

## **PAPER I**

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# Production of precipitated calcium carbonate from calcium silicates and carbon dioxide

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## Abstract

The possibilities for reducing carbon dioxide emissions from the pulp and paper industry by calcium carbonation are presented. The current precipitated calcium carbonate (PCC) production uses mined, crushed calcium carbonate as raw materials. If calcium silicates were used instead, carbon dioxide emissions from the calcination of carbonates would be eliminated. In Finland, there could, thus, be a potential for eliminating 200 kt of carbon dioxide emissions per year, considering only the PCC used in the pulp and paper industry. A preliminary investigation of the feasibility to produce PCC from calcium silicates and the potential to replace calcium carbonate as the raw material was made. Calcium carbonate can be manufactured from calcium silicates by various methods, but only a few have been experimentally verified. The possibility and feasibility of these methods as a replacement for the current PCC production process was studied by thermodynamic equilibrium calculations using HSC software and process modelling using Aspen Plus®. The results from the process modelling showed that a process that uses acetic acid for extraction of the calcium ions is a high potential option for sequestering carbon dioxide by mineral carbonation. The main obstacle seems to be the limited availability and relatively high price of wollastonite, which is a mineral with high calcium silicate content. An alternative is to use the more common, but also more complex, basalt rock instead.

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*Keywords:* PCC; Calcium carbonate; Calcium silicate; Carbonation; Carbon dioxide; Utilization

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## 1. Introduction

Calcium carbonate ( $\text{CaCO}_3$ ) is used in large amounts in the pulp and paper industry as a paper filler and in coatings to provide opacity, high brightness and improved printability due to its good ink receptivity. In Finland, 700 kt/a<sup>1</sup> of calcium carbonate is used for coating and 300 kt/a as a filler. The calcium carbonate is mined and extracted simultaneously with calcium silicate from Finnish wollastonite rock [1,2].

Integrated pulp and paper mills use carbon dioxide ( $\text{CO}_2$ ) from the lime kiln stack gas to manufacture precipitated calcium carbonate (PCC), which is synthetic calcium carbonate ( $\text{CaCO}_3$ ) with a higher purity than naturally occurring calcium carbonate (limestone). In the PCC process, purchased calcium oxide ( $\text{CaO}$ , lime) is hydrated into calcium hydroxide ( $\text{Ca(OH)}_2$ , slaked lime), followed by carbonation of the hydroxide. The lime used at the mill to manufacture PCC is typically produced by an outside vendor by calcining mined limestone. The amount of  $\text{CO}_2$  that is fixed in PCC manufacture is equal to the amount of fossil  $\text{CO}_2$  that was released from the calcination of the calcium carbonate in the lime kiln. As a result, the atmospheric net balance of  $\text{CO}_2$  is close to zero. The lime kiln needs to be heated to over 900 °C, which, in practice, causes more  $\text{CO}_2$  to be emitted than is captured in the PCC [1,3].

While the amount of  $\text{CO}_2$  captured in the PCC process is small in comparison to the overall emissions from the pulp and paper industry, the amounts can be significant for an individual pulp mill, since over 50% of the stack gas  $\text{CO}_2$  from the lime kiln<sup>2</sup> can be captured in the PCC manufacturing process. In Finland, the annual production is 400–500 kt of PCC, which binds approximately 200 kt  $\text{CO}_2$  [3]. However, the lime kiln at the mineral processing facility emits into the atmosphere a larger amount of  $\text{CO}_2$  when producing the calcium oxide required by the PCC manufacturing process, since the calcination process also requires combustion of a fuel to provide heat.

The EU emission trading scheme, which starts in January 2005, forces both the pulp and paper industry and the mineral industry to acquire  $\text{CO}_2$  emission allowances. Facilities being regulated include installations for the production of lime in rotary kilns or other furnaces with a production capacity exceeding 50 t per day and industrial plants for the production of pulp, paper and board with a production capacity exceeding 20 t per day [4]. The penalty for exceeding the allowed limit will be 40 €/t $\text{CO}_2$  during 2005–2007 and 100 €/t $\text{CO}_2$  from 2008 onwards [4]. However, the average market price of  $\text{CO}_2$  for emission trading is estimated at 26 €/t $\text{CO}_2$  [5]. If PCC was produced from a carbonate free calcium silicate rock, e.g. wollastonite ( $\text{CaSiO}_3$ ), 200 kt of  $\text{CO}_2$  emissions from lime kilns per year would be prevented. This reduction in  $\text{CO}_2$  emissions would save 5.2 M€ per year of  $\text{CO}_2$  emission allowances.

## 2. Precipitated calcium carbonate (PCC)

Calcium carbonate occurs abundantly in several natural minerals. It can be crystallized in a wide variety of morphologies, which makes it very versatile and is, therefore, used for changing

<sup>1</sup> 1 Mt = 10<sup>3</sup> kt = 10<sup>6</sup> t = 10<sup>9</sup> kg.

<sup>2</sup> Lime kilns are also used in pulp mills for regenerating  $\text{CaO}$ , which is here used as a circulating auxiliary chemical needed in the caustization process. This should not be confused with lime kilns used by the mineral industry for manufacture of commercial lime, e.g. PCC production.

physical and chemical properties of filled or coated papers. The product of a controlled synthesis that produces a desired morphology and particle size is called precipitated calcium carbonate or PCC. PCC has a higher purity than natural or ground calcium carbonate (GCC) since impurities are removed in the production process. PCC improves paper bulk, brightness, light scattering, fibre coverage and printability. The most important crystalline forms of PCC are the rhombohedral calcite type, scalenohedral calcite type and orthorhombic acicular aragonite type. The scalenohedral form is favoured in most applications. There are several various types of PCC grades, but the purity of PCC is usually over 99% with density of  $2700 \text{ kg/m}^3$ . For filler pigments 70% of the carbonate particles are smaller than  $2 \mu\text{m}$  and the specific surface area (BET) is about  $10 \text{ m}^2/\text{g}$ . The particle size affects paper smoothness, gloss and printing characteristics. Printing characteristics are also related to particle size distribution and shape, which also affects the consumption of chemical additives in papermaking. The brightness of PCC filler pigments is larger than 93%,<sup>3</sup> and the pH of 1 mol/l in an aqueous solution is 9. As a coating pigment, its average particle size is  $0.4\text{--}2.0 \mu\text{m}$  with a refraction index of  $1.49\text{--}1.67$  and a specific surface area of  $4\text{--}11 \text{ m}^2/\text{g}$ . The high refraction index and narrow particle size distribution of PCC promotes sheet light scattering. The ISO brightness for a PCC coating pigment is 95%, which requires a very pure limestone as raw material [6–9].

Important qualities of the limestone used for providing raw material for the PCC process are low manganese and iron content since these elements have a very negative influence on the brightness of the product [10]. The iron content of PCC should be lower than approximately 0.1% for a commercial product [9].

In 2002, the world's PCC consumption was approximately 6 Mt. One third of it was consumed by North American consumers and the rest mostly by Asian and Western European consumers. The largest consumers within these regions were companies in the USA, Japan, France, China and Finland. The paper industry was responsible for approximately 4 Mt of the consumption.

In Finland, there are seven PCC plants, which produced about 420 kt of PCC in the year 2001. The lime used in Finland in the PCC process was mainly quick lime burned from French and Norwegian limestones and a small part from Finnish limestone due to the high brightness required of PCC [9]. In the same year, 400 kt of PCC was used for coating and filler pigment. For comparison, 593 kt of a competing  $\text{CaCO}_3$  pigment, ground calcium carbonate (GCC), was produced. 600 kt of GCC was consumed as a coating pigment and 150 kt as a filler pigment [11–13].

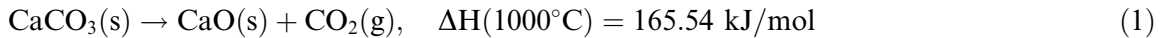
### 2.1. Production of precipitated calcium carbonate

Precipitated calcium carbonate can currently be produced by three different processes: a lime soda process, a calcium chloride process and a carbonation process. In the lime soda process, calcium hydroxide is reacted with sodium carbonate to produce a sodium hydroxide solution, from which the calcium carbonate is precipitated. This process is commonly used by alkali manufacturers, for whom sodium hydroxide recovery is the main objective, and the coarse PCC produced is only a by-product. In the calcium chloride process, calcium hydroxide is reacted with ammonium chloride, forming ammonia gas and a calcium chloride solution. After purification, this solution is reacted with sodium carbonate to form a calcium carbonate precipitate and a sodium chloride

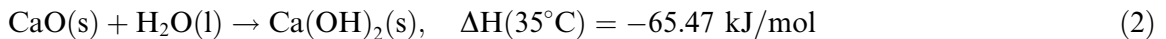
<sup>3</sup> Relative to  $\text{BaSO}_4$  reference = 100%.

solution. This process is the simplest of the three but requires a low cost source of calcium chloride to be economical. Therefore, it is usually conducted in a satellite facility adjacent to a Solvay process soda ash plant [8].

