

Workability and Retardation Effects on early CSA hydration by Phosphono and Carboxylate Chemistries

Christopher M. Childs, Oğulcan Canbek,
Kimberly E. Kurtis, Newell R. Washburn,

Presented by: Oğulcan Canbek

Carnegie Mellon University & Georgia Institute of Technology

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**Georgia
Tech**
CREATING THE NEXT

CSA CEMENTS AS AN ALTERNATIVE TO PC

- **Calcium sulfoaluminate (CSA) cements** hydrate rapidly to form ettringite
- To extend setting time beyond 30 min, important for larger scale placements, retarders are added such as citric and tartaric acids

SOME INFO ON CSA

- ❑ Developed in China ~1970
- ❑ Calcination T is 200°C less than for OPC
- ❑ Main phase ye`elinite, no alite
- ❑ Gives high early strength

MOLECULAR MECHANISM OF CSA RETARDERS

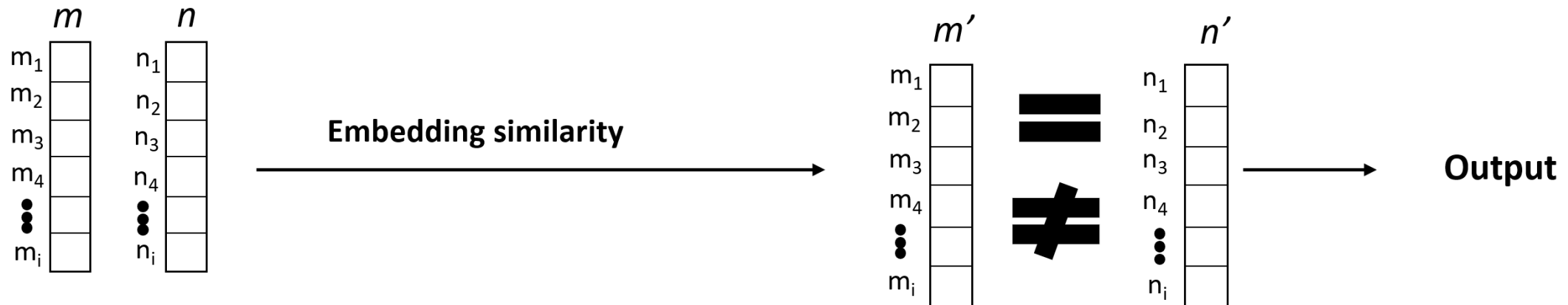
Two main mechanisms:

- 1) Binding of calcium in solution
- 2) Adsorption onto hydrating particles

Challenge: How can we screen a diversity of retarder chemistries that are suitable for CSA cements?

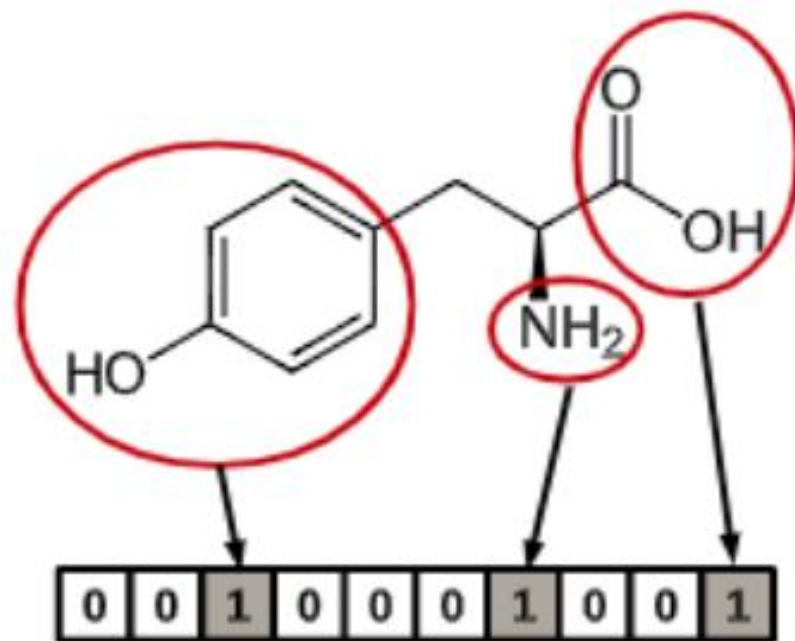
CHEMINFORMATICS

- Cheminformatics is the use of computational and informational techniques applied to a range of problems in the field of chemistry
 - Widely applied in the pharmaceutical industry for drug development through virtual screening
- In this case, quantitative methods are utilized to relate chemical structures to predict the associated increase in set time of CSA cements



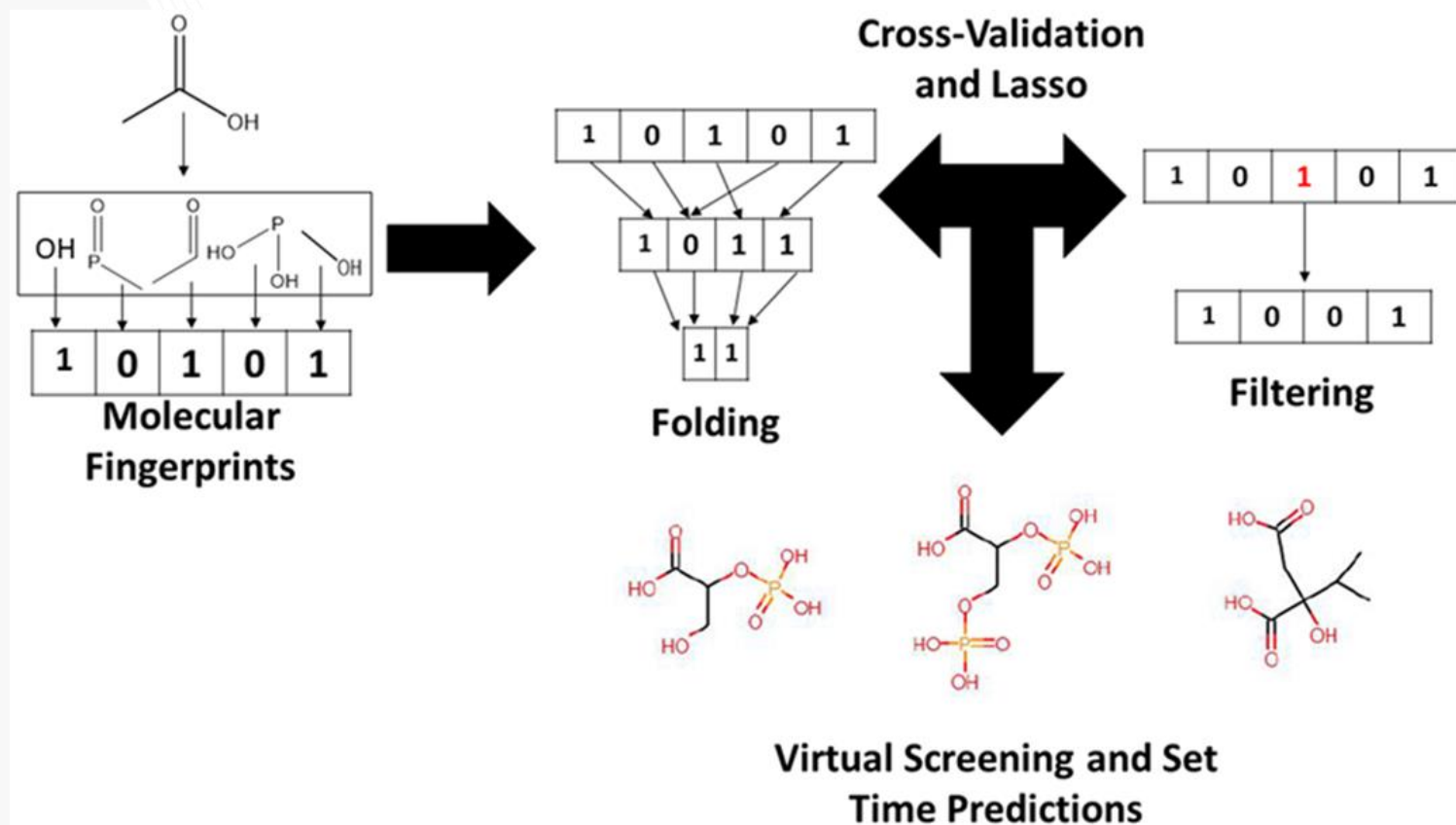
FINGERPRINT GENERATION: EXTENDED CONNECTIVITY FINGERPRINT (ECFP)

