaCO_3$ reference mineral and cement

Material	Source	Specific surface (m^2/g)	Average particle size (μm)
$CaCO_3$	Omya Canada	1.2	10
Cement	St-Laurent	1.2	20–30

Two commercially available superplasticizers were used, as received, for this study: a sodium polynaphtalenesulfonate (PNS) and a polyacrylate (PC) partially esterified with intermediate molecular weight polyethylene glycol (M_w~2000). Both superplasticizers were supplied by Handy Chemicals Ltd, as concentrated aqueous solutions (~40 wt.%). The superplasticizers were characterized by ICP spectrometry (elemental analysis), by GPC (molecular mass distribution) and by ionic chromatography (sulfate analysis); the results of this characterization are summarized in Table 3. The high sulfonate (SO_3^-) content of the PNS superplasticizer corresponds to an important negative charge density, substantially higher than that of typical PC-type superplasticizers [13].

2.2. Methods

2.2.1. Paste stability measurements

The bleeding, sedimentation and consolidation phenomena in pastes of calcium carbonate and cement were monitored through a method based on electrical conductivity measurements, developed earlier by the authors [10,14,15]. In all of the systems investigated, the aqueous phase is electrically conducting, from naturally occurring electrolytes (cement pastes) or added salts (NaCl and $Ca(OH)_2$ at constant ionic strength in calcium carbonate pastes). Since the solid phases are non-conducting, variations in the electrical conductivity of a paste measured as functions of time and depth in the sample will directly reflect the local changes in the mixture composition, which result from the combined effects of water migration and solids sedimentation–consolidation.

Typical conductivity *vs.* time curves obtained in calcium carbonate pastes, at different depths in the sample (different

Table 3
Main characteristics of the superplasticizers

Composition [a]	PNS (% w/w)	PC (% w/w)
Sodium (Na)	9.0	0.9
Potassium (K)	in traces	0.1
Calcium (Ca)	0.35	0.1
Total sulphur (S)	13.4	1.0
Sulfates (SO_4^{2-})	3.1	
Sulfonates (SO_3^-)	30.9	–
M_w (kD)	52.4	25.0
M_n (kD)	5.9	5.7

[a] All results are expressed on a dry weight basis.

electrode pairs), are illustrated in Fig. 1(a). The accumulation of bleeding water at the top of the sample results with an increase in the electrical conductivity measured by the top two electrode pairs, while sedimentation of solid particles causes a less pronounced decrease in the conductivities measured by the other electrode pairs (pairs #3–10) with time. The curves obtained for cement pastes are somewhat more complex [14,15], since the electrolytes, which dissolve upon cement hydration, change the conductivity of the solution phase with time. Nevertheless, the variance in the conductivity values at different depths at a given time is a direct measure of the heterogeneity of the sample at that instant. The local conductivity values can thus be used to define a stability index (SI), which is calculated as $\mathrm{SI}=1-(\sigma/\lambda_{\mathrm{avg}})$, where σ and λ_{avg} are respectively the standard deviation and average value of the electrical conductivities measured over the height of a sample at a given time. This parameter characterizes the overall homogeneity of the sample, which is evaluated as function of time; a stability index of 1 corresponds to a perfectly homogeneous mix [14,15]. The conductivity curves were further analyzed through a protocol described elsewhere [10,16] in order to extract density profiles over the sample depth; the latter allows the identification of two migration fronts:

- the bleeding front, which represents an interface between the clear supernatant solution and the rest of the sedimenting column, and
- the sedimentation front, which represents an interface between the sedimenting column and the compacted sediment.

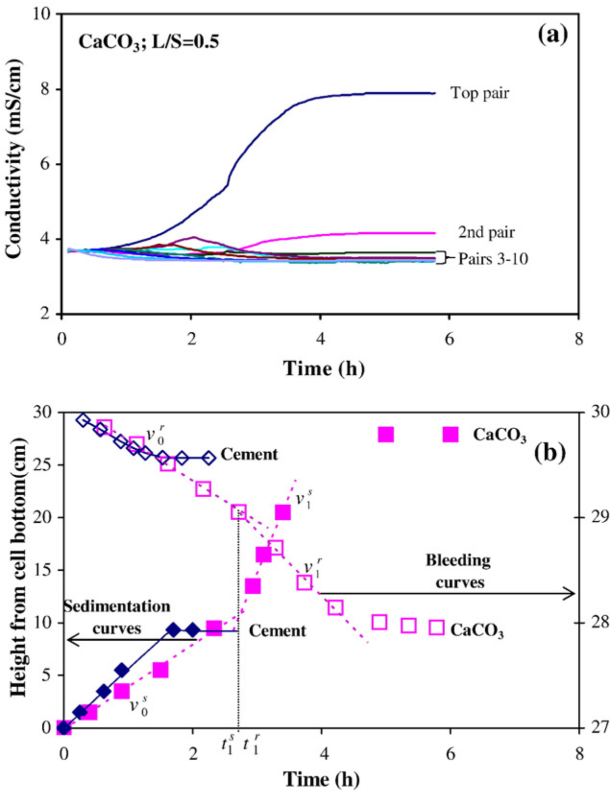

Fig. 1. (a) Typical conductivity curves obtained in experiments with $\mathrm{CaCO_3}$ pastes at L/S = 0.5; (b) bleeding and sedimentation curves of the reference limestone and cement paste obtained from conductivity measurements.

The evolution of these fronts with time defines the bleeding and sedimentation curves; Fig. 1(b) shows these curves for a reference calcium carbonate (L/S = 0.5) and cement paste (L/S = 0.55). The displacement of these fronts with time provides quantitative information on the rate of surface bleeding and the rate of formation of a compact layer at the bottom of the conductivity cell. Details on the instrumentation, optimization of the experimental parameters and data analysis procedures may be found elsewhere [10,16].

2.2.2. Rheology

Typical ranges of shear rates operating in the sedimentation of solid particles in a suspending liquid are very low. Considering the fact that displacement of particles at the top of a sample is usually lower than 1 cm and that duration of this period is about 10 000 s (before setting), the settling speed is therefore lower than 10^{-6} m/s. From the dimensional point of view, the order of shear rate generated by the displacement of a moving particle in a fluid is equal to settling speed divided by the particle diameter; given that a maximum diameter of the solids used is about 100 µm, the typical shear rate in bleeding experiment is lower than 10^{-2} s^{-1}. Hence, the rheological characterization of flocculated suspensions should be best achieved through dynamic viscosity measurements at low (and oscillating) shearing amplitude, as opposed to flow measurements. In order to obtain pastes with reproducible viscoelastic behaviour, all samples were pre-sheared for 30 s at 200 Pa and then allowed to rest for 5 min before the beginning of the dynamic viscosity measurements. In this way, each paste was reduced to a reproducible reference state prior to rheological characterization. In oscillation stress sweep experiments, the shear sweeps, usually between 0.1 and 10 Pa were run at a constant frequency of 1 Hz; the elastic and loss moduli and the phase angle were determined in the linear viscoelastic region. Frequency sweeps were also performed at frequencies ranging from 0.01–10 Hz; the applied stress during the frequency sweeps was well below the critical stress of the particular sample. From these experiments, other rheological parameters were determined, namely the relaxation time (inverse value of the frequency at which the phase angle reaches 45°) and the zero-shear viscosity (low frequency extrapolation of the measured complex viscosity).

The yield stress values of the pastes were determined via a stress-growth experiment [17]. In these experiments the pastes were sheared at a low and constant shear rate (~0.01 rad/s), and the resulting shear stress was measured as a function of time; the yield stress value was determined as the maximum stress in the stress–time curve. Both dynamic and yield stress measurements were performed with a Viscotech rheometer (ATS RheoSystems) using a vane tool at constant temperature (25 °C).