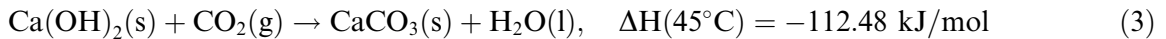
The third and most widely used process is the carbonation process because it can use cheap raw material. In this process, crushed limestone is burned in a lime kiln at about 1000 °C, where it decomposes (“calcines”) into calcium oxide and carbon dioxide:<sup>4</sup>



The dry CaO is slaked (hydrated) with water at temperatures of 30–50 °C, producing a Ca(OH)<sub>2</sub> slurry [14]. The slurry production starts with sending stored lime to a slaker tank, which is stirred by a high shear mixing agitator, after which water with the desired temperature is added and the slurry is formed:



The slurry contains undissolved calcium hydroxide, calcium ions (Ca<sup>2+</sup>) and hydroxide ions (OH<sup>-</sup>). The calcium ion concentration in the slurry is dependent on the solvent solubility limit, which decreases as the temperature increases. Before carbonation, the process slurry is screened to remove impurities originating from the limestone. The slurry is then fed to a three phase stirred tank reactor, either at atmospheric pressure or pressurized, where it reacts with CO<sub>2</sub> gas:



The particle size, particle size distribution, particle shape and change of surface properties of the calcium carbonate particles can be controlled by controlling the reaction temperature, carbon dioxide partial pressure, flow rate of carbon dioxide, lime slurry concentration and agitator speed. The carbonation temperature is in the range 41–90 °C for the scalenohedral form and –1 to 10 °C for the rhombohedral form. The threshold temperature for the aragonite structure is approximately 49 °C [15]. The usual sources of CO<sub>2</sub> gas for the carbonation process are the stack gases from power plants, recovery kilns or lime kilns. The stack gas is normally cooled and scrubbed before it is compressed into the carbonation reactor, where it dissolves into the water phase while it is bubbled through the slurry. During the reaction, the slurry is continuously under high shear agitation [15,16] and the solid content is typically about 20% [17]. The pH of the lime slurry is 12 or higher at the beginning, but it decreases as the reaction proceeds, down to an equilibrium pH of 8 ± 1. The carbonation reaction is regulated by the solution equilibrium: as the calcium ions are converted to calcium carbonate and precipitated out, more calcium hydroxide dissolves to equalize the concentration of calcium ions. The rate of dissolution of Ca(OH)<sub>2</sub> into Ca<sup>2+</sup> depends on the dissolution pressure and temperature, while the reaction rate of calcium ions combining with carbonate ions is instantaneous. Therefore, the rates of formation of calcium and carbonate ions are the primary limitations for the overall reaction rate. With a pressurized reactor, the overall reaction rate is greater than with an atmospheric reactor, since the solubility of carbon dioxide is higher at elevated pressure. Pressures in the range 1–10 bar can be used, while 2–3 bar is the recommended value. The overall reaction rate for commercially used atmospheric PCC production processes is in the range 0.5–1.5 g/lmin of Ca(OH)<sub>2</sub> [15].

<sup>4</sup> All reaction enthalpies were calculated using Outokumpu HSC Chemistry v.4.0 software.

An average paper mill uses about 20–100 kt of PCC per year, which requires large carbonation reactors of 68–76 m<sup>3</sup>. Although the net reaction of the combined calcination and carbonation process is exothermic, the heat released in the carbonation process cannot, by conventional means, provide the heat for the calcination process since the temperature of the calcination process is considerably higher. Therefore, the PCC plant uses purchased dry calcium oxide, which has been calcinated before transport. These so called PCC satellite plants use CO<sub>2</sub> emissions from the lime kiln at the paper plant for the carbonation process [6,18,19].

### 3. Calcium silicates

Mined and crushed carbonate free, calcium based minerals could be used for producing PCC. Alternative process routes are either by direct carbonation in a process plant at the mill or by producing an intermediate material, such as calcium oxide or hydroxide, which could be transported to the paper mill and carbonated using the existing PCC plant at the mill. The main source of calcium silicate is a mineral called wollastonite, CaSiO<sub>3</sub>. Since wollastonite occurrences are much less widespread than limestone, the more common calcium oxide rich rock known as basalt could provide an alternative source of raw material.

#### 3.1. Wollastonite

Wollastonite is a metamorphic fibrous mineral, which occurs mainly in crystalline limestone. The chemical composition of pure wollastonite is CaSiO<sub>3</sub> (48.3 wt.% of CaO, and 51.7 wt.% of SiO<sub>2</sub>). It has been formed in nature from the interaction of calcite (CaCO<sub>3</sub>) with silica (SiO<sub>2</sub>) under high temperatures and pressures. Its density is 2900 kg/m<sup>3</sup>, hardness 4.5 and melting point 1540 °C. Its specific surface area is very low (0.8–4 m<sup>2</sup>/g), indicating that the natural material is not porous. Other characteristic features of wollastonite include a high pH value (9.8), a low coefficient of thermal expansion and low moisture content < 0.5% [20,21].

Wollastonite is used in the plastic, ceramic and metallurgical industry as a filler and additive for various applications. The metallurgical industries are currently the only area where it is also used for providing calcium oxide [22]. Wollastonite is also used as a substitute for asbestos, since wollastonite has not been found to cause any health risks.

Although wollastonite is a common mineral in metamorphic limestones and skarns, large wollastonite ore deposits of economic value are rare. Notable occurrences of wollastonite include Willsboro and other sites in New York (Essex County 10 Mt), Texas, California and also Franklin, New Jersey, USA; the volcano Monte Somma, Vesuvius, Italy; Perheniemi, Finland; Banat, Rumania; Saxony, Germany; Zacatecas, Morelo, Chiapas, Mexico (over 100 Mt); Greece; China; Ontario and at the Jeffrey Mine, Quebec, Canada and Tremorgio, Switzerland [23,24]. For instance, the Ontario wollastonite skarn is approximately 9 Mt, containing 41.3% wollastonite [25].

Wollastonite is a common mineral, especially in limestone in the southern part of Finland, but the mineral does not form economically interesting wollastonite ore in most of the occurrences. Wollastonite commonly occurs in impure limestone, occasionally with diopside (CaMgSiO<sub>6</sub>), tremolite (CaMg<sub>3</sub>Si<sub>4</sub>O<sub>12</sub>), vesuvianite (H<sub>4</sub>Ca<sub>12</sub>Al<sub>6</sub>Si<sub>10</sub>O<sub>43</sub>), kondrodite (F<sub>2</sub>Mg<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>) and quartz (SiO<sub>2</sub>). The only deposit in operation in Finland is the Lappeenranta Ihalainen mine, where

wollastonite ore (25% pure  $\text{CaSiO}_3$ ) is quarried (18 kt/a). This deposit is estimated to contain at least 10 Mt of wollastonite and is one of Finland's largest limestone deposits. A similar deposit can be found at Savitaipale, 35 km northwest of Lappeenranta. In Puumala, a smaller diopside-wollastonite deposit of approximately 200 kt exists. Wollastonite also often forms contact walls between limestone and adjacent siliceous rocks, as in Mäntsälä, Dragsfjärd and Parainen, but there are exceptions: a limestone deposit at Lappeenranta consists of calcite grains connected by wollastonite fibres. Wollastonite has nowhere been found in pure dolomitic rocks or at their contact surfaces. A rough approximation of the limestone deposit in Vestanfjärd gives 4.6 Mt of limestone, which contains 0–4.5% of wollastonite. However, these figures do not give a realistic view of the resources available, since in most of the occurrences, the wollastonite content is low and part of the wollastonite resource data is very old [9,21,24,26].

Wollastonite is produced by mining, grinding, separation, classification and occasionally by treatment with a coupling agent. It is extracted using conventional surface mining methods. It is easily mined at places where it is the major component of metamorphosed rock. Mining is followed by several stages of crushing for size reduction. Depending on the area where the wollastonite was formed, various levels of contamination can be found in the ore. Garnet and diopside are magnetic minerals to varying degree and can be removed by dry magnetic separation. Calcite, which is the most common contamination, can be removed by using wet processing (flotation). At Lappeenranta, Nordkalk produces wollastonite concentrate as a by product of calcite flotation [20,23,27,28].

The worldwide annual production of wollastonite has been estimated to be between 550 and 600 kt in 2002 [22]. In Finland, the annual production of wollastonite was 18.4 kt in 2001, while the total calcium carbonate consumption for paper was 1.15 Mt (of which 400 kt was for PCC) [11]. The price of wollastonite on the international market ranged from \$50/ton for lump wollastonite to \$1700 for ultra-fine surface treated wollastonite in 2002. Powder grades with a maximum grain diameter of 0.1 mm could be obtained for \$60–\$80/ton. As a comparison, the average price for lime ( $\text{CaO}$ ) was \$62.50/ton [22].

### 3.2. Basalt

Basalt rocks are rich in calcium oxides and could, therefore, provide raw material for producing precipitated calcium carbonate in case wollastonite deposits are not adequate or not available. Basalt is the most common igneous rock, which is globally distributed and ubiquitous. It has a dark, alkaline surface and its elementary matter is a closed texture that can have a porosity caused by gas bubbles. Basalt has an average  $\text{CaO}$  content of 9.47% (Table 1) [29,30].

The chemical composition of basalt can vary slightly depending on the geological environment near the rock. Its main minerals are plagioclase (~45%) and pyroxene (~50%), which is usually augite ((Ca, Na)(Mg, Fe, Al, Ti)(Si, Al) $_2\text{O}_6$ ) or pigeonite ((Mg, Fe, Ca)(Mg, Fe)Si $_2\text{O}_6$ ). Plagioclase

Table 1  
Average basalt composition in % [30]

$\text{SiO}_2$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{MgO}$	<b>CaO</b>	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$
49.20	1.84	15.74	3.79	7.13	0.20	6.73	<b>9.47</b>	2.91	1.10	0.35



is comprised of albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). The other main minerals found in basalt are olivine ( $(\text{Mg, Fe})\text{SiO}_4$ ), nefeline and quartz. However, quartz is not usually found with olivine or nefeline [31].

In Finland, all igneous rocks are metamorphosed, and basalt does not exist as such. Instead, it exists in metamorphous forms, such as metabasalt, blue elvan, amphibolite and eclogite. Metamorphose changes rocks structure and grain size and also its mineral composition. In northern Finland and Karelia, igneous rocks are metamorphosed of basalt with main minerals amphibole, plagioclase and sometimes chlorite, with a CaO content of 6.8–9.2%. However, basalts have high contents of iron oxide, which is difficult to remove and affects drastically the brightness of the PCC. For instance, amphibolite has a typical CaO content of ~9%, but the iron content is usually 3–5%. The high iron content of basalts may render basalt unsuitable for PCC production [9,29].