- Each group is represented in a binary vector of presence or absence. The radius chosen for this research was three, indicating that all paths of three bonds or less are represented in the vector.
- These vectors can be folded into various lengths from 2048 down to 32 length



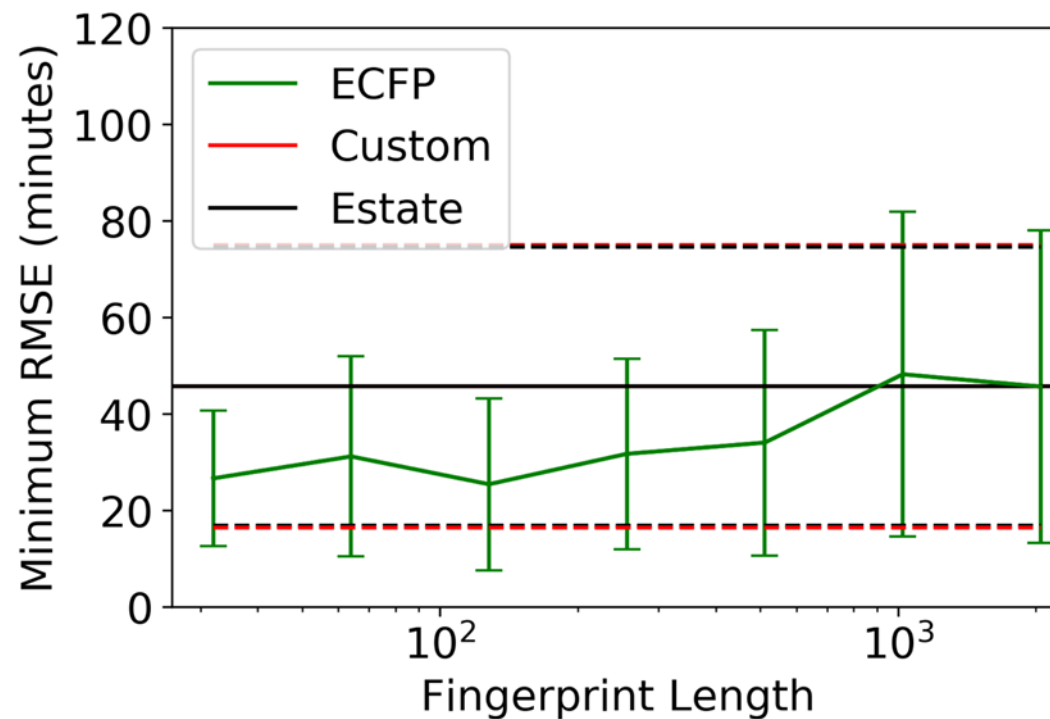
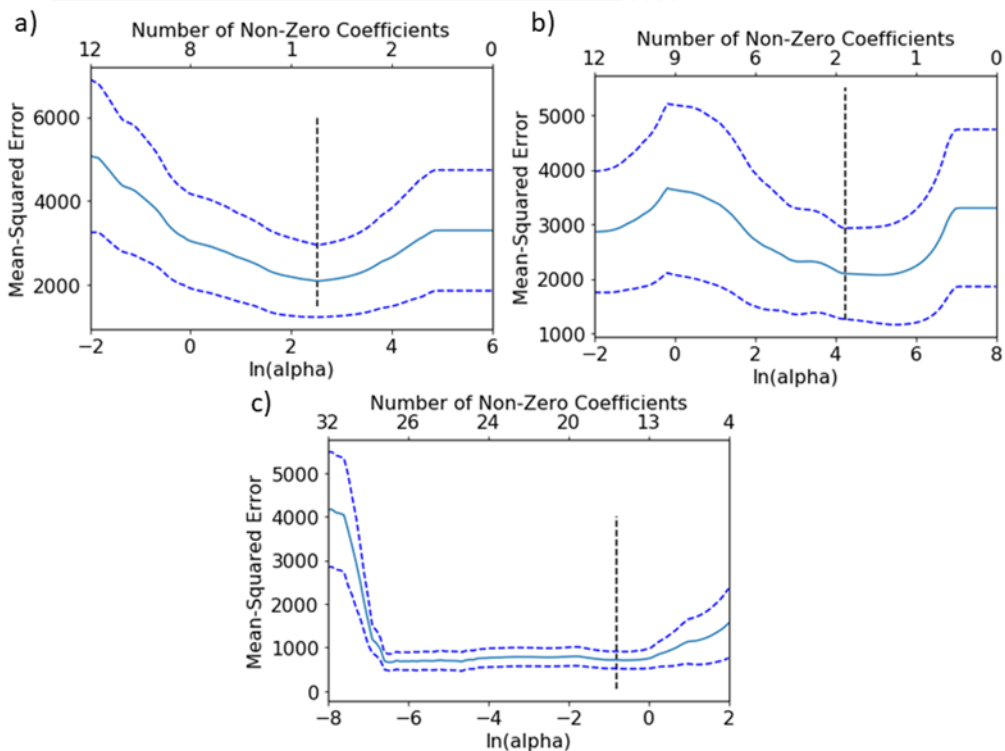
SPARSE DATASETS AND FILTERING

