Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Directed synthesis of aragonite through semi-continuous seeded crystallization methods for CO_2 utilization

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S1: Leaching and pH-swing process of the waste hydrated cement paste (HCP)

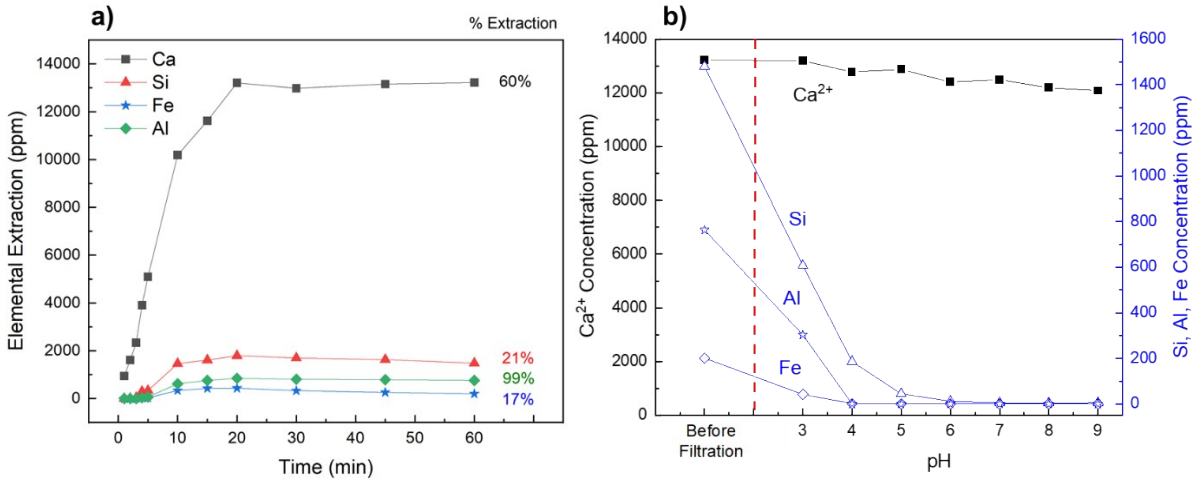

Figure S1. (a) Leaching kinetics at pH 3 of waste hydrated cement paste (HCP) over the course of 60 minutes showing the concentration of Ca, Si, Fe, and Al**. (b)** pH-swing process (pH 3 to 9) kinetics to remove the ancillary ions, Si, Fe, and Al from the reaction liquor prior to carbonation. Concentrations were verified using ICP-OES.[1,2]

