How carbon-chains may help mitigate mineral scaling

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Introduction:

Scale formation:

- Costly phenomenon for water and other fluid processing systems
- Affects process efficiency (i.e., clogging up industrial components (Fig. 1) and slowing down water-flow) [1-3].

Fig. 1. Mineral scaling reduces fluid flow

Calcium sulfate:
- common in heat exchanger or desalination
- 3 phases: bassanite, gypsum, anhydrite ($CaSO_4.0.5H_2O$, $CaSO_4.2H_2O$, $CaSO_4$)
- formation pathway is not well understood
- But $CaSO_4$ phases are useful minerals:
  - medical applications (splints)
  - construction industry (plaster)
  - sculptures

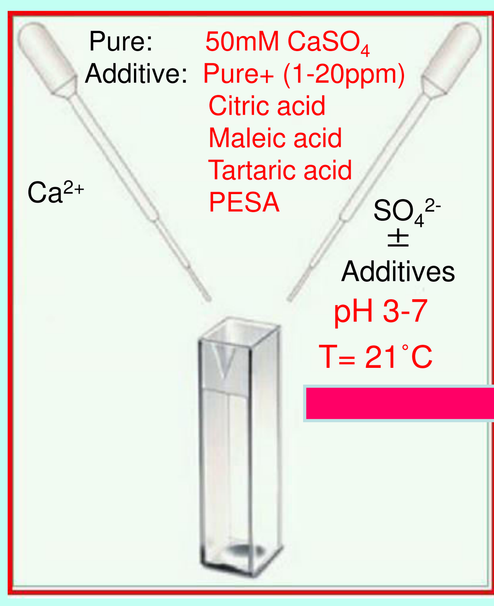
Green inhibitors:
- reduce scaling
- biodegradable(no eutrophication; Fig. 2)
- are effective at low concentrations

Fig.2. Industrial P and N containing additives cause eutrophication

Aim of Research:

- Understanding the nucleation and growth kinetics as well as the mechanisms of calcium sulfate formation
- Investigating the role + effects of green additives with different carbon-chain lengths

Experimental Procedures:



UV-VIS to measure
- Turbidity
- Induction time
- Reaction kinetics

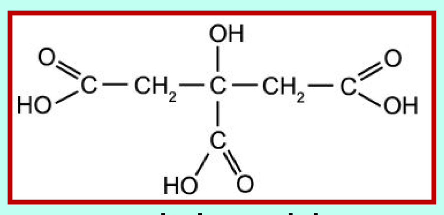
particles

Vacuum filtration

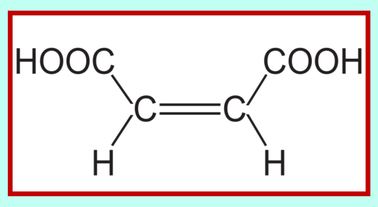
SEM

XRD

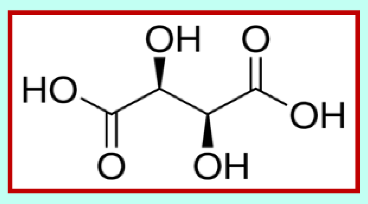
Additives



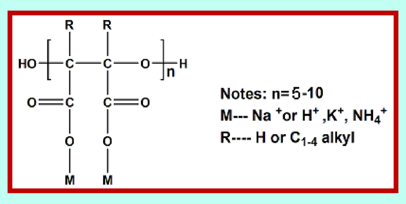
citric acid



maleic acid



tartaric acid



polyepoxysuccinic acid (PESA)

Table. 1. Dissociation constants of additives used

Additive	PK_{a1}	PK_{a2}	PK_{a3}
citric acid	3.13	4.76	6.40
maleic acid	1.92	6.23	-
tartaric acid	3.03	4.34	-
PESA	4.68	4.92	-

