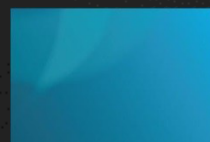




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Report on practice observations from Pilot-scale test facility unit at Aalto



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Abstract

The possibility to recycle used solvent is a necessity for the Slag2PCC process, this will minimize the chemical consumption of the process and make the technology economically feasible. Thus, a number of solvent recyclability tests were conducted. On the other, the PCC quality produced by the Slag2PCC method is of the utmost importance to the commercial viability of the technology. Thus, number of carbonation tests were carried out in order to study on how to control the precipitation conditions by varying the CO₂ feeding rate. Different steel slags like, Basic oxygen furnace (BOF), Ladle slag and AOD (Argon Oxygen Decarburization) slag was used in the pilot plant.

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1. Experimental set-up

Batches of steel converter slag (BOF), $\leq 250\mu\text{m}$ were mixed with 1 M aqueous solutions of ammonium chloride (NH_4Cl) to selectively dissolve calcium from the slag at room temperature ($\sim 20^\circ\text{C}$). The solid-to-liquid ratio (0.1 kg/L) was kept constant for all tests. In the first extraction test, a fresh batch of the NH_4Cl solvent was used, and the regenerated NH_4Cl solution after the carbonation stage was re-used. Optimizing the chemical consumption of the process by recycling the solvent NH_4Cl as many times as possible was the main objective of the extraction tests

2. Materials and Methods

The steel slag used in the pilot plant was BOF and Ladle slag provided by SSAB Ruukki, Finland, and AOD provided by Outokumpu, Finland.

3. Results

3.1. Extraction tests

3.1.1. Solvent recyclability

As shown in Figure 1, the fresh and recycled solvent have almost the same Ca extraction efficiency. The first three cycles (Cycle 1, Cycle 2, and Cycle 3) with the recycled solution show almost the same Ca extraction efficiency as the fresh solvent. The highest Ca extraction efficiency achieved was 78% with the fresh solvent and the lowest extraction efficiency (60%) was found for the third cycle (Cycle 3). The solution was recycled without chemical make-up or additional fresh solvent. Therefore, Ca extraction efficiency only deteriorated significantly (to 39%) only after the solution was recycled more than 10 times (Cycle X) including high temperature carbonation tests which can result in some evaporation of NH_3 from the solution.

On the other hand, the highest extraction efficiency was achieved only 30 minutes after the slag was added into the solution, therefore, there is no need for long calcium extraction processes, and it can be done only in 30–40 minutes.

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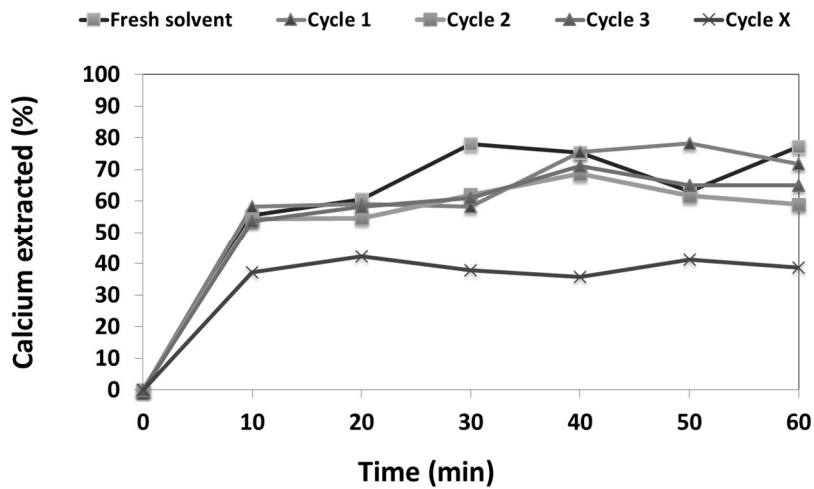


Figure 1. Calcium extraction efficiency from BOF slag with fresh and recycled solvent of 1 M NH₄Cl.