- Filtering is a process of feature selection, where only the features contributing most to the variance of the feature set are selected to model the equation



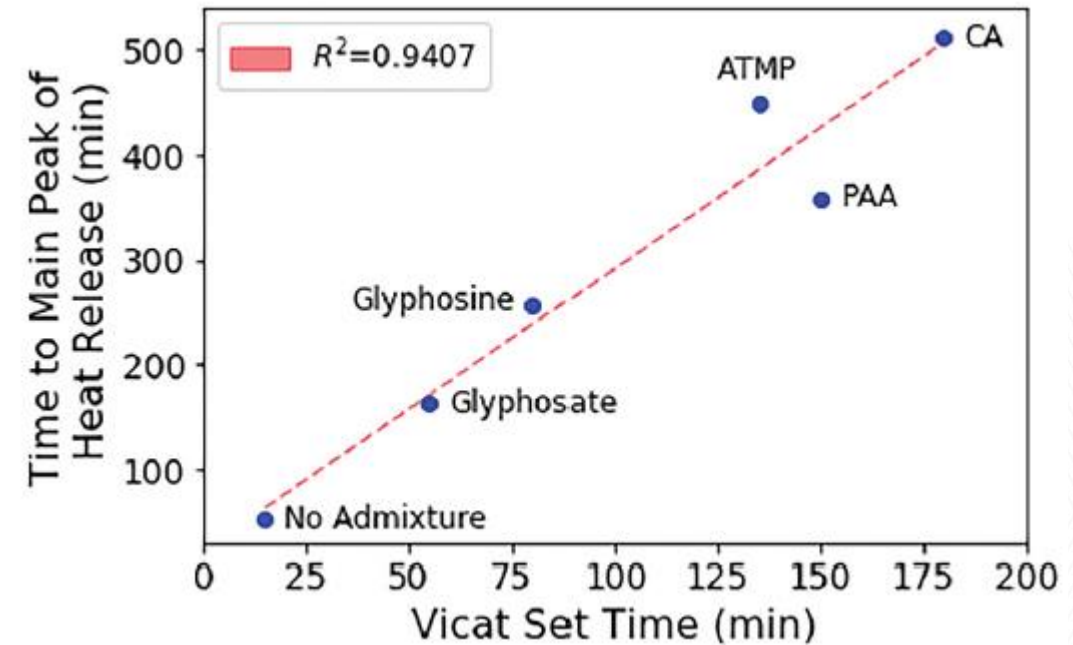
HYPERPARAMETER SELECTION

- Through cross validation, hyperparameters for both vector length (folding) and the lambda (alpha) parameter (filtering)
- The selections are conditional on minimizing the MSE, the uncertainty (standard deviation) in the MSE and having the # of features < # of training points.



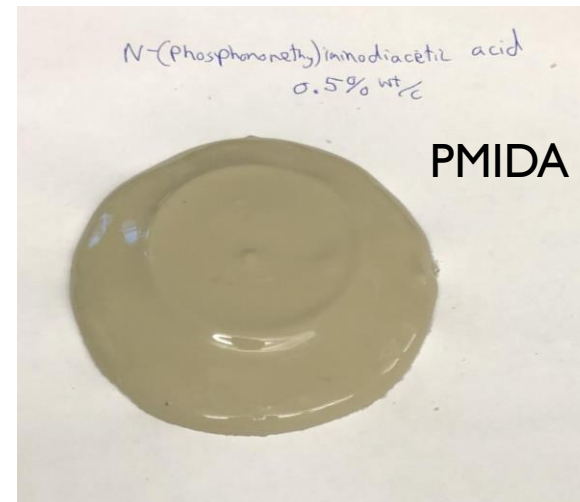
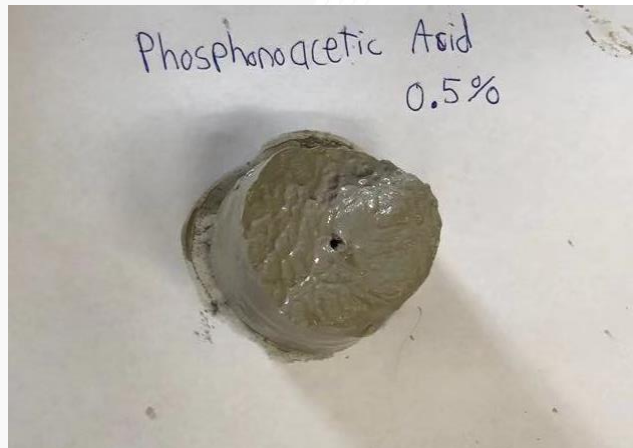
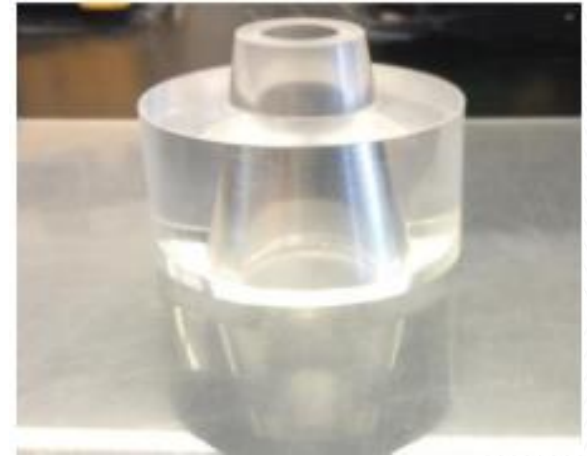
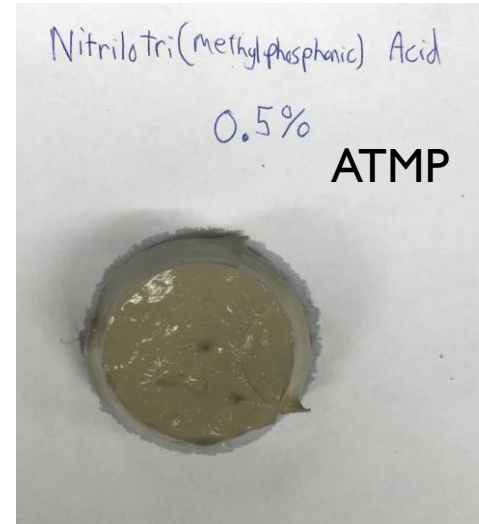
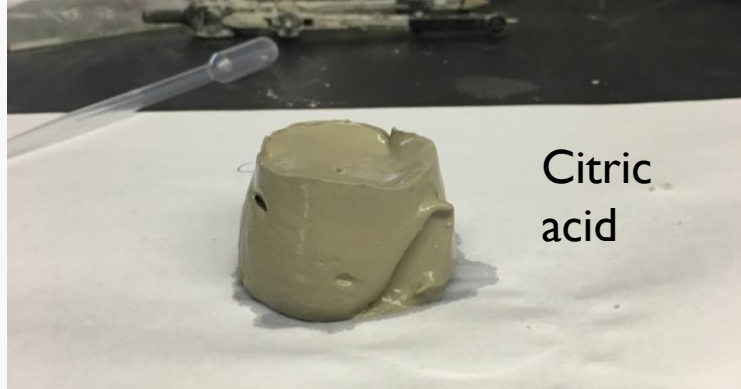
VIRTUAL SCREENING