Results

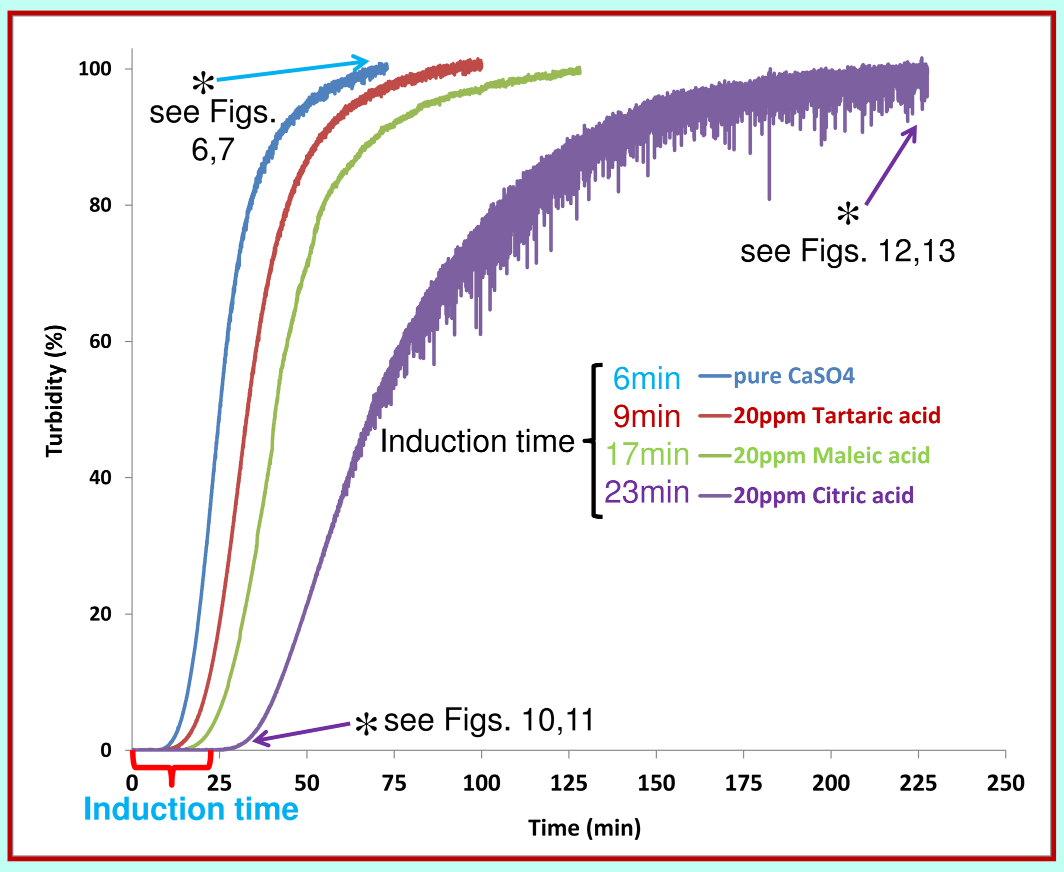


Fig. 3. The effect of various carboxylic acids on the precipitation of calcium sulfates.

