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Intelligent Cement Slurry Design Based on Molecular Level Understanding

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Abstract

Designing cement slurries suitable for diverse wellbore conditions requires a multitude of additives to meet a variety of functional needs. Unfortunately, it is most commonly assumed that an additive, intended for a specific function, will perform identically when added to a cement slurry containing multiple additives, as when tested alone. This is rarely the case, especially with additives that require adsorption onto cement surfaces. When multiple additives compete for cement surfaces, the outcome may be synergistic or antagonistic. Understanding such interactions at the molecular level will enable intelligent design of slurry formulations wherein minimum amounts of additives can be utilized to deliver optimum performance. It is the purpose of this study to develop methodologies to evaluate the competitive adsorption rates of cement chemicals (dispersants, retarders, and fluid loss control agents), to relate their chemical structures to their relative adsorption behavior, and utilize the information for intelligent slurry designs.

Adsorption rates and saturation levels of several single additives and mixtures in simulated cement slurries were evaluated. Multiple techniques such as total organic carbon analysis, UV/Vis spectrophotometry, scanning electron microscopy, oscillatory rheological measurements, and isothermal calorimetry were used to understand the cement/additive interactions and their effects. Correlations between adsorption studies and realistic cement slurry performance studies using traditional techniques such as American Petroleum Institute recommended procedures were made. The results and their significance will be discussed.

Introduction

Design of primary cement slurry formulations for diverse wellbore conditions requires inclusion of a wide variety of additives into the designs. Some of the functions the additives are designed for include rheology modification, pump time adjustment, particle settling control, fluid loss control, gas migration control, density control and gelation control. These additives are usually added in small quantities, typically less than 5% by weight of cement (bwoc). Cement formulations can also include admixtures which are added in significantly larger quantities, typically in 3-100% bwoc. Such materials include density control materials, including high density and low density materials, strength retrogression materials, fillers, and mechanical-property modifying materials. Chemical additives added in small quantities make primary cementing possible in practice. A variety of additives with a wide range of chemical structures are available in each functional category to suit diverse wellbore conditions, such as temperature, pressure, salinity, formation lithology, pore pressures and rock properties such as fracture gradient.

It is commonly assumed that the chemical activities of each functional group will remain unchanged, which implies that each chemical will function as if it is present in the slurry alone by itself. In fact, ongoing investigations by scientists have clearly shown the fallacy of such an assumption. Published literature has shown chemical interactions between additives, mix water and its components, cement surfaces, and cement hydration products in the fluid and paste phases, often leading to antagonists, synergetic and dually synergetic interactions. When additives included in the slurry design are electrically charged molecules or electron dense, often interactions of the additives with cement surfaces are involved. These may involve precipitation on cement grain surfaces, reversible or irreversible adsorptions, selective reactions with chemicals present in the different crystalline phases of cement clinker. Frequently, such interactions influence the effectiveness of the additives by negative or positive interactions. Some examples from the literature are presented here.

First, the anionic cement dispersant, sulfonated acetone-formaldehyde condensate (SAFC, Figure 1) that functions by adsorption onto cement grains and inter-particle electrostatic repulsions, antagonistically reduces the effectiveness of a anionic 2-acrylamido-t-butyl sulfonic acid (ATBS)/N,N-dimethylacrylamide (NN-DMA) copolymer, which also functions by adsorption onto cement particle surfaces (Plank et al., 2007). Similar antagonistic interaction was observed between a synthetic anionic polymer retarder, namely ATBS/itaconic acid copolymer, and the anionic fluid loss polymer, namely ATBS/NN-DMA copolymer (Tiemeyer and Plank, 2012).

On the other hand, a combination of the same fluid loss polymer with a lignosulfate cement retarder is dually synergistic, providing improved cement retardation as well as improved fluid loss control (Recalde Lummer and Plank, 2012). Furthermore, even when only one additive adsorbs onto cement and the other additive is non-adsorbing, the combination can affect the performance of either of the additives. This is observed in the synergistic combination of a

Table 1. Mechanism of additive performance.

