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Water management and separation technologies for serpentinite carbonation and for PCC production from steelmaking slag

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Report Title: D512 – Water management and separation technologies for serpentinite carbonation and for PCC production from steelmaking slag

Keywords: mineral carbonation, precipitated calcium carbonate, water management, liquid/solid separations

Executive summary

In this report the handling of aqueous streams in two processes for CO_2 mineral sequestration under development in Finland is addressed, being the so-called "ÅA route" for stepwise serpentinite carbonation, and the so-called "slag2pcc" for the production of precipitated calcium carbonate (PCC) from steel converter slag. For both processes brief descriptions are given.

For the "ÅA route" the fact that incoming serpentinite rock typically contains 10-15 %-wt crystal water gives room for losses during filtration and other processing. The high solubility of ammonium and sulphate in water gives the risk of losses of these: ammonium sulphate, being used as a "flux" for extracting magnesium from the rock should be recovered for re-use at close to 100%. Water amounts used should be kept to a minimum, although washing and drying solid products and residues may require additional water processing. Also, the iron content of the rock has great impact on water amounts necessary. Inclined settlers (to be tested!) may be useful for removing solid particles and precipitates from the aqueous streams. Filters may be necessary for final dewatering.

For the "slag2pcc" route, pH control is of great importance, as it will determine calcium extraction from steelmaking slag as well as the precipitation of PCC, not to mention its quality. Inclined settlers have been proven successful for removal of not only spent slag but also of the much finer PCC particles from the aqueous solvent streams. Nonetheless, filter elements are preferably used between the process sections as "absolute filters" that trap small amounts of material, to prevent slag particles from entering the precipitation section and PCC particles from entering the extraction section. Amounts of water used increase the amount of ammonia that will be dissolved as compared vapour phase ammonia. Again, filters may be necessary for final dewatering. The use of ion selective electrodes for on-line measurement (for process control) will not succeed as a result of slow response times, detection limits and cross-ion distortion effects.

For both processes described, hydrocyclones would offer an interesting alternative, but at the current scale of operation of the test facilities these cannot be obtained in a size that would give good separations.

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1. Introduction and scope.

CO_2 mineral sequestration becomes increasingly important as part of the CO_2 emissions mitigation and CCS (carbon capture and storage) portfolio. For Finland, it is accepted that the more "conventional" option of compressed CO_2 storage in underground formations cannot be considered due to a lack of such formations, while this approach furthermore suffers from difficulties related to CO_2 separation from flue gases, not to mention public acceptance and long-term liability issues.

At the same time, magnesium silicate mineral resources are large in Finland and many other countries worldwide. The advantages of CO_2 mineral sequestration (more than enough CCS capacity, overall heat-generating chemistry, stable product i.e. no risk for leakage, the possibility to process CO_2-containing gases directly, without a need for CO_2 separation, uses for solid product) have been well documented. Long-term storage of CO_2 using magnesium silicate minerals has been under investigation in Finland for more than ten years, with Åbo Akademi (ÅA) currently as the centre of these activities (for example, hosting the recent ACEME10 conference: www.abo.fi/aceme10), in cooperation with Aalto University/Energy Technology (Aalto/TKK) and other partners in the Cleen Oy CCSP project, besides a range of international partners.

The current status is a staged process route for magnesium silicate carbonation that involves 1) production of Mg-hydroxide from the magnesium silicate mineral and 2) carbonation of the Mg-hydroxide to Mg-carbonate. Special for the ÅA route is that the carbonation is done in a pressurised fluidised bed (PFB) reactor, at 450-550°C, CO_2 pressures above 20 bar so that the carbonation reaction heat is obtained in a valuable form, improving energy efficiency. The method uses ammonium sulphate (which is recovered for re-use later in the process) for the extraction of Mg and produce $Mg(OH)_2$. Significant amounts of iron oxides by-product are obtained, a potential feedstock for iron/steel making. (Nduagu et al., 2012a, 2012b, Fagerlund et al., 2012, Romão et al., 2012,Fagerlund and Zevenhoven, 2011, Fagerlund,2012, Nduagu, 2012).

A process schematic for this serpentinite carbonation route is given below as **Figure 1**.

The development work is so far focussing on Finnish rock (mining tailings) from a nickel mine at Hitura, whilst cooperation with international partners (incl. Singapore) involves minerals from Lithuania, Australia, Norway and Portugal. Other Finnish minerals are being considered as well, such as minerals from Vammala (less than 100 km east of Meri-Pori!) and Suomusjärvi (Zevenhoven et al., 2012). The work addresses overall energy efficiency, recovery of chemical additives and scale-up towards demonstration in Finland, Singapore and/or Portugal (Romão et al., 2011, Khoo et al., 2011).

As a spin-off of this work on large-scale CO_2 sequestration, also the fixation of CO_2 in industrial by-products and residues is being investigated at ÅA (again, in cooperation with Aalto/TKK and the other Cleen CCSP partners). This primarily involves calcium-containing slags from iron- and steelmaking. These may be converted into valuable carbonate materials, preferably high-grade precipitated calcium carbonate (PCC) that may find use in papermaking. The process operates at ambient temperature and pressure. Current work involves the scale-up to demonstration scale, with integration of the reactors and recovery and re-use of the ammonium salt used as main challenges. Large- and small-scale demonstration units are being built or taken into use at Aalto and ÅA, respectively.

A process schematic for the "slag2pcc" process is given below as **Figure 10**.

A specific set of tasks that is becoming more and more urgent is related to process- and waste water management and the handling of aqueous flows. This is the subject of this report, addressing both CO_2 mineralisation process routes.

2. Topics to be addressed:

Topics to be addressed in this report are:

- The use of water for $Mg(OH)_2$ production from magnesium silicate rocks, the recovery of water during the carbonation of $Mg(OH)_2$ and the handling of the water that is produced overall.
- Water released during the compression of flue gas and expansion of post-carbonation flue gas.
- The separation of ammonium sulphate from an aqueous stream, so that the salt can be re-used (crystallization, mechanical vapour recompression, …)
- The design of filtration devices and process units for water cleaning and separation of water from pollutants or chemicals to be recovered using membranes, mechanical or thermal methods.
- The coupling of two aqueous-solutions reactors for the steelmaking slag to PCC route, avoiding that the solutions become mixed. This involves the use of pumps combined with filters, membranes or other separators, like inclined settlers.
- Use of water for washing the solid products, improving their quality/purity and as a final recovery of chemical additives.
- Aqueous solution concentration, acidity and ion strength measurement and control.

3. Carbonation of Mg-silicate-based rock for large-scale CCS

3.1 Process description

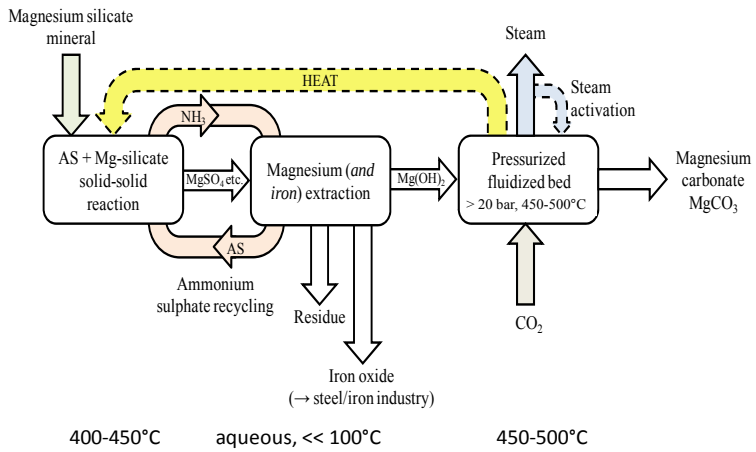

Fig. 1 Pathway for magnesium silicate-based rock carbonation: ÅA route

Figure 1 summarises the three stages of the ÅA route for magnesium silicate-based rock (preferably serpentinite, mainly containing serpentine, $3MgO{\cdot}2SiO_2{\cdot}2H_2O$, besides iron oxides and other minerals)

Stage 1: The serpentinite rock reacts with ammonium sulphate (AS) or bisulphate (ABS) and (beneficial for some rock types) some added water at 400-450°C (sometimes up to 500°C) and atmospheric pressure in order to produce XSO_4 salts (X=Mg,Ca,Fe), as first described by Nduagu et al. (2012 a,b). During the reaction considerable amounts of NH_3 (and, if temperature is so high that AS / ABS decomposition is significant, SO_3) and water are released.

The chemical reaction aimed at is:

$$Mg_3Si_2O_5(OH)_4\,(s) + 3(NH_4)_2SO_4\,(s) \rightarrow 3MgSO_4\,(s) + 2SiO_2\,(s) + 5H_2O\,(g) + 6NH_3\,(g) \quad \text{(R1)}$$

besides sulphate-forming reactions of iron and other species:

$$FeO\,(s) + (NH_4)_2SO_4\,(s) \rightarrow FeSO_4\,(s) + H_2O\,(g) + 2NH_3\,(g) \quad \text{(R2)}$$

$$CaSiO_3\,(s) + (NH_4)_2SO_4\,(s) \rightarrow CaSO_4\,(s) + SiO_2\,(s) + H_2O\,(g) + 2NH_3\,(g) \quad \text{(R3)}$$

and the AS thermal decomposition reaction

$$(NH_4)_2SO_4\,(s) \rightarrow SO_3(g) + H_2O\,(g) + 2NH_3\,(g) \quad \text{(R4)}$$

Figure 2 shows the reactors used for this purpose at ÅA (Nduagu, 2012).

