

Retarder Interactions in Oil Well Cements

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Abstract

Cement additives, their interactions with each other, and with oil well cement influence cement slurry stability, rheology, set time, and mechanical properties. The understanding of the dynamics between additives and cementitious surfaces is critical to predicting additive-additive compatibilities. This paper investigates additive-additive interactions between various cement set retarders. When cementing at elevated temperatures ($>300^{\circ}\text{F}/150^{\circ}\text{C}$), multiple retarders are often used together in the same cement slurry for extension and enhanced control of pump times and set times. The interactions of the retarding additives with one another play a critical role in the determination of the hydration kinetics in cement slurry formulations.

In this work, isothermal calorimetry is used to determine the effects of additive concentration and additive interaction on the induction period for cement setting. Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) are used to evaluate the adsorption of retarding additives on the surface of the cement. Demonstrations of the consequences of retarder interactions are also rendered through ultrasonic cement analysis under simulated well conditions at $350^{\circ}\text{F}/175^{\circ}\text{C}$. The test results underline the importance of additive interactions on slurry design which involve both intermolecular interactions in the solution phase and on cementitious surfaces. The understanding gained in this study can be helpful in selecting right retarder combinations for high temperature cementing applications.

Introduction

Oil well cement additive chemistry is fundamentally important to oil well construction and to ensuring zonal isolation throughout the life of an oil well. When sealing the casing to the wellbore formation with cement, oil well cement additives regulate many important slurry properties including rheology, suspension stability, fluid loss control of the cement slurry and set time and mechanical properties of set cement [1]. Poor engineering of oil well cement slurries can result in the loss of zonal isolation in a well potentially leading to the loss of a well and considerable hazard to field personnel. The appropriate selection of the additives in cement slurries depends on the temperature and pressure profiles down the length of the well, the depth of the well, the geological formations that the slurry contacts, as well as the presence of

gas, water, and oil in the different zones of the well. The understanding of cement additive chemistry and additive-additive interactions in oil well cements is critically important for the appropriate design of oil well cements used in wells with these well-specific parameters.

The complexity and difficulty in predicting retarder interactions are amplified by their combination with other cementing additives. For example, polycarboxylated ethers (PCE), which are powerful cement dispersants, are known to have incompatibilities with citric acid, a common cement retarder. The reason for this incompatibility has been identified by Plank et al.[2] as due to competitive adsorption by citrate onto the cement particle surface, displacing the PCE. This in turn reduces the flowability of the resulting cement slurry. In a different study of the interactions between a viscosifier, hydroxyethylcellulose (HEC), a PCE dispersant, and a retarder, sodium gluconate, it was found that there are different concentration regimes for competitive additive adsorption. At low concentrations where there are many free adsorption sites on cement grains, additives do not compete for the cement surface. As the concentration of the additives is increased, the binding to the surface becomes a competition where the strongest binding additive will preferentially occupy surface sites. These effects can lead to synergies which can benefit the design of a cement slurry with regards to engineering the rheology of the slurry along with the set time [3].

When cementing at elevated temperatures ($>300^{\circ}\text{F}/150^{\circ}\text{C}$), multiple retarders are often used together in the same cement slurry for extension and enhanced control of pump times and set times. The interactions of the retarding additives with one another and other cementing additives play an essential role in the determination of the hydration kinetics in cement slurry formulations. Cement retarders can interact both antagonistically, where the set time is reduced due to their combination, and additively / synergistically, where the set time is extended through their combination. Antagonistic interactions between different retarders are not always undesired. Such interactions can be used to fine tune setting times (induction periods) in cements and modify the nucleation and growth rates of C-S-H. On the other hand, constructive additive interactions are useful in the design of slurries for increased bottom hole circulating temperatures

where the set time needs to be maintained at higher temperature, for example.

Phosphates and phosphonates have been used as additive systems to modify set times in oil well cements [4]. These two chemical groups antagonistically compete with water for binding to surface sites in the cement. While the presence of phosphonate greatly extends the induction period in the cement, the presence of phosphate with phosphonate reduces the induction period and increases the peak hydration peak in cement containing phosphonate retarders. When sodium hexametaphosphate (SHMP) is used, the calcium complexed nitrilotris(methylene phosphonic acid) (NTMP) adsorbed to the cement particle surface is re-solubilized by the SHMP. This combination of additives has also been used as a combination for instructed cement setting [5]. An extended life slurry (ELS) can be produced with phosphonate retarded cement. This powerful retarder can be replaced with a weaker retarder, sodium hexametaphosphate. Hexametaphosphate is believed to compete with phosphonate for surface binding by dispersing the precipitated NTMP particle from the cement grain.

