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**Design and technical feasibility study of a  
magnesium silicate carbonation demo-plant  
at an industrial lime kiln**



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**Åbo Akademi University**  
**Turku, September 2013**



## **Report Title: D510 - Design and technical feasibility study of a magnesium silicate carbonation demo-plant at an industrial lime kiln**

**Key words: mineral carbonation, magnesium silicate rock, demo-plant, industrial scale lime kiln, Nordkalk/Pargas, process scale-up, exergy**

### **Abstract:**

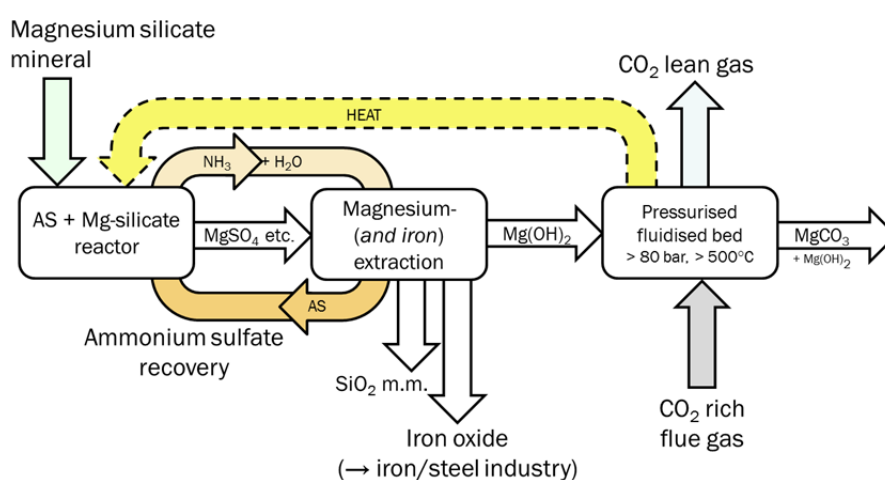
This report involves energy efficiency and chemicals use optimization and the evaluation of technical challenges when scaling up a carbon dioxide sequestration process based on mineral carbonation from laboratory to pilot scale. The case study addresses integration with the industrial lime kiln of Nordkalk at Pargas/Parainen. Aspen Plus was used to model the process. The intended pilot scale is several times larger than the laboratory scale. Some of the technical challenges can be solved by slightly modifying existing process equipment while others require custom-made equipment or alterations to the proposed process. Significant improvements to energy economy follow from the process integration while also a flue gas compression strategy is addressed and CO<sub>2</sub> pre-separation is avoided. Integration of the process with the industrial-scale lime kiln i.e. utilization of 500°C waste heat leads to exergy demand per ton CO<sub>2</sub> sequestered for heat and power of 2595 MJ and 885 MJ, respectively, processing 550 kg rock/h and sequestering 187 kg CO<sub>2</sub>/h. With the heat and power requirement equivalent to a production of 9 kg CO<sub>2</sub>/h this gives a net sequestration of 178 kg CO<sub>2</sub>/h. The calculations were made for Finnish Hitura rock, assuming a 90% conversion of Mg from rock to Mg(OH)<sub>2</sub> and a 90% carbonation conversion of this.

This report – which includes some work of forthcoming deliverable D529 – is based on journal paper “Integration of a pilot-scale serpentinite carbonation process with an industrial lime kiln” for ENERGY, Special Edition for CPOTE-12, Gliwice, Poland, September 2012 (original title “Challenges in process scale-up of serpentinite carbonation to pilot scale”), accepted /available on-line: doi 10.1016/j.energy.2013.07.009

## 1. Introduction

This report evaluates the technical challenges of scaling up, from a laboratory to pilot scale, a carbon dioxide sequestration process based on mineral carbonation whilst integrating it with an industrial CO<sub>2</sub> producer: Nordkalk's ~200 t/d lime kiln at Pargas/Parainen. The process considered in this paper is the one under development in Finland at Åbo Akademi University [1, 2], often referred to as "the ÅA route" - see Figure 1. It involves the production of magnesium hydroxide, Mg(OH)<sub>2</sub>, from magnesium silicate based material using (recoverable) ammonium sulfate salt, followed by carbonation of the Mg(OH)<sub>2</sub> in a pressurized fluidized bed (PFB) reactor at ~500°C, 20-30 bar CO<sub>2</sub> pressure. Conversion degrees for Mg(OH)<sub>2</sub> production and carbonation are taken to be 90%. Given the CO<sub>2</sub> content of ~25%-vol in the kiln gas a carbonation pressure of ~80 bar is needed.

Several challenges appear when scaling up the process with the scale considered being 187 kg CO<sub>2</sub>/h to be fixed from the flue of the Nordkalk/Pargas lime kiln [3]. Direct carbonation with the flue gas will be applied, removing the expensive and (for oxygen-containing gases) problematic CO<sub>2</sub> capture stage. The process lay-out needs to be evaluated with the availability of standard components taken into account. Besides process energy efficiency optimization (using exergy analysis) some of the challenges are the corrosive nature of fluids, the risk of salt build-up and scaling, inlet flue gas composition, high pressure and temperatures in some of the process steps, high solids content in liquids and finally the size of the pilot plant. If these issues cannot be resolved using standard industrial approaches and equipment then special materials and equipment will be needed for several of the process steps, adding considerable costs to this CCUS (carbon capture, utilisation and storage) process.



**Figure 1 A schematic illustration of the mineral carbonation process, for a flue gas with ~25 %-vol CO<sub>2</sub> content [1]**

Another challenge when going to a pilot scale is the need to operate the process in a continuous manner unlike the batch and semi-batch work done in laboratory scale. This will require sealed reactors and gas and chemicals recycling. The serpentine



processing reactor and the carbonation reactor will be the main challenges in this regard, not to mention the need for a high percentage of ammonium salt recovery. The transport of fluids and solids will also be evaluated so as to be able to find the pumps, fans and other transport equipment that would be needed for a pilot plant.

From this, the industrial feasibility of the studied process in its current layout can be evaluated. As a result the process might have to be modified or alternate process routes must be found. Exergy analysis is used for process energy and chemicals use efficiency and for the flue gas compression strategy optimization.