Stage 2: The solid products are put in water and the insoluble fraction (mainly unreacted serpentinite and SiO_2) is discarded. The NH_3 produced in the first step is used to raise the pH of the aqueous solution to ~8-9 in order to precipitate the iron and calcium in the form of hydroxides. These are separated and possibly redirected to the steelmaking industry creating the opportunity to reduce the net CO_2 emissions and replace raw materials (Romão et al., 2012). Using the NH_3 produced in the first step, the pH of the aqueous solution is raised further to ~10-12 and the magnesium precipitates to form $Mg(OH)_2$. AS is recovered from the residual solution using a crystallisation process; mechanical vapour recompression (MVR) can give significant energy savings here (Björklöf, 2010).

Fig. 2 Reactors used for solid/solid conversions at ÅA

While stage 2 has so far been accomplished as a series of batch steps, "streamlining" of the aqueous steps is part of near-future work[1] using a set-up as shown in **Figure 3**. Inclined settlers (to be discussed below) will be used for the solid/water streams separations.

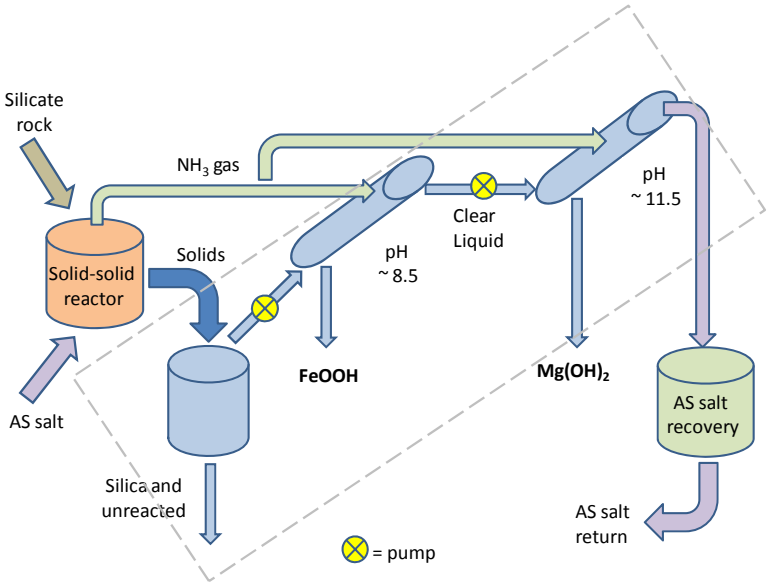

Fig. 3 Future set-up for the precipitation of $Mg(OH)_2$ and by-products at ÅA (to be built in 2013)

[1] Funding from KH Renlund Foundation (2013)

Stage 3: the $Mg(OH)_2$ is carbonated at ~500°C and 20-30 bar CO_2 partial pressure, in a pressurised fluidised bed (PFB) reactor. The carbonation method is described in more detail by Fagerlund (Fagerlund 2012, Fagerlund et al., 2012). Pictures of the test set-up at ÅA are given in **Figure 4**. The gas entering the carbonator may be a pure stream of CO_2 but may also be the entire flue gas from a process. The heat released in the carbonation reactor provides some of the energy needed to heat the serpentinite rock, aiming at an auto-thermal process (Romão et al., 2012).

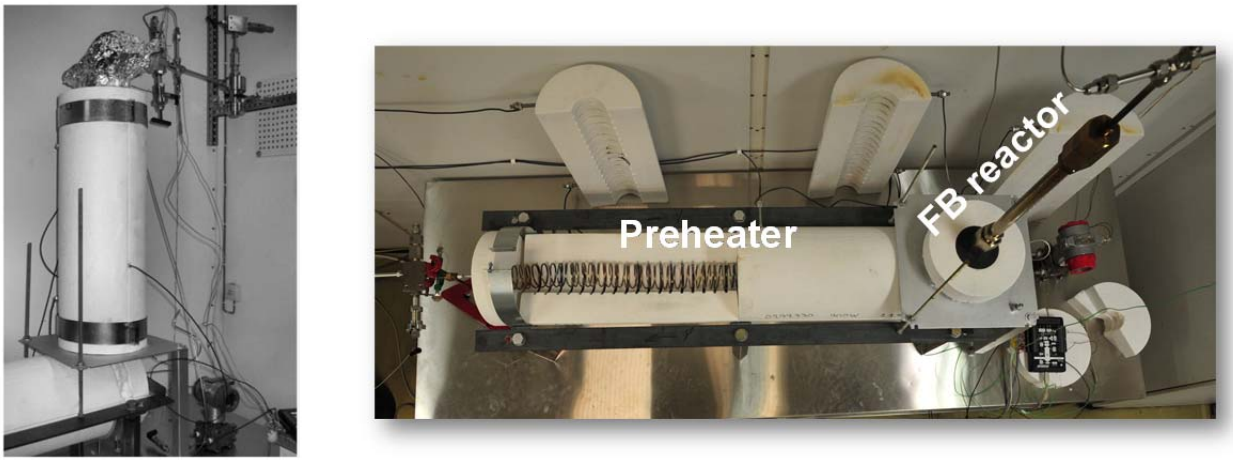

Fig. 4 Reactor used for carbonation conversion at ÅA

Figure 5 shows the solid/solid serpentinite reactor, AS (or ABS) salt regeneration and PFB carbonation reactor in an integrated process scheme; components lists are given in **Table 1** (Slotte et al., 2012)

Table 1 Process main equipment listing for Figure 5. (Slotte et al, 2012)

1	Rock silo
2	Serpentinite heater
3	Ammonium sulphate tank
4	Ammonium sulphate solution pump
5	Water tank
6	Water pump
7	Serpentinite reactor
8	Reacted serpentinite heat recovery heat exchanger
9	Dissolution tank
10	Slurry pump
11	Solids filter
12	Precipitation tank 1 (crystallizer)
13	Precipitate slurry 1 pump
14	Precipitate filter 1
15	Precipitation tank 2 (crystallizer)
16	Precipitate slurry 2 pump
17	Precipitation filter 2
18	Magnesium hydroxide heater
19	Magnesium hydroxide intermediate silo
20	Magnesium hydroxide feeder silo

21	Exhaust gas cooler
22	Exhaust gas compressor with inter coolers
23	Exhaust gas heater
24	Fluidized bed reactor (bubbling/circulating)
25	Particle separation cyclone
26	Exhaust gas expansion turbine
27	Exhaust gas heat recovery heat exchanger
28	Reaction gas recovery fan
29	Reaction gas cooler
30	Reaction gas condenser fan
31	Reaction gas condenser (scrubber)
32	Ammonium solution pump
33	Ammonium solution cooler
34	Ammonium solution dosing pump 1
35	Ammonium solution dosing pump 2
36	Ammonium sulphate regeneration
37	Regenerated ammonium sulphate solution pump
38	Steam condenser
39	Water pump

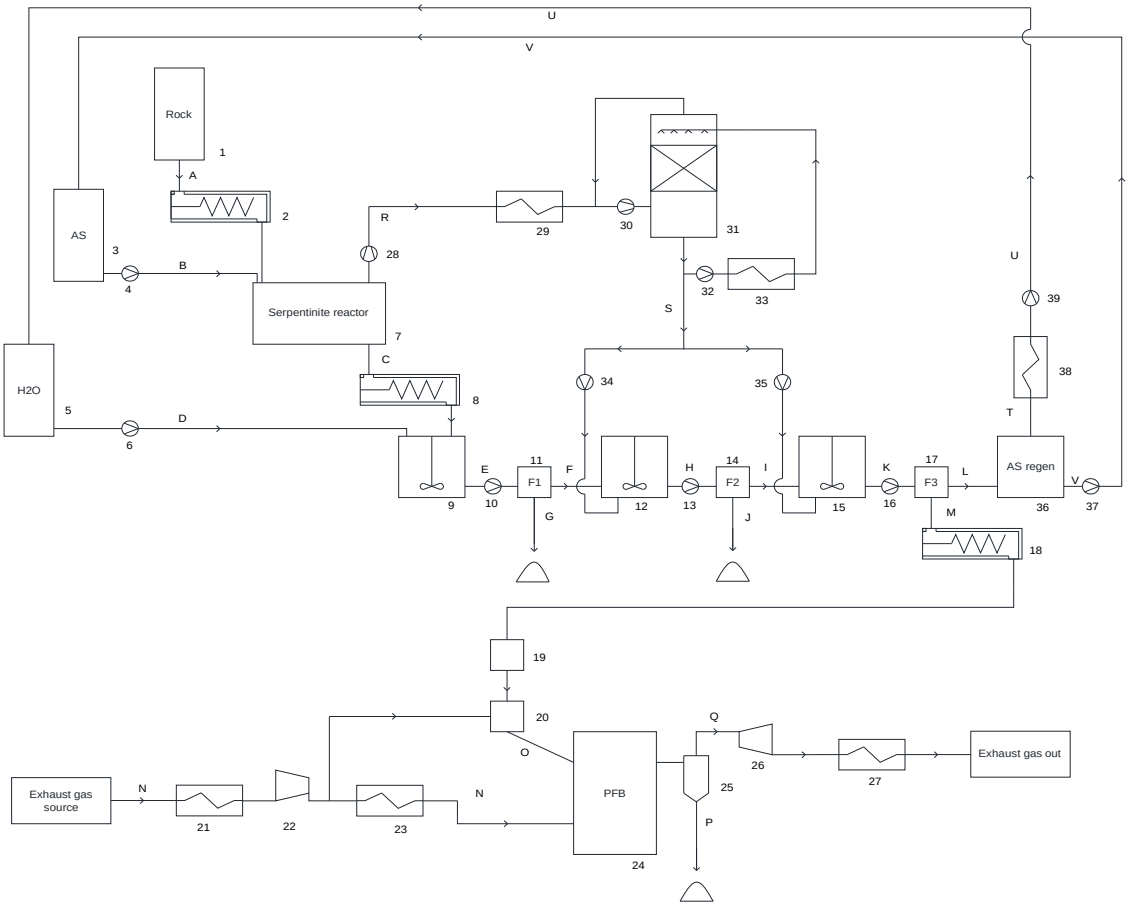

Fig. 5 Pilot plant P&I diagram (numbers explained in Table 1). (Slotte et al, 2012)

3.2 Water vapour release during the Mg-extraction solid/solid reaction

Serpentinites and several of the other Mg-silicates contain crystal water, this will be completely or partly released during the Mg extraction with AS or ABS salt. Theoretically, serpentine has a water content of ~13 %-wt. With one ton of CO_2 requiring ~ 3 ton serpentine, ~0.4 ton of water will be released too when carbonating this mineral. Together with NH_3 this will form a hot vapour that is released at the temperature of the solid-solid reaction. Water should be removed at this point in the process as much as possible. Sulphur oxides formation should be avoided, as this merely indicates that the temperature for the solid/solid reactor is too high.

