# SUPPLEMENTARY INFORMATION

# Development of a novel CaCO $_3$ PILP based cementation method for quartz sand

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1.	pH influence on CaCO₃ coating layer	2
2.	Coating Characterization	3
3.	In-situ imaging of coating formation	8
4.	Surface functionalization of sand grains	10
5.	"Continuous Flow" Technique	11
6.	Shrinkage Cracks	12
7.	Precursor Particles	13
8.	References	15

# 1. pH influence on the CaCO<sub>3</sub> coating formation

With respect to observations described in the main article, the pH influence on the calcium carbonate coating formation was investigated. It is obvious that the pH plays a major role in this process as it has an effect on not only the carbonate equilibrium but also the poly (acrylic acid) behavior (coaxervation processes) and consequently the calcium carbonate mineralization process. This results in a highly complex system, which was studied in more detail. Sodium bicarbonate or sodium carbonate were used and the pH value was adjusted with sodium hydroxide (TABLE SI1-1). This enables the investigation of the coating formation through a pH wide range (7 to 11.5).

	CaCl₂	PAA [2 kDa]	NaHCO₃	Na <sub>2</sub> CO <sub>3</sub>	NaOH	рН
106a	20 mM	1800 µg/ml		20 mM		6,92
106b	20 mM	1800 µg/ml		35 mM		8,82
107	20 mM	1800 µg/ml	50 mM			6,42
109	20 mM	1800 µg/ml	50 mM		11 mM	7,01
182	20 mM	1800 µg/ml	50 mM		14 mM	7,55
183	20 mM	1800 µg/ml	50 mM		20 mM	8,01
184	20 mM	1800 µg/ml	50 mM		26 mM	8,53
185	20 mM	1800 µg/ml	50 mM		34 mM	9,05
111	20 mM	1800 µg/ml		50 mM		9,50
112	20 mM	1800 µg/ml		50 mM	25 mM	11,52

Table SI1-1: Precursor solution composition for investigations of pH effect on CaCO<sub>3</sub> coating formation.

It is not surprising that experiments with slightly acidic and neutral pH showed no calcium carbonate formation on the quartz sand. Indeed, no calcium carbonate formation on either the quartz sand or elsewhere in the mineralization setup occurred when the pH was below pH 9. Coating formation in sample **112**, where the pH was above 11.5, was still observable but slightly thinner compared to sample **111** where the pH was not adjusted (9.50) (**FIGURE SI1-1**). The conditions of experiment **111** (20 mM CaCl<sub>2</sub>, 1800 µg/ml PAA [2 kDa] and 50 mM Na<sub>2</sub>CO<sub>3</sub>) turned out to be the most favorable to achieve a continuous calcium carbonate coating. Straightforward addition of sodium carbonate without prior or subsequent pH adjustment resulted in the most promising coating results and thus it was selected for most of the investigations carried out in this paper.



Figure SI1-1: Comparison of the coating thickness in sample 111 at pH 9.50 (left) and sample 112 at pH 11.52 (right) via SEM imaging.

# 2. Coating Characterization

The coating that has formed on the quartz sand surface has been studied extensively over the course of this work. It could be shown that the coating is composed of calcium, carbon and oxygen as EDX point analysis and mapping displayed (FEHLER! VERWEISQUELLE KONNTE NICHT GEFUNDEN WERDEN.1).



Figure SI2-1: On point EDX of the coated sample 108 (left) and EDX mapping of a coating crack and the underlying quartz sand in sample 111 (right).

