ELSEVIER

PII:S0958-9465(97)00062-0

Cement and Concrete Composites **20** (1998) 87–101

Printed in Great Britain
0958-9465/98/$19.00

Chemical Admixture–Cement Interactions: Phenomenology and Physico-chemical Concepts

Carmel Jolicoeur & Marc-André Simard

Department of Chemistry, Université de Sherbrooke, Sherbrooke, Qué. J1K 2R1, Canada

Abstract

Chemical admixtures are often used to alter the course of cement hydration reactions and the properties of fresh or hardened concrete. The admixtures, in most cases organic compounds, can perform such functions through various types of physico-chemical interactions with the hydrating cement phases. To understand the consequences of admixture–cement interactions, and to optimize the functional properties of admixtures, appropriate descriptions of their mode of action must be developed. An overview of the latter is attempted here, drawing mainly from: (1) the chemistry and phenomenology of cement hydration; (2) a review of the various types of molecular processes in which admixture molecules can be involved at the solid–solution interface; (3) selected experimental data on the influence of water reducers and superplasticizers which illustrate some basic features of admixture–cement interactions. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: cement, silica fume admixture, water reducer, superplasticizer, interaction, adsorption, hydration. rheology, colorimetry.

INTRODUCTION

Modern concretes often incorporate several chemical admixtures, each of which may interact with the various constituents of cements, and influence cement hydration reactions. The overall consequences of admixture–cement interactions on the properties of fresh or hardened concrete may thus be difficult to rationalize, particularly in cementitious systems containing mineral additives (pozzolans or fillers).

The admixture–cement interactions may in fact be viewed as the reaction between two complex chemical systems illustrated schematically in Fig. 1. Portland cements are multi-component, multi-phasic inorganic materials, comprising major components (C_3S, C_2S, C_3A, C_4AF) and minor phases (CaO, $CaSO_4{\cdot}xH_2O$, Na, KSO_4, etc.); blended cements include additional components such as supplementary materials (slag, fly ash, silica fume) and fillers (limestone, rock flour, etc.). In a similar way, chemical admixtures often contain several components which are either inherent to the nature of the admixture or a result of their manufacturing process. For example, lignosulfonate water reducers are intrinsically complex mixtures of chemical compounds derived from chemical degradation of lignin. Synthetic admixtures, for example high-range water reducers, often contain species with a broad distribution of molecular weights, reaction by-products, or other chemicals added for a specific purpose. Hence, in order to achieve understanding of

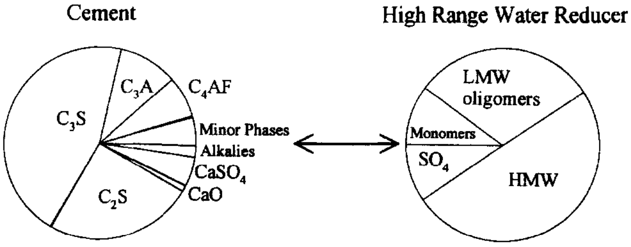


Fig. 1. Schematic illustration of the interaction between a cement (multi-phasic mineral system) and a chemical admixture (multi-component organic system).

admixture–cement (and also of admixture–admixture) interactions at a level required for optimum use of these materials, a systematic approach is essential, drawing both on experimental observations and physico-chemical concepts. The present report was prepared as an introductory overview of the phenomenology and physico-chemical concepts which currently appear relevant to cement hydration and to the influence of chemical admixtures on the cement hydration processes.

An overview of the basic chemical aspects of cement hydration will first be presented, after which the various types and purposes of chemical admixtures currently used will be recalled. The physico-chemical concepts involved in admixture–cement interactions will then be reviewed, and selected results on the influence of admixtures on cement hydration reactions will be examined. The framework will be developed with a generic perspective on all organic chemical admixtures, although most of the results cited (new or literature) will bear on water reducer and superplasticizer admixtures.

CEMENT HYDRATION

The contacting of water with Portland cement triggers a series of processes leading to hydration products which, through several types of bonding interactions, yield a dense stable matrix. An important particularity of this complex reaction is that the initial reactants are in a powdered form. Heterogeneous reactions of these powdered minerals with water involve both solution and interface (more appropriately 'interphase') processes. As shown by the broad knowledge basis derived from extensive cement hydration studies,[1–7] the formation of hydration products and the development of the microstructural features depend upon solution processes, interfacial reactions (topochemical phenomena) and, ultimately, solid-state reactions.

Cement hydration reactions: thermodynamic aspects

The hydration reactions of the major mineral phases of Portland cement have been well characterized, and generally serve as reference, or model reactions, in discussions of cement hydration chemistry, thermodynamics, or kinetics. It is broadly acknowledged, however, that the hydration reactions in Portland cement systems involve coupling of the reactions depicted in eqns (1)–(8) and thus, lead to more complex processes and products. The main pure phase hydration reactions have been given as:[8]:

$$2C_3S+6H \rightarrow C_3S_2H_3+3CH \qquad (1)$$

$$2C_2S+4H \rightarrow C_3S_2H_3+CH \qquad (2)$$

$$2C_3A+21H \rightarrow C_4AH_{13}+C_2AH_8 \qquad (3)$$

$$C_4AH_{13}+C_2AH_8 \rightarrow 2C_3AH_6+9H \qquad (4)$$

$$C_3A+3C\bar{S}H_2+26H \rightarrow C_6A\bar{S}_3H_{32} \qquad (5)$$

$$2C_3A+C_6A\bar{S}_3H_{32}+4H \rightarrow 3C_4A\bar{S}H_{12} \qquad (6)$$

$$C_4AF+3C\bar{S}H_2+29H \rightarrow C_6(A,F)\bar{S}_3H_{32}+(A,F)H_3 \qquad (7)$$

$$C_4AF+C_6(A,F)\bar{S}_3H_{32}+7H \rightarrow 3C_4(A,F)\bar{S}H_{12}+(A,F)H_3 \qquad (8)$$

Some of the key data and observations pertaining to the above reaction scheme are summarized in Table 1. Such data are used extensively in discussions of relative properties of different cements, for example, to predict the maximum heat of hydration as a function of cement composition. From the hydration reactions given above and the cement composition shown in Table 1, it can be calculated that, for common ASTM-Type I cements (Ordinary Portland Cements), the amount of water required to fully hydrate the various mineral phases is ~ 30 wt%, i.e. $W/C = 0{\cdot}30$.

The relative reactivity of the different mineral phases with water is usually given as $C_3A > C_3S > C_2S \approx C_4AF$ (absolute reactivities vary considerably depending on the degree of metal ion substitution in the phases and their crystal structure). Accordingly, the aluminate phases and their hydration products play an important role in the early hydration processes. In a general simplifying sense, the early (0–1 h)

Table 1. Hydration reactions for components of ordinary Portland cement

Component	*Typical content in OPC (wt%)*	*Hydration product*	*Hydration water (g/g_{solid})*	*$\Delta H_{hydration}$ [J/g (dry)]*
C_3S	55	C-S-H, CH	0·24	−517[a]
C_2S	20	C-S-H, CH	0·21	−262[a]
C_3A	6	Monosulfate	0·80	−1 144[a]
		Ettringite	2·13	−1 672[a]
C_4AF	9	C_6AFH_{12}	0·37	−418[a]
$CaSO_4$ (soluble anhydrite)		$CaSO_4{\cdot}2H_2O$	0·26	≈ −200[b]
$CaSO_4$ (insoluble anhydrite)	5		0·26	−124[b]
$CaSO_4{\cdot}0{\cdot}5H_2O$		$CaSO_4{\cdot}2H_2O$	0·19	−104[b]
Na, KSO_4	1	—	—	—
CaO		CH	0·32	−1 166[c]
Typical OPC		C-S-H, CH Monosulfate Ettringite	~0·3	~ −500

[a] Ref. [1], p. 232.
[b] Ref. [9].
[c] Ref. [5], p. 30.

behavior of hydrating cements is governed by reactions of the aluminate phases, particularly C_3A; the setting and early strength development behavior is mostly dependent on the hydration of silicates, particularly C_3S.