An alternate, more empirical measure of the rheological properties of mineral and cement pastes was obtained through the Kantro 'mini-slump' test frequently used in studies of cement grouts or pastes. This protocol simply involves measuring the spread area, or diameter, of a fixed volume of the dispersion

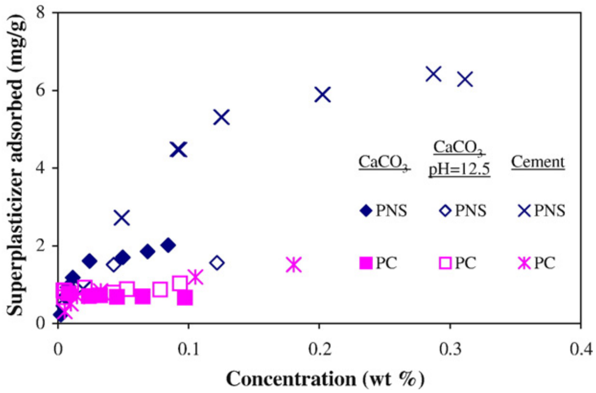

Fig. 2. Adsorption isotherms for superplasticizer molecules on $CaCO_3$ and cement particles.

confined initially in a truncated cone; the tests were carried out as described elsewhere [18].

2.2.3. Adsorption measurements

The adsorption of admixtures onto mineral particles in the pastes was determined by measuring the residual concentration of the admixtures in the liquid phase of the concentrated suspensions of limestone or cement particles. The pastes for adsorption measurements were prepared in the same way as those for stability and rheology measurements (see below). A one-hour period was considered sufficient to achieve adsorption equilibrium at ambient temperature (pseudo-equilibrium in the case of cement). After centrifugation of the paste sample, the supernatant was diluted and the residual concentration of the admixture was determined by the suitable analytical technique. The PNS-type superplasticizer adsorbs in UV/VIS, so its concentration in the solution was quantified spectrophotometrically using a Hewlett Packard 8452A diode array spectrophotometer. The residual concentration of PC-type superplasticizer in the solution was obtained by measuring the chemical oxygen demand (COD), which determines the amount of oxidizable organic material in the solution [19].

2.2.4. Zeta potential measurements

The zeta potential of concentrated limestone and cement suspensions (20 wt.%) was measured as a function of superplasticizer dosage using an electroacoustic technique. These measurements were performed by a Zeta Probe Analyser from Colloidal Dynamics.

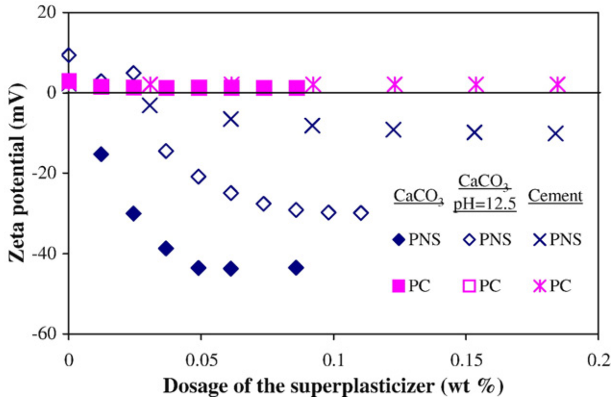

Fig. 3. Zeta potential of concentrated $CaCO_3$ and cement suspensions (20 wt.%) as a function of the superplasticizer dosage.

2.2.5. Mixing protocol and measurement sequence

The samples used for stability and rheological measurements were prepared with a Hobart mixer according to the ASTM C305 procedure. The required amount of water (in cement pastes) or electrolyte solution (in calcium carbonate pastes) together with an appropriate quantity of superplasticizer was introduced in a mixing bowl before mixing. The solids were then slowly introduced in the mixer and the time recorded as time zero for bleeding and sedimentation measurements; the total mixing time was 4 min. A portion of the sample was then transferred into the conductivity cell and conductivity readings started within 5–6 min of the initial solid/liquid contact.

The remainder of the sample was used for rheological characterization as described above, and for evaluation of air entrainment in the pastes. The latter measurements were made 6 min after mixing through the following paste protocol. A portion of the sample was transferred to overfill a Plexiglas cylinder (9.5 cm height and 5.2 cm interior diameter), and the excess paste was skimmed off with a straight edge. The air content of the sample was determined by measuring the mass of the sample in the cylinder, and by comparing this mass with the mass calculated for an air-free paste. Paste fluidity measurements (mini-slump test) were performed 8 min after mixing. The

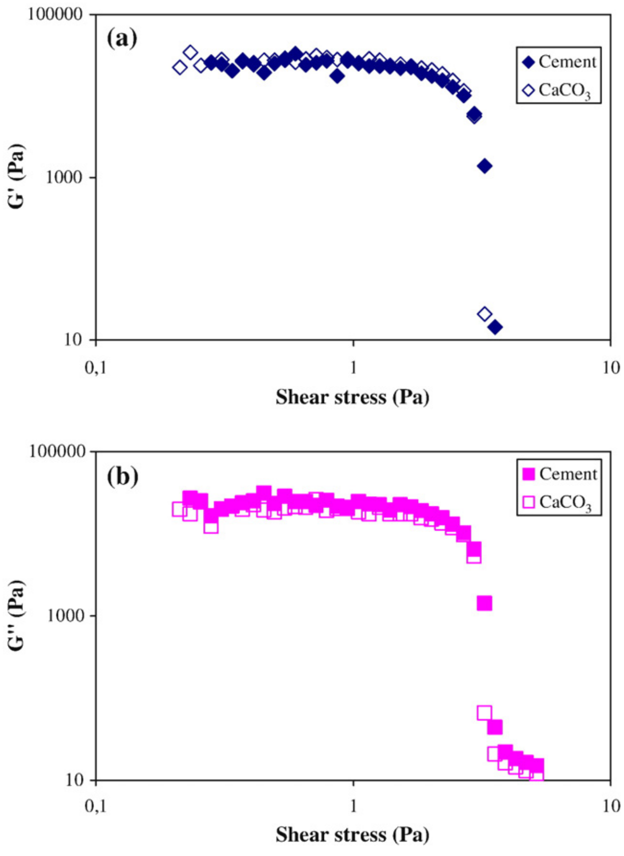

Fig. 4. Rheological properties of the reference $CaCO_3$ paste (L/S = 0.5, pH ~ 10) and cement paste (L/S = 0.55); (a) elastic modulus (G′); (b) viscous modulus (G″).

dynamic rheological measurements were performed in the following order: yield stress measurement (stress-growth technique, ~10 min after mixing), oscillatory stress sweep (~15 min) and frequency sweep (~20–25 min). The sample was gently stirred manually before each of the rheological measurements.

3. Results

The interaction of superplasticizers with limestone and cement particles is illustrated in Figs. 2–3 through adsorption isotherms and zeta potential measurements. As expected, the cement zeta potential, observed in concentrated suspensions, varies less with the PNS dosage than that observed earlier in very dilute suspensions (~0.1 wt.%) [20]. The influence of superplasticizer dosage on the bleeding/sedimentation behaviour of limestone and cement pastes is shown in Figs. 5–10. The data illustrating the stability of these pastes are collected in Table 4, while the parameters describing their rheological properties are presented in Table 5.

For discussion purposes, the following quantities were determined from bleeding volume measurements and from bleeding/sedimentation curves similar to those in Fig. 1(b):

- Bleeding volume: total volume of bleeding water accumulated at the top of the cell, at the end of sedimentation experiment, and expressed as volume of water (ml)
- v_0^r: initial bleeding rate: initial slope of the bleeding curve
- v_1^r: channel bleeding rate: accelerated bleeding rate observed after an initial period of constant bleeding rate
- v_0^s: initial sedimentation rate: initial slope of the sedimentation curve
- v_1^s: accelerated rate of sedimentation after an initial constant rate period
- t_1^r: end of initial (constant rate) bleeding period and start of channel bleeding
- t_1^s: end of initial (constant) sedimentation rate period.