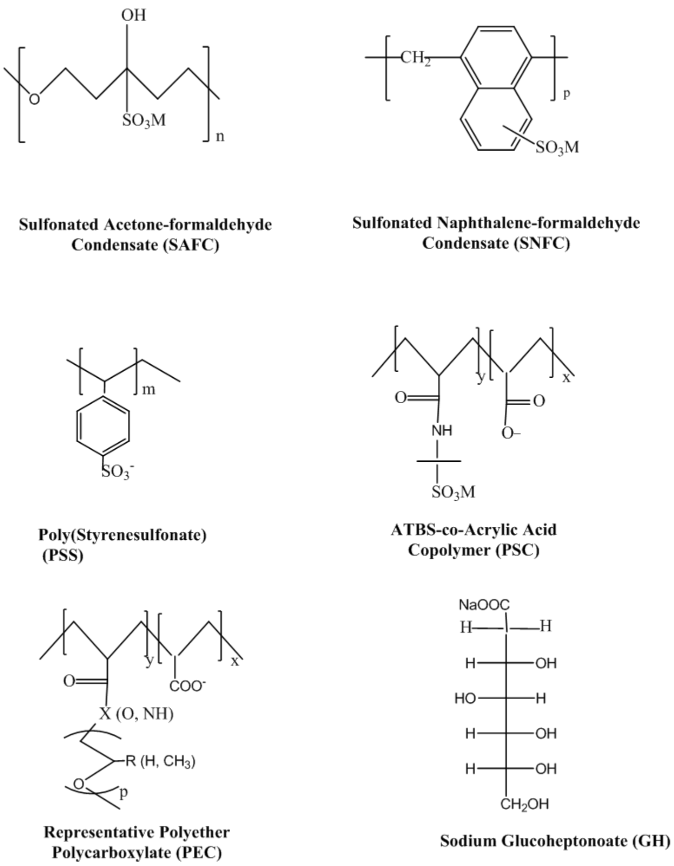
Dispersion	Retardation	Fluid Loss Control	Gas Migration Control
1) Electrostatic repulsion – adsorption dependent. 2) Steric repulsion – adsorption dependent.	1) Depletion of calcium ions generated by hydration—Ca^{2+} complexation or precipitation. 2) Adsorption on cement surface—prevention of water access to cement grains. 3) Barrier membrane formation on cement grain surface—water access is controlled by osmosis. 4) Nucleation poisoning—prevention of hydration product precipitation/ crystallization. 5) Dissolution-precipitation —combination of mechanisms 1) and 3).	1) Surface adsorption by polymers—filtercake permeability reduction. 2) Matrix fluid viscosification—decreased flow rates through filtercake permeability. 3) Water-swollen, hydrocolloidal particle plugging of flitercake porosity. 4) Elastomeric, interstitial film bridge or micelle formation in the filtercake—polymer adsorption on hydration products.	1) Elastomeric, interstitial film bridge or micelle formation in the slurry and filtercake—polymer adsorption on hydration products. 2) Hydration product dispersion—adsorption on hydration products.

sulfonated β-naphthalene formaldehyde condensate (SNFC, Figure 1) SAFC dispersant and hydroxyethyl cellulose (HEC) based fluid loss agent (Buelichen and Plank, 2011); a synergistic combination of polyethylene oxide based viscosifier and SNFC-based dispersing agent (Pickelmann and Plank, 2012); a synergistic combination of polyether polycarboxylate type superplasticizer (Figure 1) and hydroxyethyl cellulose (Bessaies-Bey et al., 2016); and a synergistic combination of SAFC and polyvinyl acetate based fluid loss control polymer (Plank et al., 2009). Lastly, an interesting case was reported of two retarders, nitrile tris(methylene) triphosphonate and sodium hexametaphosphate , when combined functioning as a cement accelerator (Pang et al., 2014).

Intelligent cement slurry design should be based on the following criteria:

1) The additives included in the slurry design should not interfere with the functions of another in an antagonistic manner.
2) The function of every additive should manifest only at the time when needed during the placement and strength development phases.

First, in order to design cement systems for diverse wellbore conditions encountered globally, a thorough understanding of the chemical interactions between additives and the mechanisms by which they perform a specific function by themselves in cement slurries, as well as in combination with multiple additives, is important. In fact, a single slurry may be designed with as few as 3 to as many as 12 additives. Additionally, a thorough appreciation of different mechanisms by which a specific cement slurry function can be accomplished during the placement and strength development phase is essential in choosing appropriate combination of additives in order to meet the two criteria listed. Some of the known mechanisms by single additives in cement slurries are listed in Table 1.



Sulfonated Acetone-formaldehyde Condensate (SAFC)

Sulfonated Naphthalene-formaldehyde Condensate (SNFC)

Poly(Styrenesulfonate) (PSS)

ATBS-co-Acrylic Acid Copolymer (PSC)

Representative Polyether Polycarboxylate (PEC)

Sodium Glucoheptonoate (GH)

Figure 1. Selected additive structures.

Intelligent cement slurry design should also take into account the mechanism by which an additive functions when used by itself, and arrive at combination of additives which will meet the requirements listed. Mechanisms by which different additives function in concrete and oil industry have been reviewed (Fink, 2003, Guilot and Nelson, 2006, Ramachandran, 1986, Smith, 1990). The next criteria describes the timing of the function and activation of an additive which requires either sequential addition of additives which is not practical in oil well cementing; or design the additive structure/composition in such a manner the active material is released at the right time in the right place, which is a non-trivial task.

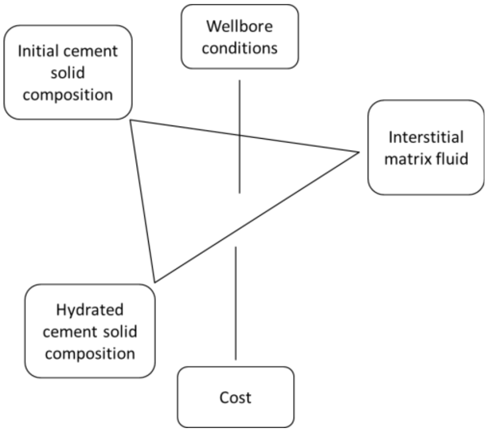


Figure 2. Factors affecting cementing additive functions, mechanisms, development and use.