#### 4. Calcium carbonate from calcium silicates—a literature review

Several alternatives for producing calcium carbonate from wollastonite have been suggested and studied to various extents. The simplest process is the direct dry or aqueous carbonation of wollastonite, suggested by Kojima et al. [32]. This process was found to be too slow for industrial applications under normal conditions. In order to speed up the reaction, Newall et al. [30] suggested dissolving calcium silicates in hydrochloric acid to create calcium hydroxide. However, there does not seem to be any experimental data available for this process. Kakizawa et al. [33] studied the carbonation of calcium silicate experimentally using acetic acid for extraction of the calcium ions and made a simple process model of a large scale  $\text{CO}_2$  sequestration facility utilizing this method. Recently, Gerdemann et al. [34] noticed that wollastonite dissolved and carbonated readily in water using an autoclave batch reactor at elevated temperatures and pressures. More details of each process are given below.

##### 4.1. Direct dry and aqueous carbonation

The direct carbonation of wollastonite was studied by Kojima et al. in a CSTR (continuously stirred tank reactor) at 25 °C and atmospheric pressure for 0–600 h. The dry carbonation rate was only briefly tested under these conditions and deemed too slow to be of interest. The kinetics of the aqueous carbonation reaction were registered by measuring the concentration of free  $\text{Ca}^{2+}$  ions that were assumed to be formed by the reaction of rock weathering:



It took 400 h before solution equilibrium was reached. The rate of  $\text{CO}_2$  absorption was measured to be 1.04 mmol/m<sup>2</sup>h and 1.46 mmol/m<sup>2</sup>h depending on the type of wollastonite. Because of the slow reaction kinetics, this process was not further investigated in this paper [32].

##### 4.2. Indirect carbonation with hydrochloric acid

Newall et al. [30] studied five different mineral carbonation processes for the purpose of long term storage of  $\text{CO}_2$ . Only one of the options uses calcium silicates as raw material. The calcium



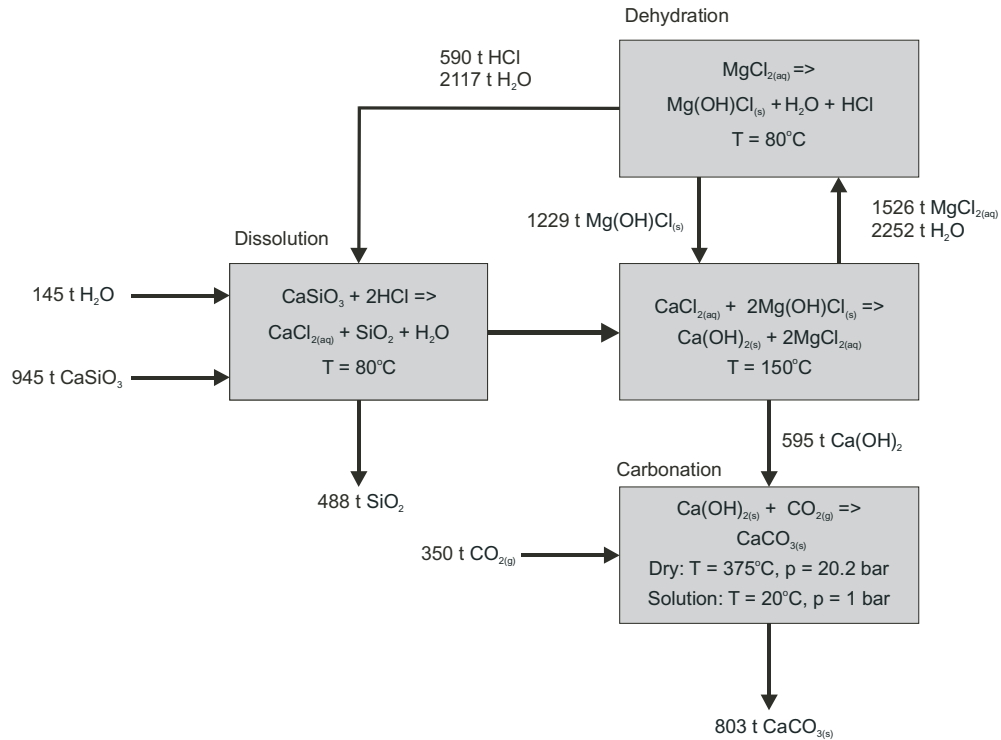


Fig. 1. Process suggestion for indirect carbonation using hydrochloric acid [30].

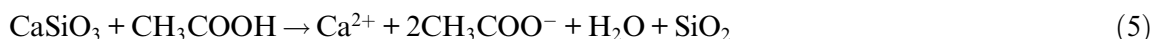
silicate carbonation process, shown in Fig. 1, dissolves basalt in hydrochloric acid. The calcium hydroxide produced (via calcium chloride) is dissolved in water and then reacted with  $\text{CO}_2$  to produce calcium carbonate. The option of using this process for long term storage of  $\text{CO}_2$  was rejected. The major drawbacks listed were the energy demand for the acid recycling stage and the very large water demand for the carbonation stage: 840 t $\text{H}_2\text{O}$ /t $\text{Ca(OH)}_2$  [30]. The process was not experimentally tested.

However, in order to dissolve calcium hydroxide in water in a continuous carbonation process, there is no need to use such large amounts of water as Newall et al. has suggested. As calcium carbonate is formed in the solution, the concentration will eventually reach the saturation point, leading to calcium carbonate precipitating out. When calcium and carbonate ions have formed calcium carbonate and precipitated, the solution will be below saturation and more calcium hydroxide can dissolve. The commercially available carbonation process for PCC production is an example of this practice: the solid content of the slurry in the carbonation reactor is as high as 20% [17]. Although the PCC production process dissolves  $\text{CaO}$ , and not  $\text{Ca(OH)}_2$ , the solubility of  $\text{Ca(OH)}_2$  in water (1.0 g/l) is similar to that of  $\text{CaO}$  (1.2 g/l) [35]. Therefore, the process suggested by Newall et al. could be used for producing  $\text{Ca(OH)}_2$  from calcium silicates and sell the produced  $\text{Ca(OH)}_2$  to a retrofitted PCC plant, which has been adjusted to carbonate  $\text{Ca(OH)}_2$  instead of  $\text{CaO}$ . In comparison with the current calcination process for producing  $\text{CaO}$ , the mass flows are several times larger for this process, while the temperatures required are lower (150 °C

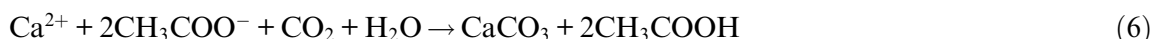
for the hydrochloride process, >900 °C for the lime kiln). This process was, therefore, selected for a deeper feasibility study using process modelling.

#### 4.3. Indirect carbonation with acetic acid

The most thoroughly examined process for carbonation of calcium silicate is the indirect carbonation process studied by Kakizawa et al. [33]. The process consists basically of two steps. The first step is the extraction of calcium ions from wollastonite using acetic acid:



The solid  $\text{SiO}_2$  precipitates and is separated in a thickener separator.  $\text{CO}_2$  is injected into the solution, which causes calcium carbonate to crystallize and deposit:



According to Kakizawa et al. the Gibbs free energy change of each step is negative, which indicates that the reactions would proceed spontaneously without requiring large amounts of energy. At 25 °C, the theoretical conversion that can be achieved is 40% at 1 bar and 75% at 30 bar. The acetic acid is recovered in this step and recycled for use in the extraction step. The process is outlined in Fig. 2.

Extraction experiments were conducted at 60 °C and atmospheric pressure in a magnetic stirrer, where the extraction ratio reached 48% in 250 min. A further pulverization of the feed of wollastonite particles was suggested for attaining a higher extraction ratio. Using an average initial particle diameter of 33  $\mu\text{m}$ , an extraction ratio of 30% was achieved in 30 min, while 125  $\mu\text{m}$  gave an extraction ratio of only 10% for a similar residence time in the stirrer. Crystallization experiments were conducted at 5–50 bar in a reactor of 0.2 l. The best carbonation conversion achieved was about 20% at 60 min under 30 bar pressure. Most of the calcium carbonate particles produced had a diameter <1  $\mu\text{m}$ , which is a suitable particle size of PCC used for industrial applications.

A carbon dioxide capture and storage process operating at 60 °C was modelled using an extraction pressure of 1 bar and a carbonation pressure of 30 bar. Under these conditions, the experimental data used for the extraction was 100% at 60 min, and the carbonation 10% at 10 min.

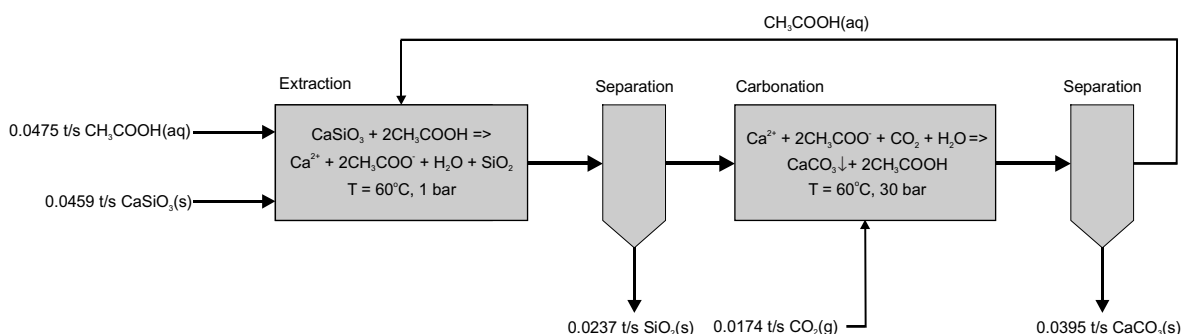


Fig. 2. Process suggestion for indirect carbonation of wollastonite [33].

Using these values and a calculated approximation for the required pulverization energy, the total energy requirements for separating CO<sub>2</sub> from a 100 MW thermal plant and using it to produce 142 t/h CaCO<sub>3</sub> from 165 t/h wollastonite was 20.4 MW. According to Kakizawa et al., the specific energy requirements for producing CaCO<sub>3</sub> using this method was 516 kJ/kg CaCO<sub>3</sub>. This process was also selected for a deeper feasibility study using process modelling [33].

