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**Report on results obtained with demo unit at
Aalto**

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Carbon Capture and Storage Program

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Report on results obtained with demo unit at Aalto



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**Aalto University
Espoo 2014**



Report Title: Report on results obtained with demo unit at Aalto

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Abstract

Despite delays and challenges during the construction of the Slag2PCC pilot plant finally we successfully opened the facility for testing. The quality of the PCC produced by the Slag2PCC process is of utmost importance to the commercial viability of the technology. If the PCC is of poor quality then it cannot be sold at a high price to the pulp and paper industry, or alternatively, a pulp and paper plant would not be able to realize significant cost savings by fully substituting Slag2PCC product for their existing PCC product due to the reduction in quality

In general, PCC can precipitate in multiple crystalline phases (calcite, aragonite, and vaterite) and many of the variables during the precipitation such as solution pH, composition, temperature, and ionic strength are interrelated and can interact with each other. Thus, a precise control over precipitation conditions is important for ensuring high quality PCC.

Therefore, we conducted three major tests designed to produce two different PCC morphologies: scalenohedral and aragonite. We successfully produced pure aragonite crystals and rhombohedral calcite. Attempts to produce scalenohedral PCC from the SLah2PCC process have not been successful on either the laboratory or the pilot scale. But we are still investigating the favor process conditions for scalenohedral PCC.

In May 2014 we final started the “real” tests: batch extraction tests and batch carbonation tests. All the experiments were performed successfully. A MSc. Thesis student Zappa. W has worked with Said. A to perform all the experimental work.



Espoo, October 2014



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1 Introduction

During commissioning of the pilot-scale Slag2PCC plant several problems were encountered which considerably delayed the experimental work. The main challenges were poor filtration system performance, corrosion problems in the CO₂ sparger in the carbonations. After considerable troubleshooting, short- and long-term solutions were put in place so that experimental work could begin. Discolouration of the PCC was found to be due to corrosion of the gas spargers in the carbonation reactor as the welding materials used by the supplier were not compatible with the corrosive NH₄Cl solvent. The solution for this was to replace the spargers with temporary spargers, and to coat the bottom of the carbonation reactors and the sparger with a corrosion-resistant Teflon coating.

As a result of these delays, only a limited number of tests could be performed in the remaining time available for the FP3. Thus, we decided that the focus of the pilot-scale test work would be to try to directly produce two of the most common commercial grades of PCC: Scalenohedral calcite and Aragonite.

2 Equipment Setup

Figure 1 shows the setup of the Slag2PCC pilot plant which has three 200L reactors: an extraction reactor (ER) and two carbonation reactors (CR). In the ER, calcium is extracted from steel slag, after which this Ca-rich solution is filtered through one of the extraction filters (1µm). Not shown in the diagram is a secondary filtration stage (two further 1µm and one 0.45 µm filter in series) after the first extraction filter that had to be added to the system during commissioning due to poor filtration performance. After filtration, the Ca-rich solution can be stored in Tank 1 or carbonated directly in Carbonation Reactor 1 (CR1) or 2 (CR2). The original design intent is for most of the Ca-rich solution to be carbonated in CR1, with a small amount of unreacted Ca-rich solution kept aside in CR2 using a flow splitting valve (V4). This is then mixed with the



carbonated liquid from CR1 to precipitate any remaining dissolved HCO_3^- and prevent it from precipitating PCC in the ER when the solvent is recycled. After carbonation is complete, the liquid from CR1 (or CR2) is filtered to collect the PCC using an identical filtration system as the extraction filters (also with a secondary filtration stage) and the solvent stored in one of the solvent tanks (ST1 or ST2) to be reused again.