Therefore, selection of a suitable additive combination depends on several factors, which are summarized in Figure 2. Published literatures, on additive development and use, primarily addresses all the factors presented in Figure 2, but only sporadically address additive interactions with cement hydration products (Ramachandran, 1986, Plank et al., 2009, Prince et al., 2002, Young, 1976). The effectiveness of additives, which function by adsorption onto cement grain surfaces, are not only influenced by other adsorbing additives, but also by competition from products, such as ettringite, amorphous calcium silicate hydrate (C-S-H) gel, and calcium hydroxide produced from cement hydration, as shown in Figure 3.

Investigation of competitive interactions among adsorbing type of additives typically used for cement slurry property management, and cement surfaces constitutes the focus of the present paper. Specifically, such interactions among polymeric cement dispersants, retarders and gas-migration control additives containing different anchoring groups, namely, carboxylate groups, aliphatic and aromatic sulfonate groups, and small molecule containing β-hydroxy-carboxylic acid group are investigated. The relative rates of adsorption of selected additives on hydrated and unhydrated cement surfaces are also investigated. In this study, relative adsorptions of two types of dispersants, namely SAFC containing aliphatic sulfonate; three polyether polycarboxylate (PEC) based superplasticizers containing carboxylate groups; a cement retarder containing both carboxylate and aliphatic sulfonate groups (PSC); and a potential gas migration control additive containing aromatic sulfonate group for cement surfaces were compared by their ability to desorb SAFC when used as binary mixtures. All the listed additives were polymers, and their representative structures are shown in Figure 1. Additionally, a small molecule retarder containing a carboxylic group and hydroxyl groups, namely sodium glucoheptonate (GH, Figure 1) was also tested in combination with SAFC.

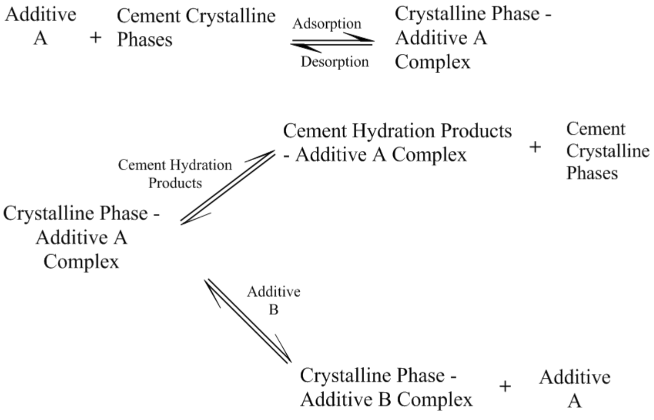


Figure 3. Adsorbing additive interactions with competitive additives and cement hydration products.

Materials and Methods

Materials

All chemicals used in this study were obtained from commercial vendors. The suppliers included Fritz Industries, Inc. (Mesquite, Texas), W. R. Grace, Construction Division, (Maryland, USA), and Akzo Nobel Corporation (Chicago, IL).

No structural information is available for the different PEC products used in the study, except for the following information available in the public domain:

PEC-1: A water reducer formulated to provide (extended slump life along with excellent workability without segregation

PEC-2: A water reducer with extended slump life and near neutral set time

PEC-3: Time-activated water reducer workability (slump and flow) enhancing mixture which when used in combination with any water reducers will significantly increase the duration of slump or flow retention.

PSS: Poly(styrene sulfonate) has a molecular weight listed as 1,000,000.

Molecular weight information of monomer ratios are not provided by the supplier for SAFC and PSC.

Methods

All adsorption kinetics studies were performed in suspensions of fresh Saudi Class G cement (5 grams) in DI water (100 ml) equipped with a stir bar, and were conducted at ambient temperature on a stirring hot plate to provide a 350 rpm stirring rate. As the solutions stirred magnetically in an open container, no special precaution was taken to protect the suspensions from atmospheric carbon dioxide.

For adsorption studies, a solution of one or more additives in specified concentrations (0.05-0.5% by weight of cement (bwoc)) was prepared. Dry cement was then added to the solution and stirred. Periodically, an aliquot from the reaction was taken and filtered through a filter disc (0.45 µm nylon). The filtrate was analyzed by total organic carbon (TOC; Shimadzu, Japan) and UV/Vis spectrophotometry (λ_{max}=420 nm; Hach, USA). Specifically, single component adsorption measurements were performed by TOC, whereas competitive adsorptions with SAFC and another additive were measured by spectrophotometry. In the latter method, the absorbance of an internal standard, SAFC, at gradient concentrations was constructed. Desorbed by the additional additive, the concentration of SAFC in the supernatant/filtrate mixture was measured from the absorbance value using the calibration curve. The difference was used to calculate the adsorbed amount of the second additive in the mixture. For experiments requiring use of pre-hydrated cement, cement was hydrated for a specified period of time using the same cement-to-water ratio and used as previously described by stirring the cement into a solution of additive(s).

For scanning electron microscopy (SEM;), the cement suspension at the end of the adsorption experiment was filtered, dried, sputter coated with palladium gold, and imaged with a Zeiss Crossbeam 540 SEM. For isothermal calorimeter measurements, the heat of hydration of cement slurries (15.8 pounds per gallon (ppg)) were prepared according to API procedure using water containing specified amounts of additive. These heat evolution measurements were made on TAM Air Calorimeter (TA Instruments, USA).

