Cement and Concrete Research 41 (2011) 1289–1309

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Impact of admixtures on the hydration kinetics of Portland cement

J. Cheung [a],*, A. Jeknavorian [a], L. Roberts [b], D. Silva [a]

[a] W.R. Grace, 62 Whittemore Avenue, Cambridge MA 02140, USA
[b] Roberts Consulting Group LLC, 44 Windsor Avenue, Acton MA 01720, USA

ARTICLE INFO

Article history:
Received 29 January 2010
Accepted 8 March 2011

Keywords:
Admixture (D)
Cement (D)
High calcium fly ash (D)
Hydration (D)
Sulfate balance (D)

ABSTRACT

Most concrete produced today includes either chemical additions to the cement, chemical admixtures in the concrete, or both. These chemicals alter a number of properties of cementitious systems, including hydration behavior, and it has been long understood by practitioners that these systems can differ widely in response to such chemicals.

In this paper the impact on hydration of several classes of chemicals is reviewed with an emphasis on the current understanding of interactions with cement chemistry. These include setting retarders, accelerators, and water reducing dispersants. The ability of the chemicals to alter the aluminate–sulfate balance of cementitious systems is discussed with a focus on the impact on silicate hydration. As a key example of this complex interaction, unusual behavior sometimes observed in systems containing high calcium fly ash is highlighted.

Contents

---

* Corresponding author.
E-mail address: Josephine.H.Cheung@grace.com (J. Cheung).

0008-8846/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2011.03.005

1. Introduction

Over the last two decades much progress had been made in cement hydration modeling [1–11]. A majority of this work has necessarily focused on simple systems, usually, but not exclusively, without admixtures. Today, application of new experimental techniques and insights are rapidly changing our conceptual understanding of the critical early hydration behavior of cement, which the mathematics of models must now capture. Recently, the strong acceleratory effects of C–S–H seeds have been demonstrated [12], and the exact timing of development of shells around hydrating alite grains has been elucidated [13]. Further, advances have been made to incorporate dissolution theory from geochemistry into early hydration models [14]. Taken together, these call into question many of the past theories which depended on invoking a continuous protective barrier during the induction period of silicate hydration. Also, a number of workers have elucidated clearly the remarkable ability of the AFm phase to intercalate many organic components of admixtures [15–21], providing an alternative to simple surface adsorption on aluminate hydration products. These findings help explain the previously noted sensitivity to the time of chemical addition, and should be accounted for in models to predict cement-admixture system behaviors.

Admixtures have been used in the production of concrete for at least two millennia, but their application has accelerated greatly in the last four decades. Today, admixtures commonly used in production concrete can contain *set retarding or set accelerating* chemicals, which obviously will directly impact kinetics. Most concrete made in developed countries also uses at least a cement dispersing agent, commonly called *water reducing* or *plasticizing* admixture. Those water reducing admixtures that can exhibit a more powerful dispersing capability, without significantly impacting setting behavior, are called a *high-range water reducing admixture* or *superplasticizer*. By virtue of the resulting improved dispersion, these materials both increase workability and reduce the amount of agglomerated cement particles. These agglomerates can lead to low w/c regions, which limits cement hydration in those areas, while allowing other regions to be higher than nominal w/c. Thus water reducing admixtures can often lead to improvement in strength and permeability even at equal w/c. If a water reduction is also taken, more substantial improvements in both are achieved. Water reducing admixture compositions may also include materials that directly impact hydration rates beyond the dispersion effects. Such admixtures frequently contain some combination of set retarding and accelerating components. This is because many dispersing materials, which meet required economic constraints, also retard hydration somewhat, and adjustment of setting time is needed to meet both industry standards and field requirements.

Other, less widely applied admixtures can inhibit corrosion of steel in concrete, adjust complex rheological behavior, entrain air to impart resistance to freezing and thawing, and provide many other attributes. Some of these materials, while having a primary impact on properties not related to hydration kinetics, may have secondary effects on hydration which must be accounted for in concrete mixture design. Therefore, understanding how hydration kinetics of cementitious systems is affected by admixtures is essential, if kinetics is to be applied for improved design and control of concrete production.

In most cases, despite the very large variety of cements, admixtures, supplementary cementitious materials (SCM's) and conditions encountered by concrete producers, predictable performance can be achieved, otherwise the concrete industry would suffer far more problems than it does. However, in some cases unexpected slump loss, excessive fast or slow set, and/or poor or absent strength development can occur. The concrete industry has had an on-going challenge to minimize these unexpected events, which can cause major disruptions of construction schedules.

As admixtures can have a very strong impact on the hydration behavior of cementitious systems, the ruggedness of models can be challenged by testing their ability to predict setting and strength development with those admixtures. It is the purpose of this paper to highlight the impact of various cement-admixture interactions on the rate of cement hydration, with the expectation of advancing the cement research community's ability to model hydration kinetics. Providing a thorough review of this highly complex topic is beyond the scope of this study. Rather, focus will be on selected cement-admixture response questions, whose analysis is expected to help contribute to a more comprehensive model of cement hydration kinetics. These questions are:

- Importance of sulfate – What is the precise mechanism whereby undersulfated cements, or C_3S in the presence of C_3A and inadequate sulfate, fail to achieve normal silicate hydration? Why do admixtures frequently exacerbate this situation?
- Impact of retarders and accelerators – What are the elementary steps for acceleration and retardation? Why is cement response to retarders so sensitive to exact chemical structure, including stereoisomerism? Why is cement response to accelerators similarly sensitive to composition, even at equimolar doses?
- Impact of water reducers and superplasticizers – Why are dispersing power and retention of dispersing power optimized by different structures of the water reducing agents? How do the dispersing agents interact with the different compositions of the cementitious matrix? How do water reducing dispersants compete with other admixtures including sulfates, and which dominates? Why do most water reducing admixtures provide improved response when added with a few minutes delay?
- High calcium fly ash interactions – Why do cementitious mixtures containing high calcium fly ash show increased sensitivity to sulfate level when admixtures are present? Why is this sensitivity enhanced by higher temperatures?

These questions have been addressed on a practical basis for many years, usually without explicit application of hydration models. Recent advances have given us the opportunity to develop conceptual models which can address these issues.

2. Importance of sulfate

As sulfate balance is important to most cement-admixture response, we will briefly introduce this issue here, with specific discussion in subsequent sections. During the last 50 years much attention has been paid to the impact that admixtures have on the requirement for the supply of sulfate by the cement. Typically, either direct penetration resistance for setting and strength measurement [22] or isothermal calorimetry [23,24] have been applied. Some early work combined both [25]. The isothermal calorimeter has been very useful, as it not only shows the rate of heat evolution from the main hydration peak, but also since the work of Lerch [26] it has been understood that the calorimeter shows the impact of sulfate phases on control of the aluminate phase hydration. Calorimetry allows one to detect the consumption of sulfate by the change in sulfate depletion point at different levels of added sulfate, and thus can be used to estimate required sulfate levels for “normal” hydration, with and without admixtures. Lerch's work further showed the suppression of silicate phase hydration when sulfate was inadequate, as depicted in Fig. 1. This suppression has been shown to be independent of iron content of the cement. Fig. 2 shows clearly that C_3A alone was capable of shutting off silicate hydration, and sulfate capable of restoring it [27]. Interestingly, the sulfate depletion point prior to a secondary exotherm, frequently ascribed to AFt conversion to AFm, was shown using in-situ XRD to correspond to the point at which solid gypsum was no longer available [24]; however, the production of ettringite in fact continued to occur for a time afterward, with no increase in the rate of consumption of C_3A [24,28]. Using stirred suspensions of C_3A, Minard et al. [29] concluded that the rapid exotherm associated with the consumption of the sulfate was due to the direct formation of calcium hydroaluminates with later conversion to monosulfoaluminates, coupled with a slow conversion of ettringite as the sulfate source. Pourchet et al. [30], building on this understanding, evaluated the difference between gypsum and hemihydrate as a sulfate source and showed that the initial reaction of C_3A was much greater with gypsum, generating ~250 J/g C_3A of heat and consuming up to 30% of the total C_3A. The reaction products formed were calcium hydroaluminates when gypsum alone was used. Partial or complete replacement with hemihydrate removed this effect. They further showed that when calcium hydroaluminates were formed, the later hydration rate was reduced. They attributed the reduction in hydration rates to the presence of calcium hydroaluminate hydration products occluding the C_3A surfaces from hydration. Gallucci et al. [13] agreed that this peak represents direct reaction of C_3A, but cite desorption of the sulfate from the C–S–H phases after gypsum depletion as the source of sulfate.

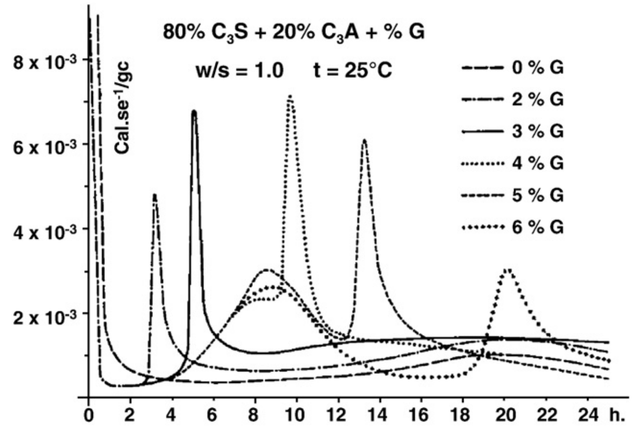

Fig. 2. Data from Tenoutasse [27] showing silicate hydration suppression in undersulfated conditions (0–3% gypsum) in the absence of C_4AF. (Graph re-labeled for clarity.)

Understanding the interaction between aluminate and silicate reactions is especially important because many workers [24,31–34] have clearly demonstrated that problems with silicate phase hydration in the presence of admixtures can be traced to inadequate control of the aluminate phase hydration by the cement sulfate. This can be caused by the fact that there is simply inadequate sulfate present, as in Lerch's original studies, or that the sulfate is in a form that does not supply sulfate quickly enough to the actively hydrating aluminate phases, either because its rate of availability is suppressed by the presence of admixtures [20,35], the temperature range is such that either the sulfate becomes more slowly available [36], or the aluminate is made more active by the higher temperature [37]. However, the exact mechanism whereby the aluminate reaction slows down or shuts off silicate reaction has not been described, although very recent work [38] does show the *μic* model capable of reproducing the sulfate depletion point.

A tremendous amount of work has been done over the last decade elegantly showing us that hydrating C_3A and C_4AF will form layered intercalates spontaneously [15–19,39,40] in model systems. This was recently thoroughly treated by Giraudeau et al. [18], so we will state only the briefest of summary. Intercalation impact on superplasticizers will be treated separately.

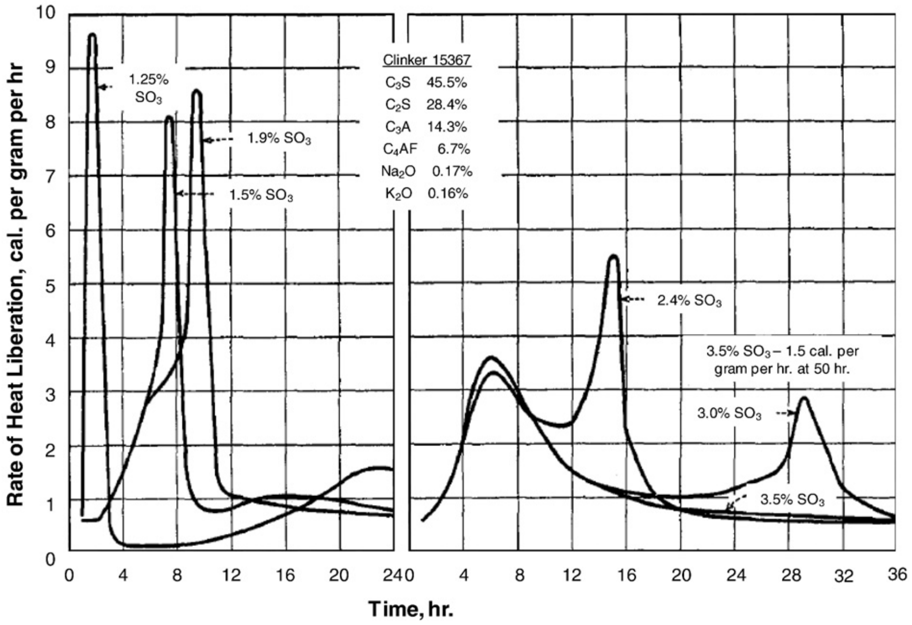

Fig. 1. Isothermal calorimetry curves generated by Lerch [26] showing suppression of silicate hydration in undersulfated condition on the left curves. (Graph re-labeled for clarity.)

At the simplest level these intercalates are metastable C_3AH_6 and C_4AH_{7-19}, but the hydroxide can be replaced by sulfate, carbonate, chloride and a whole host of organic materials. The essential point here is that the structures spontaneously self-assemble, and that the intercalating species are in competition. Sulfate is thermodynamically favored; thus sulfate concentration controls whether other anions are present, and, when it is deficient, uptake of organic materials is rapid. While this uptake is reversible, the extended time-frame of several hours renders this process to have no practical importance for workability [18]. These effects are acknowledged to be potentially important in explaining the variations in admixture performances with dosage time, which has long been recognized to be related to admixture sorption [41], and to explain at least in part the poorer performance of admixtures in undersulfated systems [31,42]. However, it has yet to be demonstrated the extent to which these intercalates form and remain stable in the complex and highly sheared environment of real concrete. Accordingly we will refer to the general case of formation of reaction products between the aluminate phases and organic admixtures, which abstract the organic material and effectively lower its dosage, as organomineral phase (OMP) formation, as used by Flatt and Youst [39].

The simple removal of admixtures by OMP formation does not explain the extremes in behavior wherein C_3S fails to hydrate. In some cases with SCM's, the sulfate content of the cement is adequate to control the aluminate reaction for the cement by itself and with the admixture being used, but not for the combination with added aluminate from the SCM. Also, aluminates can adsorb on the hydrating silicate surface, but the exact nature of this adsorption and how it influences silicate reactivity is unclear [43]. When we have a situation where an added SCM increases the reactive aluminate content without also supplying increased levels of available sulfate, the system can become unstable [44], and normal hydration can be severely delayed.

It would seem that the self-assembling nature of intercalation products, the possible presence of very early formed calcium hydroaluminates, and their relative stabilities must be taken into consideration in any theory which attempts to explain this strong retardation of C_3S seen in undersulfated systems. In the presence of admixtures which may be intercalated through early aluminate reactions under conditions of insufficient sulfate, the potential for such an intercalate, perhaps in some manner incorporated on some specific crystal surfaces of the silicates, needs to be considered. The presence of these could be responsible for the cases of extreme set retardation.

Thus, the kinetics of sulfate dissolution, aluminate reaction, and resulting silicate hydration all interact, and can individually and in combination be affected by the presence of admixtures. For kinetic models to be truly useful, they must deal with all these interactions. We will highlight some of the specific issues in the following discussions.