Because of the high reactivity of calcium aluminate and the undesirable properties of some of the products formed (e.g. hexagonal C–A–H), the aluminate hydration reaction is carried out in the presence of sulfate ions. The latter provide control of the reaction rate through the formation of mixed aluminate sulfate products namely ettringite (AFt) and monosulfoaluminate (AFm), i.e. reactions (5) and (6) respectively. Calcium sulfate added to the clinker can thus be viewed as a first 'chemical admixture' used to control the nature and properties of the aluminate hydration products. Sulfates thus play a crucial role in cement hydration, and the influence of chemical admixtures on any process involving sulfates may be expected to be significant.

Cement hydration: kinetic and mechanistic aspects

As noted previously, the overall process of cement hydration and setting results from a combination of solution processes, interfacial phenomena and solid-state reactions. To help visualize the influence of admixtures on cement hydration, it is useful to recall the main events of the hydration process, and the time scale over which they occur. A schematic representation of the evolution of a Portland cement hydration reaction with time is reproduced in Fig. 2 (adapted from Kondo and Diamon[10]). The latter identifies five distinct stages, the boundaries of which are determined by sharp variations in a reaction parameter, typically, the heat flux measured as a function of time. These five stages correspond respectively to (times shown are approximate):

I. Initial hydration processes (0–15 min);
II. Induction period or lag phase (15 min–4 h);
III. Acceleration and set (4–8 h);
IV. Deceleration and hardening (8–24 h);
V. Curing (1–28 days).

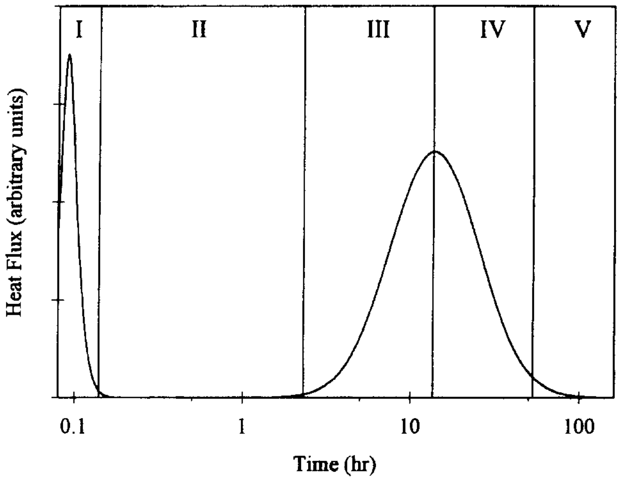


Fig. 2. Schematic cement hydration thermogram showing five distinct stages in the hydration process.

In the following examination of mechanistic aspects, we will emphasize those which may be most influenced by the presence of admixtures, particularly those occurring in the early hydration processes (e.g. 0–12 h).

Stage I: Initial hydration reactions (0–15 min)

In the first instants of the cement–water mixing, part of the easily solubilized components (Na, KSO_4, $CaSO_4{\cdot}xH_2O$) are dissolved into the aqueous phase. Simultaneously, the hydrolysis of the most reactive surface silicates and aluminates releases Ca^{2+} and OH^-, further increasing the solution concentration of these species. Since silicate and aluminate ions are soluble in highly alkaline solution, their solution concentrations will initially increase as the solution pH rises; maximum concentrations of these species however remain orders of magnitude lower than those of Na^+, K^+, Ca^{2+}, OH^- or SO_4^{2-}.[11] The most significant events occurring upon water–cement contact may thus be viewed as the wetting of the highly hygroscopic cement particles, and the solubilization of a variety of ionic species Na^+, K^+, Ca^{2+}, SO_4^{2-}, OH^-, by complete (congruent) or selective (incongruent) solubilization of the various phases present in cement. Surface hydrolysis and incongruent solubilization processes quickly lead to the formation of a thin layer of intermediate amorphous hydration products. Considering the relative reactivities of aluminates and silicates, the initial gel products should consist largely of aluminates,[12,13] though C–S–H gels can also form very rapidly on C_3S.[6]

Beyond the initial solubilization phenomena, the formation of any of the solid hydration products depicted in eqns (1)–(8) will be governed by nucleation processes; the latter may occur ‘homogeneously’ from the solution phase, or ‘heterogeneously’ at a solid–solution interface. As noted earlier, an important initial nucleation process is the formation of calcium sulfoaluminates from Ca^{2+}, SO_4^{2-} and $Al(OH)_4^-$ ions. In the case of ettringite, the reaction product can be nucleated from a homogeneous solution,[14,15] or at the C_3A–solution interface.[1,12,13] Similarly, the early nucleation of gypsum (G, $CaSO_4{\cdot}2H_2O$) following dissolution of hemihydrate (H, $CaSO_4{\cdot}0{\cdot}5H_2O$) can be initiated through solution or interface (topochemical) phenomena. The rate of these nucleation processes, particularly in homogeneous nucleation, depends on local concentration fluctuations, and on precipitation–redissolution rates, to achieve a critical size nucleus.

Following the nucleation step, the growth of the hydration products (crystalline or amorphous) will proceed at a rate determined by the bulk concentration of the solution species, the availability of water and ionic species at the reaction sites (i.e. diffusion through the solution, or through the reaction boundary), the activation energy for the molecular processes involved in the crystallization (e.g. desolvation of the ionic species) and statistical effects (e.g. orientational requirements).

As may be expected, the presence of organic admixtures which can interfere with the nucleation and/or the growth processes will influence the hydration reaction rate, the reaction products, or both.

The actual rate of the initial hydration processes (Stage I) is readily visualized in Fig. 3. The latter illustrates the heat evolved when a unit weight of clinker, or cement (from the same clinker), is immersed in excess water ($W/C = 15$) in a stirred calorimeter equipped with a fast response probe. In these systems, solubilization and early hydration are extremely rapid ($t_{0{\cdot}5} < 1$ min). Following the early heat burst, heat evolution continues at a highly reduced rate; since, in these systems, water is in large excess, it cannot be rate-limiting. The heat evolution observed beyond the first few minutes may thus be taken to reflect the progressive hydration of cement particles coated with the initial hydrate phases. As evidenced by the initial rate data in Fig. 3, after the first few minutes, the chemical admixture will be mostly interacting with hydration products.

In the latter part of Stage I (~ 15 min), the cement particles in a paste become fully coated with a layer of hydrate products. This ‘protective’ layer hinders the diffusion of reacting species in and out of the reaction interphase, thus sharply reducing the rate of the various reactions. The system enters into a period of ‘latency’ referred to as the induction, or dormant period.

Stage II: Reactions during the induction period (15 min–4 h)

As evidenced by a non-zero heat flux and changes in electrical conductance,[16,17] the pro-

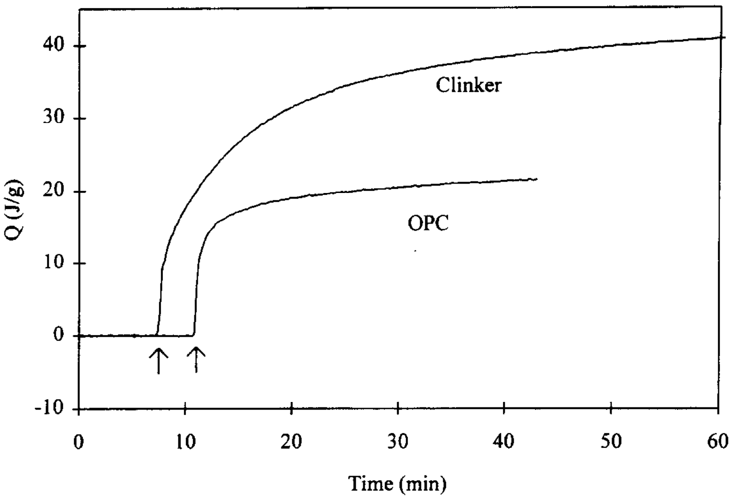


Fig. 3. Heat evolved (J/g solid) upon immersion of powdered clinker or cement in stirred excess water (W/C = 15).

cesses initiated during Stage I continue throughout the induction period. In the early part of Stage II, reactions of the aluminate phase will predominate. In addition to growth of ettringite needles (solution or interface) and to progressive thickening of the surface gel layer, other early phenomena may be observed, typically:[13] if SO_4^{2-} concentration is too low, excessive nucleation and growth of C–A–H products may occur ('flash set'); if SO_4^{2-} concentration is too high (hemihydrate, alkali sulfates), massive nucleation and growth of gypsum crystals ($CaSO_4 \cdot 2H_2O$) may be observed ('false set').