Results & Discussion

Single Additive Adsorption

The results from saturation concentration measurements by TOC for SAFC adsorption are shown in Figure 4. The additive concentrations in the mix water are by weight of cement (bwoc). The results show that the adsorption is a reversible, equilibrium process, reaching ~0.4% saturation concentration at room temperature. The dotted lines indicate the additive amount of the stock solution used for each concentration. Then, after 3 hours, adsorption increases linearly up to about a solution concentration of 0.5% bwoc (Figure 4A). An equilibrium constant of about 0.7 is observed at higher concentration (Figure 4A). All concentrations reach equilibrium after 5 minutes, except at the highest concentration at 1% bwoc, which takes about 30 minutes.

Using values at 30 minutes, Langmuir adsorption isotherm was plotted in Figure 4B using $1/q_e$ versus $1/c$:

$$\frac{1}{q_e} = \frac{1}{q_{max}K} \cdot C + \frac{1}{q_{max}} \qquad \text{(eq. 1)}$$

where the adsorption of SAFC onto cement fits the linear form of the Langmuir model, which is indicative of a monolayer on the surface (Figure 4B). The sorption capacity, (q_e), the equilibrium concentration *C*, and the empirical constant *K*, which describes the affinity of the additive to cement, are measured here. From the equation, maximum adsorption amount (q_{max}) of chemical additive, SAFC, onto cement is 8.0 mg g^{-1} with an association constant (K) of 106.0 (bwoc^{-1}). The large surface area of cement particles and TOC measurements are sensitive enough to measure adsorbance.

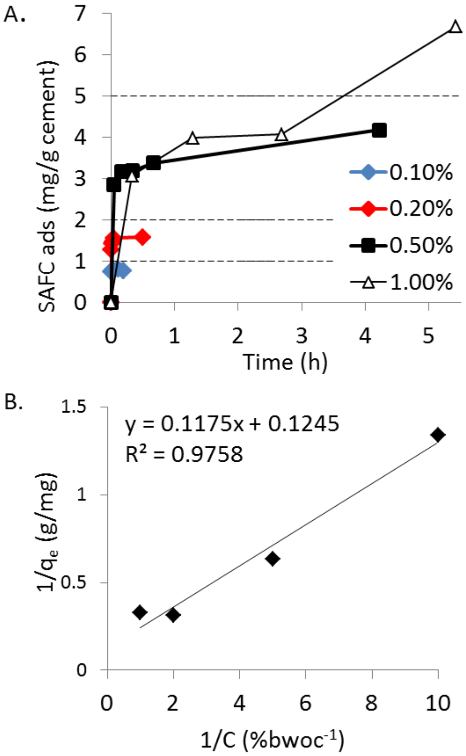


Figure 4. Time-dependent equilibrium adsorption of SAFC at different concentrations as measured by TOC (A) and the equilibrium adsorption of SAFC, Qe (mg/g-1), by cement as a function of concentration (B). Time (in hours) is the contact time of SAFC solution, and Qe (in mg/g-1) is the amount of SAFC adsorbed per gram of adsorbent.

The adsorption of polyether polycarboxylate dispersants, PEC-1, PEC-2 and PEC-3 are shown in Figure 5. Polyether polycarboxylate are powerful cement dispersants and are commonly referred to as superplasticizers by the construction industry. They function by a different mechanism than the sulfonated dispersants (SAFC and SNFC), namely by steric repulsion due to the bulky presence of ethylene oxide (EO) or ethylene oxide:propylene oxide (EO:PO) oligomeric pendant chains or combs, whereas the sulfonated dispersants function by electrostatic repulsion. The anchoring groups on PEC dispersants consist of a small number of anionic carboxylate groups which bind strongly to calcium ions on the cement grains and allow for adsorption, while the EO or EO:PO chains protrude into the matrix fluid and repel similar groups present on the other cement particles (Marchon et al., 2013). In comparison, SAFC and SNFC have large anionic charge densities due to the sulfonate groups, some which serve to bind to calcium ions on the cement grain surfaces, and the non-bound sulfonate groups protruding into the matrix fluid serve to repel similarly charged cement particles.

The adsorption values of the above mentioned dispersants along with SNFC at identical concentration (0.5% bwoc) are summarized in Figure 6. A comparison of adsorption values first graphed in Figure 4A and Figure 5 for SAFC and PEC, respectively, shows that the saturation adsorption values for sulfonated dispersants on cement surfaces are much higher than those for polyether polycarboxylates. These results are consistent with the structural aspects discussed on steric effects.