3. Impact of retarders and accelerators on the hydration of Portland cement

Recent advances in understanding early hydration chemistry require revision in our concepts of how accelerators and retarders function, and direct us to some key experiments which can advance models to deal with the impact of these admixtures:

- Makar et al. used differential isothermal calorimetry [45,46] and high resolution cold field emission SEM [47] to show that just prior to the onset of accelerated hydration, there was an exothermic event of short duration, which they ascribed to "initial C–S–H formation", and which coincided with a rapid increase in visible etch pits. However, their SEM images showed widely dispersed hydration products on the cement surface prior to this peak, and they state: "... almost all C_3S grains observed at 2.5 h of hydration had smooth surfaces". This suggests that the exotherm corresponds to the time of re-initiation of rapid C–S–H formation, and not the "initial" reaction, which clearly occurs earlier. Further, they have shown that when admixtures are present that retard and diminish the rate of heat evolution after the induction period, the energy of this transient reaction is reduced. In a subsequent paper [48], SEM images of several hydrating cements before, during, and after the period of this peak, which they called the "termination peak", were presented and they concluded that these support the model of a protective layer, despite the apparently clean surfaces, as the SEM had insufficient resolution to preclude some very thin layer being seen. In their opinion, since the continuous nucleation and growth model does not explain the presence of an event at the time of the termination peak, this model was not supported by data seen in this SEM study. Further, explanations that ascribed the acceleratory period to the beginning of calcium hydroxide nucleation were also not supported, as calcium hydroxide was found to increase before the "termination peak" at the end of the induction period. Finally, mechanisms relying on osmotic pressure breakdown of a layer were not supported as no such rupture was seen in the SEM images. Thus the exact nature of this exothermic event remains unclear, but as it appears to correspond to the time of re-initiation of C–S–H formation, and is diminished in cases of extended retardation, further investigation both experimentally and by modeling appears warranted.
- Juilland et al. [14] summarized Makar's SEM work and other findings by SEM and AFM, to show that in alite hydration, after the early reactions and before the onset of rapid hydration, there is no complete layer of hydration product formed that protects the alite surface from continued hydration. (This period, once called the dormant period, but now recognized merely to be a period of very slow reaction, will be referred to in this paper as the induction period). Rather, reactive sites at edges and dislocations exhibited coverage by reaction products, and the lack of reaction of the rest of the surface was ascribed to rapid buildup of ionic concentration in solution, such that there was inadequate undersaturation to overcome the free energy barrier to etch pitting. The dependence on dislocations and undersaturation was clearly demonstrated by the markedly greater etch pit formation with deionized water versus a saturated lime solution, by the difference in pitting seen on different crystal faces, and by the reduction of reactivity upon annealing the alite. Despite this insight as to what causes the induction period, Juilland et al. stated: "However, the exact process which brings the induction period to an end is still unclear". Application of wide angle X-ray diffraction to C_3S hydration with and without several superplasticizers [49] has confirmed preferential hydration on two of the three crystal faces of C_3S, and showed that the relative growth rates on different faces were altered by superplastizers. The authors concluded: "Furthermore, the peak at 15° due to dry C_3S is still present in samples containing SPs…….The results clearly suggest that the additives have a selective binding to preferential crystal lattice directions of C_3S". This reinforces the concept that sorption must take place on an essentially bare C_3S surface, as any amorphous C–S–H layer with a gap beneath it should not allow such an specific adsorption effect. The sorption of superplasticizers has also been shown to be competitive with sulfate [50] and with retarders [51].
- Using dilute suspensions, Garrault et al. [52] have shown the dependence of C_3S hydration on $Ca(OH)_2$ concentration. In line with the etch pit theory, lower lime concentrations gave more C–S–H nuclei, leading to shorter initial period. In the same work, AFM studies combined with modeling showed that C–S–H growth is largely parallel to the C_3S surface, with the ratio of parallel to normal growth dependent on lime concentration.
- In recent work, Bullard and Flatt [53] used the HydratiCA [10,11] model to explore the competing theories of a passivation layer of C–S–H versus an etch pit/site deactivation model along the lines discussed by

Juilland et al. [14], to explain the delay in C_3S hydration. They concluded that the site deactivation model predicts that suppression of $Ca(OH)_2$ precipitation should lead to extended setting, while the older passivation layer model does not. Based on this predicted observation, they propose experiments with materials which selectively absorb on $Ca(OH)_2$, while not affecting either C_3S or C–S–H, to determine which theory is supported. While such an additive was not identified, clearly this frames the possible experiments needed to find the relationship between retardation and the sorption of additives on $Ca(OH)_2$.

- Gallucci, Mathur and Scrivener [13] using STEM showed the details of formation of continuous shells around the hydrating cement particles soon after the end of the induction period. While these shells contained high levels of sulfur and very low levels of aluminum, they were primarily densely packed C–S–H. Somehow this layer was formed, not initially as previously thought, but at about the time of the end of the induction period, and not as a sheaf of wheat or other random form, but highly ordered parallel to the original surface. The key question of exactly how it formed was not resolved, but the high sulfur levels detected must be considered. Its relation to the "termination peak" identified by Makar is also of interest.
- C–S–H nucleation and growth has been shown to be strongly accelerated by seeding, be it by silica fume [54], calcium carbonate, slag and quartz [55], colloidal silica [12,56], C–S–H [12,57] or carbon nanotubes [58]. 2% C–S–H seeds were shown by Thomas et al. [12] to be capable of eliminating the retardation of a dose of sucrose sufficient to retard C_3S in excess of 336 h, when the seeds were added initially, and to overcome most of the retardation when the C–S–H seeds were added in a delayed fashion. Stark et al. [55] showed that the seeding of C–S–H was controlled by surface area of the seed and by both its chemistry and crystalline structure. Calcium carbonate seeds were shown to result in much higher seeding rate and a very ordered C–S–H structure at fixed orientation to the carbonate surface. Carbon nanotubes [58], in contrast, resulted in an extraordinarily fine deposition of C–S–H layers showing no structure under very high magnification cold field SEM – the tubes appear to thicken over time with a very dense layer of C–S–H which eventually appears to grow in the direction of the axis of the nanotube to greater lengths than the starting nanotubes. Ultimately a web-like network of C–S–H fibers is formed. It would appear that C–S–H is not substrate-specific in its ability to nucleate and grow, but that the substrate may alter its growth form, orientation, and rate.
- In contrast to the behavior of the above-mentioned seeding materials, addition of solid $Ca(OH)_2$ has not been found to accelerate hydration of C_3S or a laboratory-prepared alite [59]. This brings into question theories relying on rapid removal of calcium and hydroxyl ion by precipitated $Ca(OH)_2$ per se to account for the onset of rapid hydration in systems without admixtures. However in the same work, addition of $Ca(OH)_2$ did accelerate hydration in production cements, which may be related to the known retarding effect of $Ca(OH)_2$ on C_3A hydration [59], reducing its potential negative impact on silicate hydration. As pointed out by Bullard and Flatt [53], if the presence of solid $Ca(OH)_2$ limits oversaturation of Ca^{++}, acceleration could occur.

With the above as background, we can now discuss the recent findings with respect to set retarding and accelerating chemical admixtures and their implications for the various issues, which future models must be able to consider.

3.1. Impact of retarders on the hydration of Portland cement

The salts of lignosulfonic acid and hydroxylated carboxylic acids, and carbohydrates such as sucrose, glucose, glucose polymers, and sodium gluconate are among the chemical admixtures commonly used as set retarders for Portland cement hydration. Many of these compounds are also found in water reducer formulations. Citric acid, tartaric acid, and various phosphorous compounds such as nitrilotris(methylene)triphosphonate are frequently used for more specialized applications. Other higher molecular weight polysaccharides are frequently used in modifying rheology of cementitious systems, and their retarding capacity needs to be considered in product formulations.

Literature over the last 50 years is replete with efforts to apply a model for hydration retarders [60–63]. As summarized recently by Bishop and Barron [64], proposed mechanisms of set retardation generally fall into four regimes: (1) calcium complexation preventing precipitation of portlandite, (2) formation of a semipermable layer later broken down by osmotic pressure gradients, (3) surface adsorption of retarders directly on anhydrous surface, and (4) nucleation and growth poisoning of hydrates, including portlandite. The first two are now generally considered unlikely – the first because very strong chelaters can be moderate retarders while strong retarders can be moderate chelaters [63] and the second because direct SEM observation shows that during the induction period much of the C_3S surface remains bare of hydration product [14]. The special mechanism of "dissolution–precipitation" proposed by Bishop and Barron [65] for organic phosphonic acids would appear to be a special case of the third mechanism.

3.1.1. Impact of retarders on silicates

Several complexities arise when we discuss retarder effectiveness. First, retardation consists of two effects – the increase in the induction period, and the reduction (or in some cases increase) of hydration rate after hydration accelerates. This has been clearly demonstrated in a study of various polysaccharides by Peschard et al. [66], where using conductimetry in dilute cement suspensions (w/c = 20), a cellulose ether was shown to have no effect, a yellow dextrin delayed the induction period by 10 h but had no effect on the rate once the induction period was over, and a starch ether was shown not to affect the timing of the induction period, but to significantly reduce the rate of hydration afterwards (Fig. 3). On increasing to very high dilutions of w/c 8000, the most powerful retarder, the yellow dextrin, was shown not to retard significantly, even up to doses of twice the mass of cement, which led to a concentration of dextrin in the water phase equivalent to that in the w/c = 20 experiments. If retardation occurred solely by blocking at the anhydrous surface, this identical dextrin concentration should have retarded similarly regardless of the dilution. This result supports the concept that retardation by this dextrin occurs due to inhibition of nucleation and growth of reaction products, the formation of which would be affected by the dilution.

Sucrose is one of the most powerful set retarders for cement, and its mechanisms and effects have been investigated for quite some time.

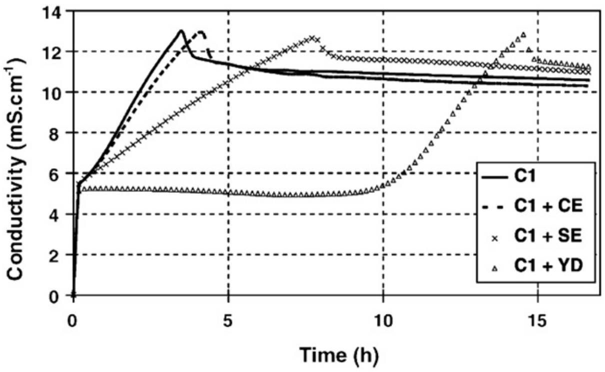

Fig. 3. Chart from Peschard [66] showing extension of induction period by yellow dextrin (YD) but normal rate of reaction afterward, contrasted to lack of extension of the induction period by starch ether (SE), but with reduction in reaction rate. Cellulose ether (CE) shows little effect as compared to the cement suspension made without chemicals (C1).

Thomas and Birchall [63] showed sucrose to apparently increase the solubility of silicate species due to its ability to chelate Ca^{2+} ions, thereby increasing the availability of silicate ions in solution. Juenger and Jennings [67] proposed that the adsorption of sugars onto C–S–H and calcium hydroxide nuclei poison the growth of these hydrates, thus promoting formation of more nuclei. Once all the sucrose has been consumed, a period of heterogeneous growth follows, producing higher surface areas due to the greater number of nuclei, and thereby inducing the "delayed accelerator" behavior of the chemical. However, the exact mechanism of interaction of sucrose with the ions and surfaces produced during cement hydration, as well as the structure of the complexes formed from this interaction, are still a matter of debate [64].

Peterson and Juenger [68,69] utilized the quasi elastic neutron scattering technique (QENS) to demonstrate the impact of sucrose on the hydration of C_3S. The technique uses neutron radiation to determine the mobility of hydrogen in the system, which can be translated into either free (more mobile) or chemically-bound (less mobile) hydrogen. The bound water index (BWI) is calculated as the ratio of the less mobile to the total hydrogen in the system, which can be read as the ratio between the chemically-bound and the total water, as a function of time. When coupled with hydration models, the method gives information on kinetic parameters of cement hydration and the diffusion coefficient of the sample. Peterson and Juenger added 0.01% and 0.05% sucrose (percentage of C_3S weight) to pastes with 0.4 water/C_3S ratio. The results of the test as shown in Fig. 4 confirmed that sucrose acted as a delayed accelerator, causing a longer induction period but increased rate and extent of formation of hydrated phases once hydration started, resulting in a higher degree of hydration after this period. The addition of sucrose also resulted in a higher diffusion coefficient [69], which they concluded to mean that the C–S–H formed was more permeable, with a higher specific surface area.

In a study of citric acid retardation [70], the hydration rate after the end of the induction period was shown to decrease proportionally to the degree of induction period delay. Most citrate was removed from solution within the first hour, and potassium concentration also reduced, so that citrate retardation was attributed to the formation of a potassium citrate complex on the anhydrous cement surface, slowing dissolution rates. Similarly, Juenger and Jennings [67] showed that at a very high (1% by weight of cement) dose of sucrose, the exotherm of the main hydration peak dropped proportionally to the extension of the induction period, yet eventually the degree of hydration with sucrose exceeded that with water alone.

Perez [71] used conductimetry and solution analysis to investigate sodium gluconate retardation as a function of dosage rate. Very high rates of adsorption were found – around 75% of added sodium gluconate was adsorbed in 5 min regardless of concentration in solutions up to 0.4% – well above any normal dose rates used in commercial applications and sufficient to delay setting for many days. Since this adsorption takes place well before significant C–S–H formation, direct adsorption of gluconate on the unreacted silicate phases is inferred, as in the case of citrate. At a 0.15% sodium gluconate dosage, higher SiO_2 concentrations were found in solutions after 5 min from contact with water, while 0.235% sodium gluconate reduced the soluble SiO_2 levels to below the reference, and the rate of dissolution was noted to decrease by a factor of 10. With both cement and C_3S, changes in the slopes of the retardation and mortar flowability versus dosage relationship were found. These break points were ascribed to a saturation dosage level beyond which the gluconate did not give additional fluidity, yet a stronger influence of retardation was noted. Perez concluded that these saturation levels corresponded to similar coverages, if alite were the only adsorbing phase considered. He further calculated this coverage to represent an adsorbed gluconate layer on the order of approximately 3 nm in thickness. The presence of this layer of sodium gluconate was believed to be adequate to completely block the surface.

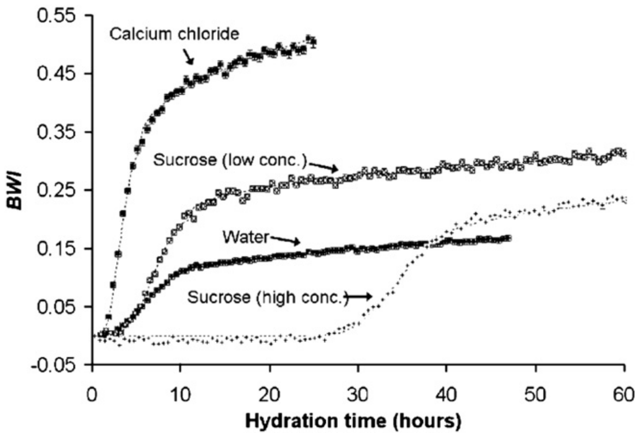

Fig. 4. BWI (Bound Water Index) data from Peterson and Juenger [69] showing QENS for C_3S hydrated with water, 2 wt.% calcium chloride, 0.01 wt.% sucrose (low conc.), and 0.05 wt.% sucrose (high conc.).

As shown recently in a study on sugar alcohols [72], stereoisomers can exhibit significantly different levels of retardation. Adonitol, arabitol and xylitol, stereochemically isomeric five carbon sugar alcohols, having respectively 0, 1 and 2 threo hydroxyl group pairs, retarded set (defined as time to 40% hydration of C_3S) to three widely different amounts – none, 1.5 days and about 20 days, respectively, at concentrations in water of 1.5, 2.0 and 4.0 mol%. In the same study, the four carbon sugar alcohol threotol, with one threo hydroxyl group pair, accelerated rather than retarded set, at both 2.0 and 4.0 mol% in water. In contrast, the five carbon arabitol with the same number of threo hydroxyl groups, retarded set 1.5 days at 2.0 mol%.

A study on the competitive adsorption between retarders and superplasticizers on cement surfaces by Plank and Winter [51] concluded that for similar sized molecules, the anionic charge density primarily controls the competitive adsorption, with the molecule having higher charge being favored.

It would thus appear that cement silicate surfaces, now known to be largely free of reaction products during the induction period, are a conflict zone, where all anionic species are competing for adsorption based on anionic charge densities, molecular conformations, and other factors not yet completely understood.

3.1.2. Interaction of retarders with aluminates

With regard to the impact of set retarders on C_3A hydration, Bishop and Barron [64] observed an acceleration of ettringite formation when up to 1.5 wt.% of sucrose was added to a C_3A/excess gypsum blend. Meyer and Perenchio [25] observed similar behavior with Portland cements, with markedly increased rates of sulfate consumption in the presence of sucrose. They showed that the consumption of calcium ions by sucrose from solution led to an acceleration of the dissolution of calcium sulfate, and an increase in availability of sulfate ions. When sucrose was used at an optimal dosage, an acceleration of calcium sulfoaluminate hydrates was noted, due to more efficient conversion of the hydrated calcium aluminates to ettringite. However, when sucrose was used at above optimal dosages, for example at 0.2 and 0.3% of sucrose by weight of cement [25], a rapid stiffening behavior of cement could result, due to the accelerated reactions of the aluminate-containing phases.