Each reactor (ER, CR1 and CR2) is equipped with temperature and pH indication as well as a three-level 2-bladed variable speed drive (VSD) agitator with a maximum speed of 202 rpm for the ER and 170 rpm for CR1 and CR2. The two carbonation reactors have gas spargers at their base with hole diameter 1mm mounted below the agitator. The pilot plant also includes two plate and frame heat exchangers (HX) which can be used to heat or cool the solvent going into the ER, or to heat or cool the Ca-rich solution to be carbonated. The HXs can be supplied with hot or cold tap water, whose maximum and minimum temperature depends on the season. In summer the maximum temperature is 60°C but in winter this may increase up to 80°C .

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Energy Engineering and Environmental Protection
Slag to PCC Demonstration Plant

- V = Valve
- MV = Manual Valve
- P = Pump
- C = Compressor

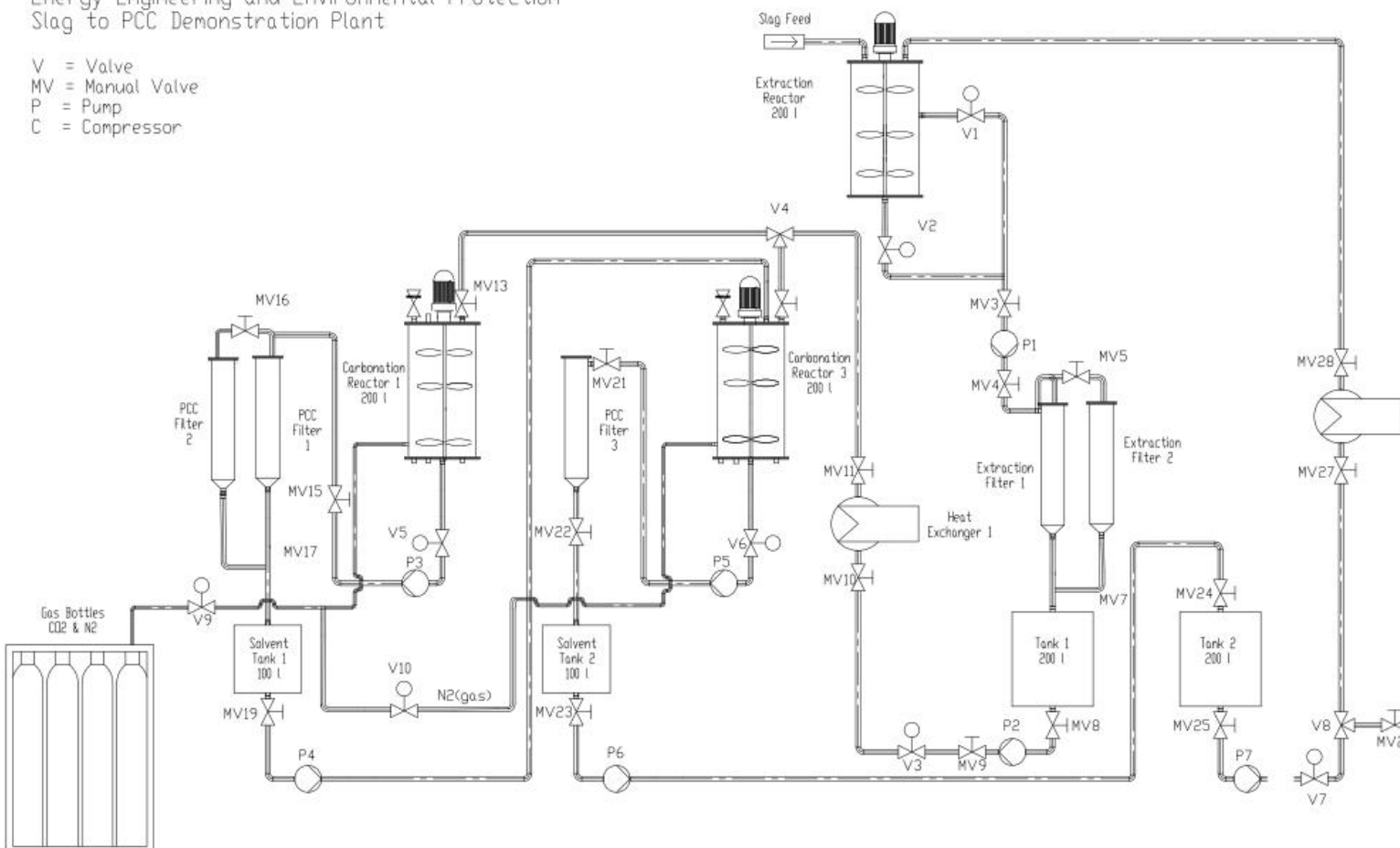




Figure 1 – Equipment Diagram of the Slag2PCC Pilot Plant

3 Test Conditions

We conducted three major tests designed to produce two different PCC morphologies: scalenohedral and aragonite. The aim of the first test (test 1) was to try to produce scalenohedral PCC by attempting to replicate the experimental conditions suggested by Hannu-Petteri Matilla from Åbo AKademi who successfully produced scalenohedral PCC at the laboratory scale. The second test (test 2) was an attempt to produce scalenohedral calcite based on conditions given in US patent 5,695,733 filed by Kroc and Fairchild [1] and in US patent 5,232,678A filed by Bleakley & Jones [2]. Although these conditions were for producing scalenohedral PCC by carbonation of $\text{Ca}(\text{OH})_2$. In the Slag2PCC process, the Ca-rich solution contains both dissolved Ca^{2+} and OH^- and so using the conditions for $\text{Ca}(\text{OH})_2$ carbonation seem to be tricky, but it is a good starting point.

The third test (test 3) was an attempt to produce aragonite simply by increasing precipitation temperature with other parameters held the same as in the scalenohedral test.