The following rheological parameters were determined (Table 5):

- Spread diameter: the paste spread diameter observed in the mini-slump test
- τ_0: yield stress of the paste
- G' and G'': elastic and loss moduli in the linear viscoelastic region, a "plateau" value on the oscillatory rheological curves similar to those presented in Fig. 4.
- δ: phase angle, a "measure" of the degree of elasticity of a sample ($\tan \delta = G'/G''$)
- η_0: zero-shear viscosity, a finite value of complex viscosity at low frequencies in frequency sweep measurements.

The stability and rheological behaviour of the following systems were examined: a $CaCO_3$ paste in a 10 g/l NaCl solution ($L/S = 0.5$) and a cement paste ($L/S = 0.55$). The L/S ratios were selected to yield stable reference pastes with similar rheological properties. Adapting the L/S compensates for slightly different particle size distributions and specific surface of cement and $CaCO_3$ particles and, more importantly, for a greater fraction of 'bound' water on cement particles due to cement hydration.

The evolution of the elastic (G') modulus as a function of shear stress for these two pastes is illustrated in Fig. 4; other relevant rheological parameters can be found in Table 5. The data confirm that the two pastes have nearly identical rheological properties, indicating similar particle–particle interactions, state of flocculation and microstructure, as observed in a separate study [10].

Fig. 1(b) illustrates the bleeding and sedimentation behaviour of the reference $CaCO_3$ and cement pastes, as derived from analysis of time-dependent conductivity data outlined above. The accurate match in the bleeding and sedimentation curves for the $CaCO_3$ and cement pastes during the initial hour or so of hydration confirms that, the key physical effects responsible for bleeding–sedimentation behaviour in cement paste are adequately represented by those which occur in the $CaCO_3$ paste. Consequently, the factors influencing the early migration of liquids and solids in cementitious systems, and the influence of chemical admixtures on these phenomena can be usefully investigated in model limestone pastes. However, after approximately 90 min, the interactions involving the hydrating cement particles begin to play a dominant role in the flocculation-coagulation process, i.e., the hydrating cement particles interact in a three-dimensional network, which inhibits the separation of the liquid and solid phases, and rapidly "freezes" the bleeding and sedimentation processes. Further discussion on the usefulness of $CaCO_3$ as a model system for cement-based materials can be found in earlier publications [10].

In order to study the influence of superplasticizers on the properties of limestone pastes under conditions comparable to those prevailing in cementitious systems, a series of stability and rheological measurements were performed at pH ~ 12.5 in the presence of $Ca(OH)_2$. In these experiments, the ionic strength of the solution was kept constant and equivalent to that of a 10 g/l NaCl solution by the appropriate addition of NaCl into a saturated solution of $Ca(OH)_2$.

4. Discussion

4.1. Particle–superplasticizer interactions

The important fluidification imparted to cementitious systems by superplasticizers depends on several physico-chemical phenomena which have been the object of considerable investigation [4–6,21–27]. The dispersing action of superplasticizers can be qualitatively understood as follows: by adsorbing on the solid phase, the superplasticizer molecules prevent the solid particles from agglomerating and trapping part of the water; the water thus remains available for paste fluidification. The dispersion mechanism depends on the type of superplasticizer, details of which are outlined below.

A first required condition for PNS- or PC-polymer molecules to act as superplasticizers is their binding to the particles in the colloidal system. The binding data shown in Fig. 2 illustrate the relative binding ability of $CaCO_3$ (pH ~ 10) and cement particles for the two superplasticizers investigated. The PC-type superplasticizer is seen to adsorb lightly onto both limestone and cement particles; PNS adsorbs approximately twice as much as PC onto limestone and approximately two-fold more onto cement particles. The higher adsorption of PNS, relative to PC, onto $CaCO_3$ particles, can be understood from the higher charge density of the PNS molecules [13]. On the other hand, the greater adsorption of PNS onto reactive cement particles is generally attributed to the incorporation (and loss of function) of adsorbed polymer molecules into the surface layers of hydration products [25–28]. This effect appears to be very important for PNS, an observation which has been explained by the chemical analogy of the sulfonate groups of the PNS and sulfate ions; both can react with aluminate phases to produce ettringite or analogous hydration products [25]. Interestingly, the adsorption of superplasticizer on $CaCO_3$ does not appear to be markedly influenced by the addition of $Ca(OH)_2$ to pH 12.5 as shown by the data in Fig. 2. Recently, it was also confirmed than not only PNS, but also PC-type superplasticizers can intercalate into cement hydration products [29].

A second required condition for superplasticizer function is the induction of some type of particle-particle repulsive forces by the adsorbed polymer molecules. Judging by the zeta potential data in Fig. 3, the PC-type superplasticizer conveys little surface charge to limestone or cement particles, while PNS molecules impart strong negative charges, particularly to $CaCO_3$ particles. Recalling that PNS is adsorbed less on limestone than on cement, and neglecting zeta potential variations which may arise from slight differences in particle size [30], the lower surface charge of the latter in the presence of PNS may result from two effects. First, a partial charge neutralization due to Ca^{+2} adsorption at high pH as can be seen from the zeta potential data for $CaCO_3$ in the presence of $Ca(OH)_2$ at pH 12.5; second, partial incorporation of the superplasticizer in the hydration products, i.e., reducing the amount of superplasticizer contributing to the surface charge. In any case, the zeta potential data shown here support the current view that PNS molecules provide mainly electrostatic dispersion forces, while PC molecules induce particle–particle repulsion predominantly through steric forces. The importance of the steric repulsive force in the dispersing effect of PNS has been a matter of speculation [31]; however, Uchikawa et al. [24] showed that the steric repulsive forces operate at very short distances, as expected, and their contribution to the total repulsive force is estimated to be about 20%.

4.2. Influence of superplasticizers on paste rheology

The rheological properties of the limestone and cement pastes, in the absence of superplasticizers, may be compared

Table 4
Stability of $CaCO_3$ and cement pastes

	Admixture	Air	System stability							
		(%)	Bleeding (ml)	Stability index	v_0^r (cm/h)	v_1^r (cm/h)	v_0^s (cm/h)	v_1^s (cm/h)	t_1^r (h)	t_1^s (h)
Model system ($CaCO_3$)	Reference	<0.1	42	0.715	0.35	0.65	4.0	10.1	2.5	2.4
	0.02% PNS	<0.1	47	0.66	0.45	0.75	4.5	8.8	2.4	2.3
	0.03% PNS	<0.1	52	0.63	0.4–0.45	0.65	4.6	6.1	3.0	3.0
	0.05% PNS	<0.1	63.5	0.585	0.4	–	3.85	–	–	–
	0.07% PNS	<0.1	72.5	0.55	0.4	–	3.0	–	–	–
	0.01% PC	<0.1	49.5	0.65	0.45–0.5	0.85	3.8	12.7	2.1	2.0
	0.02% PC	<0.1	57	0.6	0.4–0.45	0.8	3.7	11.9	2.9	2.9
	0.03% PC	<0.1	74	0.54	0.45–0.5	–	3.5	–	–	–
	0.05% PC	<0.1	89	0.48	0.4	–	2.35	–	–	–
Model system pH = 12.5	Reference	<0.1	30	0.81	0.25	0.6	4.95	9.7	2.1	2.0
	0.05% PNS		43	0.68	0.3–0.35	0.8	6.0	9.5	1.5	1.5
	0.075% PNS		52.5	0.62	0.45	0.65	4.75	6.25	1.9	1.7
	0.1% PNS		58	0.6	0.45–0.5	–	4.55	–	–	–
	0.25% PNS		143	0.4	0.65	–	2.5	–	–	–
	0.01% PC	<0.1	37.5	0.75	0.3–0.35	0.85	5.8	9.9	1.8	1.8
	0.02% PC	<0.1	53	0.61	0.35	0.85	3.9	8.55	2.2	2.1
	0.03% PC	<0.1	76	0.54	0.45	–	3.7	–	–	–
	0.05% PC	<0.1	105	0.43	0.4	–	1.55	–	–	–
Cement	Reference	<0.1	11	0.96	0.35	–	6.1	–	–	–
	0.2% PNS		23.5	0.88	0.35	1.45	6.4	13.3	1.0	0.9
	0.3% PNS		31.5	0.77	0.4–0.45	1.45	6.8	15.2	0.8	0.8
	0.4% PNS		36.5	0.73	0.45–0.5	1.65	6.85	21.0	0.7	0.6
	0.5% PNS		49	0.68	0.45–0.5	1.85	7.55	23.4	0.6	0.5
	0.03% PC	0.8	25.5	0.86	0.4–0.45	1.95	7.1	18.5	0.8	0.7
	0.05% PC	1.0	28.5	0.8	0.6	2.65	8.8	21.2	0.7	0.6
	0.07% PC	0.6	34.0	0.78	0.75	2.5	8.95	22.1	0.6	0.5
	0.1% PC	1.1	37.5	0.76	0.8	2.35	9.3	27.0	0.6	0.5