In this study a set of cement retarders are surveyed for antagonistic interactions when present in cement in combination with one another. The experiments described in this text investigate the dynamics of diethylenetriamine penta(methylene phosphonic acid) (DTPMP) and NTMP with one another and with a variety of different phosphates. The tests used to make these observations are isothermal calorimetry and high temperature / high pressure ultrasonic cement analyzer (UCA) experiments. Figure 1 illustrates the molecular structures of the different retarders used in this comparison.

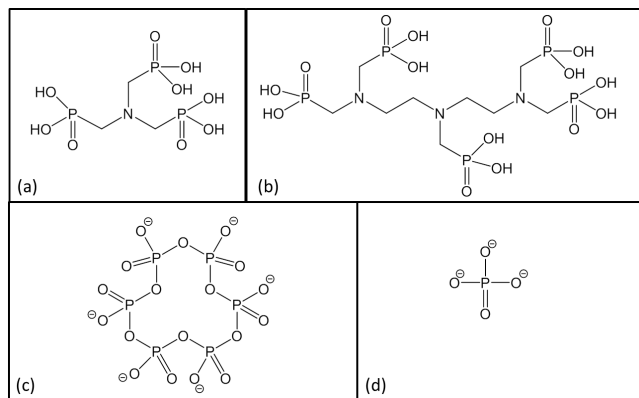


Figure 1. The molecular structures of (a) NTMP, (b) DTPMP, (c) SHMP and (d) phosphate.

Experimental Section

All cement slurries prepared in this study were based on a 15.8 pound per gallon (lb/gal) Joppa Class H Lafarge base cement slurry. The different tests vary according to additive

concentrations which are described as weight percent by weight of cement (% bwoc). All phosphates used in these studies are solids. NTMP and DTPMP are aqueous solutions with acid activities of 38-42% and 24-26%, respectively. When calculating the % bwoc value for cements with these additives, the acid activities are not factored into the % bwoc.

- Cement mixing methods

In some of these experiments, the slurries are blended according to standard API protocol [6]. In the 30 minute delay method, a primary retarder is blended with the cement slurry according to the standard API method. 30 minutes after blending, a second additive is blended with the slurry. This sequential addition method tests the displacement of one retarder with another. It allows the primary retarder to complex with the cement grains prior to the addition of a synergistic or potentially antagonistic additive. For the data reported here, API blending methods were used for the UCA's and the non-API method described earlier was used in the calorimetry experiments. Comparison of the two techniques revealed that there was not a significant change in the hydration rate of cements blended through either method when a phosphonate was used as the primary retarder.

- Calorimetry experiments

Calorimetry tests of the cement slurries were conducted on a TA Instruments Inc. isothermal calorimeter with TAM Air Assistant software version 1.3.0.151.

- UCA experiments

UCA tests were run on a Chandler 4265 HT UCA. The UCA experiments monitor the strength development in the cement through measuring the change in the speed of sound through the cement as the cement phases react with water. All UCA experiments were run on 15.8 lb/gal Lafarge Joppa Class H Portland cements with 35% of 200 mesh silica flour to mitigate strength retrogression. The cement slurries were blended according to the API recommended practice [6]. The temperature in all cases was ramped from room temperature to 350°F/175°C in 40 minutes. The pressure on the cement slurries in all cases was 3,500 psi.

- Filtration / scanning electron microscopy (SEM) experiments

To measure relative differences in surface concentrations of carbon, two different cement samples were prepared. The samples were 15.8 lb/gal Joppa Portland cement slurries with (1) 1.0% NTMP, and (2) 1.0% NTMP and 1.0% phosphate. The samples were filtered immediately after blending according to an API method. After the filtrate and filter cake were separated, the two filter cakes were analyzed for relative carbon content with SEM and energy dispersive x-ray spectroscopy (EDS).