The experimental conditions used for the pilot plant tests are given in Table 1.

Table 1. Experimental conditions for the pilot plant runs

Test	Extraction					Carbonation				
	Solvent (L)	SLR (g/L)	Slag (kg)	[NH ₄ Cl] (M)	Solution (L)	Starting T (°C)	Agitation (rpm)	CO ₂ Flow (L/min)	CO ₂ CR (min ⁻¹)	
									Est.	Act.
Scalenohehral (Test 1)	150	100	15	1.0	126	20	55	3 ^a	-	0.0032
Scalenohehral (Test 2)	150	50	7.5	1.0	120	50	170	14 ^b	0.028	0.024
Aragonite (Test3)	150	50	7.5 ^d	1.0	114	58	170	13 ^c	0.028	0.023

a) CO₂ flow scaled up from laboratory flow using GLR= 0.018 L CO₂/L.min

b) CO₂ flow set based on estimated [Ca²⁺] of 0.18M and setting CO₂CR in the typical range employed in Kroc and Fairchild [1] (0.028 min⁻¹)

c) CO₂ flow set based on estimated [Ca²⁺] of 0.18M and setting CO₂CR in the typical range employed in Kroc and Fairchild [2] (0.028 min⁻¹)

d) Slag added stage-wise in three 2.5 kg increments, waiting 5 minutes after each addition

The intention in all three tests was to have a high [Ca²⁺]/[CO₃²⁻] ratio as from the literature this seemed to be a requirement for producing scalenohedral calcite and probably aragonite as well. In traditional commercial PCC carbonation processes a very high [Ca²⁺] is typically used (1-3 M) by preparing a 5-25 weight% solution of CA (OH)₂. Thus, maximising [Ca²⁺] from the extraction stage of the Slag2PCC process to mimic the high [Ca²⁺] was considered key. However, given that slag is only 45% CaO and the range of extraction conditions studied thus far, achieving a [Ca²⁺] in the Ca-rich solution higher than 1 M is challenging. In particular, it was unclear from previous test work whether a SLR (solid to liquid ratio) of 50 or 100 g/L would lead to a higher [Ca²⁺] in solution. Doubling the SLR should result in a higher [Ca²⁺] due to the greater supply of calcium, providing the drop in extraction efficiency is not proportional. Given the uncertainty surrounding the high SLR data in a SLR of 50 g/L was used for the second two tests.

