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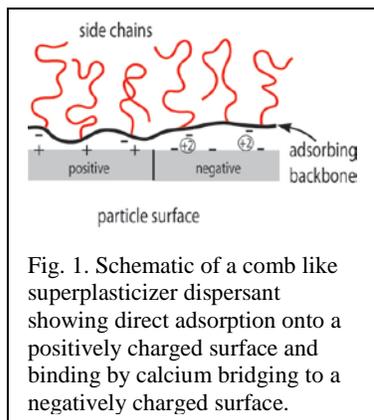
Project Title: Rational Design of Cement Dispersants for Improved Flow and Rheological Properties

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Specialized cements are widely used in petroleum drilling operations and infrastructure; for example, as a seal between casing and borehole walls and plugs during and after activities have ceased. Faulty casing and cementing cause most well integrity problems, which are extremely expensive and can result in devastating failures and environmental catastrophes such as the Deepwater Horizon accident in the Gulf of Mexico in 2010. Further, proper zonal isolation with cement is crucial to prevent fluid migration between subsurface formations in hydraulic fracturing for oil and natural gas extraction. The importance of cement and need for better cements with improved flow and rheological properties motivates the proposed studies.

Key properties of cement (and concrete) are primarily determined by the water to cement ratio (w/c), which is defined as the weight of water to the weight of cement used in cement paste. A high w/c value leads to higher capillary porosity in the cement paste, which will reduce the strength and durability of the formed material. In theory, the w/c ratio should be minimized so that there is just enough water to induce hydration reactions. However, reducing water content in cement paste significantly decreases the material workability (effort required to pump and manipulate freshly mixed cementitious materials with minimum loss of homogeneity). In general, ordinary cements have w/c ratios of 0.6 to 0.7. On the other hand, a w/c ratio of  $\leq 0.4$  is required for producing higher quality cementitious materials with low porosity and greater mechanical strength. Low water conditions can result in segregation and aggregation of solid components, which reduces the workability and flow properties of the cement. The solid components have a tendency to agglomerate via interparticle attraction, settle and segregate due to gravity resulting in reduced cement paste fluidity. Dispersants, which are also referred to as high-range water reducing additives or superplasticizers, can be added to maintain pumpability and rheological properties under low water conditions as well as mitigate undesired effects such as segregation. The focus of the proposed and carried out studies is to directly quantify how different dispersants truly act by measuring their interactions and thin film rheological properties using ultra-high resolution Surface Force Apparatus (SFA) measurements of normal and shear forces. With this fundamental understanding, it is anticipated that improved and new dispersants can be developed to more robust concrete formulations for drilling operations and infrastructure.

During the first year, we built upon our preliminary measurements of a single commercially available polycarboxylic acid ether (PCE) cement dispersant by measuring two additional PCEs with different molecular weights (MW) and physical properties. PCE's backbone consists of polyacrylic acid (PAA) with grafted side chains of polyethylene glycol (PEG) as shown in Fig. 1. For our studies we had MWs of 13k, 37k, and 51k. The ratio of carboxylic groups ( $-\text{COO}^-$ ) to PEG chain was 5:1, 2:1, and 4:1 with PEG sides chains of 2k, 2k, and 5k respectively. Note, these commercial samples as used in the field and are very polydisperse with PDIs of 2.7, 3.8, and 4.7 respectively. Our goal was to determine if the change in PCE structure led to different binding interactions and stability of the solid aggregate. To eliminate confounding chemical reactions of silica under alkaline conditions ( $\text{pH} \geq 12$ ), we used mica as a model substrate, an inert alumina silicate.



Our high-resolution force spectroscopy measurements revealed the thickness of the adsorbed dispersant under different pore solution conditions ( $0.1\text{M K}_2\text{SO}_4 + \text{saturated Ca(OH)}_2$ ) as well as conditions under which PCEs did not adsorb. Remarkably, the assumed adsorption to negatively charged surfaces (mica as a proxy for silica) in the presence of high concentrations of calcium ions did not occur (Fig. 2). This has been a long standing hypothesis for the mechanism of PCEs as cement dispersants. An exemplar force profile is shown in Fig. 2. We hypothesize that calcium ( $\text{Ca}^{+2}$ ) chelation by PEG as well as carboxylic acid groups along the PCE backbone renders the PCE is overall positively charged. However, at high, saturated calcium conditions, the negatively charged mica substrates experience charge reversal and are effectively positively charged, as well. As a result, adsorption of the overall

positively charged PCE is actually prevented in high  $\text{Ca}^{+2}$  conditions such as pore solution. In the presence of lower  $\text{Ca}^{+2}$  concentration, only the low 13k MW PCE weakly adsorbed but could be squeezed out with modest compression ( $F/R = 13 \text{ mN/m} \sim 3 \text{ atm}$  pressure).

We have continued these studies with other dispersants. Figure 3 shows the measured interaction of a commercially available polynaphthalene sulfonate (PNS) MasterRheobuild® 1000 High-Range Water-Reducing Admixture (BASF 1000). PNS based additives are a previous generation of additives that were replaced by PCEs. We also tested PCE-based MasterGlenium® 7500 Full-Range Water-Reducing Admixture (BASF 7500) under pore solution conditions and found identical behavior to our previous studies with just PCE additives in comparison to the “as prepared for use” mixtures of BASF.