S2: CO_2-loading into aqueous carbonate salts of potassium using KOH

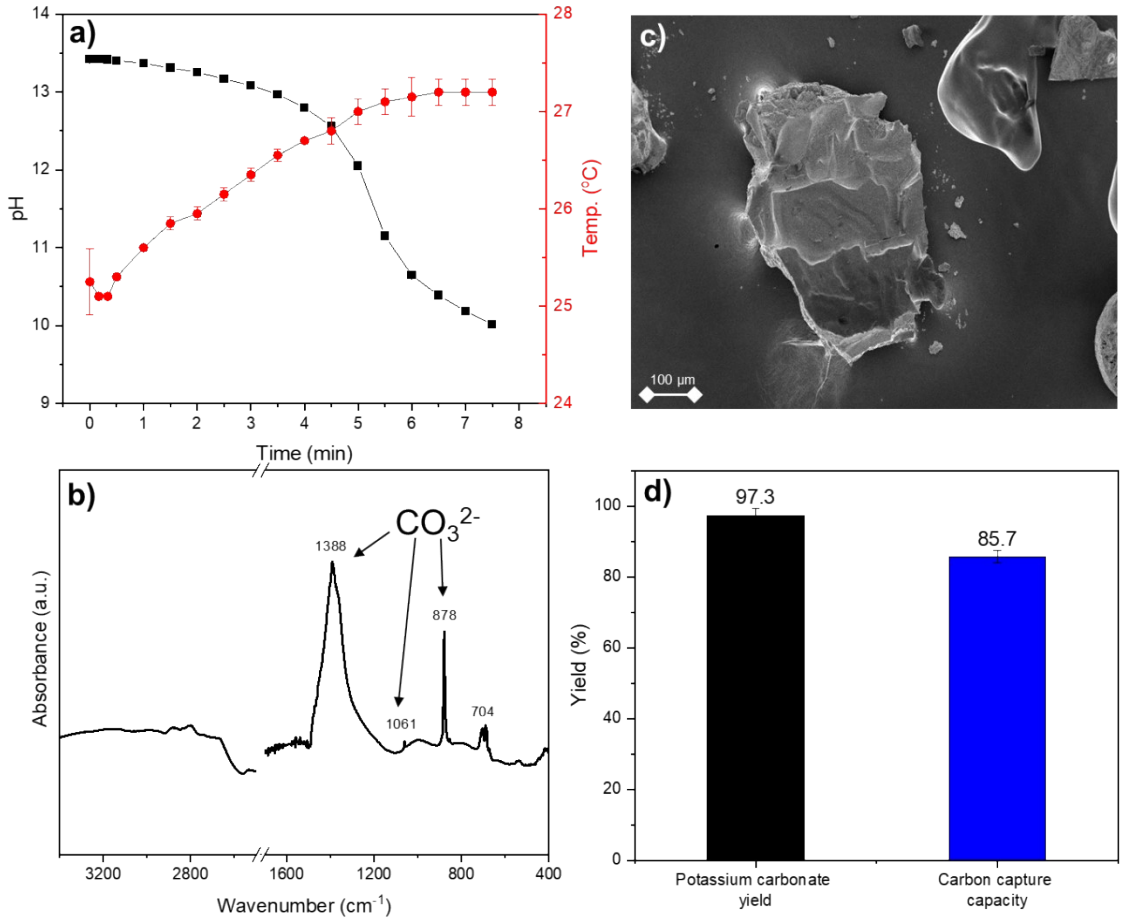

Figure S2. (a) pH and temperature kinetics for the carbonation of aqueous KOH. **(b)** FTIR spectral data confirming the appearance of carbonate peaks linked to K_2CO_3 in the solid sample and **(c)** SEM image of the produced solid. **(d)** % yield of potassium carbonate and carbon capture capacity based on the stoichiometry of the reaction and CO_2-flow, respectively.

S3: Visualization of the semi-continuous crystallization apparatus

1. Reaction vessel
2. Stirrer
3. Peristaltic pump
4. Water heating bath
5. MasterFlex tubing
6. Tubular nucleation coil (condenser)
7. Ring stand
8. Injection Pump and Syringe