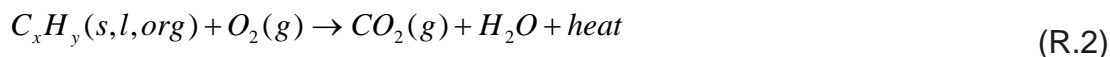
Here, the rock used is a serpentinite (~87%-wt serpentinite, ~13%-wt iron oxides) from Hitura, Finland: the use of other rock feedstock is addressed in deliverable D513: Alternative silicate raw materials for carbonation.

## 2. Process description and scale

The serpentinite rock reacts with ammonium sulfate (AS) and water at 450°C and atmospheric pressure in order to produce  $XSO_4$  salts ( $X=Mg, Ca, Fe$ ), as first described by Nduagu [4-6]. During the reaction considerable amounts of  $NH_3$ , water vapour and possibly  $SO_2/SO_3$  are released. The solids 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 in the form of (oxy-)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 [2]. Using the  $NH_3$  produced in the first step, the pH of the aqueous solution is further raised to ~10-12 and the magnesium precipitates to form  $Mg(OH)_2$ . AS is recovered from the residual solution and the  $Mg(OH)_2$  is carbonated at 500°C and 20 bar of  $CO_2$  partial pressure, in a pressurized fluidized bed reactor. The carbonation method is described in more detail by Fagerlund et al. [2,7,8]. The gas entering the carbonator may be a pure stream of  $CO_2$  but may also be the complete flue gas stream from a process. For the above mentioned lime kiln the  $CO_2$  content is 21%-vol (dry). The heat released in the carbonation reactor may provide much of the energy needed to heat the serpentinite rock, aiming at an auto-thermal process.

The production of lime is a  $CO_2$  emissions intensive process. It is produced from limestone by heating it up in a reactor, normally of rotating kiln type. The solid limestone,  $CaCO_3$ , is calcinated to  $CaO$  while  $CO_2$  is released. The heat required for the calcination reaction is generated through combustion of fuel (normally carbon based). The main reactions for the formation of the  $CO_2$  can be found below, R.1 and R.2.





During laboratory tests the maximum serpentine quantity used per batch has been a few tens of grams. The envisioned scale of the pilot plant is significantly larger and aims to process 550 kg/h serpentinite to Mg(OH)<sub>2</sub> and 620 kg/h kiln gas.

The desired process requires a significant amount of various equipments. The main components are listed in Table 1.

**Table 1 Pilot plant main equipment**

Rock silo	Flue gas cooler
Serpentinite heater	Flue gas compressor with inter coolers
Ammonium sulfate tank	Flue gas heater
Ammonium sulfate solution pump	Fluidized bed reactor (bubbling/circulating)
Water tank	Particle separation cyclone
Water pump	Flue gas expansion turbines
Serpentinite reactor	Flue gas heat recovery heat exchanger
Reacted serpentinite heat recovery heat exchanger	Reaction gas recovery fan
Dissolution tank	Reaction gas cooler
Slurry pump	Reaction gas condenser fan
Solids filter	Reaction gas condenser (scrubber)
Precipitation tank 1 (crystallizer)	Ammonium solution pump
Precipitate slurry 1 pump	Ammonium solution cooler
Precipitate filter 1	Ammonium solution dosing pump 1
Precipitation tank 2 (crystallizer)	Ammonium solution dosing pump 2
Precipitate slurry 2 pump	Ammonium sulfate regeneration
Precipitation filter 2	Regenerated ammonium sulfate solution pump
Magnesium hydroxide heater	Steam condenser
Magnesium hydroxide intermediate silo	Water pump
Magnesium hydroxide feeder silo	

### 3. Optimized process energy integration

Exergy analysis was chosen as the tool for optimizing the energy integration of the mineral carbonation process. By doing an exergy analysis, which is based on Second Law of Thermodynamics, it is possible to calculate the amount of useful work or maximum power that can be produced from a given energy form [9]. The process was simulated in Aspen Plus® and the obtained results were used to calculate the exergy for the streams using MS Excel®.

The mineral carbonation process has been discussed in several publications [1, 8,10-11] giving details on the chemistry and the energy requirements for the process. The aim of this work is to study the use of process waste heat from the

CO<sub>2</sub>-producing process to cover some of the heat required for the CO<sub>2</sub> mineralization.

Hot flue gas from the lime kiln is used as primary source of heat and as the CO<sub>2</sub> source for the carbonator.

By utilizing the hot flue gas, which is readily available, no other external source of heat is needed for the scale considered here. Other sources of heat are the exothermic reaction in the carbonator and the hot products from the same reaction. Other than the flue gas only some electricity and cooling water are needed to drive the process.

Figure 2 aims to give a clear view of the how the flue gas and waste heat is integrated in the mineral carbonation process. The stream numbers match those given in Table 2 and Figure 3. These numbers will be referred to in the text. The solid lines in Figure 2 show the material streams going through the process (left to right) as discussed above while the dashed and dash-dotted lines show the heat integration. Flue gas (stream 7) is special: it is first used as a heat source, then compressed, heated and finally used as a reactant in the carbonation process.

