

Hannu-Petteri Mattila
Hannes Hudd
Ron Zevenhoven

**Studies on the Slag2PCC process at Åbo
Akademi University**



CLEEN LTD
ETELÄRANTA 10
P.O. BOX 10
FI-00130 HELSINKI
FINLAND
www.cleen.fi

ISBN XXX-XX-XXXX-X
ISSN XXXX-XXXX



ccsp

Carbon Capture and Storage Program

CLEEN
Cluster for Energy and Environment

Åbo Akademi University
CCSP WP5.2.1, D532

Hannu-Petteri Mattila
Hannes Hudd
Ron Zevenhoven

**Studies on the Slag2PCC process at Åbo Akademi
University**



Åbo Akademi University
Turku, May 2014



H-P Mattila, H Hudd, R Zevenhoven

**Report Title: D532 – Studies on the Slag2PCC process at Åbo
Akademi University**

**Keywords: mineral carbonation, precipitated calcium carbonate,
Slag2PCC, sub-demo reactor system**



H-P Mattila, H Hudd, R Zevenhoven

Abstract

Development of the Slag2PCC process concept for the production of precipitated calcium carbonate from steel converter slags has during FP3 focused mainly on guaranteeing that the properties of the produced carbonates meet the requirements of the customers. Regarding particle morphology, i.e. particle shape, it was observed that by using low calcium and carbonate ion concentrations, the latter defined by the carbon dioxide gas flow rate, the particle shapes can be widely steered, in a similar manner as with the traditional PCC manufacturing based on limestone calcination. Low ammonium salt solvent concentrations are needed to obtain a low calcium concentration. This approach also reduces (or possibly removes completely) the need for solids washing and washing water treatment, which in the performed LCA study was found to cause an increase in environmental impacts in general, although the focus of the study was in process emissions. For the separation of solid slag residue particles from the process solution, hydrocyclones in combination with barrier filters have given promising results.

H-P Mattila, H Hudd, R Zevenhoven

Summary of the current work and FP3 progress

The research work discussed in this report has been summarized in several publications available via the CLEEN portal (see references) and, regarding earlier funding periods, also in deliverable D511. Thus, only the main findings for FP3 and the current status of the work are presented here, as well as guidelines for future work.

The process concept comprises a two-step system (Figure 1), where calcium is first selectively extracted from steel converter slag in one reactor after which the aqueous ions are contacted with dissolved carbon dioxide in another reactor to produce precipitated calcium carbonate (PCC). Quite a few solvents were studied earlier¹, and ammonium chloride was found to have good properties, ensuring an efficient and selective extraction, but also a sufficient precipitation yield.²

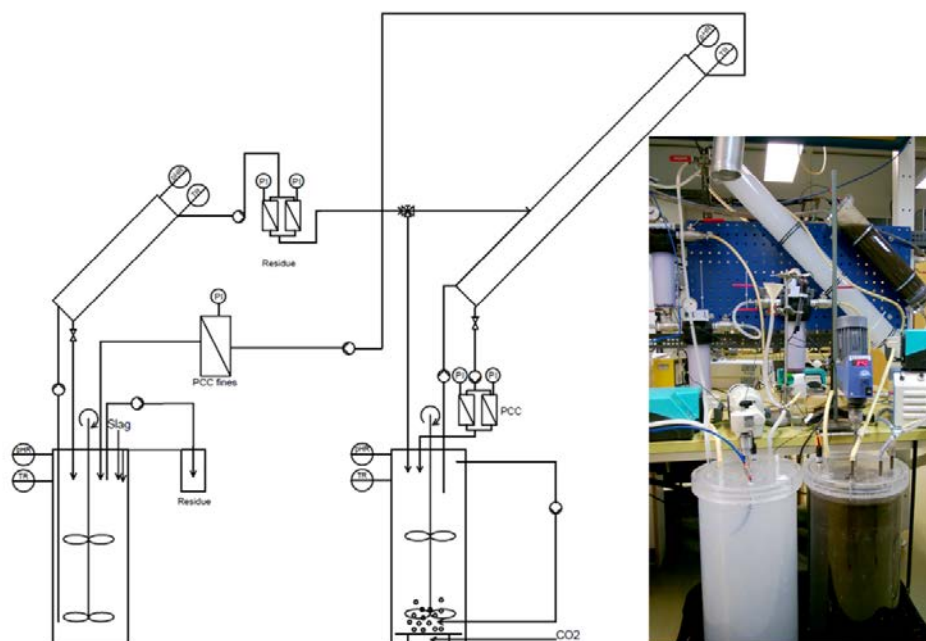


Figure 1. Process scheme and picture of the constructed demonstration setup at ÅAU.