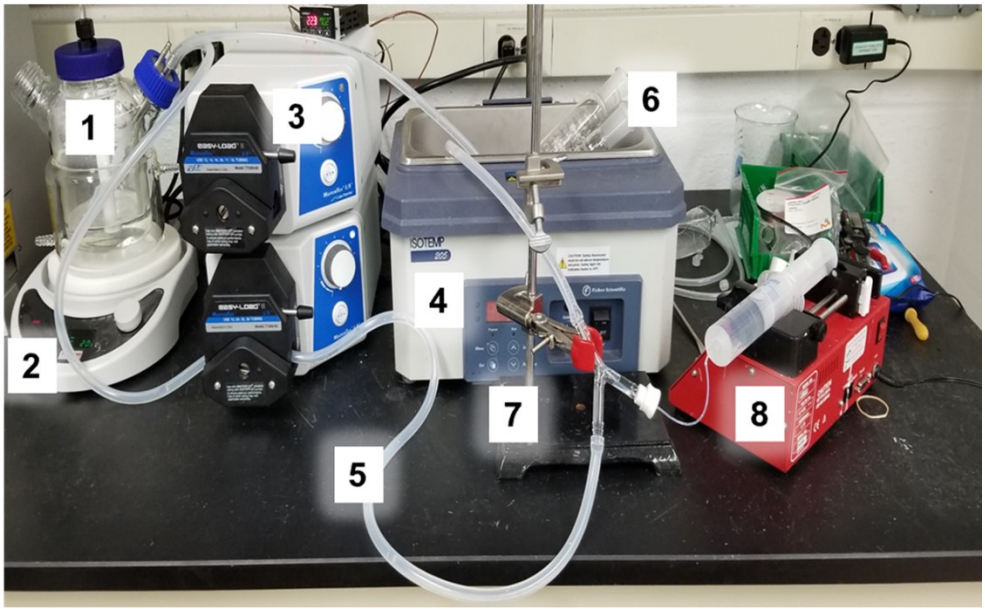

Figure S3. Semi-continuous crystallization apparatus which includes a 500 mL ChemGlass reaction vessel, peristaltic circulation pump, a heating bath and tubular nucleation coil (Graham condenser), and syringe pump for calcium injection.

S4: Calibration and flow properties of the semi-continuous crystallization reactor

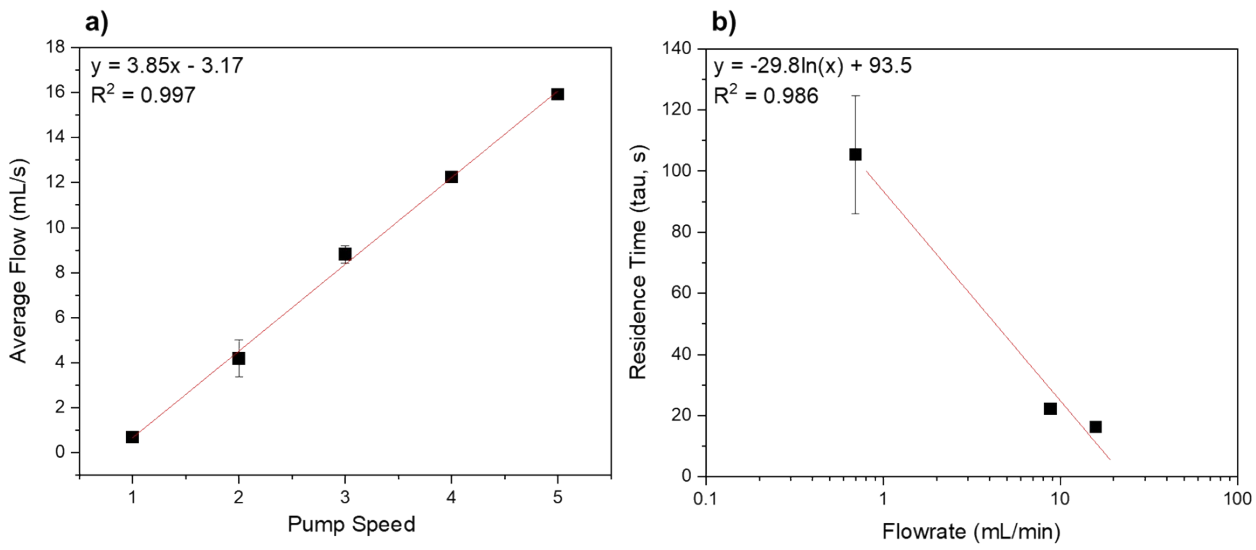

Figure S4. (a) Calibration of the circulation pump controller speed to circulation flow rate and **(b)** correlation of residence time versus semi-continuous crystallizer circulation rate as confirmed by dye-tracer tests.