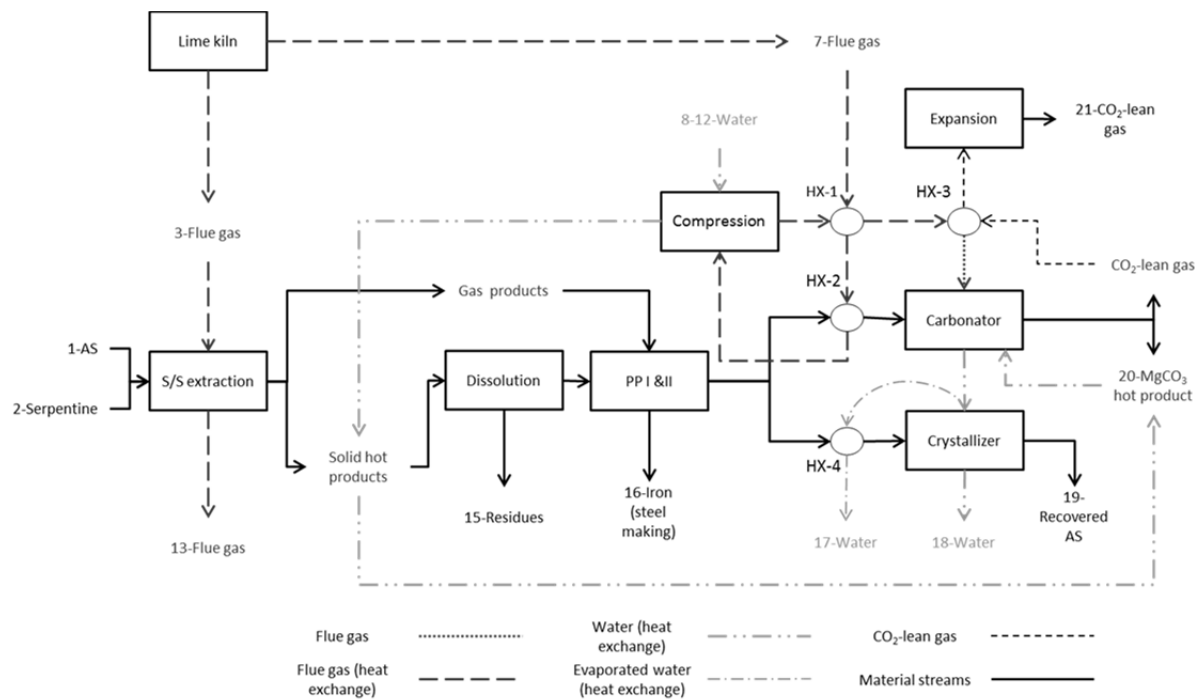


Figure 2 Mineral carbonation process block diagram





### 3.1. Heat integration and recovery

A lot of heat is required for several steps in the mineral carbonation process. The main consumers of heat are the extraction of  $\text{Mg}(\text{OH})_2$  from serpentinite, pre-heating of  $\text{Mg}(\text{OH})_2$  and compressed flue gas before the carbonation reactor and the regeneration of ammonium sulfate.

The extraction process and the pre-heating before the carbonator require high temperatures and therefore require high temperature heat to satisfy the energy requirements. Hot flue gas at  $500^\circ\text{C}$  (stream 3 in Figures 2 and 3) from the lime kiln can be used to supply the heat for the endothermic reaction in the solid/solid extraction reactor. The flue gas does not come in contact with the solids, it is only used as a heat source. After providing the heat for the extraction reaction the flue gas leaves the reactor at a lower temperature,  $440^\circ\text{C}$ , and is used to pre-heat the reactants AS and serpentine (streams 1 and 2). After the reactant pre-heating the flue gas (stream 13) still has a high temperature,  $\sim 380^\circ\text{C}$ , and can be utilized for the production of district heat. In Pargas/Parainen, the location for which this study is made a district heating system exists.

One source of high temperature heat not fully optimized in this study is the hot gas exiting the extraction reactor. The gas is mainly  $\text{NH}_3$  and water vapor but can also contain  $\text{SO}_3$  caused by thermal decomposition of the  $(\text{NH}_4)_2\text{SO}_4$  salt in the extraction reactor. Recovering heat from this gas is difficult, as soon as the gas comes in contact with a cold surface ammonium sulfate salt will form on the surface causing scaling and a lowering the heat transfer. Thus this detail needs further study. After providing heat to the process steps that require lower temperatures there is still a lot of hot water and steam at  $100^\circ\text{C}$  left. These can be used to produce hot water for distribution as district heat with a capacity of 0.8 MW.

### 3.2. $\text{Mg}(\text{OH})_2$ production from serpentinite

Before the solids exiting the extraction reactor are dissolved in water they are first cooled in two heat exchangers in series. The first uses hot water from the compressor cooling system while the second uses fresh cooling water, cooling the solids from  $440^\circ\text{C}$  to  $130^\circ\text{C}$  and then finally  $80^\circ\text{C}$ . The solids are cooled to  $80^\circ\text{C}$  as  $\text{MgSO}_4$  has the highest solubility in water at that temperature [9]. The solids are mixed with fresh water entering at  $15^\circ\text{C}$ . The solids dissolution releases heat which is removed by cooling in order to maintain an optimum temperature of  $80^\circ\text{C}$ . Due to the low temperature the heat from the dissolution tank is not considered for further use. Likewise, the undissolved solids are separated from the solution and removed without heat recovery.

Magnesium hydroxide is precipitated from  $\text{MgSO}_4$  at  $30^\circ\text{C}$  and then preheated with flue gas before entering the carbonator. As noted above, the degree of magnesium conversion from silicate in the rock to  $\text{Mg}(\text{OH})_2$  is assumed to be 90%.



The solution from the dissolution tank is cooled to 30°C before it enters the precipitation stages where ammonia (released during the solid/solid extraction) is added. The precipitated solids from the first precipitation step are removed from the process (the use of the iron oxide by-product for iron/steelmaking is the subject of a parallel study). As for the dissolution tank, the temperature of the process is too low for heat recovery.

In the second precipitation tank the  $Mg(OH)_2$  is produced. After drying this solid  $Mg(OH)_2$  is preheated in heat exchanger 2 (HX-2) in Figure 2 and fed to the carbonator. The remaining solution, which is mainly ammonium sulfate in water, is fed to the recovery crystallizer. Steam produced in the crystallizer is used to preheat this AS solution and then used for district heat (stream 17). The crystallizer is heated to 103°C using hot pressurized water and steam originating from the cooling of the carbonator. The crystallized  $(NH_4)_2SO_4$  is fed back to the solid/solid extraction process to react with serpentinite. (Alternatively, mechanical vapor recompression can be used for this salt recovery [11, 12].)

### 3.3. Flue gas compression

During the compression the flue gas heats up. This heat is removed from the compressed flue gas in intercoolers cooled with water. This cooling water is further heated by other hot units that need cooling and is used to heat process steps that require lower temperatures.

