Effects of Carbohydrates and Sulfonates During CaO Hydration on Portlandite Microstructure

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Introduction

The rising global demand for cement is driving a steady increase in cement-related CO_2 emissions, estimated between 7% and 10% from 2018 to 2022. For Portland Cement (CEM I), up to 40% of the CO_2 emissions come from fossil fuel combustion, while over 60% result from limestone calcination, essential for cement clinker production.

CO_2 capture and storage (CCS) and utilization (CCU) technologies further mitigate emissions by re-mineralizing emitted CO_2 into cement mortar or concrete.

Portlandite ($Ca(OH)_2$) plays a key role in these processes, influencing early-age cement carbonation. Furthermore, cement mortars and concrete are often formulated with the addition of organic admixtures like water reducers which affect the precipitation process of portlandite.

This research examined the effects of organic additives on portlandite microstructure, aiming to optimize its morphology for improved cement performance and sustainability, with broader applications in CO_2 sorbent design.

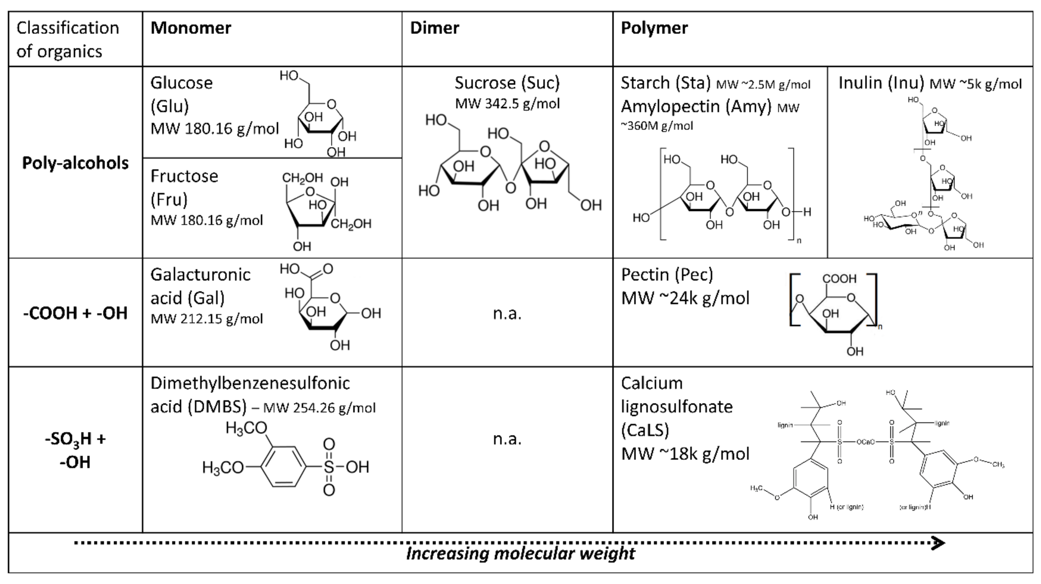

Figure 1. Matrix representing the tested additives. Left to right the increase in molecular weight of the molecules tested. Top to bottom the different families of additives.

Methods and Materials

The additives tested can be grouped into three families: hydroxyl (OH), carboxyl (COOH), and sulfonate (SO_3H). The OH family includes glucose, fructose, sucrose, starch, amylopectin, and inulin. The COOH family includes galacturonic acid and pectin, while the SO_3H family includes Ca-lignosulfonate and its monomer, 3,4-dimethoxybenzenesulfonic acid (DMBS).

To study the effects of these additives on the nucleation and growth of portlandite crystals, various water-rich lime pastes were produced by slaking quicklime in different water solutions. The effects of organic additives on portlandite microstructure were investigated by comparison with the microstructure of a control paste.

Pastes were prepared using 'Calbux Granular 15' quicklime, with organic-modified versions created using two methods: "A method" with the addition of the additives before slaking, and "B method" with the addition after slaking.

Additive dosages were based on previous studies, with a uniform dosage applied within each family to enable comparisons as summarised in Table 1.

