

PCC production from steel mill slag, update

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Appendices

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PCC saostusprosessin mallinnus, 12148-ORC-T

Project number

10018731

Key words

PCC, ammonium chloride, steel mill slag, carbonation

Avainsanat

PCC, ammonium kloridi, terästehtaan kuona, karbonointi

Abstract

This report presents the calculation of precipitated calcium carbonate (PCC) production from steel mill slag. This work is part of Carbon Capture and Storage Program (CCSP) research program. The plant capacity in these calculations was 130 000 t/a. In this Slag2PCC process calcium is leached from steel plant slag with ammonium chloride solution and the produced ammonia and calcium chloride is put to the carbonator with flue gas containing 22 vol-% carbon dioxide. In the carbonator PCC is precipitated and solution containing ammonium chloride is recycled back to the slag leaching.

This work concentrated on the individual process steps and what is the main uncertainties about them. The main problems that need to be solved were: Carbonator gas input amount and its effect to the process, PCC crystal shape and its usability to for the customers and the filtering and grinding of produced PCC.

Gas feed to the carbonator is a lot bigger than maximum gas feed to the conventional reactor. The conventional PCC production process this is not a problem probably due to the constant high pH at the process. In Slag2PCC process the pH will drop during the precipitation of PCC and this might cause the need for better CO₂ mass transfer from gas to liquid.

The PCC crystal shape that is produced in the bigger scale test work is not what originally wanted and the particle size is a lot bigger. Big particles can be grounded smaller, but the crystal shape might effect to the usability of the PCC. Also the grinding will have effect on the crystal shape.

The environmental footprint was calculated for the process. It was found out that the global warming potential (GWP) is -27.6 kt/a CO₂-equivalent for the process. It was about half of CO₂ that is captured to the PCC since the process cause CO₂-equivalent emissions mainly due to the energy consumption. This calculation gives a good base for further developing more environmental process.



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1. Introduction

This report presents update for the PCC production model from steel mill slag. The process uses NH_4Cl solution and calcium is leached from steel mill slag. The carbon dioxide is taken from the calcining drum gas.

This work was carried out in the Carbon Capture and Storage Program (CCSP) research program coordinated by CLEEN Ltd. with funding from the Finnish Funding Agency for Technology and Innovation, Tekes.

2. Process description

This process description is intentionally short and concentrates on the issues that have biggest impact on the profitability of the process. A more detailed process description is presented in the previous report [1]. The case being studied is similar to the case presented by Teir [2]. In this case, the required PCC production is 130 000 t/h and the operating time is 6257 h/a (means that the plant operates in three shifts with weekend interruption).