Table 5
Rheology of CaCO$_3$ and cement pastes

	Admixture	Spread diameter (mm)	Rheological properties				
			τ_0 (Pa)	G' (kPa)	G'' (kPa)	δ	η_0 (kPa s)
Model system (CaCO$_3$)	Reference	83	4.8	27.7	21.0	37.2	31
	0.02% PNS	96	2.75	22.7	16.7	36.4	25
	0.03% PNS	103.5	2.1	14.8	11.6	38.1	17
	0.05% PNS	118.5	0.85	5.1	3.3	32.9	6.5
	0.07% PNS	130.5	0.45	1.0	0.4	21.8	3.3
	0.01% PC	90.5	3.45	17.6	10.4	30.4	19
	0.02% PC	105.5	1.9	6.2	3.1	26.3	10
	0.03% PC	118.5	1	1.4	0.5	19.6	5.5
	0.05% PC	133	0.45	0.1	0.02	11.3	1.5
Model system pH = 12.5	Reference	74	7.5	61.4	43.5	35.3	62
	0.05% PNS	89.5	3.6	27.9	17.6	32.2	30
	0.075% PNS	101	1.85	4.65	2.6	29.2	–
	0.1 PNS%	115.5	1.1	3.2	1.4	23.6	5.5
	0.25% PNS	143	–	–	–	–	–
	0.01% PC	86	4.6	34.7	22.2	32.6	32.5
	0.02% PC	105	2.2	12.3	7.4	31	16.0
	0.03% PC	118.5	1.1	2.5	0.9	19.8	6.0
	0.05% PC	139	0.3	0.06	0.02	18.4	–
Cement	Reference	94.5	5.0	18.5	17.5	43.4	20
	0.2% PNS	110	3.25	16.5	12.5	37.1	17
	0.3% PNS	121.5	2.5	15.7	7.8	26.4	23
	0.4% PNS	140	1.2	3.3	1.4	23	12
	0.5% PNS	154	0.9	1.2	0.45	19.7	11
	0.03% PC	105	3.4	12.3	8.7	35.3	10.5
	0.05% PC	114.5	2.6	5.65	3.0	28.0	6.5
	0.07% PC	126	1.9	2.6	1.2	24.8	4.0
	0.1% PC	136.5	0.8	1.0	0.4	20.7	–

from the data reported in Table 5. As noted above and discussed previously [10], the limestone paste at equilibrium (pH ~ 10) and the cement pastes showed similar values in their key rheological parameters: yield stress, elastic and loss moduli (G' and G'') and zero-shear viscosity (η_0). As detailed below, the stability behaviour of these pastes, expressed as bleeding and sedimentation rates is also very similar. When Ca(OH)$_2$ is added at saturation (pH 12.5) to the CaCO$_3$ paste, all of the rheological parameters increase substantially, indicating a ‘stiffer’ dispersion; this change, however, is not manifested in the phase angle, which might be expected to decrease when the system becomes more ‘solid-like’. The paste stabilizing influence of Ca(OH)$_2$ is consistent with the known ability of Ca^{+2} ions to act as a flocculating agent [32]; the latter seems to be more effective at high pH where the CaCO$_3$ particles bear a greater negative charge, as it was shown in our previous study [10]. Also, it was observed that increasing the pH of a CaCO$_3$ paste to 12.5 using NaOH results with a more fluid and less stable paste relative to that containing Ca(OH)$_2$, which is readily understood from the lower concentration of Ca^{+2} ions in these pastes [10]. The fact that rheological behaviour of CaCO$_3$ pastes depends simultaneously on both pH and Ca^{2+} concentration in solution (at constant ionic strength) points out that attractive forces between particles must be of electrostatic origin. Lesko et al. [33] and Gmira et al. [34] reached the same conclusion with respect to the origin of cohesion forces between silicate hydrate surfaces; the attractive forces between slightly hydrated cement particles are likely due to the ion correlation forces, while only a marginal contribution is expected from van der Waals attraction forces. This similarity between CaCO$_3$ and cement particles is further evidence of the validity of limestone as a model system for cementitious materials.

The addition of superplasticizers has a significant effect on the rheological properties of the systems investigated (Table 5). The values of τ_0, both dynamic moduli (G' and G'') and η_0 all decrease as the concentration of superplasticizer increases in CaCO$_3$ pastes at equilibrium pH (~10), or at pH 12.5, as well as in cement pastes (here the phase angle values decrease suggesting a more solid-like behaviour, which might be the result of enhanced particle–particle correlation lengths in the presence of superplasticizers). An important fluidifying effect of the superplasticizers is also manifested by a significant increase of the measured paste spread diameters.

As is generally observed in concrete practice, the paste spread diameter and yield stress data confirm that the PC-type superplasticizer is a more effective dispersant than the PNS-type superplasticizers. In the pastes studied here, the relative effectiveness of PC- and PNS-type superplasticizers (performance ratio) apparently increases in the following order: limestone paste (pH ~ 10) < limestone paste (pH ~ 12.5) < cement paste.

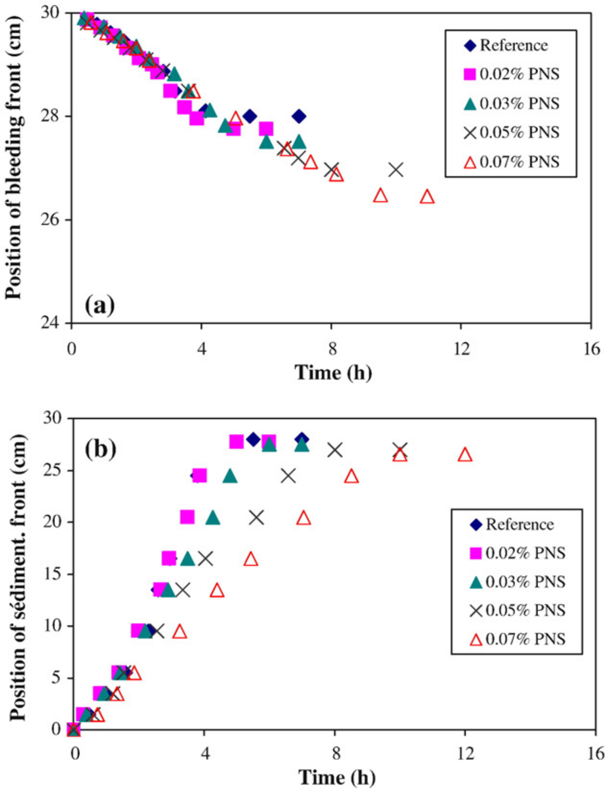

Fig. 5. Effect of the PNS-type superplasticizer on the behaviour of the $CaCO_3$ pastes (L/S = 0.5); (a) bleeding kinetics; (b) sedimentation kinetics.