The flue gas to be treated needs to be cooled before compression. This cooling is achieved by first using it to pre-heat compressed flue gas (HX-1) after which it is used to pre-heat the  $Mg(OH)_2$  (HX-2) before it enters the carbonator. After that the flue gas has a temperature of 150°C which is then lowered to 40°C with cooling water before entering the first compression stage.

The cooling causes most of the water vapor (95 %) in the gas to condense. The condensed water is separated from the gas before it enters the first compression stage. Between the compression stages the gas is re-cooled to 40°C while condensate is separated from the gas stream. The power requirement for the respective compression stages decreases slightly as the mass of gas decreases due to the water condensing in the heat exchangers. The compression ratio in the final compression step is higher than in the other steps. A higher compression ratio was selected as by that stage almost all of the water is condensed and to raise the temperature of the gas before it enters the pre-heating heat exchangers prior to the carbonator. The final compression ratios used in the simulation is 2:2:2:2:5, respectively, for the five compression steps. More detail on selection and optimization of the compression/expansion section is given elsewhere [13]. For compression of the gas up to 80 bar 118 kW is needed, assuming a mechanical efficiency of 0.8 for each step.



### **3.4. Carbonation of Mg(OH)<sub>2</sub>**

In two pre-heating heat exchangers the compressed flue gas is first heated to 473°C (HX-1) and then to 500°C (HX-3) with the CO<sub>2</sub>-lean, water rich, gas coming from the carbonator.

The carbonation reaction in the fluidized bed reactor is exothermic and the reactor needs to be cooled to maintain the desired 515°C reaction temperature. The solid and gaseous products are separated after exiting the reactor, most likely with the use of a cyclone. After preheating the compressed flue gas, the CO<sub>2</sub>-lean gas is expanded in two turbines connected in series. The gas is expanded from 80 bar down to 1 bar, producing 72.1 kW which is enough to cover 61% of the power needed for the flue gas compression. Solid magnesium carbonate and unreacted magnesium hydroxide (stream 20) exiting the carbonation reactor is cooled with water. As noted above, the degree of carbonation conversion is assumed to be 90%.

Power consumption by pumps and fans for the transport of the materials nor pressure loss in the equipment and pipes have not been considered in this study; these are expected to be small to the overall process energy picture.

After heating up the process steps that require lower temperatures there is still a lot of hot water and steam at 100°C left. These can be used to produce hot water for distribution as district heat with a capacity of 0.8 MW.

### **3.5. Exergy analysis, overall process energy requirements**

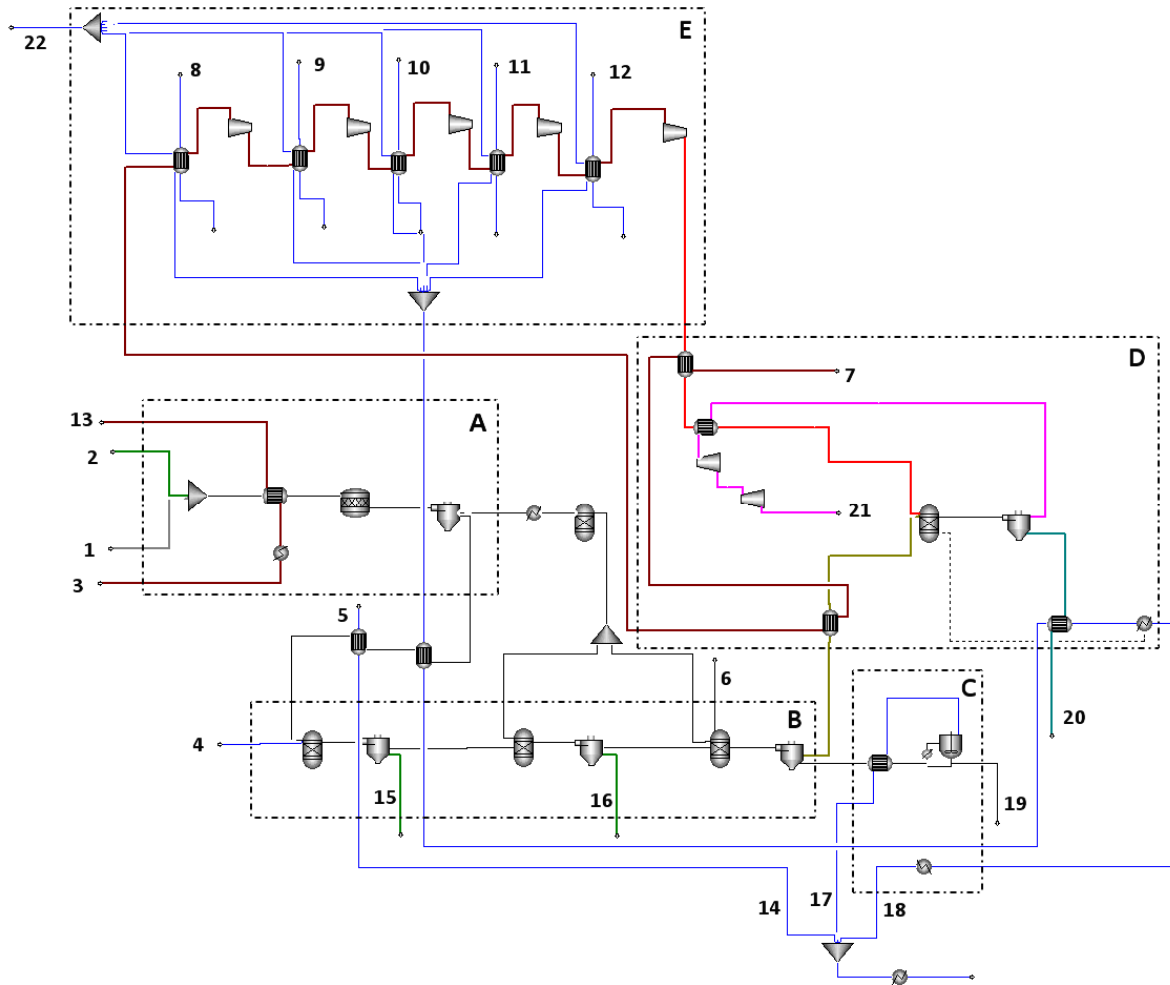
The material streams entering and exiting the mineral carbonation process given in Table 2 and can be seen in Figure 2. As most of the materials enter the process at ambient conditions their physical exergy is zero. The ambient conditions are assumed to be 15°C temperature and 1 bar pressure. The cooling water has a low exergy due to it being pressurized. The hot flue gas and the power used to drive the compressors are the only relevant sources of exergy to drive the process.