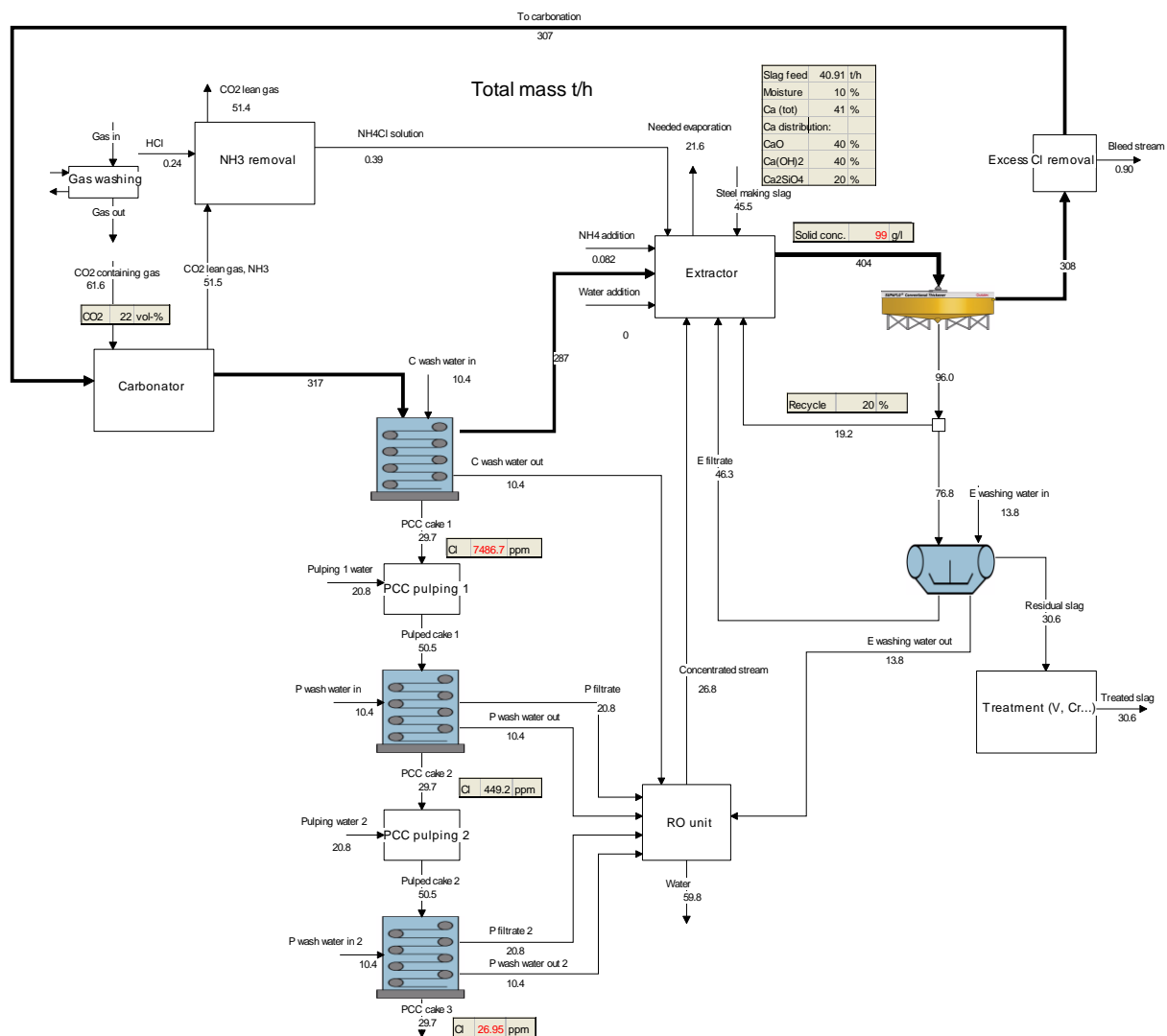


Figure 1. Process flowsheet. The PCC filtration and filter water treatment can be handled differently, in here is presented just one option.

Table 1. Overview of main process data.

Equipment	Value		Comment or reference
Extraction			
Ammonium concentration in evaporation input	30	g/l	In extraction output 9 g/l
Calcium reaction rate	50	%	Assumption based on Rinne [3]: 55-60% extraction in 2 M ammonium salt solutions
Solid concentration	100	g/l	
Thickener underflow solids	500	g/l	Thickening test 1/2012 [1]
Underflow recycle to reactor	20	%	
Filter cake moisture	10	%	Filtration test 1/2012 [1]
Filter washing efficiency	80	%	Filtration test 1/2012 [1]
Filter washing water amount	0.5	m ³ /t s.m.	Filtration test 1/2012 [1]
Carbonator			
Temperature	25	°C	
CO ₂ in the feed	22	vol-%	
CO ₂ reaction rate	50	%	
Ammonia evaporation	0.5	%	Ammonium ion not included
Needed cooling	6.2	MW	
PCC production	20.8	t/h	130 000 t/a
PCC filtration and washing			
Filter cake moisture	30	%	Values for the first filter Estimated, In [5] it was 40%, but no air drying were performed
Filter washing efficiency	80	%	
Filter washing water amount	0.5	m ³ /t s.m.	
Pretreatment of CO₂ gas			
Temperature	80-120	°C	Washing, not needed in this case 100 °C used in calculation
Moisture content	6	vol-%	
Temperature	50	°C	After pipe to the plant, estimated pipe length is 600-1200 m.*
Reverse osmosis unit			
Concentration of recovered solution	60	g/L	All salts in the solution
Recovery efficiency	100	%	Assumed that all salts go to concentrate, in reality the water needs also purification.
Evaporation			
Evaporated water	21.6	t/h	Calculated value
Needed steam	7.2	t/h	Three stage evaporator

* In calculation pipe diameter was 1.2 m, inside the pipe was air at 5 bar, air velocity was 20 m/s, initial temperature was 100°C, pipe material was AISI 110, pipe wall thickness was 6 mm, outside was air at 1 bar at 15°C. After 1000 m the gas inside the pipe is at 50°C. To get the gas temperature to 40°C the pipe length needs to be 1500 m.