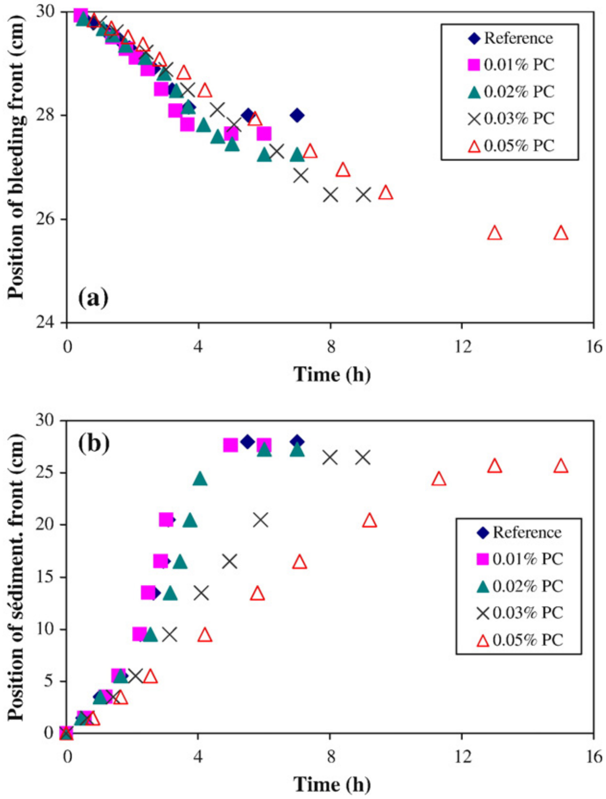

Fig. 6. Effect of the PC-type superplasticizer on the behaviour of the $CaCO_3$ pastes (L/S = 0.5); (a) bleeding kinetics; (b) sedimentation kinetics.

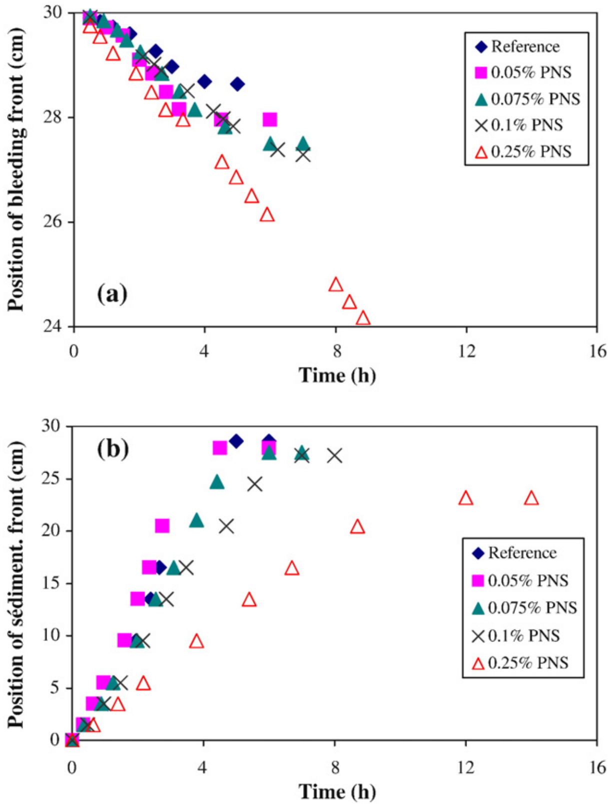

Fig. 7. Effect of the PNS-type superplasticizer on the behaviour of the $CaCO_3$ pastes in saturated $Ca(OH)_2$ solution (L/S = 0.5); (a) bleeding kinetics; (b) sedimentation kinetics.

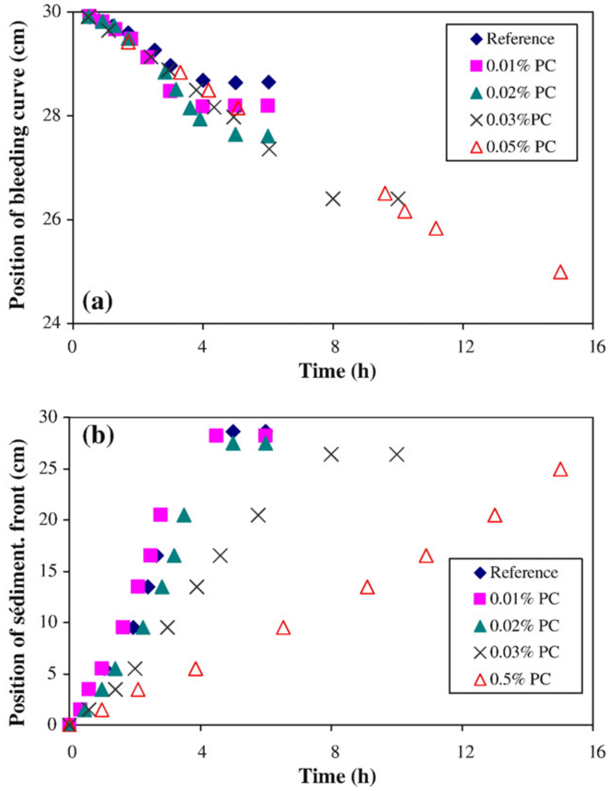

Fig. 8. Effect of the PC-type superplasticizer on the behaviour of the $CaCO_3$ pastes in saturated $Ca(OH)_2$ solution (L/S = 0.5); (a) bleeding kinetics; (b) sedimentation kinetics.

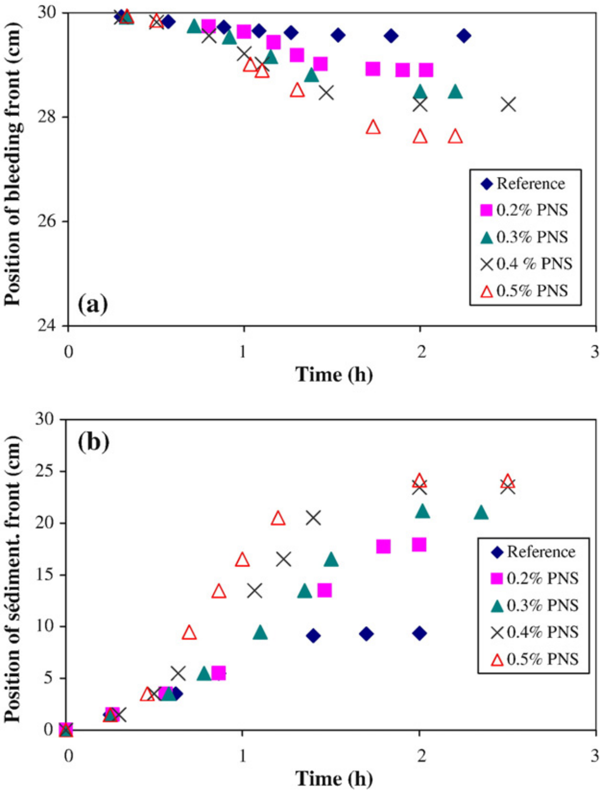

Fig. 9. Effect of the PNS-type superplasticizer on the behaviour of the cement pastes (L/S = 0.55); (a) bleeding kinetics; (b) sedimentation kinetics.

Interestingly, in $CaCO_3$ pastes at equilibrium pH (~10) the relative dosages required to achieve a given paste rheology (slump diameter, yield stress) is only slightly higher for PNS compared to PC; this contrasts sharply with observations in cementitious systems where dosages can differ by factors of 3–5 (Table 5). In the context of the present model system *vs.* cement investigation, this observation is worth emphasizing: in a non-hydrating paste of mineral particles, which exhibit colloidal properties, rheology and stability very similar to those of a cement paste [10], the two types of superplasticizers exert similar effects at comparable concentrations (although their mode of action may be different as discussed above).

It is further noteworthy that, upon increasing the pH to 12.5 with $Ca(OH)_2$, considerably higher dosages of PNS (3–5 times) are required to achieve a given paste fluidity; contrastingly, little additional PC is required in the presence of lime. The PNS adsorption data (Fig. 2) show that the increased PNS demand is unlikely due to enhanced binding to $CaCO_3$. On the other hand, PNS imparts high negative charges to the $CaCO_3$ particles (Fig. 3) and this favours (electrostatic) Ca^{+2}–particle interactions and particle–particle interactions mediated by Ca^{+2} ions; these combined effects lead to greater Ca-enhanced flocculation. Since PC-type polymers do not induce significant surface charge to $CaCO_3$ particles, the Ca^{+2}-enhanced flocculation mechanism is not effective with PC-type superplasticizers. Rather, an equal PC demand in the two limestone pastes suggests that the side chains of the polymer retain their conformation at the higher pH and Ca^{2+} content and, consequently, their effectiveness as a steric barrier to flocculation/coagulation.