In the presence of adequate SO_4^{2-} content and availability, several physico-chemical processes will later contribute to the evolution of the cement–water system,[1,12] namely: continued growth of ettringite crystals; increased production of C–S–H gel leading to an overlay ('outer layer') of C–S–H onto the initial aluminate-rich gel layer; increasing Ca^{2+} and OH^- concentrations in solution; AFt→AFm conversion when the available SO_4^{2-} is consumed; development of osmotic and mechanical pressures on the gel layer, as the hydration front moves inwards. These processes will determine the behavior of the cementitious system, particularly its rheological properties and its initial setting time.

Again, it can readily be expected that the interaction of a chemical admixture with any of the reactive species, or its interference with diffusion, nucleation and growth processes, can impact significantly on the behavior of cement pastes and concretes during the induction period.

Stage III: Cement hydration and setting (acceleration period, 4–8 h)

Near the end of the induction period, the rate of cement hydration reactions sharply increases. The number and energy of the interactions (physical and chemical) between the 'growing' particles of the system also increase, rapidly converting the system into a stiff matrix (initial set). The transition from the 'dormant' period into the acceleration stage in cement pastes is analogous to that observed with pastes of pure C_3S. In the latter case, the following effects have been considered to explain the onset of the acceleration period.[18]

1. Disruption of the hydrate protective layer by physico-chemical transformations of the hydrates (changes in composition (e.g. Ca^{2+} depletion) or structure).
2. Break-down of the protective layer by osmotic pressure effects.
3. Nucleation and growth of C–S–H products.
4. CH nucleation and growth.

Evidences reviewed and discussed by Taylor *et al.*[19] favor a mechanism wherein the integrity of the initial 'protective' hydrate layer is altered by phase transformation; the latter simultaneously promotes C–S–H nucleation and growth, while exposing further unhydrated C_3S.

The phenomena which drive the acceleration stage of hydrating cement particles are considered analogous to those occurring in C_3S hydration. However, the critical conditions required to initiate the acceleration processes in cement pastes involve more complex reactions than in a C_3S paste. In cement systems, as the initial solubilization–hydration reaction proceeds (Stages I, II), the concentrations of many ionic species are building-up simultaneously in the pore solution; this likely leads to a supersaturation condition with respect to a variety of hydrate products. The occurrence of coupled saturation equilibria will provide linkage between the different nucleation–growth processes which could either catalyze, or inhibit, the growth of the main hydrate products. Also, the greater complexity of the 'protective' layer on hydrating cement particles relative to C_3S particles can provide additional mechanisms through which the protective layer can be disrupted. For example, hydration of the aluminate phases consumes large quantities of water [eqns (3)–(6)]; the continued formation of these hydrates at the inner surface of the protective layer (reaction front) will involve considerable volume expansion and outward mechanical pressure on this gel layer.

These, and other processes which may be invoked to explain the 'self-catalytic' behavior of cement hydration in the acceleration stage, may also be affected by chemical admixtures. A potential role of admixtures may be envisaged at several levels; first, the admixtures may influence the formation and properties (structure, permeability, strength) of the protective hydrate layer; second, admixtures remaining in the pore solution at the onset of the acceleration period, or admixture released during the transformations of the initial hydrate phases, may further influence nucleation and growth of the hydration products.

CHEMICAL ADMIXTURES FOR CONCRETE

Chemical compounds are frequently introduced in concrete for the purpose of altering one or more of its properties in the fresh or hardened state. These chemical admixtures, often found by trial and error, have been classified according to the specific function they perform, typically: water reduction, set retardation or acceleration, fluidification, air entrainment, corrosion inhibition, washout prevention, impermeabilization, shrinkage control, freeze–thaw resistance, etc. The mode of action and relative performances of many of these admixtures have been investigated in various cementitious systems.[20,21]

The American Concrete Institute provides a broad classification[22] in terms of air entraining admixtures (AEA), accelerating admixtures, water reducing (WR) and set-controlling admixtures, admixtures for flowing concretes and miscellaneous other admixtures (e.g. gas-forming, expansion-producing, permeability-reducing; corrosion-inhibiting; reducing alkali-aggregate reaction, etc.).

For specific groups of admixtures, more detailed classifications have been proposed. For example, the American Society for Testing and Materials has issued a standard specification for chemical admixtures of several product groups (Types A–G), which defines more specifically their functional properties:[23] A, water reducing; B, retarding; C, accelerating; D, water reducing and retarding; E, water reducing and accelerating; F, high-range water reducing; G, high-range water reducing and retarding.

Other functional sub-classifications have occasionally been suggested, for example, first, second and third generation high-range water reducers, depending on their performances and secondary properties.

While the functional classifications are useful for application purposes, they are of limited use in formulating concrete mixes with cements having different compositions and reactivities, or mixes which incorporate several different admixtures to achieve a desired range of properties. The successful use of admixtures under a broad range of conditions requires a minimal understanding of the basic concepts of cement chemistry and admixture–cement interactions.

In the following sections, we outline several physico-chemical concepts which often apply to admixture–cement interactions; we will also attempt to illustrate how chemical admixtures can interfere in cement hydration processes and in particle–particle interactions. In doing so, we will focus on three main groups of organic chemical admixtures, namely those used to control:

- hydration rate and setting time — retarders (e.g. sugars, hydroxyacids);
- concrete workability and porosity — water reducers and superplasticizers (e.g. lignosulfonates, salts of polynaphthalene sulfonic

acids, of polymelamine sulfonic acids, of polyacrylic acids, etc.);
- freezing and thawing behavior — air entraining agents (e.g. anionic surfactants).

The physico-chemical effects examined below may apply, in part, to inorganic admixtures (e.g. calcium salts, phosphate or phosphonate salts), which are sometimes incorporated to alter the setting and hardening behavior of cement pastes. However, reactions involving these admixtures in cementitious systems tend to be specific; hence, inorganic admixtures are less amenable to classification into generic groups.

BASIC CONCEPTS IN ADMIXTURE–CEMENT INTERACTIONS

Chemical admixtures can influence cement hydration and setting in several ways, some of which have been envisaged above. An overview of the main physico-chemical effects involved is presented below and illustrated schematically in Fig. 4. To emphasize the fact that, after the first minutes of the hydration reactions, admixture–cement interactions are best described as interactions between admixtures and cement hydration products, all illustrations show the solid–solution interface with a hydrated layer.

Surface adsorption

Most organic admixtures added in cement pastes exhibit an affinity towards the surface of cement particles, or cement hydration products; this results in significant adsorption which is depicted in Fig. 4(a) for two types of admixtures. Organic molecules bearing charged groups (e.g. SO_3^-, COO^-) can interact with the particle surface via electrostatic forces (surface charges of the particles and ionic groups of the admixture molecule). Polar functional groups (e.g. OH) of organic molecules (e.g. sugars) can also interact strongly with the highly polar hydrated phases, through electrostatic forces and hydrogen-bonding interactions. A typical admixture bearing both ionic ($-COO^-$) and polar ($-OH$) groups is sodium gluconate. With polymeric admixtures (e.g. lignosulfonates) containing hydrophobic, polar and ionic groups, the adsorption results from a sum of effects and may be further assisted by entropy gains which often stabilize the adsorbed state.

Admixtures containing significant hydrophobic groups (aliphatic or aromatic), for example surfactants used as air entraining agents, can interact with the hydrating surface either through their polar groups, or through their hydrophobic moiety, depending on the prevailing nature of the surface (hydrophobic, hydrophilic).

