ÅA Thermal and Flow Engineering:
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D503   Assessment of options and a most feasible design of serpentinite carbonation applied to a lime kiln

Final version October 31, 2011
Replaces final draft October 12, 2011

Executive summary:

An assessment was made of existing process routes for CO_2 mineral sequestration at Nordkalk's lime kiln at Pargas, Finland. A prerequisite was operation on process off-gas (~ 15 t CO_2/h, ~22% CO_2 in gas), preferably carbonation of magnesium silicate (capacity calcium-based carbonation may be too low). Heat recovery from heat exchanger (470 → 270°C) is an option.

Partly expanding on an earlier study, a total of ~35 different process routes was assessed, of which ~1/3 appeared capable of operating on a CO_2-containing gas, not requiring CO_2 pre-separation. For most of these a magnesium-based material is carbonated. Four routes can be recommended for consideration by Nordkalk:

- An Mg-silicate process route under development at Nottingham University (UK)
- The ÅA serpentinite dry/wet/dry carbonation route via $MgSO_4$ and $Mg(OH)_2$
- The Aalto/ÅA "slag2pcc" route for PCC production from steelmaking slags
- The air pollution control (APC) residue gas/solid from Rome (IT), for which operation in a fluidised bed may be considered

Note that the "slag2pcc" route would require relatively pure CO_2, and will be further developed under Cleen CCSP Task 5.2 regardless of this D503 deliverable.

Process selection and first steps towards a design for large-scale processing in Pargas (as part of Cleen CCSP process year 2) shall start from this shortlist.

Information for process numbers 1-25 was collected earlier (during 2010) [ETI11], numbers ≥30 for the purpose of this project.
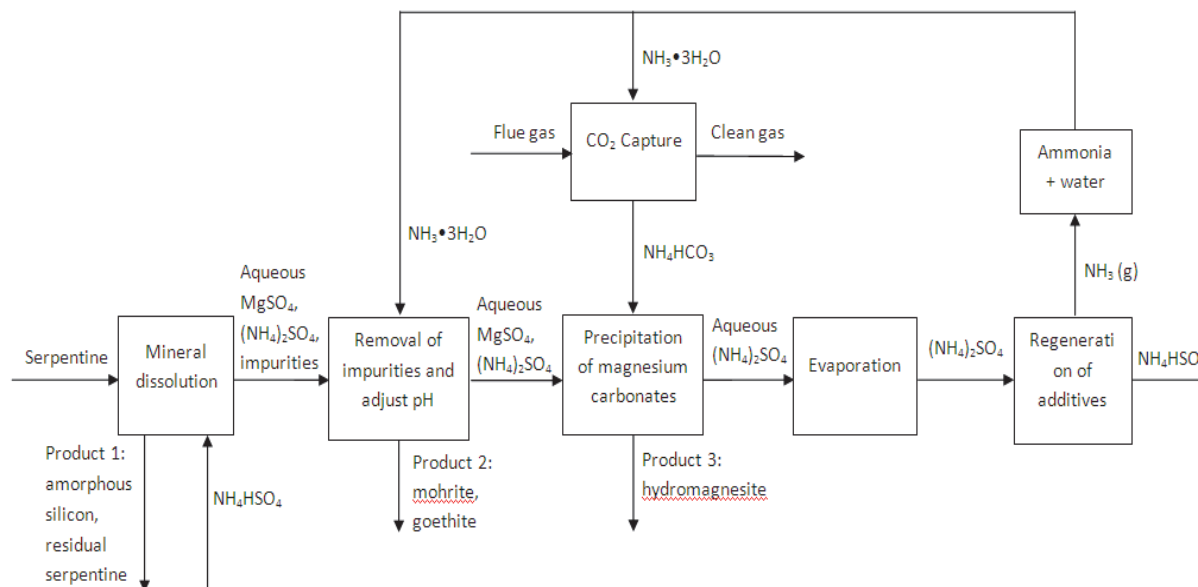
Tabelised - gray processes are considered to have potential.

	Patent?	Mg	Ca	Can use kiln gas	Comment
1 ARC Serp		X			"State of the art" 2005
2 ARC Oliv		X			"State of the art" 2005
1-2a ARC Woll			X		"State of the art" 2005: Uses wollastonite!
3 Shell Serp		X		+	
3a Shell Oliv		X		+	
4 Rau Caldeira	X		X	+	Calera Corp has patent rights
5 N'ham Univ		X		+	Gas scrubbing with NH3
6 Hunwick	X	X		+	Only theory, Gas scrubbing with NH3
7 Brent		X	(X)		~ ARC route
8 ÅA		X		+	Mg silicates route; pressurised gas
8a Aalto/AA			X		PCC production, patent Teir et al.
9 Huijgen			X	+	Pressurised CO_2
10 Baldyga					Lab concept, only part of a process
11 Munz		X			Very long reaction times
12 Lin				+	
13a Baciocchi wet			X		
13b Baciocchi dry			X	+	Calcium-based
14 Reddy	X		X		
15 Kodama			X	+	
16 Krevor		X			Very long reaction times
17 Kwak					
18 Schiller		X		+	Only theory, very complicated
19 Maroto-Valer	X	X			Dissolves rock in sulphuric acid
20 Calera	X many	X	X	+	Huge sea-water use; ←→ Inland-China?
21 Vandor	X			+	
22 Caterpillar	See 25				Confidential
23 Park	X	X			US200518910
24 Jones	X				SkyMine
25 DaCosta	X				←→ see 22
30 Novacem	X			?	Discarded by M Eriksson 22.June.2011
31 van Essendelft	X	X			WO2007106883 Strong acids and NaOH
32 Thoms, Green	X				
33 Zhong Shaojun	X				
34 Soong Yee	X		(x)		
35 Colton	X				Mine waste Strong acids and NaOH
36 Dilmore et al.	X				US7842186 Na,K (bi)carbonates
37 Riman	X				FeO & CO_2 ??
38 Smith, D.R.	X	X+..	X		WO2011019694
39 Boerrigter	X	X	X		WO2010097451 See SHELL (3)
40 Bauer et al.					Univ. Bayreuth – see ACEME10
41 Cuycha Oy	X			+, > 0.4 bar CO_2	Feldspar-type material; CCJournal Mar/Apr 2011

Process – by process brief description and assessment

The promising routes:

5) Nottingham University: Maroto-Valer et al. [MV10, MV11a,b]

With the aim to improve the efficiency of mineral dissolution and be able to recover and re-use additives, Maroto-Valer and co-workers have proposed a pH-swing CO_2 mineralisation process using ammonium salts to overcome these barriers. At 100°C, 1.4M aqueous solution NH_4HSO_4 was found to extract 100% Mg from serpentine in 3 hours. In addition, it extracts 98% of Fe and 17.6% of Si under the same conditions. The work shows similarities with a US patent from 1967 [Pun67]

The process proposed consists of five steps for which the main reactions are presented in the Figure above. In the first step, NH_3 is used to capture CO_2 from flue gas to produce NH_4HCO_3. In the mineral dissolution step, 1.4M NH_4HSO_4 is used to extract Mg from serpentine ground to a particle size range 75-125µm. The Mg-rich solution is neutralised by adding NH_4OH, after which impurities in the leaching solution are removed by adding NH_4OH. In a carbonation step, Mg-rich solution reacts with the product from the capture step NH_4HCO_3 to precipitate carbonates. Since formation and stability of hydro-carbonates is temperature dependent, $MgCO_3 \cdot 3H_2O$ (nesquehonite) can convert to $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (hydromagnesite) at temperatures above 70°C. Precipitation of hydromagnesite results in a solution that mainly contains $(NH_4)_2SO_4$. The final step is regeneration of additives, decomposition of $(NH_4)_2SO_4$ starts from 250°C and ends at 330°C producing NH_3 for the capture process and NH_4HSO_4 to be reused in mineral dissolution.

From the reaction equations CO_2 is released during "carbonation" and "carbonate forming" steps, which both also release CO_2, CO_2 sequestration efficiency 70% is attained. The last step may require a higher temperature than stated (above ~350°C, release of NH_3 would start at temperature above 350°C (from an HSC calculation).

The table below gives the chemical reactions and the thermodynamics for these.

Chemical reactions and thermodynamic data of the different steps of the process.