For this large-scale CCS process the quality and purity of the water used is not a very important issue. Using sea water is not an option, however, since accumulation of sodium and alkali in general is unwanted because high solubility will make it accumulate in the aqueous streams. Also, sodium will bind sulphate and precipitate as sodium sulphate, which has a lower solubility than magnesium sulphate. Chlorine is unwanted as well, forming ammonium chloride which may give corrosion.

For dry locations the release of crystal water from serpentine can be a great asset that can improve process economy.

3.3 Water requirements for Mg-salts dissolution after the Mg-extraction reaction

The Mg from the Mg-silicate rock will form Mg-NH_4-sulphates that decompose in water, giving Mg as dissolved $MgSO_4$. Depending on the literature source (presumably as a result of crystal water must be considered or not) the solubility of $MgSO_4$ in water ranges from 260 g/l at 0°C to 738 g/l at 100°C. (CRC, 1983).

Table 2 comprises the data used in the water consumption estimations. Despite the inconsistencies in literature data and the fact that solubility will be affected by the presence of other soluble and insoluble species this gives a first indication for the minimum amount of water needed to dissolve the solid product and the recovery of M^{2+} (Mg^{2+}, Fe^{2+}, Ca^{2+}).

Table 2 – Solubility data (g/L)

T°C	0	10	20	30	40	50	60	70	80	90	100
$FeSO_4$	103	135	174	216	265	317	385	369	336	288	246
$MgSO_4$		253	288	330	370	415	455	490	530	590	660

Iron sulphate has a solubility maximum at ~60°C while for magnesium sulphate it increases with temperature. (Cross-effects for mixtures not considered.) A scheme of the proposed process is presented in **Figure 6**. Two stages of solids dissolution are proposed. From an energy point of a view it makes more sense to first (diss A) dissolve the hot solids at ~90°C to maximise the dissolution of Mg as $MgSO_4$ (aq) and afterwards (dissB) dissolve the Fe at ~60°C.

The processing of 5000 kg of serpentine requires ~15000 kg of recyclable water. Yet, despite the considerable water losses that occur in the filtration stages (~0.47 kg water/kg solids), the process does not need a make-up stream of water as a result of three main factors: 1) the crystallization of ammonium sulphate allows for the recovery of the water from the solution, 2) the carbonation reaction produces water ($Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$) and 3) the mineral itself also contains substantial amounts of water which is released during the solid/solid reaction and recovered with the gaseous products.

Note that this work does not consider the recovery of water from the filtration cakes otherwise the process would “produce” water. The “allowable” losses of water that would still allow for operation without a net water input need are of the order of ~0.48 kg water/kg rock, depending on the purity of the rock. (For example, iron and calcium would precipitate as FeOOH and $Ca(OH)_2$ while these elements do not bring crystal water into the system, thus reducing the net water production of the Mg-extraction process.)

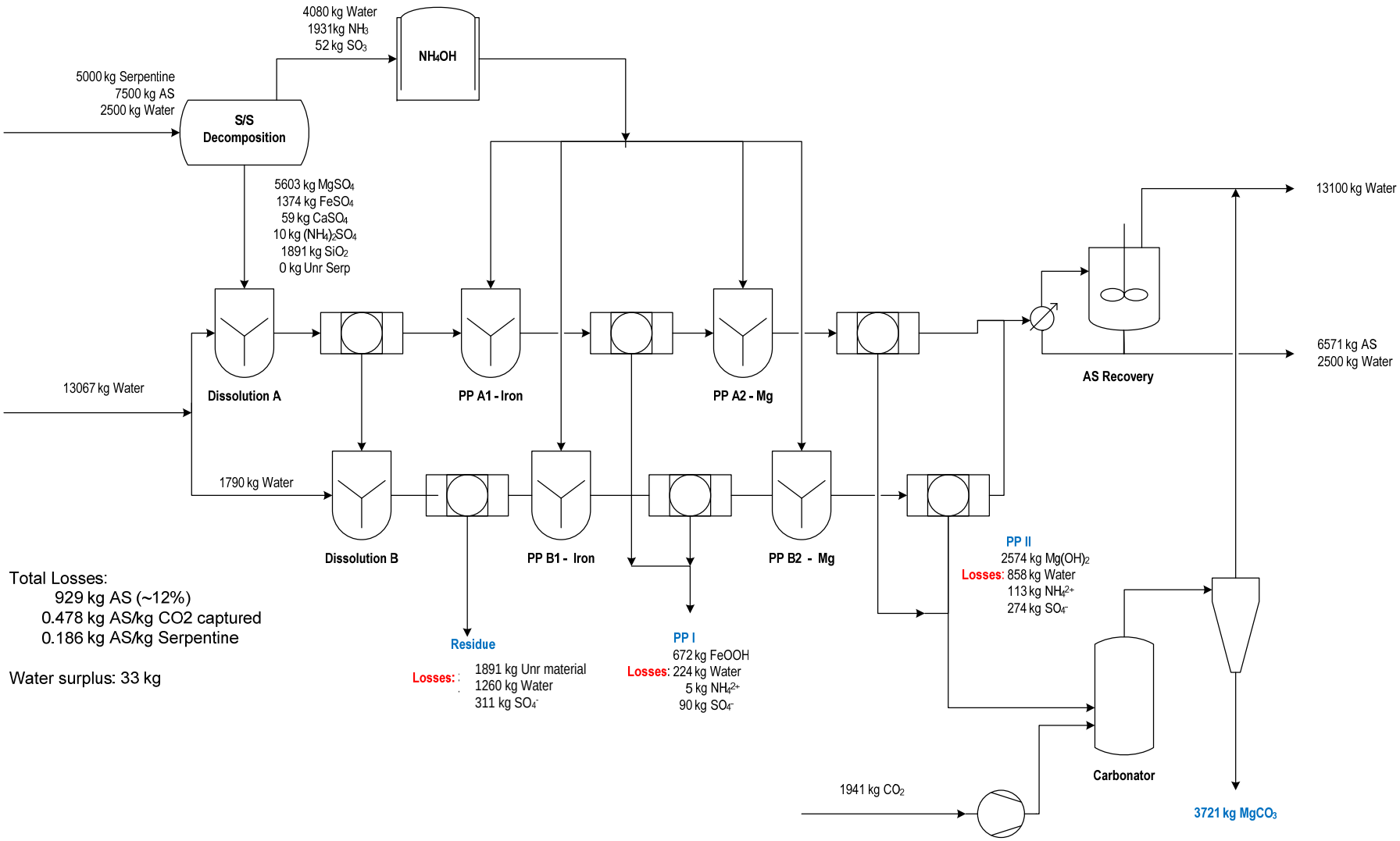

Figure 6 Process schematic with mass balances including losses of water, ammonia and sulphate

3.4 Water requirements for the precipitation steps for FeOOH, $Mg(OH)_2$ etc.

Precipitation is pH and the M^{2+} concentration dependent. Although the Fe^{2+} is fairly easy to precipitate and recover from the solution at pH ~8, the same does not happen with Mg^{2+} at pH ~11.5. Its recovery requires considerable amounts of ammonia solution (28 %-wt in water) meaning that the addition of ammonia gives a significant decrease of the Mg^{2+} concentration. Solutions for this problem may comprise the addition of gaseous NH_3, concentration of the solution before precipitation, control of temperature or addition of flocculation agents like polyethylene glycols (Pilarska et al., 2012) which, unfortunately also results in finer particles. Factors to take into account as well are the size of the particles and their surface area being these parameters important for the carbonation reaction and the PFB performance.

So-called inclined settlers may be used (this will be tested at ÅA – see **Figure 3**) for the separation of precipitates from the water streams (Davis and Gecol, 1996). Earlier this year these were tested and found successful (see photo in **Figure 7**) for related project work at ÅA VST that involves production of precipitated calcium carbonate (PCC) from steel converter slag (Filppula, 2012) – see Chapter 4.