Results and Discussion

While there is still much debate about the mechanism for cement hydration, the most widely accepted mechanism currently is the etching / pitting mechanism. In this mechanism, energy provided by the undersaturation of C3S in the cement pore solution allows for the etching of pits in the surface of the cement grain. This dissolution slows as the pore solution becomes more concentrated with the C3S dissolution products. The induction period is believed to be due to a decrease in the undersaturation of the cement pore solution to C3S leading to a decrease in the rate of solubilization of C3S. In order for the CSH particles to nucleate, its concentration in the pore solution must exceed a certain value and this is slowed due to the reduction in the rate of pitting of the C3S surface [7]. These processes can be further regulated with retarding and accelerating cement additives such as those illustrated in Figure 1.

There are four different mechanisms that are generally believed to be responsible for the retarding action of retarders in Portland cement. These are (1) calcium complexation, (2) direct surface adsorption of the retarder onto the clinker phase(s), and (3) nucleate poisoning of C-S-H and portlandite, and (4) the precipitation of a semipermeable layer on the cement grains [8]. Often it is the case that a retarding additive will retard cement through more than one of these mechanisms. For example, NTMP is believed to inhibit cement hydration through the precipitation of a semipermeable layer on the cement grains and the nucleate poisoning of C-S-H and portlandite [9]. This leads to an extension of the induction period and a decrease in the peak hydration rate of cement with NTMP as an additive.

The experiments discussed in this article highlight the effect of different set time modifiers on the rate of cement hydration in Portland cement. The mechanistic aspects are briefly discussed to explain the results. Single additive cement slurry designs are described initially followed by multi-additive designs.

The calorimetry experiments of phosphate at various concentrations in Portland cement display the basic effect of the additive on the time dependent cement hydration process. As shown in Figure 2, sodium phosphate acts as a retarder at 25°C and an accelerator at 70°C in Portland cement, in the concentration range of 0.5 to 1.5% bwoc. While the induction period of the neat cement slurry at 70°C is approximately 2 hours and peak heat flow of 16 mW/g, 0.5% phosphate has an induction period reduced to about 30 minutes and a peak heat flow rate of 17 mW/g. Relative to Portland cement with 0.5% bwoc sodium phosphate, increasing concentrations of sodium phosphate in cement result in a shortened induction period of cement hydration along with an increased peak hydration rate at both temperatures. At 70°C, 1.0 and 1.5% bwoc phosphate cements display a negligible induction period and a peak heat flow rate of 20 and 22 mW/g, respectively.

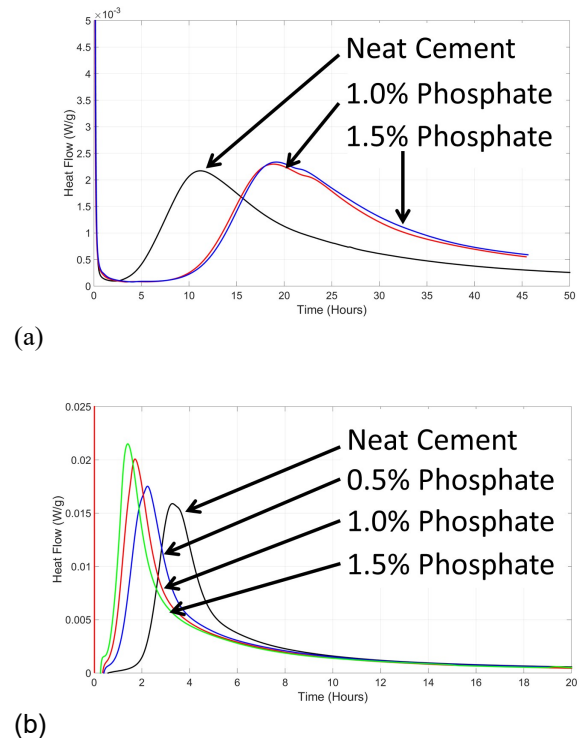


Figure 2. The effect of sodium phosphate on the hydrate rate of 15.8 lb/gal Joppa Class H cement. Phosphate plays the role of a cement set retarder and accelerator at (a) 25°C and (b) 70°C.