3.1.2 Two-stage extraction tests

One way to increase the Ca extraction efficiency is to use a two-stage extraction process. After filtration, the residual slag from the first extraction stage can be mixed with fresh (or recycled) solvent to extract the remaining calcium in the slag. Immediately after the filtration the residual slag was put back into the extraction reactor and mixed with a fresh solvent of NH₄Cl(aq). Figure 2 summarizes the results from a two-stage extraction test: Firstly, using fresh slag with fresh solvent (Extraction Stage 1), and secondly, using residual slag with fresh solvent (Extraction Stage 2). In the second extraction stage, 24% of the calcium in the residual slag was dissolved, making the total Ca extraction efficiency 83% of the original calcium content of the slag. In other words, the overall Ca extraction is the sum of extraction in first and second stages

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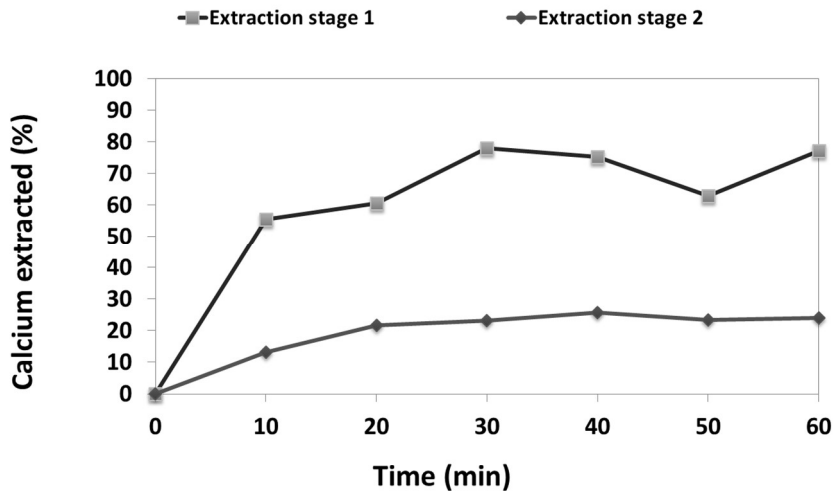


Figure 2. A two-stage calcium extraction test: Extraction Stage 1 (fresh slag with fresh solvent) and Extraction Stage 2 (residual slag with fresh solvent).

3.1.3 Calcium extraction test for AOD and Ladle slags

Batches of AOD and ladle slag were mixed with 1 M aqueous solutions of ammonium chloride (NH_4Cl) to selectively dissolve calcium from the slag at room temperature ($\sim 20^\circ\text{C}$). As shown in Figure 3 only 20% of the total calcium in the slags were extracted. However, at lab-scale tests have shown that at higher solvent concentration, e.g. 3 M NH_4Cl will result in about 50% Ca-extraction efficiency. Thus, more pilot plant test is required to maximize the extraction efficiency.

During Ca-extraction tests, we have experienced blockage in pipes and filters caused by the ladle slag. The ladle slag was stickier than the AOD that may be the reason of the blockage. Therefore, this issue must be kept in mind when dealing with the ladle slag.

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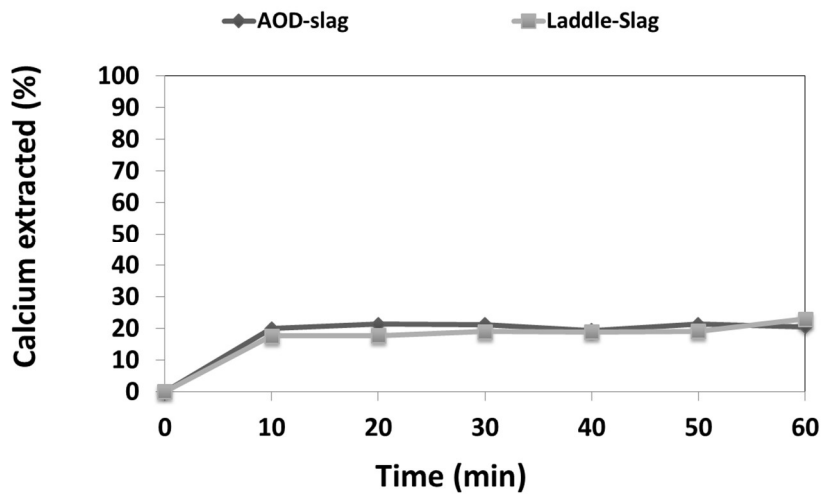


Figure 3. Calcium extraction efficiency from AOD and Ladle slag with fresh solvent of 1 M NH₄Cl.