It has now been established that the two-step Slag2PCC process can be operated according to several principles. Maximum utilization of steel slag (i.e. calcium extraction) is reached by using a solvent concentration exceeding the stoichiometric limitations defined by the calcium extraction reaction; ammonium salt must then be present in concentrations more than double the amount of reactive calcium in the slag. Higher solvent concentrations result in quicker calcium extraction, but too high levels (>1 mol/L) extract also other elements (Mg, Fe, Mn, V, Na, P). These elements may accumulate in the process solutions, precipitating eventually with the calcium

H-P Mattila, H Hudd, R Zevenhoven

carbonate and leading into reduced product purity.³ Also, at high calcium concentrations the precipitated calcium carbonate tends to form clusters of sizes 10-20µm. (Figure 2)

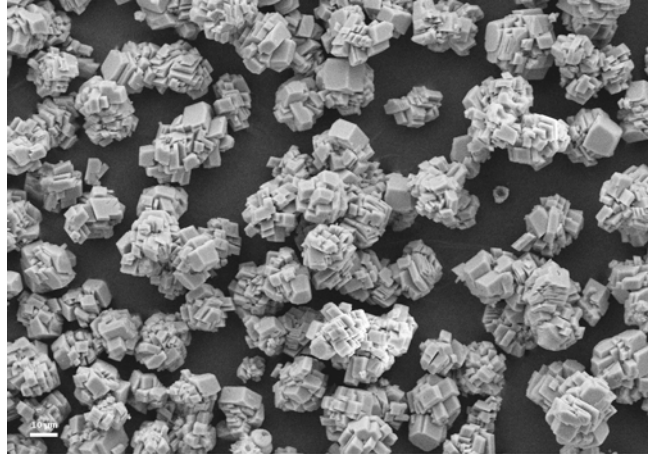


Figure 2. Clustered calcium carbonate particles from an experiment with 1.0 mol/L ammonium chloride. Scale bar 10µm.

The process can also be run with a much lower ammonium salt solvent concentration. In this way the carbonate precipitation conditions mimic the currently used industrial practices for PCC production. Experimental work with an initial NH_4Cl concentration of 0.01 mol/L produced non-agglomerated calcium carbonate particles (diameter $<1 \mu\text{m}$). However, only a small fraction ($<5 \text{ wt.-%}$) of the calcium present in steel slag is utilized in one extraction-carbonation cycle. Thus, obtaining the same calcium conversion as in the high molarity process (20-40 wt.-% depending on the slag) requires several extraction cycles using the same slag, which obviously increases the total processing time.^{4,5}

Figure 3 shows more examples of the produced PCC particles. All of these samples are from lab-scale experiments, while successful adaptation of the obtained parameters (Table 1) into the sub-demo scale is the next target. In Figure 4 a typical commercial scalenohedral PCC sample is compared to a sample produced with the Slag2PCC sub-demo setup. It can be concluded that the slag-based PCC production method is able to produce particle qualities comparable to the industrial products, even if this requires the process parameters to be chosen carefully. Low concentrations of both calcium and carbonate ions result in scalenohedral particles of a suitable particle size. A slightly larger CO_2 gas flow gives rhombohedral particles and a higher temperature yields aragonite. A high calcium concentration results in agglomerated particles, as already mentioned. Table 1 presents the experimental parameter values in detail.

