Electronic Supplementary Information (ESI) for

New Insights into the Nucleation of Magnesium Hydroxide and the Influence of Poly(Acrylic Acid) during the Early Stages of Mg(OH)$_2$ Crystallisation

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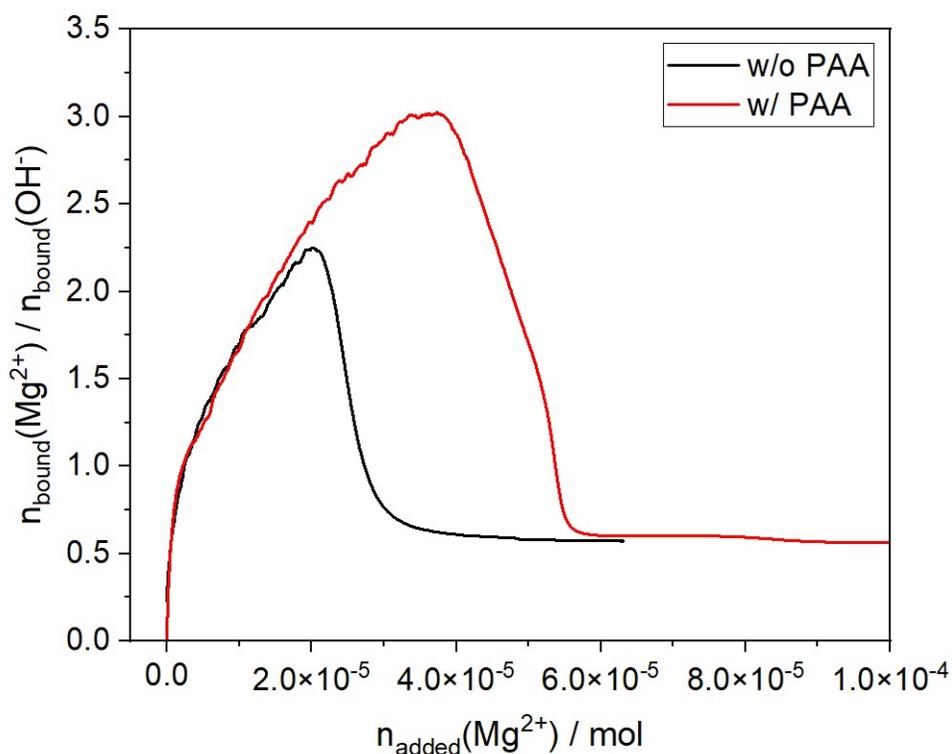[#] These authors contributed equally to this work