- The molecular structures of the three highest predicted set times, from 500,000 molecules downloaded in PubChem, are shown in the bottom figure
- Glyphosate was also predicted to extend set time beyond 1 h and is a commercially available compound at costs comparable to citric acid.
- Glyphosate was found to have a set time of 55 min, within the predicted range of error of +/- 26 min.



| Name | Glyphosate | 2-hydroxy-4-oxobutane-1,2,4-tricarboxylic acid | 4-Phosphonyl-3-carboxy-3-hydroxybutanoic acid | (3-(Formylhydroxyamino)-1-propenyl)phosphonic acid |
|---------------------|------------|--|---|--|
| Molecular Structure | | | | |
| Predicted Set Times | 61 min | 178 min | 178 min | 183 min |

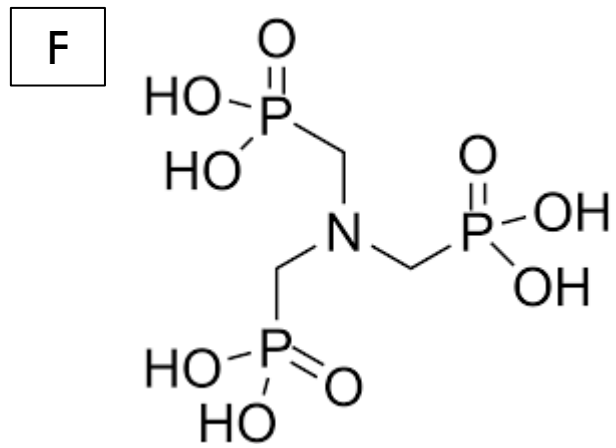
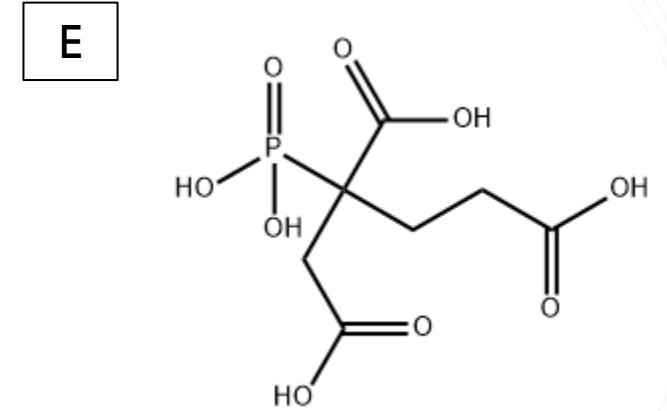
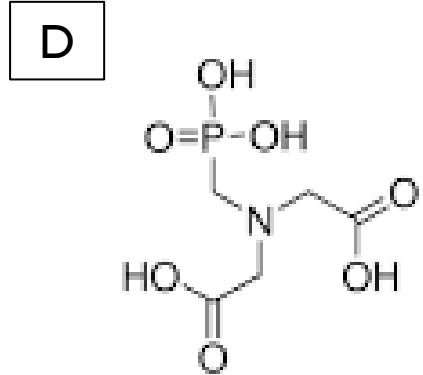
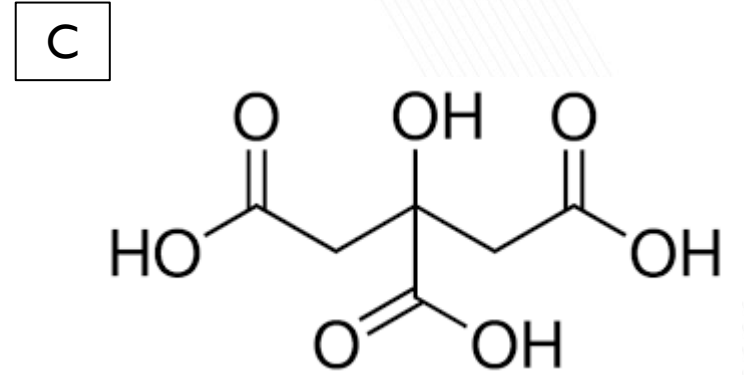
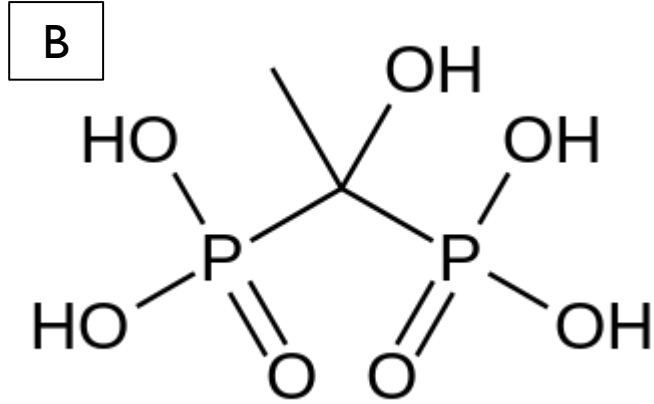
ANOMALOUS PLASTICIZATION BY PMIDA (THE BOTTOM RIGHT CHEMICAL)