2.1. Process solution

Process solution contains NH_4Cl 106 g/l (2 M). The process solution will transport the calcium from extraction to carbonation and there PCC will be precipitated. In the model 30 g/l Ca can be precipitated from the solution leaving 13 g/l Ca to the extraction feed. This gives solid concentration of 72 g/l (6.6 wt-%) in the extraction. The solution flow through the process is 288 m³/h.

2.2. Extractor

Steel making slag is fed to the extractor where the calcium from the slag will react with the process solution and calcium is leached. The solid concentration was 100 g/l after the extractor and half of the calcium will be leached.

2.3. Carbonator

Carbonator operates with 22 vol-% CO_2 gas from the calcining drum and the CO_2 efficiency is 50 %. This leads to quite large gas volumes. From Table 2 you can see that the gas volume to the carbonator is over twice what is recommended to feed to the flotation cell. However this is a normal way to operate the carbonator in a conventional PCC production. This means that the gas bubbles in a conventional PCC production are very big and they are not even tried to disperse to the solution.

The pH is a probably reason why the conventional PCC production can operate with such conditions. The solution in a conventional PCC production facility is $\text{Ca}(\text{OH})_2$ slurry with solid $\text{Ca}(\text{OH})_2$ particles and therefore pH will stay between 11 and 12 during the whole precipitation. Solid $\text{Ca}(\text{OH})_2$ will dissolve when some of alkali in solution is spend. In this new process all alkali is in the solution and the pH will drop as the PCC is precipitated, see Figure 2. The CO_2 in the gas is base and very likely therefore the gas liquid surface does not have to be a big as in other processes where gas needs to be dissolved into the solution.

Table 2. Gas volumes that various 200 m³ reactors can handle. Conventional mixing reactor is calculated with 20% gas hold up, 1 cm/s rise rate of gas bubbles and 3 m depth of the reactor.

Conventional mechanical mixing reactor	480	Nm ³ /h
Flotation cell	15000	Nm ³ /h
Fed gas volume to the carbonator	52400	Nm ³ /h

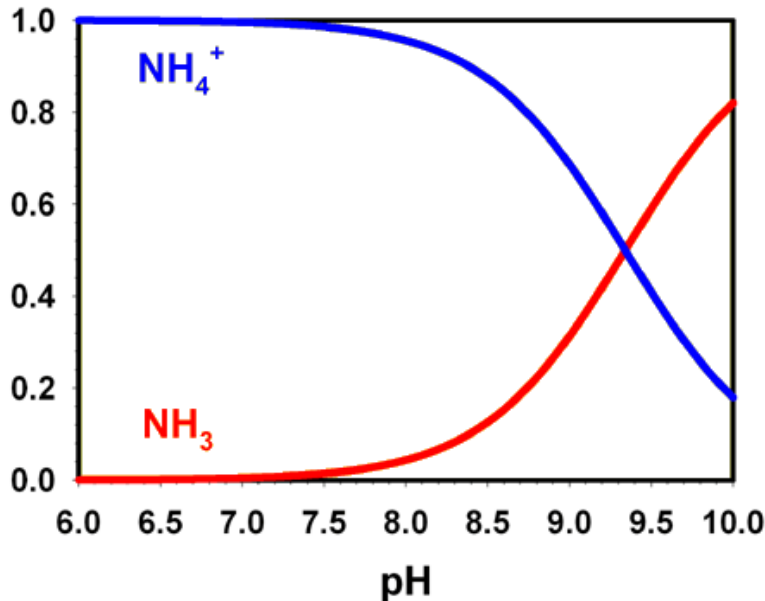


Figure 2. Relationship between pH and ammonia concentration in pure water. When 20% of ammonia is reacted the pH will be about 10.