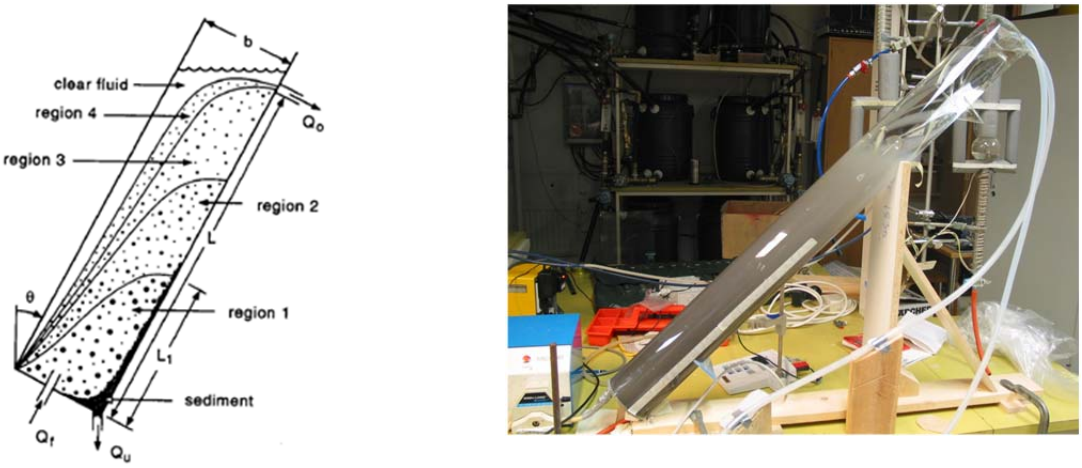

Fig. 7 Inclined settlers: concept (left) (Davis and Gecol, 1996) and tests with steelmaking slag at ÅA (right) (Filppula, 2012)

3.5 Water recovery from the unreacted rock residue and the precipitates

The main issue after the precipitation stages is the dewatering of the solids. The residue is very rich in SiO_2 and according to (Metso, 2012) this solids retain high amounts of water and the best outcome is a cake with 40-50% moisture content. In the process calculations made so far it was assumed that the residue leaves the filter with 40% while both the iron and magnesium products leave the filtration units with 25% water content. This translates in considerable losses of water, sulphates (~ 0.14 $kgSO_4^{2-}$/kg rock) and M^{2+} (~0.03 kg/kg rock) - see **Figure 6**.

Two types of filtration equipment are suitable for this process: vacuum filters which operate at low pressure or pressure filters that run at higher pressure. Due to the particle size of the solid particles, 60~125µm the second one is more advantageous when pursuing a drier cake and avoiding clogging issues. On the other hand these are expensive and heavy duty machinery which may lead to a significant energy penalty.

Unfortunately, the filtration system used in the laboratory and the filter papers used give little predictive information on larger scale operation.

3.6 Water recovery from $Mg(OH)_2$ carbonation product gas

Quite a lot of water is produced during the carbonation, following the reaction

$$Mg(OH)_2 + CO_2 \leftrightarrow MgCO_3 + H_2O \qquad (R5)$$

as a result of which the CO_2 content drops to $(1-X)\cdot p_{CO2,inlet}$ for CO_2 conversion X, giving a water content $X\cdot p_{CO2,\,inlet}$, using partial pressures p. (It is assumed that the water content of the inlet gas can be neglected as a result of the compression / intercooling system.)

During the expansion of the flue gas in the turbine, the amount of water condensed is ~ 0.05 kg / kg gas leaving the carbonator.

Water in the carbonation production gas can be recovered and potentially used as make-up water in the process, depending on the temperature at which the decarbonated flue gas is released to the atmosphere. One promising technology that could be used for efficient water recovery is a liquid desiccant dehumidification system (LDDS) (See **Figure 8**) (See also Copen et al. (Siemens), 2005). The LDDS process works by directly contacting the water vapour containing exhaust gas with a desiccant, for example LiCl, silica gel, zeolite, or $CaCl_2$ (Folkedahl et al., 2010). This would be done in a scrubber. The desiccant cools the gas and absorbs water. The desiccant is then transferred to another tank where the water is flashed at a slight under-pressure. After the water is flashed out of the desiccant it is recirculated back to the scrubber.

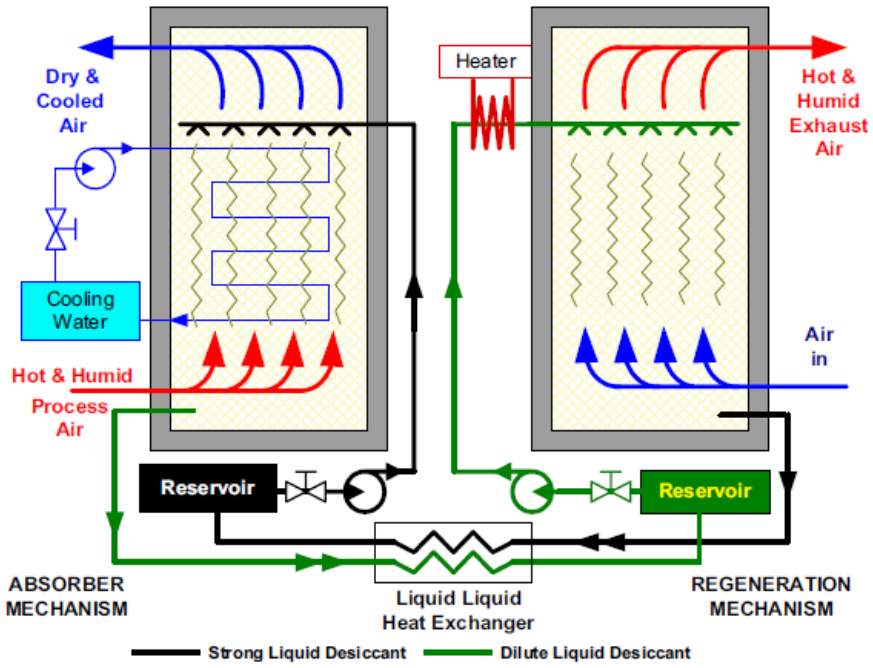

Fig. 8 A liquid desiccant dehumidification system (Jain et al., 2007)

To avoid impurities such as particles to enter the desiccant solution it is important that the gas is cleaned before the water recovery. Any sulphur oxides in the exhaust gas should also be removed as

to prevent the acidification of the desiccant solution in the scrubber. At this point in time water recovery using the LDDS technology is, however, too expensive as it requires a lot of equipment and energy.

3.7 Water recovery from AS salt recovery from dilute aqueous stream

The recovery of $(NH_4)_2SO_4$ is essential to make the process economical and environmentally feasible. Also, the LCA footprint of the process would be very high if losses of this salt cannot be reduced to a few %. The technology for AS crystallization exists and is widely used. In addition, most of the marketed ammonium sulphate derives from by-products of other processes (GEA Messo PT, 2012).

The main issue to assess at this stage is the energy penalty caused by the water removal from the AS solution which has a concentration of ~30% wt-%. Depending on the water content desired for the AS recovered, a combination of an evaporator, to concentrate the solution and a crystallizer (both using a Mechanical vapour recompressing technique) may be beneficial (Lin Liang and Dong Han, 2011).

So far it is intended to remove enough water to obtain an AS suitable for the S/S reaction and the recovered water fed back to the dissolution of the solid product. In several experiments (Romão et al., 2011) it has been shown that the presence of water may be beneficial to Mg extraction (depending on the T, type of reactor and raw material) allowing for the possibility of recycling a "wet" AS thus eliminating the need of a crystallizer.

3.8 Water produced during the compression of the CO_2 containing (flue?) gas

During the cooling stages between the compression stages water vapour in the exhaust gas will condensate. The amount of the water that condensates in the heat exchangers depend on the temperature of the cooling media, the amount of water vapour in the incoming exhaust gas and the final compression pressure. The water condensed out of the exhaust gas could potentially be used as make-up water in the process. In case the exhaust gas contains SO_2 or SO_3 it will condense together with the water vapour in the intercoolers. This will form H_2SO_3 or H_2SO_4 which might cause corrosion of the heat exchanger surfaces or on the compressor wings.

For a test case recently considered (lime kiln gas, Slotte et al., 2013) the amount of water produced during four-stage compression to 81 bar (giving ~20 bar CO_2 partial pressure) equals ~ 0.02 kg water kg / gas compressed being produced at ~150°C. The amount of NOx and SOx present in this is negligible. (These results were obtained using Aspen Plus simulation.)

3.9 Process control equipment

pH control during the process is essential because it determines iron hydroxide and magnesium hydroxide precipitation during the process. Moreover, the pH measurement during the process is straightforward but can be affected and complicated by the presence of particles. During the process, particle clusters are formed which disturbs to have homogeneous solution with the same pH. Therefore, mixing is essential which affects particle size.

Likewise, flow meters, level controllers etc. should not be blocked (may need repeated washing), the redox chemistry of iron gives coatings on surfaces that are hard to remove (unless acids are used).

Thermometers may corrode as a result of the acidic conditions (pH is < 2 using ammonium sulphate and >2 when using ammonium bisulphate) in the first precipitation solution.

3.10 Ammonia and ammoniums salt mass balance

There will be losses, particularly in the filtration units where the losses of sulphate ions (with alkali and metals as cations) will culminate in a ~12% loss of the initial 7500 kg of AS (see Fig 6). This problem may be minimized by washing the residue cake (half of the sulphates are lost with the residue) and returning this water to the S/S reaction relocating the S back in the process's loop. However, even if the solid washing is very efficient, it will be inevitable to lose some AS and water in the filtration stages. At the same time the ammonia lost in the filtration of the precipitate products is 120 kg (processing 5000 kg rock), meaning 0.03 kg/kg rock which is insignificant when compared to the 0.14kgSO_4^{2-}/kg rock losses.

3.11 Other issues

Experimental results show that the extracted aluminium (Al) ions co-precipitate along with the iron product. The percentage of Al present in it depends on the initial composition of the rock. Hitura nickel mine tailings do not have significant amounts of Al (0.21%) thus the iron product has a maximum fraction of ~1.4% of Al. On the other hand Portuguese rock contains 0.84% Al and its fraction in the Fe by-product may go up to 5%. Thus this by-product applicability to other industries, primarily steelmaking, must be well assessed.

Recent experiments at ÅA showed that Ca does not exclusively precipitate with the Fe or Mg ions. Since the major part of the alkali elements precipitate along with the iron by-product thus eliminating the necessity of a purge to avoid these elements' accumulation in the process loop.