The crystal form of C_3A is strongly influenced by alkali availability during clinkering, which in turn, is related to the amount of sulfur present in the kiln relative to the alkali level [50]. In work first reported in this paper (Fig. 5), the marked differences in the degree of retardation sodium gluconate gives with the different crystal forms of C_3A are shown. First, the hydration of the orthorhombic C_3A in presence of sulfate at SO_3:C_3A mole ratio of 2.5 and excess calcium hydroxide (at 13.7 g/l) occurred earlier and at a faster rate than that of

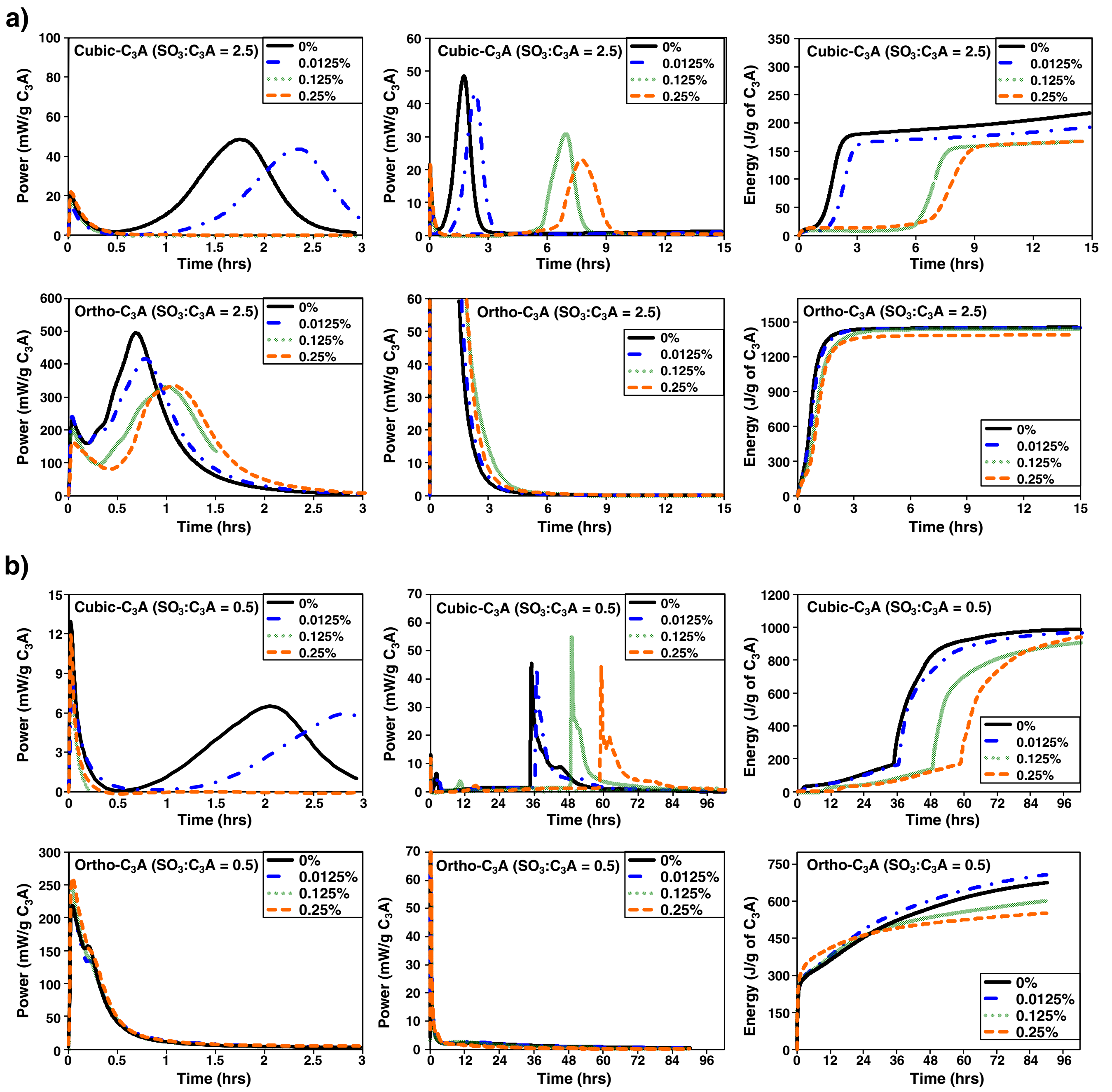

Fig. 5. Calorimetry curves at 23 °C showing impact of different dosages of sodium gluconate on (a) cubic-C_3A:hemihydrate:$Ca(OH)_2$:water and orthorhombic-C_3A:hemihydrate:$Ca(OH)_2$:water (1:1.5:0.05:3.75 by weight) pastes, and (b) cubic-C_3A:hemihydrate:$Ca(OH)_2$:water and orthorhombic-C_3A:hemihydrate:$Ca(OH)_2$:water (1:0.3:0.05:3.75 by weight) pastes.

the companion cubic C_3A systems. The extent of retardation by sodium gluconate was significantly less for the orthorhombic-C_3A system than for the cubic-C_3A system. In the cubic-C_3A systems with sufficient sulfate content (SO_3:C_3A of 2.5 by mole), only one exothermic peak occurred after the initial dissolution peak. The retardation by sodium gluconate grew linearly with increasing dosage up to 0.125%, after which the rate of retardation increase slowed down from 0.125% to 0.25%. In the cubic-C_3A systems with lower sulfate content (SO_3:C_3A of 0.50 by mole), two exothermic peaks, at 1–20 h and 30–80 h, occurred after the initial dissolution peak. The extent of retardation for the cubic-C_3A systems with low sulfate content increased almost linearly from 0 to 0.25%. It was also observed that, in the presence of sulfate and calcium hydroxide, exothermic reactions of orthorhombic-C_3A occurred significantly faster and released 10 times more initial heat than that of the corresponding cubic-C_3A systems. The initial peak is believed to stem from rapid hydrolysis of C_3A, followed immediately by the formation of calcium aluminate hydrates. The total energy released for the first 10 h was about 6–8 times higher for the orthorhombic-C_3A than for the cubic-C_3A blends, when both are made with a good supply of sulfate. However, for under-sulfated blends, the total energy released from the cubic system in the first 4 days was higher by about 50% than that from the orthorhombic system, showing that the different crystal forms are markedly different in response to the undersulfated condition. This case presents a simple but illuminating example where set retardation is impacted by the mineralogy of the C_3A phase, which is known to be altered by relatively minor changes in kiln operation such as changes in sulfur level of fuel.

3.1.3. Requirements for modeling the impact of retarders

Thus, it would appear that there are multiple possible mechanisms for retardation, and each chemical can have a different impact on the extension of the induction phase and reaction rate after hydration begins, depending on the various complex mechanisms. For models to help unravel this complexity, they will have to deal with the following potential portions of the overall mechanism of retardation of the silicate phases:

- initial chelation ability – the ability of set retarding admixtures to more readily solubilize Ca^{2+} and therefore increase SiO_4^- and sulfate ion concentrations in solution, which can promote more C–S–H nuclei. This is in contrast to the older theory of formation of chelates directly preventing CH precipitation. In terms of the newer etch pit theories, set retarders could continue etch pitting causing greater levels of calcium dissolution. This could result in either set accelerating or retarding behavior depending on the fate of the dissolved species,
- ability of set retarding compounds to form directly bonded adhered layers on the anhydrous silicate and aluminate surfaces, thereby reducing their ability to dissolve. These adhered layers could be divided into directly adsorbed species, or formation of a calcium or potassium salt which precipitates and adheres onto the surfaces,
- ability to poison nucleation of CH
- ability to poison growth of CH
- ability to poison nucleation of C–S–H, and
- ability to poison growth of C–S–H.

Poisoning of nucleation and growth are unfortunately referred to as one mechanism by some studies, but they must be separated, as their impact on reaction rate after the induction period would be expected to differ greatly depending on which effect dominates.

Aside from these mechanisms of action, the models will have to deal with two possible methods of removal of retarders in hydrating cementitious mixtures:

- alkaline hydrolysis, as shown by Previte [60], and
- removal by OMP formation, which will be strongly influenced by the amounts and forms of calcium aluminate hydrates, the forms and availability of sulfates, and as shown by Sandberg et al., Perez [24,34] and others, by the chemical and dispersive impact of the set retarder on the rate of reaction of the aluminate phases, especially in the critical first few minutes.

Finally, the model must predict not only the delay in the end of the induction period, but also the reaction rates subsequent to that. It would be surprising if any one retarder impacted only one of these parameters. Good models need to be able to reflect how all aspects are impacted by a particular material.

3.2. Impact of accelerators on the hydration of Portland cement

The most common accelerators are grouped as soluble inorganic salts (chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates, and alkali hydroxides), and soluble organic compounds (such as triethanolamine (TEA) and triisopropanolamine (TIPA). Other organic compounds are less frequently encountered such as calcium formate, calcium acetate, and other calcium salts, and admixtures for shotcrete (alkali silicates, alkali aluminates, aluminum chloride, sodium fluoride fluorides, and alkali-free accelerators, mainly based on acid solutions of aluminum salts) whose primary acceleratory target is the aluminate phase, normally resulting in rapid workability loss. In this review, we will focus on the first two groups.

3.2.1. Impact of accelerators on silicates

The mechanisms of interaction between inorganic salt accelerators and hydrating cement have been the subject of research for many decades [73–77]. While most older explanations have focused on disruption of barrier layers caused by faster nucleation of CH, changes in the hydration reaction products have also been noted. For instance, Ramachandran and Feldman noted in 1977 that the reaction products of Portland cement with calcium chloride tend to be of lower density.

The shorter induction period in the presence of $CaCl_2$ has also been attributed to the smaller ionic size and higher diffusivity of the Cl^- relative to OH^-, which would result in an early rupturing of a layer of adsorbed ions on the surface of hydrating C_3S particles [78]. The rate of formation of hydrated phases and the degree of hydration at early ages were observed to increase with the salt. In addition, the diffusion coefficient was higher, indicating a more permeable C–S–H with higher specific surface area. The authors believed that the more permeable initial C–S–H layer was responsible for the faster hydration of cements with calcium chloride [79].

As with retarders, acceleration is not a one-parameter effect. Both the time to the end of the induction period and the hydration rate after the onset of hydration are affected, and not necessarily in proportion. Few papers dealing with acceleration consistently separate these effects. Edwards and Angstadt gave an early example in 1966 [74], using isothermal calorimetry and equimolar doses of a variety of salts. $CaCl_2$ accelerated the end of the induction period and sharply increased the rate of hydration. In contrast, $Ca(NO_3)_2$ accelerated the induction period approximately the same amount, but the rate of hydration afterward was substantially less than with $CaCl_2$, although greater than the reference. Conversely, various chloride salts showed a consistent relationship between the acceleration of the induction period and the reaction rate thereafter. Any complete model for acceleration behavior would have to deal with this discontinuity between effect on induction period and effect on subsequent reaction rate. Furthermore, the utility of equimolar doses was shown, and is to be recommended for any experiments in support of model development; unfortunately, this has not usually been the case with prior studies.

In their 1975 review of possible mechanisms of set accelerator performance, Skalny and Maycock [75], citing work by Collepardi, observed that divalent cations are stronger accelerators than monovalent, and within each series, the smaller ionic radius species are the more powerful accelerators. As with most prior studies, there was no differentiation in the discussion between acceleration of induction period and rate of hydration thereafter. However, the authors further insightfully observed: “The chloride ion content of fully hydrated C_3S ($<0.3\%$) could be quite misleading, particularly if lattice defects in the C_3S grain play a role in hydration. If defects do play a role, it is the number and mobility which are important-. Therefore, an increase in impurity content, possibly by the diffusion of Cl^- ions into the C_3S lattice will increase the lattice defects”. The potential for this model, essentially analogous to models of metal corrosion, is especially intriguing in light of the recent understanding of “bare” surfaces and etch-pit model outlined by Juilland et al. [14].

Modern techniques are allowing researchers to investigate the interaction between accelerators and hydrating cement more closely. Using quasielastic neutron scattering (QENS) Juenger et al. [68,69] tracked the hydrogen in chemically-bound water – the bound water index (BWI), compared the results to isothermal calorimetry, and derived parameters describing nucleation and growth and diffusion limited kinetic periods. Fig. 4 shows the results of BWI using QENS obtained by Peterson and Juenger [68] when analyzing C_3S pastes with 2% calcium chloride by weight of C_3S. As can be seen, calcium chloride shortened both the induction period and the later rapid reaction period. Using these results, Juenger et al. proposed that the relative effect of the accelerator anions and cations generally followed the Hofmeister series, and that acceleration of $CaCl_2$ was due to its ability to flocculate hydrophilic colloids, so that the C–S–H layer that forms around the cement grains from the very early stages of hydration would be more permeable, and therefore would allow a faster diffusion of ions and water. As a consequence, the hydration reactions would be accelerated. With the new understanding that much of the surface is not covered with reaction products, this model can perhaps most easily be seen to account for the faster reaction rate after the end of the induction period, when reaction products are known to cover most of the surface. There remains the possibility that such alterations in the reaction products at the widely distributed points of reaction during the induction period may influence the rate of supply of Ca^{2+} and SiO$_4^-$ through those points of reaction, accounting for the earlier end of the induction period, but this remains to be shown. Alternatively, a more open C–S–H morphology may simply provide a greater number of growth surfaces, leading to overall faster reaction. Also, the relationship of this effect to the different growth direction of C–S–H as a function of Ca^{++} concentration [52] needs exploration.

Jupe et al. [28] investigated calcium chloride acceleration in oilwell cement slurries using in-situ synchrotron X-ray diffraction, and showed marked difference between an API Class A cement (similar to a normal ASTM Type I cement) and Class H cement (similar to an ASTM Type V cement but at lower fineness). While the Class A cement showed increased acceleration, in terms of thickening time, the Class H cement reached a maximum acceleration at 2% CaCl$_2$ by weight of cement, and at 4% both thickening times and C$_3$S depletion by XRD showed a reduction in reaction rate. In addition, the C$_4$AF consumption was found to be greater with the 4% CaCl$_2$. As chloride is known to solubilize iron and the class H cement contained very high levels of C$_4$AF, 15.3%, the potential for solubilized iron to be involved in the reduction in set acceleration needs to be considered. The authors postulated that production of an amorphous iron containing reaction product may interact with the C$_3$S and retard hydration.

3.2.2. Interaction of accelerators with aluminates

As early as 1964, Rosenberg [73] explored how abstraction of chloride by reactions with aluminate could reduce the amount available to accelerate the silicate phases. He showed using solution analysis that chloride consumption is usually minimal, to well beyond the time period of acceleration, and that the chloride eventually consumed is proportional to the sum of the molar amounts of C$_3$A and C$_4$AF, less 1/3 of the SO$_3$ (Fig. 6). Tenoutasse [27] further elucidated the mechanism that chloride is consumed by the aluminate phases in the hydrating cement in a way similar to the sulfates; however, the consumption of chlorides only starts after the sulfate has been depleted. Associated with this mechanism, the chlorides keep AFt phases stable in cement containing chlorides and sulfates. It is only after the consumption of all chloride available in solution that there is the conversion of AFt to AFm phases. Thus more chloride will remain in solution during the acceleratory period in systems with sufficient sulfate content (relative to the aluminate activity) to continue ettringite formation until after the peak of the main hydration exotherm. In cases where the sulfate is depleted prior to the main silicate peak, due either to inadequate added sulfate or more active aluminates, acceleration can be diminished. Thus, sulfate balance is again a critical factor with respect to set acceleration by CaCl$_2$.

The impact of sulfate balance is even more strongly seen with non-chloride accelerators, which in some cases have been shown to become retarders in severely undersulfated conditions. In such cementitious mixtures, calorimetry shows that the accelerator is inducing higher levels of aluminate reaction prior to silicate hydration, and that the effect is more prevalent with alkali-modified orthorhombic C$_3$A. Sandberg et al. [24] used synchrotron XRD and calorimetry to show that calcium nitrite, in contrast to calcium chloride, speeds gypsum consumption and ettringite formation, which implies an acceleration of C$_3$A activity (Fig. 7). This would be expected to lead to possible concerns with undersulfated cement systems.

In Fig. 8, isothermal calorimetry curves are seen for a Type V cement with low sulfate and ASTM C 618 class F fly ash at 15% by cement mass, with 0.2% SO$_3$ as gypsum and 1.0% SO$_3$ as plaster. The admixtures used were a 250 ml/100 kg lignin-carbohydrate-triethanolamine water reducer and 2000 ml/100 kg calcium nitrate-calcium nitrite based accelerator. Dosages were on cement plus fly ash basis, except where noted. X-ray diffraction indicated essentially no alkali-modified C$_3$A in this sample of cement. Only mild acceleration was seen, but no anomalous C$_3$A hydration.

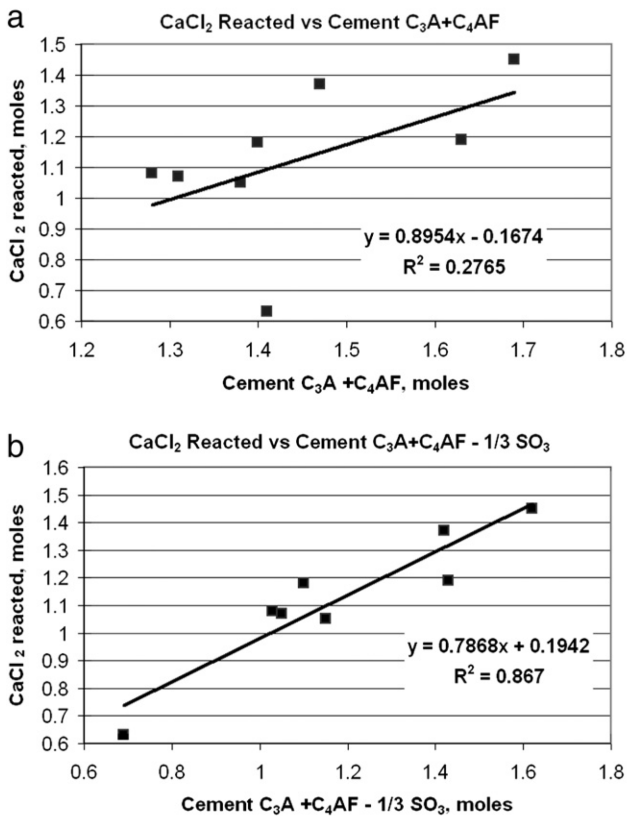

Fig. 6. Chart after data from Rosenberg et al. [73], showing abstraction of chloride from liquid phase is proportional to the C$_3$A and C$_4$AF remaining beyond that which can be reacted to AFt by the available SO$_3$ content.

In Fig. 9, similar results are reported for a companion cement from the same plant, with similar levels of sulfate, 0.05% as gypsum and 1.4% as plaster, but with high levels of alkali modified C$_3$A. Due to the technical service nature of this work, exact composition of the cement is not available. While the cement and ash without admixture behaved normally, the combined water reducer and non-chloride accelerator caused numerous early unidentified reaction peaks to occur, but no significant main silicate reaction was seen until well after that of the untreated samples. The initial heat flow was also much more intense than with the other cement. Addition of sulfate as plaster was shown to eliminate the problem, but the much higher initial exotherm remained.