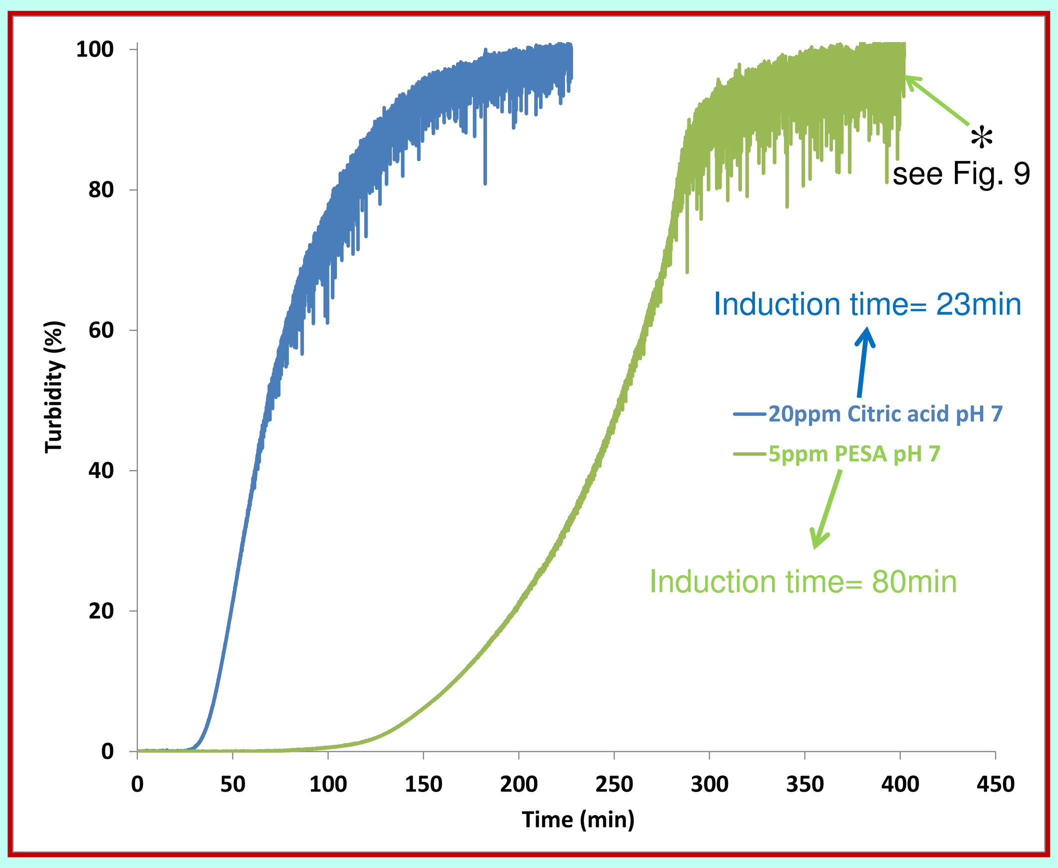


Fig. 4. Comparison between the effect of 20 ppm citric acid and 5 ppm PESA on calcium sulfate precipitation.