The temperature of the gas fed to the carbonator has an effect on the carbonator energy balance. Now the temperature is 50°C and this is reached with just a pipe if the outside temperature is 15°C, see the initial values for the calculation from Table 1. This means that during rain and winter the gas temperature will be significantly lower. If the gas temperature is 25°C the carbonator cooling energy consumption will be about 1 MW lower. Moisture will start to condensate to the pipe at about 35°C temperature.

2.4. NH_3 removal from carbonator gases

Ammonia in the carbonator off gas needs to be washed with acidic solution since the ammonia gas has relatively big partial pressure even at low temperatures. In the current calculation the ammonia partial pressure after the carbonator is 122 Pa. If the gases are washed in the scrubber with water at 25°C and the ammonia water concentration is allowed to rise to 0.5 wt-% (5 g/l, 0.12 M) with circulating the same water we can extrapolate from Figure 3 that the ammonia partial pressure in such system would be above 1000 Pa. This is far more than initial ammonia partial pressure from the carbonation and means that the allowed maximum ammonia concentration in the scrubber would never be reached and all ammonia would be lost with the gases exiting the scrubber. This phenomenon can be explained with significant partial pressure that ammonia has even in low temperatures. The gas flow would strip the ammonia from the scrubber water in a similar way as described in articles [8] and [9]. The acidic washing is the only option to capture small ammonia concentrations from gases and ensure the ammonia free outlet gas.

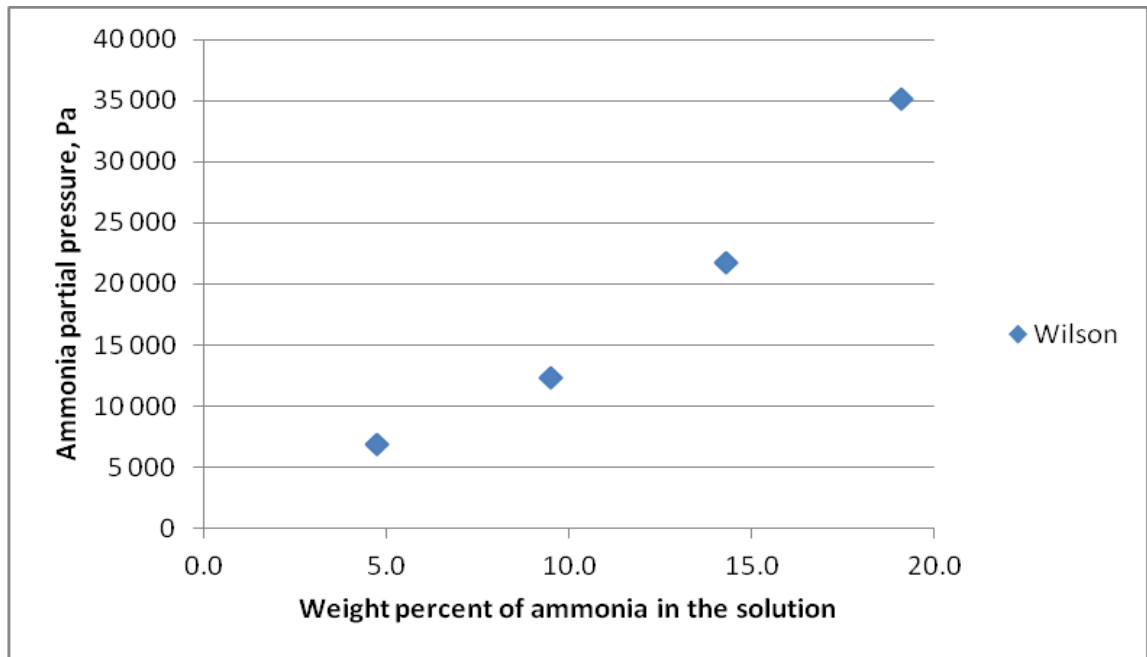


Figure 3. Ammonia gas partial pressure above the solution in the water-ammonia system [7].

