Adsorption of Air-Entraining Agents in Fly Ash/Cement Systems
A Study of Surfactant Interaction in Cement Systems

Lori E. Tunstall, Robert K. Prud'homme, and George W. Scherer

Princeton University, School of Engineering and Applied Science

INTRODUCTION

It is well documented that proper air-entrainment in concrete is required for protection against frost damage, yet our ability to control air-entrainment is limited by deficient information on the interaction of surfactants in cement systems. The work presented here seeks to contribute to this understanding, using surface tension as a novel method for elucidating surfactant behavior in a simulated cement pore solution.

This presentation also highlights the usefulness of γ experiments in measuring adsorption. With the environmental incentive to partially replace cement with waste materials such as fly ash, the control of air in concrete has become increasingly difficult. This is especially true for carbon contaminated fly ash (which is now the most abundant variety), since the carbon adsorbs air-entraining agents (AEAs) in an unpredictable manner. Using γ, we can quantify the amount of AEA adsorbed onto ash and calculate the remaining AEA in solution able to contribute to air-entrainment.

EXPERIMENTAL PROCEDURE

Surface tension was measured using the drop-weight method, which correlates surface tension with drop size. Once the drops were collected and weighed, the surface tension was calculated as

$$\gamma = \frac{W}{2\pi r f(r/V^{1/3})}$$

where $f(r/V^{1/3})$ is a corrective function for drop shape, r is the outer radius of the syringe tip, and W is the average drop weight.

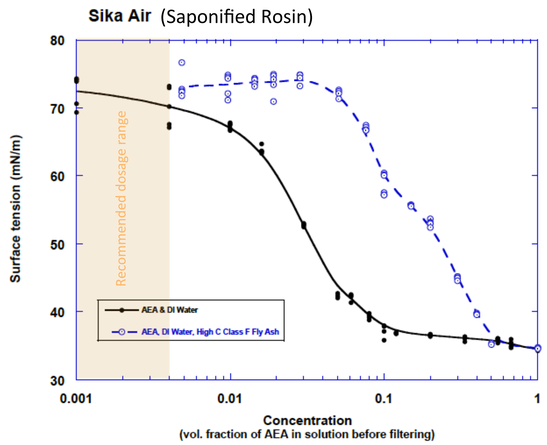
Surface tension experiments were conducted on various solutions. First a baseline critical micelle concentration curve (CMC) was made using only DI water and AEA. In each other case, the AEA was mixed with the solution of interest, filtered and the filtrate was analyzed. Since surface tension decreases with increase in surfactant concentration, removal of AEA via adsorption or coagulation would result in a filtrate with a higher surface tension.

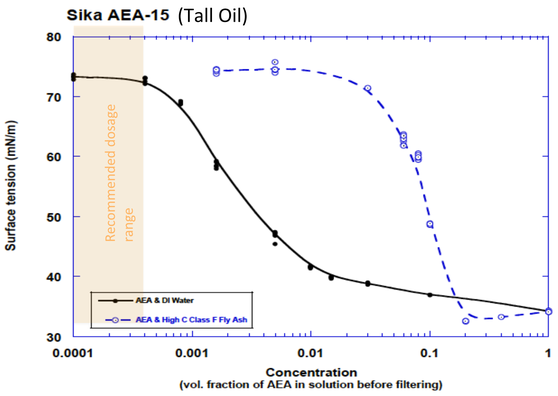
Four AEAs were used in these experiments, three carboxylates and one sulfonate, but only two are presented here: Sika Air (a carboxylate made by saponifying rosin) and Sika AEA-15 (a carboxylate from tall oil). For the adsorption studies, a high and low carbon Class F fly ash were used (LOI ~11% and ~3%, respectively).