Thermogravimetric analysis shows a significant mass loss from 650 to 750 °C due to the decomposition reaction of CaCO<sub>3</sub> into CaO and CO<sub>2</sub> (Fehler! Verweisquelle konnte nicht gefunden werden.2). Only minor amounts of water (0.4-1.1 wt%) and PAA (0.1-0.4 wt%) were still left in these samples (FEHLER! VERWEISQUELLE KONNTE NICHT GEFUNDEN WERDEN.2). However, the standard error associated with the apparatus is ± 1.5 weight-% and it was not possible to conclude on the incorporation of PAA and/or in the presence of water in the coating layer. Using the weight loss from 650-750 °C the portion of calcium carbonate in the given sample was calculated (FEHLER! VERWEISQUELLE KONNTE NICHT GEFUNDEN WERDEN.1). It is worth mentioning that TGA measurements were conducted on coated sand samples excluding mineral that has formed elsewhere. Hence, an accurate collection of coated sand grains is essential to quantify the precise amount of coating mineral. As expected, the weight percentage of CaCO<sub>3</sub> is higher when less sand was coated. For low amounts of sand, thicker coatings could be achieved; however, the overall weight percentage for calcium carbonate did not increase in a linear manner. Double amount of sand from 50 to 100 mg did also not halve the portion of calcium carbonate, as one would expect. This suggests a nonlinear coating behavior where early coating stages seem to be favored. Nevertheless, it can be stated that up to 55% (11.07 mg out 19.99 mg possible) of the CaCO<sub>3</sub> could be mineralized in form of a coating on the quartz sand surface. This percentage however might increase in a system where only quartz sand surfaces are provided in contrast to the glass/water interface in this test system. It also needs to be considered that the results only provide an average value, not representing deviations caused by local inhomogeneity within the sample.



Figure SI2-2: Thermogravimetric analysis of varyingly thick coated quartz sand samples 148 (left), 149, 150A and 150B (right).

	Sand	TGA mass loss	ωt% (CaCO₃)	m(coating)
148	25.1 mg	8.50 %	19.33	4.60 mg
149	48.3 mg	8.86 %	20.15	8.58 mg
150A	99.6 mg	5.30 %	12.05	10.42 mg
150B	100.5 mg	5.56 %	12.65	11.07 mg

**Table SI2-1: Evaluation of TGA data provided in** Fehler! Verweisquelle konnte nicht gefunden werden. **and extrapolation of how much coating mass has mineralized on the quartz sand**.

In order to identify the CaCO<sub>3</sub> phase/s of the coating layer, ATR-IR measurements, TEM analysis and PXRD measurements were performed. Coated samples that have been grinded in an agate mortar show significant signals for the carbonyl stretching vibration at around 1400-1500 cm<sup>-1</sup>, which is characteristic for calcium carbonate. The absence of carbonyl vibrations between 1500 and 1700 cm<sup>-1</sup>, which are usually characteristic for PAA-Na or bidentate PAA-calcium complexation, combined with no observable aliphatic vibration suggest that no detectable amount of poly (acrylic acid) is contained within the coating (**FIGURE SI2-3 AND SI2-4**). Further evaluation of the ATR-IR data reveals  $u_2 = 871$  cm<sup>-1</sup> and  $u_4 = 712$  cm<sup>-1</sup> specific vibrations for the coated sand sample as well as the colorless precipitation that has formed on the surrounding glass surface. Those signals can be assigned to the calcite polymorph of the calcium carbonate. Traces of water remained within the sample as indicated by the broad band around 3000 to 3500 cm<sup>-1</sup>. In addition, the  $u_3$  band that is usually specific at 1396 cm<sup>-1</sup> is slightly shifted towards higher wavenumbers with a shoulder around 1454 cm<sup>-1</sup> in the case of the coated sand sample. According to literature<sup>1, 2</sup>, this suggests that the carbonate groups are slightly distorted and in a less crystalline state.



Figure SI2-3: ATR-IR spectra of grinded sample 111 and an uncoated quartz sand reference (left) and the spectra of colorless precipitation that has formed on the surrounding glass surface (right).



 $Figure \,SI2-4: Extended \,ATR-IR \,spectra \, of grinded \, sample \, 111 \, showing \, the \, absence \, of \, signals \, between \, 1500 \, and \, 3000 \, cm^{-1}.$ 

Selected area electron diffraction (SAED) carried out during TEM analysis of the coating resulted in no or very weak diffraction patterns. The patterns that could be evaluated however, displayed distinct reflexes that could be matched with calcite as shown in **FIGURE SI2-5**. PXRD measurements also confirm calcite as the main CaCO<sub>3</sub> phase of the coating layer (**FIGURE SI2-6**).



Figure SI2-5: TEM image of a coating piece mineralized in sample 146 (left) and the corresponding SAED pattern with the assigned Miller indices for the crystal planes (right).