3.2 Carbonation tests

The initial carbonation temperature was identified as the most important parameter in determining the crystal morphology of the PCC. In the conventional PCC processes, aragonite PCC is produced at higher temperatures (>55°C), but in the Slag2PCC method such a high carbonation temperature will result in the evaporation of ammonia NH₃(aq) in the ammonium chloride solution. This in turn reduces the solution strength and lead to less calcium extraction when the solution is recycled back to the extraction stage. Figure 4 shows the concentration of NH₃(g) in the gas from the carbonation process at 45°C, 50°C, and 60°C. The analysis was performed with a Fourier transform infrared spectroscopy gas analyzer. At 60°C more than 2 vol.-% (20355 ppm) of NH₃ was detected in the off gas and at 50°C it was 0.65 vol.-%, while at 45°C the NH₃ concentration in the off gas was only 0.11 vol.-% (1137 ppm). The ammonium loss occurs when heating up the solution. As shown in Fig.4 when the solution temperature is stabilized and the CO₂ is pumped to the reactor, the concentration of the ammonium in the flue gas becomes constant.

Thus, to avoid an unnecessary higher carbonation temperature, a number of experiments were conducted at 45°C, aiming to produce aragonite PCC by varying the CO₂ flow rate. As shown in the XRD analysis (Fig. 5), the aragonite

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mass fraction in the PCC is subjective to the CO₂ flow rate. The highest mass fraction of aragonite (80 wt.-%) was achieved at 0.05 L CO₂ / L reactor (10 L/min CO₂ and 200 L reactor) and the lowest (25 wt.-%) at 0.07 L CO₂ / L reactor (14 L/min CO₂ and 200 L reactor). The ratio of the calcium concentration to the CO₂ in the solution could be the reason for some shifts from calcite to aragonite at a lower CO₂ feeding rate and from aragonite to calcite at a higher CO₂ feeding rate (beyond 10 L/min). However, more studies are needed to investigate carbonation kinetics and maximize the mass fraction of aragonite precipitated at 45°C.

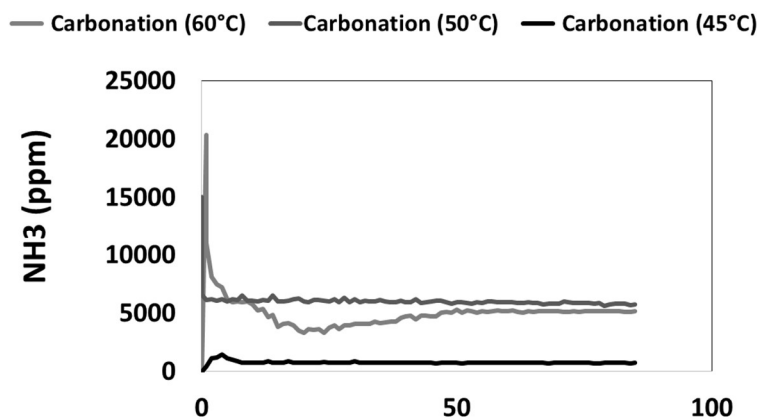


Figure 4. The concentration of ammonia in the off gas in the carbonation stag

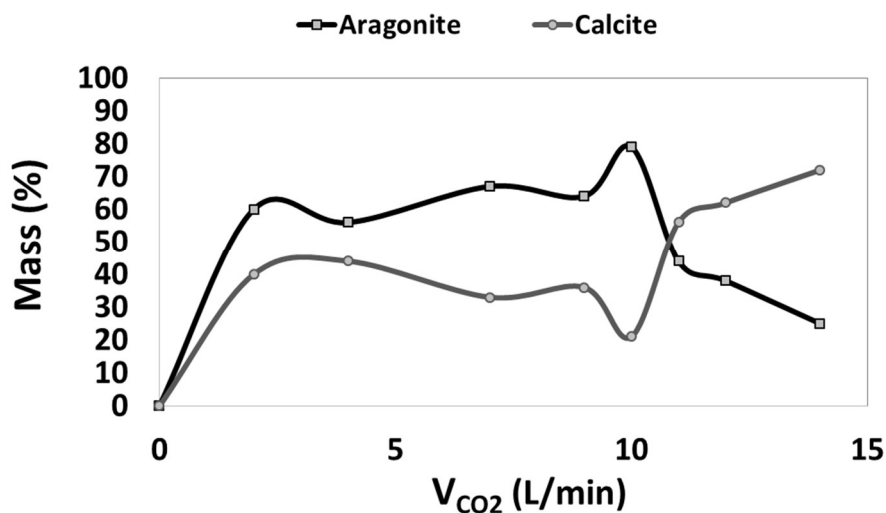


Figure 5. The content of aragonite and calcite fin PCC precipitated at 45°C by XRD analysis

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When the CO₂ feeding rate was 10 L/min, calcium concentration after the carbonation was 5730 mg/L, while the initial calcium concentration was 19600 mg/L, resulting in a calcium conversion of 71%. According to the online gas flow meter (FM12, Fig. 6), the average CO₂ coming out from the carbonation reactor was 0.001 kg, while incoming CO₂ was 0.76 kg. This indicates that almost all the CO₂ was converted into PCC, while 29% of the calcium in the Ca-rich solution was not converted into PCC because of the low feed rate of CO₂. The Ca conversion could be maximized by increasing the CO₂ flow rate, but an excess amount of CO₂ will have a direct effect on the PCC quality either by 1) losing its homogeneous crystal shape or 2) increasing particle agglomeration. Therefore, there is a need for process optimization to maximize the Ca conversion and the PCC quality.