#### 4.4. Direct aqueous carbonation at elevated pressures and temperatures

The carbonation of wollastonite in a batch autoclave reactor was recently tested by Gerdemann et al. [34] at Albany Research Center, USA. It was noted that a carbonation conversion of more than 70% could easily be reached in less than an hour in distilled water at elevated pressures and temperatures (185 °C and 152 bar). The rate of carbonation was not significantly increased in a bicarbonate (HCO<sub>3</sub><sup>-</sup>) solution. The wollastonite had been grinded in a high energy attrition mill to a particle size (d<sub>50</sub>) of less than 2–4 μm. While keeping the pressure constant at 152 bar, similar conversion rates were achieved in the temperature range 100–200 °C during one hour. While keeping the temperature constant at 185 °C, similar conversion rates were achieved as low as 50 bar, while a 10% lower conversion was achieved at ~10 bar. However, the product was a mixture of calcium carbonate and silicate, which would require further separation processing to produce pure carbonate. Therefore, this process was not further investigated in this paper.

## 5. Process modelling

In order to determine the feasibility of possible PCC production from calcium silicate, three processes were chosen for modelling and comparison of power and heat requirements: indirect carbonation with hydrochloric acid (Newall et al.), indirect carbonation with acetic acid (Kakizawa et al.) and the current PCC production method by carbonation. Since the heat demanding step of the current PCC production process is the calcination of limestone in a lime kiln, the calcination process was studied in detail separately. All processes were modelled assuming a clean source of pure CO<sub>2</sub>, available at room temperature and atmospheric pressure. The processes were modelled using Aspen Plus 12.1<sup>®</sup> and Outokumpu HSC-4 software.

### 5.1. Data for feasibility comparison

The current international market price for calcium carbonate and wollastonite is summarized in Table 2. While the current bulk price for untreated (Chinese) wollastonite is slightly higher than the price for ground calcium carbonate, it is only one fourth of the price of PCC. Unless a tax benefit is gained from the avoided CO<sub>2</sub> emissions by the calcite to wollastonite shift, the production process for wollastonite PCC is not allowed to be more expensive than the process for calcite PCC for the product to be competitive on the market. The national market prices in Finland are different from the international prices, but prices vary heavily depending on mineral origin, processing and quality (Table 3). For comparing heat content, CO<sub>2</sub> emissions and price for energy from various fuels, the data presented in Table 4 was used in all calculations. CO<sub>2</sub> emissions estimates for a 500 MWe pulverised coal fired power plant including flue gas desulphurisation (Table

Table 2  
International market price for raw minerals and PCC [35]

Mineral	€/ton
<i>Calcium carbonate</i>	
GCC ex-works UK chalk, uncoated	45–78
High brightness for paper (1.5 $\mu\text{m}$ )	138–146
PCC ex-works UK	244–339
FOB (Free on Board) USA, Fine (0.4–1 $\mu\text{m}$ )	203–220
Ultrafine, surface treated (0.02–0.36 $\mu\text{m}$ )	305–610
<i>Wollastonite</i>	
US ex-works, 200 mesh (74 $\mu\text{m}$ )	154
US ex-works, 400 mesh (38 $\mu\text{m}$ )	210
Chinese, FOB, 200 mesh (74 $\mu\text{m}$ )	65–81
Chinese, FOB, 325 mesh (45 $\mu\text{m}$ )	73–89

Table 3  
Mineral prices supplied by Nordkalk Finland [37]

Mineral	€/ton
<i>Calcium carbonate</i>	
Lumps (for e.g. calcination), from Gotland, Sweden	11
PCC (cheapest)	120
<i>Calcium oxide</i>	
Bulk (for e.g. PCC production)	100
<i>Wollastonite</i>	
Powder (unprocessed, average price), from Lappeenranta	200

Table 4  
Prices for electricity power and heat [38]

Fuel	Heat content (GJ/t)	CO <sub>2</sub> emissions (gCO <sub>2</sub> /MJ)	Price (€/MJ)
Heavy fuel oil	41.1	77.4	0.0056
Electricity	–	–	0.0225

Table 5  
CO<sub>2</sub> emissions from a pulverized coal fired power plant with FGD [39]

Plant	SO <sub>2</sub> (%)	Size (MW)	Efficiency (%)	CO <sub>2</sub> emissions (kg/MWh)
Subcritical	90	500	40	830
Subcritical	95	500	40	830
Subcritical	90	250	40	830
Supercritical	90	500	43	770

5) were used to compare the feasibility of the various processes. The CO<sub>2</sub> emission value for a sub-critical condensing power plant was used.

5.2. PCC production by carbonation

A simplified model of the PCC production process was constructed in Aspen Plus® (Fig. 3). Since the process was modelled as an atmospheric carbonation process, there are no power requirements from compression and pumping in the model. The only heat requiring step is the calcination step, since both the hydration (slaking) step and carbonation step are exothermic. However, the exothermic steps are at very low temperatures and, therefore, produce no useful heat (1533 kJ/kg CaCO<sub>3</sub> at 35 °C and 680 kJ/kg CaCO<sub>3</sub> at 45 °C). Therefore, only the calcination step was studied in detail.

The lowest possible temperature at which the calcination reaction (1) can occur at atmospheric pressures can be found by calculating the Gibbs free energy for the components involved and plotting the logarithm of the equilibrium constant against temperature. According to the results, calcination is possible for temperatures over 894 °C for 1 bar CO<sub>2</sub> (Fig. 4). Taking pressure

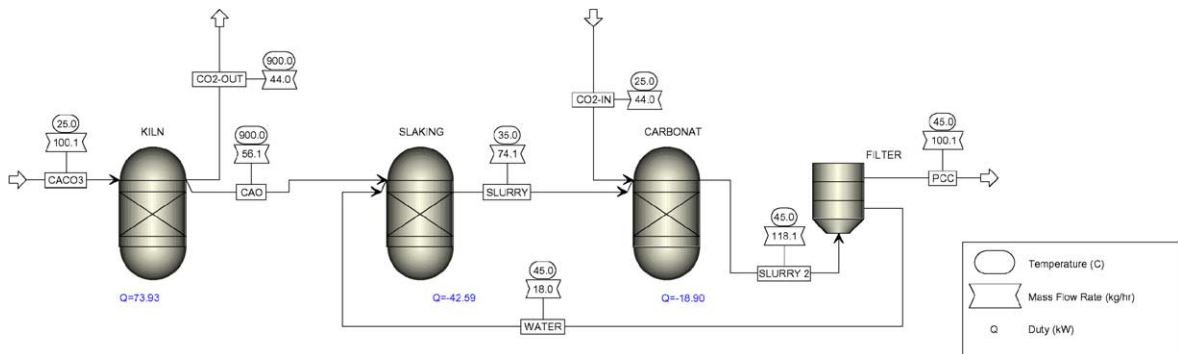


Fig. 3. PCC production process by calcination and carbonation.

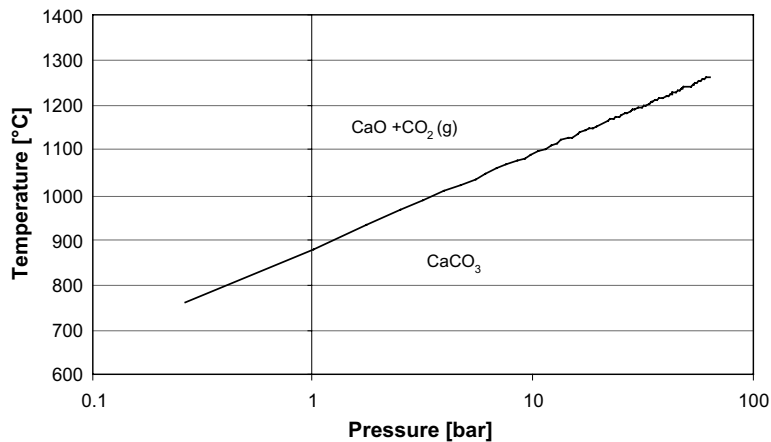


Fig. 4. Equilibrium composition plot for CaCO<sub>3</sub> = CaO + CO<sub>2</sub>(g), temperature–pressure dependency.

dependency into consideration, it is possible to calcine calcium carbonate at temperatures lower than 900 °C, but then sub-atmospheric reactor pressures are required. The current calcination process runs at atmospheric pressure.

The calcination process was modelled using a multi-phase reactor module that calculates the product composition by Gibbs free energy minimization (Fig. 5). Since the mineral needs to be heated to 900 °C and the calcination reaction is an endothermic process, the lime kiln is very energy intensive: 2669 kJ/kg CaCO<sub>3</sub> is needed for calcining calcium carbonate (with an initial temperature of 25 °C) at 900 °C. The released carbon dioxide can be used for preheating the lime feed, lowering the external heat requirements to 2244 kJ/kg CaCO<sub>3</sub> (Fig. 6). The process produces 0.44 kg CO<sub>2</sub>/kg CaCO<sub>3</sub>, which later is bound in the PCC production process. If heavy fuel oil were combusted for providing the heat required, an additional 0.21 kg CO<sub>2</sub>/kg CaCO<sub>3</sub> would be emitted, making the total emissions from the calcination process 0.65 kg CO<sub>2</sub>/kg CaCO<sub>3</sub>. If the waste heat could be fully utilized, the emissions from the additional combustion are reduced to 0.17 kg CO<sub>2</sub>/kg CaCO<sub>3</sub> (0.61 kg CO<sub>2</sub>/kg CaCO<sub>3</sub> total emissions from the calcination step). In a real lime

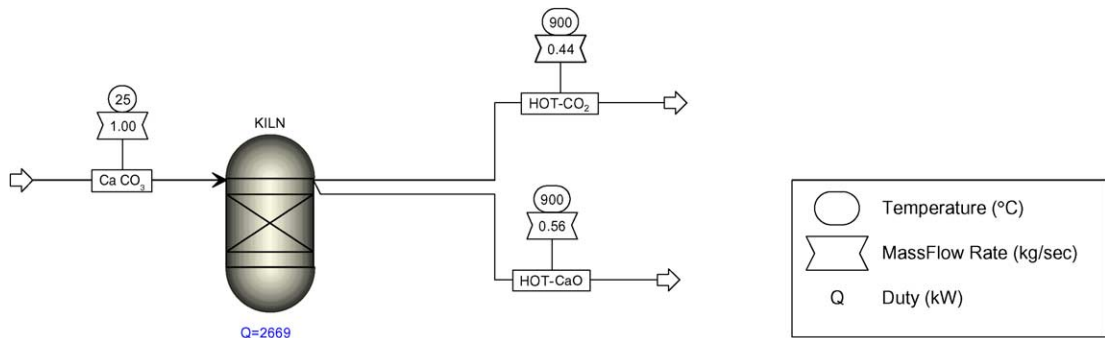


Fig. 5. Basic lime kiln model.