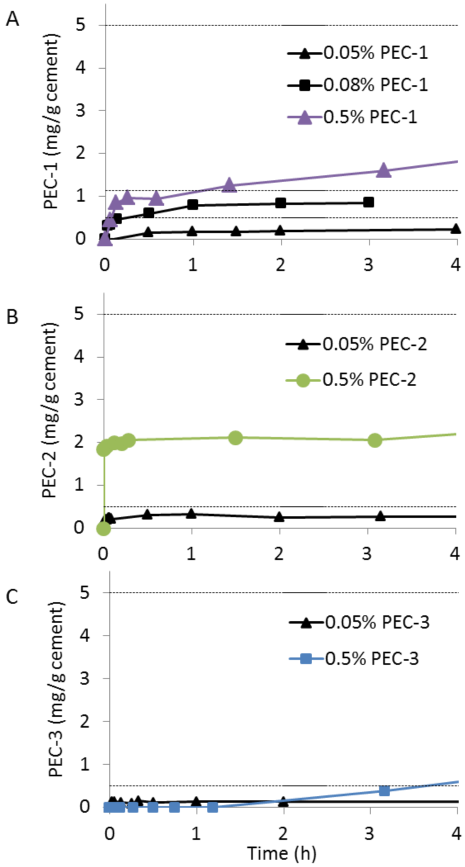


Figure 5. Adsorption of polyether polycarboxylate superplasticizer, PEC-1 (A), PEC-2 (B), and PEC-3 (C).

In contrast, a recent report by Plank showed that electron dense functional groups, such as carboxylates, have greater ionic strength to adsorb onto cement. It presents an interesting case as to whether the depletion method used in this work can distinguish between an additive that may precipitate out of the solution in the presence of cement or that truly adsorbs on the cement surface. He concludes in his report that carboxylates have greater affinity than sulfonates (Plank et al., 2007). Here, this may be explained by the significant difference in molecular weight of the polymers or the number of anchoring points especially for PEC, where steric also affects adsorption rates.

Furthermore, the effects of dispersants on cement hydration were studied by isothermal calorimetry (Figure 7). Here, the control cement, or neat, contains no additive and hydrates at two different peaks at 7 and 8 hours. The second peak has been characterized as the formation of ettringite, which consists of the aluminate phase in cement, or when the aluminate to sulphates ratio increases (Marchon et al., 2013).

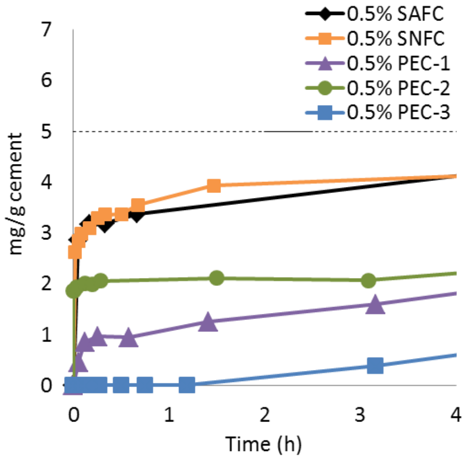


Figure 6. Adsorption of individual dispersants.

There are some interesting observations that become apparent from the heat of hydration patterns. First, the sulfonated SNFC and SAFC products had no significant effect on the time cement hydrates, which occurs in less than 10 hours and which occurs earlier than with PEC (Figure 7). Also, the maximum rate of heat for SNFC yielded the greatest peak. This may be indicative of the accelerating effects of SNFC on the hydration of C_3A (Ramachandran, 1973). Interestingly, with the addition of these sulfonated dispersants, the secondary ettringite formation peak observed for the control sample is also observed for SNFC, but not for SAFC. This may suggest differences in adsorption of the sulfonated polymers onto the aluminate phases.

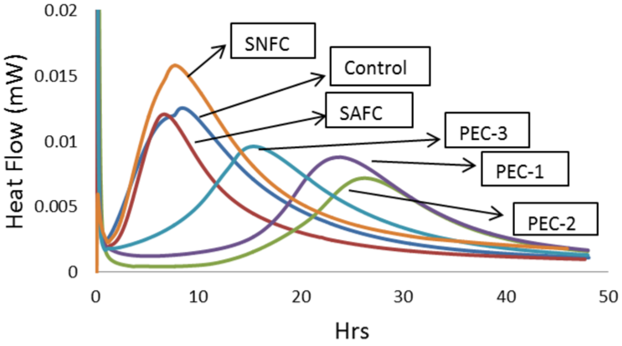


Figure 7. Isothermal heat of hydration measurements for different dispersants at 0.5% bwoc.

Also in Figure 7, the polyether carboxylates are surprisingly more retarding than the sulfonated SNFC and SAFC products. PEC-3 is a less retarding dispersant, because it is designed to be a delayed-release dispersant. But also, from Figure 5, PEC-3 adsorbs the least of the three products. This may be the reason PEC-3 allows the cement to hydrate faster than other PEC additives. In contrast, PEC-2 adsorbs the fastest and remains constant as seen in Figure 6, but has the strongest strength of retardation for up to 25 h. PEC-1 adsorbs next fastest (Figure 6) and retards the cement for up to 23 h. This also illustrates the high ionic functional groups of PECs that adsorb strongly onto cement (Shin et al., 2008).

The addition of PEC to cement is shown in Figure 8. Normally hydrated cement will form needle-shaped ettringite crystals after three hours of hydration as the aluminate to sulphates ratio increases, as previously discussed.