	Reaction equations	T (°C)	ΔH (kJ)	ΔG (kJ)
CO_2 capture	$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$	10	−127.0	−26.3
Mineral dissolution	$Mg_3Si_2O_5\cdot(OH)_4 + 6NH_4HSO_4 \rightarrow 3MgSO_4 + 2SiO_2 + 5H_2O + 3(NH_4)_2SO_4$	90	−141.1	−431.8
pH adjustment	$NH_4HSO_4 + NH_4OH \rightarrow (NH_4)_2SO_4 + H_2O$	25	−116.0	−134.4
Removal of impurities	$(Fe,Al,Cr)_2(SO_4)_3 + 6NH_4OH \rightarrow 2(Fe,Al,Cr)(OH)_3\downarrow + 3(NH_4)_2SO_4$	25	−673.0	−545.1
	$(Zn,Cu,Mn)SO_4 + 2NH_4OH \rightarrow (Zn,Cu,Mn)(OH)_2\downarrow + (NH_4)_2SO_4$	25	−191.4	−144.4
Carbonation	$MgSO_4 + 2NH_4HCO_3 \rightarrow Mg(HCO_3)_2 + (NH_4)_2 SO_4$			
	$Mg(HCO_3)_2 + 2H_2O \rightarrow MgCO_3\cdot 3H_2O\downarrow + CO_2\uparrow$			
	Overall reaction			
	$MgSO_4 + 2NH_4HCO_3 + 2H_2O \rightarrow MgCO_3\cdot 3H_2O\downarrow + (NH_4)_2SO_4 + CO_2\uparrow$	80	−6.6	−37.4
	Carbonate formation change			
	$5\ MgCO_3\cdot 3H_2O \rightarrow 4MgCO_3\cdot Mg(OH)_2\cdot 4H_2O + CO_2\uparrow + 10H_2O$	80	69.5	−18.2
Regeneration of additives	$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3\uparrow$	300	111.6	90.4

It is important to note that all reactions are exothermic, except the last listed i.e. the regeneration of the ammonium bisulphate. Note also that that has ΔG > 0, which indicates that it is thermodynamically unfavourable.

In [MV11a] it is stated that the conversion of ammonium sulphate into bisulphate is accomplished by evaporating water followed by further heat-up to 300°C which causes NH_3 to be released, regardless of ΔG > 0 in the table.
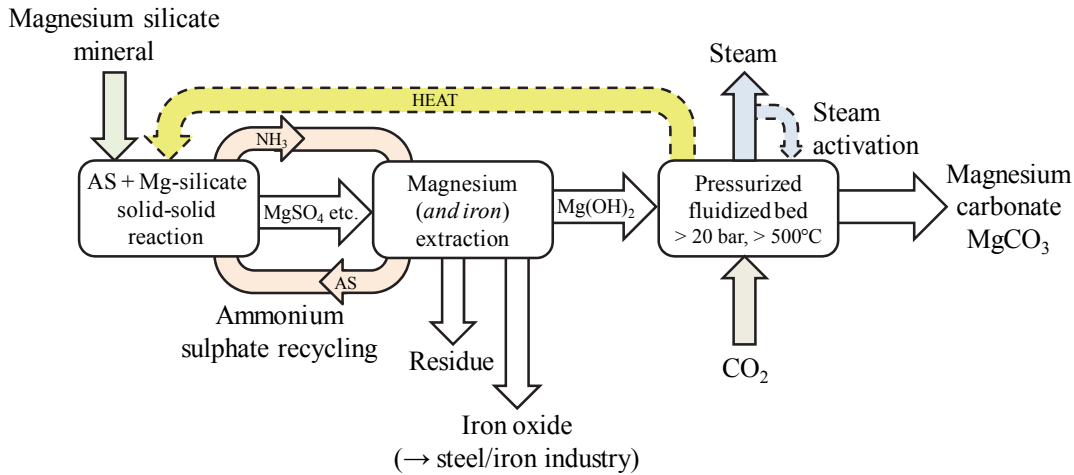
An estimate of energy (heat) need can be made: for the water to be evaporated it may be assumed that the amount used is given by the solubility of MgSO4 in the first step of the process, which corresponds to 7.8 t H_2O/t CO_2. To evaporate this water 17 GJ heat is needed per ton CO_2. In a Mechanical Vapour Recompression (MVR) unit it would instead require ~ 2 GJ electricity for compressors (see: MSc thesis T Björklöf ÅA 2010). For the chemical reaction of ammonium sulphate into bisulphate 5 GJ/ton CO2 must be added.

Alternatively, if it is assumed that ammonium sulphate can be converted to bisulphate by release of NH3 only, without evaporation of water then a pressure > 85 bar is needed to increase the boiling temperature for water to 300 ºC. Under these conditions the sulphate into bisulphate conversion requires 7.8 GJ/t CO_2 (HSC Chemistry) . (ΔH = 171 kJ/mol NH4HSO4, while one t CO2 requires 6 t of it, according to first step

$Mg_3Si_2O_5(OH)_4 + 6NH_4HSO_4 \rightarrow 3MgSO_4 + 2SiO_2 + 5H_2O + 3(NH_4)_2SO_4$.
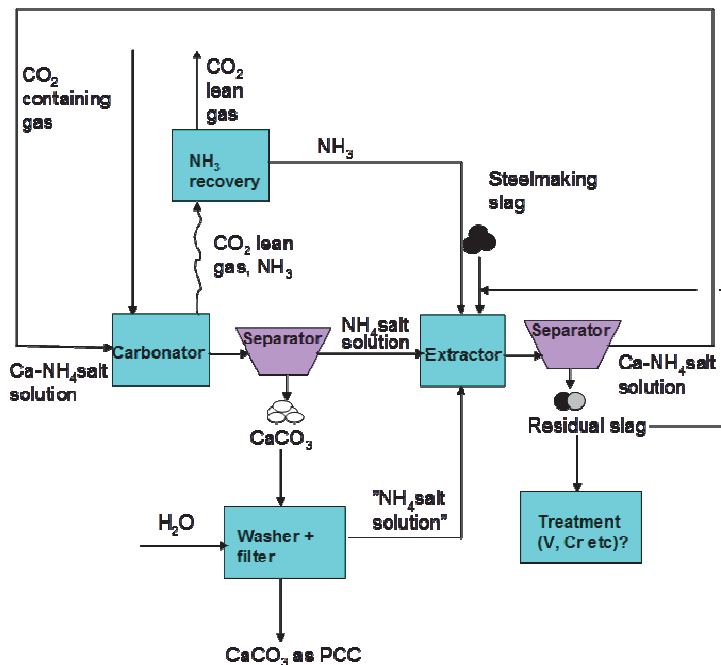
In a recent paper the energy input requirements were not addressed [MV11b], where the box "evaporation" is no longer part of the process schematic.

8 = ÅA two-stage serpentinite carbonation

This process involves production of water soluble MgSO4 from reaction of serpentine with recoverable ammonium sulphate (400-450°C, ~20 min) followed by precipitation of $Mg(OH)_2$ (and by-products) from aqueous solutions. The $Mg(OH)_2$ is carbonated in a gas/solid pressurised fluidised bed (~20 bar CO_2 pressure, ~500 °C, ~10 minutes), producing recoverable heat mainly in the form of pressurised steam. Described in detail elsewhere, see for recent reporting [JF11, IR11]. Achieved so far: ~75% Mg extraction, ~65% Mg carbonation.

8a = Aalto /ÅA Slag2pcc concept

Selective extraction of Ca from steel converter slag using ammonium chloride, nitrate or acetate followed by carbonation to give PCC while regenerationg the solvent salt. Operates at ambient conditions, residence time in both reactors ~30 min. Extensive proof-of-concept testing and a patent (application); scale-up to demonstration ongoing. Described in detail elsewhere – a major CLEEN CCSP task 5.2 activity….

13. Baciocchi et al. (Italy) b: dry [Bac09]

Comparision of diferent routes for carbonation of APC (air pollution control) residues

b. The dry carbonation experiments were perfomed in a TGA system, at 300~500°C with gas 10-50% vol CO_2/Argon. The experimental results are very good (1 bar, 400°C, 50% vol CO_2, ~2 min, ~70% conversion & 1 bar, 400°C, 10% vol CO_2, ~5 min, ~75% conversion). The process has mainly adavantages: no extra chemicals are added, it can run on flue gases, atmospheric pressure, fast kinetics, good conversion, It may be applied to incinerator waste, cement kiln dust, steel slags, etc. In the case of IW, carbonation leads to a decrease on the heavy metal leaching (Pb, Zn, Cu). The heat required can be provided by Nordkalk's waste heat. Still, it is important to stress that this process is a very good option to stabilize ashes, but there are not enough "residues" available to solve the GHG issue.