Finally, in a hydrating cement paste, still higher dosages of both PNS and PC are required for a given fluidity; the incremental dosages over those required for fluidification of pH 12.5 limestone pastes containing $Ca(OH)_2$, can be accounted for by incorporation of the superplasticizer molecules into cement hydration products as discussed above. In the light of observation of limestone pastes, it appears that the dispersion ability of both types of superplasticizers is influenced by this phenomenon.

The model system approach and the data presented here thus offer a more detailed description of the mode of action of PNS and PC types of superplasticizer. In the description outlined above, the influence of Ca^{+2} ions and the consequences of cement hydration on paste rheology can now be properly distinguished. The influence of polymer charge density on surface binding and on Ca^{+2}-mediated flocculation are better understood, and can later be used in the interpretation of superplasticizer performance. As in related studies with $Mg(OH)_2$ and PC-type superplasticizers, it is likely that the effects reported here will depend on many of the molecular properties of the superplasticizer, i.e., molecular weight, charge density, structure, etc... [35].

4.3. Effect of superplasticizers on paste stability

The bleeding and sedimentation curves derived from paste conductivity measurements (Figs. 5–10) show related features,

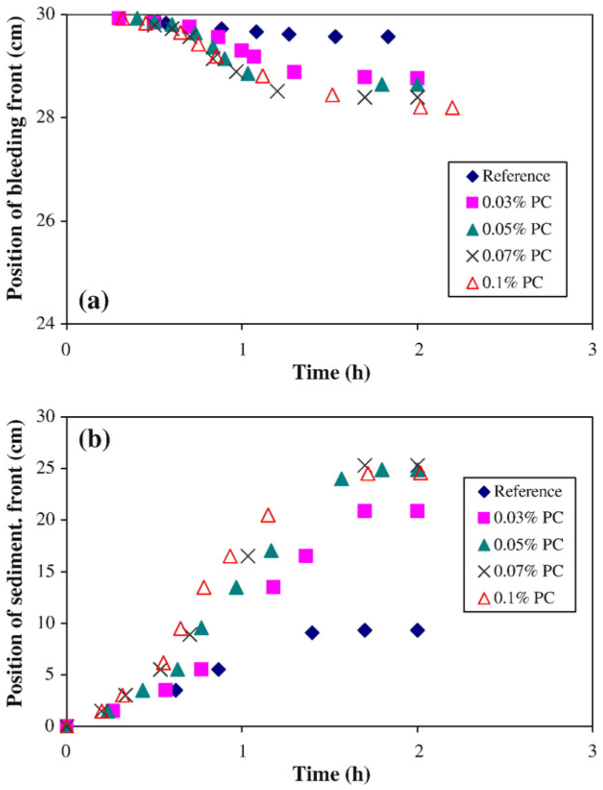

Fig. 10. Effect of the PC-type superplasticizer on the behaviour of the cement pastes (L/S = 0.55); (a) bleeding kinetics; (b) sedimentation kinetics.

as might be expected since the bleeding and sedimentation processes are inherently coupled. In the absence of superplasticizers, the general shape of these curves (for limestone pastes) features an initial period where bleeding and sedimentation occur at nearly constant rates. This is followed by an acceleration period, where both the bleeding and sedimentation rates increase sharply; the rates later decrease slowly to zero as the system reaches a pseudo-equilibrium state. As described elsewhere [10], the marked rate increases occurring several hours into the phase-separation process indicate the onset of 'channelling', i.e., liquid migration through preferential, least-resistance paths.

The relationship between liquid channelling and the settling mechanism of solid particles in a paste can be understood as follows. In pastes with relatively high solids contents (limestone: L/S = 0.5, cement: L/S = 0.55), and in which flocculation is important, the solid particles may either sediment in a cooperative fashion irrespective of their size (so-called zone settling [2,36]), or undergo homogeneous compaction (consolidation). Alternately, the solid particles can also settle independently creating a density gradient, especially when the solid particles are completely deflocculated. Indeed, it was observed experimentally that channelling occurs when a settling system is between a regime of zone settling and fully established uniform compression [36]. Loh et al. [37] found that channelling occurs in cement-based systems when the governing process is sedimentation in the upper part, while consolidation is taking place in the sedimented zone at the bottom; if the settling is due to consolidation only, no channelling occurs.

The data presented in Table 4 provide various measures of the influence of PNS- and PC-type superplasticizers on the bleeding–sedimentation processes in $CaCO_3$ and cement pastes. First, with increasing superplasticizer dosage, the overall stability of the pastes (stability index) decreases, and the total volume of bleeding water collected over the pastes increases. These observations are readily understood from the combined particle de-flocculation effect of the superplasticizer, and an increase in the amount of 'free' water, which can migrate upward through the paste. A more accurate description of the effect of superplasticizers on the bleeding and segregation processes can be achieved from the kinetic parameters presented in Table 4 and examination of Figs. 5 and 6.

In $CaCO_3$ pastes, the initial rate constants show that the superplasticizers affect the initial bleeding and sedimentation rates only marginally, i.e., rates remaining constant or increasing slightly. However, at later stages of the phase-separation process, superplasticizers exert a marked influence on the accelerated bleeding and sedimentation rates (v_1^r,v_1^s). Generally, at low dosages, both superplasticizers tend to increase v_1^r and v_1^s values; as the superplasticizer concentration is increased, the bleeding and sedimentation rates are significantly reduced and become comparable to the initial rates at the highest concentrations examined, i.e., bleeding and sedimentation processes occurring at nearly constant rates. From previous discussions on channelling phenomena, the changes in the bleeding and sedimentation kinetics with increasing superplasticizer dosage imply a change in the sedimentation mechanism, with the repression of channel bleeding. At high superplasticizer concentration, sedimentation occurs more slowly at a near constant rate; the bleeding rate is also slightly lower, but carries on for a longer time, so the bleeding volume is larger. Hence, from the sedimentation rates, the limestone pastes would appear stabilized by the superplasticizer, whereas from total bleeding volumes, the pastes would seem destabilized (as noted above). Clearly, in these types of systems, the definition of stability is related to specific criteria.

The addition of $Ca(OH)_2$ to $CaCO_3$ pastes (pH 12.5) reduces the duration of channel bleeding, as is apparent by comparing the 'reference' data in Figs. 5–8 and Table 4; the sedimentation rates in the 'accelerated' period is also moderately decreased, both observations being consistent with paste stabilization due to Ca-mediated flocculation. The addition of superplasticizers enhances bleeding with either PNS or PC; at constant fluidity, PNS enhances bleeding rate and volume, more so than PC. From the data in Table 4, a reverse effect is found in the relative sedimentation rates.

In cement pastes without superplasticizers, the initial bleeding and sedimentation rates are comparable to those of the limestone pastes; however, the duration of these processes is much shorter than in limestone pastes and no significant channel bleeding occurs. The addition of superplasticizers to the cement paste results in an important destabilization as seen by a significant increase of both the bleeding and sedimentation rates (note change in x-axis scale). The magnitude of the effect depends on the nature and concentration of the superplasticizer. The kinetic parameters in Table 4 show that the initial bleeding and sedimentation rates increase slightly as the concentration of PNS increases; however, the channelling behaviour, which was not observed in the reference cement paste, is induced and promoted by PNS, as manifested by an increase in the v_1^r and v_1^s values. A similar effect is observed with the PC-type superplasticizer; in this case, the effect appears somewhat larger for PC than for PNS, as is apparent from the bleeding and sedimentation rates data for the two superplasticizers.