Figure SI2-6: PXRD analysis of pure (left) and coated (right) quartz sand samples. The underlying reflexes show quartz (blue, Entry\_96-900-9667) and calcite (green, Entry\_96-900-0967) reference data obtained from the *Match!* database.

To quantify the degree of mineralization, the mass of mineralized material was determined and compared to theoretical values. Assuming thermodynamic equilibrium in the solution (20 mM CaCl<sub>2</sub> and 50 mM Na<sub>2</sub>CO<sub>3</sub>) respect to calcite ( $K_{sp}$ =10<sup>-8.4</sup>), a total amount of 1.99  $\cdot$  10<sup>-4</sup> moles of CaCO<sub>3</sub> should be formed using 10 ml of standard precursor solution (PAA effect not considered). That corresponds to 19.99 mg of CaCO<sub>3</sub>. The measured weights over the course of experiments shown in FEHLER! VERWEISQUELLE KONNTE NICHT GEFUNDEN WERDEN.2 reveal that more than 90% of the calcium carbonate mineralized within 6 days regardless of the amount of quartz sand present. TGA measurements described above show negligible amounts of water (0.4-1.1 wt%) and PAA (0.1-0.4 wt%) in the samples (FEHLER! VERWEISQUELLE KONNTE NICHT GEFUNDEN WERDEN.2). Few amounts of loose mineral were washed off due to experimental procedures. The residues from the washing procedure were collected, centrifuged and analyzed, confirming that they are loose micrometer-sized CaCO<sub>3</sub>. This also implies that CaCO<sub>3</sub> mineralization is not limited to the quartz sand surface. FEHLER! VERWEISQUELLE KONNTE NICHT GEFUNDEN WERDEN.7 shows how spherical particles settled down on the bottom of the glass.

Nonetheless, they can be clearly distinguished from the dense coating that is forming on the glass and the quartz sand surface.

	CaCl <sub>2</sub>	PAA [2 kDa]	Na <sub>2</sub> CO <sub>3</sub>	Sand	Coating	Mineral
159	20 mM	1800 µg/ml	50 mM	-	-	18.4 mg
133A	20 mM	1800 µg/ml	50 mM	12.5 mg	~50 μm	-
148	20 mM	1800 µg/ml	50 mM	25.1 mg	~30 µm	17.7 mg
149	20 mM	1800 µg/ml	50 mM	48.3 mg	~25 μm	19.3 mg
150A	20 mM	1800 µg/ml	50 mM	99.6 mg	~17 μm	19.4 mg
150B	20 mM	1800 µg/ml	50 mM	100.5 mg	~10 µm	18.9 mg

Table SI2-2: Increasing coating thickness with decreasing amount of quartz sand after mineralization for 6 days in 10 ml of precursor solution with the given concentration.



Figure SI2-7: CaCO<sub>3</sub> coating of a single sand grain and its surrounding glass vial bottom in sample 164 via SEM imaging.

# 3. In-situ imaging of coating formation

The growth process of the sand coating was observed in-situ in order to get time-resolved insights into the mineralization process. A new mineralization setup was developed, which allowed light microscopic observations during coating formation. The set up was sealed to avoid evaporation of the precursor solution (**Figure SI3-1**).



**Glass Cover Slide** 

Figure SI3-1: Image of the prepared time series mineralization setup sealed with silicon grease.

For standard conditions (20 mM CaCl<sub>2</sub>, 1800  $\mu$ g/ml PAA and 50 mM Na<sub>2</sub>CO<sub>3</sub>), it could be observed that mineralization starts slowly within the first 3 hours in form of small globules predominantly on sloping and rough areas. During the following 6 hours the amount of globules on the sand surface increases drastically until the complete sand grain is covered in globules. At this point mineralization continues on the underlying glass surface (background) starting in special proximity to the sand grains and further advance over time. This is a further indication towards an interaction of the precursor droplets with the quartz surface rather than just homogeneous mineralization events (**Figure SI3-12**).



Figure SI3-2: LM time series experiment for 24 hours of mineralization in sample 117 using standard concentrations.



Figure SI3-3: SEM images of sample 146 64 (20 mM CaCl2, 1800  $\mu$ g/ml PAA[2 kDa], 50 mM Na2CO3) coated for 48 hours (left) and 7 days (right). The coating thickness has almost doubled.