This approach may very well be applied to operation in an atmospheric fluidised bed (FB) reactor, making use of waste heat of ~ 400 °C. Calcium-based input material (APC residue) availability may be limited, though.

The other routes considered:

1-2) Albany Research Center (USA) wet process : "state of the art 2005" [ARC05]

In this process, powdered serpentinite (preheated to 630°C), olivine or wollastonite is carbonated in a pressurized aqueous solution. Optimisation of solution chemistry (using 0.64 M $NaHCO_3$ and 1 M NaCl), heat treatment (615-630°C for serpentine) and grinding gave 65% conversion after 1 h and 80% conversion within ½ h at 185°C/150 bar for olivine, 155°C/115 bar for heat treated serpentine or 40 bar/100°C for wollastonite. A cost assessment gave 54, 78 and 64 US$/ton CO_2, respectively for these three minerals. (The process costs are unfortunately an overestimation since heat input requirements are charged the same way as power which is roughly twice as expensive Also the use of heat of reaction is not explicitly addressed.)
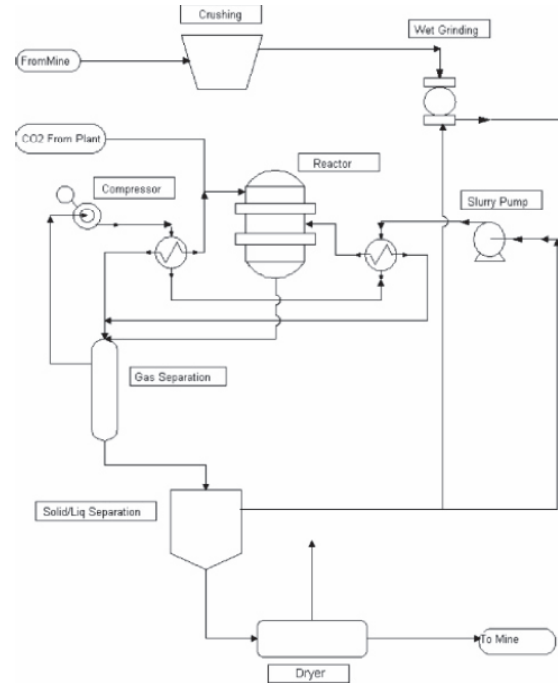
Process parameters for the ARC process experimental work (two tables) from [ARC05]

Table IV. Energy consumption by feed material and specific pretreatment methodology.

	Feed Material History					Pretreatment Energy Consumption, kW•h/ton					
Region	Ore mineral & grade	Pretreatment methodology	Code	Crush.	Bene.	Grinding			Heat treatment	Total
						Stage 1	Stage 2	Stage 3		
1	Olivine, 100%	Ball mill (-200 mesh)	1A	2		11				13
		Ball mill (-400 mesh)	1B	2		11	70			83
		SMD mill	1C	2		11	70	150		233
2-4	Serpentine, 100% (lizardite)	Ball mill (-200 mesh)	2-4A	2		11				13
		Heat treatment (-200)	2-4B	2		11			326	339
5	Olivine, 70%	Ball mill (-200 mesh)	5A	2	2	15				19
		Ball mill (-400 mesh)	5B	2	2	15	70			89
		SMD mill	5C	2	2	15	70	150		239
6	Serpentine, 100% (antigorite)	Ball mill (-200 mesh)	6A	2		11				13
		Heat treatment (-200)	6B	2		11			293	306
		Heat treatment (-400)	6C	2		11	70		293	376
7	Wollastonite, 50%	Ball mill (-400 mesh)	7A	2	4	21	70			97
		SMD mill	7B	2	4	21	70	70		167

Table V. Parasitic energy loss by pretreatment.

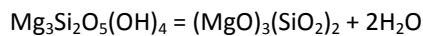| Feed Code	R_{CO2}	R_X, %	Ore/conc., kt/day	Pct total plant energy
1A	1.8	16	286	15
1B	1.8	61	75	26
1C	1.8	81	56	55
2-4A	2.5	9	706	37
2-4B	2.5	40	158	222
5A	1.8	16	286	22
5B	1.8	61	75	28
5C	1.8	81	56	56
6A	2.1	12	445	24
6B	2.1	62	86	110
6C	2.1	92	58	90
7A	2.8	43	165	67
7B	2.8	82	87	61

The ARC process is not suitable for Nordkalk purposes because the high pressures would make direct flue gas carbonation unfeasible. In addition, the authors claim the process works best with olivine and wollastonite. Serpentine carbonation is expected to be very expensive as a result of thermal pre-treatment (as noted above, an incorrect conclusion).

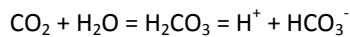## 3) Shell flue gas (see reporting Verduyn et al. [Ve09, Ve10]

Although direct flue gas carbonation seems to be possible, the CO_2 capture efficiency is very low (20-30%). This process also depends on energy intensive grinding (< 10µm).
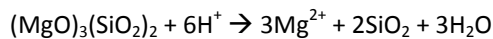

1. Thermal activation step

$$Mg_3Si_2O_5(OH)_4 = (MgO)_3(SiO_2)_2 + 2H_2O$$

Dissolution of CO2 and dissociation of carbonic acid

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-$$

2. Leaching Mg^{2+}

$$(MgO)_3(SiO_2)_2 + 6H^+ \rightarrow 3Mg^{2+} + 2SiO_2 + 3H_2O$$

3. Precipitation of $MgCO_3$

$$Mg^{2+} + 2HCO_3^- \rightarrow MgCO_3 + CO_2 + H_2O$$

4) Rau and Caldeira "Advanced weathering of limestone" (AWL01)
WO0010691; US7655193; US2001022952; US6890497; AU5568099

Using stable carbonates (limestone wastes, for example useless fines) to capture CO_2 and transform into less stable bicarbonates has several drawbacks:

- Large amounts of water to contain the bicarbonates
- Availability of carbonates
- End use/storage difficulties – although in principle disposal of products into sea/ ocean.
- Note: see research papers by G. Rau (et al.)

6) R.J. Hunwick [Hun08, Hun10]
System, apparatus and method for carbon dioxide carbonation

Hunwick came up with a method for capture and sequestration of CO_2 from power station flue gases. Carbon dioxide sequestration is carried out in the following steps: The first step involves mixing an aqueous slurry of metal silicate-containing rock (30% solids) with ammonia to form an ammonia/water/metal silicate slurry. Serpentine is the preferred silicate rock, finely ground to 90% finer than 40 microns. Secondly, a flue gas stream is exposed to the solution from stage (1) hence absorbing the CO_2 into the reactive slurry. Finally, the reactive slurry is pumped to a reactor at an elevated pressure of 100 bar and at a temperature of 225°C so as to enhance the rate of a reaction between CO_2 and serpentine reaction to produce magnesium carbonate and ammonia which is thus regenerated.

The two reactor types proposed by the inventor are: a pipeline reactor preferably with multiple flow paths and an underground chamber reactor. In the pipeline reactor, one flow path supplies ammonia/water/silicate slurry from the mining area for CO_2 absorption at the power plant. Another pipeline acting as a reactor connects the power plant to the serpentine mine site where the reaction product would be stored.

The second type of reactor set up as proposed by Hunwick is an underground chamber reactor. The reactor is a form of a chamber that may be excavated from bed rock at a depth of several 100m sufficient to allow for the carbonation reactions to occur quick enough (a depth that provides sufficient pressure to enhance the reaction). The left-hand Figure above shows a schematic diagram of the process utilising a pipeline as a (horizontal) reactor while the right-hand Figure shows a caved-in (vertical) chamber located at such a depth that it provides sufficient pressure to enhance the reaction between the CO_2 and the metal silicate.

Energy is required to pump material from one end to the other, large transport distances for chemicals (including those that fixed the CO_2), and quite fine mineral grinding.

Corrosion in the pipe can't be ruled out since ammonia is corrosive while also the slurry may be abrasive.

Looks very promising and deserves further assessment and testing.

Note: RZ has communicated (Aug. 2-3, 2011) with Hunwick about "proof of concept" experimental work done at CSIRO, Australia, as mentioned in [MPS09]. The reply was that a non-disclosure agreement must be signed before this information will be made available. (There have been problems with IP made use of by one UK university.)