Neubauer et al. [80] used combined isothermal calorimetry and X-ray diffraction to follow hydration with 2.5% calcium formate as well as 0.1% triethanolamine. While the induction period was shortened, the specific heat flow maximum was reduced by the calcium formate, and the early heat flow was not increased as would be expected if the aluminate phases were strongly accelerated.

Nevertheless, more ettringite was found at 0.07 h, right after mixing – 11.1% with calcium formate, in comparison to 7.9% in the reference without addition of chemicals. Also, the crystallite size of ettringite was dramatically increased during the induction period, relative to the reference. The reference crystal size measurement at 0.07 h was approximately 40 nm, growing to ~60 nm by 2.5 h, while with the calcium formate the initial size was ~78 nm growing to ~105 nm at 2.5 h. The implication of these observations to the

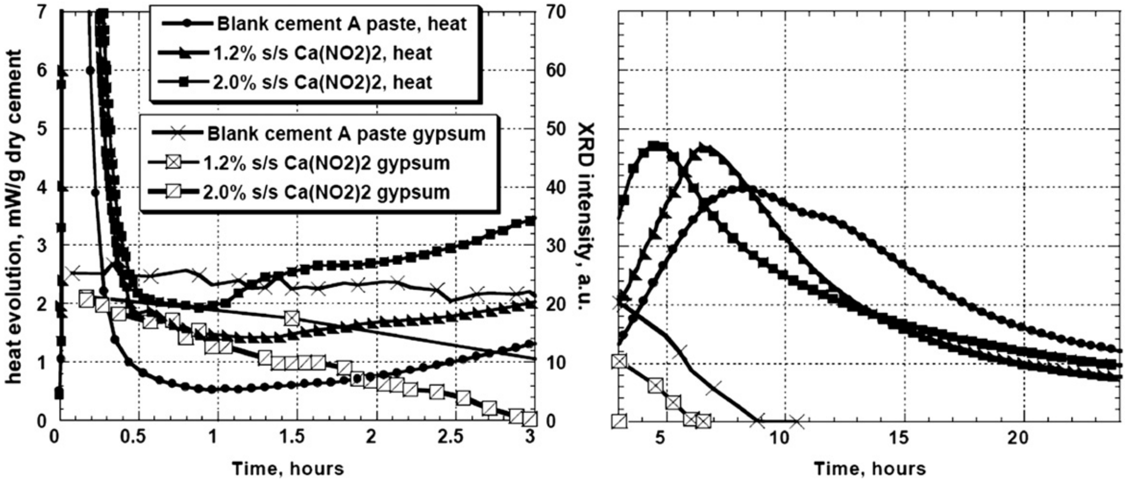

Fig. 7. Chart from Sandberg et al. [24] showing faster depletion of sulfate with increasing doses of calcium nitrite, with depletion points by isothermal calorimetry (solid markers) corresponding to disappearance of gypsum by synchrotron XRD (hollow markers).

acceleration behavior was not discussed, nor was the impact of varying the sulfate level. However, the findings provide important measureable results which can be used to test new models.

3.2.3. *Impact of triethanolamine and triisopropanolamine*

Tertiary alkanolamines, such as triethanolamine (TEA) and triisopropanolamine (TIPA), have been used as cement grinding additives and concrete admixtures to accelerate setting times and strength development of cement. When used at the appropriate dosages, TEA promotes set acceleration and early strength development, while TIPA enhances development of later-age strengths [81]. When TEA is used at levels higher than 0.1%, the opposite effects of set-retardation or flash-set and strength-loss have been noted. Possible mechanisms of how TEA and TIPA influence the hydration of Portland cement and how TIPA influences the hydration of limestone blended cement at different dosage rates will be discussed.

3.2.3.1. Influence on strength developments and set times. The chemical structures of TEA and TIPA are shown in Fig. 10. When the two amines were used at dosage levels of 0.02% s/c, different strength enhancement behaviors were noted as shown in Fig. 11. For this cement, 0.02% of TEA promoted strength enhancement at 1 day, while 0.02% of TIPA gave strength enhancements at 2 and 28 days. When TEA was used at higher dosage levels ranging from 0.1 to 1.0%, Ramachandran [81] showed an increasing loss in strength both for paste and mortar samples from 1 to 28 days.

On examination of the set behaviors induced by different dosages of TEA, Dodson [82] showed TEA to be an accelerator at 0.02% and a retarder at 0.25%. At 0.5%, TEA caused an early initial set, but final set was not reached in 8 h. At 1%, TEA led to flash setting. See Fig. 12.

3.2.3.2. Mechanistic understanding of hydration of Portland cement with TEA. Ramachandran [81,83,84] conducted studies to show the influence of TEA on the hydration of tricalcium aluminate, tricalcium silicate phases and OPC. He concluded that TEA, when added in amounts of 0.1% or more, retarded the hydration of tricalcium silicate, but accelerated the hydration of C_3A and the formation of ettringite. Neubauer et al. [80] showed that the size of the AFt for 0.1% TEA started off at ~60 nm, but decreased to ~48 nm at 2.5 h. The reason as to why TEA induced development of much smaller AFt crystals in comparison to the blank and the accelerating 2.5% calcium formate is a topic worthwhile to pursue.

Gartner and Myers [85] further pointed out that excessive quantities of TEA could result in flash setting behavior where the aluminate hydrates were formed rapidly, while retarding the silicate phase hydration. Under these circumstances, the cement would exhibit poor strength development. The poor strength development reported by Ramachandran likewise seemed to be a result of excessive

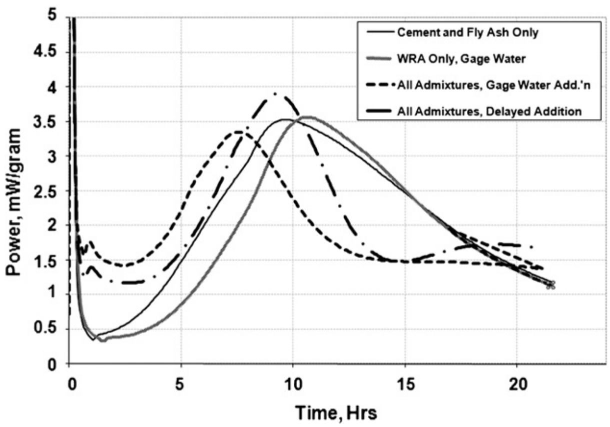

Fig. 8. Effect of addition of water reducer alone and water reducer plus non chloride accelerator to the isothermal calorimetry curves of undersulfated mixes with Type V cement and fly ash, in which the cement's C_3A is largely in the cubic form. Normal level of acceleration is seen.

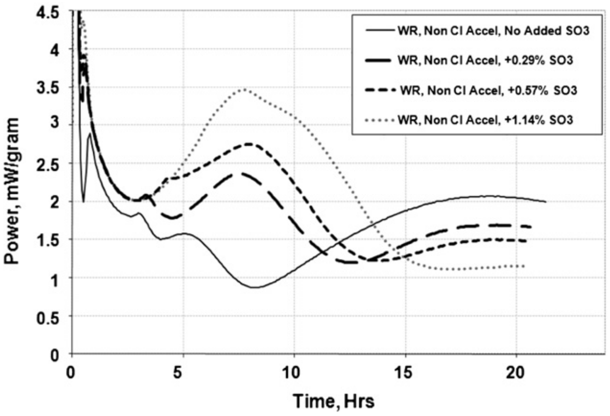

Fig. 9. Isothermal calorimetry curves showing the effect of addition of water reducer and non chloride accelerator to mixes of undersulfated Type V cement with fly ash, in which the cement's C_3A is largely in the alkali-modified orthorhombic form. Curves also show the improvement in acceleration and hydration by adding extra sulfate (as plaster) to such mixes.

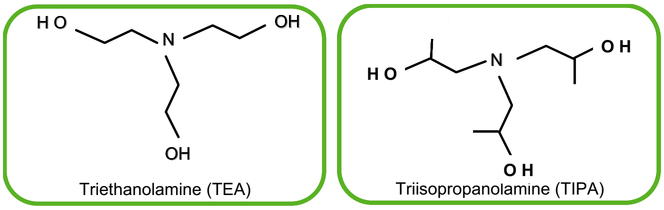

Fig. 10. Chemical structures of TEA and TIPA.

addition of TEA. In practice, TEA is typically used at levels of less than 0.03% by weight of cement or cementitious content.

The ability for TEA to enhance strength was ascribed to the formation of amine-iron complexes under high pH conditions [86]. Gartner and Myers [85] and Perez et al. [87] observed an increase in dissolution of iron at 10–14 h and saw earlier onset of the sulfate depletion point when TEA was added at 0.24% and 0.54%. However, one of the authors of the present article (Cheung) believes that the mechanism observed at these dosage levels may not reflect the hydration kinetics of TEA when used at the typical strength-enhancing dosage of less than 0.03%, because an increase in dissolution of iron was not seen by Cheung at 30 and 120 min at this lower dosage level with a gray cement analyzed by QXRD to have 6.9% C_4AF. Notable amount of soluble iron was observed only when TEA was increased to 0.5%. In this case, 0.48 mM and 0.14 mM of iron is seen at 30 min and 2 h, respectively. The detailed mechanisms on how much, how quickly and why the low dose TEA (at 0.01 – 0.03%) lead to acceleration should be studied to elucidate the observations generally seen by the cement and concrete industries.

3.2.3.3. Mechanistic understanding of hydration of ordinary Portland cement with TIPA. As demonstrated by Gartner and Myers [85], 0.01% TIPA could produce remarkable strength increases in many OPCs. The increase was demonstrated to result from an increase in the degree of hydration, particularly for cements with a higher C_4AF content.

Fig. 13 showed a comparative study made with 0.02% TEA and 0.02% TIPA [88]. The results showed a much higher and prolonged dissolution of iron with the TIPA sample. This phenomenon known as the "facilitated iron-transport" mechanism was believed to be the main driving force to explain the unexpected late-strength gain for cements treated with TIPA. In this case, TIPA helped dissolve the insoluble ferric hydroxide "gel" formed around the silicate phases. Gartner and Myers [85] noted that in order for the facilitated transport process to work efficiently, the binding constant of the iron-amine complex must neither be too high nor too low. "If it is too low, no significant increase in dissolved iron will be observed, whereas, if it is too high, the complex will form but will not break up to redeposit iron at the growth site". The main reason why TIPA can act as an efficient "facilitator" is said [85] to be a result of TIPA not being adsorbed by cement hydrates at the early stage of hydration. Gartner [89] also postulated that an increase in rate of ferrite phase reaction could lead to an increase in the rate of silicate phase hydration as most cement grains are polymineralic. While these postulates correlate well with the observed greater strength enhancement of TIPA with higher iron and lower surface area cements, further work will be required to fully understand why TIPA works better in some clinkers and less with others.

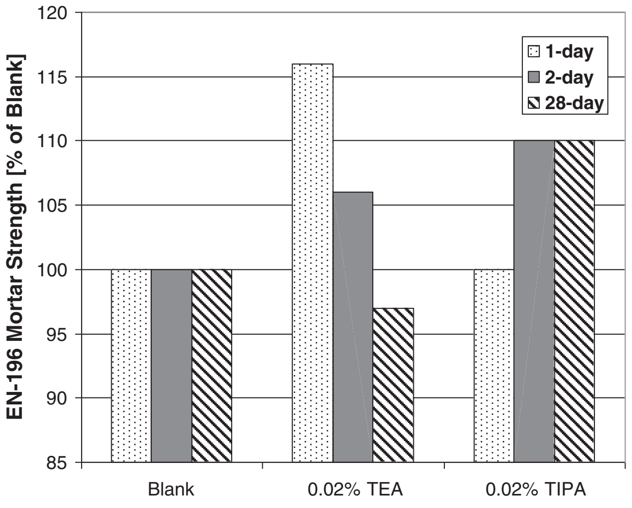

Fig. 11. EN 196 mortar strength results on cement with 6.9% C_4AF, 3.6% *cubic*-C_3A, 3.3% *ortho*-C_3A, 68.5% alite, 4.4% belite, 5.5% gypsum, 0.7% plaster, 4.4% calcite, 1.6% periclase by QXRD, Sol. Alkali (Na_2O eq.) = 0.08%, BSA = 385 m^2/kg. Data represented as % of blank (no chemicals) mortar strengths.

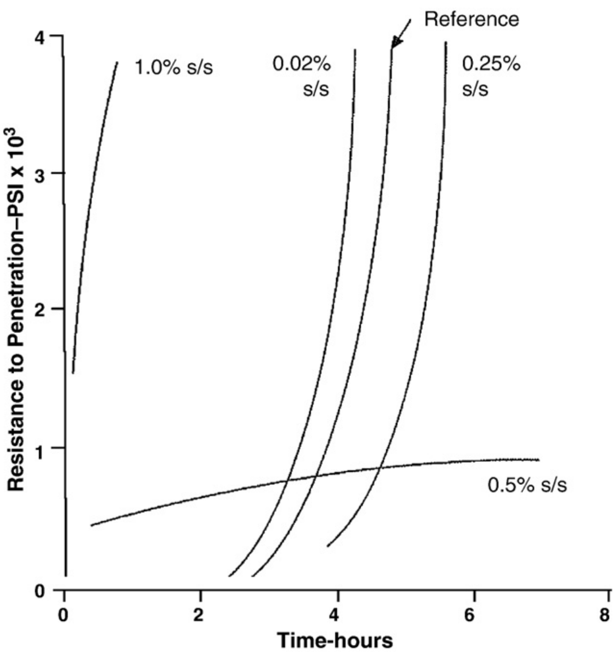

Fig. 12. Data from Dodson [82] showing the time of setting characteristics of concretes treated with triethanolamine. (Graph re-labeled for clarity.)

3.2.3.4. Mechanistic understanding of hydration of limestone blended cements with TIPA. As reported by Gartner [90], TIPA, when added in industrial cement grinding mills, provided strength enhancement

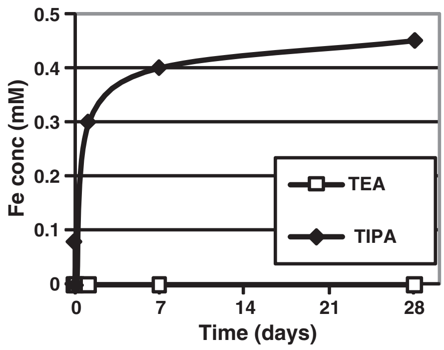

Fig. 13. Data from Sandberg et al. [88] showing comparison of iron dissolution in pore water from cement paste containing 0.02% TEA and 0.02% TIPA.

beyond three days, and is especially useful in blended cements made with 5% or more of limestone. Mortar strength results reported by Ichikawa et al. [91] using a cement made from a clinker with 9% C_4AF content and gypsum added to 2.0% SO_3 level showed an increasingly larger impact on 28-day strength enhancement with increasing substitution of limestone, as shown in Fig. 14. X-ray diffraction studies made with corresponding paste showed an acceleration of the conversion of ettringite (AFt) to monosulfoaluminate (AFm) and also an enhancement of the formation of the hemicarboaluminate and monocarboaluminate phases with 0.01% TIPA. The results indicated that TIPA and limestone participated in the late-age hydration and the acceleration of the ferrite phase hydration promoted the AFt to AFm conversion and carboaluminate hydration as shown by the following schemes.

$$C_3A \bullet 3C\bar{S} \bullet 32H + 2C_3A + 4H_2O \rightarrow 3[C_3A \bullet C\bar{S} \bullet 12H] \qquad [1]$$

$$C_3A + C\bar{C} + 11H \rightarrow C_3A \bullet C\bar{C} \bullet 11H \qquad [2]$$

$$2C_3A + C\bar{C} + CH + 23H \rightarrow (C_3A)_2 \bullet C\bar{C} \bullet CH \bullet 23H \qquad [3]$$

$$3[C_3A \bullet C\bar{S} \bullet 12H] + 2CC + 18H \rightarrow C_3A \bullet 3C\bar{C} \bullet 32H + 2[C_3A \bullet C\bar{C} \bullet 11H] \qquad [4]$$

Another X-ray diffraction study conducted by Gartner et al. [89] to understand the influence of 0.04% TEA and TIPA on rates of reaction of C_3A and C_4AF with calcite under conditions typical of Portland cement hydration showed:

- the addition of TEA or TIPA had little effect on the course of reaction of C_3A-calcite blends,
- the addition of TEA had no effect on reaction or kinetics of C_4AF-calcite blends,
- the addition of TIPA strongly impact the reaction kinetics of C_4AF-calcite blends and the following phenomena were observed:
  - acceleration in the consumption of calcite,
  - acceleration of C_4AF hydration,
  - increase in the formation of monocarboaluminate if sufficient calcite was available, and
  - increase in the formation of the hydrogarnet phase especially when the alkali level was high and calcite level was not in excess.