H-P Mattila, H Hudd, R Zevenhoven

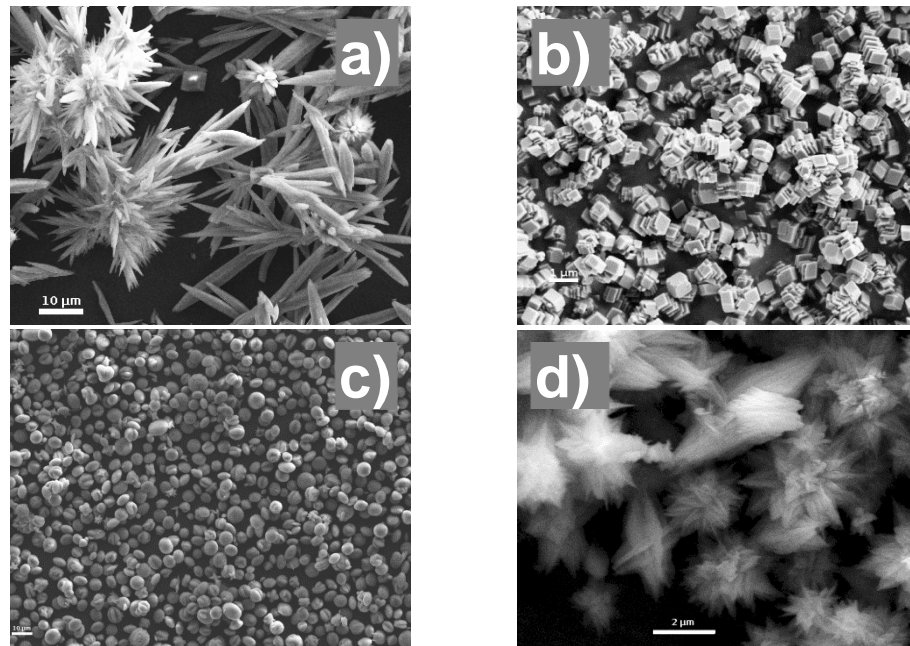


Figure 3. Scanning Electron Microscope (SEM) pictures of a) aragonite, b) rhombohedral calcite (from a low solvent concentration experiment), c) vaterite and d) scalenohedral calcite particles produced with the Slag2PCC process. Scale bars 10 µm in a) and c), 1 µm in b) and 2 µm in d).⁴

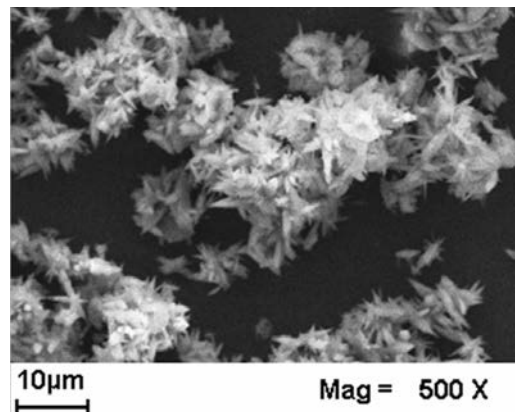
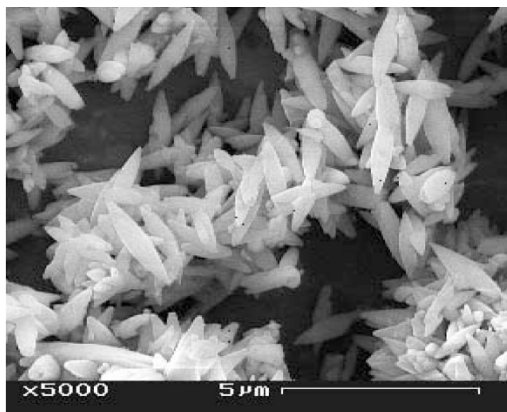


Figure 4. SEM pictures of Schaefer Kalk GmbH & Co. KG PRECARB 150⁶ (left) and scalenohedral calcite particles produced with the sub-demo scale Slag2PCC process setup under low CO₂ concentration conditions (right).

H-P Mattila, H Hudd, R Zevenhoven

Table 1. Production conditions of the PCC particles in Figures 2-4.