CHEMISTRY

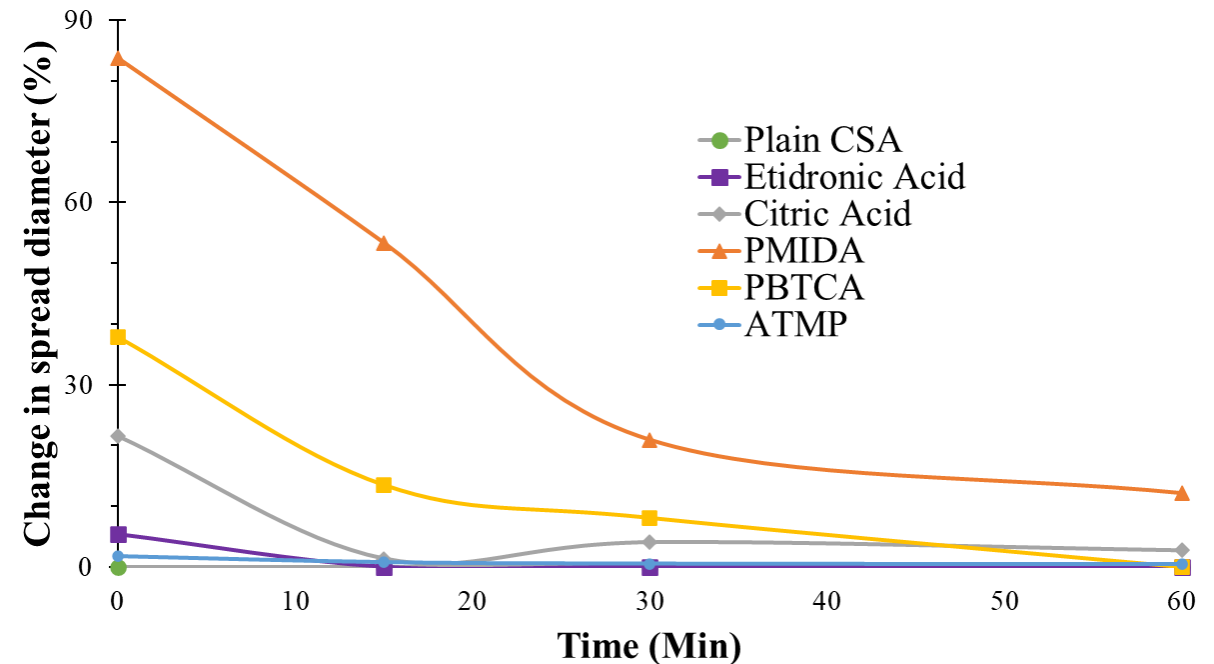
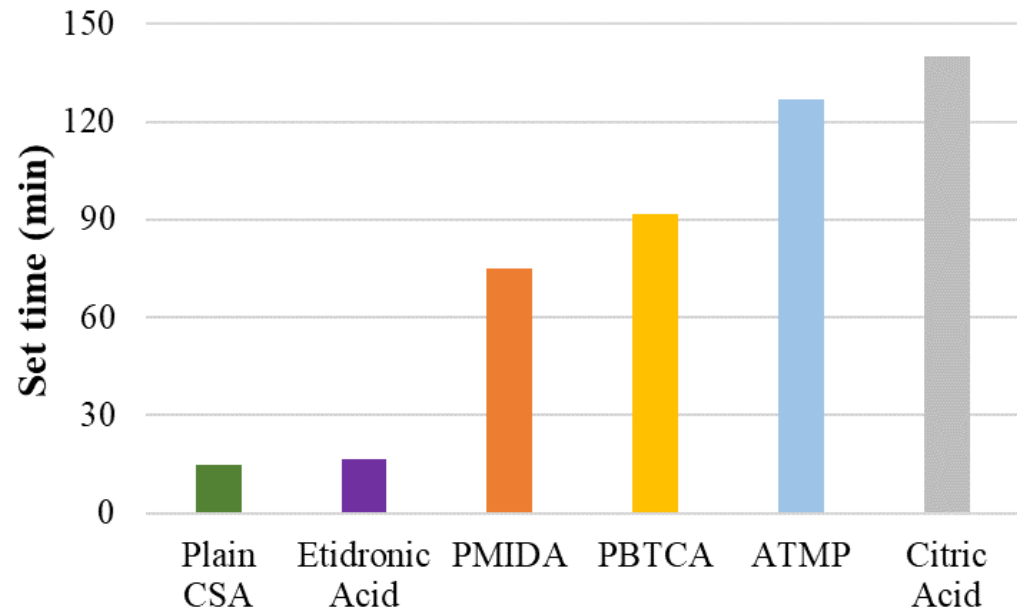
Labels for presentation:

- A - None
- B - Etidronic acid
- C - Citric acid
- D - PMIDA (the bottom right chemical)
- E - PBTCA
- F - ATMP