Characterization included SEM for micromorphology, XRD for mineralogical analysis, laser diffraction for particle size distribution, and BET for specific surface area.

Table 1. List of tested additives with related methods and concentration.

Preparation method	Additive	Additive concentration in solution (wt.%)/ g additive per L water	Sample Name
"A" Method (additive dissolved in slaking water)	Glucose	5 wt.%	Glu-A
	Fructose		Fru-A
	Sucrose		Suc-A
	Starch		Sta-A
	Amylopectin		Amy-A
	Inulin		Inu-A
	Galacturonic acid	0.5 wt.%	Gal-A
	Pectin		Pec-A
	DMBS acid	1.5 wt.%	DMBS-A
	Ca lignosulfonate		LS-A
"B" Method (additive introduced as a dry powder to the slaked lime)	Glucose	50 g	Glu-B
	Fructose		Fru-B
	Sucrose		Suc-B
	Starch		Sta-B
	Amylopectin		Amy-B
	Inulin		Inu-B
	Galacturonic acid	5 g	Gal-B
	Pectin		Pec-B
	DMBS acid	15 g	DMBS-B
	Ca lignosulfonate		LS-B
Control	-	-	C

Results

- The presence of carbohydrates and sulfonate compounds in $Ca(OH)_2$ aqueous dispersions promotes the formation of platelet-shaped portlandite crystals. This is a highly-valued characteristic in the conservation industry that is traditionally achieved by maturing plain lime putty for 2-12 months. The addition of small dosages of selected carbohydrates or sulfonate compounds showed to be a rapid method to obtain similar characteristics of matured lime putty.

- Four main groups can be identified according to the effects produced on the micromorphology as observed by SEM: i) Glu-A, Fru-A, Suc-A, and Inu-A showed crystals of irregular morphology, with the former two showing a coarser texture and the latter two showing a finer texture; ii) LS-A and LS-B showed large, plate-like crystals, as already observed; iii) Gal-A, Gal-B, Pec-A, and Pec-B showed slightly more abundant granular crystals than the control; iv) all other samples showed crystal shapes similar to the control.

- Most additive-modified samples showed a higher abundance of platelets, smaller crystallite size, and higher specific surface area.

More marked effects were observed when the organics were added before slaking (method A) with respect to after slaking (method B) suggesting that the interaction of the organics with $Ca(OH)_2$ responsible for the microstructural modifications occurs during the nucleation and early growth stages of portlandite crystals.

- The OH family brings overall more marked effects. Three sub-groups can be identified: i) glucose and fructose, which induce low crystallite size and low specific surface area when added in the A mode; ii) sucrose and inulin, which lead to low crystallite size and high specific surface area when added in the A mode; iii) starch and amylopectin, which were the less active compounds in the family. Moreover, glucose, fructose, sucrose, and inulin can actively enhance the solubility of calcium hydroxide, bringing more calcium ions into solution.

- The COOH family leads to an increase in granular crystals and specific surface area, with more marked effects obtained with the galacturonic acid samples, which also show a remarkably low crystallite size.

- The SO_3H family show differentiated effects across the different compounds tested. While the monomer DMBS is rather inactive, the polymer lignosulfonate induced strong crystallite size reduction and specific surface area increase, together with a strong modification of the crystal habit.