Sodium phosphate has been widely reported as a retarder [10]. The mechanism for this action in Portland cement is still not completely resolved but phosphate is believed to slow the dissolution of C3S [11]. Also similar to sodium phosphate, iron phosphate acts as a mild retarder at room temperature. Figure 3 illustrates the effects of 0.5 to 1.5% bwoc iron phosphate on the cement induction period and peak hydration rate. Induction period for these cements increases from 2 hours, in the case of neat cement to 5, 7.5, and 10 hours for cement with 0.5, 1.0, and 1.5% bwoc iron phosphate, respectively. The peak heat flow remains similar across the different samples shown in Figure 3 at 2.1 mW/g. Similar to iron phosphate, SHMP and sodium pyrophosphate also act as retarders at 25°C in Portland cement for hydration [12]. As with phosphate, SHMP displays a non-linear behavior with respect to concentration. Beyond about 0.5% bwoc in a 15.8 lb/gal Joppa Class H cement slurry, the effect of retardation is diminished such that the induction period for a 1.0% bwoc slurry with SHMP will be shorter than that of a 0.5% bwoc slurry. Furthermore, the peak hydration rate begins to increase to values higher than both the neat cement and cements retarded with less than 1.0% bwoc SHMP, when the SHMP concentration is raised beyond 1.0% bwoc.

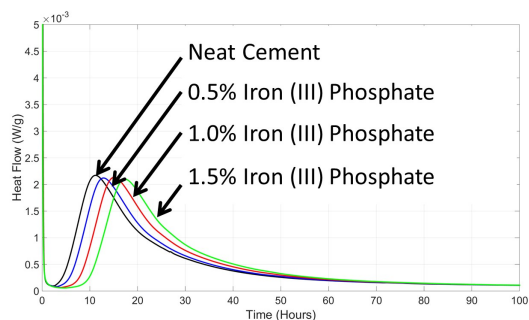


Figure 3. Isothermal calorimetry of 15.8 lb/gal Joppa Class H cement with different amounts of iron phosphate at 25 °C. Iron phosphate acts as a mild retarder in Portland cement as evidenced by the change in induction period.

NTMP is a much stronger retarder than any phosphate surveyed. Based on a class of powerful phosphonate retarders, NTMP is thought to bind to calcium in the cement pore solution, precipitate onto the surface of cement grains and poison the growth of C-S-H nuclei. Figure 4 shows the effect of NTMP on the hydration rate. While 0.5% bwoc NTMP (accounting for the activity of the NTMP solution the actual molecular loading of retarder is 0.25% bwoc) extends the cement hydration time to 310 hours at room temperature, the same amount of iron phosphate only delays cement hydration by a few hours. The peak heat flow is reduced with increasing concentration from 2.2 mW/g to 1.4 mW/g for neat cement and cement with 0.5% bwoc NTMP, respectively. The retarding action of the NTMP can therefore be anticipated to slow the rate of mechanical strength development of the set cement as it continues to hydrate. The width of the hydration peak with NTMP can be seen to broaden as the concentration of NTMP is increased, indicating the longer acceleration period after the induction period. The delay in induction period can be readily modified through the introduction of a secondary additive.

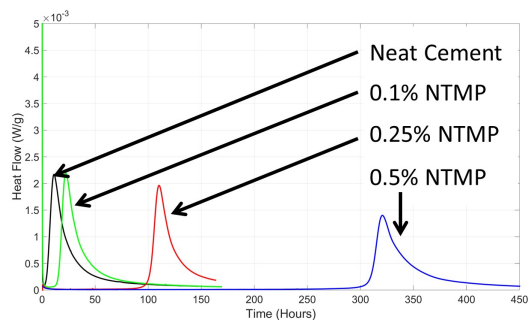


Figure 4. NTMP concentration and the effect of NTMP on the induction period of 15.8 lb/gal Joppa Class H cement at 25 °C.

The influence of secondary additives on cement hydration in different slurry designs containing NTMP and DTPMP is presented in Figures 5 through 11. The secondary additive can either be a retarder, as is the case for sodium hexametaphosphate (SHMP) and sodium pyrophosphate [12],

or an accelerator in Portland cement hydration, as is the case for sodium phosphate at temperatures 70°C and higher. As shown in Figure 5, when these secondary additives are added to NTMP retarded cement, the hydration rate is increased in all cases except for that of iron phosphate. The induction period is decreased with the addition of all the phosphates described in Figure 5. The decreased induction period has been hypothesized, in the case of SHMP, to be due to the resolubilization of the NTMP complexed cement with the secondary retarder. With NTMP redispersed and solubilized, it no longer functions as a nucleate inhibitor and the induction period is drastically reduced. This effect is now extended to a variety of other phosphates, beyond the SHMP that has previously been reported.