XRF was used to analyze the purity of the PCC produced from the pilot plant. The PCC samples were not washed but dried for XRF analysis. Table 1 summarizes the major components detected in the PCC samples when fresh or recycled solvent was used in the Ca extraction process. The concentration of all other species increased except for chloride that was decreased due to the weakening of the solvent strength. However, the purity of the PCC produced from the pilot plant was higher than 99.5% and it can be improved by washing.

Table 1. XRF analysis of the PCC samples produced from the pilot plant.

Element	Fresh solvent	Recycled solvent (recycled 10–20 times)	Differences (ppm)
CaCO ₃ (%)	99.53	99.76	
Si (ppm)	1473	2710	1237
V (ppm)	801	936	135
Mg (ppm)	1392	1450	58
Cl (ppm)	7963	5267	-2696

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3.3. Material consumption

Raw material consumption and production capacity of the Slag2PCC pilot plant are summarized in Table 2. In each test, 20 kg of slag and 180 L (183 kg) of solvent was fed into the extraction reactor, resulting in 170 L (175 kg) of Ca-rich solution and 19 kg of wet residual slag where the moisture content is about 37%. Almost 9 kg of the input material could not be accounted for after filtration. All the Ca-rich solution was fed into the carbonation reactor, resulting in about 12 kg of wet PCC with a 15% moisture content. Nearly 10 kg of the material could not be accounted for after both the extraction and carbonation process steps, therefore a better filtration design is important to avoid or minimize the material losses.

Table 2. The raw material and production capacity of the Slag2PCC pilot plant.

In		Out		Description
Extraction reactor		kg		kg
Solvent	183	Ca-rich solution	175	
		Residual slag	19	37% moisture content
Slag	20	(wet)		
Total	203	Total	194	
		Lost	-9	lost due to filtration
Carbonation reactor		kg		kg
Ca-rich solution	175	Solvent	162.4	
CO ₂	0.76	CO ₂	0.001	
Total	175.76	CaCO ₃ (wet)	11.8	15% moisture content
		Total	174.20	
Lost			-1.56	lost due to filtration



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3.4. Waste water analysis

We have analyzed the concentration of different species in the waste water collected after washing of the residual slag and the PCC samples (0.2 g solid/L). Table 3 summarizes the concentration of the most significant species observed in the waste water. As expected the concentration of NH_4^+ and Cl^- was high in both cases.

Table 3. Waste water analysis

Waste water contents				
	washed water from residual slag		washed water from PCC sample	
	mg/l		mg/l	
NH_4		4071		4224
Cl		8000		8300
Si		4.1		12.2
V		1.5		0.5
Mg		0.5		1.9

4. Discussions

During the first set of tests (after the commissioning of the pilot plant in 2014) a deep blue color on the Ca-rich solution was observed after the extraction filters. It was later observed that the deep blue color was due to the copper complex ion $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, formed from the reaction between $\text{NH}_3(\text{aq})$ and copper ions, resulting from the chemical attack upon the brass components in the filter connectors.

In aqueous solutions copper ions are actually present as hexaaquacopper (II) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions, which will react with NH_3 to produce the complex $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. This was confirmed by the addition of acid to the deep blue solution, which converted the copper-ammonium complex back to the characteristic pale blue hexaaquacopper (II) ion. From this finding it was concluded that no brass materials (mainly present in drain valves and threaded connections in the extraction filters) should be used in the Slag2PCC system due to the incompatibility of copper with the NH_4Cl solvent.

Another observation during the initial tests at the pilot plant was that the PCC₁ produced from the carbonation reactor had a yellow or brownish color.

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Inspection of the reactor identified that the welding material used in the sparger had corroded, causing iron and rust to discolor the PCC. Also some corrosion was observed on the welding surfaces of the reactors. This problem was resolved by replacing the sparger with a new sparger, then both the new sparger and the corroded surface of the reactors were coated with a rust preventive pigment known as POR-15[®].