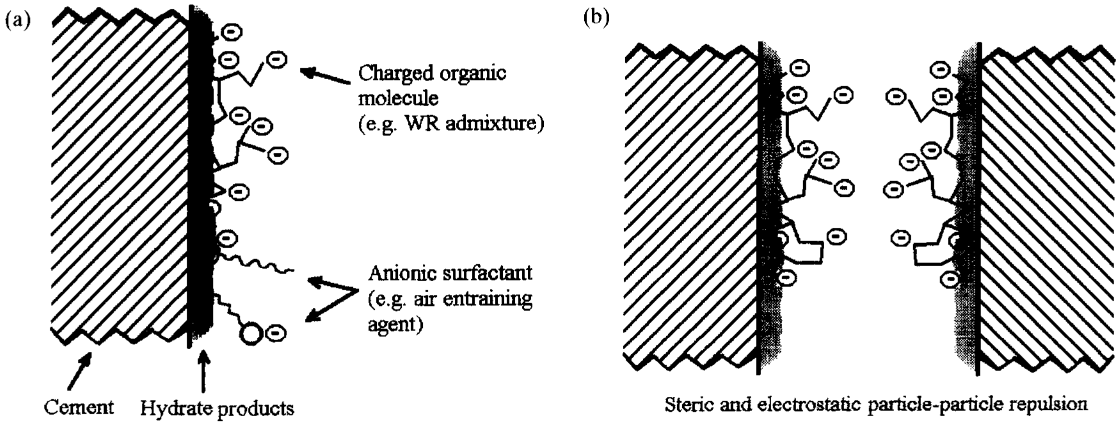
Consequences of admixture adsorption on surface properties

Precluding chemical reactions between the cement phases and the organic admixture, the adsorbed compounds will alter the surface properties of the cement particle and thus its interactions with the solution phase, as well as with other cement particles. Typically, adsorbed anionic surfactants (e.g. AEA) and polymers (e.g. WR) will convey a net negative electrical charge to the particle surface, i.e. negative zeta potential). This will induce repulsion between neighboring cement particles and thus contribute to increased dispersion [Fig. 4(b)]. In the case of high molecular weight polymers, physical interference (steric) will lead to additional short-range repulsive forces. Thus, both the 'electrostatic' and 'steric' forces contribute to the fluidification of the cement paste.[24,25] The steric effects can be seen to play an important role, since low molecular weight dispersants usually exhibit weak water reduction and low paste fluidification properties. In general, the relative importance of electrostatic and steric effects in particle–particle repulsion will depend on both the chemical nature of the polymer (composition, structure) and its molecular weight.

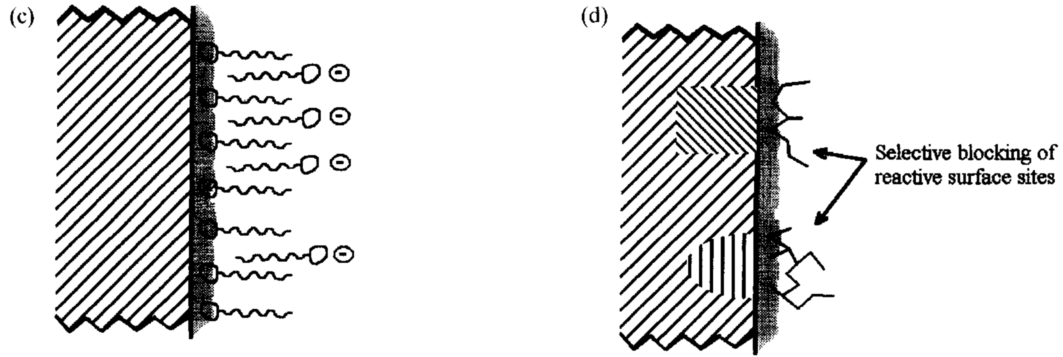
In the case of AEA, adsorption of the surfactant molecules at the cement–solution interface can induce molecular assemblies such as found in lipid layers (or bilayers) and micelles. These assemblies lead to formation of films at air–solution, or solid–solution interfaces, schematically depicted in Fig. 4(c).

Chemical processes in adsorption of admixtures

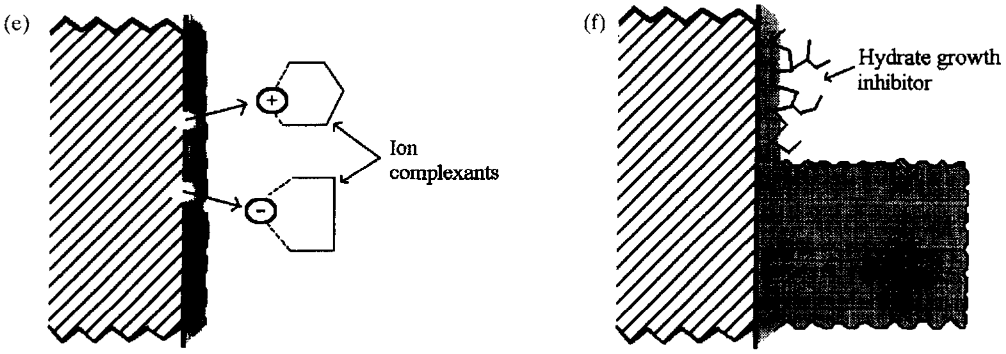
Because of the high reactivity of the various mineral phases of cements, organic admixtures can participate in, or interfere with several distinct chemical phenomena.

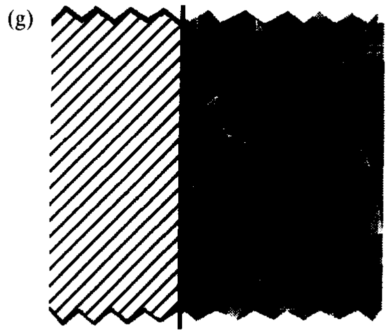


Steric and electrostatic particle-particle repulsion



Film formation at solid-solution (or air-soltion) interface





Cement hydration phases modified by admixture intercalation

Fig. 4. Schematic illustration of various physico-chemical effects which may occur upon interaction of chemical admixtures with cement particles at the interface (interphase) with the pore solution. Particle surfaces are shown with a hydrate layer, depicting the situation prevailing very shortly after contact between cement and water: (a) adsorption of organic molecules at the cement–solution interface; (b) particle–particle repulsion due to electrostatic forces (repulsion between like charges) and steric repulsive forces; (c) layered molecular organization (films) resulting from adsorption of surfactants at solid–solution interfaces; (d) preferential adsorption of organic admixtures on specific surface sites; (e) complexation and solubilization of ionic species; (f) hydrate crystal nucleation and growth inhibition by adsorbed organic admixture; (g) intercalation of the admixture in the cement hydrate products with structural alteration.

First, specific surface reactions can occur at the most reactive sites of the cement particle surface; this is illustrated schematically in Fig. 4(d), with organic molecules chemically adsorbed (reacted) at specific surface sites. As noted earlier, SO_4^{2-} ions act as a specific admixture reacting preferentially with aluminate phases exposed on the particle surface. Sulfonated superplasticizers (e.g. polynaphthalene sulfonates [PNS]) have also been shown to interact more specifically with aluminate phases,[26–30] competing with SO_4^{2} ions. As evidenced by the rate-controlling effect of SO_4^{2-} ions on the hydration of C_3A, specific cement–admixture interactions can exert a profound influence on the cement hydration rate from the very beginning of the hydration process.

Many organic admixtures, for example sugars and hydroxy carboxylic acids, can help solubilize ionic species (e.g. Ca^{2+}, SiO_x^{n-}, $Al(OH)_4^-$[1,31]), through association or complexation, as illustrated schematically in Fig. 4(e). On the one hand, complexation reactions can accelerate dissolution processes and initial reaction rates (e.g. sugar adsorption on C_3A[31]). On the other hand, complexation allows higher concentrations of the ionic species in the solution phase, which can delay the precipitation of insoluble hydrates [e.g. $Ca(OH)_2$, C–S–H]. However, complexation reactions are usually stoichiometric, so their influence vanishes once the admixture has been consumed.