Nonetheless, even if some Ca and Mg remains in the aqueous solution, the losses in the filtration stages may be enough to avoid accumulation, especially for alkali, in the AS recovery loop. For example, calcium is present in small amounts in "good'' serpentine rock like Hitura (FI) and Bragança (PT), at ~1% of the rock as $CaSiO_3$. This means that the fraction of $CaSO_4$ in the soluble products is less than 1 %. Some of it will be lost in the filtrations along with the water, and still if no calcium is precipitated at all, in the end the recycled AS (after the evaporation) will at most contain 0.18 %-wt Ca. Similar values apply other (earth-)alkali elements, with Na and K salts being more soluble. The sulphates of Na and K will eventually precipitate, as will also calcium sulphate (as gypsum) if calcium amounts in rock are higher.

Finally, not quantified issues in detail in this report:

- washing during crushing, grinding and milling can reduce fine particle losses. The effects on mass balances are assumed negligible.
- processing of waste water and other process water is needed before it can be disposed off, using regular process industry water treatment.

The figure below (**Figure 9**) shows the overall mass balance of the process: for a typical serpentinite with ~10 %-wt crystal water the maximum allowable losses of water are of the order of 1.2 ton per ton CO_2 fixed.

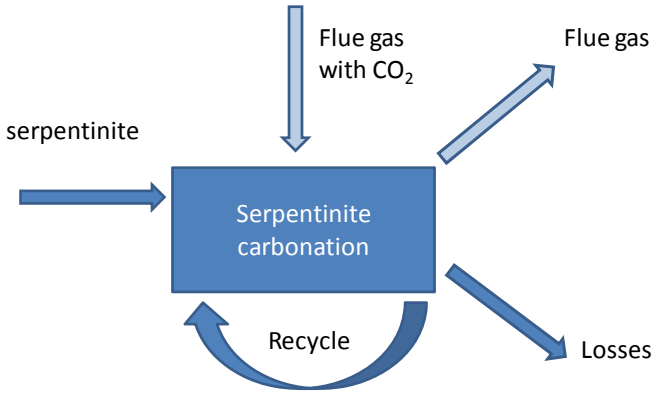

Fig. 9 Overall process mass balance for serpentinite carbonation

4 Production of PCC from steel converter slag ("slag2pcc")

4.1 Process description

In "slag2pcc" process route, carbonation of calcium-containing steel converter slag is studied. More specifically, the focus is on a two-step pH swing process, where the formed carbonates can be separated as marketable precipitated calcium carbonate (PCC).

The two-step pH swing process consists of two separate reactors between which an ammonium salt solution is circulated (see **Figure 10**). As a solvent ammonium salts such as ammonium nitrate, chloride or acetate can be used. In the first step calcium from the steel slag is extracted to the process liquid, which is then lead to the second step where CO_2 is pumped through the solution and calcium carbonate is precipitated. So far, most of the experimental work was done batchwise, either with a fresh solvent, or by re-using the solvent from previous experiments. (Eloneva, 2010, Eloneva et al., 2012, Mattila, 2009, Mattila et al., 2012a,b,c). The concept is now developed towards larger scale continuous operation, with a small-scale demo (reactor volumes ~25 liter) being taken into use at ÅA and a larger demonstration unit (reactor volumes ~200 liter) at Aalto/Energy technology in Espoo. At a steel converts slag production rate of ~ 25 t/h, eventually the process may be scaled up to produce ~10 t/h PCC.

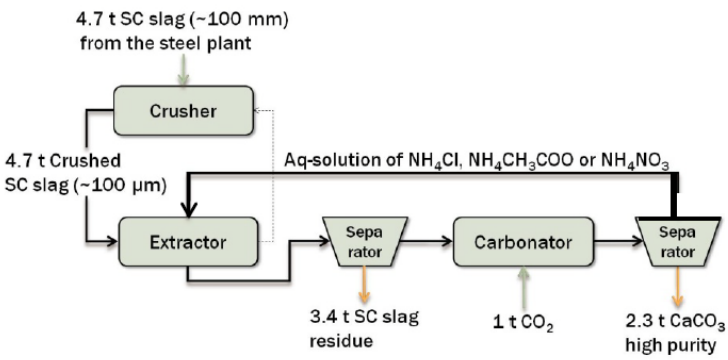

Fig. 10 Pathway for steelmaking slag carbonation for synthetic calcium carbonate or PCC production: Aalto/ÅA "slag2pcc" route

An impression of the test set-up at ÅA (December 2012), showing inclined settlers and filters, several of the five pumps and the reactors is given in **Figure 11**.

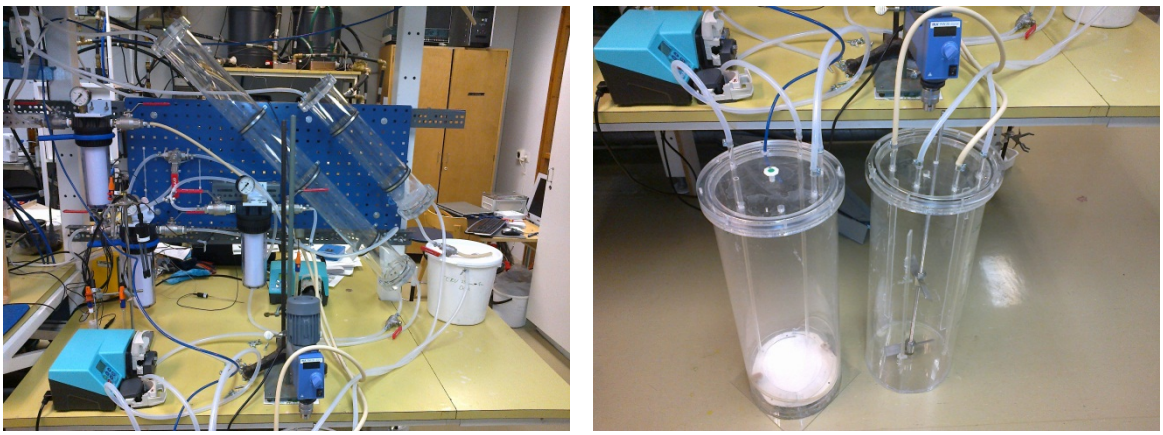

Fig. 11 Impression of the "slag2pcc" test set-up at ÅA (December 2012)

4.2 Water needs for the Ca extraction from steelmaking slag

Minimum and maximum amounts of water and ammonium salts needed for successful, efficient but also selective extraction of calcium depends strongly on the steelmaking slag type. XRD analysis will reveal whether the calcium is present as free lime (CaO) or in more complication forms, primarily silicates. The "slag2pcc" process was found to successfully extract Ca present as free lime, and as larnite, $2CaO{\cdot}SiO_2$. The assumed main reactions present in the process can be listed as follows:

$$CaO(s) + 2NH_4X(aq) + H_2O(l) \rightarrow CaX_2(aq) + 2NH_4OH(aq) \quad \text{(R6)}$$

$$2CaO * SiO_2(s) + 2NH_4X(aq) + H_2O(l) \rightarrow CaX_2(aq) + CaO * SiO_2(s) + 2NH_4OH(aq) \quad \text{(R7)}$$

$$2NH_4OH(aq) + CO_2(g) \leftrightarrow (NH_4)_2CO_3(aq) + H_2O(l) \quad \text{(R8)}$$

$$(NH_4)_2CO_3(aq) + CaX_2(aq) \leftrightarrow CaCO_3(s) + 2NH_4X(aq) \quad \text{(R9)}$$

(R6) and (R7) describe the extraction stage reactions, while (R8) and (R9) present the carbonation stage. Thus, it is obvious that water is necessary for the system, not only as the reaction medium, but also as a reactant for extraction. The minimum amount of water is one mol for one mol dissolved calcium, but more water is needed to enable ion dissolution. In the carbonation step, the water consumed in the extraction step is regenerated. On the other hand, with low solid-to-liquid ratios it is possible to obtain remarkably high calcium extraction rates (up to 70%), but this is impractical for larger scale use, since the required process equipment would require too much space.

Regarding quality (i.e. purity, particle size distribution, crystal form) of the PCC product, the main issues are related to concentration levels of calcium and carbon dioxide (or carbonate ions) during carbonation, since these together with pH are the main parameters controlling the crystal size and shape of the product. In extraction, by increasing the amount of solids per amount of liquid, concentration of calcium can be varied. However, at the same also pH of the aqueous solution is changing. Also the change of ammonium salt solvent molarity affects in a similar way. **Figure 12** represents the observed relation between pH and dissolved calcium concentration, while in **Figure 13** a similar graph for silicon concentration is shown. Included in the Figures are also trendlines, indicating linear behaviour.

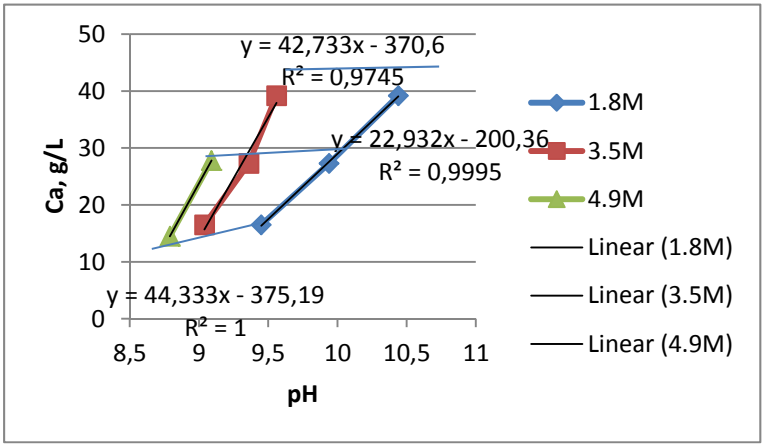

Fig. 12 Extraction of Ca in various extraction solution strengths

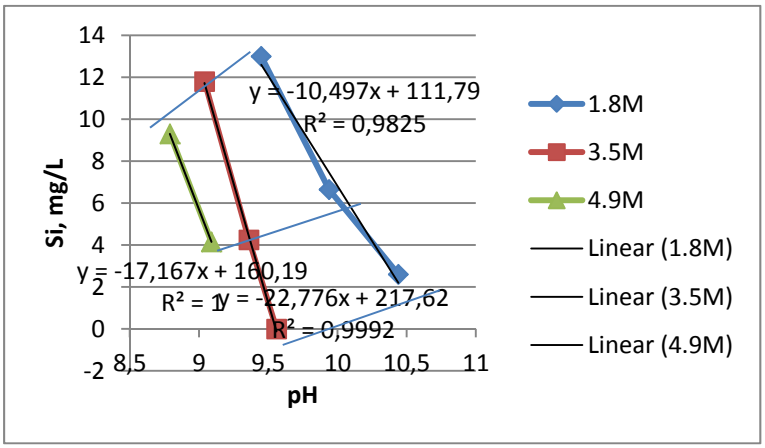

Fig. 13 Extraction of Si in various extraction solution strengths

The correlation between concentrations of dissolved calcium and silicon in water is a widely studied area in cement and concrete industry, where it has been observed that a) solubility of silicon increases noticeably at pH values above 9-9.5 (Alexander et al., 1954) and b) if silicon solubility is high, then calcium solubility will be restrained. (Chen et al., 2004) By plotting the results from **Figures 12** and **13** in a one figure - see **Figure 14** - this behaviour can be confirmed also for the case of ammonium chloride solutions. By increasing the ammonium salt molarity the pH of the solution after extraction is decreased.

