Crystallization of calcium carbonate in alginate and xanthan hydrogels

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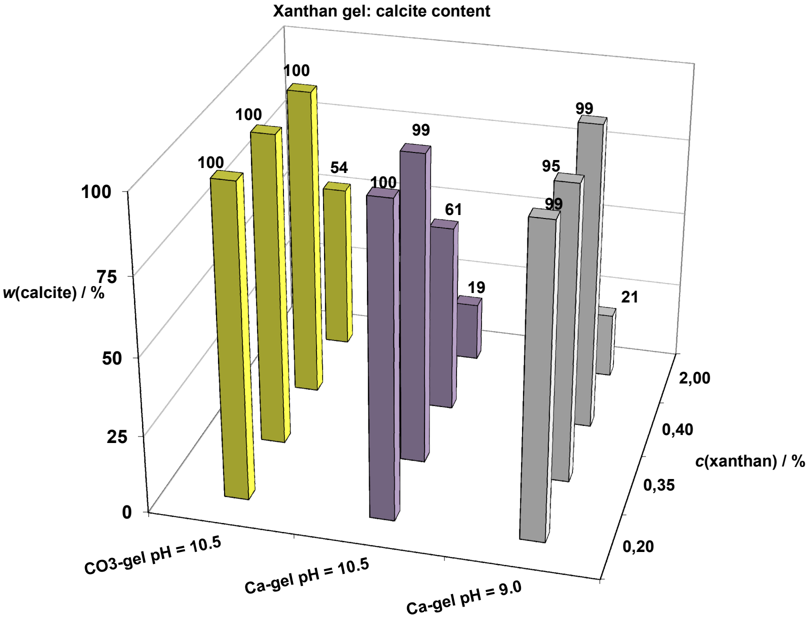
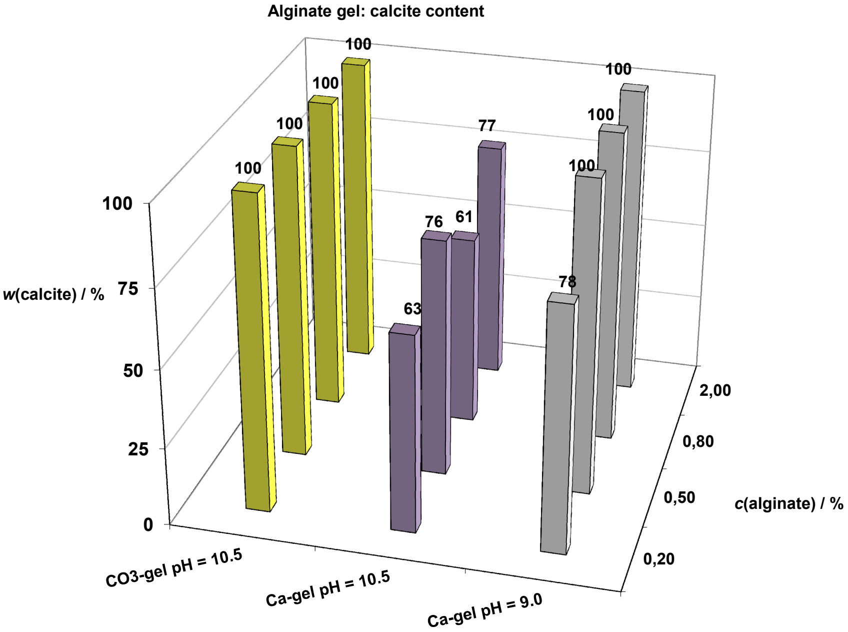
SUPPORTING INFORMATION



a



b

Figure. S1 *Content of calcite observed after 5 days of aging and determined by means of P-XRD, in respective systems: (a) xanthan and (b) alginate.*