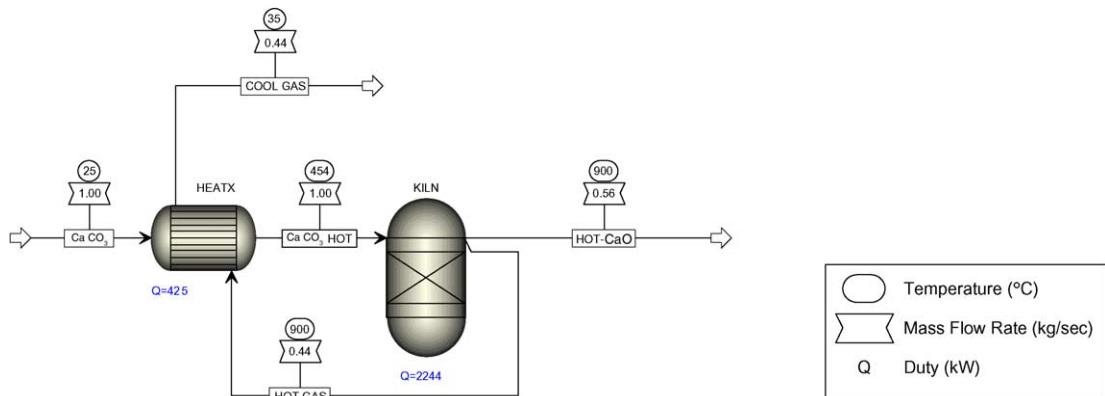


Fig. 6. Basic lime kiln model using extracted CO<sub>2</sub> to preheat limestone.

kiln, more heat is needed since not all heat released in the combustion can be effectively utilized by the calcination reaction in the kiln.

### 5.3. Indirect carbonation with hydrochloric acid

The process suggested by Newall et al. for carbonation of calcium silicates was modelled both without a carbonation reactor (Fig. 7) and with a carbonation reactor (Fig. 8). All chosen reactor models use Gibbs free energy minimization for determining the product compositions and heating/cooling requirements. The only significant variation between the results from the process modelling and Newall's calculated process values was the temperature requirement for the dehydration unit for recycling all  $\text{Mg}(\text{OH})\text{Cl}$  ( $227\text{ }^\circ\text{C}$  instead of  $150\text{ }^\circ\text{C}$ ). The dehydration unit was, as expected, the most energy demanding step, requiring  $11830\text{ kJ/kg Ca}(\text{OH})_2$  (or  $8760\text{ kJ/kg CaCO}_3$ ). This requirement alone is over three times the heat needed for calcining limestone. The only additional energy requirement for the process was for the calcium hydroxide separator, requiring  $240\text{ kJ/kg Ca}(\text{OH})_2$  (or  $178\text{ kJ/kg CaCO}_3$ ). If heavy fuel oil were combusted for providing the heat for the process,  $0.69\text{ kg CO}_2/\text{kg CaCO}_3$  would be emitted in the  $\text{Ca}(\text{OH})_2$  production process, which is more than the current calcination process emits.

A carbonation reactor was integrated with the hydroxide production process model in order to investigate the possibility for reducing the heat requirements by using waste heat from the carbonation process (Fig. 8). Because of the exothermic nature of the carbonation process, the reaction temperature was lifted to  $560\text{ }^\circ\text{C}$ , which was the maximum sustainable operating temperature for the carbonation process without any external heat demand. Higher temperatures could speed up the dry carbonation reactor and the heat from the process streams could be utilized for the hydration step. The results from the integration showed that the heat from the carbonation process can only supply  $7.6\%$  of the total heat demand for the dehydration unit. This equals a net emission of  $0.20\text{ kg CO}_2/\text{kg CaCO}_3$  (using heavy fuel oil for supplying heat), which is almost as much as the

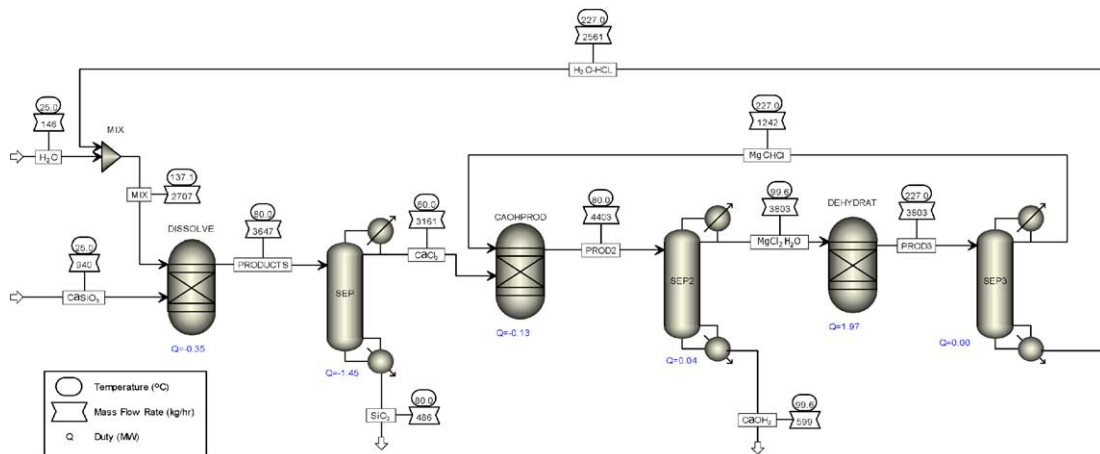


Fig. 7. Calcium hydroxide production from calcium silicate.



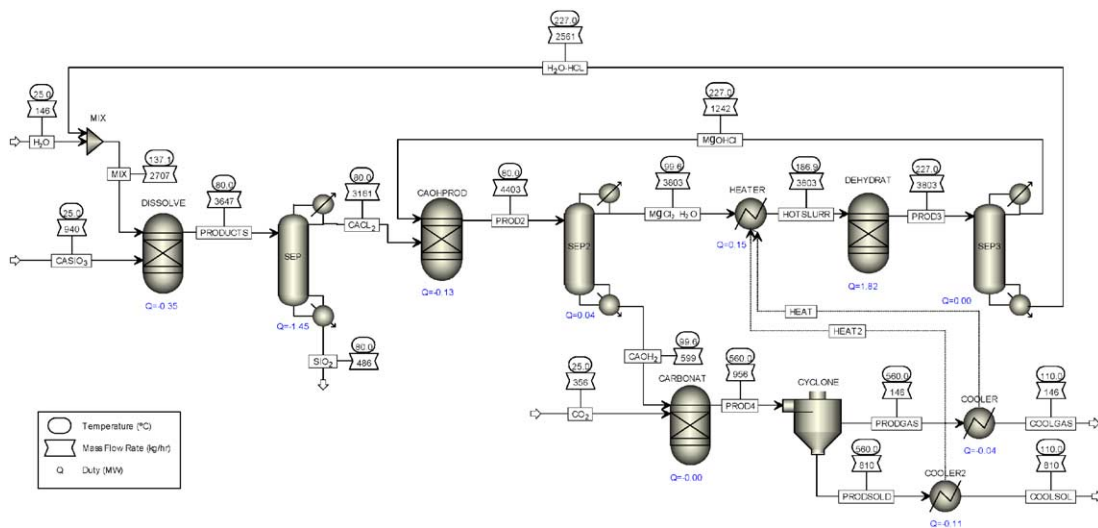


Fig. 8. Calcium hydroxide production from calcium silicate with carbonation reactor integrated.

current net emission of the combined calcination and PCC production process. Therefore, the process (Fig. 1) is not suitable for enhancing the CO<sub>2</sub> utilization of the PCC production.

#### 5.4. Indirect carbonation with acetic acid

The elemental composition of the filtered solids from the crystallization experiments made by Kakizawa et al. was never chemically analyzed. Therefore, thermodynamic equilibrium calculations were performed to verify the possible products of the process. The overall reaction was studied at atmospheric pressure by calculating the thermodynamic equilibrium constant. It shows that the process should be thermodynamically possible up to 280 °C at atmospheric pressure.

According to the equilibrium content calculations made with HSC for the extraction reaction (Fig. 9), the maximum attainable conversion of calcium ions from the calcium silicate drops with temperature. For instance, at 60 °C, the maximum attainable conversion is 98.8%, while it is 95.6% at 80 °C. Most of the components involved are either liquids or solids, and the effect of pressure upon the equilibrium composition is negligible. The equilibrium composition of the crystallization (carbonation) reaction (Figs. 10 and 11) is more sensitive to carbonation pressure due to the presence of a pressurized gas (CO<sub>2</sub>). According to Kakizawa et al., the theoretical conversion that can be achieved at 25 °C is 40% at 1 bar and 75% at 30 bar. An attempt to reconstruct the results using Gibbs free energy calculations for ionic solutions gave even lower results: 9% at 1 bar and 41% at 30 bar. This is not a serious limitation of the process, since the solution is filtered from precipitated carbonate and recycled. Therefore, almost complete conversion can be obtained by sufficient recycling of the solution.