Figure S1. Evolution of the molar ratio of bound magnesium and hydroxide ions upon continuous addition of 20 mM $MgCl_2$ solution (at a rate of 0.01 mL/min) into a reservoir of water (initially 50 mL) containing no (black line) or 10 ppm (red line) poly(acrylic acid) (cf. Figures 1b and 4b in the main text). Note that the Mg^{2+}/OH^- ratio in the associated species increases during the pre-nucleation stage from ca. 0.3 to >2.2 at the time of nucleation in the additive-free experiment, while values up to 3.0 are reached in the presence of PAA. After nucleation, the Mg^{2+}/OH^- ratio decreases rapidly and approaches the expected level of 0.5, whereby any remaining deviations from the 1:2 stoichiometry are tentatively ascribed to the ideal treatment of the non-ideal solutions (cf. Figure S3).
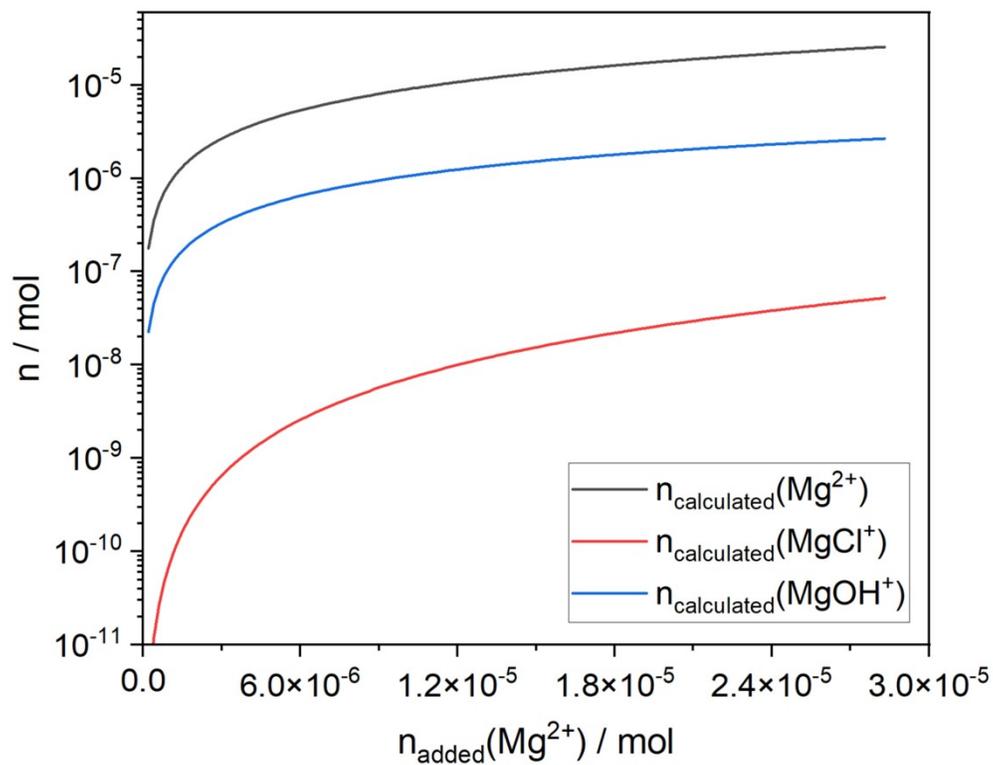
Figure S2. Plot of the molar amounts of Mg^{2+}, $MgCl^+$ and $MgOH^+$ predicted to occur in solution at pH 11.0 during titration of 50 mL water with 20 mM $MgCl_2$ at a rate of 0.01 mL/min (cf. Figure 1a in the main text). Calculations were performed for the pre-nucleation regime (i.e. up to the maximum in Figure 1a) with the PHREEQC software package[S1] using the Thermoddem database[S2] and excluding equilibration with atmospheric CO_2.
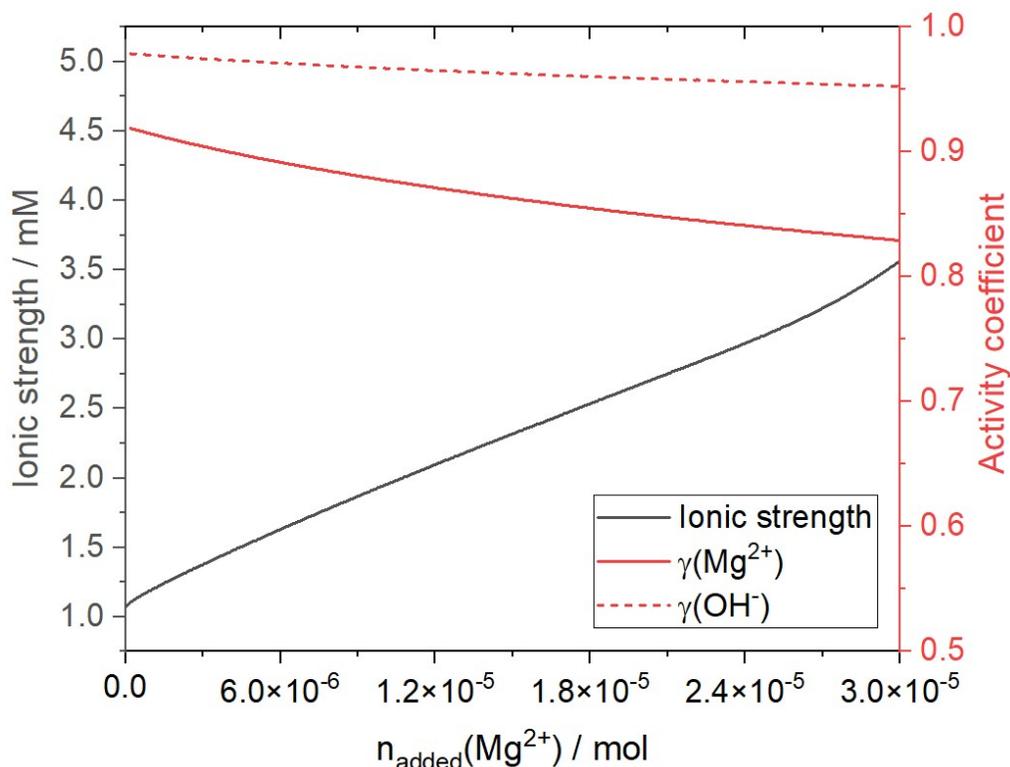
Figure S3. Development of the total ionic strength (grey line, left y-axis) and the activity coefficients of magnesium (full red line, right y-axis) and hydroxide (dashed red line, right y-axis) ions during titration of 50 mL water with 20 mM $MgCl_2$ at a rate of 0.01 mL/min and a constant pH of 11.0 (cf. Figure 1a in the main text). The ionic strength was calculated based on the dosed amounts of $MgCl_2$ and NaOH, assuming complete dissociation and no complexation. Activity coefficients (γ) were obtained from solution speciation modeling performed with the PHREEQC software package[S1] using the Thermoddem database[S2] and excluding equilibration with atmospheric CO_2. Note that the deviation from ideality ($\gamma \approx 1$) increases in the course of the titration experiment and is more pronounced for the divalent magnesium cation, which most likely accounts for the parallel offset of the $n_{bound}(Mg^{2+})$ and $n_{bound}(OH^-)$ profiles after nucleation in Figure 1b of the main text (considering that lower activity coefficients will lead to stronger apparent binding for ideal treatment, as described in detail elsewhere[S3]).

References

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S3. M. Kellermeier, A. Picker, A. Kempter, H. Cölfen and D. Gebauer, *Adv. Mater.*, 2014, **26**, 752-757.