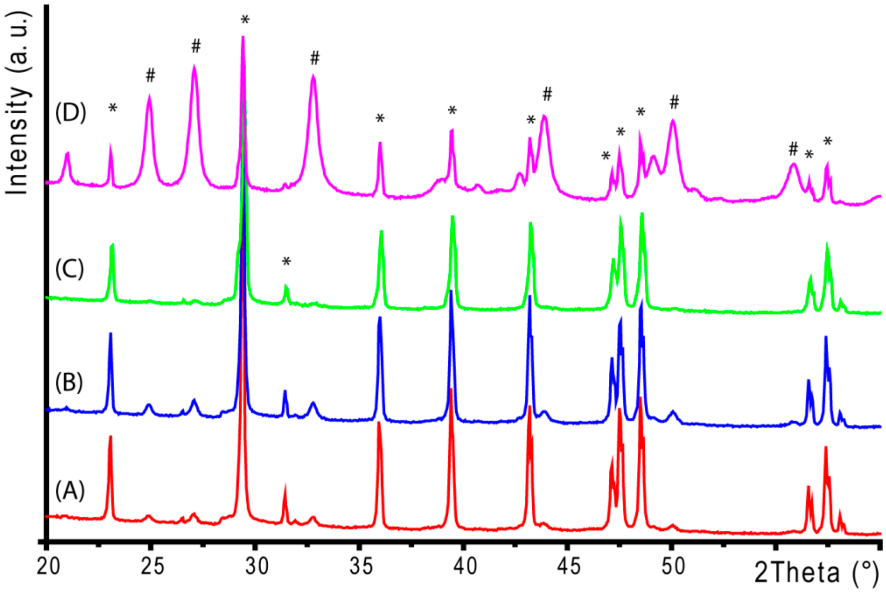


Figure S2 *XRD patterns of precipitate obtained in xanthan Ca-gel pH = 9.0. Concentrations of xanthan are: (A) c = 0.2%, (B) c = 0.35%, (C) c = 0.4% and (D) c = 2.0 %. * indicates the diffraction peaks of calcite and; # indicates the diffraction peak of vaterite.*

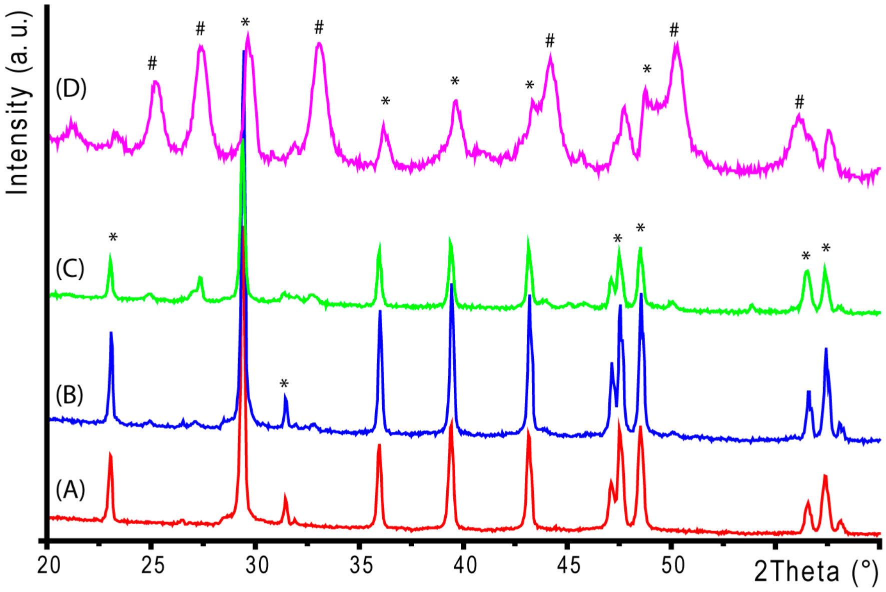


Figure S3 *XRD patterns of precipitate obtained in xanthan Ca-gel pH = 10.5. Concentrations of xanthan are: (A) c = 0.2%, (B) c = 0.35%, (C) c = 0.4% and (D) c = 2.0 %. * indicates the diffraction peaks of calcite and # indicates the diffraction peak of vaterite.*