The process was also modelled using Aspen Plus<sup>®</sup> (Figs. 12 and 13). The design allows for recirculation of the calcium ion solution to the extraction reactor, which results in a net conversion dependent on both the single step crystallization conversion and the number of circulation cycles.

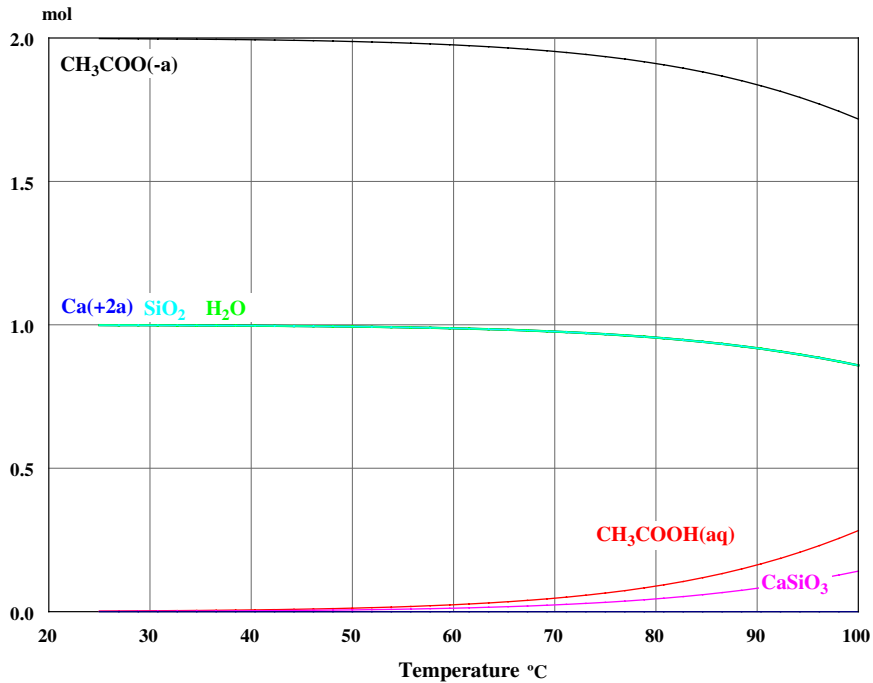


Fig. 9. Thermodynamic equilibrium composition of the extraction reaction: 1 mol  $\text{CaSiO}_3$  with 2 mol  $\text{CH}_3\text{COOH}(\text{aq})$ .

Stoichiometric reactor models were used since the products were known, and the model allows the user to specify the conversions of the reactants. A compressor for raising the pressure of  $\text{CO}_2$  was also included in the model, which may not be needed if the  $\text{CO}_2$  for the process is separated and compressed elsewhere and transported by pipeline to the PCC plant. A cooler was also included for lowering the temperature of the compressed  $\text{CO}_2$  stream before entering the reactor, which, in practice, may be unnecessary if the hot stream can be directly fed into the crystallization reactor for covering the heat demand. A pump for raising the pressure of the solution before the crystallization reactor was also included in the model, along with a valve for reducing the pressure of the recycled solution to the level of the extraction reactor. The isentropic efficiency of the compressor modelled was set to 0.8, and the total efficiency for the pump was set to 0.8.

Two variations of the process were constructed: one model with a crystallization conversion of 100% (Fig. 12) and another with a crystallization conversion of 10% (Fig. 13). The mass flow of the model with a crystallization conversion of 10% agreed quite well with the model created by Kakizawa et al., except for the thickener flow, which was higher than expected (Table 6). Another surprising difference was noticed in the crystallization reactor model, which was found to be endothermic instead of exothermic. However, the extraction reactor releases more heat than the crystallization reactor demands, so the heat demand can be covered by heat recovery of the heat released in the extraction reactor. The temperature for the exothermic extraction reactor was, therefore, raised to 80 °C in order to be able to supply heat for the crystallization step (operating at 60 °C). This reduces the theoretical maximum allowable extraction conversion from 98.8% to 95.6% but makes the heat exchange in the process self supporting. However, the conversion of the

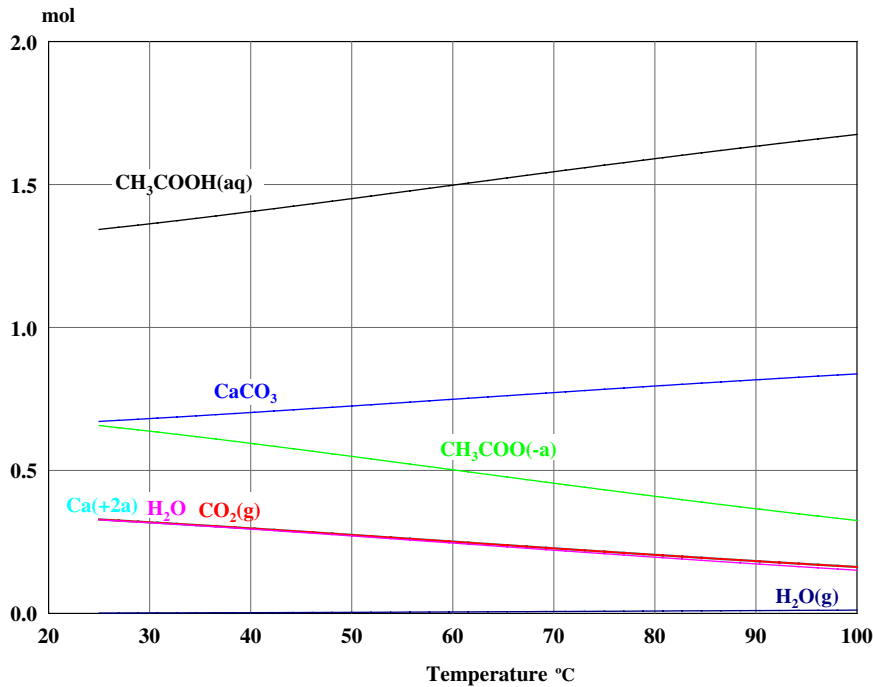


Fig. 10. Thermodynamic equilibrium composition of the carbonation reaction: 1 mol  $\text{Ca}^{2+}$ , 1 mol  $\text{H}_2\text{O}$  and 2 mol  $\text{CH}_3\text{COO}^-$  with  $\text{CO}_2$  at 1 bar.

extraction reactor was modelled as 100%, in order to be able to compare the results with those presented by Kakizawa et al.

The power demand of the pump for raising the pressure of the solution before the crystallization reactor was found to be heavily dependent on the number of circulation ratio cycles of the liquid and the pressure level of the extraction step. Therefore, the power consumption of the process is mostly dependent on the solution circulation ratio and the pressure level of the crystallization reactor (Fig. 14).

A benefit of the current PCC process is that it can use very coarse calcium oxide particles for the hydration process. Granules of up to 15 mm are currently used without need for pulverization. For the Kakizawa process, very fine particles may be needed (20  $\mu\text{m}$ ) to enhance the reaction rate. Therefore, the pulverization of wollastonite particles will consume additional power, which must be taken into consideration when determining the feasibility of the process. To approximate the energy need for pulverization, Bond's equation [40] was used.

$$E_0 = W_i \left( \frac{\sqrt{F} - \sqrt{P}}{\sqrt{F}} \right) \sqrt{\frac{100}{P}} \quad (7)$$

where  $E_0$  is the energy required for pulverization [kWh/t];  $P$  is the sieving size that passes 80% of the pulverized particles through [ $\mu\text{m}$ ];  $F$  is the sieving size that passes 80% of the feed particles through [ $\mu\text{m}$ ];  $W_i$  is the work index for the specific rock type [kWh/t].

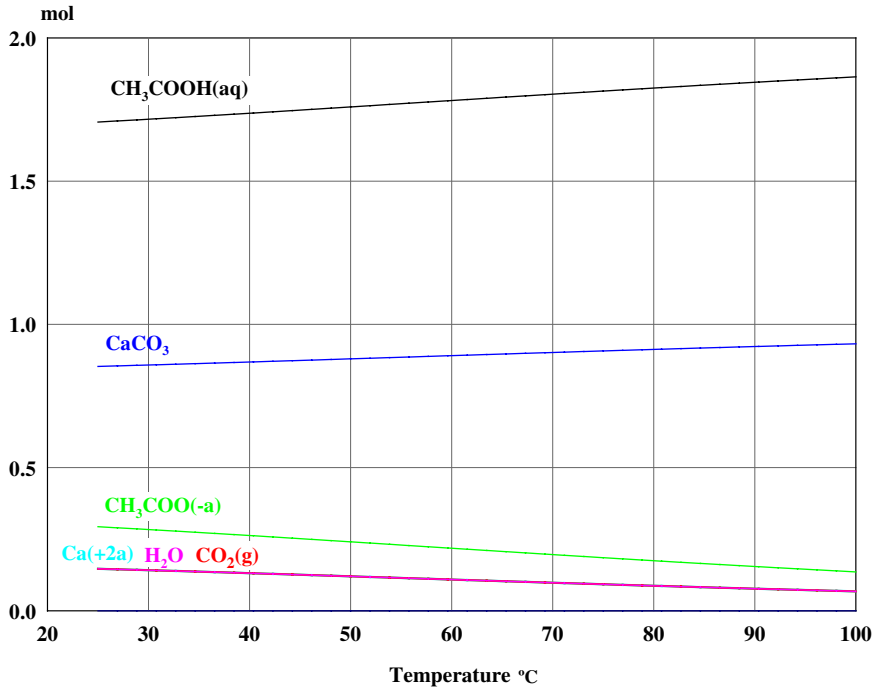


Fig. 11. Thermodynamic equilibrium composition of the carbonation reaction: 1 mol Ca<sup>2+</sup>, 1 mol H<sub>2</sub>O and 2 mol CH<sub>3</sub>COO<sup>-</sup> with CO<sub>2</sub> at 30 bar.