The time series experiments were repeated while imaging the coating formation under polarized light so that the crystallinity of the coating could be determined in its early stages. If an amorphous coating forms on the birefringent quartz sand grains, the intensity of the polarized light should decrease and therefore prove the aforementioned. It could be observed that the light intensity decreases within the first 18 hours of mineralization indicating the formation of an amorphous coating (**Figure SI3-4**). However, the strong birefringence of the underlying quartz sand might overshadow the effect. Additionally, small disordered calcite particles would also cause a decrease in intensity due to light scattering.



Figure SI3-4: Polarized light microscopy images of a time series experiment during 24 hours of mineralization in sample 151 using standard concentrations.

Another hint towards coating growth can be found in the high-resolution SEM images of the coating surface. Spherical particles that have formed elsewhere in solution probably sediment at the coating surface at some point during the coating growth. As growth continues, these particles are embedded in the coating until they are trapped completely (FIGURE SI3-5).



Figure SI3-5: SEM images of spherical particles being enclosed by the growing coating in sample 148.

#### 4. Surface functionalization of sand grains

In order to investigate the influence of surface properties on the mineralization behavior for quartz surfaces,  $CaCO_3$  mineralization of hydrophilized and hydrophobized quartz sand surfaces was examined. Hydrophilization of silica surfaces was achieved through treatment with a mixture of  $H_2O_2/H_2SO_4$  (ratio 1:3), hydrolyzing the remaining Si-O-Si bonds. Subsequently introducing fluoroalkanes ((3-3-3 trifluoropropyl)-trimethoxysilane) by use of silane chemistry resulted in hydrophobized quartz surfaces. The degree of wetting was determined from contact angle measurements by using the Washburn method and the Washburn equation.<sup>3</sup>

For the full mineralization time of 6 days, both samples showed only minor differences regarding coating thickness, and "mud cracking". There was also no difference in the adhesion of the coating towards the sand surface. However, for shorter mineralization times, there was a significant difference in coating thickness as displayed in **FIGURE SI3-1**. The coating thickness for the hydrophobic sand was only about 4  $\mu$ m compared to the hydrophilic sand with around 12  $\mu$ m.



Figure SI4-1: SEM images of coated samples after 72h of mineralization (in 20 mM CaCl2, 1800 µg/ml PAA[2 kDa], 50 mM Na2CO3) for hydrophilized (left) and (3-3-3 trifluoropropyl)-trimethoxysilane hydrophobized (right) quartz sand.

# 5. "Continuous Flow" Technique

The used test systems feature an extremely high precursor solution to sand volume ratio. Coating a few milligrams of sand requires at least 200 times the volume of precursor solution. Furthermore, mineralization had to be carried out in a sealed container over the course of several days, which poses difficulties to any scaled up application. These drawbacks motivated the development of a more feasible mineralization setup regarding technically applicable on site construction. Our previous experiments (Multiple Coating) showed that it was possible to continuously grow a CaCO<sub>3</sub> coating on the quartz sand by restoring consumed precursor solution. This led to the idea of generating a continuous flow of freshly prepared precursor solution, which runs slowly through a batch of sand. To monitor solution flow and coating formation, a "continuous flow" chamber was designed between two microscope glass slides, sealed with a rubber. In order to produce a fresh precursor solution in situ, CaCl<sub>2</sub>/PAA- and Na<sub>2</sub>CO<sub>3</sub>-solutions were mixed just before entering the chamber where sand grains are contained (**FIGURE SI5-1**). Concentrations were adjusted so that both solutions can be mixed in a 1:1 ratio with the same flow rate resulting in the standard precursor solution concentration (20 mM CaCl<sub>2</sub>, 1800 µg/ml PAA [2 kDa] and 50 mM Na<sub>2</sub>CO<sub>3</sub>). The lowest possible flowrate of 0.001 ml/min per solution was chosen and mineralized for 10 days under a continuous flow of precursor solution.



Figure SI5-1: Experimental setup for the continuous flow technique before (left), during (middle) and after (right) continuous mineralization for 10 days.