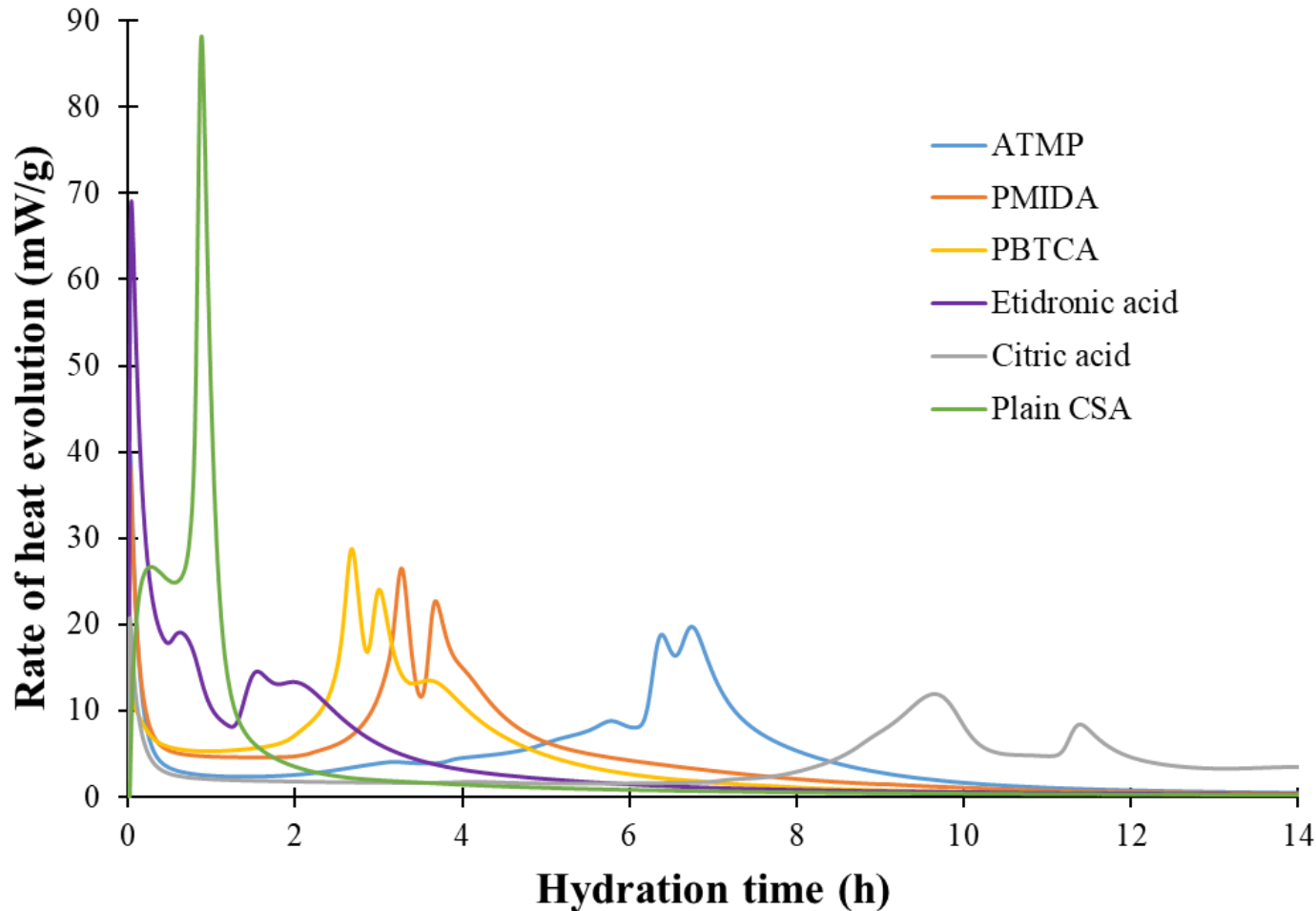


SET TIME AND MINI SLUMP SPREAD VARY SIGNIFICANTLY ACROSS RETARDERS

- Although Citric acid exceeds PMIDA on Vicat retarding time by 65 min, PMIDA maintains slump throughout the entire first 60 min.
- By 90 min, no further spread was observed for any of the retarders



Calorimetry curves show similar trends to set time

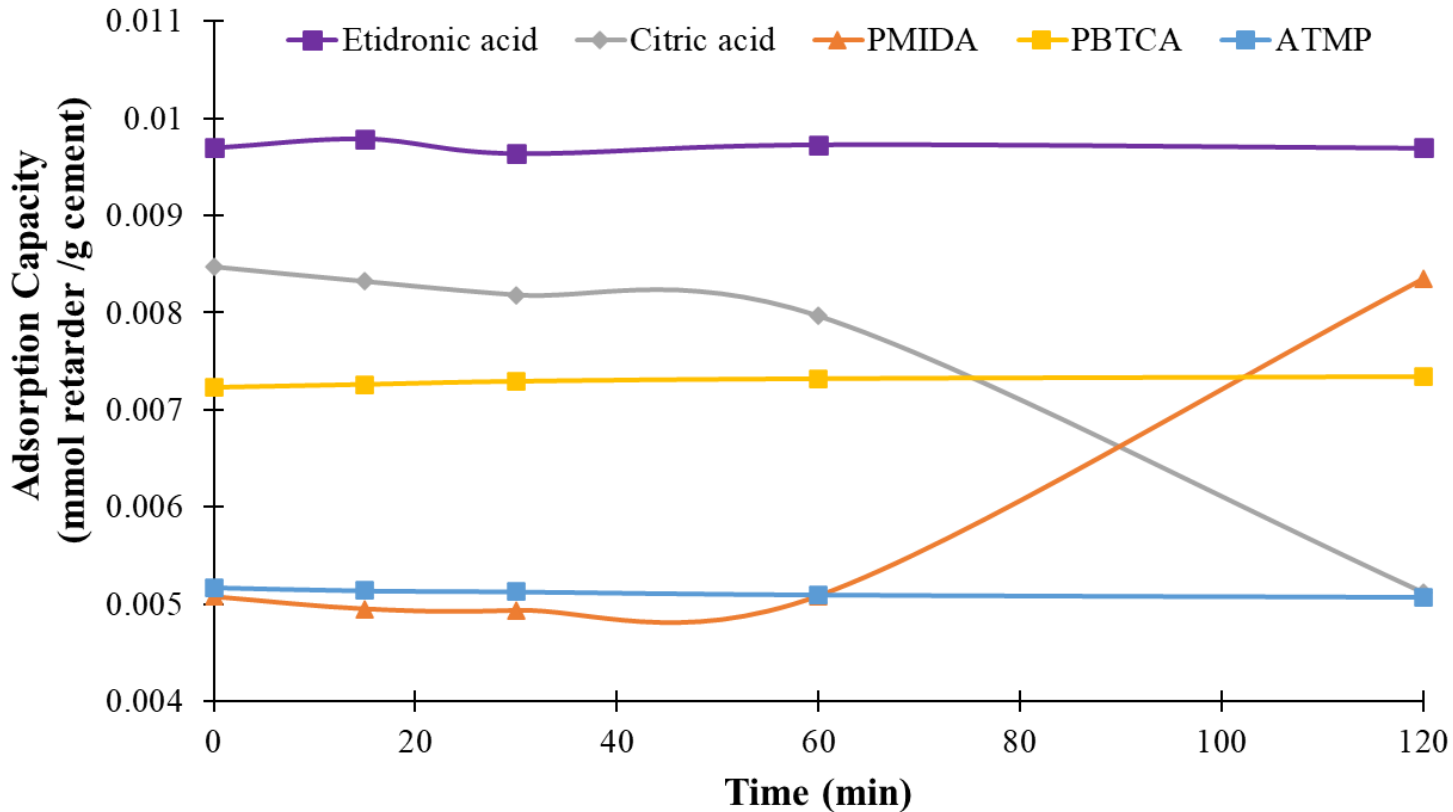


- A single peak was observed with plain CSA around ~55 min, whereas dual peaks were observed with retarders