Thus, while alkanolamines are common chemicals used for cement grinding and in concrete admixtures, and differing behavior is known, the basic mechanism of how the amines interact with the interstitial phases and the subsequent effect on silicate hydration at realistic dosages is a research topic to pursue, both by experimentalists and modelers.

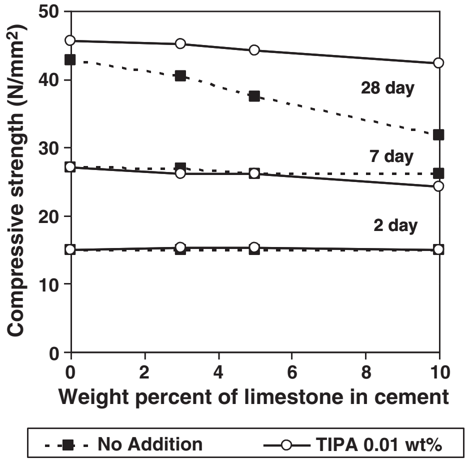

Fig. 14. Data from Ichikawa et al. [91] showing relationship between limestone content in cement and strength enhancement of mortar by TIPA.

3.2.4. Requirements for modeling the impact of accelerators

Therefore, with accelerators, we arrive at a set of requirements for effective models analogous to what we described for retarders. To completely describe the interaction of an accelerator with cement, the models must separately deal with:

- direct acceleration of the pitting of the essentially bare (to SEM micrographs) silicate surfaces seen during the induction period,
- acceleration of CH nucleation, which may control saturation levels and influence etch pitting,
- acceleration of C–S–H nucleation leading to more growth sites which will impact reaction rate after the end of the induction period, and
- acceleration of C–S–H growth after nucleation, which may be due to an increase in permeability of the reaction products promoting faster reaction after the induction period.

Aside from these mechanisms of action, the models also have to deal with the interaction of accelerators with the aluminate phases, reflecting:

- the increase in silicate reaction brought about by increased aluminate and aluminoferrite reactions through organic chelaters such as TEA and TIPA, which expose silicate surfaces otherwise occluded, and
- the decrease in silicate reaction caused by excessive aluminate reaction induced by accelerators, which includes interaction with the availability of sulfate and the crystallographic form of the C_3A, and the interaction of these with other anions such as carbonate which may react with aluminate. The role of iron from accelerated C_4AF also needs to be considered here.

4. Impact of water reducers and superplasticizers on the hydration of Portland cement

Normal and high range water reducing admixtures or superplasticizers (WR/HRWRA) are used quite extensively for the production of both normal and high performance Portland cement concretes [92,93]. The improved rheological performance of concrete mixtures admixed with WR/ HRWR chemical admixtures is attributed to dispersion of agglomerated cement and hydrating cement particles [93]. Such agglomerates, formed during the initial mixing of Portland cement with water, result from relatively large Van der Waals forces of attraction, which operate at inter-particle distances in the range of 5 to 7 nm. Loosely entrapped quantities of water are associated with the agglomerated network of particles. WR/HRWR admixtures have the ability to overcome the Van der Waals attractive inter-particle forces by imparting a stronger repulsive force at the surface-liquid interface, freeing the entrapped water. This process was described by Spiratos et al. to occur as follows [93]: (1) the mixing actions break down the cement agglomerates and distribute the WR/HRWR agents, fully miscible in the high ionic strength pore water, through the cement slurry; (2) an attractive force between the WR/HRWR admixtures, which usually bears a negative charge at the relatively high pH of the pore water, and the positively charged cement surfaces, causes fairly rapid adsorption of the WR/HRWR onto the cement particles; and (3) the adsorbed compounds, forming a layer of a certain thickness and conformation, produce some combination of electrostatic and steric repulsive forces (i.e. "electrosteric") that prevent re-agglomeration of cement particles and liberate the water trapped within the flocculated structure. This can be used to lower the yield stress and viscosity of the cementitious mixture. Alternatively, the mixture proportions can be redesigned with a lower water content to increase strength or reduce permeability, while maintaining approximately similar yield stress (related to slump) and plastic viscosity. Due to the complexities of rheology, the exact relationship between yield stress and plastic viscosity is likely to change, with plastic viscosities of samples with plasticizers remaining higher at equal yield stress.

In conjunction with their cement dispersing function, WR/HRWR admixtures almost invariably retard the rate of the cement hydration process. Various accelerators are added when needed to keep the setting behavior within standards requirements. The influence on hydration rate can be dependent on numerous factors including: (1) cement fineness, chemistry, mineralogy, and degree of pre-hydration; (2) the chemistry of the cement dispersing ingredient (especially where modern chemical admixtures are rarely comprised of single compounds or polymers); (3) the differences in behaviors of different dispersants with respect to sulfate availability; (4) the time of addition relative to the initiation of cement hydration; and (5) the addition rate. Further complicating our understanding of the impact of these additives on cement hydration are the complex interactions between the type of additive and the major and minor compounds and phases of the cement. Specifics on the latter four factors will be described below.

4.1. Chemistries of the HRWRs

The structural features of polycarboxylate-polyether comb polymer (PCE)-type superplasticizers such as charge density and side chain length can significantly influence cement hydration kinetics [19], depending on the extent of OMP formation versus surface adsorption conducive for cement dispersion. The induction period during early cement hydration can be prolonged with increasing charge density, i.e. decreasing side chain length and increasing ratio of carboxylate to PEO groups on the polymer backbone. Possible hydration mechanisms may include [19,94] (1) reduced diffusion of water and calcium ions at the cement surface because the adsorbed polymers is hindering the process; (2) complex formation between calcium ions and PCE in the pore solution; and (3) a change in the growth kinetics and morphology of hydrated phases caused by the dispersive action of the PCE. However, as Winnefeld et al. [19] further stated “there is not much evidence from literature that calcium ions form strong complexes with PCE-based superplasticizers. Thus, it can be concluded that the retardation of cement hydration by PCEs is mainly due to adsorption of the polymers on the surface of the cement particles and due to growth kinetics and morphology of early hydrates, which is supported by investigation of Ridi et al. and Rieger et al.” [95,96]. Although it is noted that a PCE with more carboxylate groups can give more retardation, the exact cause and mechanism for retardation, in particular on how it is related to the molecular structures of the water reducers, remain to be an area that requires more research.

4.2. Interaction between water reducers/high range water reducers and sulfates

The adsorption processes that occur with WR/HRWR during the initial minutes of cement hydration have major consequences on subsequent dispersion performance and hydration rate effects. The fate of most, if not all, WR/HRWR admixtures depends most strongly on the balance between the reactivity of the interstitial aluminate phases of the cement and sulfate availability. The rate of availability of soluble sulfate that can participate in the aluminate reactions can be influenced by the form and fineness of the interground calcium sulfate, soluble alkali (sulfate) content, adsorption of selected admixtures on calcium sulfate altering sulfate solubility [20], and temperature [22,23]. The critical role of this balance results from OMP formation – the adsorption or intercalation of organic compounds by aluminate hydrates [15–20,39,40,46,97–99], which can form when any portion of the hydrating cement surface experiences an under-sulfated condition. As this can be impacted not only by the dispersion per se causing higher very early aluminate reactivity, but by the various chemical effects imparted by the retarding and accelerating components which may be present, the performance of a WR/HRWR can only be understood in the context of knowing the degree of sulfate availability of the cementitious system.

A number of recent studies have focused on the behaviour of polycarboxylate-type (PCE) dispersants in the context of the rate of sulfate availability and the reactivity of the aluminate phases in Portland cement [39,50,97]. Three types of possible outcomes have been proposed to describe the state of the PCE dispersant upon addition to a cement slurry [39]: (1) When the very early available sulfate is below a certain threshold sulfate concentration required for normal AFt formation, and the PCE is already present, OMP formation will dominate rendering some portion of the PCE inactive for dispersion. (2) When adequate sulfate is available, the PCE is found to adsorb onto particle surfaces to help disperse cement agglomerate. (3) Conversely, an excess of sulfate can decrease the desired PCE dispersing performance due to competitive adsorption and a reported reduction of the hydrodynamic volume of the PCE. Several studies [50,97,100] clearly showed that sulfate is adsorbed on the surface of cement grains virtually immediately in competition to the polycarboxylate superplasticizer adsorption.

4.2.1. Formation of organo mineral phases (OMPs)

The uptake of water reducing agents such as NSFC and PCE with aluminate phases has been verified by various analytical techniques such as XRD, elemental analysis, IR spectroscopy, and TEM. Fernon et al. [101] confirmed the formation of intercalated OMP during the preparation of calcium aluminate hydrates with polynaphthalene sulfonate. The proposed schematic view of is shown in Fig. 15. Fernon et al. also noted that the FTIR spectroscopy corroborates the assumption that sulfonate groups are chemically bound to the principal layers, which represents the driving force for intercalation. In the presence of sulfate, both ettringite and intercalated hydrocalumites are found and their proportions are found to be dependent on the initial molar ratios of sulfonate levels from the NSFC to sulfate levels in solution [101].

Formation of intercalates has also been demonstrated for polycarboxylates by Planck et al. [16,17]. The intercalation of PCEs was found to depend heavily on the amounts of calcium and sulfate in contact with the hydrating aluminate phase, as well as the structure of the PCE. With a very low sulfate concentration in the pore water, PCEs can become rapidly intercalated within the hydrocalumite layer of the cement paste [18]. Conversely, at high sulfate levels such intercalates do not form.

4.2.2. Uptake of NSFC by C_3A, C_4AF and C_3S as a function of interground sulfate

The uptake for an NSFC-type HRWR on individual cement compounds interground with different forms of sulfate is illustrated by Nawa et al. [102] in Fig. 16. Of note is the nearly 100 fold higher uptake of the NSFC by the aluminate and ferrite phases versus the C_3S and the reduction in NSFC adsorption by the aluminates (unlike with C_3S) in the presence of added sulfate. The much higher uptake of NSFC by the aluminate and ferrite phases when made without addition of sulfate is most likely a consequence of the formation of intercalated NSFC with the calcium hydroaluminates which would have high specific surface areas. When sulfate is added, the amount of NSFC uptake is reduced. However, the extent on how much of the NSFC molecules exist as intercalates or chemisorbed on the different phases, how the intercalated NSFC phases survive in real cementitious system, and how these phases impart retardation should be studied to help elucidate the mechanism.

4.2.3. Effect of polymer structure on the sulfate-PCE competition

Flatt et al. [103,104] have recently derived and confirmed experimentally a relationship between the structures of PCEs and their tendency to adsorb onto CSH surfaces as a function of sulfate availability. They observed that the sulfate sensitivity of a PCE to

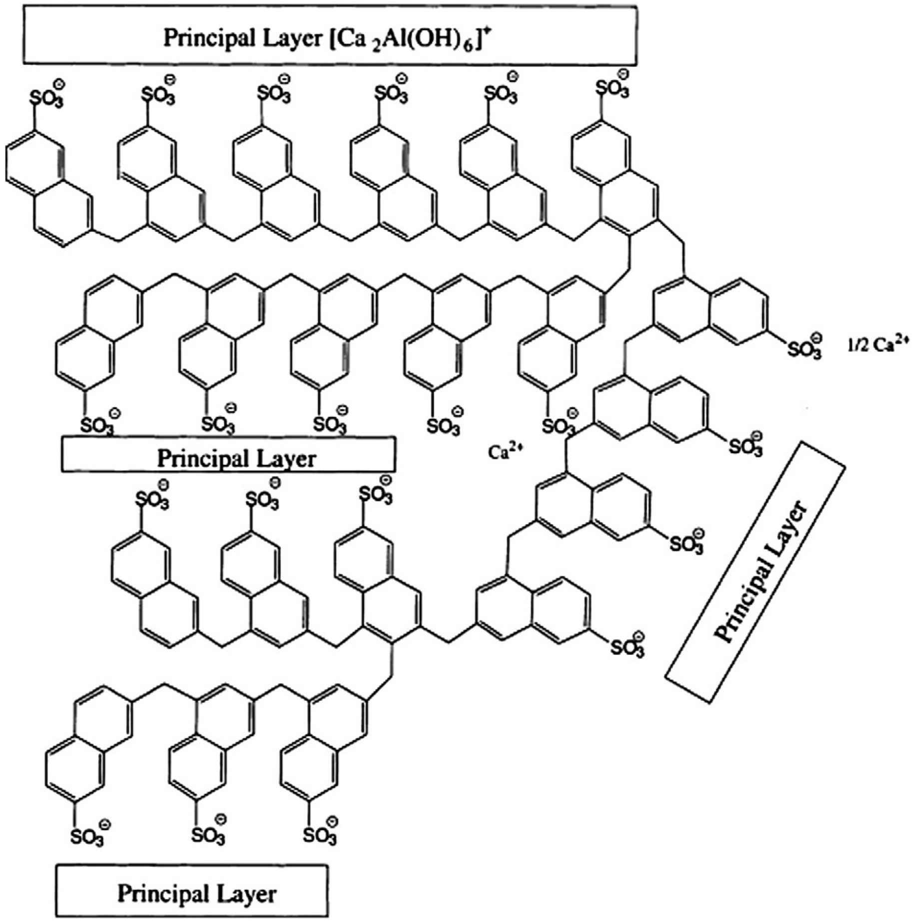

Fig. 15. Structural model proposed by Fernon et al. [101] for C_4AH_x with polynaphthalene sulfonate.

increase with the length of the side chain of the PCE (a parameter named "P") and decrease with the grafting degree or the number of monomers in the backbone per side chain or the carboxylic to ester ratio ("N"). This sulfate sensitivity parameter (SSP) is defined as:

$$SSP \approx \frac{p^{4/5}N^{3/5}}{(N-1)^2}$$

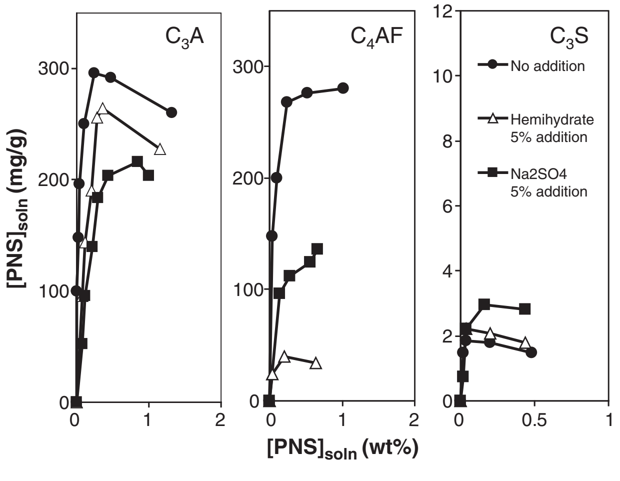

Fig. 16. Data from Nawa et al. [102] showing the uptake of polynaphthalene sulfonate as a function of interground sulfate.

To the authors' knowledge, this is the first quantitative criterion derived for evaluating the impact of sulfate adsorption competition on yield stress. It should be noted that since this work was conducted on equal mass dose basis, the various ratios and dosage of each moiety are not mutually independent; thus as SSP changes with P, at equal N and equal mass dose, the molar dose of carboxylate attaching groups must decrease, which may account for the increased sulfate sensitivity. Similar experiments on equimolar basis could further elucidate these relationships.

4.3. Impact on the time of addition

Varying the time of addition for water reducing admixtures can have a significant impact on the rheology and setting characteristics of cementitious mixtures. Fig. 17 represents the mortar penetration data for four mortar mixes obtained using a modified ASTM C359 Early Stiffening of Mortar test. One mortar was prepared without any admixture. The other mortars were prepared with a blend of lignosulfonate-corn syrup-triethanolamine water reducer. In one case, the admixture was added with the mixing water. For the other mortars, the admixture was added 1 and 2 min after cement-water contact. As shown in Fig. 17, the mortar without admixture exhibits some early stiffening as a function of time as evidenced by the drop in penetration results. When the water reducing admixture is introduced with the mix water, early stiffening is actually increased significantly. However, as the delay in admixture addition time is increased up to 2 min, the dispersing benefit of the admixture can begin to be realized by the elimination of all the early stiffening in the mortar.

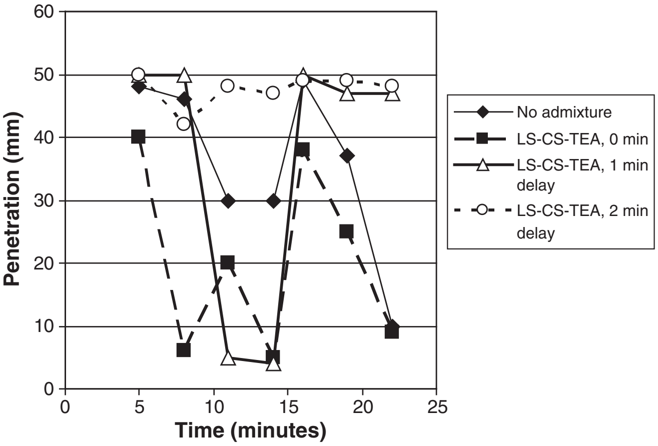

Fig. 17. Impact of lignosulfonate-corn syrup-triethanolamine addition time on ASTM C359 mortar stiffening.