Fig.	[NH ₄ Cl] (M)	Solid-to-liquid (g/L)	Slag amount (g)	Temperature (°C)	CO ₂ gas flow (L _{CO2} /(L _{H2O} *min))	Reaction type	Mixing (rpm)
2	1.0	100	30	20	3.333	batch	0
3a)	0.65	100	80	60	0.075	batch	240
3b)	0.01	100	80	20	0.075	batch	240
3c)	1.0	67	50	20	0.187 (no gas flow in this vessel)	semi-continuous	0
3d)	1.0	67	50	20	0.187 (no gas flow in this vessel)	semi-continuous	0
4*	1.0	100	-	20	0.018	batch	55

* Particles removed from filter unit 24h after experiment

Table 2. Chemical composition of PCC samples produced with the Slag2PCC method (XRF analysis) compared to a commercial quality: 1) 0.50 mol/L NH₄Cl, 2) 0.65 mol/L NH₄Cl, 3) 1.84 mol/L NH₄Cl, 4) Schaefer Kalk GmbH & Co. KG PRECARB 150⁶. Weight loss by heating to 950°C in the last column. n.a.: no information available.⁴ n.d.: not detected.

[%]	CaO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	MnO	P ₂ O ₅	S	Cl	950 °C
1	55.3	0.02	0.01	<0.01	<0.01	0.03	<0.01	0.03	<0.01	<0.01	0.08	n.d.	43.9
2	54.0	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.02	n.d.	44.4
3	53.3	0.02	<0.01	<0.01	0.02	0.03	<0.01	0.02	0.03	<0.01	0.04	2.8	44.3
4	55.5	0.04	n.a.	0.04	0.02	0.33	n.a.	n.a.	0.01	n.a.	0.02	n.a.	n.a.

Besides the particle size and morphology, also the possible contamination of the products by the impurities originating from the slag material is an aspect of importance for the Slag2PCC process. As shown in Table 2, the contents of various elements measured with XRF analysis do not significantly deviate from those of a typical commercial product (PRECARB 150⁶). The main concern is the possible chlorine from the process solution, which can, specifically with high solvent molarities and without washing of the produced PCC, remain in the product as NH₄Cl.

Removal of the chlorine contamination from PCC and from the residual slag by washing was also studied during FP3.⁷ According to the results, washing would require such a large amount of water that it would strongly impair the process feasibility (Figure 5).⁵ For example, if the PCC product contains 1 wt.-% NH₄Cl and is washed in three steps to a concentration of 0.01 wt.-%, the process requires a 5.2 times larger amount of water than PCC on mass basis. In case of the slag residue, washing from 1.0 to 0.1 wt.-% would require water at 11 times the amount of PCC (kg) produced from the same slag amount. The most problematic issue is the purification of the washing water. If it is accomplished by evaporating the aqueous phase, the process for heat production can possibly emit more CO₂ than what is actually stored in the solid carbonates. An alternative approach to evaporation should be used for purifying the washing waters.⁵

H-P Mattila, H Hudd, R Zevenhoven

The chlorine contamination problems can also be resolved by using low solvent concentrations.⁵ With the solvent molarity of 0.01 mol/L NH₄Cl, the product is estimated to contain only 0.1 wt.-% solvent salt even without any washing.

