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Steering particle morphology in the Slag2PCC process

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Abstract

During FP 1-4 the Slag2PCC process concept has been developed further from lab-scale and a pilot plant now exists at Aalto University. The work at Åbo Akademi University has recently focused on steering the particle quality of the precipitated calcium carbonate product. In detail, this includes control of particle sizes and morphology, and is continuation for work reported as D527 and D532. Interesting findings regarding novel particle forms have been made also at Aalto University. Results about the dependencies of product properties on parameters such as concentrations of calcium, ammonium chloride and carbon dioxide as well as pH, solution conductivity, temperature and agitation efficiency are presented. The Slag2PCC method can produce a wide variety of commercially available PCC qualities, such as scaleno- and rhombohedral calcite, aragonite and nano-scale precipitate.

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Summary of the obtained results regarding product properties

Several deliverables and other publications about the Slag2PCC process in general as well as the earlier results are available in the CLEEN CCSP portal. This report presents a summary of the so far obtained PCC particle qualities, regarding both particle size and morphology. Another important quality aspect, chemical purity of the products has been discussed in e.g. D532.

Based on the open scientific literature and experimental work, the following parameters have been identified to affect the calcium carbonate precipitation process and thus to change the properties of the obtained product: reaction temperature, concentrations of calcium and carbonate ions (Ca^{2+}, CO_3^{2-}), their molar ratio, total concentration of ammonium chloride, solution pH and conductivity, and mass transfer rate from gas phase to liquid solution. The latter is affected by for example solution agitation rate and pore size of the gas feeding equipment.

The parameters are correlated; some of them can be independently changed while some depend on the other parameters. Table 1 presents the effect of changes in independent parameters on the dependent parameters. The arrow shows the direction of change, when the value of the independent parameter increases. Grey arrows represent weak or indirect effects.

Table 1. Parameter dependencies

Dependent:	Ca^{2+}/CO_3^{2-}	pH	cond.
Independent: $[Ca^{2+}]$	↑	↑	↑
$[CO_2]_{total}$	↓	↓	↑
$[NH_4Cl]$	⇡	↓	↑
Temp.	⇡	⇣	↑
Agitation/ bubble size	Affects via CO_2 concentration		

Via experimental work a rather wide area of possible combinations of independent parameters has been studied (Table 2). Scanning Electron Microscope (SEM) pictures of the produced precipitates illustrate the variations in product properties (Figure 1).