7) Brent PCT/AU patent [Bre09, Bre10]

Basically the ARC process (see 1)) with heat integration/optimization. Same reasons apply.
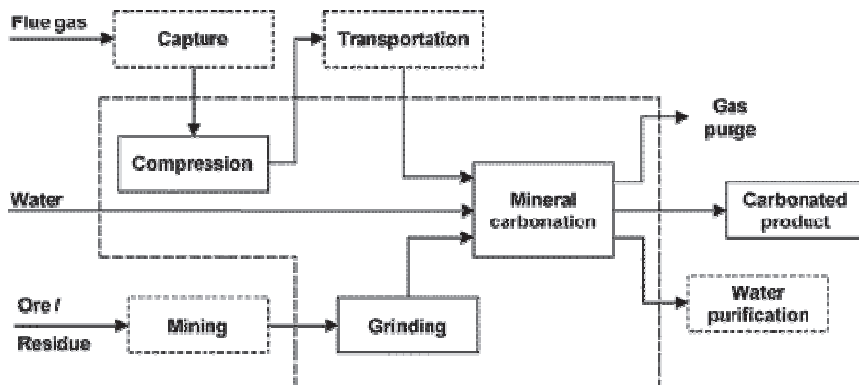
9. Huijgen et al. [Huij07]

Energy consumption and net CO_2 sequestration of Aqueous Mineral Carbonation

  The author addresses the carbonation of wollastonite and steel slags.
  The wollastonite/steel slags are grinded and mixed in water with CO_2. The Ca is extracted and precipitated in form of $CaCO_3$.

The optimum experimental conditions are 200°C, partial pressure of CO_2 of 20[1] bar, d<38 µm, reaction time 15 minutes, L/S ratio of 5kg/kg, with a carbonation degree of 69% for the steel slags and 75% for wollastonite.

The moderate temperatures allow for the use of waste heat, the conversions are reasonable in short reaction times. The sequestration efficiencies in the energy consumption assessment are clearly first law efficiencies thus the estimated values are misleading. Moreover, the author sugests only the use of pre-captured CO_2 and not flue gases making the process less suitable for Nordkalk.

10. Baldyga et al. [Bal01]
Utilization of carbon dioxide by chemically acelerated mineral carbonation

This is a two-step process including extraction of calcium from wollastonite by dissolving it in succinic acid at 80°C, for 120 minutes with a 300 rpm agitation. The author claims 100% extraction. In a seconf step the Ca is crystalized in the form of $CaCO_3$ at 30 bar, 80°C and a 300 rpm agitation. This second step takes 1 hour and the author claims 90% of conversion.

The author does not assess the chemicals recovery/recycling or gives any information on the $CaCO_3$ particle size and purity. The reaction times are long (a total of 3 hours) and a pure CO_2 stream must be used. Besides wollastinite is not a suitable input material.
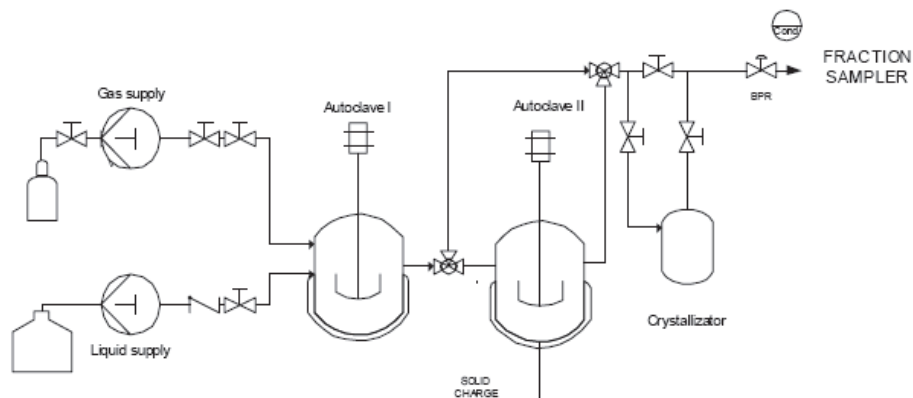
11. Munz et al. (Norway) [Mun09]
A continuous process for manufacture of magnesite and silica from olivine, CO_2 and H_2O.

In this aqueous process the CO_2 is dissolved in water at 150°C and 150 bar. This solution is used to dissolve the olivine and extract magnesium which is precipitated in the form of MgCO3 by increasing the temperature to 250°C.

No information about CO_2/water ratio is given but it looks like it needs big amounts of water (although the CO_2 solubility increases, at the operating conditions, to 4.3gCO_2/100gH_2O). Reaction times are not repported (but seem to be very long). The whole process runs at a constant pressure of 150 bar and a temperature range of 130 ~250°C. The silica recovery from the outlet solution, as suggested by the author, requires water

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[1] For steel slags carbonation this pressure does not need to be higher than 10 bar according to their experimental results.

evaporation. No information about conversion is given and the process is very energy intensive. Besides it's only applicable to pure CO_2 streams.

12. Lin et al. [Lin08]

Magnesium hydroxyde extracted from magnesium rich mineral for CO_2 sequestration ina a gas solid system

The magnesium rich mineral is subjected to hydrothermal treatment with HCl, at 125°C for 24 hours. The solutions pH is then raised with NaOH to 8 (to recover silica) and further to 11 (to recover the Magnesium in the form $Mg(OH)_2$). The gas/solid carbonation proceeds at 325°C, atmospheric pressure in a fixed bed with gas 10%vol CO_2/N_2.

The extraction takes too long and is very energy consuming. Also, the chemicals recovery is not assessed. Although the process has the advantages of running at atmospheric pressure and it can be applied to combustion gases, the conversion is very low: 26% conversion to $MgCO_3$ of the 90% Mg extracted.

13. Baciocchi et al. (Italy) a: wet; [Bac09]

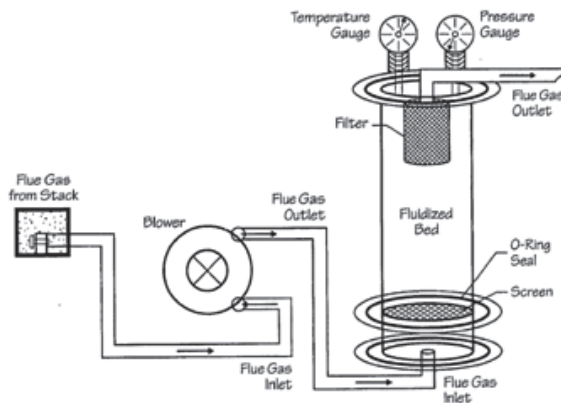Comparision of diferent routes for carbonation of APC residues

The author presents two routes to carbonate APC residues: wet and dry carbonation.

a. In the wet carbonation route the residues are reacted with water and CO_2, in a stainless steel reactor at 3 bar and 30°C. After 1 hour a conversion of 70% is reached.The process looks good since it has no extra adition of chemicals, runs at low temp and pressure and presents a good conversion. It may be applied to incinerator waste, cement kiln dust, steel slags… But the this wet route is not suitable for Nordkalk because a stream with high CO_2 concentration is required.

14. Reddy et al. (Wyoming, USA) [Red09]

Patent WO 2007/081561 ; US 7,879,305 B2, Feb 2011

A fluidized bed reactor for simultaneous capturing and mineralizing coal combustion flue gas with fly or bottom ash is patented. It operates at 15-150°C (more likely at the temperature that flue gas leaves the stack). After 15 minutes only 4% of the CO_2 going into the reactor is captured. Besides this the reactor does not look suitable (yet) for a large-scale continuous operation.
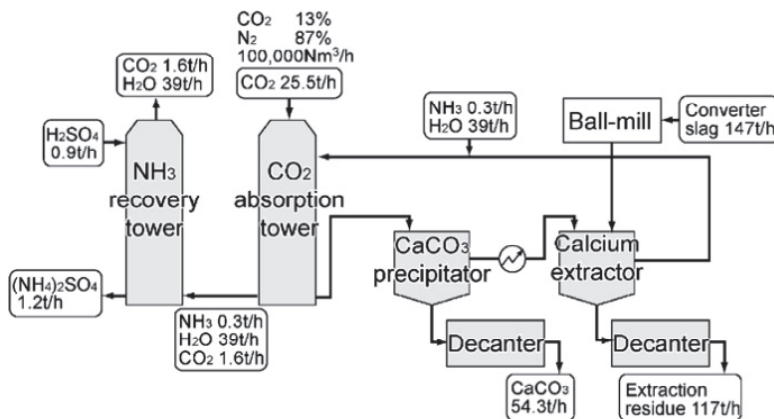
15. Kodama et al. (Japan) [Kod08]

Development of a new pH-swing CO_2 mineralization process with a recyclable reaction solution

    Slags, pre-treated at 950°C for 30 min, (with a particle size < 63 µm) are dissolved in a NH_4Cl solution, at 80°C, ~300rpm, for 1 hour. The carbonation (in aqueous solution) is done with flue gas at 80°C for 2 hours. According to the mass balance performed by the author, a conversion of 37% of the Ca in slag to $CaCO_3$ is achieved.