Figure 6 shows the design of the Slag2PCC pilot plant and Table 4 summarizes the key components of the pilot plant

Table 4. The key components of the pilot plant.

Name	Number of units	Type	Description
Reactor	3	Stainless steel, AISI 304	V = 200 L, h = 1 m, d = 50 cm
Reserve tanks	5	Plastic tanks	2 x 200 L, 1 x 300 L, 2 x 100 L
Quantitative Filters	5	Amazon bag filters	Bag filter housing: 1µm
Qualitative Filters	3	HOH filter housings	2 x 1 µm and 1 x 0.45 µm
Slag feeder	1	Rotary valve	RV-RVR 02, 10 rpm
Pump	8	Pump SELF, Mag 22T8	0.35 kW, 20 L/min
Heat exchange	2	Fixed plate	FP 40-59-1-NH
Agitators	3	Pitched blade impeller	CML and HLS, 0.37 Kw, 202 and 170 rpm
Pipes		Stainless steel, AISI 316	¾ inch
Hose		VEPA, 19 X 27 mm	EPDM 110C, 15 bar, ¾ inch
pH sensor	3	Jumo, 0030u151	0–12 pH
Temperature sensor	5	pt- 100	
Liquid flow meters	10	210, DN10	Max 32 L/min
Gas flow meters	2	Rotameter and Aalberg, GFM57	

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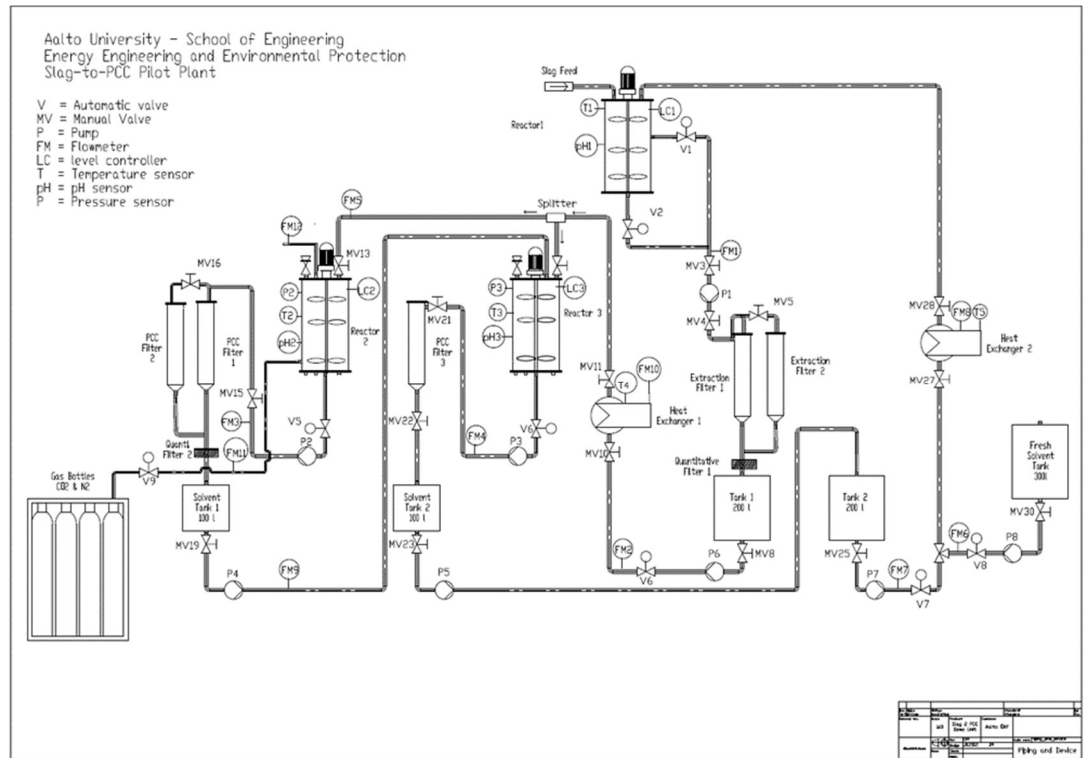


Figure 6. The process design of the Slag2PCC pilot plant test facility at Aalto University, Finland

5. Conclusions

The scale-up work of the Slag2PCC process was very successful the pilot plant operated as designed and the achieved results are very promising.

As future work (after the Clic CCSP project period), study on the carbonation kinetics is important in order to enable to control the PCC quality, for example, morphology, agglomeration, and PSD. The design of a demonstration plant for pre-commercializing the technology is in a progress and it is planned to be ready in 2017.