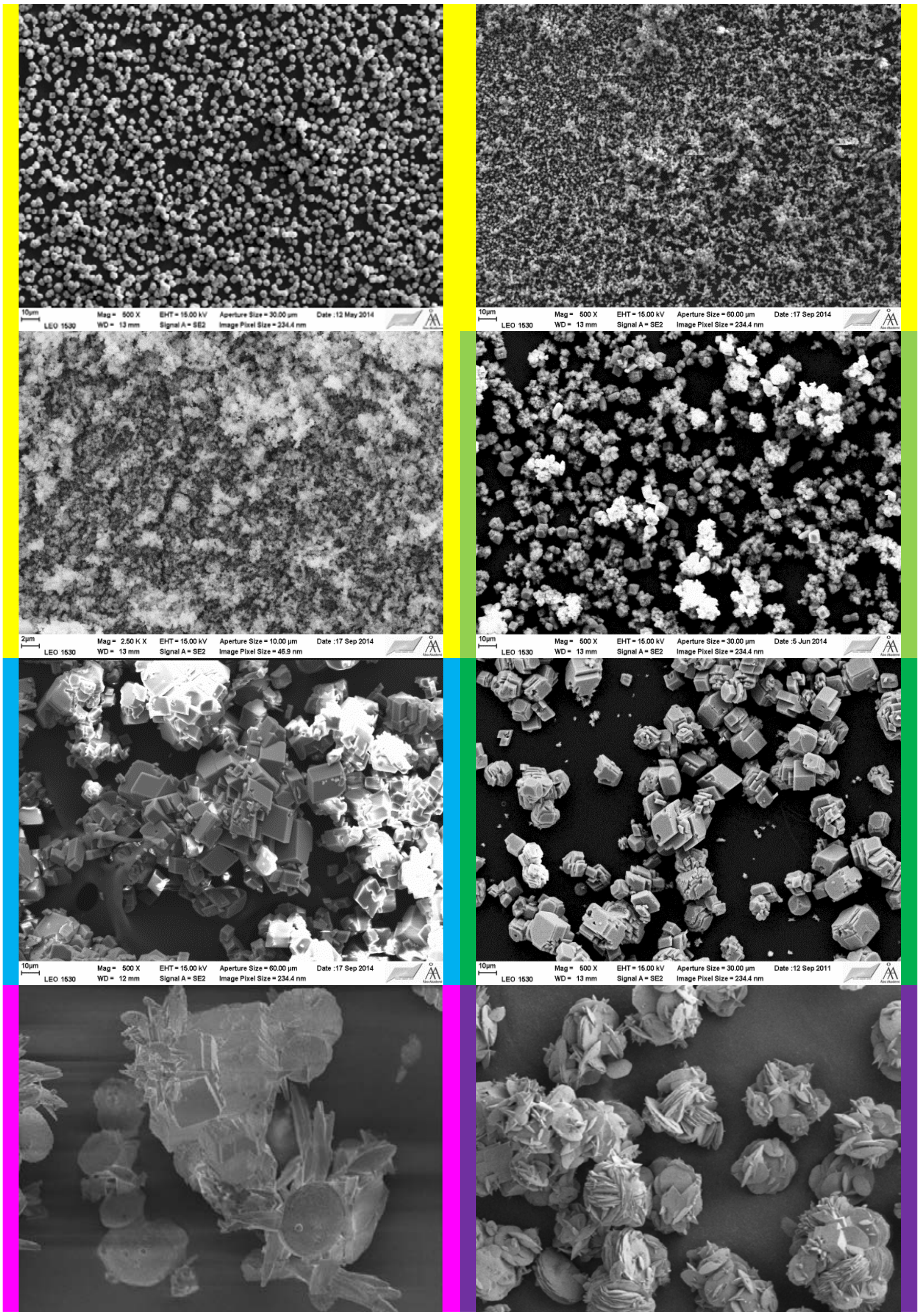
Our findings can be summarized as:

- High molar concentrations of ammonium salts or calcium (i.e. the high slag-to-liquid ratio in extraction reaction) result in larger PCC particles as agglomerates of individual crystals.
    - o Depending on the temperature the precipitate is either calcite (rhombohedral) or aragonite, the latter requiring a higher solution temperature.
- Vaterite is formed at high solvent concentrations and short reaction times.
- Smaller, individual crystals are formed at low calcium and ammonium concentrations.
- Additional parameters controlling the crystal size are the reaction time and the CO_2 throughput rate from gas phase into the solution, affected by the gas flow rate, but also by agitation.
    - o Shorter reaction time and higher gas throughput rate favor the formation of smaller particles. Even nanometer-size PCC has been produced in lab-scale experiments.
- Producing prismatic and scalenohedral particles is also possible with the Slag2PCC method using low concentrations, even though this requires obtaining and maintaining specified levels of conductivity and pH to be successful.

Table 2. Parameter combinations tested in experimental work. The colors represent the produced particle types as shown in Figure 1 and described below the Table.