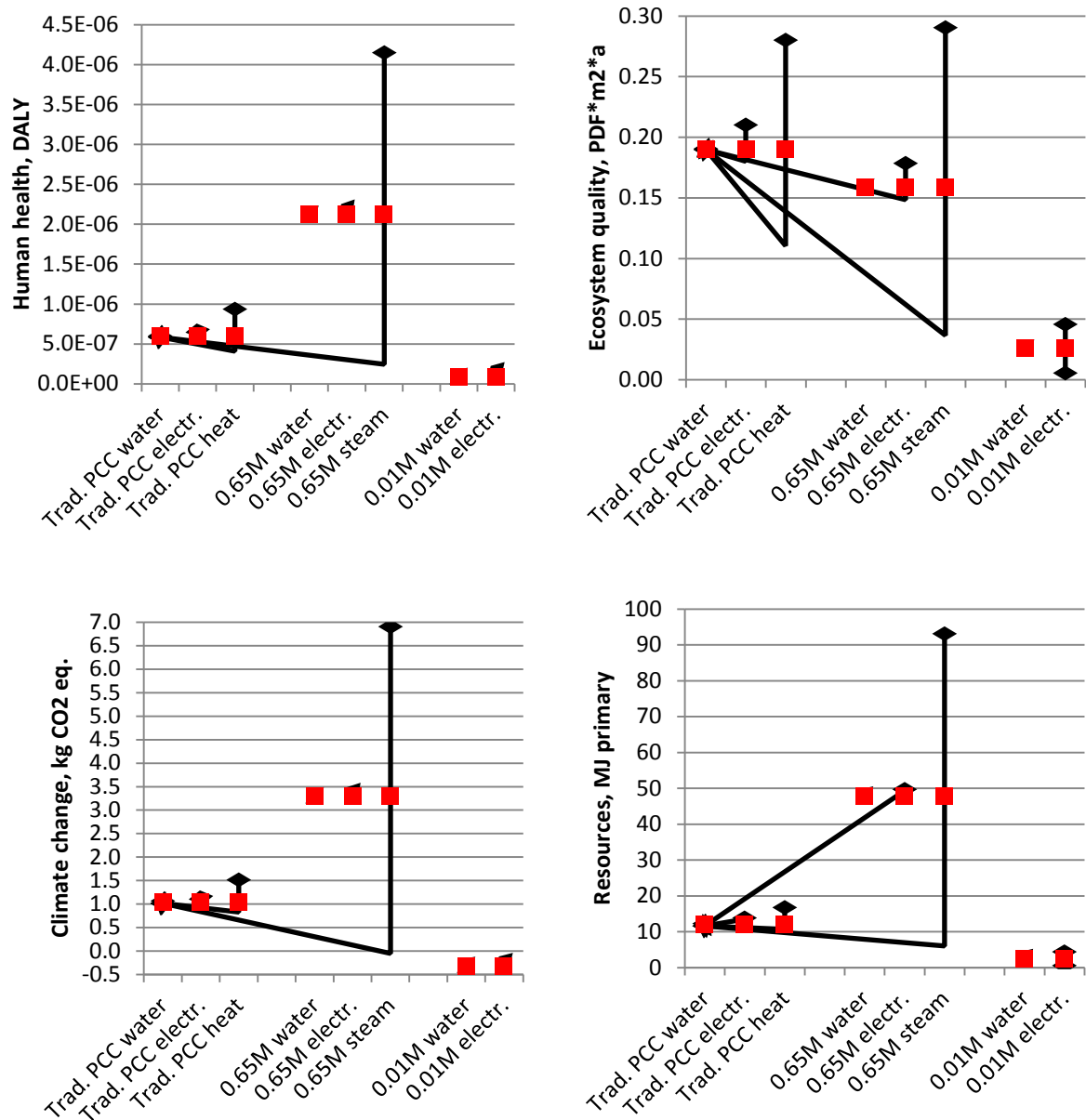


Figure 5. Life cycle impact assessment results per impact category for traditional PCC production and for Slag2PCC with 0.65 and 0.01 mol/L solvent concentrations. Black lines indicate the uncertainty limits for the various commodities used in processes.⁵

H-P Mattila, H Hudd, R Zevenhoven

Separation of solid slag residues from the process solution by a hydrocyclone (Figure 6) was tested during FP3. The cyclone was purchased from Chemindustrial Systems, Inc., USA⁸ and it has a throughput capacity of 2.6 L/min with a 2 bar inlet pressure (5 L/min with 8 bar). In the preliminary experiments performed so far, overflow from the cyclone was adjusted to 0.5 L/min, resulting to efficient separation and pre-clarification. Only <5% of the slag residue entered the barrier filters (type AWP109-1, 1µm pore size, 10" housing, recommended max. throughput 17 L/min and MMP921AAS, 0.2µm pore size, 10" inch housing, throughput of clean water 3.8 L/min with 0.02 bar Δp) located downstream the hydrocyclone while the rest was recycled back to the extraction reactor from the cyclone underflow.