S5: Additional characteristics and properties of the produced PCC crystal seeds

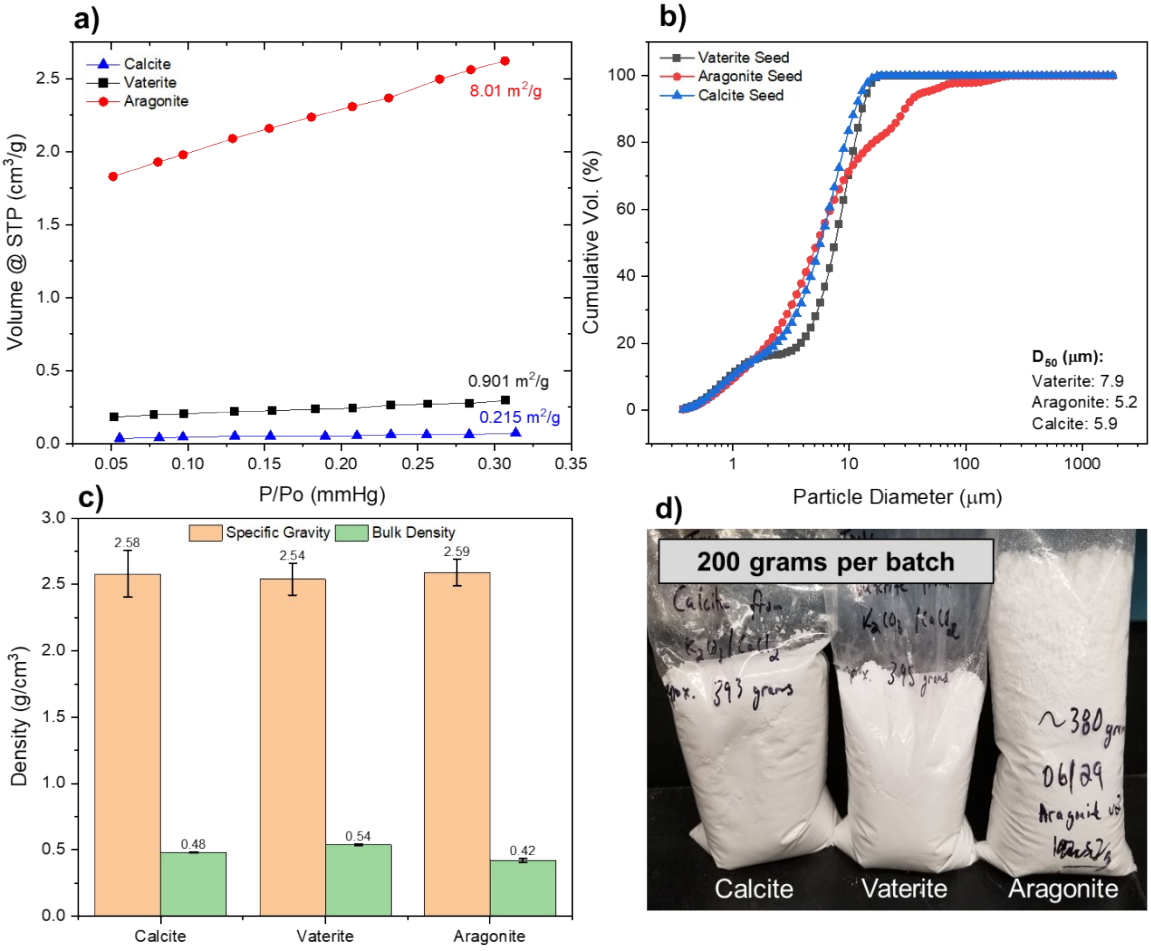

Figure S5. (a) BET surface area, **(b)** particle size distributions, **(c)** measured bulk and specific gravities, and **(d)** optically visual differences in bulk densities for scaled-up batches.

S6: SEM images of the PCC produced by un-seeded *batch* crystallization at various temperatures