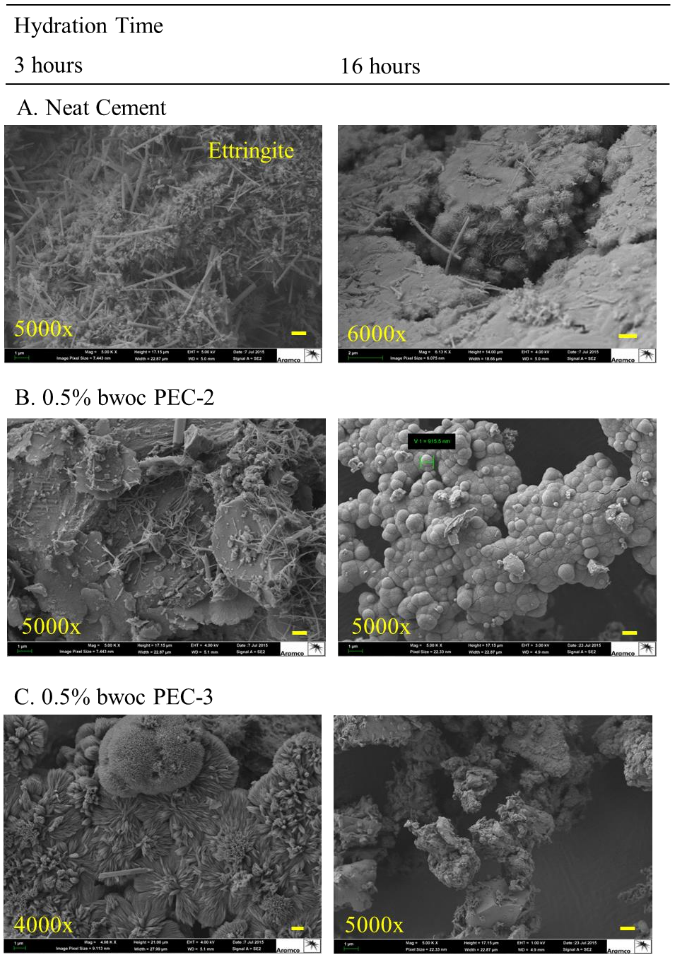


Figure 8. SEM images of hydrated cement at 3 and 16 hours in the presence of PEC additives. Cement morphology changes with addition of PEC (B & C) in comparison to cement with no additive (A). The change is proposed to be caused by either a small amount of ettringite, or some unhydrated cement particles. Scale bar in yellow is 1 µm.

With the addition of PEC at 0.5% bwoc, the formation of ettringite is reduced because of the delay in hydration, as shown in Figure 7. After 16 hours, neat cement precipitates and gels as it starts to set. But, as seen in Figure 8, addition of large molecular PEC alters the shape and structure of cement in comparison. PEC-2 forms emulsion-like thin-films that coat the surface of the cement; whereas PEC-3, as a time-activated polymer, coats the surface of the cement less and is more crystalline at both 3 and 16 hours, than PEC-2.

Adsorption of SAFC on Pre-hydrated Cement

Many of the additives studied above showed a sharp increase in adsorption after several hours of exposure to cement suspensions (Figure 9). Based on isothermal calorimeter results, it was suspected that increased adsorption of additives with time may be due to competition between hydration products, such as C-S-H gel, $Ca(OH)_2$, ettringite, or sulfate-free aluminate hydrate phases. To confirm this probability, cement was hydrated in additive-free water for different periods of time (up to 6 days) before adding SAFC. Then aliquots of the hydrated cement were separated by filtration and SAFC in the filtrate over time was measured by spectrophotometry (Figure 9b). The results clearly show that hydrated cement has a significantly higher capacity for adsorption of the dispersants than unhydrated fresh cement. The adsorption of SAFC increased shortly after exposure to water, the time of total saturation of SAFC was dependent on hydration time of the cement, and with increased hydration caused immediate SAFC saturation onto cement. Further studies are needed to measure the maximum adsorption capacity of the hydrated cement for SAFC and other dispersants, and whether such adsorptions are reversible equilibrium adsorptions. This study with hydrated cement also confirms the suspected reason for the increase in the adsorption of dispersants with prolonged hydration (Prince et al., 2002).

Competitive Additive Adsorption in the Presence of SAFC

These studies were conducted using mixtures of SAFC with another additive by dissolving the additives in mix water followed by addition of cement. At specified intervals, aliquots were collected, filtered and absorbance was measured using spectrophotometry. The absorbance curve of single additive SAFC onto cement by spectrophotometry was graphed as a control (Figure 10, black line). In comparison, the data shows the effect of a second additive in the mix water on SAFC adsorption. The objective of the study was to establish the relative strengths of adsorption of different additives in comparison to SAFC by measuring the adsorption level of SAFC on cement in the presence of selected additives. The additives that were selected to compete with SAFC included carboxylated dispersants, namely polyether polycarboxylates (PEC-1, PEC-2 and PEC-3); retarders, namely ATBS-co-acrylic acid copolymer (PSC); a high molecular-weight poly (styrene sulfonate (PSS) and a non-polymeric hydroxyl carboxylic acid, small molecule retarder, namely glucoheptonate (GH). The results are discussed in the following paragraphs.

Polyether polycarboxylate-based superplasticizers—all additives were used at 0.5% bwoc. The results are shown in Figure 10. The most interesting observation is that PEC-3 which adsorbed least when used alone, reduced the adsorption of the SAFC the most (66% reduction). PEC-1 and PEC-2 decreased the adsorption of SAFC by about 38%. SAFC adsorption reaches an equilibrium plateau for a short period of 1-2 hours and then increases rapidly. This may be due to the generation of hydration products with time on which SAFC adsorbs the strongest, or it may be due to the displacement of PEC products by SAFC with time. The initial adsorption patterns suggest that PEC adsorption may be kinetically controlled, whereas SAFC adsorption is thermodynamically controlled.