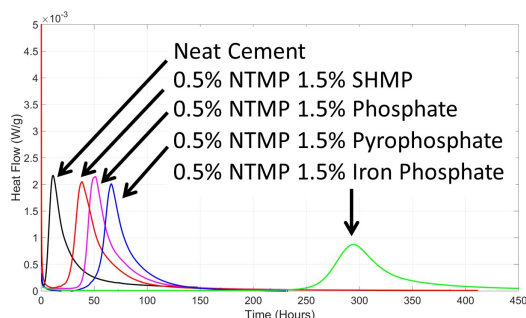


Figure 5. The effect of different phosphates at 1.5% bwoc on the induction period of Joppa Class H cement retarded with 0.5% bwoc NTMP at 25 °C.

From Figure 5, it can be noted that iron phosphate does show a significant effect in shortening the induction period of cement. While 15.8 lb/gal Portland cement has an induction period of 300 hours at 25°C in the presence of NTMP, the induction period of the cement is reduced to 250 hours when 1.5% bwoc iron phosphate is added to the cement, 30 minutes after API blending of the cement with NTMP. This effect, is however significantly less than that observed with SHMP, trisodium phosphate, and sodium pyrophosphate which are much more potent in this regard. By weight, SHMP, trisodium phosphate, and sodium pyrophosphate are much more potent in modifying the cement set time. Figure 6 shows the hydration of cement with both 0.1% and 0.5% bwoc NTMP with and without the combination with 1.5% bwoc iron phosphate.

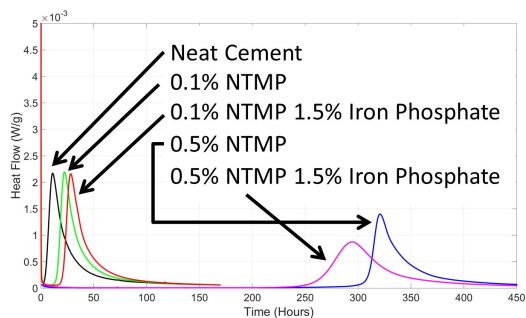


Figure 6. The effect of 1.5% bwoc iron phosphate on the induction period of Joppa Class H cement with different amounts of NTMP retarder at 25 °C.

The addition of sodium phosphate to cement retarded with NTMP (Figure 7) results in a shortening of the induction period until at 1.5% bwoc the induction period is identical to that of neat Portland cement. However, at 16 mW/g, maximum heat flow, the peak hydration rate is estimated to be the same as 1.5% bwoc phosphate. The analogous exchange with NTMP and phosphate is presented in Figures 8 and 9 as UCA experiments.

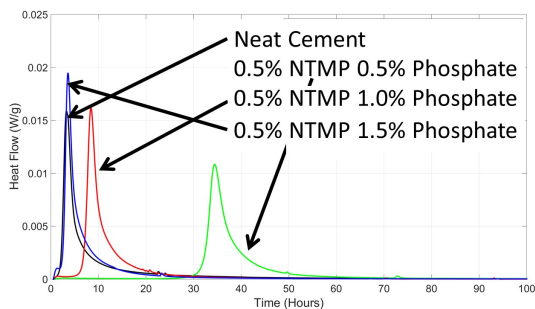


Figure 7. The effect of different concentrations of sodium phosphate on the induction period of 15.8 lb/gal Joppa Class H cement retarded with 0.5% bwoc NTMP at 70 °C.

As would be anticipated from the calorimetry experiments, the rate of strength development in cements retarded with the NTMP and phosphate combination show increasing rates of strength development with increasing proportions of phosphate to NTMP. A cement slurry which is retarded with 1.0% NTMP has an initial strength development (> 0 psi compressive strength) delayed to about 5.6 hours while 1.0% NTMP with 0.5% sodium phosphate shows the initial development of compressive strength to develop at 56.5 minutes. The times for each of these slurries to reach compressive strengths of 500 psi were 8.8 hours and 1.5 hours for 1.0% bwoc NTMP and 1.0% bwoc NTMP with 1.0% bwoc phosphate, respectively. As would be anticipated, the sample with 0.5% phosphate and 1.0% NTMP hydrates at a time in between the other two slurry designs.