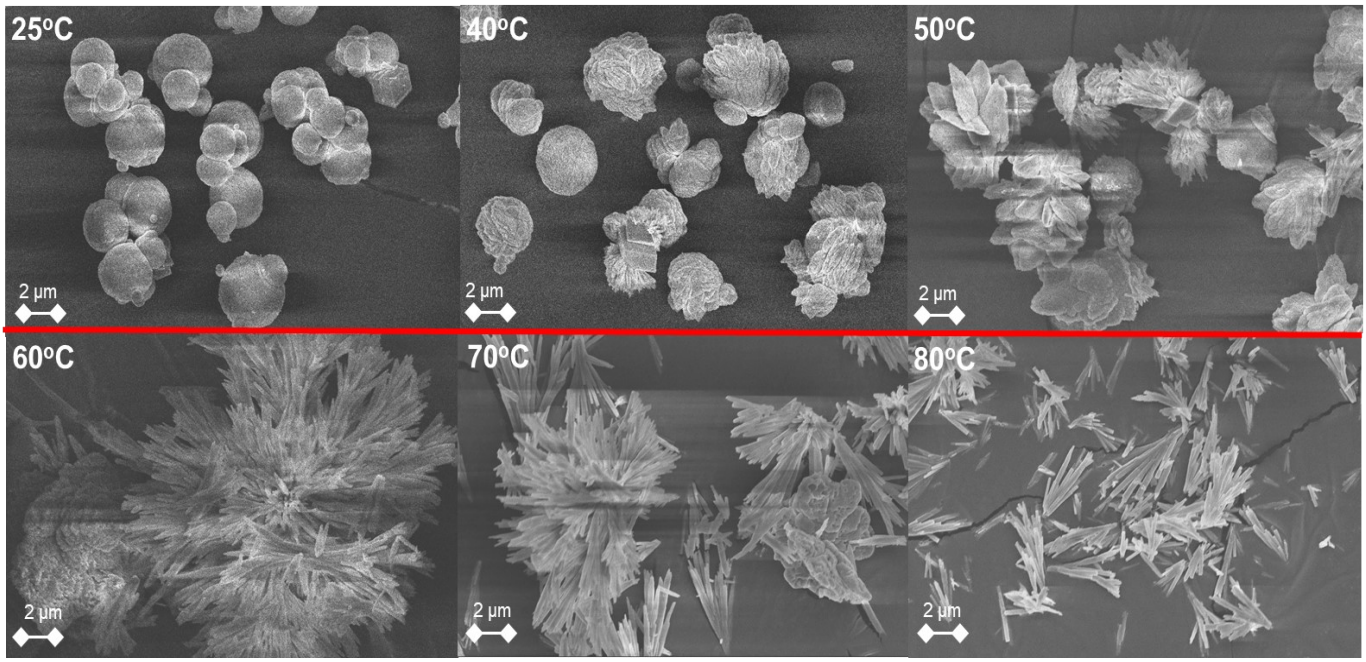

Figure S6. SEM images of the produced PCC at 25, 40, 50, 60, 70 and 80°C (from left to right) using the un-seeded batch crystallizer.

S7: SEM images of the PCC produced by un-seeded *semi-continuous* crystallization at various temperatures