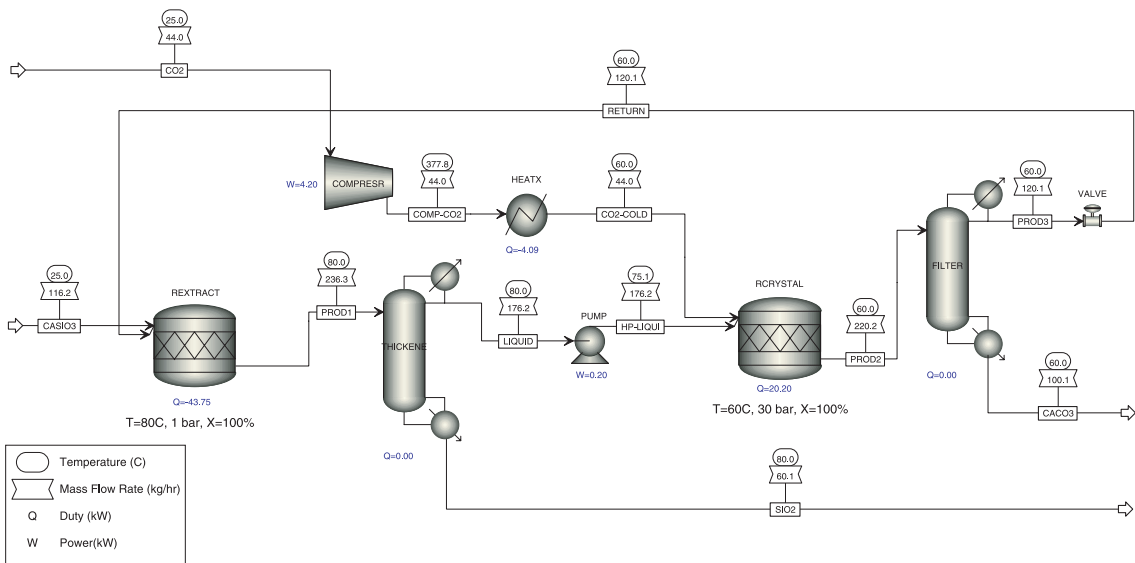


Fig. 12. Calcium carbonate production from calcium silicates assuming 100% carbonate conversion (30 bar crystallization pressure).

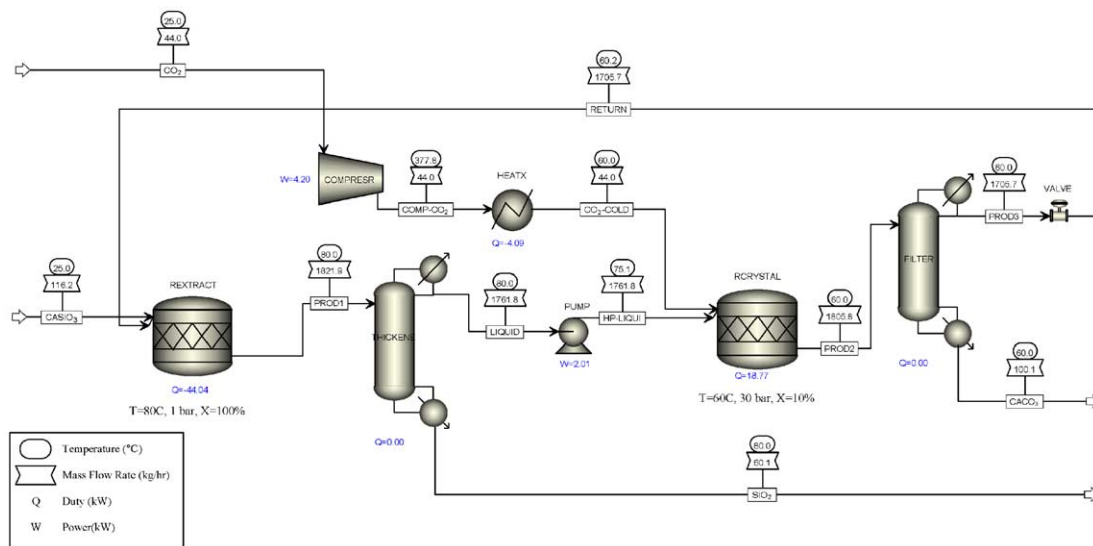


Fig. 13. Calcium carbonate production from calcium silicates assuming 10% carbonate conversion (30 bar crystallization pressure).

Table 6

Mass flow comparison of process models (carbonation pressure 30 bar)

	Kakizawa (kg/h)	Aspen Plus® (kg/h)
CaSiO <sub>3</sub> input	116.2	116.2
CO <sub>2</sub> input	44.0	44.0
	160.2	160.2
CaCO <sub>3</sub> output	100.0	100.1
SiO <sub>2</sub> output	60.0	60.1
	159.9	160.2
Regenerated acid	120.2	120.1
Thickener flow <sup>a</sup>	1422.3	1761.8

<sup>a</sup> Liquid flow from thickener to crystallization reactor.

For the work index of wollastonite, which is a slightly harder rock material than limestone, the work index of limestone (13.8 kWh/t) multiplied by a factor of 1.1 was used [41]. Using this equation, a graph was constructed (Fig. 15), which shows the energy requirement for pulverizing particles of various initial sizes down to 20  $\mu\text{m}$ . As can be seen from the graph, the curve approaches 34 kWh/t wollastonite (equal to 142 kJ/kg CaCO<sub>3</sub>) as the lump size grows. Although this is a considerable amount of power demand, it was not included in the analysis given below, because the price comparison was made with purchased wollastonite of a sufficiently small particle size.

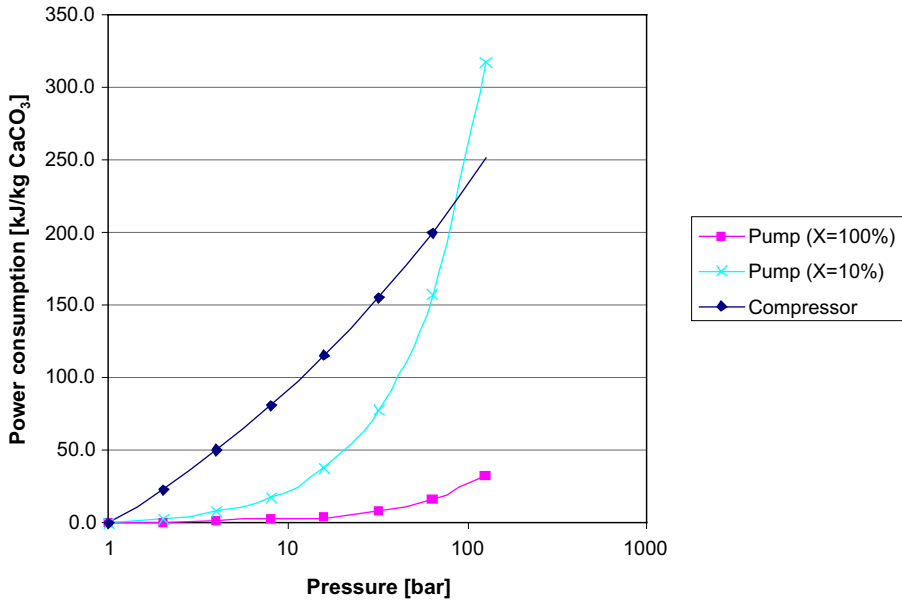


Fig. 14. Power consumption dependency of carbonation pressure.

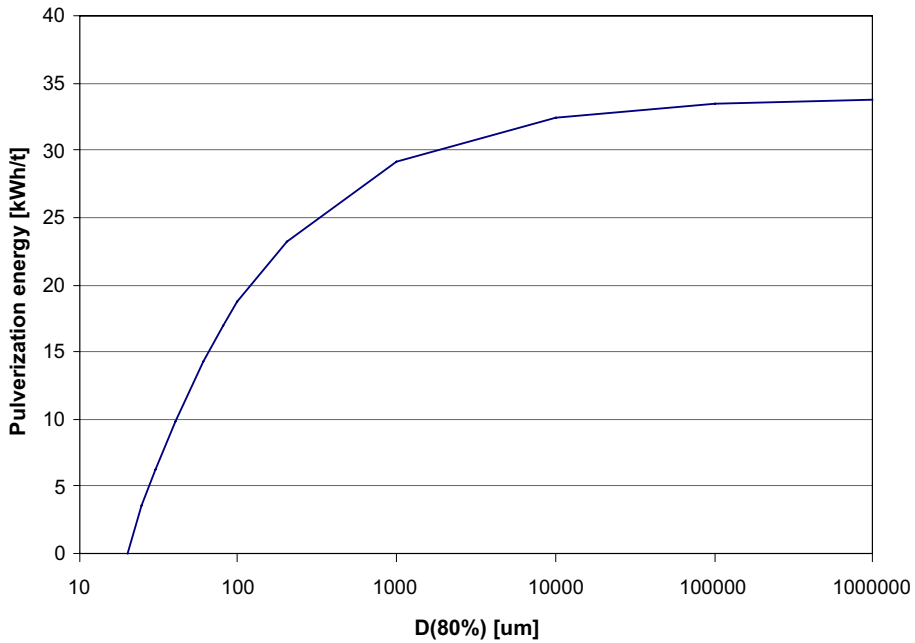


Fig. 15. Pulverization energy requirement for pulverizing particles of 20–10<sup>6</sup> μm to 20 μm.

The total power demand of the modelled process with 10% carbonate conversion (Fig. 13) was 223 kJ/kg CaCO<sub>3</sub>. Since the process is based on a carbonate free raw material, the net process

binds 0.44 kg CO<sub>2</sub>/kg CaCO<sub>3</sub> produced, which was the main motivation for this research. Assuming power is supplied from a coal fired subcritical power plant (emission data from Table 5), 0.096 CO<sub>2</sub>/kg CaCO<sub>3</sub> will indirectly be emitted from the power plant. The net sequestration of CO<sub>2</sub> will then be 0.34 kg CO<sub>2</sub>/kg CaCO<sub>3</sub>.