Fig. 18 represents the isothermal calorimetry profiles of the same C359 mortar mixtures. Note the significant delay in cement hydration associated with the delay in the addition time of the admixture, as well as a decrease in the very early exotherm. The greater initial exotherm observed when the admixture was added to the mixing water implies a higher early aluminate reaction. Thus, the extended set times and lowered initial exotherm with the delayed addition of admixture could be partially due to less admixture being chemisorbed or intercalated by the aluminate phase, forming OMP, leaving higher amounts of chemical in the solution to retard hydration.

It is proposed that the delayed addition of admixture allows the normal sulfoaluminate phases to form thus minimizing OMP formation. As a results of understanding how early C_3A reactions can decrease the effectiveness of water reducers, a number of technical approaches [21,105] have been applied to give controlled release of the materials, so that the early aluminate reactions will not render them inactive.

4.4. Impact on addition rates

A relative indication of the impact that several normal and high range water reducing agents can have on the rate of cement hydration is illustrated in Fig. 19. The slump versus set time data were obtained by dosing each additive over a range (0.03%–0.45%, dosage is dependent on WR/HRWR used) to produce slump values from 100 to 225 mm in a concrete mixture with 300 kg/m^3 of cement and 0.51 w/c. When the set times of the concrete mixture are normalized for slump, a dramatic difference in set time is evident among the various dispersants, which results from a combination of dispersant chemistry and amount adsorbed on the cement surface. Thus, while the inherent retardation of water reducers is important, the critical measure is retardation at a given water reduction. This example suffices to show that dispersing ability and retardation are not directly related in a linear manner.

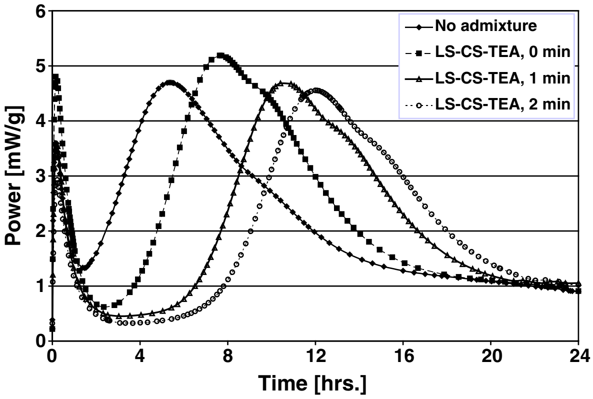

Fig. 18. Isothermal calorimetry profiles of ASTM C359 mortar mixtures with and without lignin-corn-syrup-TEA blends (same mortars shown in Fig. 17), highlighting effect of delayed addition (1 and 2 min delay) on the rate of hydration.

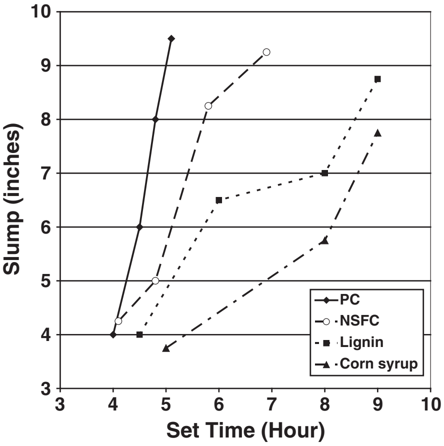

Fig. 19. Slump and set performance of polycarboxylate-based (0.03–0.12% s/s), NSFC-based (0.10–0.45% s/s), lignin-based (0.10–0.35% s/s), and corn syrup-based (0.1–0.30% s/s) water reducing agents. Dosage rates are expressed as percent of active admixture by weight of cement.

4.5. Requirements for modeling the impact of water reducing dispersant

In light of the discussions above, it would appear that multi-component models will be needed to describe the behaviors of the hydration of cement containing water reducing dispersants. We expect the results generated from molecular-scale simulations will need to be parameterized as input for coarser-scale models to describe the different systems. Some aspects for the models to show are:

- how the molecular architectures of the water reducing dispersants affect both the surface sorption behavior, the dispersing power and the retention of that dispersing power. This is the first order requirement to model and the recent work by Yamada et al. [97] and Flatt et al. [103,104] and many others have shed much light on this aspect,
- what type of competitive reactions are generated when water-reducing dispersants with different chemistries and molecular architectures are present (i.e. how much dispersants is abstracted – forming either truly intercalated hydrocalumites or chemisorbed on hydrating aluminates (both of which comprise OMP); how much is adsorbed on the different surfaces of cement particles and hydration products producing dispersion; how much are remains dissolved in the pore solutions; and how these aspects are affected when the dispersants are formulated with other, non-dispersant components),
- how the above competitive reactions are impacted by the presence of different amounts and forms of sulfates, and of other chemicals present which can compete for the surfaces,
- how the above competitive reactions are impacted by the different times of additions of the water-reducing dispersants,
- how the above competitive reactions are impacted by the different dosages of the water reducing dispersants, and
- how the very early rates of hydration, and especially sulfate demand, are impacted by dispersed cement particles versus agglomerated cement particles.

Once the above can be understood, reduced to theories and to mathematical formalisms, we can then put better predictive models together. The effectiveness of these models must be tested using well-characterized cements with different sulfate conditions and water-reducing components (as single components and multiple mixed systems) that are added at different addition rates and at different times of additions.

5. High calcium fly ash interactions as a modeling opportunity

One of the more frequently encountered negative interactions between cement, supplementary cementitious materials and admixtures occurs with high calcium fly ashes. These are classified as ASTM C 618 Class C. These fly ashes are found mostly in the US, but they also occur in other parts of the world. In this article, we will designate them as "high calcium fly ash" while recognizing their behavior is due to the fact they are truly high calcium aluminate fly ashes, as discussed below. Due to their complexity of composition, high calcium ash interaction with cement and admixtures affords a particularly interesting challenge to model. These ashes typically contain significant levels of calcium aluminates, both in crystalline and glassy form. The crystalline forms typically include C_3A, but at CaO contents above 25% Klein's compound, $Ca_4(AlO_2)_6SO_4$, may also form [106,107], when sufficient sulfate is available in the coal. The glassy forms reflect various compositions, again depending on calcium content [107]. The gross compositions are widely variable, while generally falling into groups depending on the coal source [106,107]. However, since each ash particle is generated from an individual coal particle entrained in the gas stream, they will have unique composition; further these individual particles are heterogeneous [107,108]. It is seen that many such ashes contain significant sulfate, generally in the form of soluble anhydrite condensed from the gas stream onto the surfaces of the particles and thus making the sulfate readily available [107]. In others a significant amount of the sulfate may be included in the glassy phases where the sulfate becomes available only well after the initial hydration and setting [109].

The extra available aluminates and limited sulfate availability can create a special case of the undersulfated conditions discussed earlier, leading to rapid slump loss and severely reduced early strength.

Surprisingly, such problems may be especially prevalent when low C_3A cements are used. In these cases the low added sulfate levels required for the cement alone limit any excess to be available for the ash.

Even without admixtures, retardation of silicate hydration with high calcium ash has been reported [110,111]. In some cases no slump loss is seen; in some the loss of early strength is mild, in others severe. This has been discussed in numerous papers [31,32,36,111], and it is generally understood to be due to inadequate control of the total aluminate phases, both from the cement and from the fly ash, leading to the aluminate reaction preceding the silicate to the extent that the silicates are suppressed, as originally shown possible by Lerch. In the specific case with high calcium fly ash, it has been shown to be a function of the composition of the materials, the ratios selected, and the temperature. Generally the more ash used, or the more admixture used, or the higher the temperature, the more likely the problem is to occur. The better sulfated the cement is, that is the later the sulfate depletion point on the calorimetry curve occurs relative to the main peak maximum, the more robust the system is likely to be [42].

In cases when admixtures are used, poor performances can result for a number of reasons. First, dispersion alone can cause negative interaction to occur as a result of the extra aluminate surface available for reaction in the critical first few minutes when the sulfate must dissolve rapidly enough to control the aluminate reactions. Second, an increase in C_3A content brought on by the use of high calcium fly ash compounded with the increased calcium chelating effects brought on by retarders can cause unexpected excessive retardation. This effect was reported by Hanehara and Yamada [50] who attributed the excessive retardation to "..the initial hydration of C_3A was not controlled effectively because of the increase in the effective C_3A content brought about by the high replacement level of Class C ash and the effect of retarders 'capturing' Ca^{++} ions from the solution phase. With the lack of an adequate amount of sulfate and Ca^{++} ion supply, C_3A is thought to react with abnormally high activity and this results in the delay of C_3S hydration". Taking the simplest case of a cement with no admixtures, with adequate sulfate the surface would be expected to have sulfate adsorbed on all available sites; with low sulfate it would not. Despite the fact that C_3S will hydrate normally in water, Lerch showed 65 years ago that cement without adequate sulfate will not. Thus, it can be inferred that adequate sulfate coating on alite is critical to hydration, while in the presence of aluminate phases. As expected from the role calcium ion plays in stabilizing ettringite, problems with excessive reaction of the calcium aluminate would also be expected to occur if insufficient calcium hydroxide is released in the early reactions. Recent work in 50:50 cement high calcium fly ash blends has shown the addition of 5% calcium hydroxide to overcome excessive set retardation, which occurred even with added sulfate. This confirms adequate calcium hydroxide to be critical in at least some instances [112,113].

Fajun et al. [110] evaluated high calcium fly ash versus the same ash leached in water, and found a reduction in retardation by leaching. They ascribed this lesser retardation to a reduction in calcium consumption by the leached fly ash due to lower available reactive aluminate. Taken together, these would suggest a potential relationship to calcium hydroxide supplied by alite hydration. Thus both low C_3S content and prehydration will be predicted to reduce initial flush of Ca^{++} ions resulting in non-optimal set and strength development, but we are unaware of any reported work exploring this relationship.

This sensitivity can lead to the very unusual circumstance of slight increases in temperature causing increases in aluminate reaction, either due to the temperature per se, or to the depression in sulfate solution rate from plaster, which then leads to very strong suppression of silicate reaction and reduction in strength, while set and workability during placement appear normal [37,42,111,114]. This sequence of events can lead to markedly less reaction at higher temperature, a deviation from normal Arrhenius behavior. Moreover, when the materials and conditions favor the problem, the difference between total failure and slow but acceptable strength gain can be as little as 6 °C [37] or 0.2% early available sulfate. We will discuss these in some detail to point out the issues seen in the field.

Such systems can be on a very fine edge. 20 years ago, one of the authors (Roberts) encountered a field problem with such a combination, with an ASTM C 618 Class C ash, a 200 ml/100 kg dose of lignin-corn syrup-triethanolamine water reducer and a Type II cement, where concrete showed rapid slump loss and at one day had failed to develop enough strength to allow demolding of the strength specimens. On analysis the cement was found to have 2.3% SO_3, which by discussion with the cement producer was determined to consist of a 40% gypsum/60% anhydrite blend. The gypsum was largely dehydrated because of the heat experienced during the grinding process. When the manufacturing SO_3 set point was raised to 2.9%, the problem disappeared. As this increase would contribute only 0.2% readily-soluble SO_3 as plaster, it is clear that minor changes in sulfate level can have large effects.

This was recently dramatically demonstrated by Cost and Gardiner [114] using semi-adiabatic calorimetry. At 32 °C with a ~520 ml/100 kg dose of a corn syrup-amine type water reducing admixture and 15% high calcium fly ash, several plant run cements were tested over a normal range of SO_3 production variation from 3.08 to 3.28%, having a standard deviation of 0.09%, which is well within normal plant control. The 3.28% cement showed a normal, but delayed exotherm and gave 12.5 MPa at one day by ASTM C 109. 3.21% SO_3 gave a diminished exotherm and ~9.8 MPa, while 3.16, 3.08, and 3.06% SO_3 all yielded a severely truncated calorimetry pattern and less than 1 MPa at one day. For the same cements, at the same temperature but a ~260 ml/kg dose of chemical admixture, all calorimetry results showed normal main hydration peak exotherms, with only a slightly increased delay at 3.06% SO_3.

The technical and economic challenge here is clear. Especially in the North American market, where the decisions about amounts of fly ash to substitute are being made at the level of the Ready Mix quality control department, it is very hard to avoid problems in a situation where both cost and environmental considerations favor the use of the maximum possible ash. Few are aware of the strong impact of temperature, so that mixtures evaluated and found acceptable in laboratory conditions of about 20 °C can fail totally at 30 °C.

From a practical mixture proportioning point of view, this means that any mix selected for use should be challenged by testing at higher temperatures. Since it is difficult to represent an increase in active aluminate or a decrease in available sulfate, tests at higher doses both of ash and admixture or higher temperatures can be used to determine if the system is near to a problem. From the modeler's point of view, the apparent non-Arrhenius behavior of this system must be accommodated. Clearly aluminate reactivity and sulfate availability are at the heart of the issues, but the exact mechanism whereby the silicate reaction can be shut down so dramatically needs to be elucidated as well.

5.1. Normal impact of differing materials

Wang et al. [115] showed the differences in response of two different cements blended with a high calcium fly ash containing 30.5% CaO, at 20% addition on cement, with an unidentified mid-range water reducer. The first cement, shown in Fig. 20, had a 0.48 SO_3 to C_3A mass ratio, and the reduction of the main hydration calorimetry peak height is only 7.5%. Note the sulfate depletion points represented by the inflections in the curves remain at similar points in time, but different in relation to the main hydration peak. With a different cement at slightly lower SO_3 to C_3A mass ratio of 0.42, Fig. 21, the sulfate depletion points are not obvious. With the high calcium ash and admixture, depletion may be at the slight inflection seen near the foot of the much more seriously retarded and suppressed main hydration peak. The split peak with the cement alone may indicate the depletion is at about 9 h, but as this shape can result from depletion occurring before the silicate peak, this cannot be stated with confidence. In both cases, tests with added sulfate would be able to determine the actual depletion points. In any case, the sulfate is depleted substantially earlier in relation to the silicate when compared with the results in Fig. 20, and greater suppression of the main hydration results. Effects as mild as this may or may not be visible in the field.

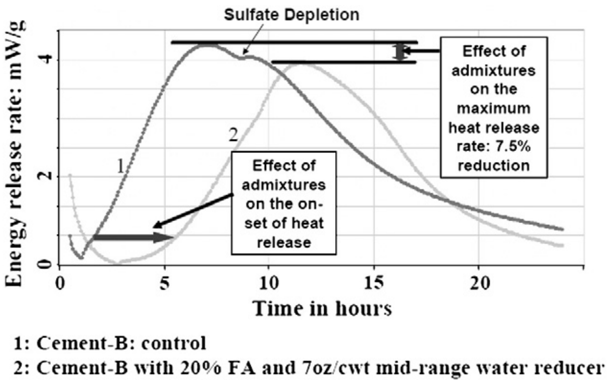

Fig. 20. Isothermal calorimetry curves from Wang et al. [115], with added indication of sulfate depletion, showing moderate suppression of silicate hydration peak with 20% added class C fly ash in a well-sulfated cement.

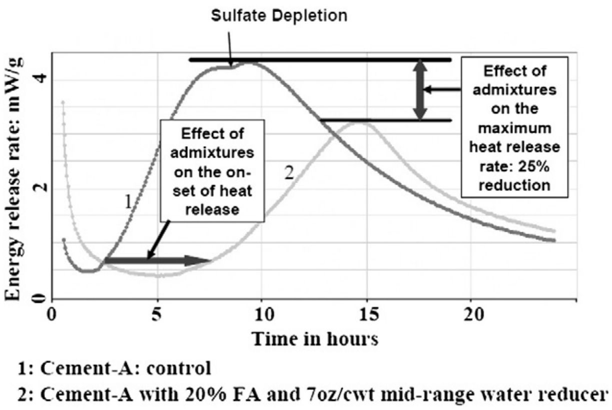

Fig. 21. Isothemal calorimetry curves generated by Wang et al. [115], with added indication of sulfate depletion, showing more serious suppression of silicate hydration peak with 20% added class C fly ash in mildly undersulfated cement.

5.2. Serious impact at higher high calcium fly ash dose

A more serious case of performance impact is seen in data from Roberts and Taylor [42]. A section of pavement containing high calcium fly ash and a lignin-triethanolamine water reducer at 325 ml/100 kg of cementitious failed to set and was removed. The mix was designed at the maximum ash replacement which was found acceptable in the laboratory – 32%. A number of changes, both in cement – a minor reduction in SO_3 content in a new shipment, and in placement conditions – a much higher temperature – led to the failure. Without the water reducer, Fig. 22 shows the suppression of the hydration was marked, but hydration still occurred. With the water reducer, an early high reaction rate in the first 4 h was followed by no silicate hydration. In this case, the water reducer dispersed the cement and fly ash particles which led to a condition where problem-causing calcium aluminate hydrates were formed and the combination of the above condition also resulted in the shutting down of the silicate hydration. When the amount of this high calcium flyash was reduced to 20%, or when other ashes or other cements were used, proper setting and hardening performances were restored.