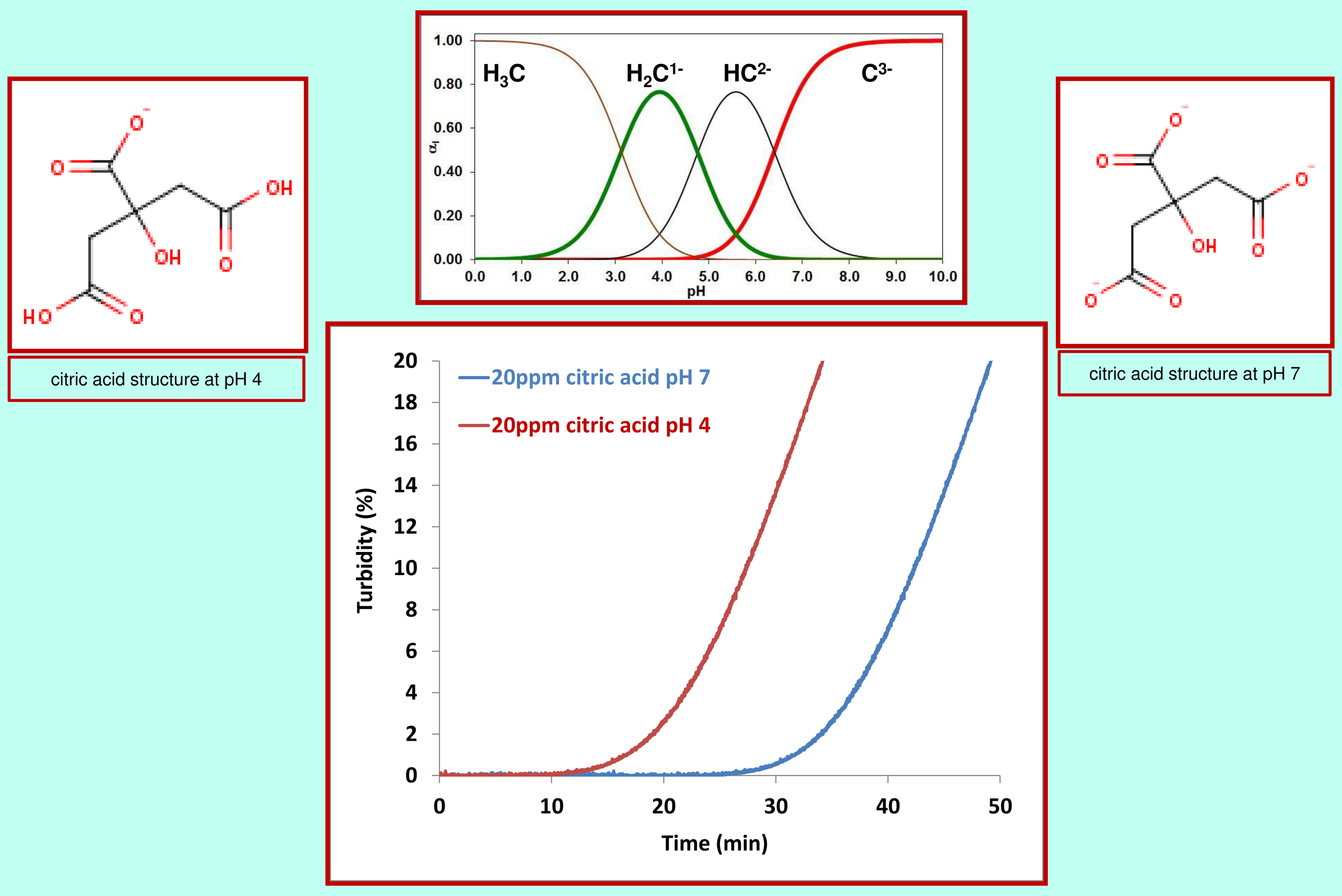
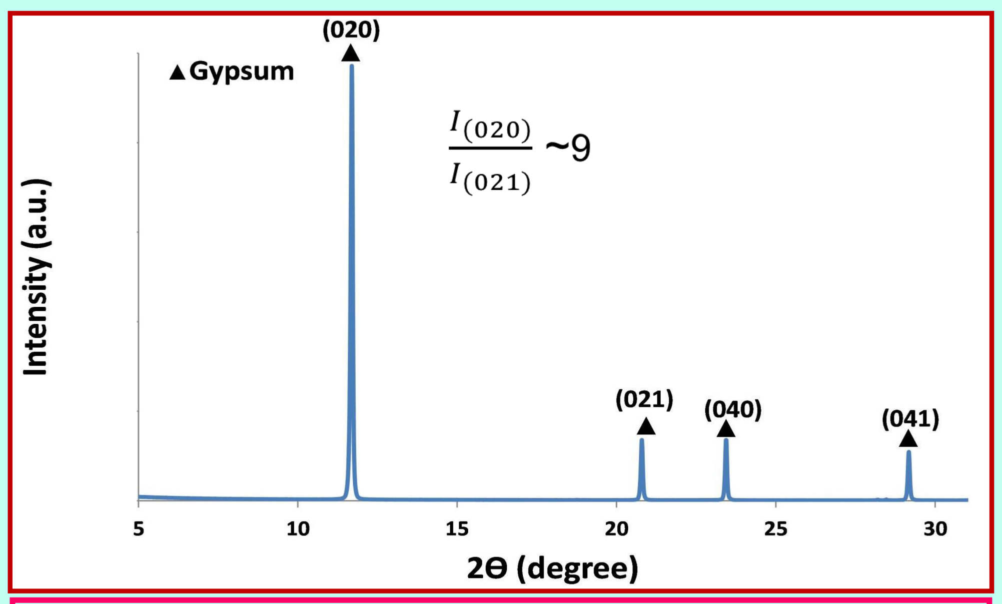


Fig. 5. How the pH dependent citric acid speciation is affecting the inhibition performance in the calcium sulfate system

Fig. 6. Photomicrograph of gypsum needles formed without additives



$\frac{I_{(020)}}{I_{(021)}} \sim 9$

Fig. 7. XRD pattern of precipitates from the additive free system after 75min

The differences in $\frac{I_{(020)}}{I_{(021)}}$ of XRD patterns can be related to the shape modification (Figs. 7 and12)