    The process diagram includes a NH_3 recovery tower and a CO_2 absorption tower and looks a complicated. The author reports problems with NH_3 losses making its make-up and recovery expensive. The pre-treatment is at too high temperatures and energy intensive. For this and also due to its low conversion the process does not appear to be promising.

16. Krevor et al. [Krev09]

Enhancing Process Kinetics for mineral carbonation sequestration

    Magnesium silicate is dissolved in a solution containing different dissolved salts (citrate, EDTA, or oxalate) under a CO_2 atmosphere at 120°C, 20 bar for 6 to 24 hours.

    The total extraction of Magnesium might take up to 10-20 hours. Reaction times are too long, the extra chemicals added are not recovered and the proces is not suitable for flue gases. ---- see also Park (#21)
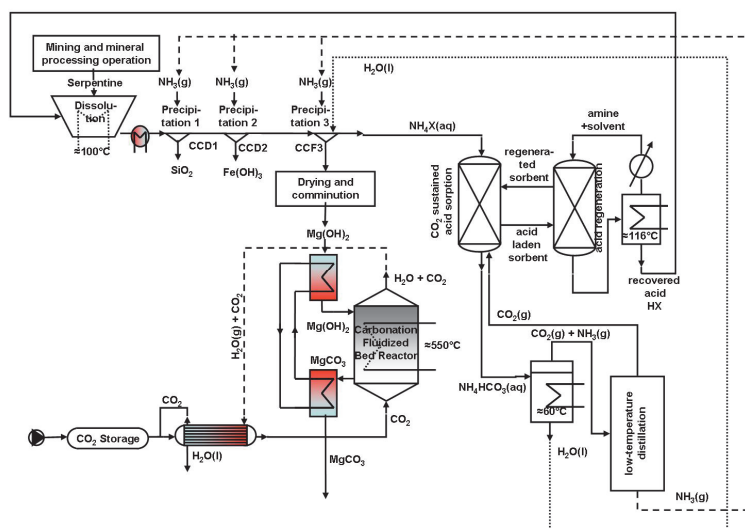
17. Kwak et al. [Kwak10]

Enhancing Process Kinetics for mineral carbonation sequestration

The experiments are done with fosferite which is crushed to 37 μm and mixed with water. A stream of pure CO_2 is pumped into the solution. The process runs at ~20-80°C, 80-97 bar, for 20h-7days. The highest conversion reported by the author is 8% after 20 hours. Clearly this is not a prossiming process.

18. Schiller [Sch06]

Schiller's process (decribed in an MSc thesis only) is theoretical investigation for mineral carbonations. This proces does not suit to Nordkalk because no experimental results are reported. Strong acids are used for mineral dissolution.

19. Maroto – Valer et al. [MW04]

US 7,604,787; US 2005/0002847

The patent describes carbonation of silicate based materials in CSTR reactor. Process temperature is in a range of 15-90 °C, pressure can be applied in a range of 14 -700 psig (approximately 1-50 bar).

Magnesium is dissolved using acids (H_2SO_4, CH_3COOH, H_2PO_4, HNO_3 in general protic, diprotic and triprotic acids) from minerals.

70 % of magnesium was dissolved from serpentine. Conversion of magnesium was about 73% after 3 hours (carbonation reaction at ambient temperature and 600 psig).

This process is not suitable for Nordkalk because:
- Too many chemicals;
- Energy intensive;
- Pure CO_2 is used;

Not logical (to produce a sorbent by adding amine in order to capture CO_2 from flue gases).
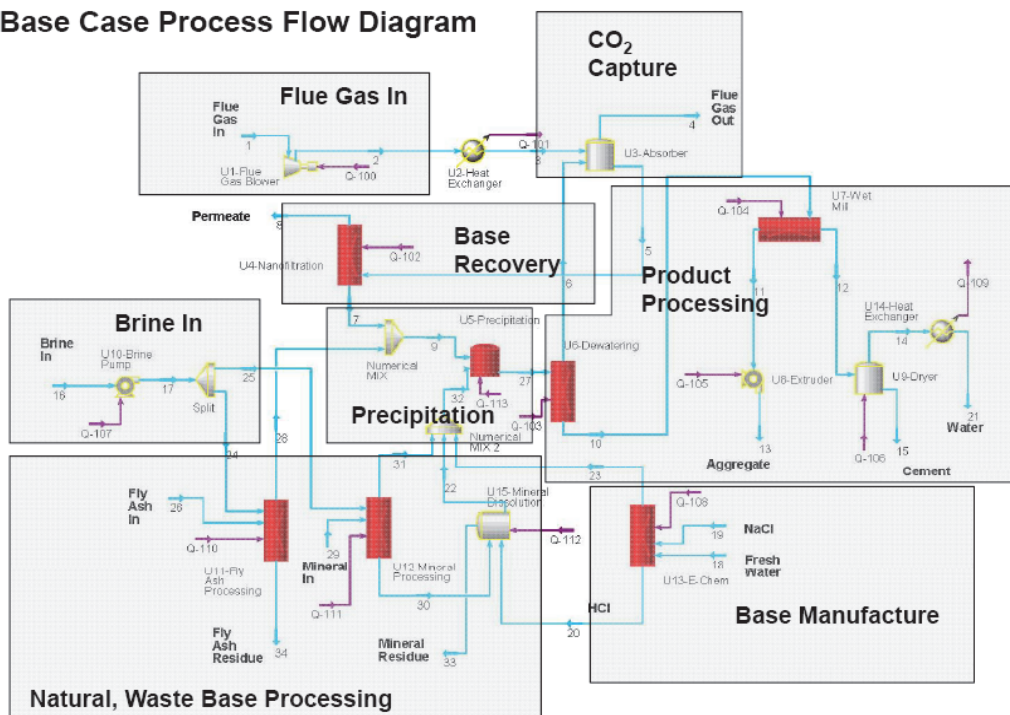
20. Calera Corporation – *[Cal09, Cal10a, Cal10b, Con09]*

This patent describes how carbonation can be applied in desalination processes in different embodiments precipitating carbonates and other salts using flue gas. Due to the fact that flue gases contain gases other than CO_2, some other salts than carbonates may be precipitated as well. For this process, brine, and sea water are used.

Solution (brine or sea water) is charged by flue gas in the beginning of the process. Afterwards precipitation of various salts occurs when pH is adjusted by employing ashes, steel slags, oxides, hydroxides, and/ or electrolyses of water.

This process may not be suitable for Nordkalk because they do not produce brines. Nonetheless, because Calera is very visible, claims much media attention and also appears to license or purchase other patents, some description is given here:

The invention involves contacting a volume of an aqueous solution of divalent cations (Mg^{2+}, Ca^{2+}) with a source of CO_2, then subjecting the resultant solution to conditions that facilitate precipitation. The alkaline-earth-metal-ion-containing water proposed include: seawater (35-50 ppt salt), brackish water (0.5-35 ppt salt) and brine (+50 ppt salt) (ppt = parts per thousand). An alternative source of alkaline-earth-metal-ion-containing water may be prepared by adding one or more divalent metal ions (oxides or hydroxides of Ca or Mg) to water. A magnesium ion source added to initial water may be finely ground solids or aqueous solution including: serpentine, olivine, mafic and ultramafic minerals and brucite (but not limited to this).