➤ Hemihydrate to gypsum

➤ Ettringite formation

TOC ADSORPTION

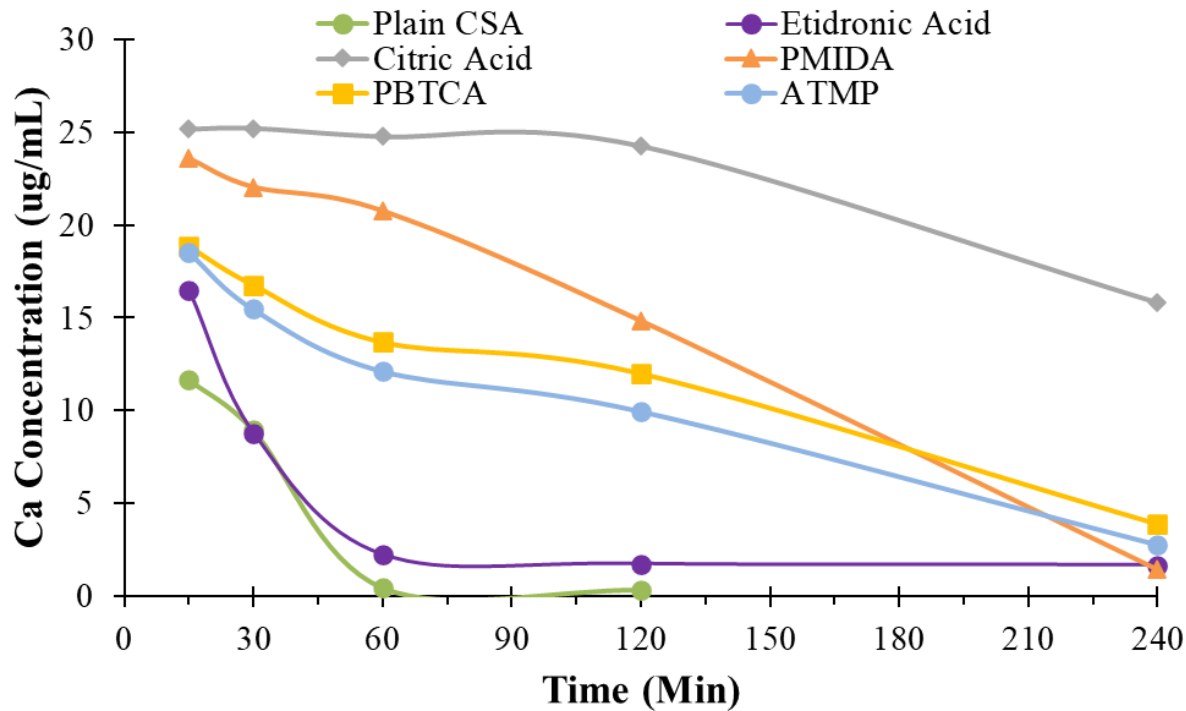


- Relatively lower adsorption is observed with PMIDA that leads to higher spread
- Decreasing citric acid adsorption but increasing PMIDA adsorption over time

ICP Pore Solution Concentrations of Ca and Al

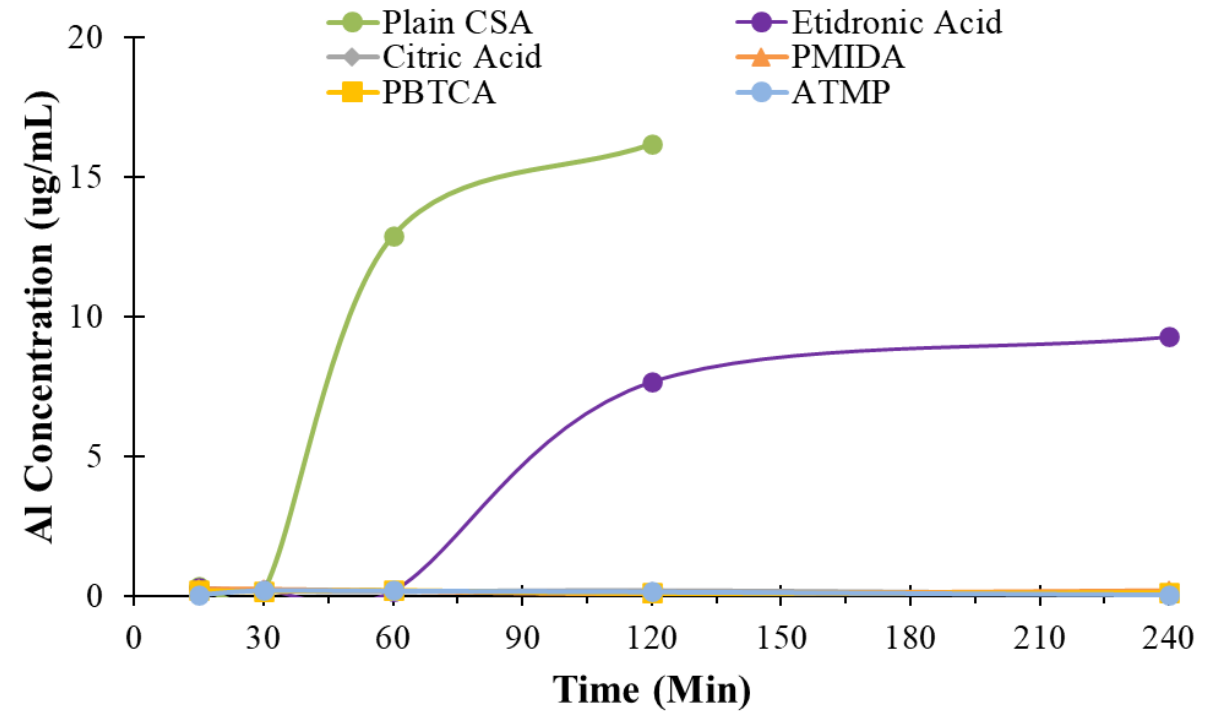
- Plain CSA and etidronic acid → Low Ca concentration in pore solution

Rapid set by ettringite formation?



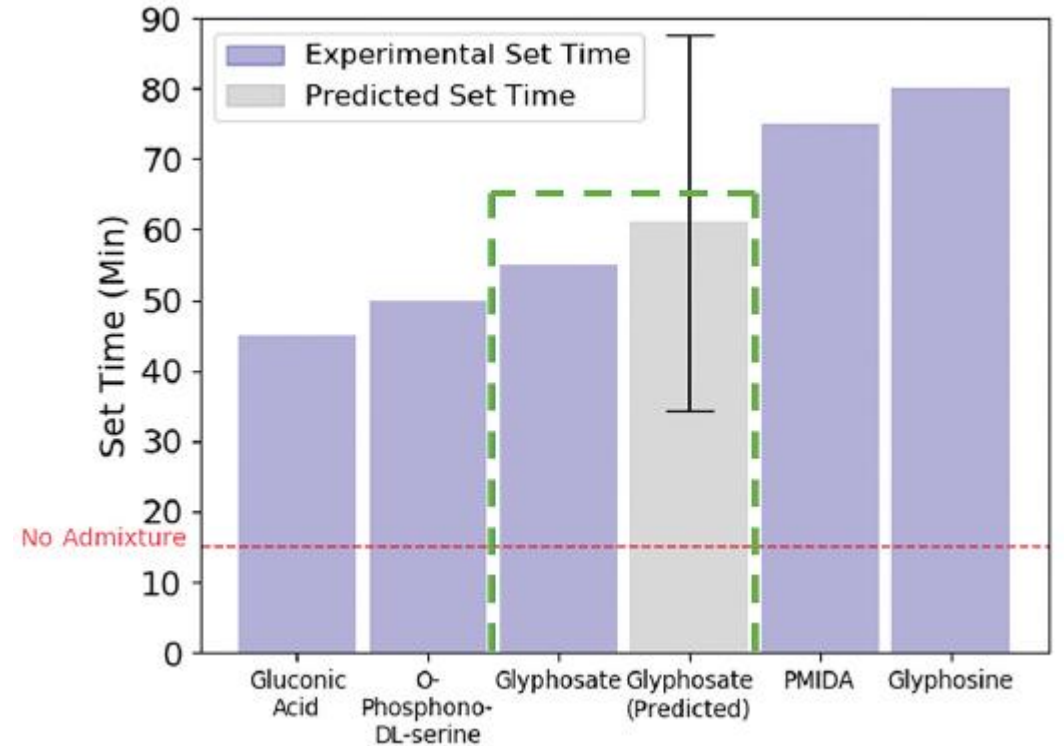
- Retarders except etidronic acid → Almost zero Al concentration in pore solution

Curbed ye`elimited dissolution?