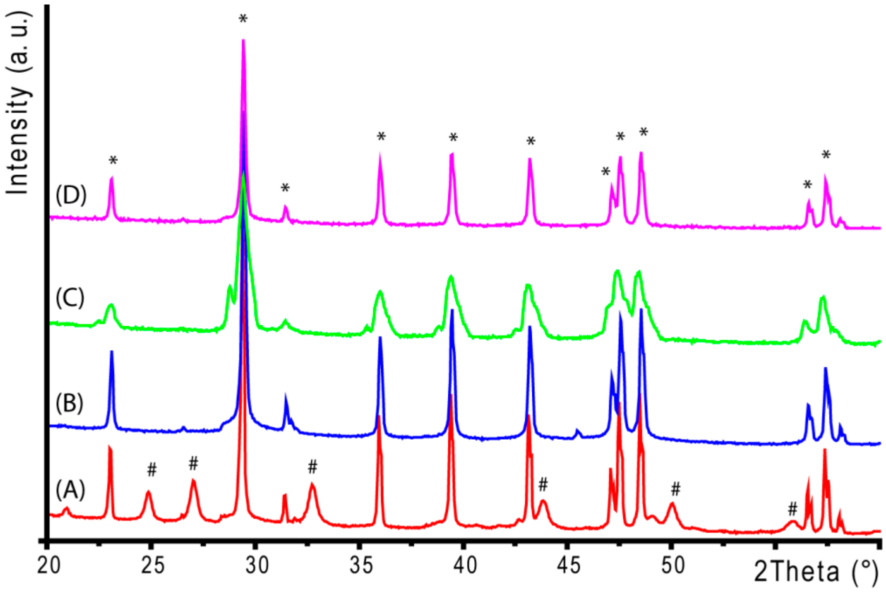


Figure S4 *XRD patterns of precipitate obtained in alginate Ca-gel pH = 9.0. Concentrations of alginate are: (A) c = 0.2%, (B) c = 0.5%, (C) c = 0.8% and (D) c = 2.0 %. * indicates the diffraction peaks of calcite and # indicates the diffraction peak of vaterite.*

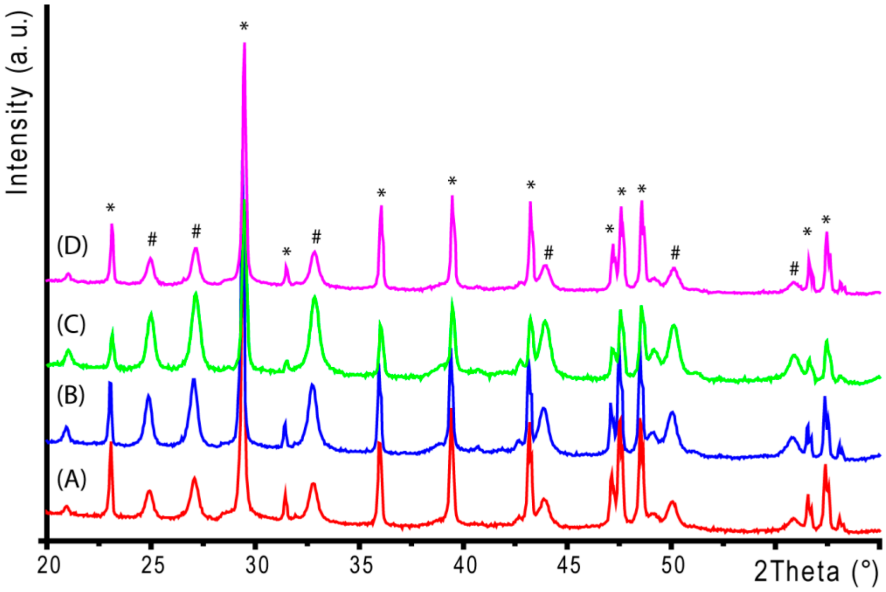


Figure S5 *XRD patterns of precipitate obtained in alginate Ca-gel pH = 10.5. Concentrations of alginate are: (A) c = 0.2%, (B) c = 0.5%, (C) c = 0.8% and (D) c = 2.0 %. * indicates the diffraction peaks of calcite and # indicates the diffraction peak of vaterite.*