The CO₂ flow for the test 1 was set based on a GLR (gas: liquid ratio) of 0.018 L CO₂/L.min that was used by H-P Matilla in his test. The CO₂ flow for the scalenohedral test was set based on the CO₂ flows, reaction volumes and calcium concentrations used in the patent by Kroc and Fairchild to produce scalenohedral calcite particles. From analysis of the work of Kroc & Fairchild it was found that for each of example tests producing scalenohedral PCC given in their patent (see Appendix), the



moles of CO₂ added per mole of calcium per minute varied between 0.01 and 0.05 with an average of ~0.028. This level was supported by the patent of Bleakley & Jones which recommended a CO₂ flow of 0.02 to 0.10 moles per mol Ca(OH)₂ per minute in order to produce scalenohedral PCC. This quantity – the moles of CO₂ added per mole of calcium per minute, is hereafter referred to as the *CO₂ to calcium ratio* (CO₂CR), defined in equation) as

$$CO_2CR = \frac{Q_{CO_2}}{c_{Ca^{2+}} \hat{v}V}$$

where Q_{CO_2} is the flow rate of CO₂ gas (L/min), \hat{v}_{CO_2} is the molar volume of ideal gas at the calibration temperature and pressure (24.05 L/mol at 20°C, 1 atm), $c_{Ca^{2+}}$ is the concentration of calcium (M) and V is the volume of the Ca-rich solution being carbonated (L).

4 Experimental Procedure

A fresh batch of 1M NH₄Cl solvent was prepared for each test by dissolving 8 kg of solid NH₄Cl in 150L of water and agitating thoroughly at room temperature (~20°C). Being strictly accurate this means that the solvent was actually 1 molal (1 mol NH₄Cl/kg H₂O or 0.962 M) and not 1 molar, but in the large volumes dealt with the difference is small, and because qualitative results (i.e. PCC morphology) were of primary concern rather than quantitative results, a nominal concentration of 1M was considered sufficient. In the first two tests the slag was added all at once but in the aragonite test, the slag was added stage-wise in three 2.5 kg increments, waiting 5 minutes after each addition to see if this would improve extraction efficiency.

For each test, 150L of solvent was pumped from the Fresh Solvent Tank (FST) into the ER. The required amount of slag (ground to <250µm) was weighed, then added at the top of the reactor with agitation at 202 rpm. Extractions were run for one hour. After extraction was complete, the Ca-



rich solution was filtered and pumped to CR1 with CR2 isolated so that all the available solution went to CR1. The design of the filtration system, tanks, and piping meant that some 20-30L of the Ca-rich solution remains in the dead volume of the system and could not be easily recovered for carbonation, which is why the solvent and Ca-rich solution volumes in Table 1 differ. The agitation rate was set by modifying the setting on the agitator drive frequency converter. The CO₂ flow was set using a CO₂-calibrated rotameter and carbonation time begun when the flow of CO₂ started. Pure CO₂ was used in all tests. The pH and temperature of the carbonating solution were logged automatically at 5 second intervals.

The carbonation tests were stopped at specific pH levels. In test 1 the carbonation was stopped once pH reached approximately 7. The scalenohedral test was stopped at pH 7.5, the level used in the patent. The aragonite test was stopped at pH 7 as, due to the lower starting pH, it was thought that stopping at pH 7.5 may not provide sufficient reaction time. Samples of the PCC produced in each test were taken for SEM imaging. The PCC was washed with deionised water and filtered using 0.25µm paper.

5 Results

Figure 2 -4 show the pH and temperature data from all tests. The pH readings recorded at the start of each carbonation showed that the higher solution temperature reduced the starting pH, to be expected from the temperature dependence of the water dissociation equilibrium.