## 6. Logistical issues and resources

In current processes, calcium oxide is produced at a limestone mine and transported to the PCC plant at the paper mill. If calcium silicates are used as raw material for PCC production, the transportation costs are likely to be higher, since none of the processes produce calcium oxide, which is less heavy than both silicates and carbonates (Table 7) as an intermediate material. The alternatives for the calcium silicate based processes using the techniques presented above are either to produce PCC at the mine and transport that to the paper mill, or to transport calcium silicates to a paper mill retrofitted for PCC production by calcium silicates. As can be seen from the material requirements for producing PCC in Table 7, all options for PCC production from calcium silicates require more material to be transported; up to over twice the amount of the current PCC process. A third alternative would be to integrate a calcium silicate carbonation process to use the CO<sub>2</sub> released from limestone calcination. However, the CO<sub>2</sub> from the calcination process is mixed with flue gases from the fuel burned for sustaining the calcination temperature and may not have a sufficiently high CO<sub>2</sub> content for the calcium silicate carbonation process. Therefore, to minimize the transportation and retrofit costs of the PCC plant, it would be of interest to find another method that could separate CaO from calcium silicates.

In order to replace calcium carbonate completely in the PCC production in Finland, 530kt/a of pure calcium silicate is needed, which is as large as the current world wide production rate of wollastonite. The CaO content of Finnish wollastonite from the Lappeenranta mine (25% pure) is 12%, while the CaO content of Finnish basalt is 7–9%. The average calcium carbonate content

Table 7  
Material requirements (assuming 100% compound purity)

Compound	Tonnes needed to produce 1 ton PCC	Transportation need in comparison with CaO (%)
CaO	0.56	100
Ca(OH) <sub>2</sub>	0.74	132
CaCO <sub>3</sub>	1.00	178
CaSiO <sub>3</sub>	1.16	207

Table 8  
Scale of mining activity based on average CaO-content of Finnish rocks

	Limestone (68%)	Wollastonite (25%)	Basalt (8%)
CaO-content	38%	12%	8%
Scale of mining	100%	315%	476%



Table 9  
Comparison of processes

	Calc.	PCC	PCC + calc.	N-Carb.	N + Carb.	K	CaO
Raw material	CaCO <sub>3</sub>	CaO	CaCO <sub>3</sub>	CaSiO <sub>3</sub>	CaSiO <sub>3</sub>	CaSiO <sub>3</sub>	
– Market price	11 <sup>a</sup>	100 <sup>a</sup>	11 <sup>a</sup>	200 <sup>a</sup> 75 <sup>b</sup>	200 <sup>a</sup> 75 <sup>b</sup>	200 <sup>a</sup> 75 <sup>b</sup>	€/ton €/ton
Product	CaO	CaCO <sub>3</sub> (PCC)	CaCO <sub>3</sub> (PCC)	Ca(OH) <sub>2</sub>	CaCO <sub>3</sub> (PCC)	CaCO <sub>3</sub> (PCC)	
– Market price	100 <sup>a</sup>	120 <sup>a</sup> 200 <sup>b</sup>	120 <sup>a</sup>	150 <sup>a</sup>	120 <sup>a</sup> 200 <sup>b</sup>	120 <sup>a</sup> 200 <sup>b</sup>	€/ton €/ton
Heat demand							
– Ext. heat demand	2669	0	2669	8936	8269	0	kJ/kg CaCO <sub>3</sub>
Power demand							
– Pulverization						68.0	kJ/kg CaCO <sub>3</sub>
– Pump						72.3	kJ/kg CaCO <sub>3</sub>
– Compression						151.1	kJ/kg CaCO <sub>3</sub>
– Extraction stirrer <sup>c</sup>						32.2	kJ/kg CaCO <sub>3</sub>
– Crystallization stirrer <sup>c</sup>						65.8	kJ/kg CaCO <sub>3</sub>
– CaCO <sub>3</sub> separation <sup>c</sup>						25.6	kJ/kg CaCO <sub>3</sub>
– Total power demand						414.9	kJ/kg CaCO <sub>3</sub>
– Fuel price <sup>d</sup>	15			49	45	0	€/t CaCO <sub>3</sub>
– Electricity price <sup>e</sup>						9	€/t CaCO <sub>3</sub>
Minimum product price:	26	0	26	249 <sup>a</sup> 124 <sup>b</sup>	245 <sup>a</sup> 120 <sup>b</sup>	84 <sup>a</sup> 209 <sup>b</sup>	€/t CaCO <sub>3</sub> €/t CaCO <sub>3</sub>
CO <sub>2</sub> emissions							
– Heat generation	0.21	0	0.21	0.69	0.64	0	t CO <sub>2</sub> /t CaCO <sub>3</sub>
– Power generation <sup>f</sup>						0.096	t CO <sub>2</sub> /t CaCO <sub>3</sub>
– Process release	0.44	–0.44	0		–0.44	–0.44	t CO <sub>2</sub> /t CaCO <sub>3</sub>
<b>Net CO<sub>2</sub> emissions</b>	<b>0.65</b>	<b>–0.44</b>	<b>0.21</b>	<b>0.69</b>	<b>0.20</b>	<b>–0.34</b>	t CO <sub>2</sub> /t CaCO <sub>3</sub>

Calc. = calcination process;

PCC = PCC production process;

PCC + calc. = PCC production including calcination;

N-Carb. = Newall's process without carbonation;

N + Carb. = Newall's process with carbonation;

K = Kakizawa's process.

<sup>a</sup> Average price data for CaO, Ca(OH)<sub>2</sub>, bulk CaCO<sub>3</sub>, and cheapest PCC supplied by Nordkalk Oy, June 2004 [37].

<sup>b</sup> Average international market price for chinese wollastonite used, assuming 74 μm particle size [36].

<sup>c</sup> Data from Kakizawa et al. [33].

<sup>d</sup> Calculated using the heat content and average market price of heavy fuel oil 2002 [4].

<sup>e</sup> Calculated using the average annual electricity price 2002 [4].

<sup>f</sup> Data from Table 5, assuming 100% availability.

of limestone mined in Finland is 68% [28], which means that the average CaO content of Finnish limestone is 38%. This means that over three times more rock must be mined to produce the same

amount of PCC when using wollastonite instead of limestone (Table 8). If basalt were used instead of limestone for carbonate production, almost five times more rock must be mined.

## 7. Comparison of process models

The comparison of the processes in Table 9 presents the major power and heat demands of the various processes and an estimate of the cost for supplying this energy. Heat or material losses were not taken into account. Transportation costs were not included either. The energy need is calculated as kJ/kg CaCO<sub>3</sub> produced (also for processes producing CaO or Ca(OH)<sub>2</sub>, assuming a later 100% conversion into carbonate). The table shows also a rough approximation of the cost of PCC. No investment costs were included, only process energy requirements and raw material price. As can be seen from the cost comparison, the process suggested by Kakizawa et al. is cheaper than the current process considering its energy consumption, but depending on the cost data used, the feasibility of the idea of using calcium silicates varies. According to the international market prices, the process suggested by Kakizawa et al. could be competitive with the current processes, and an additional benefit could come from selling CO<sub>2</sub> emission allowances. However, using Finnish wollastonite for domestic PCC production, the price would be several times higher than the current domestic PCC produced from limestone. To compensate for the higher raw material prices, the avoided CO<sub>2</sub> emissions (0.21 + 0.34 t CO<sub>2</sub>/t CaCO<sub>3</sub>) would have to be sold as emission allowances for 300 €/t CO<sub>2</sub>, which is several times higher than the price for the penalty fees will be. On top of this, it must be remembered that good quality calcium silicates are scarce.

## 8. Future studies

Raw white magnesium carbonate, magnesite, is also used as a paper filler because it is chemically inert and relatively soft. However, it is normally utilized only as a minor filler because the shape of its crystal is not appropriate for paper bounding, and its hardness of five contributes to premature wearing of machinery. It also has a tendency to yellow in time. The investments required for modifying processes and machinery to get a valid filler material from magnesium carbonate is not usually considered as worthwhile since other filler materials are more abundant [42]. However, if magnesium carbonate is manufactured using magnesium silicates as a sequestration method for CO<sub>2</sub>, it might also be worth using it as a paper pigment for fillers and coatings [43]. The possibility to use the process suggested by Kakizawa et al. for carbonating magnesium silicates is currently under investigation.

## 9. Conclusion

The feasibility of precipitated calcium carbonate production from calcium silicates was studied by literature reviews, thermodynamic equilibrium calculations, process modelling and preliminary cost comparison. A two step carbonation method using acetic acid was found to be the most fea-

sible process for PCC production with calcium silicate. Using this process, 0.34 t CO<sub>2</sub> could be fixed per ton PCC produced. There are no external heat requirements, and the total energy requirements could be much lower than the existing calcination and PCC process combined. However, the process produces carbonate directly and not calcium oxide, which means that existing PCC plants could not be used without heavy modifications. Twice the amount of minerals would also need to be transported, and 3–5 times more rock would have to be mined.

The largest problem seems to be the availability of wollastonite, which is much more rare than limestone (hence the price). Therefore, it is definitely not feasible to use mineral carbonation of wollastonite solely as a method for disposal of CO<sub>2</sub>. However, if the product can be sold as PCC including a CO<sub>2</sub> taxation benefit, there might be a possibility. A modified process might also be able to handle basalt, which is common and inexpensive. However, the process costs for utilizing basalt may be too high, and the high iron oxide content of basalt probably renders the rock unsuitable for PCC. With current national mineral prices and CO<sub>2</sub> taxation, producing PCC from calcium silicates does not seem to be feasible in Finland.

A more thorough study of resources and a detailed comparison with the current PCC production process are needed. Experiments should also be conducted to determine if the quality of the PCC produced from various calcium silicates is sufficient for use as a paper filler.

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