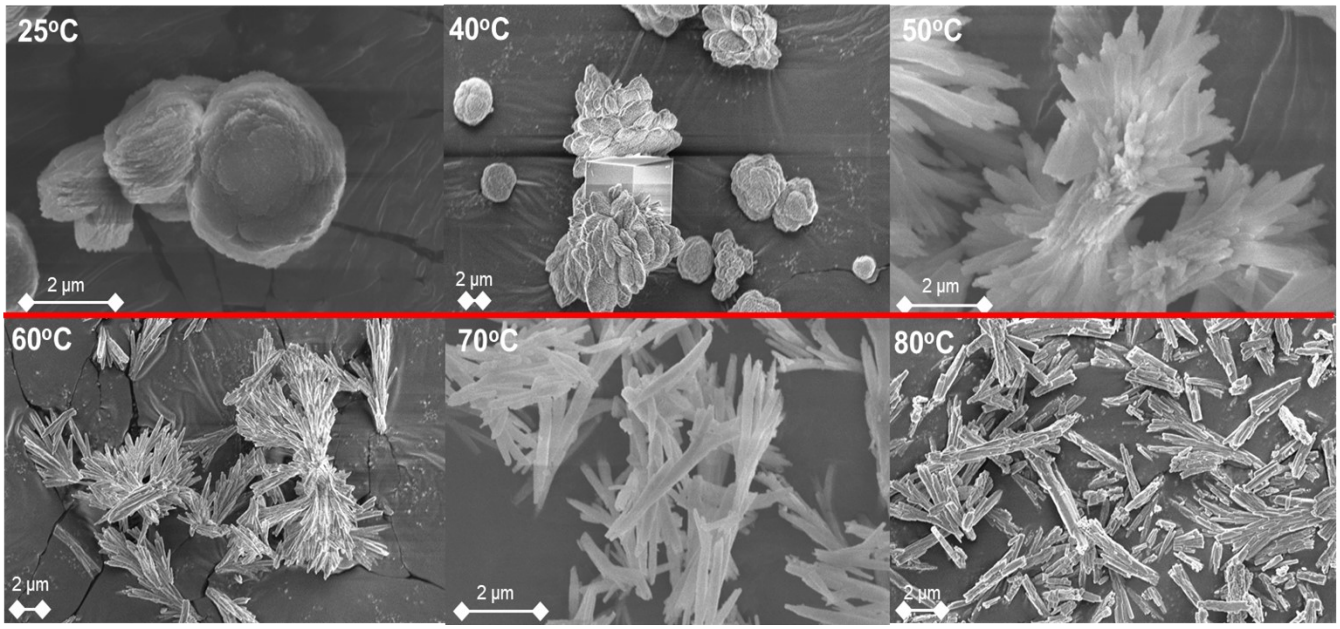

Figure S7. SEM images of the produced PCC at 25, 40, 50, 60, 70 and 80°C (from left to right) using the un-seeded semi-continuous crystallizer.

S8: Aragonite seeded temperature FTIR data for batch and semi-continuous crystallizer operation

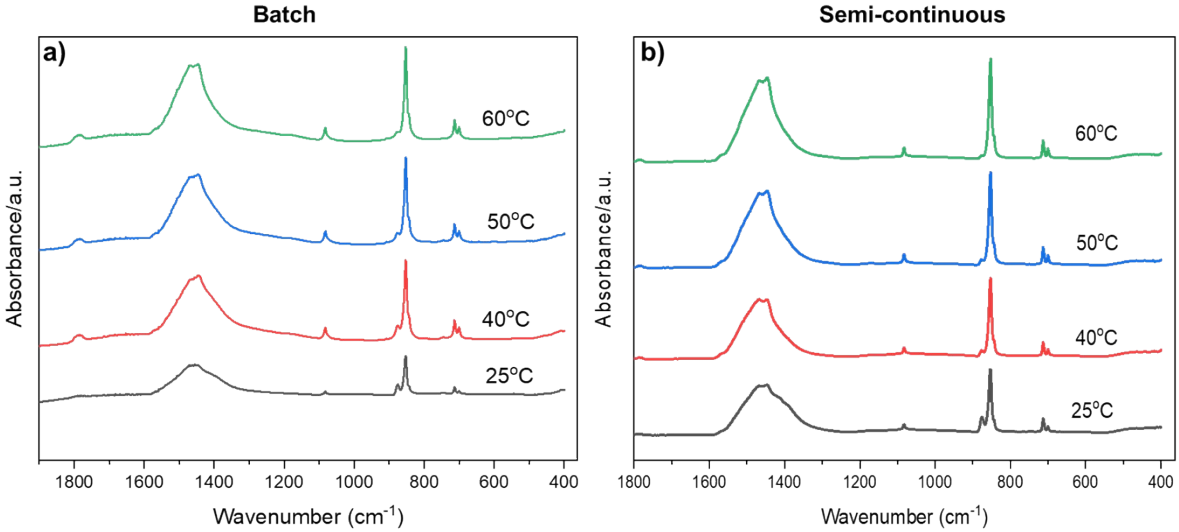

Figure S8. FTIR data for the PCC samples produced using aragonite seeding in **(a)** batch and **(b)** semi-continuous crystallization modes. 1 wt.% seed load of aragonite was used in all cases.