In light of the above discussion on the mode of action of superplasticizers and their influence on rheological properties of pastes, the influence of superplasticizers on the stability of limestone and cement pastes is clearly the result of several phenomena, which are coupled in complex ways. With some generalization, the current observations can be understood from the following:

- the superplasticizers de-flocculate the particles in the paste, liberating water trapped within flocs;
- the dispersing action of superplasticizers opposes the sedimentation, so the sedimentation process occur more slowly;
- the dispersed particles settle and consolidate more homogeneously as dense sediments (lower sediment volumes than for flocculated systems), avoiding the formation of bleeding channels;
- in the case of cement pastes, the superplasticizers retard the early hydration, so the cement pastes behave more like

limestone pastes, showing channel bleeding and enhanced sedimentation in the presence of superplasticizers;

- the greater influence of PC, relative to PNS, on the cement pastes (at constant fluidity) is likely due to the surfactancy of PC-type superplasticizers, as suggested from earlier surfactant studies [12];
- finally, since superplasticizers will disperse the finest particles most effectively, the motion of these fines (Brownian, or upward driven by water migration) may also oppose the phase separation and contribute to differences in the stability of the pastes.

4.4. Relation between rheological properties and bleeding/ sedimentation behaviour

As noted in the introduction, the present investigation also aimed to establish whether there exist useful correlations between the rheological properties and the stability of cementitious or model systems. To that effect, a stability parameter (equilibrium stability index) was plotted against a rheological parameter (paste spread diameter) in Fig. 11, for all of the pastes examined. The spread diameter was chosen over other rheological parameters to represent the overall fluidification effect of superplasticizers, because of its practical relevance and wide accessibility. However, from the data presented in Table 5, it can be seen that spread values are well correlated with yield stress and the dynamic rheological parameters. An exponential function proposed by Flatt et al. [38] to provide the relation between slump spread diameter and yield stress for cement pastes having an intermediate fluidity level fits well with our data; a different exponential function for cement and $CaCO_3$ could be either due to the highly thixotropic nature of cement paste compared to limestone suspensions or possibly due to surface tension effects [39]. Similar experimental correlation may be established between dynamic rheological parameters (both dynamic moduli, η_0) and spread diameter. Hence, the following comments can be considered quite general.

Fig. 11 shows a linear correlation between the fluidity (mini-slump) and stability (stability index) of the $CaCO_3$ and cement pastes at varying superplasticizer concentration. This correlation depends on the nature of the solid phase, but appears relatively independent of the solution composition (pH, presence of Ca^{2+} ions), or type of superplasticizer. The correlation lines for $CaCO_3$ and cement are quasi parallel, but the cement paste appears more stable than the limestone paste of the same fluidity by about 0.2 stability index units. The observed difference may be due, in part, to properties of the solids (particle size distribution, specific surface), but largely to the different volume fraction of the 'bound', or 'free' water in the two types of pastes at the time of the stability index determination, i.e., while rheological properties are measured at short times after sample homogenization, the bleeding–sedimentation experiments extend over several hours, during which the cement hydrates partially, reducing the amount of 'free' water. Nonetheless, the results show that, in a given cementitious system, the superplasticizers do not impact negatively on the fluidity–stability relationship.

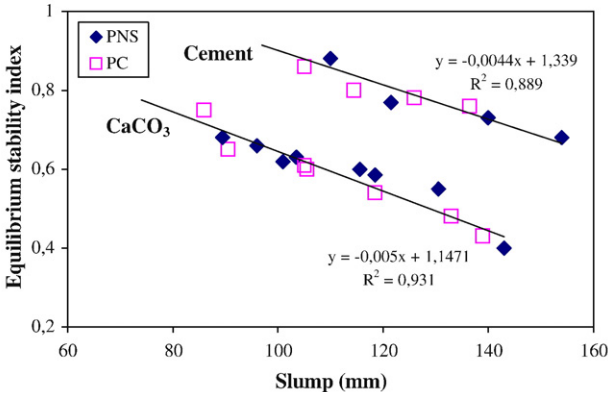

Fig. 11. Stability of the $CaCO_3$ and cement pastes expressed in terms of stability index as a function of the paste fluidity (mini-slump spread diameter).

On the other hand, attempts to relate the rheological parameters and the bleeding and sedimentation rates failed to show significant correlations. Again, this is not so surprising since the rheological parameters are obtained initially on a homogeneous system, whereas bleeding and sedimentation are time-dependent processes in increasingly heterogeneous systems. Hence, in a general sense, the rheological properties of a system will impact on its overall stability, but early rheology data on a cementitious system should not be expected to predict its detailed bleeding and segregation behaviour. The time evolution of particle–particle interactions and of flocculation–consolidation processes will affect the mechanism through which the solids can sediment or consolidate in the sample column, as well as the water transport through and out of the consolidating materials. The different behaviours of limestone and cement pastes confirm that, as should be expected, the stability of the system depends on the reactivity of the solid phase.

5. Conclusions

The systematic comparison of limestone and cement pastes provides valuable information for the elucidation of chemical effects specifically related to the cementitious system. In the present study, this 'model' or reference system approach provides a basis for an improved phenomenological description of the rheology and stability of these pastes, and the influence of superplasticizers on their behaviours.

Dynamic rheological parameters, or simple flow observations (spread diameter), on limestone pastes under varying conditions (pH, Ca) and on cement pastes, provided new insight into the mode of action of superplasticizers and on differences between PNS- and PC-type molecules. In a water–limestone paste, the dispersing effectiveness of PNS- and PC-type superplasticizers are comparable; the greater dispersion ability of PC appears when $Ca(OH_2)$ is added to the limestone paste (pH 12.5) and can be understood from electrostatic interactions and flocculation effects. On the other hand, cement hydration reactions apparently affect both PNS and PC in similar ways (partial incorporation into hydration products), significantly decreasing their dispersing ability.

Evaluation of the stability of the various pastes investigated also leads to a better understanding of bleeding and sedimentation processes occurring in fresh cementitious systems. Limestone–water pastes undergo phase separation through a channelling process occurring after a few hours of solid settling. Superplasticizers can prevent the channelling processes through particle de-flocculation and dispersion; at a given paste fluidity, the action of both superplasticizers is comparable. In the presence of $Ca(OH_2)$, the initial stability of limestone pastes is enhanced (Ca-induced flocculation), but the addition of superplasticizers leads to kinetic effects similar to those observed at pH 10, again, comparing at constant fluidity. In comparison, cement pastes exhibit less bleeding and sedimentation than limestone pastes, with little or no channelling behaviour. In these pastes, the presence of superplasticizers promotes channelling, and enhanced bleeding and sedimentation; again, at comparable fluidities, the influence of PNS and PC are similar.

Finally, the various results collected in this work suggest that, in a given cementitious system, there can be a relationship between the initial rheology of the system and its stability towards bleeding and sedimentation. This was observed, for example, as a linear relation between the paste fluidity (paste spread diameter) and a stability index, which characterizes the heterogeneity of the paste sample at phase-separation equilibrium. In such a system, the initial rheological properties can provide predictive indications of stability, for example, following the addition of different admixtures. However, the same type of relation cannot be expected to apply broadly to a variety of cementitious materials, since the time evolution of the interactions which control the phase-separation processes are dependent on the chemical composition and reactivity of the various solids.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by the Natural Sciences and Engineering Research Council of Canada, and Handy Chemicals. The help of Marc-André Simard and Jeff Sharman in the preparation of this article, as well as frequent discussions are also gratefully acknowledged.

References

[1] Self-compacting concrete, in: O. Wallevik, I. Nielsson (Eds.), Proceedings of the 3rd International RILEM Symposium, Reykjavik, Iceland, 2003, p. 1056.

[2] L. Svarovsky, Sedimentation, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons Inc., 1997.

[3] A.W. Saak, Characterization and modeling of the rheology of cement paste: with applications towards self-flowing materials, Ph.D. Thesis, Northwestern University, 2000.