**Table 2 Overall simulated material streams**

Total process		Mass flow kg/h	Temperature °C	Enthalpy flow (total) W	Pressure bar	Exergy (physical) W
<b>In</b>						
1	Ammonium sulfate	1100	15	-2267300	1	0
2	Serpentine	550	15	-2166800	1	0
3	Flue gas in	28000	500	-20826000	1	1729984
4	Dissolution water	900	15	-3976800	1	0
5	Cooling water for solids	90	15	-397680	1	0
6	NH <sub>3</sub>	0.1	15	-76	1	0
7	Flue gas	620	500	-461140	1	38308
8	Cooling water I	290	15	-1281400	4	4
9	Cooling water II	130	15	-574420	4	12
10	Cooling water III	130	15	-574420	4	12
11	Cooling water IV	130	15	-574420	4	12
12	Cooling water V	120	15	-530240	4	2
	Compressors					118139
	Exergy in (heat in material streams)					1768333
	Exergy in (power)					118139
<b>Out</b>						
13	Flue gas out	28000	384	-21849000	1	1119993
14	Hot water from solids cooling	90	100	-386050	1	1726
15	Undissolved solids	298	80	-1119800	1	49836
16	Precipitate I	36	30	-64808	1	16066
17	Evaporated water	523	100	-2023100	1	60353
18	Medium hot water	800	100	-2952300	1	124374
19	Recovered AS	1441	103	-4682300	1	128015
20	Solid product (MgCO <sub>3</sub> )	386	150	-1421300	80	127770
21	CO <sub>2</sub> -lean gas	489	92	-289180	1	5398
22	Condensate	21	41	-91746	1	26
	Turbines					72153
	Exergy out (heat in material streams)					1633557
	Exergy out (power)					72153

As can be seen in Table 2 most of the exergy exiting the process is in the unprocessed flue gas. The other main carriers of exergy are the medium hot water, recovered AS and the solid product. Another significant source of exergy is the expansion turbines used to recover power. By utilizing waste heat generated inside the CO<sub>2</sub> mineralization process the need for hot flue gas from the lime kiln to cover the heat requirement of the process can be reduced by 32%, from 42434 kg/h flue gas reported earlier [10], with less process heat integration with the kiln process to 28620 kg/h flue gas. This shows that there is a possibility to increase the scale of the envisioned pilot plant based on the available heat, while preventing the need for a separate CO<sub>2</sub> capture process. (With 32% more heat available the amount of CO<sub>2</sub> fixed may be increased from ~180 kg/h to ~260 kg/h.)



**Figure 3 Aspen Plus model of envisioned process**

The simulated Aspen Plus model for the mineral carbonation process can be seen in Figure 3. The model is made up of five main modules: solid/solid extraction module, dissolution and precipitation module, AS recovery module, carbonation with pre-heating and power production and finally the gas compression module, modules A, B, C, D, E, respectively. The material streams, with their mass flow, temperature, enthalpy, pressure and physical exergy, entering and exiting the modules are shown in Tables 3-7.



As can be seen in Table 3 the hot flue gas entering the module is the only source of physical exergy. The difference in physical exergy entering and exiting module A is due to exergy destruction and conversion of physical exergy to chemical exergy.

**Table 3 In and out flows to module A**

A	Mass flow	Temperature	Enthalpy flow (total)	Pressure	Exergy (physical)
	kg/h	°C	W	bar	W
In					
Ammonium sulfate	1100	15	-2267300	1	0
Serpentine	550	15	-2166800	1	0
Flue gas in	28000	500	-20826000	1	1729984
Out					
Ammonia + steam	732	440	-1749100	1	132483
Reacted solids I	942	440	-2849000	1	350870
Flue gas out	28000	384	-21849000	1	1119993

Table 4 shows that even though 35% of the mass entering module B is water the dissolution of ammonia and sulfate greatly increases the mass of liquid exiting the module.

**Table 4 In and out flows to module B**

B	Mass flow	Temperature	Enthalpy flow (total)	Pressure	Exergy (physical)
	kg/h	°C	W	bar	W
In					
Reacted solids II	942	80	-2943900	1	40471
Dissolution water	900	15	-3976800	1	0
NH <sub>4</sub> I	58	40	-189370	1	149
NH <sub>4</sub> II	674	40	-2207300	1	1733
NH <sub>3</sub>	0	15	-76	1	0
Out					
Undissolved solids	298	80	-1119800	1	49836
Precipitate I	36	30	-64808	1	16066
Mg(OH) <sub>2</sub>	275	30	-1212000	1	18528
AS solution	1964	30	-7041300	1	478

The hot water entering module C is only a heat carrier and exits at a lower temperature as medium hot water. Water in the AS solution is evaporated, the AS and evaporated water are recovered separately.

**Table 5 In and out flows to module C**

C	Mass flow	Temperature	Enthalpy flow (total)	Pressure	Exergy (physical)
	kg/h	°C	W	bar	W
In					
AS solution	1964	30	-7041300	1	478
Hot water	800	144	-3299600	4	56671
Out					
Evaporated water	523	100	-2023100	1	60353
Medium hot water	800	100	-2952300	1	124374
Recovered AS	1441	103	-4682300	1	128015

The two biggest exergy streams exiting module D are in the solid product and as power from the expansion turbines, as can be seen in Table 6.