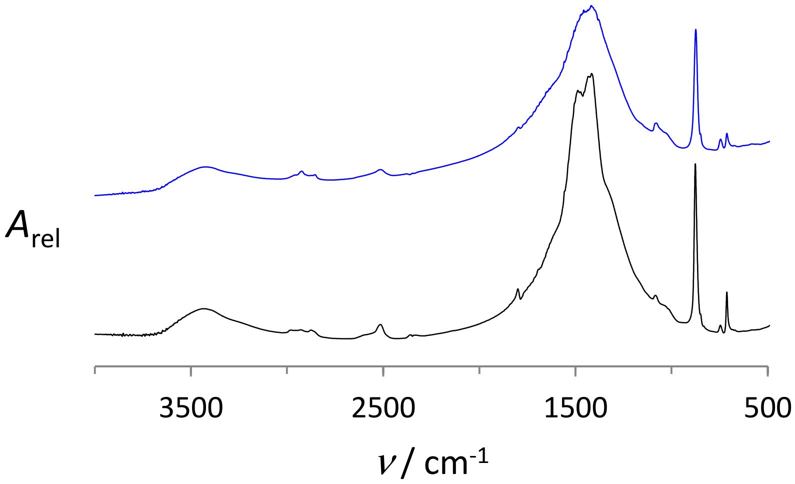


Figure S6 *Typical FT-IR spectra of* $CaCO_3$ *samples isolated from xanthan Ca-gel, pH = 10.5. Concentrations of xanthan: c = 0.4%, (black line) and c = 2.0 % (blue line)*

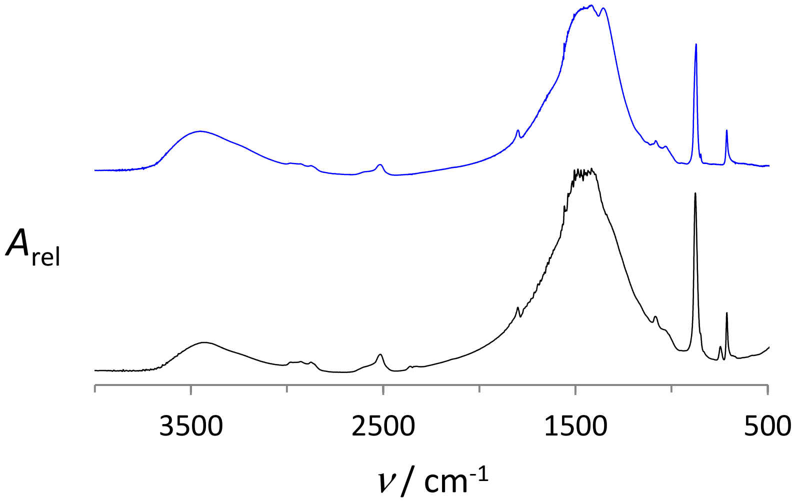


Figure S7 *Typical FT-IR spectra of* $CaCO_3$ *samples isolated from alginate Ca-gel, pH = 9.0. Concentrations of alginate: c = 0.2%, (black line) and c = 2.0 % (blue line)*

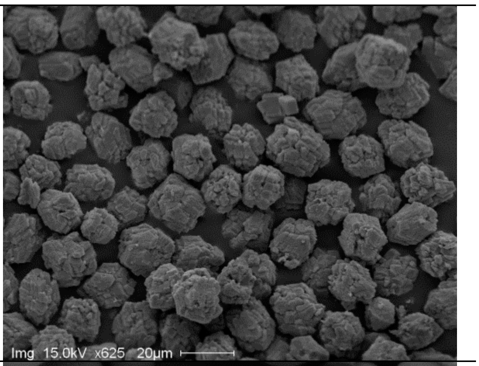
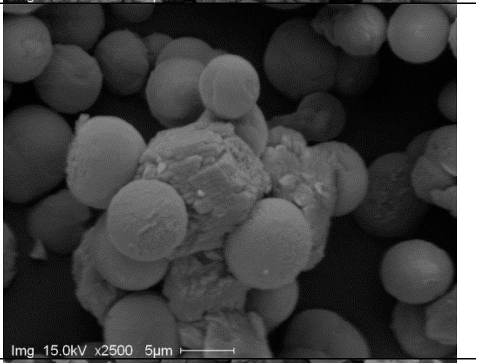
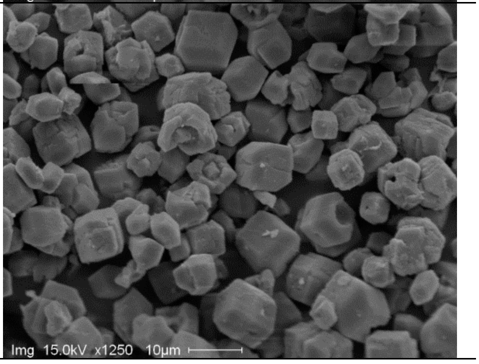
Xanthan system	***w* (calcite) / %**	**SEM**
Ca-gel pH = 9.0 *c* = 0.4 wt%	99	
Ca-gel pH = 10.5 *c* = 2.0 wt%	19	
CO3-gel pH = 10.5 *c* = 0.4 wt%	100	