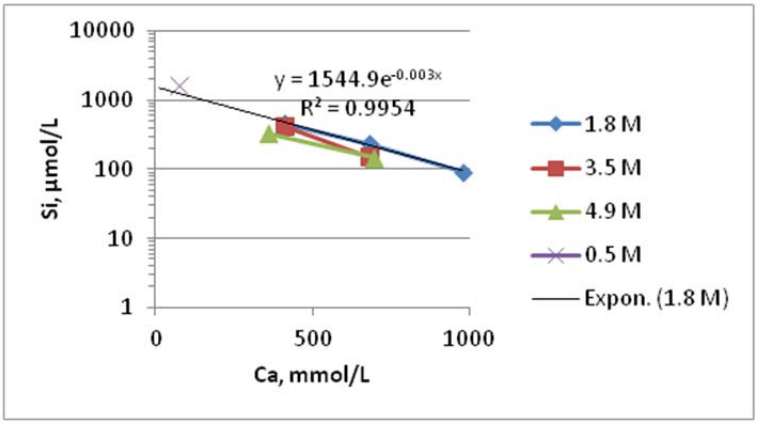

Fig. 14 Extraction of Si versus Ca in various extraction solution strengths

Also, it is known that compared to equilibrium calculations (based on Gibbs energy minimization), the calcium extraction efficiency is lower than predicted at higher slag-to-liquid ratios. Thus, a following hypothesis can be made about the process control; it would be beneficial to limit the increase of pH in order to have a lower solubility of silicon and thus a higher solubility of calcium in the solutions. The simplest way of obtaining this is usage of moderately high ammonium salt concentrations (1-2 mol/L, 1.5 mol/L is a good “guideline” value) together with also moderate solid-to-liquid ratios.

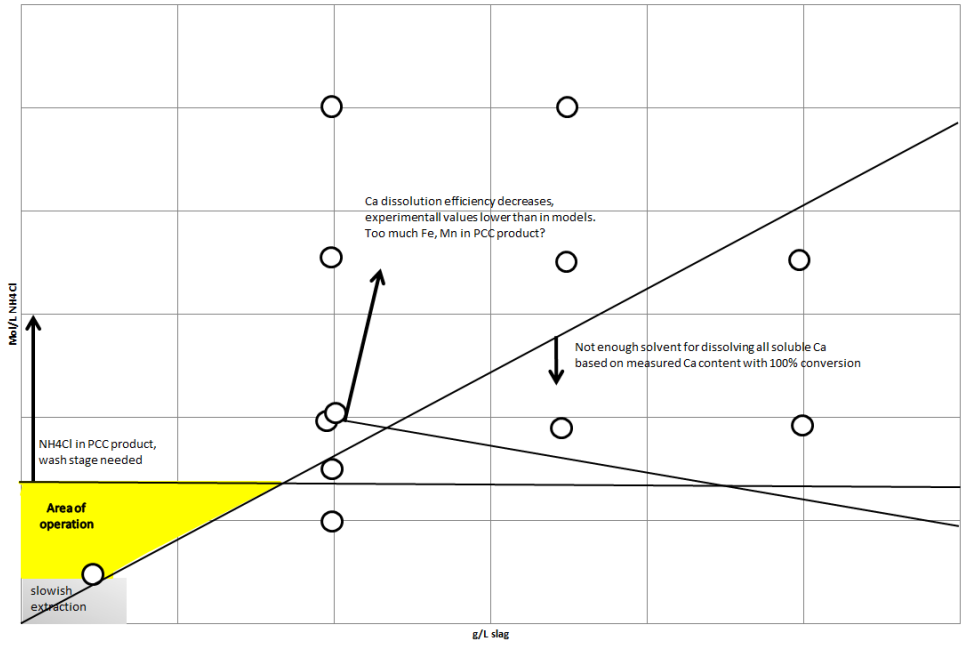

Fig. 15 Preferable region of operation for extraction of Ca in various extraction solution strengths and liquid/solid ratio's

The experimental observations are summarized in **Figure 15**, where the spheres represent performed experiments and the yellow area is the region within which the process should preferably be run. In the Figure, also the different reasons for limitations are shown. Increased solvent strengths were also shown to give increased extraction of Fe and Mn, as also discussed in Mattila et al. (2012b).

4.3 Separation of residual slag or PCC from aqueous streams

Separation is one of the most essential steps in different industries because of high cost of this step. As a consequence, gravimetric sedimentation is usually employed to separate solids from slurries. **Table 3** lists various conventional separation ways used in industries.

Table 3 Solid- liquid separation (PAControl, 2012)

Settling:	Filtration:
• By gravity	• By gravity
• By centrifugal force	• Vacuum filtration
• By air flotation	• Pressure filtration
• By dance media flotation	• Centrifugal filtration
• By magnetic properties	

Although the varying composition of the slag forms a challenge in itself when it comes to guarantying PCC quality and smooth process operation, feeding solid materials at a controlled rate into a process is less of a challenge than getting particulate material out of it. For the "slag2pcc" process, the separations involve removal of spent slag and PCC, respectively, of significantly different size (several 100 µm and < 20 µm, respectively) from low temperature water streams with low concentrations of dissolved salts. For a continuous process, continuous filtration or settlers are preferable, avoiding

(too) frequent stops of part of the process and the high costs or installing multiple units (one in operation, another stand-by or being cleaned or regenerated).

The Figure below (**Figure 16**) shows an Aspen Plus process scheme where the various separators are labelled "...SEP" or "...SEPAR" and "SETTLER".

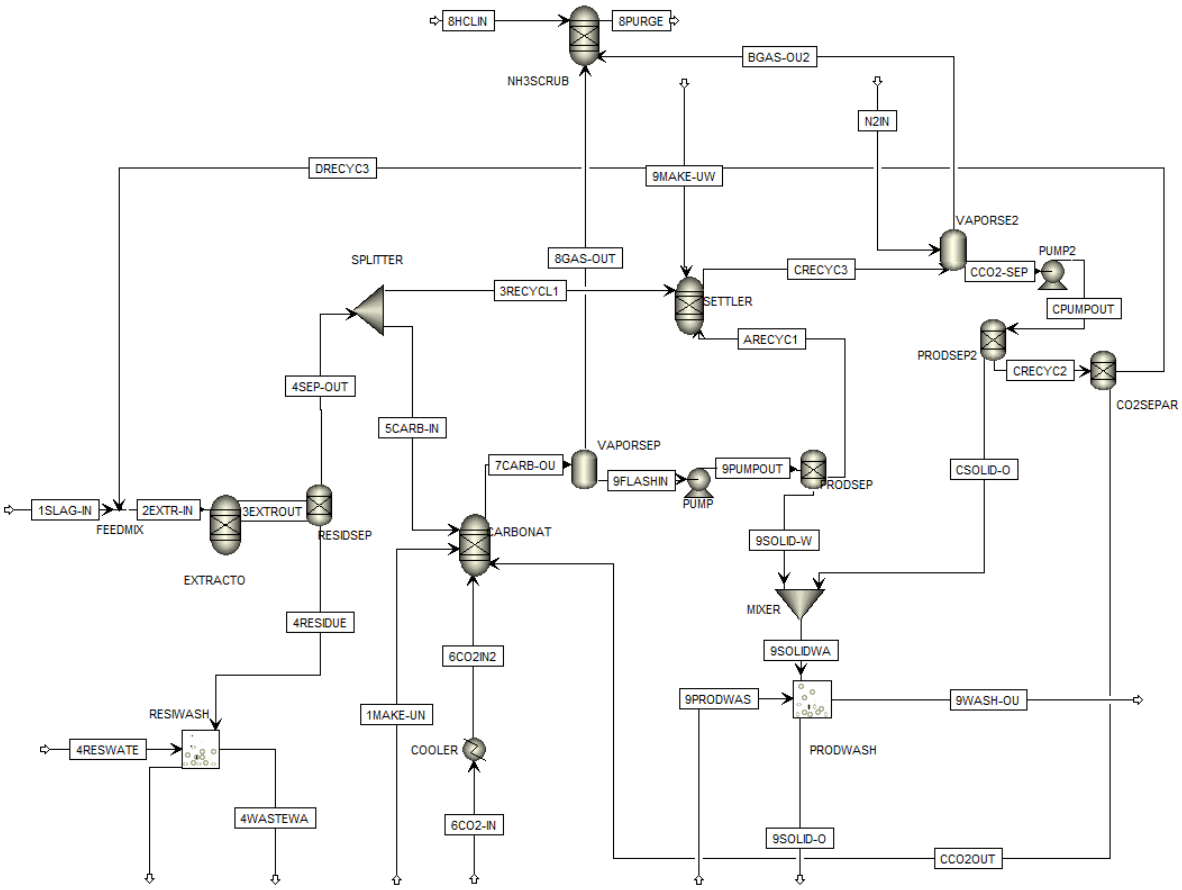

Fig. 16 Aspen Plus process scheme

Table 3 lists methods based on either using a force to alter the path of dispersed particles, or filters where a geometric barrier cannot be passed by the particles. The effect of external forces becomes smaller with decreasing particle sizes, dictating the use of (electro-)filters necessary for particles smaller than 5-10 µm in small process units, or smaller than 20-50 µm in larger units (depending on the density difference between the fluid and the dispersed particles.