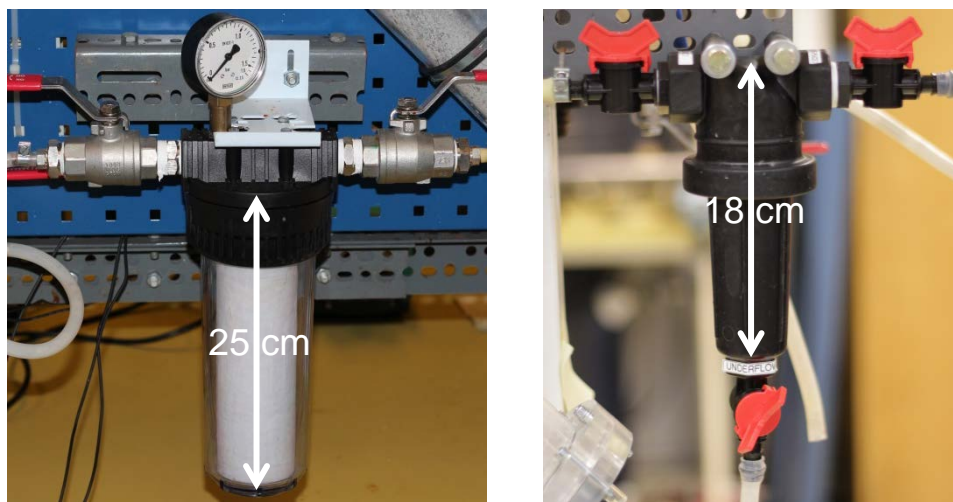


Figure 6. A cartridge filter unit with a pressure gauge for the barrier filters (left) and a hydrocyclone⁸ used in the experimental work (right).⁴

Based on these results, during FP4 the established experimental parameters producing near-commercial quality PCC will be tested with the sub-demo scale setup. Assuming that the washing of the solids can be avoided, the low ammonium salt concentration approach will be developed further, including efficient separation of solids from the process solution using the above described separation equipment.



H-P Mattila, H Hudd, R Zevenhoven

Conclusions

- The Slag2PCC process can produce “near-commercial” quality PCC
- Low ammonium salt solvent concentrations are more suitable for this purpose
- Washing of the solid products is then not necessarily required
- The performed LCA study has verified negative CO₂ emissions for the low-concentration process
- Also other environmental impacts are reduced compared to traditional PCC manufacturing
- During FP4 the research focus will remain in improvement of the product quality as well as of certain details of the overall process design

References

1. Eloneva, S. *Reduction of CO₂ Emissions by Mineral Carbonation: Steelmaking Slags as Raw Material with a Pure Calcium Carbonate End Product. Doctoral Dissertation.* Aalto University, School of Science and Technology: Espoo, Finland, 2010.
2. Mattila, H.-P.; Grigaliūnaitė, I.; Zevenhoven, R. Chemical kinetics modeling and process parameter sensitivity for precipitated calcium carbonate production from steelmaking slags. *Chem. Eng. J.* **2012**, *192*, 77-89.
3. Mattila, H.-P.; Zevenhoven, R. Design of a continuous process setup for precipitated calcium carbonate production from steel converter slag. *ChemSusChem* **2014**, 903-913.
4. Mattila, H.-P. *Utilization of steelmaking waste materials for production of calcium carbonate (CaCO₃). Doctoral Dissertation.* Åbo Akademi University. Manuscript under preparation. 2014.
5. Mattila, H.-P.; Hudd, H.; Zevenhoven, R. Partial life cycle assessment of precipitated calcium carbonate production from steel converter slag. Accepted manuscript, In Press. *J. Clean. Prod.* **2014**.
6. SCHAEFER KALK GmbH. *SCHAEFER PRECARB 150 - Technical Data Sheet, Typical Values.* **2012**.
7. Hudd, H. *Post-treatment of precipitated calcium carbonate (PCC) produced from steel converter slag. M.Sc. thesis.* Åbo Akademi University: Turku, Finland, 2014.
8. ChemIndustrial Systems, Inc. *ChemIndustrial Hydroclone Miniclones.* <http://hydroclone.com/products/miniclone.htm> (accessed 05.02.2014).