The force profiles reveal that in 0.1 M  $\text{K}_2\text{SO}_4$ , PNS in the BASF 1000 admixture adsorbed on mica, inducing a strong, relatively short-range steric repulsion. In 5 mM  $\text{Ca}(\text{NO}_3)_2$ , a slightly thicker PNS adsorption layer also formed, exhibiting an additional weak electrostatic repulsion before a similar steric repulsion. Increasing the  $\text{Ca}(\text{NO}_3)_2$  concentration to 0.1 M doubled the adsorption layer thickness, but only steric repulsion was detected. Small cohesion ( $-0.5$  to  $-1 \text{ mN/m}$ , load and  $\text{Ca}^{+2}$  ion concentration independent) was detected in both 5 mM and 0.1 M  $\text{Ca}(\text{NO}_3)_2$  solutions presumably due to  $\text{Ca}^{+2}$  ion bridging between the opposing PNS layers. These findings reveal that divalent  $\text{Ca}^{+2}$  ions have a much stronger ability to assemble PNS molecules to develop a multi-layer adsorption than monovalent  $\text{K}^+$  ions. Furthermore, divalent  $\text{Ca}^{+2}$  ions can link PNS-coated cement particles, which would cause additional fluidity (workability) loss. The inter-layer interaction forces strongly suggests that PNS’s lubrication and dispersion mechanism in the cement pore solution is steric repulsion from the adsorbed PNS films.

Again, the PCE BASF 7500 admixture did not adsorb onto mica in high calcium conditions of 0.1 M  $\text{Ca}(\text{NO}_3)_2$ . This behavior is consistent with our previous studies with pure PCEs and occurs due to charge reversal of both mica ( $\text{Ca}^{+2}$  ion condensation on mica) and PCE ( $\text{Ca}^{+2}$  ion chelation).

Such high resolution force spectroscopy measurements clearly reveal how cement additives adsorb and modify (or not) the interactions of silica like particles in cement. The present measurements bring new understanding of the interactions between PCE and negatively charged surfaces in high-calcium aqueous solutions and suggest that some of the added PCE functions as a “free” lubricant between cement particles in the cement pore solution instead of the long hypothesized adsorption due to calcium.

Impact: In terms of research, cement is an entirely new experience for the PI. It is daunting working in such a well developed field, and this would not have happened without the support of the PRF. It has been very exciting to see the novel results! The students have become experts in high-resolution force spectroscopy measurements. One, Bo Wu received his PhD and has authored one of the papers supported by the PRF grant.

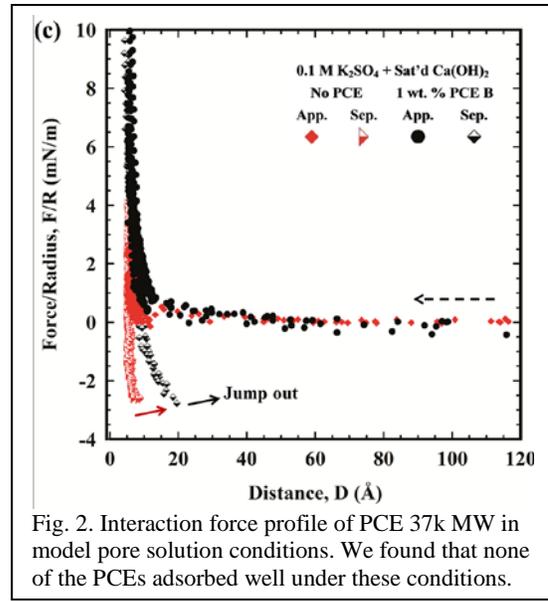


Fig. 2. Interaction force profile of PCE 37k MW in model pore solution conditions. We found that none of the PCEs adsorbed well under these conditions.

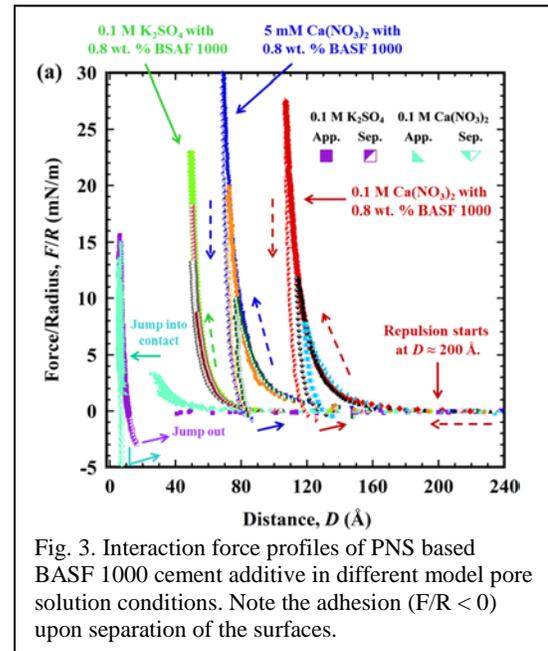


Fig. 3. Interaction force profiles of PNS based BASF 1000 cement additive in different model pore solution conditions. Note the adhesion ( $F/R < 0$ ) upon separation of the surfaces.