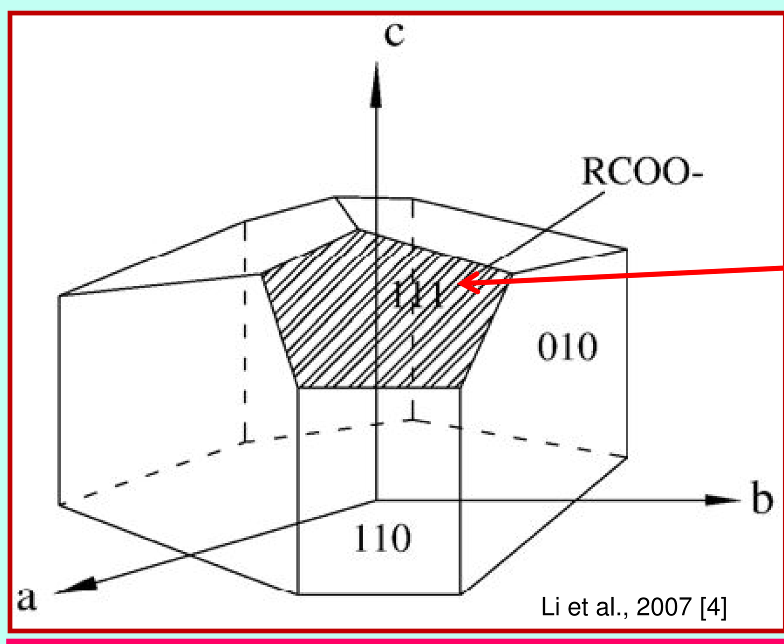


Fig. 8. Schematic of likely sorption of carboxylic group on gypsum growth site

The small platy gypsum crystals can easily pass through membranes without clogging them. They also stick less to surfaces.

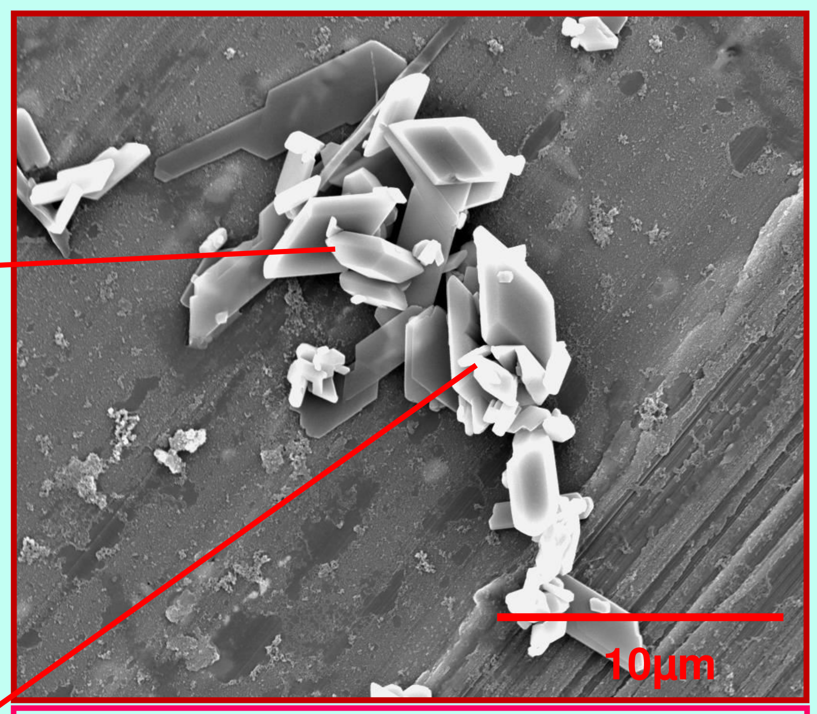


Fig. 9. Photomicrograph of gypsum crystals in the system with 5ppm PESA and pH 7 after 400min