Whether the adsorption of admixtures occurs in a specific, or in a non-specific way, it is likely to influence the cement hydration processes. The presence of organic molecules at the solid–solution interface can inhibit crystal nucleation and growth [Fig. 4(f)]. Adsorption occurring on a nucleation center may prevent the nucleus from achieving a minimum critical size. On the other hand, the growth of hydrate products in the presence of sorbed admixtures may result in structural alteration by intercalation depicted in Fig. 4(g), and/or changes in the morphology of the hydrate particles.[30,32] It is noteworthy, however, that adsorption of either lignosulfonate, sugar or gluconate does not appear to retard the formation of ettringite.[33]

CHEMICAL ADMIXTURE–CEMENT INTERACTIONS: SELECTED EXAMPLES

The manifestations of admixture–cement interactions have been extensively investigated in dilute slurries and pastes of cements, or of pure C_3S, C_3A, etc. phases.[14,17,24–36] Selected experimental observations are presented below which illustrate the consequences of admixture–cement interactions on the hydration reaction, on the rheological behavior and on the setting of cementitious systems. The data shown pertain mostly to PNS superplasticizers and will be discussed in relation to the concepts outlined above on cement hydration and on the behavior of organic molecules at reactive solid–solution interfaces.

Initial admixture–cement interactions (Stage I)

The adsorption of a PNS superplasticizer on OPC, and OPC with 8% silica fume (OPC–SF) and silica fume (20 m^2/g), is illustrated in Fig. 5. The data were obtained 10 min after initial contact of the material with the solution containing the admixture. The quantities adsorbed were normalized to unit BET (N_2) surface area of the dry solids (mg/m^2) and plotted as a function of the free PNS concentration ($[PNS]_{soln}$) in solution at the time of the measurement.

Under the conditions of the experiment (near neutral pH, negative surface potential), silica (silica fume or powdered quartz) adsorbs relatively low amounts of PNS, independently of the solution concentration; the adsorption data for the cements, normalized at unit surface area, show 5–10 fold higher PNS adsorption values, the latter depending on the solution concentration of the admixture. It is noteworthy that the normalized adsorption of the cement

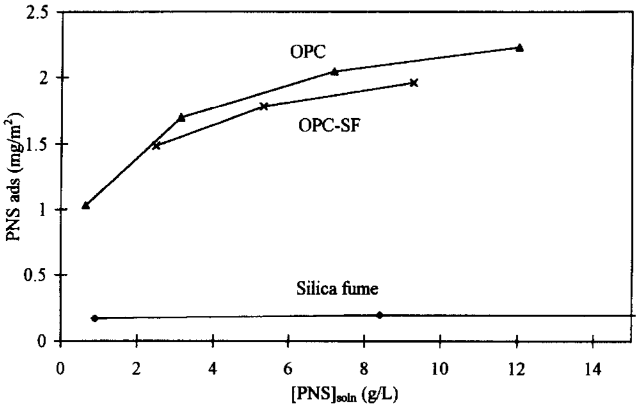


Fig. 5. Adsorption of PNS measured at 10 min in pastes of cements (OPC, OPC+8% SF) and silica fume (20 m^2/g) as a function of 'free' PNS concentration in solution. Cement pastes: $W/C = 0{\cdot}35$;[42] SF paste: $SF/W = 0{\cdot}5$, pH 13 (data derived from ref. [37]).

containing silica fume (the latter accounting for a large fraction of the surface area) is comparable to that of the OPC. This has been attributed to the influence of Ca^{2+} ions which promote PNS adsorption on silica and on other 'inert' minerals.[37–40]

As noted in the preceding section, the adsorption of PNS (and many other chemical admixtures[31]) occurs preferentially onto the aluminate phases. It has also been reported to depend on the alkali content (Na_2SO_4, K_2SO_4) of cements; in the presence of these salts, the amount of adsorbed PNS is reduced.[41]

The consequences of initial adsorption of the PNS admixture can be seen in various ways, namely in paste rheological properties and in the early hydration rates, as illustrated in Fig. 6 and Fig. 7.

The fluidity of cement pastes (same pastes as in Fig. 5) and of a paste of ground quartz (mean diameter 8 μm; W/Q = 0·38) is illustrated in Fig. 6 as a function of the total amount of PNS added to the system. Due to the repulsive forces (electrostatic, steric) induced between particles by adsorbed PNS molecules [Fig. 4(b)], the fluidity of all systems increases markedly in the presence of the admixture. Clearly, however, much greater amounts are required to achieve high fluidity in cementitious systems, relative to inert systems (quartz); this is consistent with the adsorption data shown in Fig. 5. As mentioned above for PNS adsorption, the presence of Ca^{2+} ions ($CaCl_2$) has a marked effect on the fluidity of pastes of silica minerals (in this case, quartz). Also, a greater amount of PNS admixture is required to achieve particle–particle repulsion and fluidification with the OPC–SF pastes, in agreement with the larger surface area of this blended cement.

Figure 7 shows the initial heat of hydration for several systems under conditions identical to those of data shown in Fig. 3, i.e. heat of immersion at W/C = 15. Figure 7(a) illustrates the influence of $CaSO_4$ and a PNS admixture on the initial heat of hydration of clinker (immersion in water, or in a solution of the admixture). For comparison, the heat evolution observed with a pure powdered C_3A sample is also included in Fig. 7(a). The results of these experiments show that polynaphthalene sulfonates can sharply reduce the heat generated during the very early hydration processes. The inhibitory influence of PNS on the surface

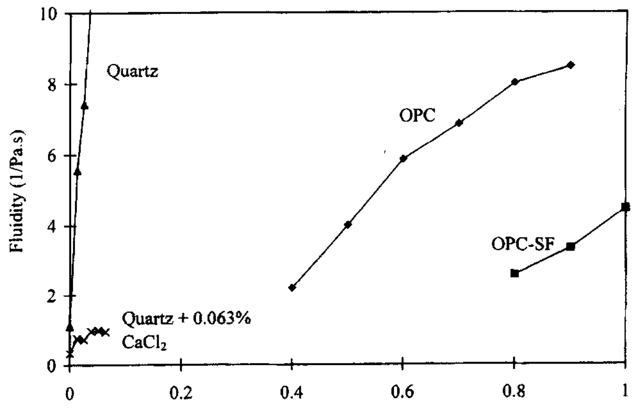


Fig. 6. Fluidity (1/η) values obtained at shear rate ~95 s^{-1} for pastes of cements (as in Fig. 5) or quartz (W/Q = 0·38), the latter having a surface area close to that of the OPC cement (here, the PNS concentration shown is the total added) (data from refs [38,42]).