Moreover, hydrocyclones (**Figure 17**) are widely used in solid liquid separation as well. Compared to more conventional solutions, such as filtration and gravitational settling, a liquid/solid hydrocyclone has several advantages, such as compact dimensions, operational simplicity and high separation efficiency (Wang et al., 2006) but their construction is more complicated compared to gravitational settlers. Also, pressure drop may become an issue.

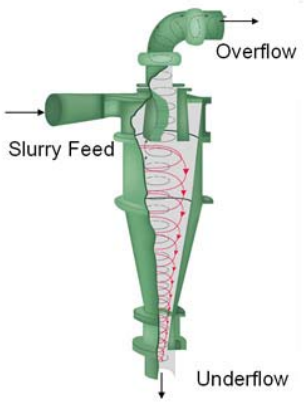

Fig. 17 Flow principle in a hydrocyclone (Picture from http://www.aeroprobe.com)

For the purpose of "slag2pcc" scale-up at ÅA and (at 15x larger scale) at Aalto, a hydrocyclone could offer continuous operation for suitable particle sizes, but had to be discarded: for ÅA the size of a hydrocyclone would be in the several mm range, while also at Aalto the stream volumes to be processed are still too small to give a the throughput velocities needed for solid/water separation. (More detail is given in Filppula, 2012, the Appendix, for SWECO hydrocyclones: see reference).

Due to the construction simplicity and high efficiency inclined tubular settler was investigated for the separation of steel slags and PCC from the dispersions - See **Figure 18**.

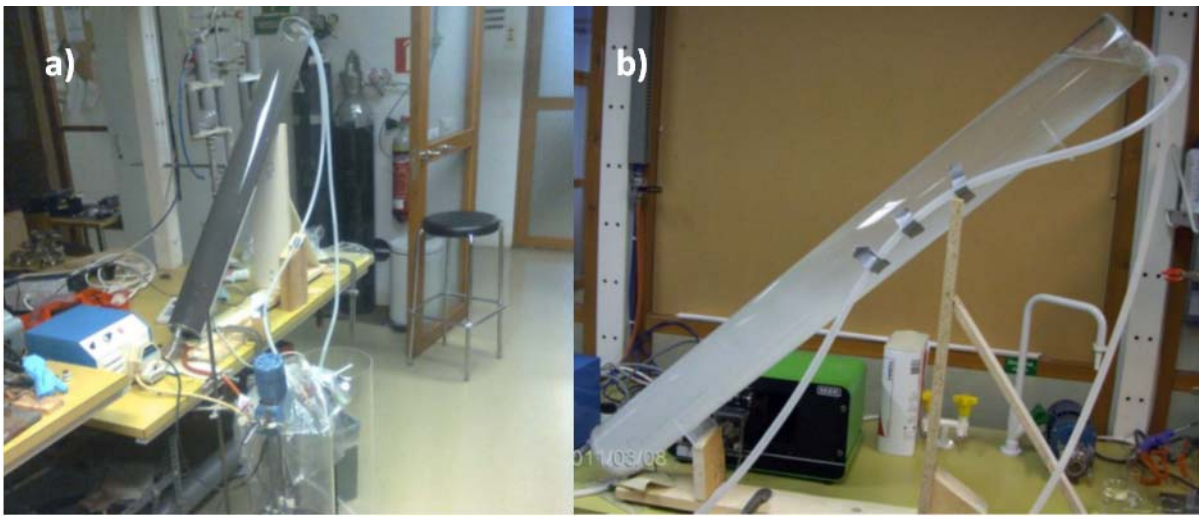

Figure 18 a) inclined settler for slag sedimentation; b) inclined settler for PCC sedimentation (Filppula, 2012)

An inclined settler was built from a circular perspex tube with 10 cm diameter and 110 cm length. The flow principle for the inclined settler is illustrated in **Figure 7** (in Chapter 3).

During inclined settler testing several experiments with steel slags and Ballotini glass bead were carried out in order to determine the optimal inclination angle of the settler (See Table 4). Experiments with the steel slags with a particle size in a range of 63-125 µm, with a volumetric inflow

rate of 40 l/h and with a volumetric underflow rate of 7 l/h, and at different inclinations (0 °, 30°, and 45°) did not show differences in the separation efficiencies (see **Table 4**).

Separation efficiency was calculated using (**Eq. 1**) where η is the separation efficiency, c_0 is the overflow particle concentration (mol/l), and c_{in} is the initial particle concentration in the inclined settler.

$$\eta = 1 - \frac{c_0}{c_{in}} * 100\% \quad (1)$$

Table 4 Separation efficiency of slag particle and glass beads (Filppula, 2012)

Material	Size fraction (µm)	Inclination	c_{in} (g/L)	c_o (g/L)	η
BOF slag	<125	10°	90	0.129	99.86 %
	63-125	30°	90	0.129	99.86 %
	63-125	45°	90	0.127	99.86 %
Glass beads	125-212	0°-45°	90	0	100 %

Despite of the fact that inclination angle did not have much influence on separation efficiency, it effected a length of sedimentation layer along the settling tube. At 10° inclination 110 cm (the entire settling tube) sedimentation layer was formed along the settler and at 30° and 45° inclinations 82 cm and 80 cm long sedimentation layers were formed respectively. Moreover, if particles are recycled back into the extraction reactor and become smaller all the time, a longer sedimentation layer will be formed; as a consequence it is advisable to use a higher inclination angle for the settling tube (45°).

A 97.8% separation efficiency of PCC with a particle size of 6-20 µm in the inclined settler was achieved. This separation efficiency may not be sufficient because the aim of this project is to produce as small particles as it is possible (target 2-8 µm, paper industry) and with decreasing particle size, the separation efficiency will decrease as well. It is suggested to use alternative separation technique to separate PCC from the slurry.

Thus, current work at ÅA employs a 110 cm inclined settler for PCC removal and a shorter, 50 cm inclined settler for spent slag removal. Filter units (with cut size 1 µm) are used downstream the settlers, acting as "absolute filters" to make sure that no PCC particles enter the extraction step, or slag particles enter the PCC precipitation vessels. An important goal with the work is to optimise a separation system that can also be used at larger scale at Aalto, avoiding a situation where complete water flows must be put through filter units.

Figure 19 shows one of the filter elements (HOH Separtec type: HOH Pure5, with spun PP filter medium) in more detail.

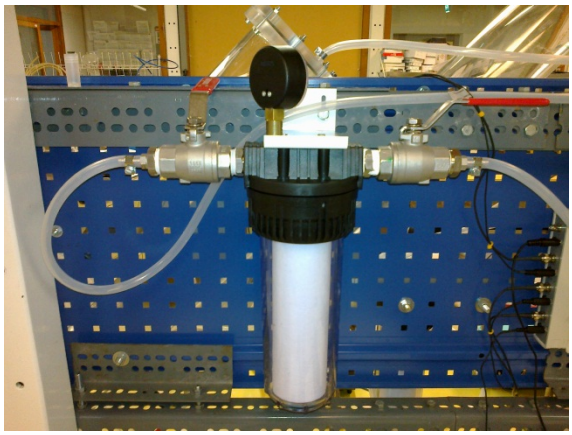

Figure 19 Filter element used after inclined settlers at ÅA

4.4 Recovery of water (and solvent salt) from steel slag residue (before V-recovery)

The water content of slag residue leaving the process is 10% based on batch and semi-batch experiments conducted at ÅA. However, this does not only involve losses of water, but also losses of the ammonium salt that is used as the process chemical. Based on SEM-EDX analysis of the slag residues it was determined that the chlorine content in the dry solids would be 5%, although this value needs to be confirmed by repeated analysis. Thus, depending on the further utilization of the processed slag, a washing step might have to be applied after the slag separation step. As a drawback, this will bring more water to the process, and this water will contain dilute ammonium chloride and possibly also some metals that are leached from the residue.

More consideration can be given to this issue when experimental results and experience with the small and large scale "slag2pcc" demonstration units. For the recovery of water from the PCC product as well as from the spent slag, filter press units may be most beneficial.

4.5 PCC product drying and after-treatment

The criteria for pure PCC include limits for iron, chlorine, manganese and other impurities. Also, the crystal size and shape should not be destroyed by the after treatment procedures, which depend on the application for the product. Obviously, this processing should as much as possible be integrated with water recovery (see previous point).

4.6 Process control equipment (incl. ion selective electrodes)

Although the "slag2pcc" process in principle operates at ambient temperature and pressure some benefit may result from slightly elevated temperatures (depending on solubility ranges). Nonetheless, pH meters will give the most useful information on the process, followed by thermometers, flow meters (that can handle dispersed particles) and static pressure (difference) meters.