[4] C. Jolicoeur, P.-C. Nkinamubanzi, M.-A. Simard, M. Piotte, Progress in understanding the functional properties of superplasticizers in fresh concrete, in: V.M. Malhotra (Ed.), Proceedings of the 4th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Montreal, Canada, 1994, pp. 63–88, ACI SP-148.

[5] A. Pierre, R. Mercier, A. Foissy, J.M. Lamarche, The adsorption of cement superplasticizers onto mineral dispersions, Adsorp. Sci. Technol. 6 (1989) 219–231.

[6] A. Foissy, A. El Attar, J.M. Lamarche, Adsorption of polyacrylic acid on titanium dioxyde, J. Colloid Interface Sci. 96 (1983) 275–287.

[7] A. Pierre, J.M. Lamarche, R. Mercier-et, A. Foissy, Adsorption d'un fluidifiant du ciment sur le carbonate de calcium, Cem. Concr. Res. 19 (1989) 692–702.

[8] C. Comparet, A. Nonat, S. Pourchet, M. Mosquet-et, P. Maitrasse, The molecular parameters and the effect of comb-type superplasticizers on self-compacting concrete: a comparison of comb-type superplasticizer adsorption onto a basic calcium carbonate medium in the presence of sodium sulphate, Proceedings of the 7th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Berlin, 2003, pp. 195–209, SP-217-13.

[9] E. Sakai, D. Atarashi, A. Kawakami-et, M. Daimon, Influence of molecular structure of comb-type superplasticizers and inorganic electrolytes on the dispersion mechanisms of limestone powder, Proceedings of the 7th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Berlin, 2003, pp. 381–392, SP-217-25.

[10] N. Mikanovic, C. Jolicoeur, K. Khayat, M. Pagé, Model systems for investigation of the stability and rheological properties of cement-based materials, Supplementary Papers of the 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology, Montréal, 2006, pp. 267–304.

[11] J. Wheeler, S. Chatterji, Settling of particles in fresh cement pastes, J. Am. Ceram. Soc. 55 (9) (1972) 461–464.

[12] N. Mikanovic, C. Jolicoeur, M. Pagé, Influence of surfactant chemical admixtures on the stability and rheological properties of calcium carbonate and cement pastes, in: V.M. Malhotra (Ed.), Proceedings of 8th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Sorrento, 2006, pp. 321–343, SP-239.

[13] X. Zhang, M. Pagé, Y. Dénommé, C. Jolicoeur, Novel polymer blends as concrete superplasticizers, in: V.M. Malhotra (Ed.), Proceedings of the 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology, Montréal, 2006, pp. 217–239, SP-235-15.

[14] C. Jolicoeur, K.H. Khayat, T. Pavate, M. Pagé, Evaluation of effect of chemical admixtures and supplementary cementitious materials on stability of cement-cased materials using *in-situ* conductivity method, in: V.M. Malhotra (Ed.), Proceedings of the 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Nice, 2000, pp. 461–483, SP-195-29.

[15] T.V. Pavate, K.H. Khayat, C. Jolicoeur, *In-situ* conductivity method for monitoring segregation, bleeding, and strength development in cement-based materials, in: V.M. Malhotra (Ed.), Proceedings of the 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Nice, 2000, pp. 535–559, SP-195-33.

[16] N. Mikanovic, Méthode conductométrique pour l'étude des phénomènes de ressuage et de sédimentation dans les matériaux cimentaires, Ph.D. Thesis, Université de Sherbrooke (Canada), 2006.

[17] A.W. Saak, H.M. Jenning, S.P. Shah, Influence of wall slip on yield stress and viscoelastic measurements of cement paste, Cem. Concr. Res. 31 (2001) 205–212.

[18] D.L. Kantro, Influence of water-reducing admixtures on properties of cement paste. A miniature slump test, Cem. Concr. Aggreg. 2 (1980) 95–102.

[19] APHA Standard Methods19th ed., , 1995, pp. 5–15, method 5220 D.

[20] M. Daimon, D.M. Roy, Rheological properties of cement mixes, zeta potential and preliminary viscosity studies, Cem. Concr. Res. 9 (1979) 103–110.

[21] V.S. Ramachandran, V.M. Malhotra, C. Jolicoeur, N. Spiratos, Superplasticizers: Properties and Application in Concrete, CANMET, Canada, 1998.

[22] V.S. Ramachandran, V.M. Malhotra, Superplasticizers, in: V.S. Ramachandran (Ed.), Concrete Admixtures Handbook, Noyes Publications, 1984, pp. 211–268.

[23] C. Jolicoeur, M.A. Simard, Admixture–cement interactions: phenomenology and physico-chemical concepts, Cem. Concr. Comp. 20 (1998) 87–102.

[24] H. Uchikawa, S. Hanehara, D. Sawaki, The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture, Cem. Concr. Res. 27 (1997) 37–50.

[25] V. Fernon, Étude de nouveaux solides lamellaires obtenus par coprécipitation d'hydrate aluminocalcique et de sulphonate aromatique, Ph. D. Thesis, Université d'Orléans (France), 1994.

[26] K. Luke, P.C. Aïtcin, Effect of superplasticizer on ettringite formation, in: S. Mindess (Ed.), Advances in Cementitious Materials, 16, National Institute of Standards and Technology, Gaithersburg, 1990, pp. 147–166.

[27] N. Mikanovic, Interaction superplastifiant-ciment durant l'hydratation initiale, M.Sc. Thesis, Université de Sherbrooke, Sherbrooke, 2002.

[28] R.J. Flatt, Y.F. Houst, A simplified view on chemical effects perturbing the action of superplasticizers, Cem. Concr. Res., 31 (2001) 1169–1176.

[29] J. Plank, Z. Dai, N. Zouaoui, D. Vlad, Intercalation of polycarboxylate superplasticizers into C3A hydrate phases, in: V.M. Malhotra (Ed.), Proceedings of the 8th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Sorento, 2006, pp. 201–213, SP-239-14.

[30] R.J. Flatt, C.F. Ferraris, Acoustophoretic characterization of cement suspensions, Mat. Struct. 35 (2002) 541–549.

[31] P.F.G. Banfill, A discussion of the papers "Rheological Properties of Cement Mixes" by M. Daimon and D.M. Roy, Cem. Concr. Res. 9 (1979) 795–796.

[32] P.-C. Nkinamubanzi, Influence des dispersants polymériques (superplastifiants) sur les suspensions concentrées et les pâtes de ciment, Ph. D. Thesis, Université de Sherbrooke (Canada), 1993.

[33] S. Lesko, E. Lesniewska, A. Nonat, J-C. Mutin, J.-P. Mutin, Investigation by atomic force microscopy of forces at the origin of cement cohesion, Ultramicroscopy 86 (2001) 11–21.

[34] A. Gmira, M. Zabat, R.J.-M. Pellenq, H. van Damme, Microscopic physical basis of the poromechanical behavior of cement-based materials, Mat. Struct. 37 (2004) 3–14.

[35] A.M. Kjeldsen, R.J. Flatt, L. Bergstrom, Relating molecular structure of comb-type superplasticizers to the compression rheology of MgO suspensions, Cem. Concr. Res. 36 (2006) 1231–1239.

[36] E.B. Fitch, Sedimentation process fundamentals, transactions of the American Institute of Mining, Metall. Pet. Eng. 223 (1962) 129–137.

[37] C.-K. Loh, T.-S. Tan, K.-Y. Yong, T.-H. Wee, An experimental study on bleeding and channeling of cement paste and mortar, Adv. Cem. Res. 10 (1998) 1–16.

[38] R.J. Flatt, D. Larosa, N. Roussel, Linking yield stress measurements: spread test versus Viskomat, Cem. Concr. Res. 36 (2006) 99–109.

[39] N. Roussel, C. Stefani, R. Leroy, From mini-cone test to Abrams cone test: measurement of cement-based materials yield stress using slump tests, Cem. Concr. Res. 35 (2005) 817–822.