2.5. PCC filtration

Filtration of PCC is the most expensive part of the process since the chloride containing solution needs to be washed from the solids [1]. The other problem is that a small particle size is not easy to produce with this process. The particle size of PCC should be about 1 μm and in laboratory produced PCC the particle size has been about 20 μm from large batches [6]. The washing of PCC is more difficult if the particle size is smaller.

To solve these problems Janne Kauppi proposed that the PCC would be grinded after filtration. The advantage would be easier washing and filtration of PCC (=smaller equipment and smaller end chloride concentration in the PCC). Also making of smaller PCC particles in laboratory scale means lower temperature, smaller Ca^{2+} and NH_4^+ concentration, smaller CO_2 flow and more intensive agitation according to Zappa [6]. All of those have a big effect on the process economy and very likely they would make the process uneconomical. The grinding equipment for this duty would be based on shear forces since the particles are soft and power need is small. According to Kauppi this kind of equipment are already in use in conventional production of PCC.

The estimated EPC cost of PCC filtration plant is about 17 million euros.

3. Environmental impact of research results

The environmental footprint of the process was calculated with GaBi program. The results are presented as yearly emissions and initial values are as hourly basis (8000 h/a). The PCC production was 130000 t/a. Table 3 presents the information fed to GaBi.

Table 3. Data used in environmental footprint calculation.

Material	Comment	Value	Unit
Carbon dioxide	CO ₂ from flue gas captured by the PCC production process	7140	kg/h
Electricity for carbonator cooling		6.2	MW
Electricity for pumps, agitators, ...	Estimated	0.85	MW
Hydrochloric acid (33%)		184	kg/h
Ammonium chloride		65	kg/h
Steam for evaporation	From heavy oil fired burners	2500	kg/h
Steam for evaporation	From steel mill	2500	kg/h
Water (tap water)		20	t/h
Slag	For landfill	21.5	t/h
Waste water	Estimated	10	t/h
PCC transportation, dry mass	50 % slurry, 40 km, 50 t/truck	16.3	t/h

Steam from steel mill did not have environmental impact in the calculation and ammonium chloride was left out from the calculation since it was not found from the GaBi database.

The yearly value for global warming potential (GWP) was -27.6 kt CO₂-equivalent for this case. The impact of different reagents and consumable is presented in Figure 3. The same calculation for acidification potential (AP) is presented in Figure 4.