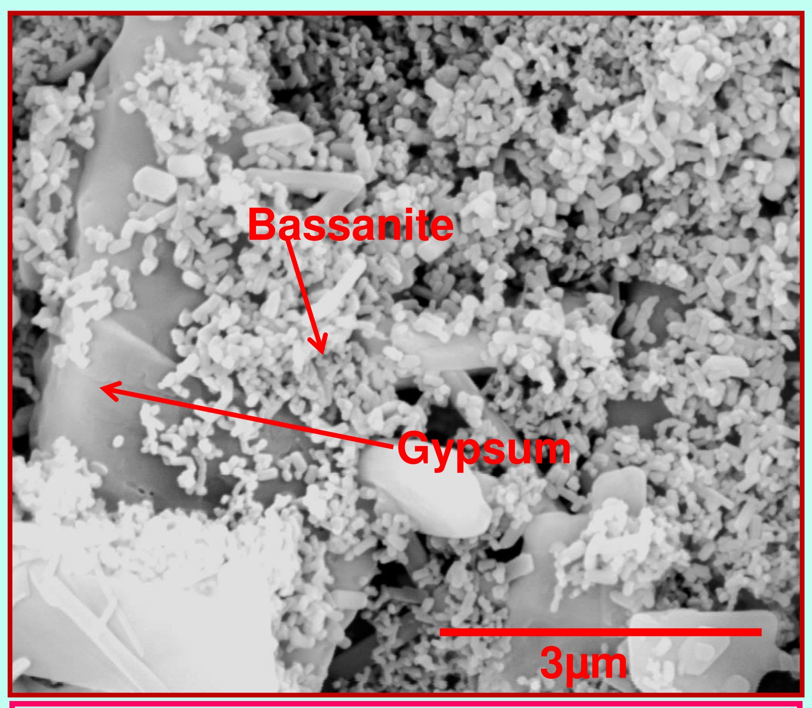


Fig. 10. SEM image of gypsum and bassanite formed at pH 7 with 20ppm citric acid after 28min

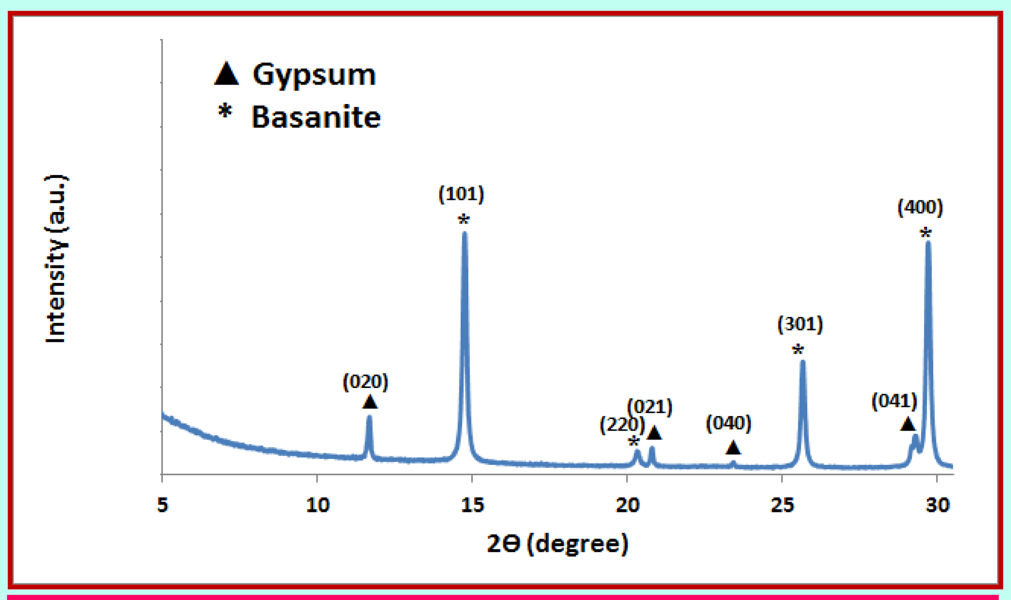
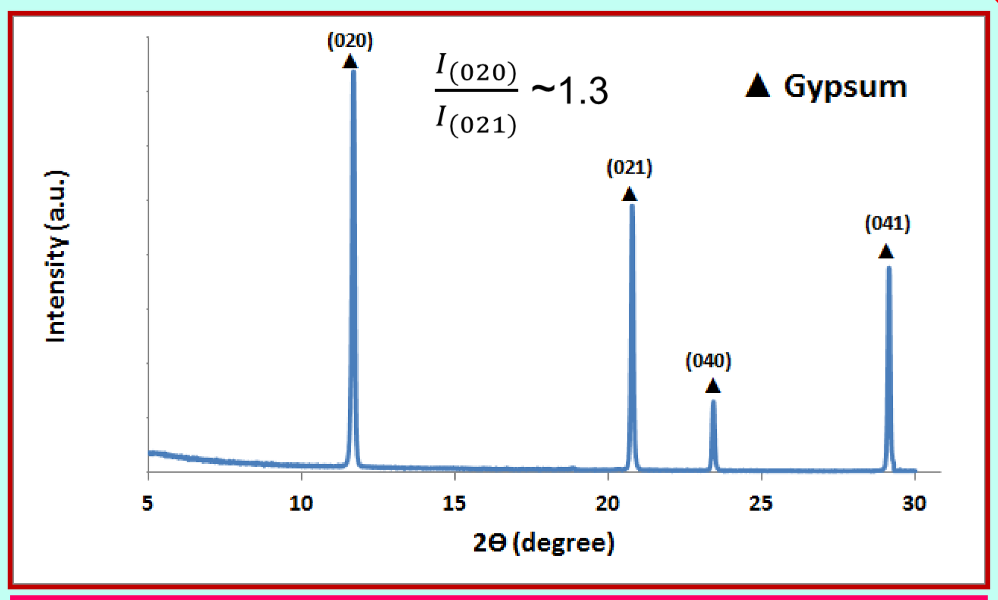