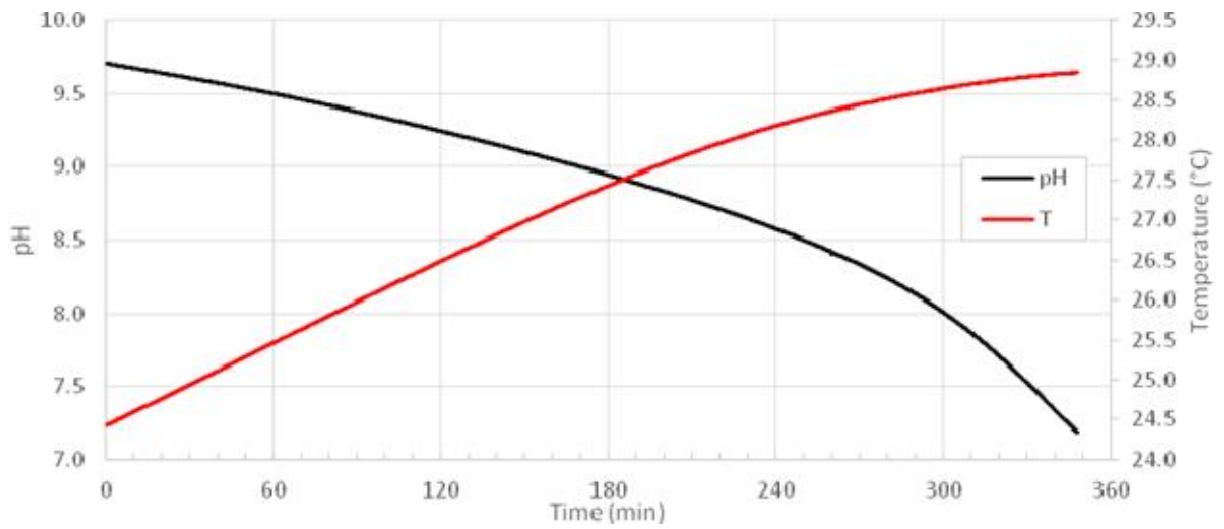


Figure 1. Recorded pH and temperature during the test 1

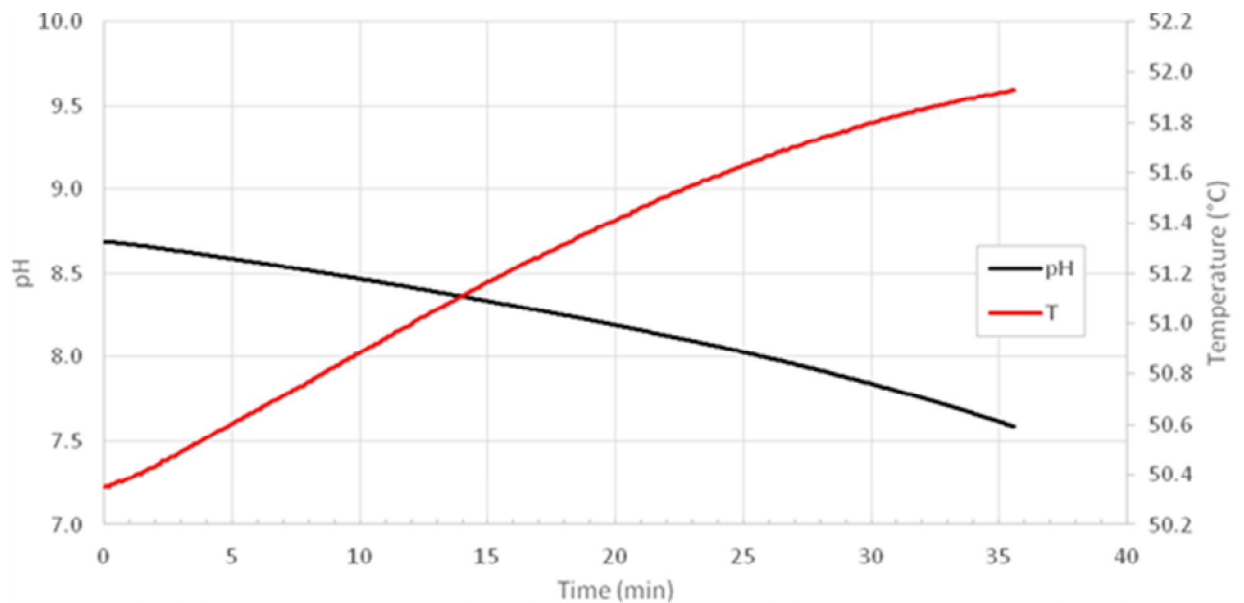


Figure 3. Recorded pH and temperature during the test 2

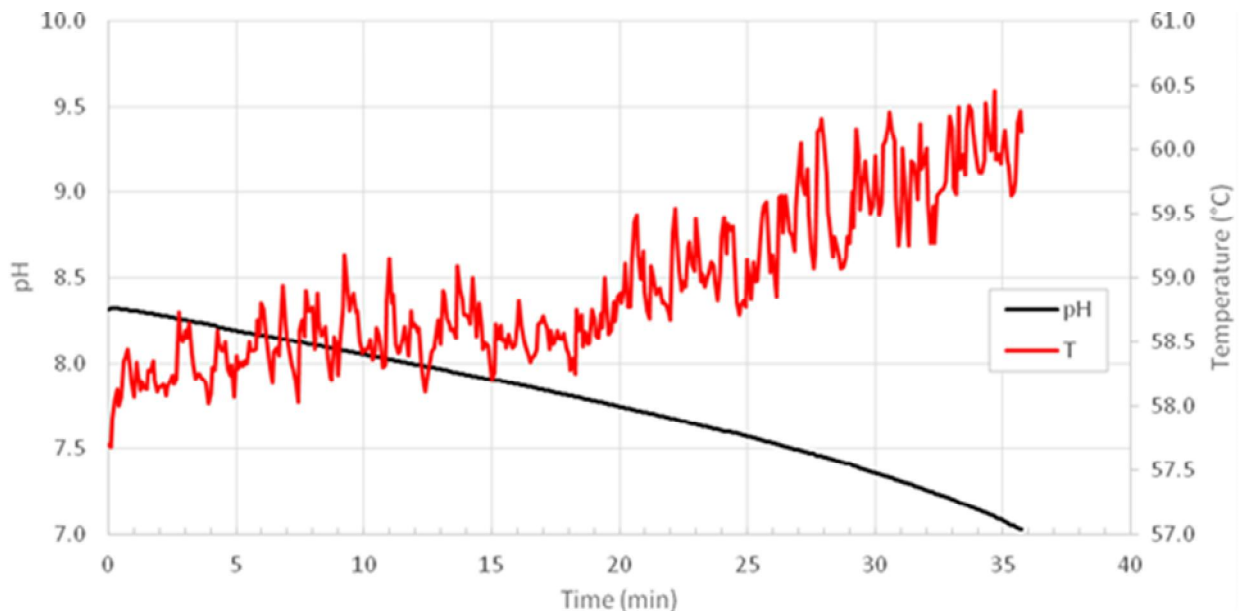


Figure 4. Recorded pH and temperature during the test 3 pilot plant test

The SEM micrographs taken of PCC samples from each of the pilot plant tests show in Figure 5. Due to the very long duration of the test 1, a few additional samples were taken during the course of carbonation to look at how the morphology changed over time. When these samples were taken from the reactor, the solution was quite transparent and contained very few solids. After some minutes, the sample began to turn cloudy indicating PCC was precipitating. A sample taken during the test 1 after 270 minutes of carbonation (pH 8.3) indicated that the PCC precipitating was spherical vaterite of approximately 10 μm (a). At the end of carbonation, a mixture of rhombohedral calcite and cotton wool ball-like structures of presumably vaterite were formed (b). The attempt to make scalenohedral calcite according to Kroc & Fairchild, rather than producing scalenohedral PCC, instead yielded large agglomerates of a variety of crystals morphologies including spherical and disclike vaterite, rhombohedral calcite, as well as aragonite (c-d). The aragonite test was