Figure SI5-2: LM (left) and SEM images of the border area between sparsely (C and D) and highly (A and B) mineralized regions in the "continous flow" method experiment.

#### 6. Shrinkage Cracks

The formation of the so-called "shrinkage cracks" has been investigated and it could be shown that these cracks do not develop until the sample is dried. Light microscopic time series experiments show how the cracks develop over the course of several hours, when a freshly coated sand sample was exposed to drying at room temperature (**FIGURE SIG-1**). This implies that a significant amount of water is contained within the calcium carbonate coating in its initial state. That is probably due to the transformation of ACC into calcite.



Figure SI6-1: LM time series experiment during drying of coated quartz sand sample 164. Shrinkage crack formation can be investigated, beginning at the bottom right sand grains.

#### 7. Precursor Particles

The depicted findings described in the main article strongly suggest that the 30-40 nm sized particles play a key role in the coating formation. However, it was still unknown what structure and composition these particles inherited. Calcite nanoparticles, ACC nanoparticles, PILPs or liquid-liquid phase separated droplets are only a few possibilities that come to mind. Preparative ultracentrifugation is the appropriate way to separate those particles from solution in order to analyze them in more detail. In the case of liquid-liquid phase separated particles, it needs to be considered that this might result in unwanted coalescence/agglomeration.

Ultracentrifugation of a freshly prepared precursor solution was performed at 55000 RPM for 65 minutes resulting in a transparent gel-like material after removing the supernatant. The sedimented material was analyzed via ATR-IR, TEM and SAED. Due to the absence of the  $v_4$  band and the shift of the  $v_2$  band towards 860 cm<sup>-1</sup> in the ATR-IR, an amorphous calcium carbonate species was indicated according to literature<sup>4</sup> (Figure SI7-1). Therefore, it was expected to observe ACC particles of appropriate size in the TEM images. However, a continuous film without distinguishable particles was detected. SAED confirmed that the material is amorphous as no reflexes could be observed. The previously described 30-40 nm size particles present in the precursor solution, seem to have vanished after centrifugation according to DLS measurements (Figure SI7-2). Thus, it is consequential that they coalesced at the bottom in the process of centrifugation resulting in the observed gel-like ACC structure. This suggests a liquid character of the observed particles in the precursor solution.



Figure SI7-1: ATR-IR (left), TEM (right) and SAED (inlet, scale bar: 0.5 1/Å) analysis of the sedimented material of a freshly prepared precursor solution after 65 minutes of ultracentrifugation at 55000 RPM.

The density of stabilized particles in solution can be obtained through an AUC experiment where the sedimentation coefficient in two solutions of different density is determined. In aqueous solutions, this can be achieved by varying the H<sub>2</sub>O to D<sub>2</sub>O ratio. Due to the differences in density of calcite, ACC and CaCO<sub>3</sub> liquid precursors, it is possible to conclude on the nature of these particles by means of AUC experiments. The calculated density for the particles with a size of d = 39.1 nm and a sedimentation coefficient of s = 20.20 S is  $p_{Particle} = 1.024$  g/cm<sup>3</sup>. This value however, needs to be considered as an approximation for several reasons. For example, the particle size obtained in DLS measurements reflects the hydrodynamic radius. The real density might be therefore slightly higher. Nonetheless, it can be stated that this result suggests a liquid precursor particle state rather than solid nanoparticles due to its low density. This also coincides with previous findings where the sedimented material obtained from ultracentrifugation was identified as a gel-like amorphous material with high water content.



Figure SI7-2: Raw DLS data of the supernatant from a standard precursor solution after 64 minutes of ultracentrifugation at 55000 RPM shows no noticeable particle concentration.

# 8. References

- 1. S. Gunasekaran, G. Anbalagan and S. Pandi, *Journal of Raman Spectroscopy*, 2006, **37**, 892-899.
- 2. T. Dupuis, J. Ducloux, P. Butel and D. Nahon, *Clay Minerals*, 1984, **19**, 605-614.
- 3. E. W. Washburn, *Physical review*, 1921, **17**, 273.
- 4. M. F. Khouzani, D. M. Chevrier, P. Guttlein, K. Hauser, P. Zhang, N. Hedin and D. Gebauer, *Crystengcomm*, 2015, **17**, 4842-4849.