**Table 6 In and out flows to module D**

D	Mass flow	Temperature	Enthalpy flow (total)	Pressure	Exergy (physical)
	kg/h	°C	W	bar	W
In					
Flue gas	620	500	-461140	1	38308
Compressed gas	599	263	-432630	80	65945
Mg(OH) <sub>2</sub>	275	30	-1212000	1	18528
Pres. medium heat water	800	144	-3360100	4	37976
Out					
CO <sub>2</sub> -lean gas	489	92	-289180	1	5398
Low pres. cold gas	620	149	-527730	1	4649
Solid product	386	150	-1421300	80	127770
Hot water	800	144	-3299600	4	56671
Turbines					72153

**Table 7 In and out flows to module E**

E	Mass flow	Temperature	Enthalpy flow (total)	Pressure	Exergy (physical)
	kg/h	°C	W	bar	W
In					
Low pres. cold gas	620	149	-527730	1	4649
Cooling water I	290	15	-1281400	4	4
Cooling water II	130	15	-574420	4	12
Cooling water III	130	15	-574420	4	12
Cooling water IV	130	15	-574420	4	12
Cooling water V	120	15	-530240	4	2
Compressor					118139
Out					
Compressed gas	599	263	-432630	80	65945
Condensate	21	41	-91746	1	26
Cooling water out	800	113	-3443400	4	12896

The destruction of exergy is clearly visible in Table 7. As there is no chemical reactions taking place in the compression module the difference in exergy in and out is exergy destroyed. Here 64% of the exergy entering the module is destroyed. This is a significant loss.

Finally it is possible to calculate the overall exergy demand per ton CO<sub>2</sub> sequestered for heat and power to be 2595 MJ and 885 MJ (equivalent to 9 kg CO<sub>2</sub>/h using the national emission average value for Finland of 200g CO<sub>2</sub> per kWh [14]), respectively, processing 550 kg rock/h and sequestering 187 kg CO<sub>2</sub>/h, which gives a net sequestration of 178 kg CO<sub>2</sub>/h.

## 4. Technical challenges of pilot scale plant

There are several properties, such as density, viscosity and solid fraction of the liquids and slurries, that must be determined before the equipment such as pumps, tanks and filters can be properly selected. For the bulk solids and the particles in the process it is also important to determine size, shape and hardness. Once the optimum conditions are fixed these can be found from laboratory scale tests.

### 4.1. Magnesium extraction

One of the main challenges will be the design of the serpentinite/ammonium sulfate reactor for the extraction of Mg from Mg-silicate-based rock. In the first part of the extraction reactor the ammonium sulfate is mixed with the serpentinite and heated up to ~400-440°C. The volume of the reactor for the extraction stage needs to be





minimized (especially the overhead gas space) in order to keep the gases in contact with the solids for an extended period to facilitate optimum conversion of rock. The gases released during the reaction are to be recovered for use in later stages of the process. It is therefore important that the reactor is gas tight.

The serpentinite conversion reaction is endothermic and requires an external source of heat. Hot flue gas taken from the lime kiln can be used as this heat source. The flue gas cannot be in direct contact with the solids as this would interfere with the conversion reactions. This can be avoided by using heat transfer tubes inside the reactor or by building the reactor with a double wall where the flue gas can flow between the walls.

After the reaction gas leaves the serpentinite reactor it has a temperature of ~400°C. Recovering the thermal energy in the gas is difficult because of its composition. When the gas reaches 420°C its components may start to react and form solid ammonium sulfate (AS) according to HSC Chemistry [15]. The fouling of the heat transfer surface in the heat exchanger will reduce the availability of the heat exchanger. To reduce the rate of fouling the heat transfer surface needs to be warm enough to prevent the formation of AS. Preferably, the gases released from this solid-solid reactor do not contain SO<sub>x</sub> species, as this basically indicates that the temperature in the reactor is too high, giving AS salt decomposition.

## 4.2. Solids handling, Mg(OH)<sub>2</sub> production

After a first dissolution tank for removing unreacted rock and insoluble products like silica, the precipitation in two sequential precipitation tanks is based on the change of solubility with pH. The tanks work in series: iron oxyhydroxide is precipitated in the first tank at a pH of ~8-9 and magnesium hydroxide in the second tank at pH ~10-12. Process control is important to ensure that the resulting particles are of a suitable size distribution. The optimum size distribution is dependent on the requirements of a potential end user. For the magnesium hydroxide the optimum particle size and distribution was studied by Fagerlund [8].

The process requires that solid particles are removed from aqueous streams at several stages. Due to the process being continuous two or more automatic parallel coupled batch filters need to be used at each stage. One filter is operated while the solids captured by the other filter are removed. To reduce the loss of solution it is important that the solid cake formed in the filter is as dry as possible. By using heated press filters the water content can be kept to a minimum.

The amount of liquid flowing through each filter is very similar and therefore the same type of filter housing can be used for the filters, only the filter mesh needs to be different.

The large amount of solids handled in this process, which comprise dry solid



powders and wet precipitates are to be transported by conveyors. Different types of conveyors, such as screw conveyors, will be needed depending on the varying solids properties such as temperature and particle size.

### 4.3. Gas handling and $Mg(OH)_2$ carbonation

In several stages of the process hot flue gas from the lime kiln will be used as a heat source. Flue gas used for heating purposes has to be taken from the end of the kiln in order for it to be hot enough [3]. This will set some restrictions on the use of the flue gas. As the gas contains steam and can contain small amounts of sulfur dioxide small amounts of sulfurous acid may form if the gas is cooled too much or comes in contact with cold surfaces. Another factor that limits the use of the hot flue gas directly from the lime kiln is the amount of particles. These particles will build-up in heat exchangers causing increased pressure drop and affecting heat transfer on the gas side.

Flue gas going to the compressor should contain as little  $SO_x$ , water vapor and particles as possible. The  $SO_x$  and water vapor can (after condensation) cause corrosion and the particles can cause damage to the compressor wings.

According to the process description by Fagerlund et al. [1] the  $CO_2$  partial pressure needs to be 20 bar in the fluidized bed reactor. As the flue gas contains only around 20%  $CO_2$  the needed total gas pressure will be 80 bar. Reaching 80 bar will require high pressure compressors. For efficient compression intercoolers will be needed. The inlet gas should contain as little  $SO_x$  as possible as it will condense during the compression and cooling stages. As noted, together with condensed water the  $SO_x$  may form sulfuric and sulfurous acid, causing corrosion in the compressors and intercoolers.