The dissolution of CO_2 into the aqueous solution of divalent cations produces carbonic acid. In order to produce carbonate – containing precipitate, protons (H+) are removed from the solution so as to shift the equilibrium towards carbonate. PH is important during precipitation since it is the factor that prevents the shift back to acidic and also precipitation of hydroxides. To attain this and to maintain a substantial constant pH value (9.5-11) or maximize the amount of CO_2 absorption the inventors propose
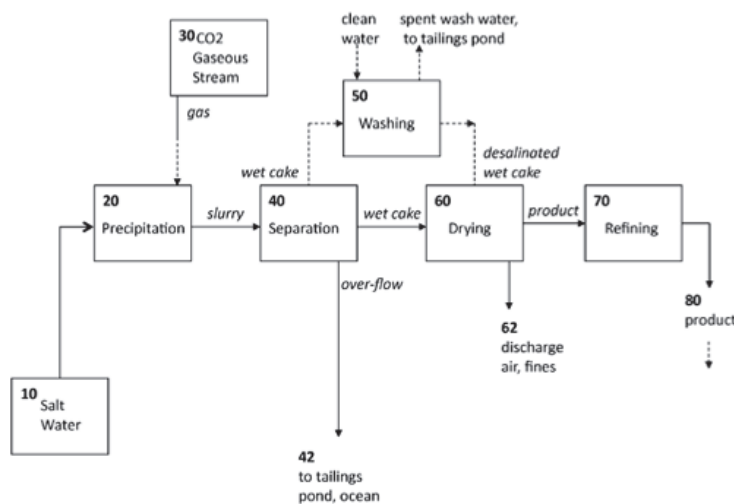
- Natural occurring proton- removal agents e.g. lime (CaO), periclase (MgO), alkaline lakes

- Electrochemical means - this comes along with acid generation stream such as HCl which could be used to enhance dissolution of Mg-bearing minerals.
- Use of microorganisms and fungi that produce alkaline protease enzymes e.g. aspergillus ustus and bacilluspasteulli.
- Synthetic chemical proton removal agents e.g. NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$

The precipitation temperature may be 0-100°C (the inventors are not specific on the temperature range), pH of 9.5-11.
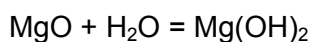
Process description

In the Figure below, water source 10 draws sea water into the precipitation reactor 20. Industrial flue gas containing CO_2 is charged into the reactor through source 30. The precipitation reactor may have a number of design features such as temperature regulators, chemical additives for raising pH, electrochemical components, mechanical agitation and monitoring parameters. The output from the reactor is directed to a separator 40. Precipitated carbonate mineral is separated from the mother liquor mechanically (mechanical pressing, vacuum filters, gravity sedimentation or centrifugation). The filter cake (precipitated carbonate) is washed to remove salt (50) and dried in drying station 60. The dried precipitate can further undergo milling 70 before use as a building material.
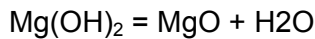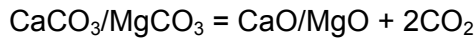

The inventors state the source of pH raising agent to be NaOH which is expensive while $Mg(OH)_2$ is not naturally occurring in large amounts. The proposal of using HCl as dissolute serpentine for example will result in $MgCl_2$ hence the need for expensive hydroxide to convert this to $Mg(OH)_2$.

Magnesium hydroxide is not a common mineral - because of its reactivity. The same holds for magnesium oxide. So, aiming at producing magnesium hydroxide one typically takes magnesium carbonate and calcines this to an oxide, and then react this with water to the hydroxide. The reactions are:

$MgCO_3 = MgO + CO_2$

$MgO + H_2O = Mg(OH)_2$

CO_2 is released when calcining magnesium carbonate - thus producing CO_2 from the process. Energy expenditures follow from calcining and reacting with water.

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University

D503 Assessment of options and a most feasible design
of serpentinite carbonation applied to a lime kiln

One cannot react dolomite with seawater to form magnesium hydroxide. One has to calcine to dolomite to "dolime" (a mix of CaO and MgO) - this reacts with seawater to precipitate magnesium hydroxide (magnesium hydroxide is much less water soluble than calcium hydroxide). The reactions are:

$$CaCO_3/MgCO_3 = CaO/MgO + 2CO_2$$

$$CaO/MgO + 2H_2O + MgCl_2 = 2Mg(OH)_2 + CaCl_2$$

$$Mg(OH)_2 = MgO + H2O$$

Again this produces significant amounts of CO_2.

An electrochemical approach will be energy intensive.

The Calera process is being demonstrated and two pilot plants based in the USA and Australia have given promising results. – *Status should be followed up.*

21.Vandor [Van10]

WO2010042294; WO2010042294; US201008415

Alkali + methanol (non-aqueous solution) → methoxide + MeOH
H_2O + flue gas + solvent suspension (methoxide) → carbonate + H_2O + heat
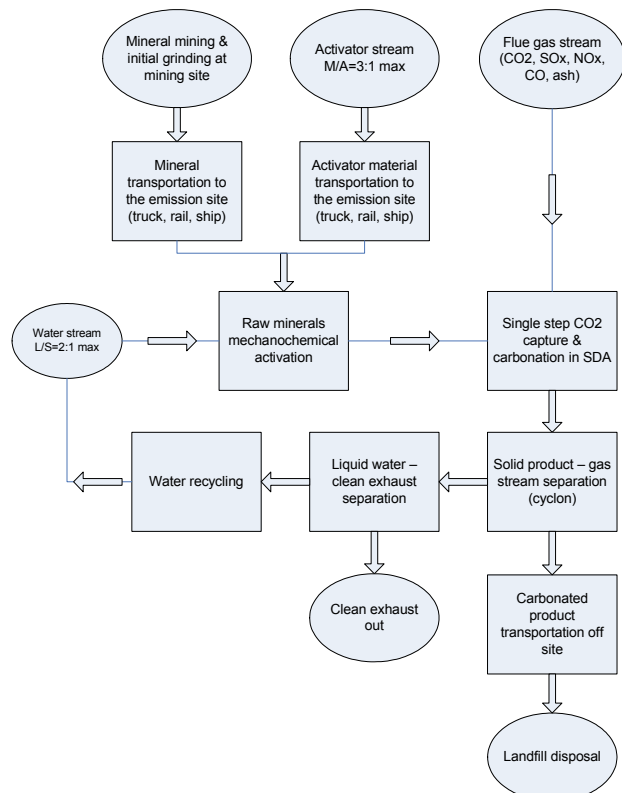
This process is less suitable for Nordkalk because:
- Too many chemicals;
- There is no data about conversions;
- Too complicated.

22 + 25. DaCosta + Caterpillar
US 2010/0221163 A1 [DaC10]

The patent describes direct mineral carbonation using flue gas and metal silicates (olivine, serpentine), alkaline earth metal oxides and combinations in bed reactor at a temperature range of 100 - 500 °C.

This process is not suitable for Nordkalk because there is a fundamental problem with reaction stoichiometry and mass balance, while conversion rate and conversion time are unknown.
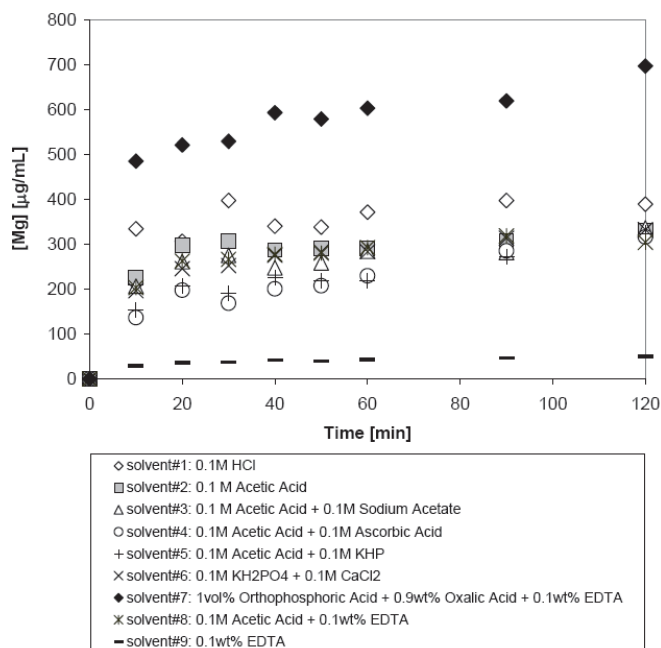
23. Park et al.,

Patent US200518910 [see also Park03, Park04]

CO_2 Mineral Sequestration: Chemically Enhanced Aqueous Carbonation of Serpentine

This article describes dissolution of Mg from serpentine and carbonation of serpentine in three-phase fluidized bed reactor.