$[Ca^{2+}]$ (initial)		low	moderate	high	
CO_2 gas flow	very low	low	moderate	high	very high
$[NH_4Cl]$	very low	low	moderate	high	very high
Temperature		low	moderate	high	
pH (initial)		low	moderate	high	
Conductivity (initial)		low		high	

nm-µm – scale calcite	calcite and vaterite	agglomerated calcite	agglomerated calcite	calcite and vaterite
disc-like vaterite	aragonite	aragonite and calcite	prismatic and scalenohedral calcite	scalenohedral calcite



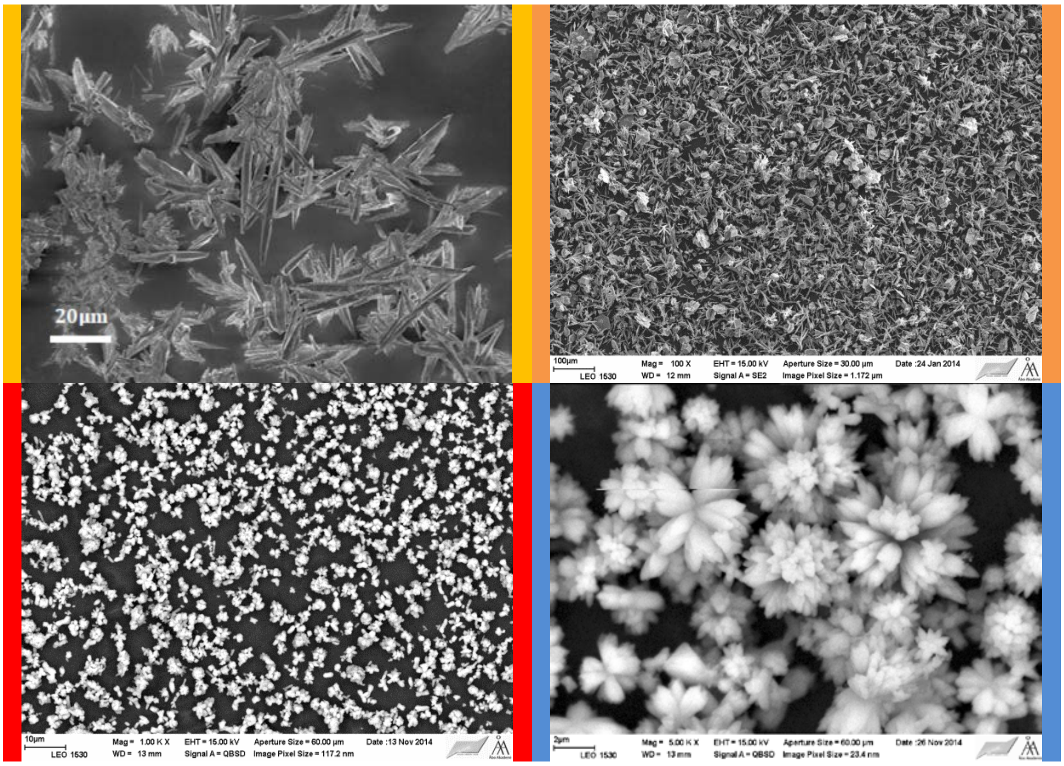


Figure 1. Scanning electron microscope (SEM) pictures of the produced PCC particles.

The particles shown in Figure 1 have mainly been produced in lab-scale tests at ÅA, though aragonite, clustered rhombohedral calcite and vaterite have been formed also in pilot-scale experiments at Aalto. The disc-like vaterite particles from the pilot-scale tests seem to be a novel form of a precipitate.

Conclusions

- The Slag2PCC process can produce PCC with the particle sizes and crystal morphologies corresponding to commercial products.
- Several of the commonly available particle morphologies such as prismatic, rhombo- and scalenohedral calcite as well as aragonite can be manufactured.
- Ammonium salt residues can lower the product quality (see D532)
- Low ammonium salt solvent concentrations in general enable a better product control.
- Moreover, certain novel morphologies such as disc-like vaterite and nano-scale calcite have been produced.
- In the future the possible applications for these rarer particle qualities are to be investigated.
- Most of the product qualities have been produced in both lab-scale and pilot scale.