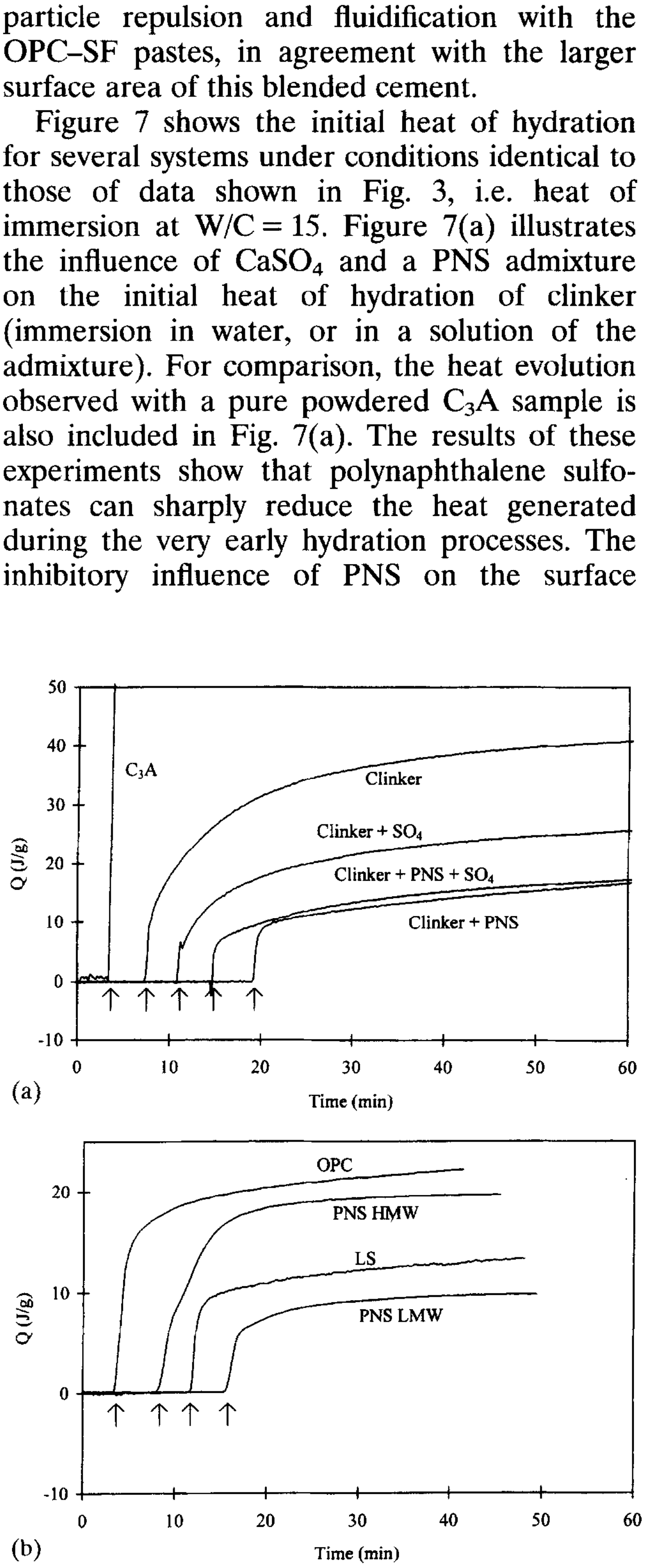


Fig. 7. Heat evolved upon initial (contact) hydration when cementitious materials are immersed in water or in solution of various admixtures A. The arrows indicate the beginning of the experiment (data from ref. [27]). (a) SO_4: calcium sulfate; [SO_4^{2-}] = 0·08 g/100 g solution; SO_4^{-2}/C = 1·3%. PNS: polynaphthalene sulfonate; [PNS] = 0·42 g/100 g solution; PNS/C = 6·9%. PNS+SO_4: same concentrations as above. (b) PNS HMW, LMW: respectively high and low molecular weight PNS; LS: lignosulfonates; [A] = 0·42 g/100 g solution, A/C = 6·9%.

hydration of clinker may even exceed that observed with $CaSO_4$ [the $CaSO_4$ solution concentration was 4 mM, while that of PNS (monomeric unit) was 16 mM]; the combined influence of $CaSO_4$ and PNS is comparable to that of PNS alone.

As shown by the data in Fig. 7(b), the inhibitory effect of admixtures on hydration reactions is also marked with the Portland cement. The effectiveness of admixtures is further seen to depend on their chemical nature and molecular features; moreover, low molecular weight (LMW) PNS appears significantly more effective than the high molecular weight (HMW) analog, at the same solution concentration. Lignosulfonates (LS) also induce a major reduction of the initial heat of cement hydration.

The specific behavior of admixtures reflected by the initial heat of hydration data strongly argues in favor of selective admixture–cement interactions involving: (1) preferential adsorption at most reactive sites [Fig. 4(d)] and (2) efficient inhibition of nucleation and growth of the hydrate products [Fig. 4(f)]. Variations in the shape of the hydration thermograms of different admixtures (e.g. comparing LS and PNS) point to further specificity in the mode of action of these admixtures. Although the latter effects have not yet been investigated in detail, the observations discussed above emphasize the significance of admixture–cement interactions in the first instants of the hydration process (Stage I).

Admixture–cement interactions during the induction period (Stage II)

The influence of admixture–cement interactions on phenomena occurring during the induction period can be seen from the time dependence (15 min–2 h) of the reaction parameters used to characterize Stage I effects, namely adsorption, rheology and heat evolution.

Fig. 8 illustrates the decrease of 'free' PNS superplasticizer in the solution phase of pastes (OPC, OPC–SF) as a function of time. The adsorption data plotted in this way, i.e. fractional concentration of free PNS, further illustrate the importance of admixture adsorption during the first few minutes of the hydration reaction. Beyond the rapid initial adsorption (to 'saturate' the most reactive phases), the admixture uptake by the hydrating cement continues at a reduced rate. At that stage, continued adsorption occurs, mainly due to the growth of new hydrate particles.

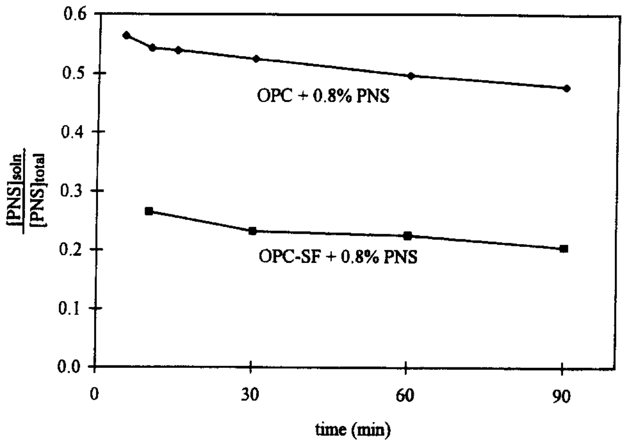


Fig. 8. Evolution of the solution concentration of PNS in pastes of OPC and OPC–SF cements as a function of time (W/C = 0·35; $[\mathrm{PNS}]_{\mathrm{total}}$ = 0·8 wt%).[42]

The progressive consumption of the PNS admixture impacts on the reaction rates and rheological properties of the hydrating pastes. This is readily seen from the evolution of paste fluidity data as a function of time in Fig. 9. As the solution concentration of 'free' admixture decreases, the fluidity of the cement pastes progressively decreases with time. While slump loss is expected from the evolution of the cement hydration reactions (see below), the fluidity would readily be maintained by a periodic redosage of small amounts of PNS into the paste. In a more detailed study of cement paste rheology as a function of time, temperature and PNS concentration, fluidity measured by mini-slump data was found qualitatively correlated to $[\mathrm{PNS}]_{\mathrm{soln}}$, beyond a certain threshold value of the latter. This threshold was found to depend

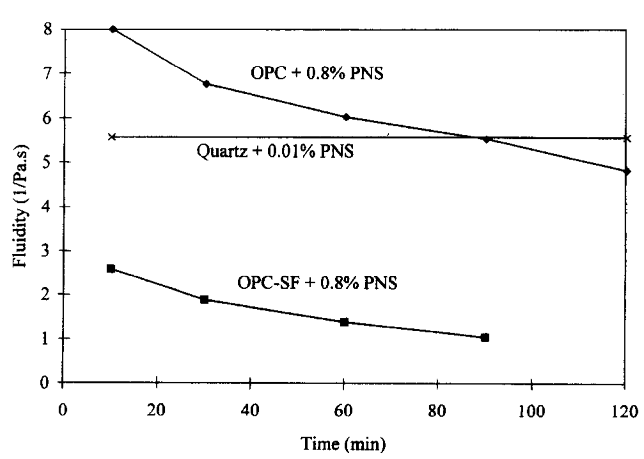


Fig. 9. Fluidity ($1/\eta$, shear rate 95 s^{-1}) of pastes of cements (OPC, OPC–SF; W/C = 0·35; 0·8 wt% $[\mathrm{PNS}]_{\mathrm{total}}$ and ground quartz (W/Q = 0·38; 0·01 wt% $[\mathrm{PNS}]_{\mathrm{total}}$) (data from refs [38,42]).

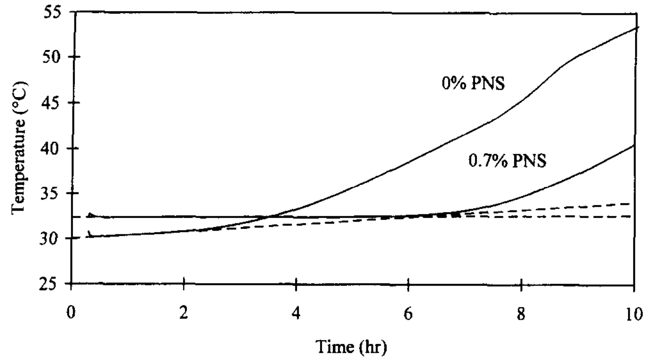


Fig. 10. Hydration thermogram (adiabatic) of OPC cement pastes (W/C = 0·35) with and without PNS ($[PNS]_{total}$ = 0·7%) measured at 30°C.[42]

on cement type and temperature,[42] and its magnitude likely reflects the minimum PNS concentration required to counteract the slump loss due to the cement hydration processes.