The construction of the pressurized fluidized bed reactor may be challenging and it seems that it cannot be supplied by Finnish fluidized bed boiler manufacturers. During normal operation the reactor needs to be able to withstand a total pressure of 80 bar and a temperature of 500°C. Due to the fluidization of the magnesium hydroxide and bed particles the inner walls of the reactor will be in erosive conditions thus the construction material for the reactor has to be carefully selected.

The intended 600 kg/h lime kiln gas is about 70 times the scale used in the laboratory. This means that the pilot scale fluidized bed reactor would have an inner diameter of about 10 cm for the first level of scale-up considered in this paper, compared to the 1.6 cm lab scale reactor used in the lab at ÅA [7,8].

After the fluidized bed reactor it is important to capture as many of the particles as possible to reduce the wear on the expansion turbine used to utilize the high pressure and temperature after the reactor.

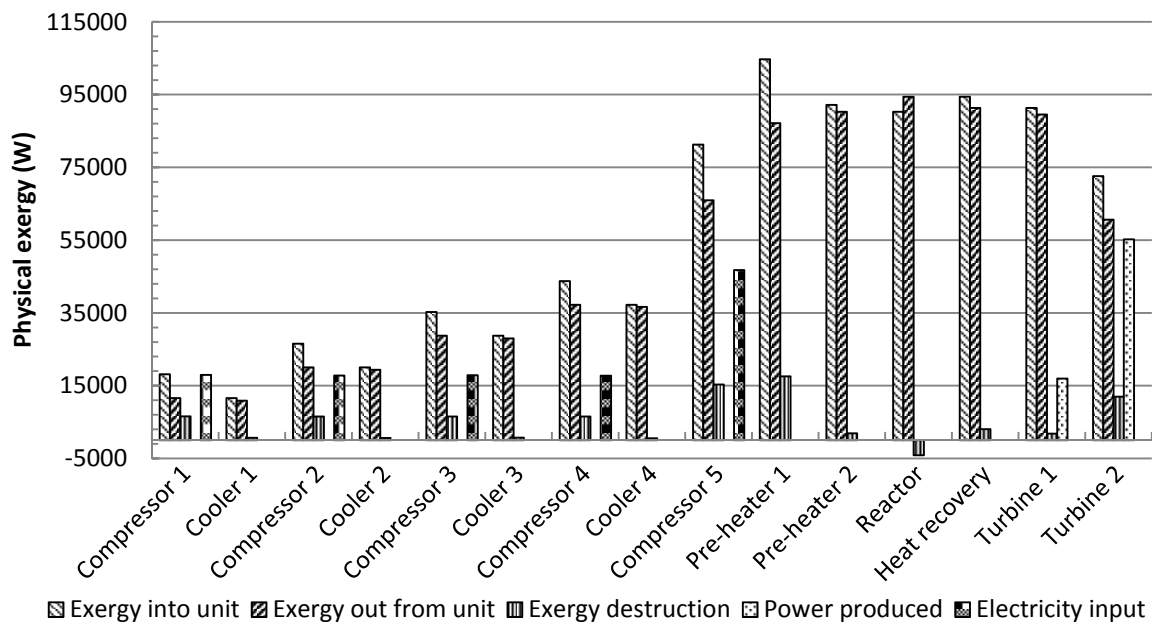
After recovering some of the heat content of the gaseous products leaving the



extraction reactor the ammonia must be recovered to be used in later stages of the process. This ammonia can be recovered by a wet absorber. When the ammonia and water vapor come in contact with the scrubbing liquid they are cooled and condensed. By recirculating the scrubbing liquid a close to saturated solution of  $NH_3$  can be obtained. This solution can then be used for the pH control of the precipitation tanks. The penalties of using a wet absorber are the loss of heat to the scrubbing solution, the need to pump the scrubber solution and the necessary cooling of the scrubbing solution.

## 5. Flue gas compression optimization

A five-stage compression process with intercooling was selected for this study was selected as it has a low power requirement compared to compression with fewer steps and a lower exergy loss [13]. Despite the optimization still quite some exergy is lost during the cyclic process of compression and cooling of the gas between.



**Figure 4 Physical exergies for the gas treatment units**

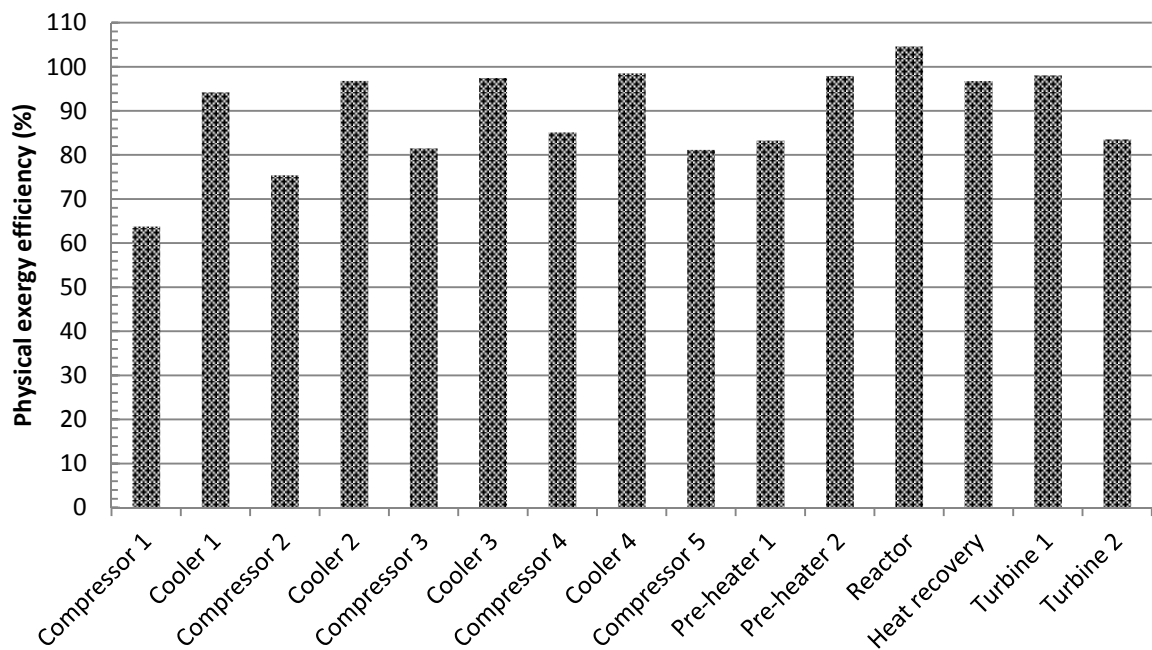
Compressors and expansion turbines with an efficiency (polytropic / isentropic) of 72% and a mechanical efficiency of 80%, pressurized-water cooled counter-current heat exchangers and a heating unit were selected and used to calculate the loss of exergy in the system. The exergy was calculated separately for each stream and the effect the different units have on the exergy of the streams was assessed. See Figure 3 for the Aspen Plus model used for the calculations.