S9: SEM images showing the effect of seed load on aragonite crystallization at ambient conditions

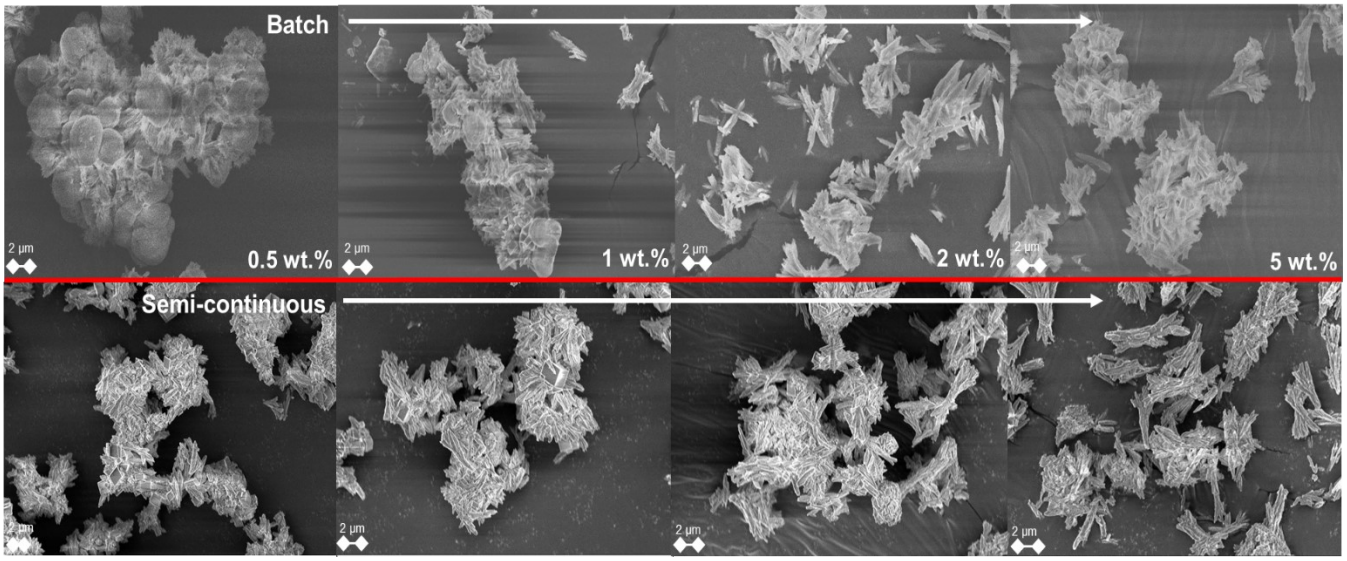

Figure S9. SEM images of the PCC produced at ambient conditions (25°C) by varying the seed load from 0.5 to 5 wt.% slurry density.

S10: FTIR data for batch and semi-continuous crystallizer aragonite seeding at ambient conditions