Initial adsorption of PECs on cement surfaces may prevent approach of SAFC molecules because of steric repulsion. Direct measurement of adsorption amounts of PECs in the presence of SAFC would be useful in the clarification of the mechanism. It should be noted that PEC suppliers generally discourage the use of the combination of PECs with conventional dispersants such as SNFC, and sulfonated melamine formaldehyde condensates.

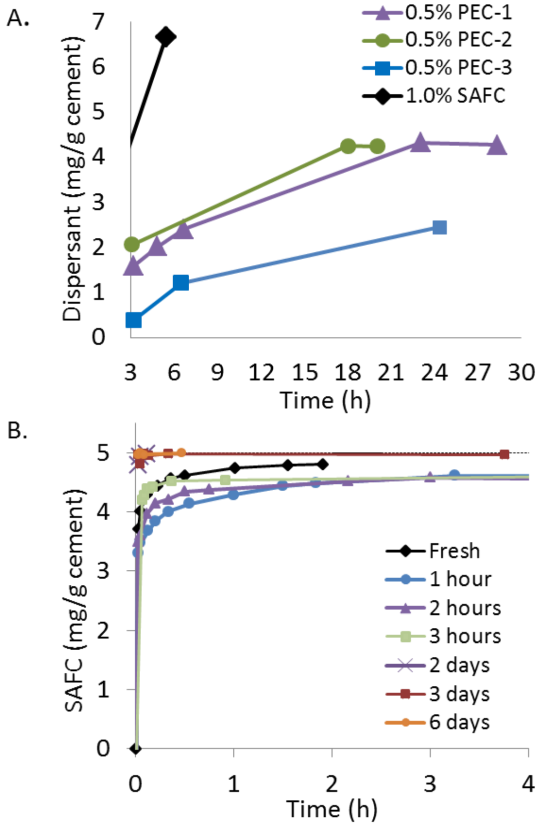


Figure 9. Adsorption of additives as a function of hydration time (A) and pre-hydration time (B). Time dependent adsorption of additives (0.5% bwoc) by cement.

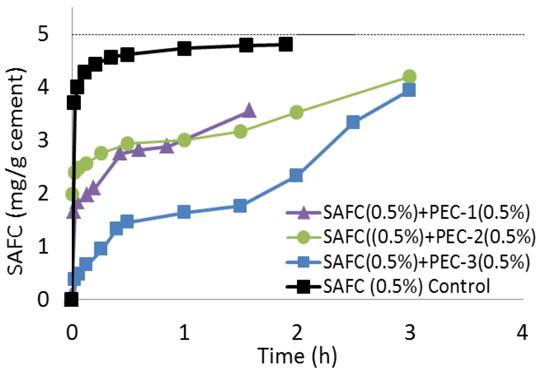


Figure 10. Competitive adsorption of dispersant combinations containing SAFC –sulfonate vs carboxylate.

ATBS-co-Acrylic acid (PSC) Based Cement Retarders—the synthetic polymer PSC is an effective cement retarder for temperatures up to 300°F. It is also an effective dispersant. Retarders of this type are expected to be good calcium complexing agents. The results shown in Figure 11A suggest that SAFC adsorption decreased by 35% and 66% at PSC concentrations of 0.2% and 0.5%, respectively. These results suggest that PSC adsorbs onto cement either directly or by precipitation onto cement surfaces. The adsorption of SAFC does not increase again as seen for PEC products, most likely because cement hydration is delayed due to the strong retardation effects of PSC. The results appear to be consistent with the mechanism proposed for PECs that carboxylate groups allow for kinetically controlled rapid adsorption compared to the sulfonate groups on SAFC (Plank et al., 2007). PSC molecular weight is significantly higher than that of SAFC. The molecular weight differences between SAFC and PSC may also be playing a significant role in the adsorption trends. Both compounds have high density charges. Rheological measurements of cement slurry with SAFC (0.2% bwoc) with PSC (0.5% bwoc) shows the faster adsorption and dispersing effects of PSC, where the rheology of the mixture is identical to the single additive slurry (Table 2).

Poly(styrene sulfonate)-based gas migration control agent—in studies containing only a single additive, SNFC had similar adsorption pattern as SAFC (Figure 6). Yet, SNFC and PSS polymers contain aromatic sulfonate groups unlike SAFC and PSC polymers, which contain aliphatic sulfonate groups or organic sulfite groups.

Table 2. Rheology of cement slurries of combination of 0.2% bwoc SAFC with 0.5% bwoc additive.

Additive	%bwoc	3	6	100	200	300	600
Neat		10	15	44	62	88	152
SAFC	0.20	11	16	37	52	71	113
PSC	0.50	1	1	9	19	27	62
SAFC + PSC		1	1	8	19	28	60
GH	0.25	4	7	15	26	35	78
SAFC + GH		3	3	13	25	38	81

The polymer with aromatic sulfonate groups was least effective in competing with the adsorption of SAFC (Figure 11B). At 0.2% bwoc PSS, there was little effect on the adsorption of SAFC, but reaching equilibrium was delayed by about 1 hour. Even at the highest PSS concentration of 2.0% bwoc, there was only 24% decrease in the amount of SAFC adsorbed compared to more than 60% decrease with 0.5% bwoc additives containing carboxylate groups (Figure 10).