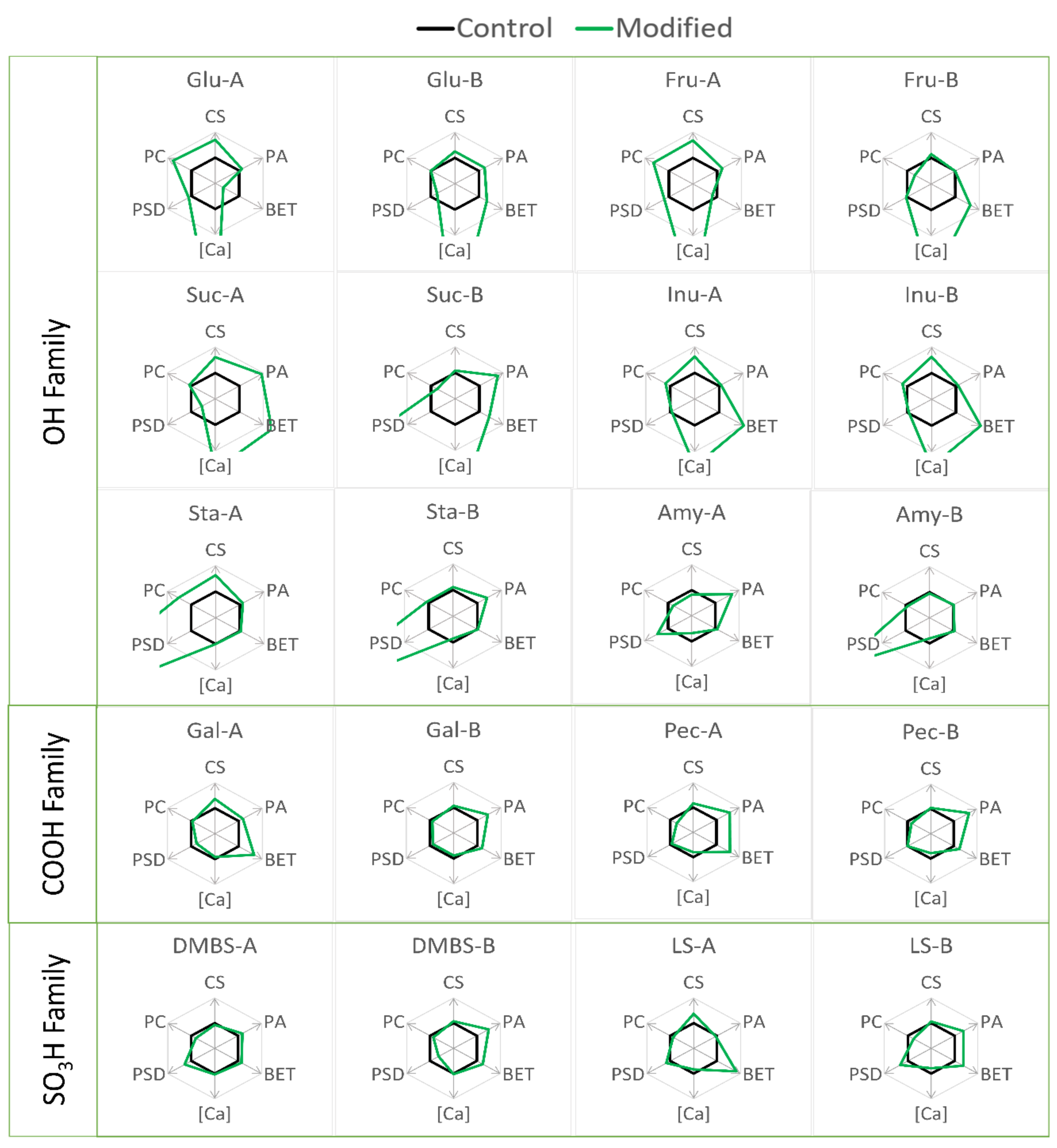

Figure 2. Overall effects of the tested additives on the characteristics of lime putty. The black plots show the reference values of the control sample represented as zero and the green plots show the values of the additive-modified samples in terms of percent difference from the reference (the outer grey circle is 100% increase and the centre point is -100%). The additives keys are: Glu = glucose; Fru = fructose; Suc = sucrose; Inu = inulin; Sta = starch; Amy = amylose; Gal = galacturonic acid; Pec = pectin; DMBS = dimethoxybenzenesulfonic acid; LS = lignosulfonate. The characteristics investigated are: CS = crystallite size reduction; PA = platelets abundance; BET = specific surface area; [Ca] = calcium concentration in solution; PSD = particle size distribution (d50); PC = polycrystallinity

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