Figure S8 *SEM micrographs of* $CaCO_3$ *precipitated in different xanthan systems and isolated after 5 days of aging. The images show the calcite crystals with spherical imprints probably caused by dissolution of vaterite, or coexistence of two polymorphs in the system in which dissolution of vaterite was retarded.*

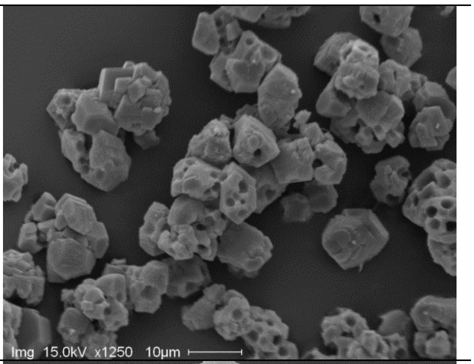
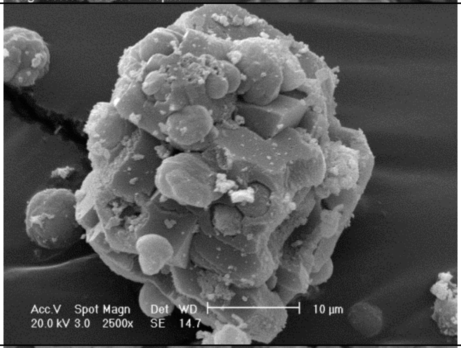
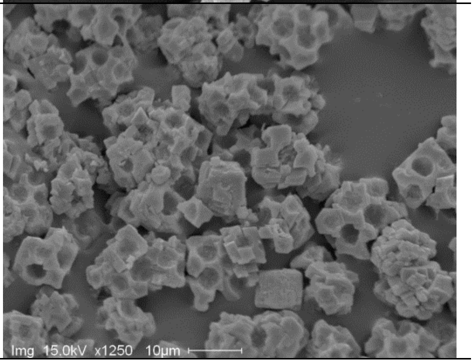
Alginate system	***w* (calcite) / %**	**SEM**
Ca-gel pH = 9.0 *c* = 0.8 wt%	100	
Ca-gel pH = 10.5 *c* = 0.8 wt%	61	
CO3-gel pH = 10.5 *c* = 0.8 wt%	100	

Figure S9 *SEM micrographs of* $CaCO_3$ *precipitated in different alginate systems and isolated after 5 days of aging. The images show the calcite crystals with spherical imprints caused by dissolution of vaterite, or coexistence of two polymorphs in the system in which dissolution of vaterite was retarded.*

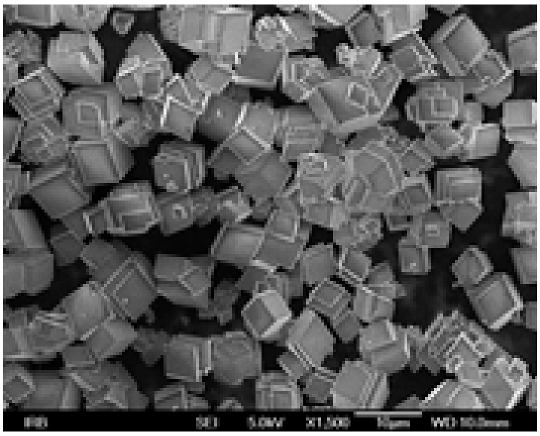
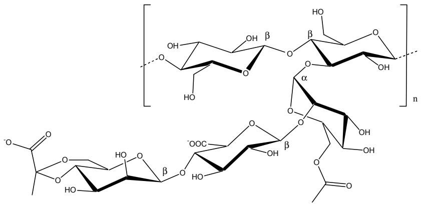


Figure S10 *SEM micrographs of calcite crystals precipitated in the model system. Precipitation was initiated by fast mixing of reactants (c(*$CaCl_2$*) = c(*Na_2CO_3*) = 0.066 mol dm*$^{-3}$*). The samples are aged for 24 hours.*