Glucoheptonate salt, a small molecule cement retarder—GH has been used as a cement retarder in oil well cementing and construction industry for many years. It is one of the most effective retarders available. This can be seen in the heat of hydration data for different retarding polymers used in this study at 0.5% bwoc (Figure 12).

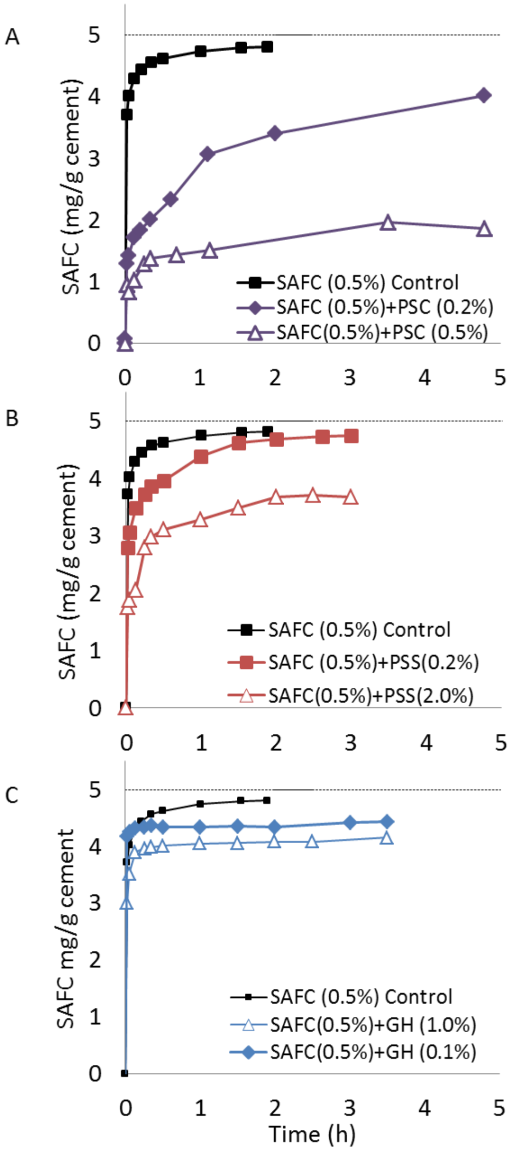


Figure 11. Competitive adsorption of retarders against SAFC. Sulfonated vs. carboxylated+sulfonated (A). Aliphatic sulfonated vs. araomatic sulfonated (B). SAFC with sodium glucoheptonate (C).

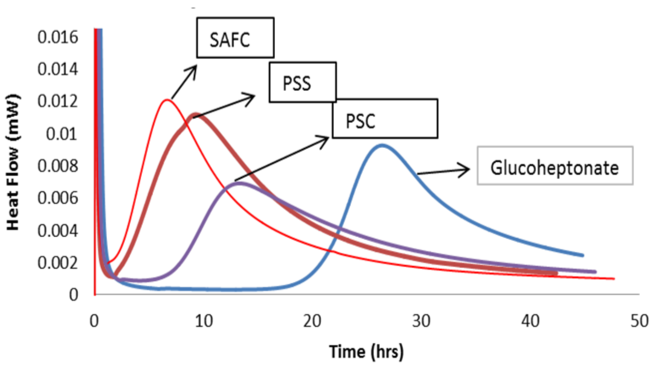


Figure 12. Heat of hydrations for retarders.

The effect of GH retarder on the adsorption of SAFC is shown in Figure 11C. The results clearly show that glucoheptonate salt does not affect the adsorption of SAFC significantly even when the concentration of glucoheptonate was increased ten times. This can be rationalized by assuming that glucoheptonate co-adsorbs with SAFC by adsorbing onto sites not occupied by SAFC. This is unlike PSS where co-adsorption with SAFC is not likely because of the very high molecular weight of PSS and, hence high volume requirements for the polymer chains in adsorbed conformation. Rheological data in Table 2 confirms the co-adsorptive behavior of SAFC and the dispersing effectiveness of GH.

Conclusions

Based on the results from this analytical study on the adsorption rates of cement chemical additives onto Saudi G cement, the following conclusions are given:

1) TOC measurement show the dispersant with the most affinity to cement: SAFC = SNFC > PEC2 > PEC1 > PEC3, which may be due to steric effects.
2) The hydration time of cement with sulfonated additives occurs faster than with carboxylated additives.
3) Calorimeter data shows PEC dispersants have significantly strong retarding effects, as does GH, at high concentrations (0.5% bwoc).
4) SEM illustrated the production of ettringite and the deposition of polymeric additives onto cement.
5) Pre-hydrated cement of more than one hour shows an increase in reactivity
6) A binary mixture with SAFC dispersant and a retarder can be competitive: PSC > PSS > GH, being the least competitive.
7) Co-adsorbance of SAFC and GH was observed.

Acknowledgments

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