Dissolution:

For this study nine sets of different acids and/ or chemicals were tested to dissolve 3 g of serpentine (< 75 μm) in 200 ml of solution at ambient temperature and pressure. The best performance had a mixture of 1 vol% orthophosphoric acid, 0.9wt% oxalic acid and 0.1wt%EDTA (80% of Mg was leached out in first 10 min).
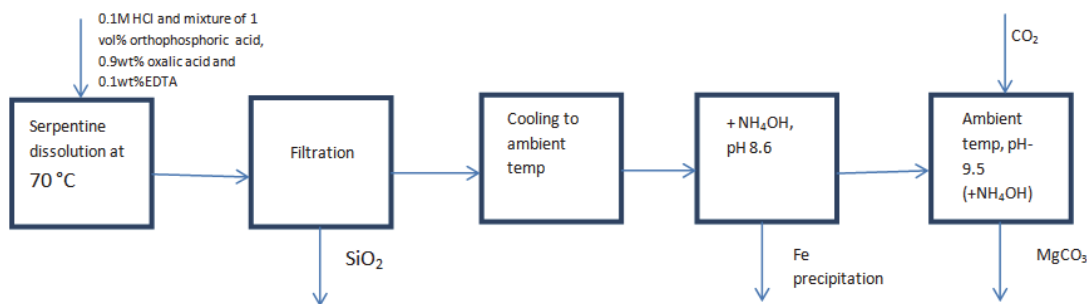

- solvent#1: 0.1M HCl
- solvent#2: 0.1 M Acetic Acid
- solvent#3: 0.1 M Acetic Acid + 0.1M Sodium Acetate
- solvent#4: 0.1M Acetic Acid + 0.1M Ascorbic Acid
- solvent#5: 0.1M Acetic Acid + 0.1M KHP
- solvent#6: 0.1M KH2PO4 + 0.1M CaCl2
- solvent#7: 1vol% Orthophosphoric Acid + 0.9wt% Oxalic Acid + 0.1wt% EDTA
- solvent#8: 0.1M Acetic Acid + 0.1wt% EDTA
- solvent#9: 0.1wt% EDTA

Carbonation:

Carbonation was done in three- phase fluidized reactor by bubbling CO_2. It was found that the conversions were 32% and 90% for 160°C and 20°C respectively of carbonation reaction at 15 atm in approximately 1 hour.

This process is not suitable for Nordkalk because too many chemicals are needed. In addition, this process is energy intensive (grinding).

CO_2 Mineral sequestration: physically activated dissolution of serpentine and pH swing process
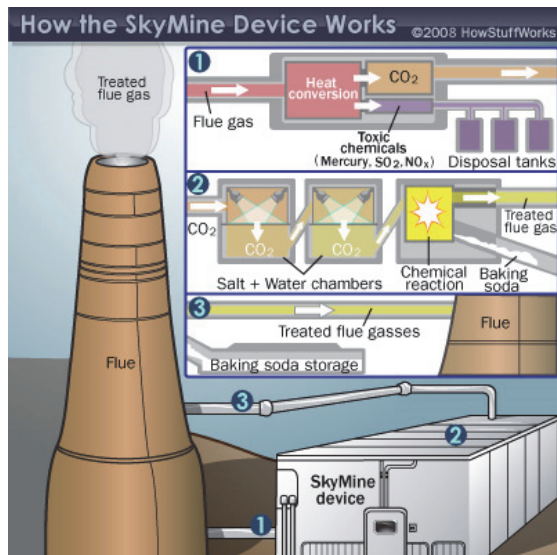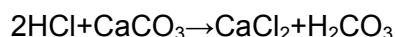

This process is not suitable for Nordkalk because:
- too many chemicals are needed;
- this process is for pure CO_2;
- energy intensive

24. Jones – see also the SkyMine concept [Jon10]

This process describes a removal of CO_2 from gas stream using various chemicals such as hydroxide, chlorine to produce carbonates and/ or bicarbonates. Afterwards calcium chloride

is formed from carbonates. In addition, electrolysis chamber can be used for the process to produce hydroxide, hydrogen and chlorine for the process.
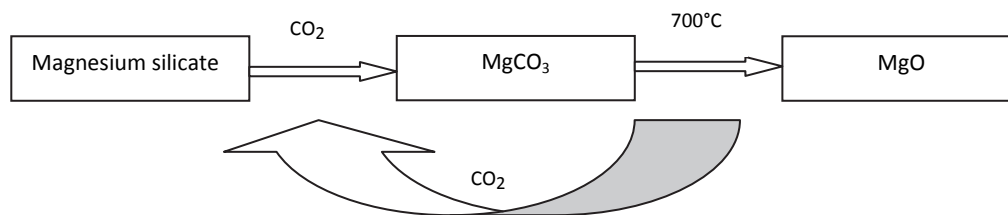
$$2HCl+CaCO_3 \rightarrow CaCl_2+H_2CO_3$$

This process is not suitable for Nordkalk because it is too complicated, there is no data about conversions, and there may not be markets for the products.
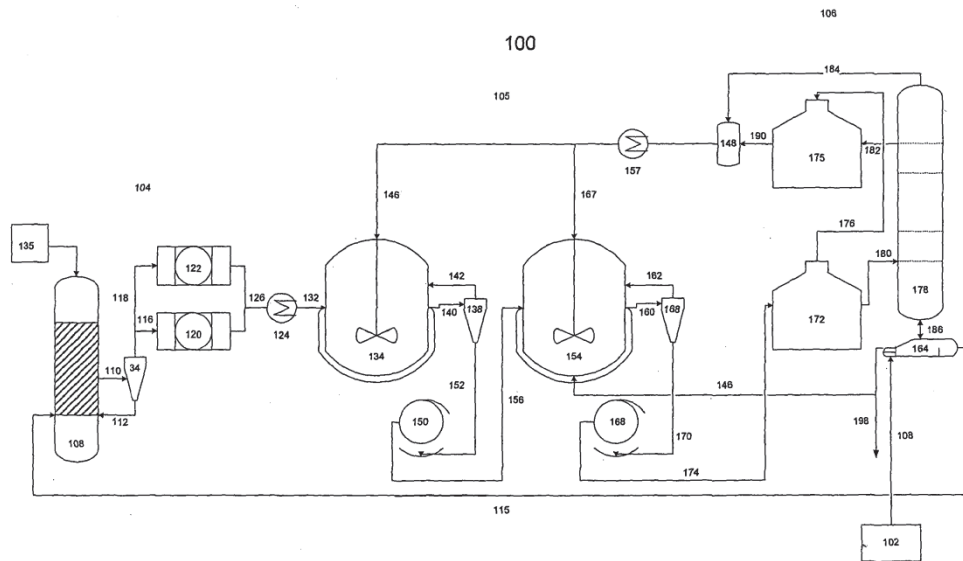
30. Novacem
WO/2009/156740; GB2009/001610

This patent describes cement production which is composed of magnesium oxide and magnesium carbonates. In addition, Novacem product has a negative footprint due to the fact that during hardening time it absorbs CO_2 from the environment.

This process looks promising and it may be a market for Nordkalk to sell magnesium carbonates which would be produced during mineral carbonation.

31   D.T van Essendelft, flue gas CO_2 sequestration WO patent 2007 [vEs07]

A process for trapping CO_2 from flue gases, reacting it with a base as to precipitate a metal carbonate, such as magnesium carbonate. Complex process, includes heat recovery but may be complicated when it comes to base recovery using heat, ion exchange resins, membranes, molecular sieves. Cost effective?

32 G. Thoms, K. Green, Australian patent 2010 [Tho10]

"Further improved methods of converting captured carbon dioxide to bicarbonate anions and then sequestering as bicarbonates of alkali and alkaline earth elements in aqueous solution", expands on patent applications "Improved method…… sodium bicarbonate" or "…. calcium bicarbonate" in aqueous solution. Clearly, dissolved carbonate is an objective – doesn't really "sequester" CO_2.

The reaction rate with magnesium silicate will presumably be quite low (natural weathering..)

33 Zhong Shaojun Method for sequestering carbon dioxide US patent 2011 [Zho11]

CO2 is absorbed in an ammoniated aqueous solution, after which basic materials such as cement kiln dust, steel and iron slag or silicate rocks or mining wastes are added. CO_2 ends up eventually as dissolved bicarbonate ions.