At ÅA, ion selective electrodes (ISE's) were tested for measurement of Ca^{2+}, NH_4^+, were tested for possible on-line use (similar to pH meters). The aim was to use the information to control the process during steel slag conversion into valuable calcium carbonate, as it is very important to monitor pH, temperature and concentrations of various ions. By controlling concentrations of various ions it is possible to control process and morphology of the final PCC product. By following the pH and

temperatures it is possible to determine how the reactions proceed and approach completion, and when the slurry can be transferred into the other reactor. For this purpose pH meter, temperature probe and Ion Selective Electrodes (ISE, Nico2000) have been employed in the experimental work to control and monitor the process and its parameters. In the process solutions, unfortunately, concentrations were typically too high, requiring sampling and sample dilution.

The biggest drawback of using ISEs is that their accuracy depends on ion concentration in the solution, dilutions, measurement time, and the calibration curves.

If concentrations of ions are very low, it takes a long time to get a stable reading. Moreover, if the concentrations are too high, samples have to be diluted and this increases error of the measurement. To calculate the error (**Eq. 2**) was used, giving results as in **Table 5** for calcium concentration measurements.

Table 5 Errors during Ca ion concentration measurements at different dilution ratios

	error, %			
Dilution / Measurement	x 5	x 7	x 9	x 20
1	2	5	9	2
2	3	7	15	7
3	8	12	19	27
4	14	13	16	1
5	3	2	4	8
6	1	6	10	4
7	2	6	8	30
Average:	5	7	12	11

The error margin was calculated using

$$error, \% = \frac{c_1 - c_2}{c_1} * 100 \quad (2)$$

where c_1 – concentration of initial/the lowest dilution solution, mol/l and c_2 – concentration of diluted solution, mol/l.

Thus, to detect ion concentrations in the solution a set of ISEs were purchased with the intention to employ them in 'on-line' concentration measurements but during the experiments it was found that the response time is 2-5 min which is too long for 'on-line' monitoring. Moreover, if the solution contains ions that interfere with each other, the measurement error increases. This was in fact observed in practice during Ca^{+2} concentration measurements when in the solution nitrate (NO_3^-) and ammonium (NH_4^+) ions were also present. According to the ISEs manual (Nico2000), it is advisable to calibrate the electrodes in a matrix with all ions present as in the solution to be analysed but in this case calibrating the Ca^{+2} electrode correctly was not possible due to too strong NH_4^+ , NO_3^-, and Ca^{+2} ions interactions. Instead of a straight, monotonic calibration line, a parabolic curve was obtained.

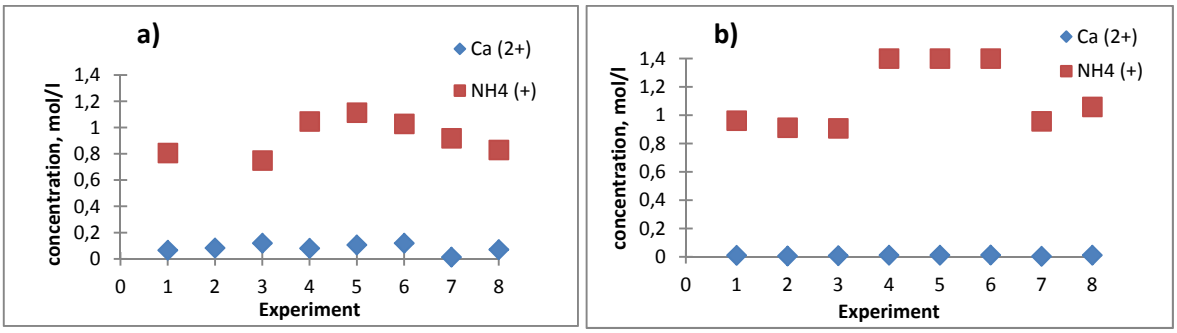

Fig 20 a) Ca (+2) and NH_4 (+) ion concentration measurements in extraction reactor (a) and in carbonation reactor (b) by using ISEs

Figure 20 depicts ammonium and calcium ion concentration measurements during the extraction and carbonation experiments with dilutions 10x and 15x, respectively. The dilutions were chosen according to ammonium ion concentrations and aiming at the detection range of $2 \cdot 10^{-6}$ to 0.1 mol/l and for Ca lower than $5 \cdot 10^{-6}$ mol/l. Samples were diluted 15 times where 1.5 mol/l ammonium chloride solution was used and 10 times where 1 mol/l ammonium chloride salt solution was used for the steel slag leaching.

Due to the fact that NH_4^+ ions are substituted with mainly Ca^{+2} ions during the extraction reaction it is possible to compare ammonium and calcium ion measurements. One calcium ion replaces two ammonium ions and thus ammonium ion concentration can be calculated using **Eq. (3)**.

$$[NH_4^+] = ([NH_4^+] + [NH_3])_0 - ½ * [Ca^{2+}] \quad (3)$$

The deviation between measured and calculated concentrations varies up to 18%, as shown in **Figure 21,** which clearly shows the importance of accurate calibration before measurements. It was furthermore noted that the electrode calibration "drifts" with ~3 mV per day, which is ~1% of the full measurement scale.

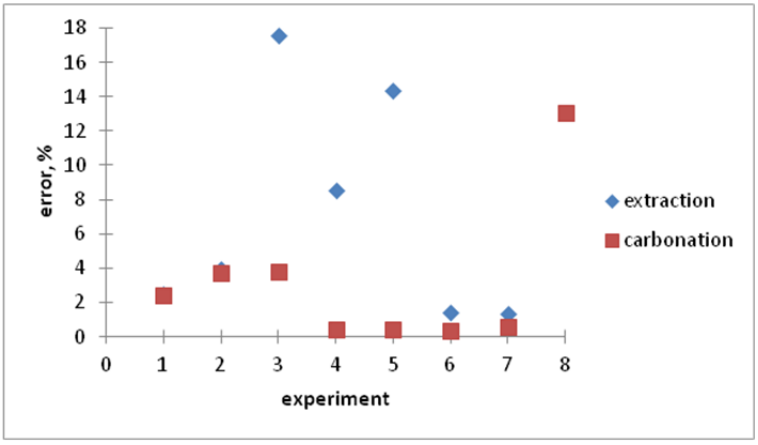

Figure 21 Deviation between calcium and ammonium ions measurements

4.7 Loss of water with off-gas

Losses of water should be controlled also because ammonia vapour will have a strong tendency to leave the system with it. Depending on the ammonium salt that is used as solvent, adding small

amounts of acid to the process purge gas stream can be used to recover both water and ammonia vapours: for NH_4Cl, hydrochloric acid can be used to bind NH_3 to NH_4Cl and recover water. (For NH_4NO_3 and NH_4Ac the corresponding acids are nitric acid and acetic acid, respectively.)

4.8 Other issues

Based on experimental work, other elements such as silicon, magnesium, manganese, sulfur and vanadium are also leached from the steel slag to some extent, depending on the chosen solvent strength and solid-to-liquid ratio. Since they are not precipitating with PCC, it means that they are accumulating in the aqueous process solution. However, except for manganese, which has been observed to precipitate and colour the liquids/ process equipment black with solvent molarities above 2 mol/l (M=2), it seems that e.g. silicon and sulphur are not disturbing the process or the product quality, since their concentrations level out after a few cycles of extraction – carbonation experiments. (Mattila 2009, Mattila et al., 2012b)

Also, because some water is leaving the system with slag residue and produced PCC, there might not be a need for a separate water purge. Inevitably, however, there may be need for make-up ammonium chloride solution, partially also because of water losses with the off-gas stream from the system. On the other hand, if both the residue and product wash stages are applied, the process will suffer from a large excess of diluted ammonium salt solution.

5 Conclusions

For two CO_2 mineralisation processes the control of water streams and the separation of dispersed particles or dissolved salts are addressed.

For both processes:

- Water losses or purges will tend to contain significant amounts of dissolved ammonia as a result of high solubility of ammonium salts. In the serpentinite carbonation process the sulphates losses are more important.
- Solubility of $MgSO_4$/$CaCl_2$ in NH_4-sulphate/ chloride solutions will determine minimum water amounts and hence minimum pumping power for water.
- Filters and inclined settlers can be used in solid-liquid separation, hydrocyclones may be used for solid-liquid separation process if the process scale were larger;

For the "ÅA route":

- The AS losses can be minimised by solids washing and more efficient filtration equipment. Obviously this efficiency comes at the expense of energy penalties and more machinery investment. Ammonia and sulphate losses are a bigger problem than water losses for serpentinite carbonation since, in theory, this process can run without a make-up stream of water.
- Water may give better Mg extraction when present during the 1st step (solid-solid reaction), of $Mg(OH)_2$ production so water from ammonium sulphate probably need not be removed completely.
- For rock containing Fe: more AS salt is needed and increased amounts of water will be involved.
- Serpentinites bring ~100 kg water per ton rock into the carbonation process (this will not be the case for olivines / forsterites). This will help balancing the water losses in the filtration stages.
- AS recovery is important; it will be very different if ABS (more expensive than AS) is the preferable lixiviant. Although the regeneration costs of ABS will almost certainly be higher, the savings on serpentine pre-processing (mining, transportation, crushing and grinding) may be compensated by a better Mg extraction.
- Water quality not critical, but no sea water should be used: alkali and chlorine should be avoided. As these will accumulate in the AS recycling loop. Otherwise those elements are not an issue for the serpentine process.

For the "slag2pcc" route:

- The optimum ammonium chloride concentration for the process is in a range of 1.5-2 mol/l;
- Losses of water should be controlled in order to prevent ammonia losses from the system;

- Adding small amounts of acid to the process purge gas stream can be used to recover both water and ammonia vapours: for NH_4Cl, hydrochloric acid can be used to bind NH_3 to NH_4Cl and recover water;
- The use of ion selective electrodes for Ca^{2+} and other ions for on-line use and process control is not feasible, due to: a response time of 2-5 min; detection limits ($5 \cdot 10^{-7}$ – 0.1 mol/l), while dilution by 10x gives 10-20 % error) and distortion effects by different ions.

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