Fig. 11. XRD pattern of precipitates from system with 20ppm citric acid and pH 7 after 28min



$\frac{I_{(020)}}{I_{(021)}} \sim 1.3$

Fig. 12. XRD pattern of precipitates from system with 20ppm citric acid and pH 7 after 200min

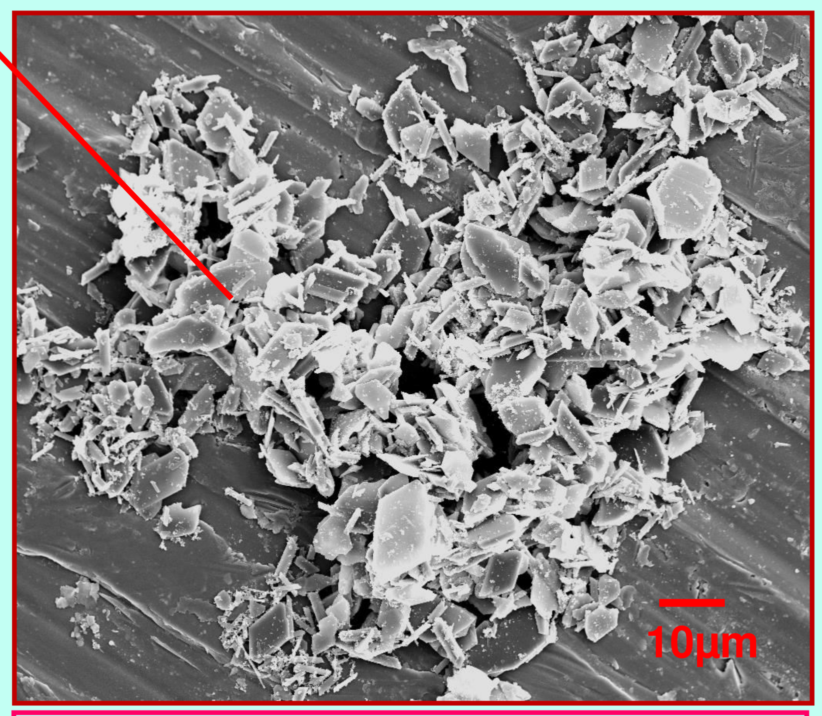


Fig. 13. Photomicrograph of gypsum plates in system with 20ppm citric acid and pH 7 after 200min

Summary and Implications:

(1) Carboxylic acids (citric, maleic, tartaric) and PESA all increase the induction time of $CaSO_4$ formation (Fig. 3 and 4) and are thus adequate inhibitors.
(2) The increase in induction time depends on solution pH and carbon-chain length of the additive.
(3) The polymeric nature of PESA (more functional groups), delays the $CaSO_4$ formation more than the citric acid which has just 3 functional groups (Fig. 4, 5) and is a better green additive.
(4) Citric acid stabilize bassanite as a precursor for gypsum formation; [5] PESA and citric acid also act as a shape modifier (Fig 9, 10 and 13) in that they change the bassanite and gypsum morphologies to more isometric nanoparticles (bassanite) and platelets (gypsum) respectively.

Acknowledgements:

- This project has received funding from the European Union's Seventh Framework Programme (Marie Curie, MINSC ITN) for research, technological development and demonstration under grant agreement no. 290040.

References:

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