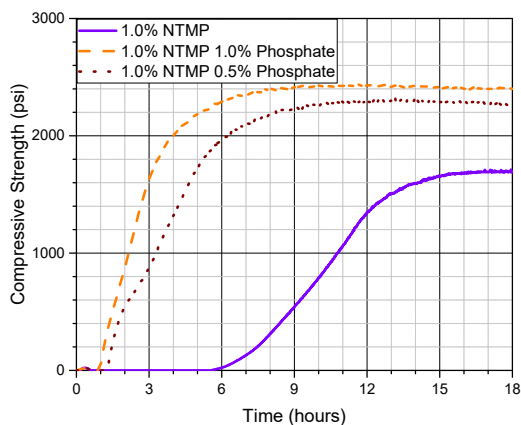


Figure 8. A 15.8 lb/gal Portland cement slurry retarded with

1.0% NTMP and then subsequently activated with 0.5% and 1.0% phosphate at 350°F.

This effect of increasing rate of strength development with increasing concentrations of phosphate can be tuned produce a cement slurry meeting certain specific cement set times. Figure 9 shows the effect of a range of concentrations of sodium phosphate, from 0.0625% bwoc to 0.25% bwoc. The times to 500 psi for 0%, 0.0625%, 0.125%, and 0.25% bwoc in a 15.8 lb/gal slurry retarded with 1.0% NTMP are 8.8, 7.1, 6.6, 4.9, and 4.3 hours, respectively. This further demonstrates the ability to tune the set time for the cement slurry through varying the secondary additive concentration, in this case phosphate.

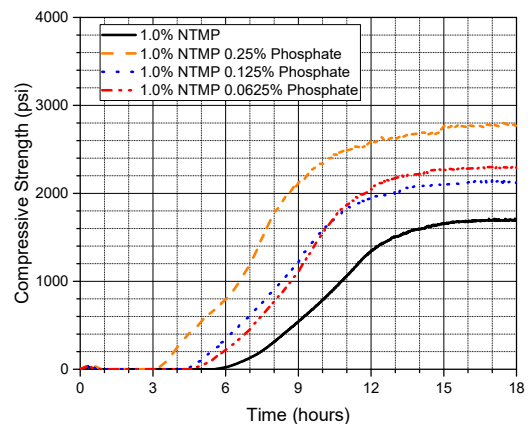


Figure 9. A 15.8 lb/gal Portland cement slurry retarded with 1.0% NTMP and various quantities of phosphate ranging from 0.0625% to 0.25% bwoc at 350°F.

DTPMP shows similar interactions with phosphate as does NTMP. UCA data for a 1.0% bwoc DTPMP slurry is shown in Figure 10. When 0.25% phosphate is added to the slurry design, the time to 500 psi is shortened from 13.5 hours to 7.4 hours. Similarly, the 250 psi time is shortened from 3.3 hours to 2.7 hours. There is a plateau at 350 psi which is more pronounced in the absence of phosphate. The addition of phosphate to the slurry reduces the time that the cement compressive strength dwells at 350 psi.

When 1.0% bwoc DTPMP is combined with 1.0% bwoc NTMP, the time to building compressive strength is greatly lengthened. As illustrated in Figure 11, the initial set of the cement did not occur until 40 hours into the experiment when the temperature was set at 350°F/175°C. When 0.25% DTPMP and 1.0% NTMP are combined in a Portland cement slurry, the time to 250 psi is 20 hours.

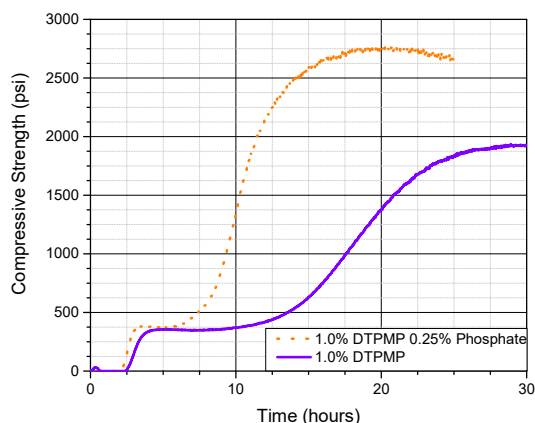


Figure 10. A 15.8 lb/gal Portland cement slurry retarded with 1.0% DTPMP and with 1.0% DTPMP and 0.25% Phosphate at 350°F.