The role of the PNS admixture on the hydrating reactions in the induction period can also be seen from thermograms such as that reproduced in Fig. 10. The rate of the hydration processes is substantially reduced in the presence of the PNS admixture, in agreement with the inhibitory effect of PNS on the initial hydration reactions in dilute slurries. The low heat output observed in the cement paste containing PNS suggests, in fact, that very limited amounts of new hydrate products are formed during the dormant period. In such a case, the PNS consumption would mainly result from adsorption on nucleating hydrate particles and intercalation into hydrate phases already formed. With this type of WR admixture, intercalation yielding new 'organo-mineral' phases has been observed experimentally with ettringite.[32,43] The main role of the PNS admixture during the induction period is thus to inhibit the development of hydrate particles.

Admixture–cement interactions in the acceleration period (Stage III)

As a result of admixture–cement interactions in Stages I and II, the onset of the acceleration period can be substantially postponed. This is indeed observed from measurements of initial setting times, or from calorimetric data such as that shown in Fig. 11.[29] While a low concentration of PNS (0·5 wt%) decreases the apparent setting time (as a result of improved dispersion and water–cement contact), increasing PNS concentrations are seen to lengthen the induction period and retard setting of the pastes. Judging from the shape of the hydration thermograms, the PNS admixture has, however, little influence on the hydration processes in the acceleration period and throughout the hardening period, i.e. 24 h. A weak reduction of the maximum heat flux indicates a minor role of the PNS admixture in this part of the hydration process.

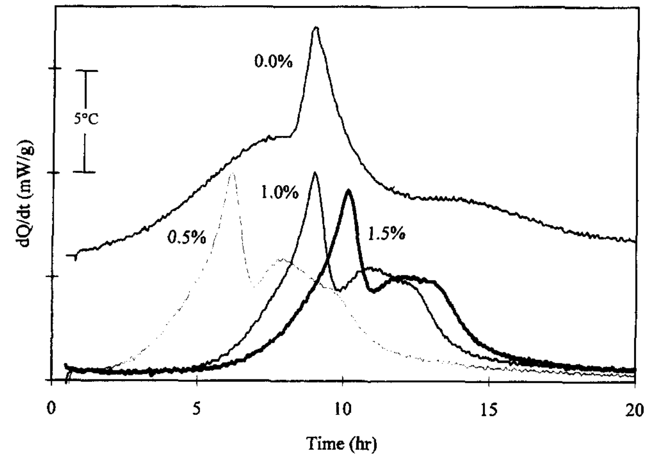


Fig. 11. Heat flux evolved from OPC cement pastes (W/C = 0·35) under adiabatic conditions with varying concentrations of PNS admixture. For clarity of presentation, the reference curve (PNS = 0) is vertically offset.[29]

This is readily understood since, at the end of the induction period, there remains only low quantities of free PNS in the intersticial solution. The latter is insufficient to control the massive nucleation–reaction–precipitation processes triggered when the initial (protective) hydrate layers are disrupted. More significant effects of the admixture could be observed if the admixture itself participated in, or catalyzed, the hydrate formation (e.g. Ca^{2+} salts). Likewise, more important effects might be seen if some phase transformations of the hydrates products released the admixture into the solution during the acceleration stage.

CONCLUSION

Admixture–cement interactions, examined above through selected results for high-range water reducers in cement pastes, involve a diversity of phenomena. Tentatively, these can be rationalized from the physico-chemical processes associated with cement hydration and several concepts of surface and colloid chemistry.

In Stage I of the cement hydration reaction (0–15 min), the PNS admixture is promptly adsorbed in multi-layer quantities; this results in a highly efficient control of the early hydration reactions and rheological properties, through a combination of the following mechanisms:

- bulk adsorption occurs on all mineral components of pastes or concretes;
- the adsorbed PNS molecules induce repulsive interactions (electrostatic, steric) between neighboring particles, increasing dispersion and fluidification;
- via their SO_3^- groups, PNS molecules (particularly low molecular weight species) adsorb more specifically on the hydrating aluminate phases, competing effectively with SO_4^{2-} ions for reaction sites;
- surface-adsorbed PNS inhibits the growth of the hydrate products;
- PNS molecules remaining in the intersticial solution inhibit homogeneous nucleation of hydrate products.

PNS can further interfere with sulfates by adsorbing onto the hemihydrate and delaying conversion of the latter into gypsum.[44] On the other hand, complexation of ionic species by PNS molecules does not appear to play a significant role.[45]

During Stage II (induction period), a continuous slow uptake of the PNS admixture takes place on the hydration products of the different mineral phases. The following effects appear involved:

- relatively low concentrations of $[PNS]_{soln}$ efficiently inhibit nucleation and growth of the hydrate phases, as well as the interactions between these phases;
- modified hydrate products appear, incorporating the admixture (intercalation);
- PNS molecules reducing the production rate of hydrates, and maintaining repulsive forces between neighboring particles, ensure retention of paste fluidity.

Synergy between $CaSO_4$ and PNS molecules could provide further control of hydration and rheology if PNS adsorbed early on hemihydrate (H) crystals is released upon H→G (gypsum) conversion.

The influence of admixture in Stage III (acceleration) of cement hydration is indirect (unless the admixture participates in the reaction, e.g. some Ca^{2+} salts) and more difficult to generalize. For PNS, at the end of the induction period, there remains little 'free' PNS molecules and the hydration processes do not appear to be altered once the admixture has been 'consumed'. Secondary effects can, however, be envisaged as follows:

- the induction period being extended, the hydrated phases may have undergone partial transformation, and their reactivity may be altered;
- PNS molecules may be released into the pore solution upon phase transformation of hydrate products during the acceleration period.

The effects summarized above in the case of PNS superplasticizers should apply to other types of high-range water reducers, allowing for intrinsic differences due to chemical composition and reactivity. Likewise, the physicochemical concepts used to describe the phenomena can, to varying degrees, be used to explain the mode of action of a broad variety of concrete admixtures, namely water reducers and retarders. The integrated approach presented here to describe the chemical 'admixture–cement' interactions, although limited by the lack of detailed relevant data and the simplicity of the concepts used, should prove useful in optimizing admixture properties and applications. It should also help develop more accurate models to simulate the evolution of the chemistry and microstructure of hydrating cementitious systems.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec and Handy Chemicals Ltd. The assistance of Mr. Jeff Sharman, Pierre Gagné, Pierre-Claver Nkinamubanzi and Martin Piotte for data collection and treatment is also gratefully acknowledged. The authors are also grateful to Professor Pierre-Claude Aïtcin for numerous discussions on admixture–cement interactions.