Description of the molecular gelling process

Xanthan

Xanthan gum consists primarily of a 1,4-linked β-D-glucose backbone with side chains containing two mannoses and one glucuronic acid on every other glucose at the C-3 position. Approximately half of the terminal mannose units carry a pyruvic acid residue and the non-terminal residue usually carries an acetyl group at C-6. These side chains represent about 60% of the molecule and give xanthan gum specific properties. The structure of xanthan gum is shown in Figure 1. According to the proposed model of gelling, a colloidal dispersion of xanthan molecules dissociate by desorbing water molecules during the initial stage of annealing and the firm gel is formed by homogenization of the system and subsequent formation of junction zone between liberated xanthan molecules. After annealing, xanthan molecules most probably form rather stiff double stranded helical conformation, on contrary to less stiff and elongated single stranded structure of not treated compound. An additional important property of xanthan gels is the thixotropy, i. e., low viscosity at high shear and returning in full viscosity immediately on release. Such behavior is a consequence of hydrogen bonding between the side chains of the highly extended molecules.

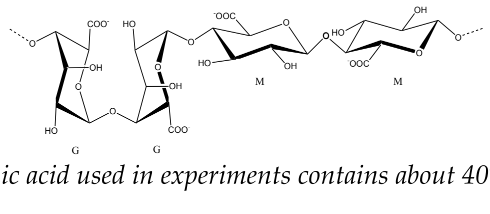


Structure of xanthan gum

Alginate

The alginates are natural polysaccharides - unbranched block copolymer containing β-(1→4) linked D- mannuronic acid (M) and *α*-(1→4)-linked L-guluronic acid (G) residues with different M/G ratio. The epimers, D-mannuronic acid and L-guluronic acid differ only at C5, but their conformations are quite different: D-mannuronic acid residues are connected by diequatorial, while L-guluronic residues are connected by diaxial links. The idealized structure of alginate is shown in Figure 2. Due to diaxial links, L-guluronic residues form stiff 2-fold screw helical chains, preferring intra-molecular hydrogen bonding between carboxyl and hydroxyl groups, on contrary to 3-fold left-handed helix of equatorially linked D-mannuronate residues, with weak hydrogen bonding between hydroxyl groups and ring oxygen.

The alginate forms strong and stable gels with divalent cations, like Ca^{2+}. Gelling occurs when the divalent cations take part in the interchain binding between G blocks, thus leading to a three-dimensional network. In such conformation Ca^{2+} coordination is saturated with oxygen ligands from hydroxyl and carboxyl groups, as well as with oxygen from glycoside linkage of guluronate chains and is stabilized by hydrogen bonding between other carboxylate and hydroxyl groups. The affinity of alginates for divalent ions increases with increasing the L-guluronic residue in the polysaccharide chain, thus promoting the formation of GG-blocks, instead of MM and MG blocks. At that, it is found that in the systems in which L-guluronic units are more abundant than the D-mannuronic, the affinity of alginates for the alkaline-earth metal ions follows the order: Ba^{2+} >Sr^{2+} >Ca^{2+} >>Mg^{2+} .



Structure of alginic acid Alginic acid used in experiments contains about 40% of α-L-guluronic acid units.

Table S1. *TG analyses of the $CaCO_3$ samples isolated at respective time intervals, from the alginate system: Ca-gel, pH = 9.0, c_{alg} = 0.8 wt%. The calcite/vaterite content was determined by FT-IR analyses.*

Time / h	*w*(calcite) / %	*w*(vaterite) / %	m_{water} / %	$m_{organic}$ / %
0	21,5	78,5	6,8	3,1
1	54,9	45,1	1,5	4,6
2	62,9	37,1	1,8	3,6
4	65,7	34,3	2,1	4,4
24	100	0	0,7	1,5
120*	61	39	3.2	5.3

** Sample obtained after 120 h corresponds to the system Ca-gel, pH = 10.5, c_{alg} = 0.8 wt%*

Table S2. *TG analyses of the calcite samples isolated after 120 h in the system Ca-gel, pH = 10.5 and different concentrations of xanthan.*

c_{xan} / wt%	m_{water} / %	$m_{organic}$ / %
0.20	0.8	1.0
0.35	0.3	0.9