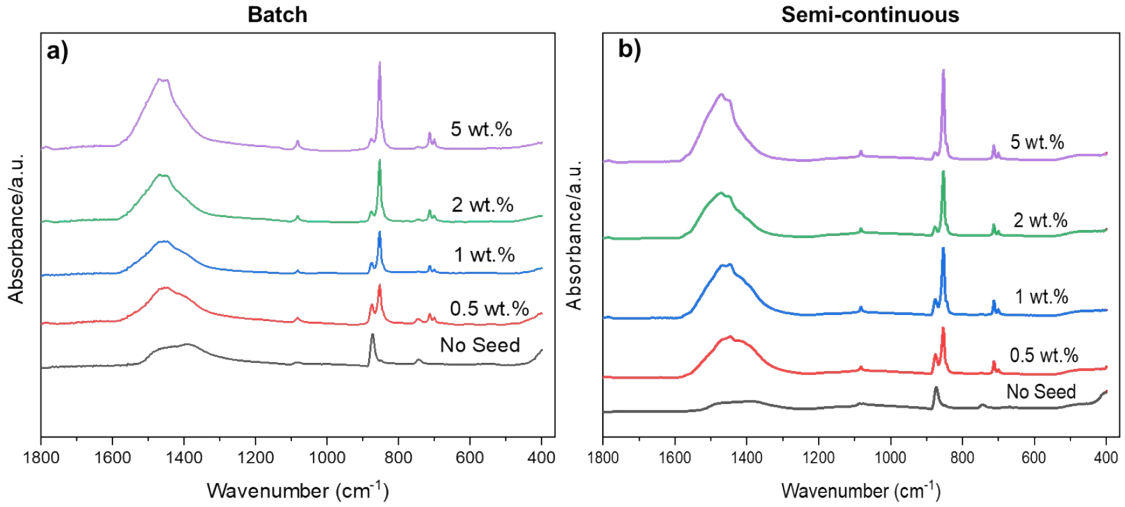

Figure S10. (a) Batch and **(b)** semi-continuous seeded production of aragonite at ambient conditions (25°C) by varying the seed load from 0.5 to 5 wt. % slurry density.

S11: PCC carbonate purity from Ca-leachate from waste cement paste at pH 3 and pH 9

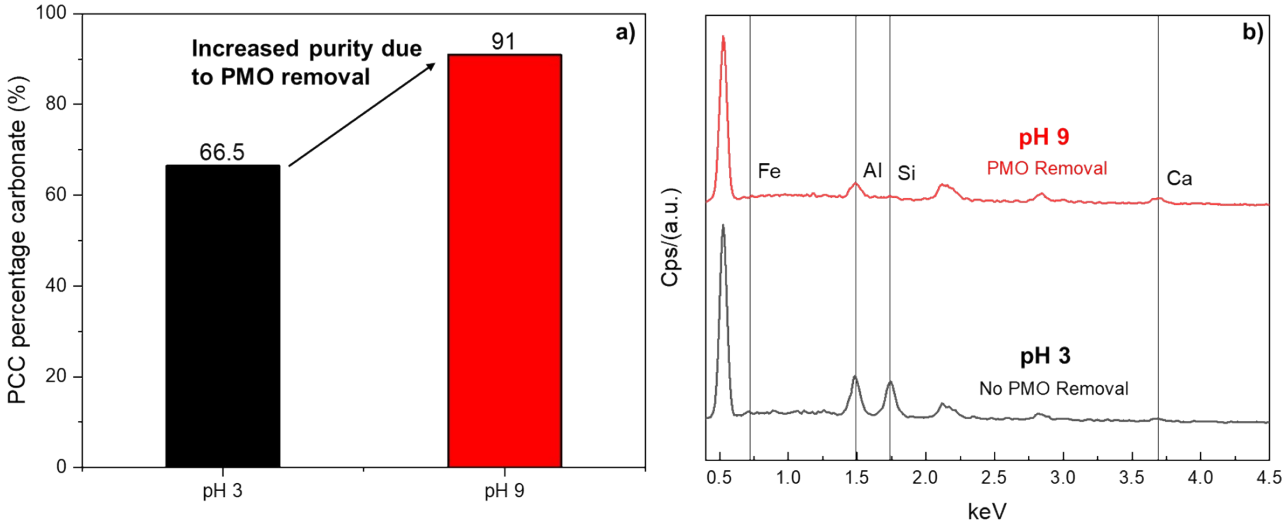

Figure S11. (a) Carbonate product purity as determined by coulometric carbon analysis for pH 3 PCC and pH 9 PCC. **(b)** EDS measurements of pH 3 PCC and pH 9 PCC showcasing the removal of certain ancillary ions such as Fe, Al, and Si.

References:

1 G. Rim, N. Roy, D. Zhao, S. Kawashima, P. Stallworth, S. G. Greenbaum and A.-H. A. Park, *Faraday Discuss.*, , DOI:10.1039/d1fd00022e.

2 N. Zhang and A. Moment, *ACS Sustain. Chem. Eng.*, , DOI:10.1021/acssuschemeng.2c04241.