Various levels of sulfate were added to determine if the system could be restored to proper performance. Fig. 23 shows the results with 1.6%–2.1% SO_3 added as plaster, and shows that, 1.6% and more achieve full hydration. This is fully in line with what Lerch found 65 years ago – when there is enough sulfate – more does not help. The

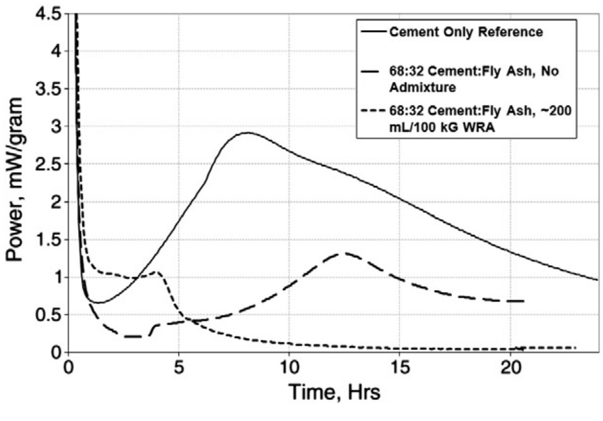

Fig. 22. Isothermal calorimetry curves after Roberts and Taylor [42] showing complete suppression of silicate hydration with 32% high calcium fly ash replacement and lignin-triethanolamine water reducing admixture at 325 ml/100 kg cementitious dosage.

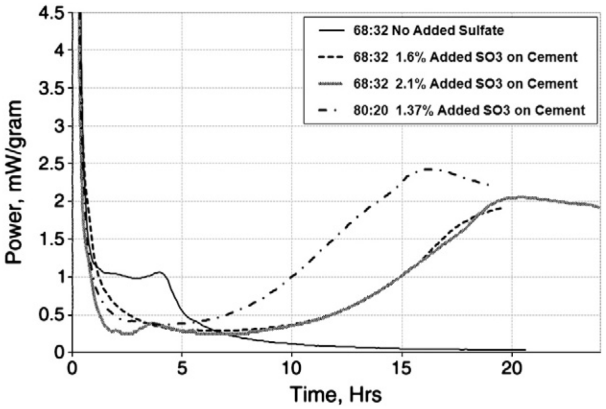

Fig. 23. Isothermal calorimetry curves after Roberts and Taylor [42] showing restitution of silicate hydration by addition of 1.2% to 2.2% SO_3 by cement mass (as plaster), with 32% high calcium fly ash replacement, lignin-triethanolamine water reducing admixture at 325 mL/100 kg cementitious. Includes added data showing the impact of reducing blend ratio to 80:20 (cement:fly ash ratio).

initiation of hydration is nevertheless still delayed. Reduction of the ash content to 20% plus added sulfate resulted in a normal hydration exotherm and approximately 5 h faster hydration.

5.3. Extreme non-Arrhenius behavior with higher temperatures

The correlation of calorimetric response and strength measurement for these systems was shown clearly by Cost [37]. In this work on exploring the interaction of a carbohydrate-triethanolamine water reducer admixture at 390 ml/100 kg cementitious with cement SO_3 level and temperature, semi-adiabatic calorimetry and mortar strength testing showed that the higher the temperature, the more sulfate was needed to obtain normal hydration and achieve normal strength. At lower sulfate levels high temperature was seen to suppress not only 1 day, but also 3 day strengths. At the highest temperature of 100 °F or 38 °C, even 28 day strength was reduced at the lower sulfate levels. The data were re-plotted by Roberts and Taylor [43], Fig. 24, to show the dramatic nature of this apparent non-Arrhenius behavior. In another study Muhhopahyay et al. [111] studied two admixtures – a so-called mid-range water reducer and a water reducing retarder not further identified, at 10, 24 and 35 °C, and showed that retardation was much greater with ASTM C 168 Class C ash as compared to Class F ash. Also very strong excessive retardation with almost complete suppression of the main hydration peak was shown with only a double dose of the retarder, equivalent to 0.4% by total cement binder weight.

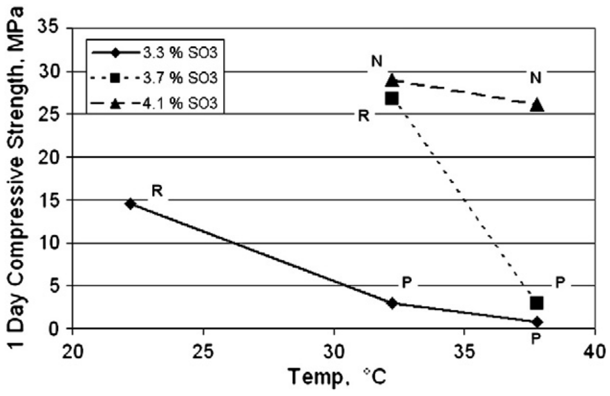

Fig. 24. Chart adapted from Roberts and Taylor [42] analyzing data from Cost [29], showing extent of non-Arrhenius behavior and its sensitivity to SO_3 content. N = Normal semi-adiabatic calorimetry curve, R = Reduced calorimetry curve with evident silicate reaction before 24 h, P = Poor curve with little evident silicate reaction before 24 h.

Thus, the behavior of a number of high calcium fly ash mixtures is well characterized and a number of different sensitivities are easily reproduced. The materials are available, and those conversant with the effect could supply material to researchers exploring ways to model such systems.

5.4. Requirements for modeling the behavior of systems with high calcium fly ash

The combination of admixtures with of high calcium fly ash and cement at varying ratios affords modelers a system with known extremes of behavior. If a model can accommodate these extremes, its ruggedness will be shown. Materials are available for experimental correlation with modeling, and the methodology for those experiments is widely known and efficient.

Among the requirements would be that the model:

- show the sensitivity both to amount and availability of sulfate and calcium in solution,
- be able to reproduce the mild and sometimes complete suppression of hydration seen in the real systems,
- reproduce the non-Arrhenius behavior with temperature, and
- show the sharp, trigger like change at the critical sulfate ratio, admixture dose, sulfate level or temperature typical of field results.

6. Closing the gaps: a road map for future research

Although better insights on the mechanisms of Portland cement hydration in the presence of chemicals are being provided by modern research, there are still many gaps in the knowledge that hinder the development of hydration models. A number of the specific requirements needed to model the behaviors of retarders, accelerators, water reducing dispersants and systems with high calcium fly ashes were listed at the end of their respective sections. In the following, we will present the more global issues that we see are important to address. We will divide our discussion into three categories – experimental condition issues, possible new experiments, and modeling goals. None of these lists are complete as we can only touch on some of the main challenges facing us.

6.1. Experimental condition issues

- One of the gaps resides in the variety of experimental conditions used by different researchers. The starting materials (OPC, C_3S, C_3A, etc), the ratio between the compounds of the mix (cement, water, chemical), and the mixing conditions, among others, are critical factors that have enormous impact on the reaction behavior of the mix. Even for the same type of starting materials, the characteristics and therefore reactivity can differ depending on the raw materials used for the synthesis, the thermal treatment, the particle size distribution of the powder, and the presence of impurities. Often the details are missing from the reported literature. As an example, the recent etch pit theory emphasizes the effect of ionic concentration on site deactivation, yet many experiments are carried out in highly excessive w/c for instrument and other reasons, bringing into question the applicability of the results of those experiments. Another example is the large difference between C_3A crystal form reactivity and response to admixtures, necessitating thorough characterization of any C_3A used.
- Another experimental gap lies in the sulfate source used in experiments. In most of the researches the full analysis is not provided. This limits the ability for modelers to simulate these systems.

- In many research programs our understanding would be advanced by deliberate addition of extra calcium sulfate to determine if the system under investigation is in an undersulfated condition, and what changes occur when corrected.
- The dosage of chemical admixtures used in mechanistic studies is yet another issue that deserves attention. In many cases, very large dosages of admixtures are used in mechanistic studies. Although the probable intent is to promote a measurable impact in the system, we must note that the high dosage of chemicals used in these studies may result in behavior markedly different from when realistic dosages are used in the field, due to the almost exclusively non-linear response of cementitious systems to admixture dose.
- In a number of studies on the impact of chemical structure on performance, constant mass dosage is used. In many cases, better information would be obtained if constant molar doses were used, either alone or in addition to the constant mass doses. Then direct impact of structural differences would be evident, which can be masked by the fact that at constant mass, if one moiety is increased, another must be decreased.
- Finally, it is important to have in mind that, in most systems, more than one chemical product will be present at the same time. It is well known, from performance studies, that chemicals do interact in synergistic or antagonistic fashion. Understanding the mechanisms of such interactions, and modeling them in cementitious systems, is yet another challenge.

6.2. Key experiments

There are a number of potentially useful experiments that to the authors' knowledge have not been reported that would appear to offer useful insights:

- AFM and SEM tracking studies similar to those reported by Juilland [14] on C_3S or alite surfaces hydrated in saturated limewater in the presence of C_3A, with deliberately varied levels of sulfate. Hydration could be tracked by companion calorimetry studies. This would reproduce the results of Tenoutasse [27], but let us see what happens to the surface as sulfate availability changes and silicate hydration is reduced.
- If the above yielded interesting results, addition of similar studies including a typical water reducing chemical known to have issues with undersulfated conditions would add extra knowledge about changes in the alite surfaces as the system begins to exhibit extended retardation.
- Further investigation into Makar's [45.48] observation of a transition peak at the beginning of rapid hydration, in conjunction with varied doses of those admixtures known to have differing impact on the relation of acceleration of induction period versus hydration rate thereafter.

6.3. Modeling goals

Thus the goal is to develop models sufficiently flexible to give predictions which reflect the several major impacts of admixtures. Among the requirements would be to:

- model the various mechanisms of retardation separately, so that the relative impact of any retarder on each potential mechanism type can be reflected, yielding predictions which cannot only reproduce the delay in the onset of hydration, but also the differing relative reaction rates after the end of the retarding period,
- model the various mechanisms of accelerators separately, which can yield prediction of not only the acceleration of the end of the induction period, but also the hydration thereafter. In particular, model the interaction of non-chloride accelerators, wherein the sensitivity to sulfate demand can lead to retardation by accelerators when adequate sulfate is not available. The impact of different C_3A crystal form must be accommodated in this model,
- model the varying impact on strength development by alkanolamines of differing chelating capacity, including their impact on sulfate demand and interaction with cement iron content,
- for dispersing admixtures, model the competition for cement surface between dispersant, sulfate, accelerators and retarders that can be added separately or together as components of the dispersing admixtures, while taking into consideration the sulfate effect on OMP formation,
- model differing tendencies to form OMP, which alter the admixture's response to variation in dosage time, aluminate activity and sulfate availability, in such a way that delineates true intercalation from surface adsorption on reaction products,
- model the various effects dispersion can have on the hydrating cement system, separating the potential very early higher sulfate demand or OMP formation due to faster aluminate reaction from the known fluidizing effects, and the later sometimes-encountered strength and permeability improvements due to more even w/c on the microscopic level,
- model the complex interactions which occur when aluminous SCM's such as high calcium fly ash are added.

Acknowledgements

This paper is an outcome of the International Summit on Cement Hydration Kinetics and Modeling. The authors acknowledge financial support for that conference from the National Science Foundation (NSF) through Grant Award Nos. OISE-0757284 and CMS-0510854, the Federal Highway Administration (FHWA), Mapei, W. R. Grace, BASF, the Tennessee Technological University (TTU) Center for Manufacturing Research (CMR), the Canadian Research Center on Concrete Infrastructure (CRIB) and the Natural Science and Engineering Research Council of Canada (NSERCC). The authors would also like to acknowledge the organizers of the Summit including Joseph J. Biernacki (TTU), Will Hansen (University of Michigan), Jeff Bullard (National Institute of Standards and Technology) and Jacques Marchand (Laval University). The authors would also like to thank Joseph J. Biernacki (TTU) for providing input and edits for the paper and for his dedication in coordinating the efforts for the Summit. The support of W.R. Grace in affording the time required is appreciated. Finally, the authors appreciate the detailed and challenging review of the paper, which has helped us greatly refine our presentation.

References

[1] J.M. Pommersheim, J.R. Clifton, Mathematical modeling of tricalcium silicate hydration, Cem. Concr. Res. 9 (1979) 765–770.
[2] P.W. Brown, J. Pommersheim, G. Frohnsdorff, A kinetic model for the hydration of tricalcium silicate, Cem. Concr. Res. 15 (1985) 35–41.
[3] J.J. Thomas, H.M. Jennings, Effects of D_2O and mixing on the early hydration kinetics of tricalcium silicate, Chem. Mater. 11 (1999) 1907–1914.
[4] O. Bernard, F.J. Ulm, E. Lemarchand, A multiscale micromechanics-hydration model for the early-age elastic properties of cement-based materials, Cem. Concr. Res. 33 (2003) 1293–1309.
[5] J.J. Thomas, A new approach to modeling the nucleation and growth kinetics of tricalcium silicate hydration, J. Am. Ceram. Soc. 90 (2007) 3282–3288.
[6] S. Garrault, A. Nonat, Hydrated layer formation on tricalcium and dicalcium silicate surfaces: experimental study and numerical simulations, Langmuir 17 (2001) 8131–8138.
[7] D.P. Bentz, Three-dimensional computer simulation of Portland cement hydration and microstructure development, J. Am. Ceram. Soc. 80 (1997) 3–21.
[8] D.P. Bentz, Modelling cement microstructure: pixels, particles, and property prediction, Mater. Struct. 32 (1999) 187–195.
[9] S. Bishnoi, K. Scrivener, Studying nucleation and growth kinetics of alite hydration using µic, Cem. Concr. Res. 39 (2009) 849–860.
[10] J.W. Bullard, A determination of hydration mechanisms for tricalcium silicate using a kinetic cellular automation model, J. Am. Ceram. Soc. 91 (2008) 2088–2097.
[11] J.W. Bullard, A three-dimensional microstructural model of reactions and transport in aqueous mineral systems, Model. Simul. Mater. Sci. Eng. 15 (2007) 711–738.

[12] J.J. Thomas, H.M. Jennings, J.J. Chen, Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, J. Phys. Chem. C 113 (2009) 4327–4334.

[13] E. Gallucci, P. Mathur, K. Scrivener, Microstructural development of early age hydration shells around cement grains, Cem. Concr. Res. 40 (2010) 4–13.

[14] P. Juilland, E. Gallucci, R. Flatt, K. Scrivener, Dissolution theory applied to the induction period in alite hydration, Cem. Concr. Res. 40 (2010) 831–844.

[15] J. Plank, Z. Dai, H. Keller, Organo-mineral phases formed during cement hydration, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[16] J. Plank, Z. Dai, P.R. Andres, Preparation and characterization of new Ca–Al–polycarboxylate layered double hydroxides, Mater. Lett. 60 (2006) 3614–3617.

[17] J. Plank, D. Zhimin, H. Keller, F. Hossle, W. Seidl, Fundamental mechanisms for polycarboxylate intercalation into C_3A hydrate phases and the role of sulfate present in cement, Cem. Concr. Res. 40 (2010) 45–57.

[18] C. Giraudeau, J.B.E. Lacaillerie, Z. Souguir, A. Nonat, R. Flatt, Surface and intercalation chemistry of polycarboxylate copolymers in cementitious systems, J. Am. Ceram. Soc. 92 (2009) 2471–2488.

[19] F. Winnefeld, S. Becker, J. Pakusch, T. Gotz, Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems, Cement Concr. Compos. 29 (2007) 251–262.

[20] V.H. Dodson, T.D. Hayden, Another look at the Portland cement/chemical admixture incompatibility problem, Cem. Concr. Aggreg. 11 (1989) 52–56.

[21] L. Raki, J.J. Beaudoin, L. Mitchell, Layered double hydroxide-like materials: nanocomposites for use in concrete, Cem. Concr. Res. 34 (2004) 1717–1724.

[22] L.H. Tuthill, R.F. Adams, S.N. Bailyey, R.W. Smith, A case of abnormally slow hardening concrete for tunnel lining, J. Am. Concr. Inst. 57 (1961) 1091–1110.

[23] S.M. Khalil, M.A. Ward, Influence of SO_3 and C_3A on the early reaction rates of portland cement in the presence of calcium lignosulfonate, Am. Ceram. Soc. Bull. 57 (1978) 1116–1122.

[24] P. Sandberg, C. Porteneuve, F. Serafin, J. Boomer, N. LoConte, V. Gupta, B. Dragovic, F. Doncaster, L. Alioto, T. Vogt, Effect of admixture on cement hydration kinetics by synchrotron XRD and isothermal calorimetry, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[25] L.M. Meyer, W.F. Perenchio, Theory of concrete slump loss as related to use of chemical admixtures, ACI Concr. Int. 1 (1979) 36–43.

[26] W. Lerch, The influence of gypsum on the hydration and properties of Portland cement pastes, Proc. Am. Soc. Test. Mater. 46 (1946) 1252–1292.

[27] N. Tenoutasse, The hydration mechanism of C_3A and C_3S in the presence of calcium chloride and calcium sulphate, Proceedings of the 5th International Symposium on the Chemistry of Cement (ISCC), Tokyo, Supplementary Paper II-118, 1968.

[28] A.C. Jupe, A.P. Wilkinson, K. Luke, G.P. Funkhouser, Slurry consistency and in-situ synchrotron X-ray diffraction during the early hydration of Portland cements with calcium chloride, J. Am. Ceram. Soc. 90 (2007) 2595–2602.

[29] H. Minard, S. Garrault, L. Regnaud, A. Nonat, Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum, Cem. Concr. Res. 37 (2007) 1418–1426.