more successful, yielding essentially 100% aragonite needles of various sizes, ranging from 2-50 μm in length and maximum width of around 3 μm (e-f).

While the test at 58°C (test 3) in the pilot plant successfully produced aragonite, neither the test 1 nor the test 2 at 50°C using the conditions of Kroc & Fairchild produced the scalenohedral PCC morphology.

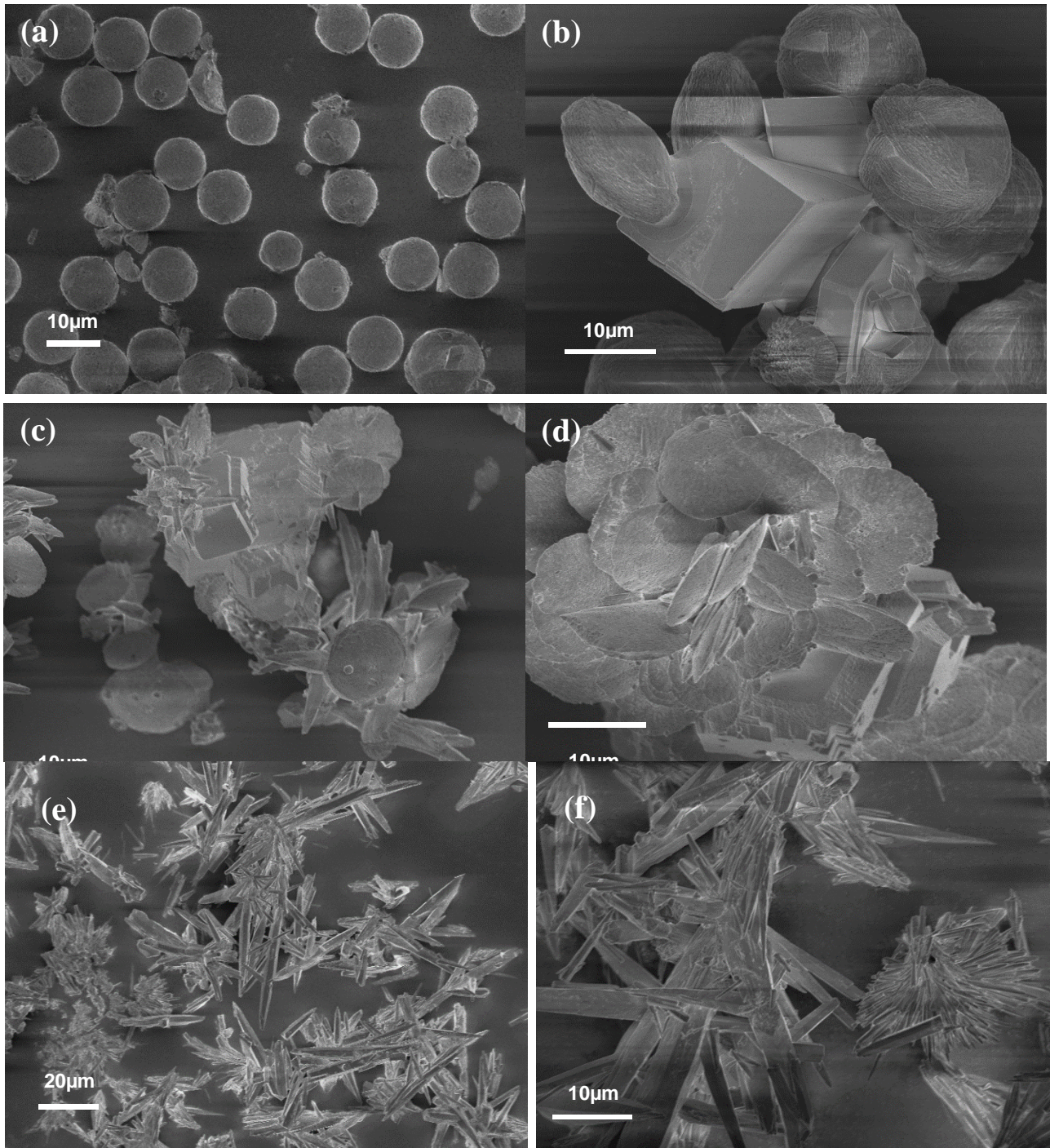


Figure 5 – SEM micrographs from pilot plant tests a) test1, sample taken after 270 min, pH 8.3, 1000x b) tests 1, samples taken after carbonation stopped, pH 7.1, 1750x c) test2, 1000x, d) test 2, 1500x, e) test 3, 500x, f) test 3, 2000x



6 Discussion

6.1.1 Agitator Design

During commissioning of the pilot plant it was found that the outlet of the extraction reactor would continuously block with solid material preventing normal drainage. This was because the coarse slag solids were settling to the bottom of the reactor, even with agitation at the maximum setting of 170 rpm. Not only did the settled slag cause blockages, but it would also reduce the calcium extraction efficiency as the mass transfer from solid to liquid would be significantly impaired. To try to alleviate the problem, subsequent slag was sieved through a 250 μm sieve before being added to the reactor. This reduced the frequency of blockages, but grinding the slag particles to 250 μm requires more energy than grinding to 1mm and this should be taken into account in the overall process.

6.1.2 Ammonia Release

During the commissioning stage of the pilot plant equipment it was noticed that a considerable amount of NH_3 gas was being given off by the solvent solution during and after the calcium extraction stage. If not recaptured, this loss of NH_3 will gradually weaken the strength of the solvent and reduce the calcium extraction efficiency. Mannisto [3] tried to quantify the loss of NH_3 experimentally during carbonation tests using 500 mL of 2 M NH_4NO_3 and NH_4Cl solvents, with