The exergy of the streams was calculated from the stream data given by Aspen Plus and normalized with data for similar streams at ambient conditions (1 bar and 15°C).

As can be seen in Figure 4 the exergy of the flue gas entering the compression process is very small compared to the necessary input of exergy for the compressors. The temperature and pressure increase for the gas can clearly be seen as an increase of physical exergy of the streams. The exergy in Figure 4 is physical exergy.

As it can be seen in Figure 4 and Figure 5, the units with the highest loss of exergy are not always the same as the units with the lowest exergy efficiency. The exergy destruction for a unit is from as little as 1.5% (intercooler four) up to almost 40% (compressor one) depending on the type of unit. For the carbonator the physical exergy loss is negative (-4131W) as the carbonation reaction is exothermic. The compressors have higher losses than the intercoolers while the highest exergy losses can be found in the first pre-heater. Another large exergy penalty can be found in the second expansion turbine.

Figure 5 shows the difference in exergy entering a unit and the exergy exiting the unit. The physical exergy for the carbonation reactor in Figure 4 is above 100% as chemical exergy is converted into physical exergy.



**Figure 5 Physical exergy efficiency of the carbonation gas compression and expansion units**

The heat-generating carbonation reactor will provide for some of the heat needed to pre-heat the gas after compression to the carbonation reactor temperature. As to avoid unnecessary detail only physical exergy for the gas and cooling water is considered and the exergy of the solids exiting the reactor are assumed to be the same as for the solids entering the reactor. Heat from the carbonation reactor will be used to pre-heat the gas.



Some of the exergy added to the flue gas, after its compression, before the entering the carbonator can be recovered with expansion turbines. The preferable option for using the power from the expansion turbines is to have one or more of the compression stages connected on the same axis as the turbines.

## 6. Alternatives for scale of equipment

The intended pilot scale is much larger than what has been accomplished in laboratory tests but it is still very small when compared to an industrial scale mineral carbonation process at a lime kiln plant that processes all flue gases. This is problematic as equipment designed for laboratory use is too small while industrial sized equipment is too large. In this regard the biggest problem is the flue gas compressor: compressed flue gas will be stored in an intermediate tank that would continuously feed the carbonator. The pressure in the tank will drop below a set target thus the compressor will be run periodically at nominal capacity.

In the process described by Romão et al. [2] the ammonia gas released from the solid/solid extraction reactor is fed to the precipitation tank with the use of fans. This could be problematic due to insufficient pressure generated by ordinary gas fans to overcome the static pressure caused by the liquids in the tanks. This is also problematic as the pH control is more difficult when dealing with gaseous ammonia. As an alternative, in this paper it is suggested to contact the ammonia gas with water in a scrubber to form an ammonia solution that can easily be pumped into the precipitation tanks with normal chemical dosing pumps.

## 7. Conclusions and future work

Integrating the mineral carbonation process with an industrial lime kiln (Nordkalk's ~200 t/d kiln at Pargas/Parainen) and by using waste heat generated in the process the need for external exergy can be reduced significantly. Compared to the exergy requirement reported by Romão et. al. [10] the need for hot flue gas to drive the process is reduced by slightly over 30%. This is a significant reduction. The integrated process utilizing waste heat has an exergy demand per ton CO<sub>2</sub> sequestered for heat and power of 2595 MJ and 885 MJ, respectively, processing 550 kg rock/h and sequestering 187 kg CO<sub>2</sub>/h.

This leaves a considerable amount of flue gas heat available for processing more serpentinite to Mg(OH)<sub>2</sub> and in turn sequestering more CO<sub>2</sub>: the 30% improvement on heat economy would allow for expanding to fixing ~260 kg/h CO<sub>2</sub>.

Technical challenges in the design of a small industrial scale demonstration installation arise when evaluating the carbon dioxide storage by mineralization process being developed at Åbo Akademi University. Some can be solved by



slightly modifying existing process equipment while others require custom-made equipment or alterations to the proposed process. One major challenge is the relatively small scale of the test installation as it is too small to utilize standard industrial process equipment. The use intermediate storage tanks and pressure vessels may overcome this challenge at the expense of energy and cost efficiency.

As the  $Mg(OH)_2$  production and carbonation processes have been reported on earlier, more attention was given to the flue gas compression. A significant part of the exergy fed to the compression system is lost due to inefficiencies in the compressors and due to the cooling between the compression stages. Because of the considerable loss of exergy in the compression process the exergy released in the carbonation reactor and the expansion turbines are not enough to avoid the input of exergy from outside the system.

The exergy and energy balances for the mineral carbonation process should be studied with varying ambient conditions. Variations in the ambient temperature (-30 to 30°C) due to annual temperature variations can have an impact on the process. During winter with low ambient temperatures more heat will be needed to heat up the rock and ammonium sulfate while less cooling water will be needed due to the lower temperature of cooling water. This might have a clear impact on the exergy use and energy efficiency for the system.

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