This synergistic / additive interaction between NTMP and DTPMP highlights the differences in the ways that retarders can influence the hydration of Portland cement together. Furthermore the high temperature tolerance of phosphonate additives such as NTMP and DTPMP show the suitability of these additives for high temperature / high pressure wells where temperatures exceed 300°F/150°C.

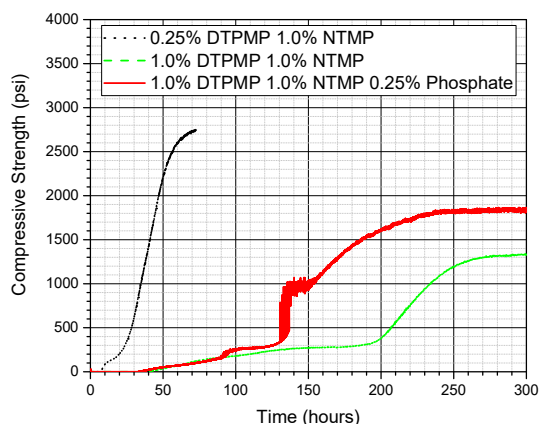


Figure 11. 15.8 lb/gal Portland cement slurries retarded with 0.25% DTPMP and 1.0% NTMP, with 1.0% DTPMP and 1.0% NTMP and with 1.0% DTPMP, 1.0% NTMP and 0.25% Phosphate at 350°F.

From the filtration / SEM experiment described in the experimental section, the EDS data from the filter cake solids indicate that there was a 5% higher content of carbon on the surface of the cement sample with NTMP than with cement sample that was treated with NTMP and sodium phosphate. This indicates that there was a removal of carbon, presumably in the form of NTMP, when phosphate was added to cement with calcium complexed NTMP. This result is consistent with the model previously proposed for the cement slurry

containing phosphonate and SHMP, where the NTMP is solubilized after the addition of phosphate [5].

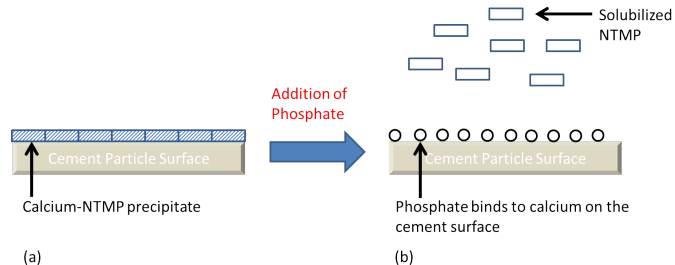


Figure 12. Simplified representation of the dynamic exchange of additives from the cement surface.

Phosphate, pyrophosphate and iron phosphate all show the capacity for reducing the induction period and also increasing the maximum hydration rate of cement during the acceleration period. Similar to the phosphonate / SHMP dynamic exchange, these phosphates could also follow a similar mechanism as depicted in Figure 12. In this Figure, NTMP forms a precipitated coating over the cement grain. This coating is then solubilized through the addition of phosphate and the phosphate in turn binds to the cement surface.

Conclusions

A variety of different cement additives were tested for their retarding effects on class H Portland cement. When these additives were tested in combination with one another, some of them interacted antagonistically to reduce the setting time of the cement and some of them interacted synergistically to lengthen the cement set time. In all cases, phosphates decreased the induction period for cement hydration whether the primary retarder was NTMP or DTPMP. This kind of cement system can be used in the activation of extended-life cement slurries.

NTMP and DTPMP, both known powerful retarders for cements, were found to interact constructively with each other in cement to greatly lengthen the induction period for cement hydration at 350°F/175°C. In particular, it was demonstrated that a cement with 1.0% DTPMP and 1.0% NTMP would not develop compressive strength until 40 hours at 350°F. This combination of retarders could be of benefit to use in high temperature, high pressure wells where many retarders fail to perform.

Acknowledgments

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Nomenclature

bwoc = By weight of cement
lb/gal = Pounds per gallon

DTPMP = diethylenetriamine penta(methylene phosphonic acid)

EDS =Energy dispersive x-ray spectroscopy

ELS =Extended life slurry

NTMP =Nitrilotris(methylene phosphonic acid)

SEM =Scanning electron microscopy

SHMP =Sodium hexametaphosphate

UCA =Ultrasonic cement analyzer

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