RESULTS

ADSORPTION STUDIES

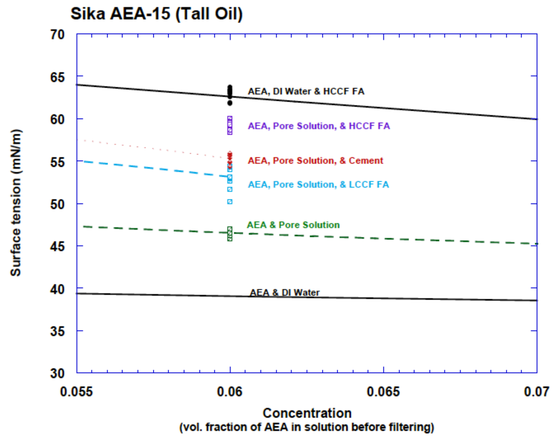
In comparing the surface tension plots of each AEA, it is immediately evident that certain AEAs interact more strongly with the fly ash. It is also clear that the fly ash alone is able to remove all of the AEA at concentrations much higher than the recommended dosages.





Even though the fly ash is a powerful adsorbent, recent studies indicate that it is actually not as strong of an adsorbent as the cement particles. So there will be competition between the fly ash carbon and the cement particles for the AEA in solution.

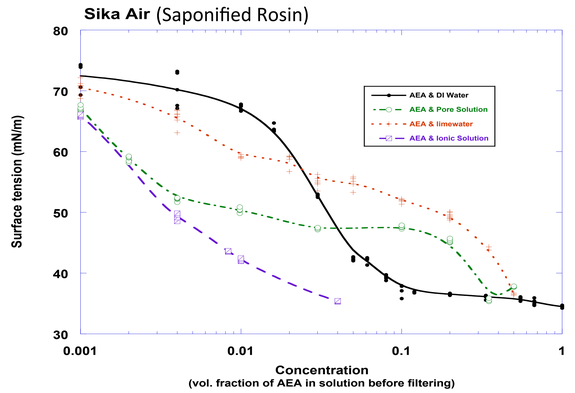
For the tall oil, for instance, at a concentration 0.06 times the as-received material, assuming a starting solution of 50 g, the cement is able to adsorb 2.75 x 10^{-4} g/m^2 while the high carbon ash is only able to adsorb 0.334 x 10^{-4} g/m^2.

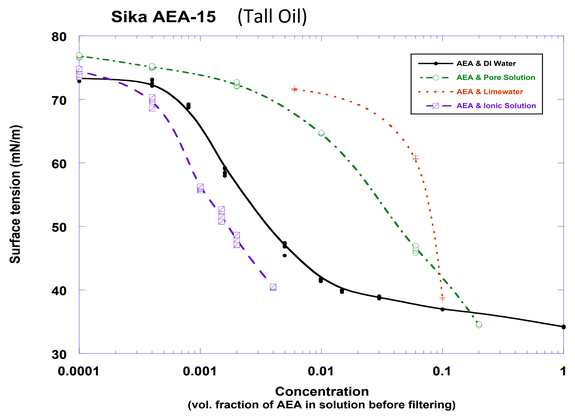


AEA INTERACTION IN CEMENT SYSTEMS

Results show that the ionic strength reduces γ, while Ca^{2+} increases γ by removing surfactant from solution via coagulation. The γ of the pore solution is then a balance of these two effects. The distinct response of each AEA to these effects can be explained by molecular structure.

Sika Air, which has a branchy hydrocarbon tail, does not crystallize easily and is therefore not as sensitive to Ca^{2+}. It is, however, sensitive to ionic strength. It is also notable that AEA-15 actually shows an increase in γ at the recommended dosage, since bubble formation usually requires significant decrease in γ. This suggests that AEA-15 and Multi Air may stabilize bubbles by some other mechanism, perhaps by forming Ca^{2+}-rich shells at the air void/cement paste interface.





CONLUSIONS

This work demonstrates the usefulness of a simple γ measurement in quantifying adsorption and studying surfactant interaction in cement systems. These results suggest that the mechanism for air entrainment may vary depending on surfactant structure, some stabilizing air voids via γ reduction and other stabilizing via calcium interaction.

ACKNOWLEDGEMENTS

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