a fixed gas flow of 2 L/min and different CO_2 concentrations. Bubbling CO_2/N_2 gas through the carbonation solution effectively acts a stripping operation, and so NH_3 losses may be high. He found that for CO_2 concentrations from 25-100% the loss of NH_3 in each case was below 1 wt%, and that in fact the loss of water from the solution as vapour was 2-3 times higher. No studies have been done to quantify the loss of NH_3 during extraction, but it is likely to be lower than from carbonation as there is no gas-liquid mixing and hence there will be no stripping effect.

6.1.3 Copper Compatibility

During test work with the pilot plant it was noticed that the Ca-rich solution leaving the ER and filters would at times take on a deep blue colour, which was particularly strong when residual extraction solution was left in the system for several hours or days. After some investigation



it was theorised that the deep blue colour was due to the complex ion $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, formed from the reaction between NH_3 and copper ions resulting from chemical attack of brass components in the system. In aqueous solutions copper ions are actually present 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 addition of acid to the deep blue solution, which converted the copper-ammonium complex back to the characteristic pale blue hexaaquacopper (II) ion. Final proof came from the addition of NaOH to the pale blue solution which precipitated insoluble light blue copper(II) hydroxide dihydrate. This also explained the presence of a light blue scale observed around the extraction filters. From these findings it was concluded that no copper-containing materials should be used in the Slag2PCC system due to the incompatibility of copper with the NH_4Cl solvent and the brass components (mainly drain valves and threaded connections in the extraction filters).

7 References

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