There will be ammonia (salt) recovery issues here, and it may not work in Mg-silicates – see tests at ÅA by E Nduagu (MSc thesis 2008).

34 Soong Yee, et al. patent US 7922792B (2011-4-12) [SY11]
Method for sequestering CO_2 and SO_2 utilizing a plurality of waste streams

Uses bauxite residues and brine waste waters from oil/gas production processes.

Not suitable for Nordkalk application.

35   D. Colton, mineral sequestration using mine waste. WO patent 2011 [Col09]

Contacting CO_2 with an aqueous slurry of mine waste, recovering metals and recycling CO_2. Expensive / exotic additives are used, it is not clear how much CO_2 is sequestered *versus* recycled. CO_2 is supercritical, at 74.9 bar.
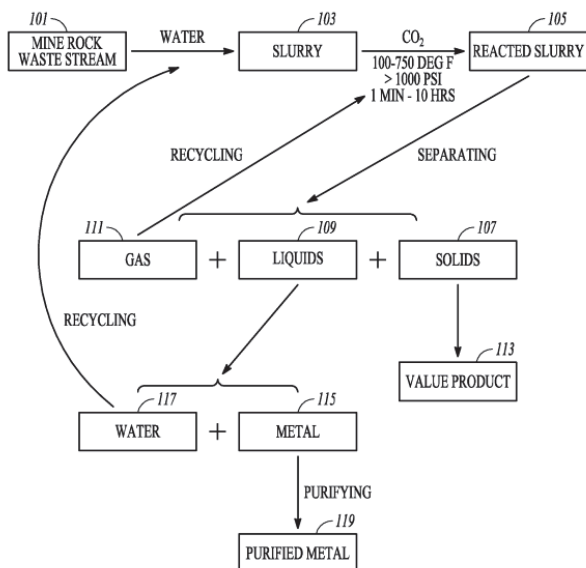

FIG. 1

Not suitable for Nordkalk application: high pressures.

36   R. Dilmore et al., separation of CO_2 from low-temperature flue gases [Dil08]
US patent application 2008

A process that uses $Na_2CO_3/NaHCO_3$ or $K_2CO_3/KHCO_3$ to concentrate CO_2.

Not suitable for Nordkalk application: no sequestration.

37   Riman, R. carbon capture and sequestration of gases WO patent 2009 [Rim09]

The method involves a reaction between CO_2 and a reagant in solution, followed by contacting the solution with a porous matrix (metal oxide, sulphate, silicate) wherein a product is formed that fills pore space and hence sequesters CO_2. Water-soluble organic solvents are needed. Energy use/costs and chemical recovery may be problematic.

38   Smith, D.R., Method and apparatus to sequester CO_2 gas, WO patent 2011 [Smi11]

CO_2 is prevented from entering the atmosphere by "combustion with metal fuels", which involves cyclic processes with metals such as magnesium. For the regeneration, electrolysis is used. See Figure below.

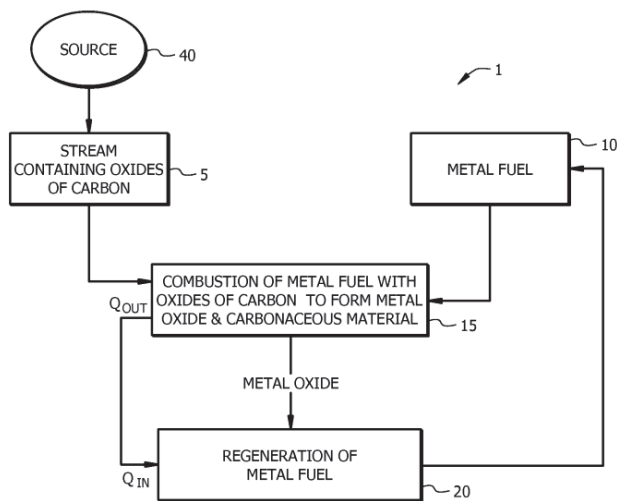Not suitable for Nordkalk application – complex and expensive.

FIG. 1

39.   Boerrigter et al., Shell Amsterdam WO 2009/092718
        A PROCESS FOR PREPARING AN ACTIVATED MINERAL

Describes heating serpentine to convert it into olivine. Apparently a forerunner of work by Verduyn and co-workers – see #3.

        Boerrigter et al., Shell Amsterdam WO 2010/097451
        PROCESSES FOR PREPARING AN AQUEOUS BICARBONATE SOLUTION, FOR CARBON DIOXIDE SEQUESTRATION AND FOR PREPARING ACTIVATED SILICATE HYDROXIDE MINERAL PARTICLES

A combination of mineral preheating and size reduction for activation, and carbonation in aqueous solutions. Long reaction times (up to 16 hours) for "leaching".

40.   M. Bauer, S. Peiffer et al., University of Bayreuth, DE, [Ba11a, Ba11b]

The group of Bauer and co-workers at Bayreuth Germany (see also 2 abstracts and presentations at ACEME10, Turku 29.11-1.12.2010) works on wet and semi-dry reaction concepts that are applied to alkaline wastes but have also been tested on CaO and MgO. Not surprisingly, Mg carbonate production was much less than calcite precipitation and some work is to be done on Mg-species carbonation.

MgO is not a common mineral resource. The semi-dry concept looks promising for Ca-containing wastes.

41. Cuycha Oy: Carbon capture and neutralization (CCN) [CCJ11, Cuy11]

The method involves the use of feldspar-type minerals to bind CO_2 as water-soluble HCO_3^- ions (counter-balanced by Ca^{2+}, K^+ or Na^+ ions, depending on the feldspar used) while at the same time producing significant amounts of aluminum hydroxide. The process operates with aqueous solutions at low (~ ambient) temperatures; for the CO_2 a (partial) pressure of at least 0.4 bar is necessary for sufficient dissolution of CO_2 in the aqueous solution. Amounts of material needed to bind a ton of CO_2 are of the order of 3 - 6 ton feldspar. The mass of aluminium hydroxide produced is roughly equal to the mass of CO_2 fixed. The numbers given are theoretical or based on reaction stoichiometry.

Unfortunately, different from other ongoing work in the field of CO_2 mineral carbonation there is no proof-of-concept information for this CCN technology. The reporting in Carbon Capture Journal refers to work done at the Univ. of Jyväskylä, but the results from experimental work (as reported by J. Huttunen in his MSc thesis from April 2009) are disappointing, presumably because the CCN technology is based on process conditions that are too mild for a significant chemical conversion rate. The technology was discussed with prof. Eklund, ÅA Geology & Mineralogy, concluding that these mild conditions won't give a significant chemical conversion. (Hangx and Spiers [HS09] report on tests at elevated temperatures and pressures.)

EMBODIMENT 1

[0027]   The method is shown schematically in FIG. 1. The flue or other gas at normal pressure is passed via connection 11 to heat exchanger 21, from which it exits into compressor 22 equipped with water injection. From it the flow proceeds at a pressure of, say, 5 bar into washing column 23, into which cold water is sprayed via connection 12. The majority of the CO_2 dissolves into the water flow and the CO_2 solution formed is passed into neutralization space 24 containing gravel, sand, or crushed rock, from which the neutralized solution exits via connection 13 into bauxite settling pool 25. The bauxite precipitate is collected from this pool at regular intervals. A part of the solution is recycled back into the washing process via connection 14 to reduce the consumption of water and the remainder is removed via connection 31. The crushed rock or other such material of the neutralization space is exchanged at regular intervals.

[0028]   The flue gas exiting from the top of column 23 is warmed in heat exchanger 21 and passed into exhaust gas turbine 26 that is coupled to compressor 22. The flue gas exits the process from turbine 26 via connection 30. In the input flow of the turbine is placed a steam injector 27, with which the unit is started and which can be used to elevate the pressure level of the dissolution if required. Depending on the CO_2 content of the flue gas and the temperature and pressure conditions of the process, the combination of turbine and compressor may produce surplus mechanical energy, which can be utilized with a generator coupled to it (not shown).

Since there is no proof-of-concept experimental data, nor a good picture energy efficiency and net CO_2 binding efficiency this seems not a useful process for application at Nordkalk Oy. (Nordkalk would not want to flush the CO_2 into the archipelago as dissolved HCO_3^- ions, nor produce very large amounts of $Al(OH)_3$).

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D503 Assessment of options and a most feasible design
of serpentinite carbonation applied to a lime kiln

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