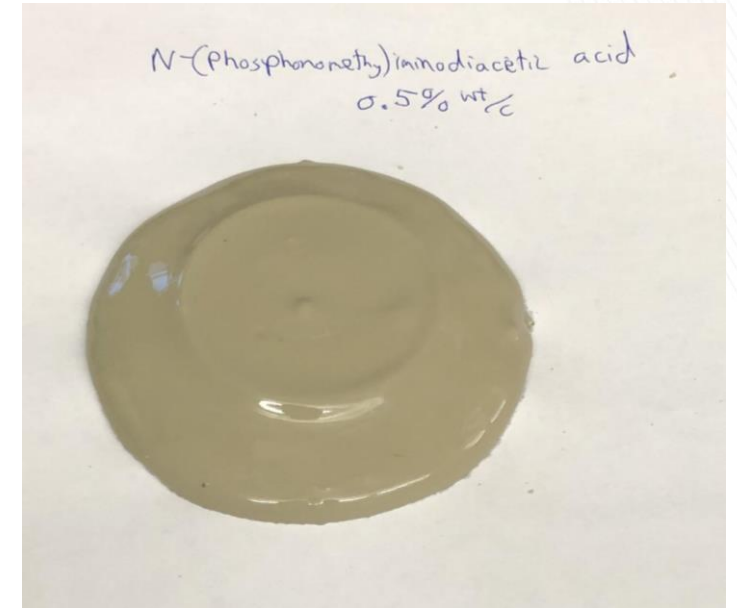
CONCLUSIONS

- ✓ Cheminformatics was used to accurately predict set time for anionic retarders
 - We identified glyphosate as a novel set retarder for CSA



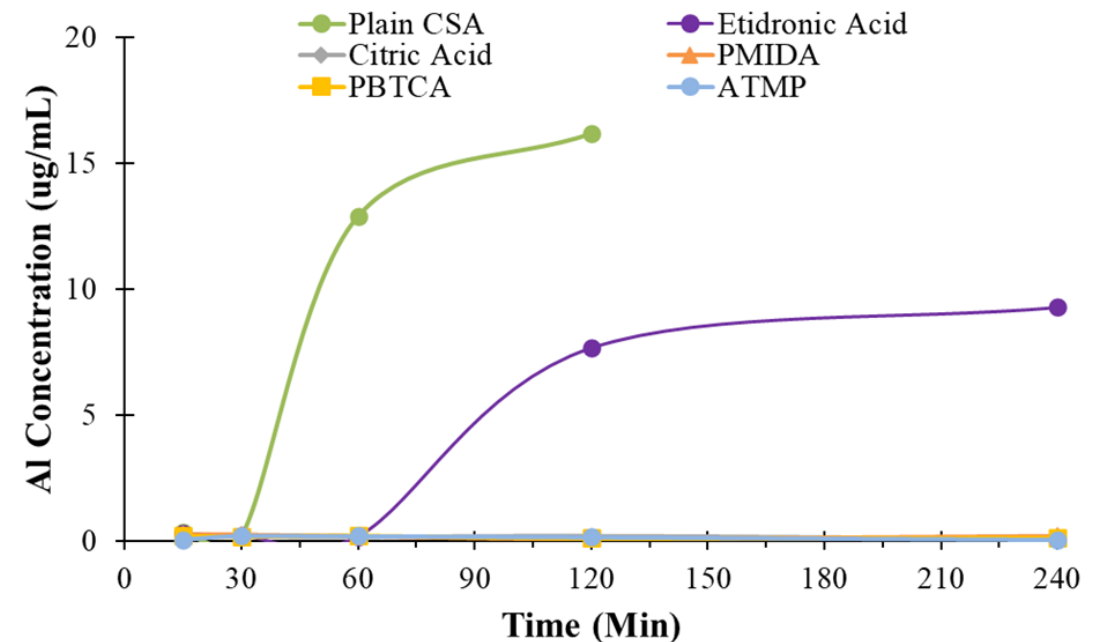
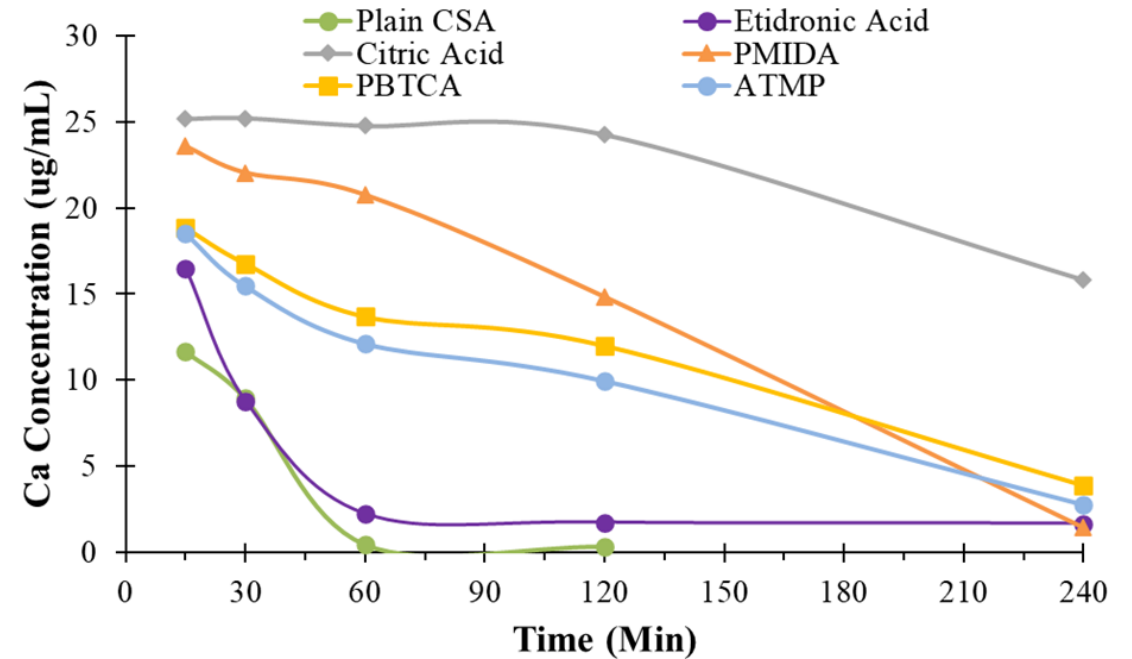
CONCLUSIONS

- ✓ Screening a small library of anionic set retarders led to the observation anomalous plasticization by PMIDA
 - Set time around 75 min with mini slump spread retention



CONCLUSIONS

- ✓ Mechanistic studies indicate a complex relationship between setting and plasticization
 - Adsorbed retarders preventing dissolution
 - Retarders in pore solution binding calcium and possibly other phases



Acknowledgements

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