REFERENCES

1. Taylor, H. F. W., *Cement Chemistry*. Academic Press, London, 1990, 475 pp.

2. Skalny, J. & Young, J. F., Mécanismes d'hydratation du ciment portland. In *Proceedings of 7th Congrès international de la chimie des ciments*, Paris, Vol. 1, 1980, II.1/4–1/52.
3. Taylor, H. F. W., Chemistry of cement hydration. In *Proceedings of 8th International Congress on the Chemistry of Cement*, Rio de Janeiro, Vol. I, 1986, pp. 82–110.
4. Massazza, F. & Daimon, M., Chemistry of hydration of cements and cementitious systems. In *Proceedings of 9th International Congress on the Chemistry of Cement*, New Delhi, Vol. 1, 1992, pp. 383–446.
5. van Breugel, K., Simulation of hydration and formation of structure in hardening cement-based materials. Ph.D. Thesis, Proefshrift Technische Universiteit, Delft, The Netherlands, 1991, 295 pp.
6. Damidot, D. & Nonat, A., Investigations of the C_3S hydration process during the first hours of hydration. In *Hydration and Setting of Cements, Proceedings of the International RILEM Workshop on Hydration and Setting*, Eds. A. Nonat & J. C. Mutin, Dijon, 1991, pp. 23–35.
7. Ramachandran, V. S. & Feldman, R. F., Cement science. In *Concrete Admixtures Handbook, Properties, Science, and Technology*, Ed. V. S. Ramachandran. Noyes Publications, Park Ridge, NJ, 1984, pp. 1–53.
8. Mindess, S. & Young, J. F., *Concrete*. Prentice Hall, Englewood Cliffs, NJ, 1981, pp. 76–83.
9. Bénard, J., Calcium, combinaisons avec le soufre. In *Nouveau traité de chimie minérale*, Ed. P. Pascal, Tome IV. Masson, Paris, 1958, pp. 424–431.
10. Kondo, R. L. & Diamon, M., cited in Young, J.-F., A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures. *Cement and Concrete Research*, **2** (1972) 415–433.
11. Taylor, H. F. W., *Cement Chemistry*. Academic Press, London, 1990, p. 227.
12. Scrivener, K. L., Ph.D. Thesis, University of London, 1984, cited in ref. [1], p. 222.
13. Skalny, J., Jawed, I. & Taylor, H. F. W., Studies on hydration of cement, recent developments. *World Cement Technology*, September (1978) 183–195 (and refs [5] and [6] cited in this reference).
14. Bassant, J.-B., Nouvelles méthodes d'étude de formation d'hydrates des ciments-applications à l'analyse de l'effet d'adjuvants organiques. Ph.D. Thesis, Université de Franche-Comté, 1990, 194 pp.
15. Mehta, P. K., Scanning electron microscopic studies of ettringite formation. *Cement and Concrete Research*, **6** (1976) 169–182.
16. Vernet, C., Demoulian, E., Gourdin, P. & Hawthorn, F., Cinétique de l'hydratation du ciment Portland. In *Proceedings of 7th Congrès international de la chimie des ciments*, Paris, Vol. 2, 1980, II-219–II-224.
17. Vernet, C. & Noworyta, G., Conductometric test for cement–admixture systems. In *Proceedings of 9th International Congress on the Chemistry of Cement*, New Delhi, Vol. 4, 1992, pp. 627–633.
18. Taylor, H. F. W., *Cement Chemistry*. Academic Press, London, 1990, p. 163.
19. Taylor, H. F. W., Barret, P., Brown, P. W., Double, D. D., Frohnsdorff, G., Johansen, V., Smidth, F. L., Ménétrier-Sorrentino, D., Odler, I., Parrott, L. J., Pommersheim, J. M., Regourd, M. & Young, J. F., The hydration of tricalcium silicate. *Matériaux et constructions. Essais et recherches*, **17** (1984) 457–468.
20. Dodson, V., *Concrete Admixtures*. Van Nostrand Reinhold, 1990, 211 pp.
21. Rixom, M. R. & Mailvaganam, N. P., *Chemical Admixtures for Concrete*, Eds. E.&F. N. Spon, 2nd edn., 1986, 275 pp.
22. ACI Committee 212, Chemical admixtures for concrete. In *ACI Manual of Concrete Practice 1996. Part I: Materials and General Properties of Concrete*. American Concrete Institute, 1996, 212.3R-1–212.3R-31.
23. ASTM C 494-90, Standard Specification for Chemical Admixtures for Concrete.
24. Jolicoeur, C., Nkinamubanzi, P.-C., Simard, M.-A. & Piotte, M., Progress in understanding the functional properties of superplasticizers in fresh concrete. In *Proceedings of 4th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, Ed. V. M. Malhotra. ACI SP-148, 1994, pp. 63–88.
25. Uchikawa, H., Hanehara, S. & Sawaki, D., The role of steric repulsive force in the dispersion of cement particles in fresh pastes prepared with organic admixture. *Cement and Concrete Research*, **27** (1997) 37–50.
26. Ramachandran, V. S. & Malhotra, V. M., Superplasticizer. In *Concrete Admixtures Handbook, Properties, Science, and Technology*, Ed. V. S. Ramachandran. Noyes Publications, Park Ridge, NJ, 1984, pp. 211–268.
27. Gagné, P., Chaleur d'hydratation initiale de ciments en présence de divers adjuvants. M.Sc. Thesis, Université de Sherbrooke, Canada, 1993.
28. Bonen, D. & Sarkar, S. L., The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss. *Cement and Concrete Research*, **25** (1995) 1423–1434.
29. Simard, M.-A., Nkinamubanzi, P.-C., Jolicoeur, C., Perraton, D. & Aïtcin, P.-C., Calorimetry, rheology and compressive strength of superplasticized cement paste. *Cement and Concrete Research*, **23** (1993) 939–950.
30. Massazza, F. & Costa, U., Effects of superplasticizers on the C_3A hydration. In *Proceedings of 7th Congrès international de la chimie des ciments*, Paris, Vol. IV, 1980, pp. 529–534.
31. Young, J.-F., A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures. *Cement and Concrete Research*, **2** (1972) 415–433.
32. Luke, K. & Aïtcin, P.-C., Effect on superplasticizer on ettringite formation. In *Conference on Advances and Cementitious Materials*, National Institute of Standards and Technology, Gaithersburg, MD, July 1990, 17 pp.
33. Collepardi, M., Monosi, S., Moriconi, G. & Pauri, M., Influence of gluconate, lignosulfonate or glucose on the C_3A hydration in the presence of gypsum with or without lime. *Cement and Concrete Research*, **14** (1984) 105–112.
34. Ramachandran, V. S., Interaction of chemical admixtures in the cement–water system. *Il Cemento*, **83** (1986) 13–38.
35. Ramachandran, V. S., Interaction of calcium lignosulfonate with tricalcium silicate, hydrated tricalcium silicate and calcium hydroxide. *Cement and Concrete Research*, **2** (1972) 179–194.
36. Ramachandran, V. S., Use of superplasticizers in concrete. *Il Cemento*, **84** (1987) 273–298.
37. Diamond, S. & Struble, L. J., Interaction between naphtalenesulfonate and silica fume in Portland cement pastes. *Mater. Res. Soc. Symp. Proc.*, **114** (1988) 117
38. Nkinamubanzi, P.-C., Influence des dispersants polymériques (superplastifiants) sur les suspensions concentrées et les pâtes de ciment. Ph.D. Thesis, Uni-

versité de Sherbrooke, Canada, 1993.

39. Pierre, A., Carquille, C., Lamarche, J. M., Foissy, A. & Mercier, R., Adsorption d'un polycondensat d'acide naphtalène sulfonique (PNS) et de formaldehyde sur le dioxyde de titane. *Cement and Concrete Research*, **18** (1988) 18–28.
40. Pierre, A., Lamarche, J. M., Mercier, R. & Foissy, A., Adsorption d'un fluidifiant du ciment sur le carbonate de calcium. *Cement and Concrete Research*, **19** (1989) 692–702.
41. Nawa, T., Eguchi, H. & Fukaya, Y., Effect of alkali sulfate on the rheological behavior of cement paste containing a superplasticizer. In *Proceedings of the 3rd CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, Ed. V. M. Malhotra. ACI SP-119, 1989, pp. 405–424.
42. Jolicoeur, C., Sharman, J., Otis, N., Lebel, A., Simard, M.-A. & Pagé, M., The influence of temperature on the rheological properties of superplasticized cement pastes. To be presented at the *Proceedings of the 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, Ed. V. M. Malhotra. ACI Symposium, Rome, 1997, pp. 379–405.
43. Fernon, V., Étude de nouveaux solides lamellaires obtenus par coprécipitation d'hydrate aluminocalcique et de sulfonate aromatique. Ph.D. Thesis, Université d'Orléans (France), 1994.
44. Jolicoeur, C., Simard, M.-A., Aïtcin, P.-C. & Baalbaki, M., Cement–superplasticizer compatibility in high-performance concretes. In *Proceedings from the Half-day Open Presentations of the 4th Semi-annual Meeting of the Network of Centres of Excellence on High-Performance Concrete*, Toronto, 1992, pp. 9–29.
45. Piotte, M., Caractérisation du poly(naphtalènesulfonate). Influence de son contre-ion et de sa masse molaire sur son interaction avec le ciment. Ph.D. Thesis, Université de Sherbrooke, Canada, 1993.