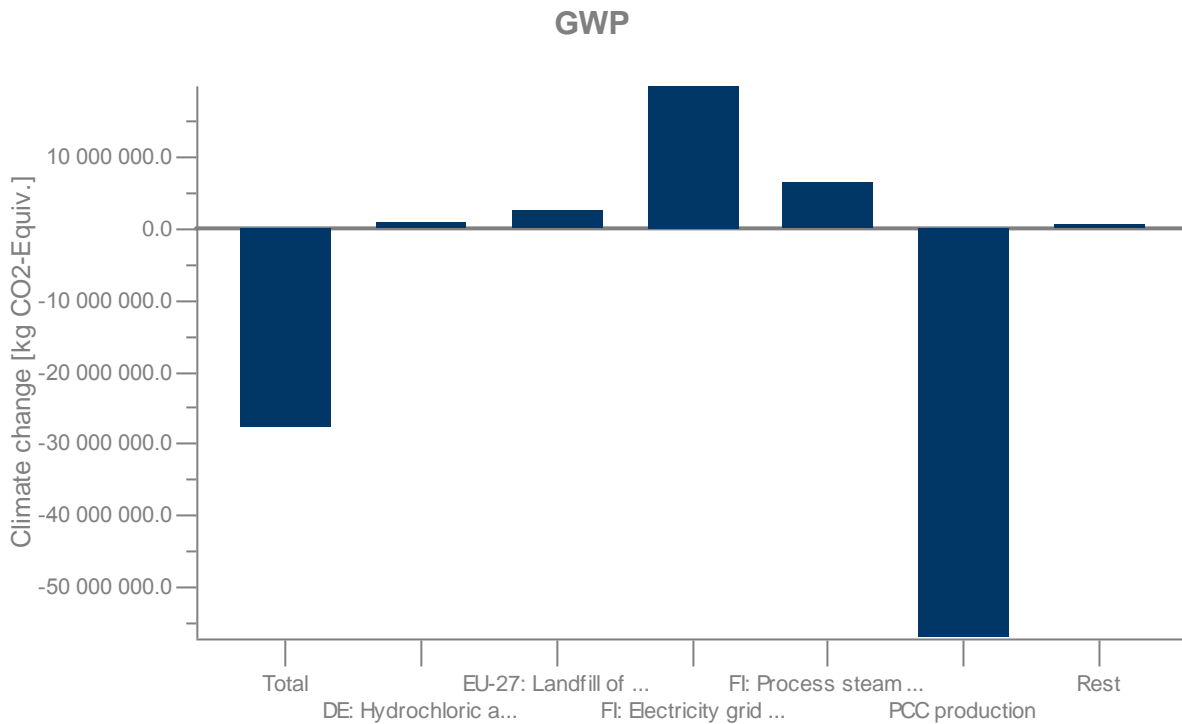


Figure 3. Global warming potential of PCC production process. From the left after total is hydrochloric acid, landfill of slag, electricity consumption, steam consumption and PCC production.

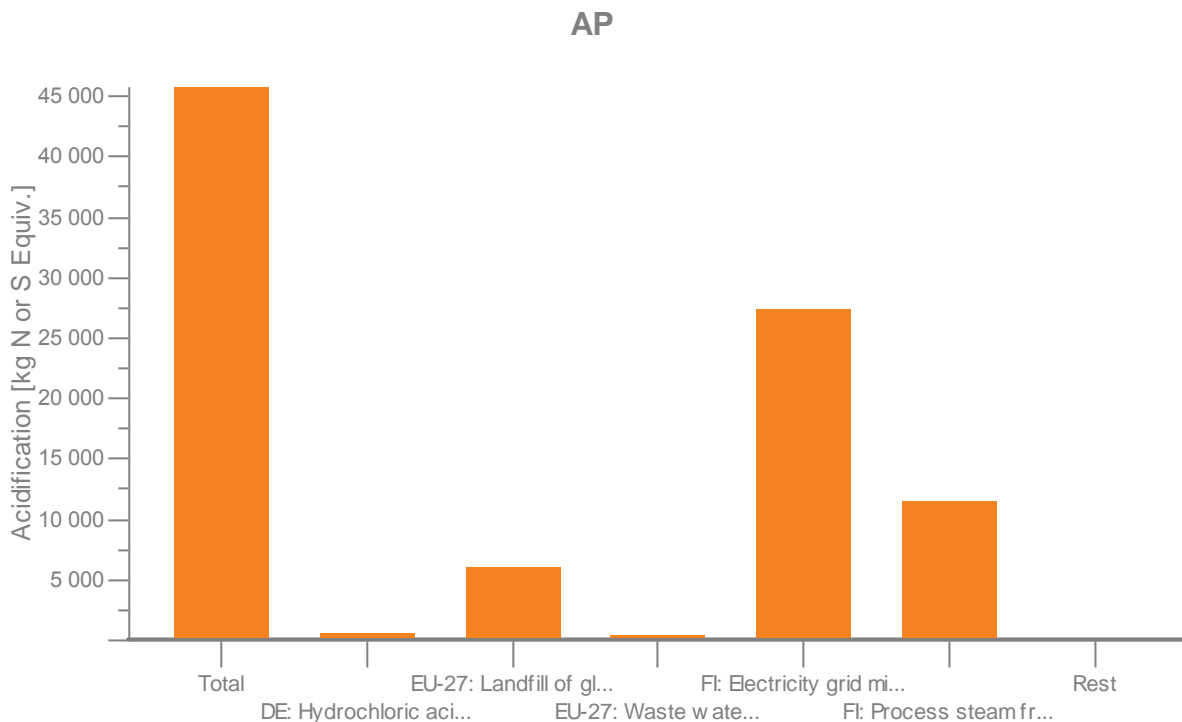


Figure 4. Acidification potential. From the left after total is hydrochloric acid, landfill of slag, waste water treatment, electricity consumption and stream consumption.

From the GWP we can see that PCC production reduces the CO₂ emissions, but half of captured CO₂ will be discharged due to the utilities used in the process. These figures help to identify where the emissions are created and where they can be reduced.