[30] S. Pourchet, L. Regnaud, J.P. Perez, A. Nonat, Early C_3A hydration in the presence of different kinds of calcium sulfate, Cem. Concr. Res. 39 (2009) 989–996.

[31] P.J. Sandberg, L.R. Roberts, Studies of cement-admixture interactions related to aluminate hydration control by isothermal calorimetry, ACI SP-217 (2003) 529–542.

[32] P.J. Sandberg, L.R. Roberts, Cement-admixture interactions related to aluminate control, J. ASTM Int. 2 (2005) 219–232.

[33] P.C. Taylor, L.A. Graf, J.Z. Zemajtis, V.C. Johansen, R.L. Kozikowski, C.F. Ferraris, Identifying incompatible combinations of concrete materials: volume I – Final report, FHWA Publication No. FHWA-HRT-06-079, US Department of Transportation, 2006.

[34] J-Ph. Perez, D. Sorrentino, Influence of aluminate hydrate and iron hydroxide precipitation on early-age C_3S hydration kinetics, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[35] C. Rössler, B. Möser, J. Stark, Influence of superplasticizers on C_3A hydration and ettringite growth in cement paste, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[36] J.P. Bombled, Influence of sulfates on the rheological behavior of cement pastes and on their evolution, Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, 3, 1980, pp. VI 164–VI 169.

[37] V.T. Cost, Incompatibility of common concrete materials – influential factors, effects, and prevention, Proceedings of the 2006 Concrete Bridge Conference, Reno Nevada, 2006.

[38] K. Scrivener, Challenges in modeling cementitious materials, Proceedings pro076: Mat. Sci. - HetMat - Modelling of Heterogeneous Mat. - Theme 2 (2010) 33–42.

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

[40] H. Pöllmann, S. Stefan, E. Stern, Synthesis, characterization and reaction behaviour of lamellar AFm phases with aliphatic sulfonate-anions, Cem. Concr. Res. 36 (2006) 2039–2048.

[41] V.H. Dodson, E. Farkas, Delayed addition of set retarding admixtures to Portland cement concrete, Proc. Am. Soc. Test. Mater. 64 (1965) 816–826.

[42] L.R. Roberts, P.C. Taylor, Understanding cement–SCM–admixture interaction issues, Concr. Int. 29 (2007) 33–41.

[43] I. Jawed, J. Skalny, Surface phenomena during tricalcium silicate hydration, J. Colloid Interface Sci. 85 (1) (1982) 235–243.

[44] H. Wang, C. Qi, H. Farzam, J. Turci, Interactions of materials used in concrete – effects of fly ash and chemical admixtures on Portland cement performance, Concr. Int. 28 (2006) 47–52.

[45] J.M. Makar, G.W. Chan, Derivative conduction calorimetry, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[46] J.M. Makar, G.W. Chan, K.Y. Esseghaier, A peak in the hydration reaction at the end of the cement induction period, J. Mater. Sci. 42 (2007) 1388–1392.

[47] J. Makar, High resolution cold field emission scanning electron microscopy of cements, Proceedings of the 29th International Cement Microscopy Association Conference, Quebec City, 2007, pp. 472–489.

[48] J.M. Makar, G.W. Chan, End of the induction period in ordinary Portland cement as examined by high-resolution scanning electron microscopy, J. Am. Ceram. Soc. 91 (2008) 1292–1299.

[49] E. Fratini, F. Ridi, S.H. Chen, P. Baglioni, Hydration water and microstructure in calcium silicate and aluminate hydrates, J. Phys. Condens. Matter 18 (2006) S2467–S2483.

[50] S. Hanehara, K. Yamada, Rheology and early age properties of cement systems, Cem. Concr. Res. 38 (2008) 175–195.

[51] J. Plank, Ch. Winter, Competitive adsorption between superplasticizer and retarder molecules on mineral binder surface, Cem. Concr. Res. 38 (2008) 599–605.

[52] S. Garrault, E. Finot, E. Lesniewska, A. Nonat, Study of C–S–H growth on C_3S surface during its early hydration, Mater. Struct. 38 (2005) 435–442.

[53] J.W. Bullard, R.J. Flatt, New insights into the effect o calcium hydroxide precipitation on the kinetics of tricalcium silicate hydration, J. Am. Ceram. Soc. 93 (7) (2010) 1894–1903.

[54] L.R. Roberts, Microsilica in Concrete, in: I.J. Skalny (Ed.), Materials Science of Concrete I, American Ceramic Society, Westerville, 1989, pp. 197–222.

[55] J. Stark, B. Möser, F. Bellmann, Nucleation and growth of C–S–H phases on mineral admixtures, in: C.U. Grosse (Ed.), Advances in Construction Materials, Springer, New York, 2007, pp. 531–538.

[56] Z.Q. Wu, J.F. Young, The hydration of tricalcium silicate in the presence of colloidal silica, J. Mater. Sci. 19 (1984) 3477–3486.

[57] R. Alizadeh, L. Raki, J.M. Makar, J.J. Beaudoin, I. Moudrakovski, Hydration of tricalcium silicate in the presence of synthetic calcium–silicate–hydrate, J. Mater. Chem. 19 (2009) 7937–7946.

[58] J.M. Makar, G.W. Chan, Growth of cement hydration products on single walled carbon nanotubes, J. Am. Ceram. Soc. 92 (2009) 1303–1310.

[59] H. Uchikawa, The role of free lime in early hydration of alite – retarder or accelerator? Am. Ceram. Soc. Bull. 63 (1984) 1143–1146.

[60] R.W. Previte, Some insights on the mechanism of saccharide set retardation of Portland cement, Cem. Concr. Res. 1 (1971) 301–316.

[61] J.F. Young, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures, Cem. Concr. Res. 2 (1972) 415–433.

[62] B. Casu, M. Chiruzzi, F. Tegiacchi, G. Zoppetti, Interaction of aluminates with carbohydrates and aldonates, Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, 4, 1980, pp. 558–563.

[63] N.L. Thomas, J.D. Birchall, The retarding action of sugars on cement hydration, Cem. Concr. Res. 13 (1983) 830–842.

[64] M. Bishop, A.R. Barron, Cement hydration inhibition with sucrose, tartaric acid and lignosulfonate: analytical and spectroscopic study, Ind. Eng. Chem. Res. 45 (2006) 7042–7049.

[65] M. Bishop, S.G. Bott, A.R. Barron, A new mechanism for cement hydration inhibition: solid-state chemistry of calcium nitrilotris(methylene)triphosphonate, Chem. Mater. 15 (2003) 3074–3088.

[66] A. Peschard, A. Govin, J. Pourchez, E. Fredon, L. Betrand, S. Maximilien, B. Guilhot, Effect of polysaccharides on the hydration of cement suspension, J. Eur. Ceram. Soc. 26 (2006) 1439–1445.

[67] M.C.G. Juenger, H.M. Jennings, New insights into the effects of sugar on the hydration and microstructure of cement pastes, Cem. Concr. Res. 32 (2002) 393–399.

[68] V.K. Peterson, M.C.G. Juenger, Hydration of tricalcium silicate: effects of $CaCl_2$ and sucrose on reaction kinetics and product formation, Chem. Mater. 18 (2006) 5798–5804.

[69] V.K. Peterson, M.C.G. Juenger, Time-resolved quasielastic neutron scattering study of the hydration of tricalcium silicate: effects of $CaCl_2$ and sucrose, Phys. B 385–386 (2006) 222–224.

[70] G. Moschner, B. Lothenbach, R. Figi, R. Kretzschmar, Influence of citric acid on the hydration of Portland cement, Cem. Concr. Res. 39 (2009) 275–282.

[71] J-Ph. Perez, The mechanism of action of sodium gluconate on the fluidity and set of Portland cement, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[72] L. Zhang, L.J.J. Catalan, R.J. Balec, A.C. Larsen, H.H. Esmaeili, S.D. Kinrade, Effect of saccharide set retarders on the hydration of ordinary Portland cement and pure tricalcium silicate, J. Am. Ceram. Soc. 93 (2010) 279–287.

[73] A.M. Rosenberg, Study of the mechanism through which calcium chloride accelerates the set of Portland cement, J. Am. Concr. Inst. 61 (1964) 1261–1270.

[74] G.C. Edwards, R.L. Angstadt, The effect of some soluble inorganic admixtures on the early hydration of Portland cement, J. Appl. Chem. 16 (1966) 166–168.

[75] J. Skalny, J.N. Maycock, Mechanisms of acceleration by calcium chloride: a review, ASTM J. Test. Eval. 3 (1975) 303–311.

[76] R. Kondo, M. Daimon, E. Sakai, H. Ushiyama, Influence of inorganic salts on the hydration of tricalcium silicate, J. Chem. Technol. Biotechnol. 27 (1977) 191–197.

[77] V.S. Ramachandran, R.F. Feldman, Time-dependent and intrinsic characteristics of Portland cement hydrated in the presence of calcium chloride, Cemento 75 (1978) 311–322.

[78] N.B. Singh, P.N. Ojha, Effect of $CaCl_2$ on the hydration of tricalcium silicate, J. Mater. Sci. 16 (1981) 2675–2681.

[79] M.C.G. Juenger, P.J.M. Monteiro, E.M. Gartner, G.P. Denbeaux, A soft X-ray microscope investigation into the effects of calcium chloride on tricalcium silicate hydration, Cem. Concr. Res. 35 (2005) 19–25.

[80] J. Neubauer, F. Goetz-Neunhoeffer, U. Holland, D. Schmitt, P. Gaeberlein, M. Degenkolb, Crystal chemistry and microstructure of hydrated phases occurring during early OPC hydration, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[81] V.S. Ramachandran, Hydration of cement – role of triethanolamine, Cem. Concr. Res. 6 (1976) 623–632.

[82] V.H. Dodson, Concrete Admixtures, Van Nostrand Reinhold, New York, 1990, pp. 92–95.

[83] V.S. Ramachandran, Influence of triethanolamine on the hydration characteristics of tricalcium silicate, J. Appl. Chem. Biotech. 22 (1972) 1125–1138.

[84] V.S. Ramachandran, Action of triethanolamine on the hydration of tricalcaium aluminate, Cem. Concr. Res. 3 (1973) 41–54.

[85] E. Gartner, D. Myers, Influence of tertiary alkanolamines on Portland cement hydration, J. Am. Ceram. Soc. 76 (1993) 1521–1530.

[86] S. Chaberek, A.E. Martell, Organic sequestering agents, John Wiley & Sons, Inc., New York, 1959.

[87] J. Perez, A. Nonat, S. Garrault-Gauffinet, S. Pourchet, M. Mosquet, C. Canevet, Influence of triisopropanolamine on the physico-chemical and mechanical properties of pure cement pastes and mortars, Proceedings of the 11th International Congress on the Chemistry of Cement, Durban, 2003, pp. 454–464.

[88] P.J. Sandberg, The effect of 4 alkanolamines on pore water composition and strength development of mortar, Proceedings of the 11th International Congress on the Chemistry of Cement, Durban, 2003, pp. 484–494.

[89] E. Gartner, R. Hu, J.H. Cheung, Influence of tertiary alkanolamines on rates of reaction of C_3A and C_4AF with calcite under conditions typical of Portland cement hydration in concrete, World Cement 29 (1998) 74–90.

[90] E.M. Gartner, CBA® processing additions for ordinary and blended Portland cements – a technology update, Proceedings of the PCA Manufacturing Process Committee Annual Meeting, California, September 1996.

[91] M. Ichikawa, M. Kanaya, S. Sano, Effect of triisopropanolamine on hydration and strength development of cements with different character, Proceedings of the 10th International Congress on the Chemistry of Cement (ICCC), 1997,, 3iii005.

[92] R. Rixom, N.P. Mailavaganam, Chemical Admixtures for Concrete, third ed.E & F Spon, London, 1999.

[93] N. Spiratos, M. Pagé, N.P. Mailavaganam, V.M. Malhotra, C. Jolicoeur, Superplasticizers for concrete: fundamentals, technology and practice, AGMV Marquis, Quebec, 2003.

[94] M.Y.A. Mollah, W.J. Adams, R. Schennach, D.L. Cocke, A review of cement-superplasticizer interactions and their models, Adv. Cem. Res. 12 (2000) 153–161.

[95] F. Ridi, L. Dei, E. Fratini, S.-H. Chen, P. Baglioni, Hydration kinetics of tri-calcium silicate in the presence of superplasticizers, J. Phys. Chem. B 107 (2003) 1056–1061.

[96] J. Rieger, J. Thieme, C. Schmidt, Study of precipitation reactions by X-ray microscopy: $CaCO_3$ precipitation and the effect of polycarboxylates, Langmuir 16 (2000) 8300–8305.

[97] K. Yamada, S. Ogawa, S. Hanehara, Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase, Cem. Concr. Res. 31 (2001) 375–383.

[98] W. Prince, M. Edwars-Lajnef, P.C. Aïtcin, Interaction between ettringite and polynaphthalene sulfonate superplasticizer in a cementitious paste, Cem. Concr. Res. 32 (2002) 79–85.

[99] J. Roncero, S. Valls, R. Gettu, Study of the influence of superplasticizers on the hydration of cement paste using nuclear magnetic resonance and X-ray diffraction techniques, Cem. Concr. Res. 32 (2002) 103–108.

[100] C. Haehnel, H. Lambois-Burger, L. Guillot, E. Borgarello, Interaction between cements and superplasticizers, Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, 2007.

[101] V. Fernon, A. Vichot, N. Le Goanvic, P. Colomber, F. Corazza, U. Costa, Interaction between Portland cement hydrates and polynaphthalene sulfonates, Fifth CANMET/ACI conference on superplasticizers in concrete, ACI, 1997, pp. 225–248, SP-173.

[102] T. Nawa, H. Eguchi, Effect of cement characteristics on the fluidity of cement paste containing an organic admixture, Proceedings of the 9th International Congress on the Chemistry of Cement (ICCC) IV, 1992, pp. 597–603.

[103] J. Zimmermann, C. Hampel, C. Kurz, L. Frunz, R.J. Flatt, Effect of polymer structure on the sulphate-polycarboxylate competition, in: T.C. Holland, P.R. Gupta, V.M. Malhotra (Eds.), Proceedings of the 9th ACI Int. Conf. Superplasticizers and Other Chemical Admixtures in Concrete, American Concrete Institute, Detroit, 2009, pp. 165–176,, SP-262-12.

[104] R.J. Flatt, J. Zimmermann, C. Hampel, C. Kurz, I. Schober, C. Plassard, E. Lesniewska, The role of adsorption energy in the sulphate-polycarboxylate competition, in: T.C. Holland, P.R. Gupta, V.M. Malhotra (Eds.), Proc. of the 9th ACI Int. Conf. Superplasticizers and Other Chemical Admixtures in Concrete, American Concrete Institute, Detroit, 2009, pp. 153–164,, SP-262-12.

[105] L. Raki, J.J. Beaudoin, Controlled release formulation of chemical admixtures, Canadian Patent CA 2554347, US Patent Application US 2007/0022916 A1 (2007).

[106] G.J. McCarthy, J.K. Solem, O.E. Manz, D.J. Hassett, Use of a database of chemical, mineralogical, and physical properties of North American fly ash to study the nature of fly ash and its utilization as a mineral admixture in concrete, Mater. Res. Soc. Symp. Proc. 178 (1990) 3–33.

[107] J.K. Tishmack, P.E. Burns, The chemistry and mineralogy of coal combustion products, in: R. Giere, P. Stille (Eds.), Energy, Waste and the Environment: a Geochemical Perspective, Special Publications, 236, Geological Society, London, 2004, pp. 223–246.

[108] R.T Chancey, Characterization of crystalline and amorphous phases and respective reactivities in a Class F fly ash, PhD Dissertation, University of Texas at Austin, 2008.

[109] J.K. Tishmack, J. Olek, S. Diamond, Characterization of high-calcium fly ashes and their potential influence on ettringite formation in cementitious systems, Cem. Concr. Aggr. CCAGDP 21 (1) (June 1999) 82–92.

[110] W. Fajun, M.W. Grutzeck, D.M. Roy, The retarding effects of fly ash upon the hydration of cement pastes: the first 24 hours, Cem. Concr. Res. 15 (1985) 174–184.

[111] A.K. Mukhopadhyay, S. Jung, Using cement paste rheology to predict concrete mix design problems, Technical Report FHWA/TX-09/0-5820-1, 2009.

[112] D.P. Bentz, C.F. Ferraris, Rheology and setting of high volume fly ash mixtures, Cement Concr. Compos. 32 (2010) 265–270.

[113] D.P. Bentz, Powder additions to mitigate retardation in high volume fly ash mixtures, ACI Mater. J. 107 (2010) 508–514.

[114] V.T. Cost, A. Gardiner, Practical concrete mixture evaluation via semi-adiabatic calorimetry, Fourth Annual Concrete Technology Forum, Focus on Performance Prediction, NRMCA, Cincinnati, 2009.

[115] H. Wang, H. Farzam, G. Lansing, E. Leigh, Cement performance – significances of the absence and presence of mineral and chemical admixtures, Proceedings of the Third International Conference on Construction Materials: Performance, Innovations and Structural Implications, Vancouver, 2005, p. 410.