The electricity consumption causes the main emissions and it is mainly consumed in cooling of carbonator. The cooling of carbonator was assumed to be made with electricity since the carbonation needs 25 °C temperature and it is too low for use of more economical ways to cool the liquid. If the temperature can be increased to about 40 °C the electric cooling can be replaced with cooling towers or cooling with sea water.

The second big emission source is steam production. Steam is used in evaporation of water from the process solution. The evaporation need can be reduced if the water inputs can be reduced to the process. However this might be difficult since solid materials needs to be washed and other water sources are quite small. The emissions caused by the steam are calculated so that half is assumed to come from heavy oil fired burners and half does not cause emissions since it comes from steel mill. In reality steam is coming from the steel mill, but it is hard to estimate the emissions of steam produced in a steel mill since steel mill has many other products.

4. Conclusions and recommendations for the experimental work at Aalto

The process seems to be economical if price for carbon dioxide emissions is big enough. However there are few issues that need more testing before we can be confident that the process can be build. One thing is that the process needs to be piloted in a continuous operated test setup with big enough scale. Aalto University has taken the first step in that direction, but apparently they operate the equipment with too dilute solution: the scale of

their reactors is two hundred liters, which is big enough, but they get only about five kilograms of PCC per cycle. This is either caused by operational difficulties (recovery of material difficult) or a dilute solution is used for avoiding problems. It is important to test the calculated operation conditions since then we know what kind of problems we are going to have in a bigger scale plant. Zappa [6] presented some test equipment related problem in his master's thesis, but only few process related problems, mainly about the particle size and shape.

Dilute ammonium chloride solution is not economical. For example the ammonium chloride concentration will define the solution amount in the circulation. If the NH_4Cl concentration would be 0.01 M, like Zappa [1] proposed as one solution for the problems, the needed solution flow for the same PCC production would be approximately 44500 m^3/h , i.e. 200 times the solvent volume used in this case study. This would require much larger equipment leading to much higher investment cost. By raising the ammonium chloride concentration the needed solution flow will decrease, but also the solid concentration will increase, making the process possibly more difficult to handle. Most of the tests so far have been focusing on a small solid concentration.

The precipitation of PCC needs a lot of carbon dioxide. Commercially operated PCC production uses flue gases that contain about 20 vol-% CO_2 . It is bubbled through $\text{Ca}(\text{OH})_2$ slurry to produce PCC. In Slag2PCC process there have been indications that the bubble size might need to be smaller than in the commercial operated PCC production. For example Zappa [1] proposed to increase the agitation speed to produce smaller PCC. Also the bigger scale tests in Aalto are very likely made with very small CO_2 feed and therefore also the bubble size in the carbonator reactor is small. It would be interesting to see the carbonator operated at high concentrations and CO_2 fed as 22 vol-% strong.

Since the gas amount is so big in the commercial scale plant it is very important to notice that if in laboratory experiments the process works only if the CO_2 gas is well dispersed (to bubbles, which rise about 1 cm/s) to the solution it means that we cannot use same kind of carbonators than in conventional PCC production. The carbonator volume with conventional mechanical mixing reactors would be in worst case 70 times bigger than in conventional PCC production.

The particle size of the produced PCC from the larger scale experiments is currently too big for the end user. However, it can be ground to smaller size after filtration. Filtration and washing would be a lot simpler if the particle size is bigger.

5. Further measures

Currently there are three issues that need to be solved:

- Can we feed the needed amount of gas to the carbonator? If the bubble size needs to be very small then the reactor size will be very big and the process is not economically viable.
- Are the currently produced PCC crystal shapes acceptable for the end user? Currently, rhombohedral and aragonitic PCC can be produced with a relatively large particle size (20-40 μm). Although the particles can be ground smaller, particle shape might be unfavourable, as scalenohedral PCC is needed for paper filler purposes. Grinding will also change the crystal shape of PCC particles.
- Filtration and grinding of PCC has not been tested. It should be tested to get information what kind of end product we can get. Grinding is hard to test with small scale laboratory equipment since usually they produce more fine particles than bigger equipment.

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