

## ÅA Thermal and Flow Engineering

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# D504 A technology survey report on the feasibility of large-scale CO<sub>2</sub> mineralisation in Finland

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### Executive summary:

An update is given on mineral resources in Finland and their most feasible use for large-scale CO<sub>2</sub> mineral sequestration. Besides the widely known vast resources in central Finland, special focus lies here with minerals in south/southwest Finland, and their use at important CO<sub>2</sub> emission point sources such as the Meri-Pori coal-fired power plant and a lime kiln at Parainen. As was reported earlier, mineral resources are not the limiting factor but distances between mineral deposits and CO<sub>2</sub> point sources may be considered problematic. The quality of the materials found in south/southwest could offer solutions for long enough time periods for the two mentioned applications although technology development on the carbonation process (the ÅA route) is needed, especially if the rock to be used is not a serpentinite. CO<sub>2</sub> mineralisation process technology was reviewed in Deliverable D503 (Oct. 2011).

### 1. Introduction and scope.

This text summarises and updates earlier reporting on the possibility of large-scale sequestration of CO<sub>2</sub> produced in Finland by CO<sub>2</sub> mineralisation, using Finland's vast mineral resources. There are several motivations for the ongoing R&D work on this CCS route for Finland, which started in year 2000 at TKK (nowadays Aalto University) and after 2005 had its main centre at Åbo Akademi University:

- It is known for quite some time (and has repeatedly been confirmed) that underground storage capacity for CO<sub>2</sub> is not available in Finland [e.g., 1,2]. As reported recently, based on findings from the EC FP7 project CGS Europe the same appears to hold for the Baltic region<sup>1</sup> in general, apart from CCGS capacity in Poland, a country that produces a lot of coal-derived CO<sub>2</sub> emissions [3].
- Finland has vast amounts of magnesium silicate-based mineral resources; assessments by the Geological Survey of Finland typically mention 2-3 Gt CO<sub>2</sub> storage capacity in minerals of the Outokumpu-Kainuu region of central Finland alone [6-8]
- Underground storage capacity in west-Russia may seem attractive but export of CO<sub>2</sub> to outside the European Economic Area is prohibited under the EU directive on CCS (which in effect addresses only CCS that implies underground storage) [9].<sup>2</sup>

<sup>1</sup> There would be some CO<sub>2</sub> underground storage capacity in Latvia but in 2011 a political decision was made against CCS in Latvia [4]. As noted recently, Poland seems to go in the same direction [5].

<sup>2</sup> This can become more flexible if the concepts Clean Development Mechanism (CDM) and Joint Implementation (JI) under the Kyoto Protocol may be applied to CCS.

- Implementation of the above mentioned EU directive on CCS in Finnish legislation is ongoing and may result in CO<sub>2</sub> underground storage being forbidden within Finland's borders [10-11].

Thus, Finland's hope, as for several other countries with which cooperation is ongoing (Lithuania [12], Portugal [13], Singapore<sup>3</sup> [14]) for CCS implementation appears to be largely narrowed down to CO<sub>2</sub> mineral sequestration.<sup>4</sup>

In recent years, research into CO<sub>2</sub> mineralisation has taken a leap forward as demonstrated by the rate at which new process routes are suggested, patented and in several promising cases developed to large-scale application [15]. Many of these processes do not require pure CO<sub>2</sub>, but can be run with flue gases directly, such as the process routes suggested by Nottingham University [16], Hunwick [17] and also the ÅA route [18]. A general trend is the use of ammonium salts for extracting Mg from rock, and a more clear division between direct (one-step) methods, and indirect (multi-step methods). The latter benefits greatly from the separately obtained and hence more valuable, (by-) product solids [19].

Thus, CO<sub>2</sub> mineral sequestration will preferably be operated on flue gases (or other CO<sub>2</sub> containing gases) directly, especially if the gases contain oxygen. According to BASF [20] there is no market for CO<sub>2</sub> solvents for gases that contain oxygen<sup>5</sup>. Chilled ammonia processes (CAP) are an important alternative for alkanol amine type sorbents for CO<sub>2</sub>; the resulting ammonia (bi-)carbonate can be made to react with activated magnesium, for example in an aqueous solution [16,17].

Of course, the distance between the flue gas / CO<sub>2</sub> production source and the mineral deposit limits the possibilities of transporting complete flue gas flows, not to mention large amounts of mineral. As noted by Brent [21,22], the preferable way to apply CCS to power plant –generated flue gas would be to have the power plant at a mineral deposit and transport the coal (or other fuel for that matter) to that site.

The table below gives four options for CO<sub>2</sub> mineralisation; depending on the market value of the produced solids the costs for these schemes will presumably be lower when going downwards in the table.

Table 1: CO<sub>2</sub> mineralisation options for operation

CO <sub>2</sub> capture	Transport of	Mineralisation on	Location
yes	CO <sub>2</sub>	CO <sub>2</sub>	At mineral mine
yes	rock	CO <sub>2</sub>	CO <sub>2</sub> -producing site
no	rock	CO <sub>2</sub> -containing gas	CO <sub>2</sub> -producing site
no	CO <sub>2</sub> -containing gas	CO <sub>2</sub> -containing gas	At mineral mine

If CO<sub>2</sub> pre-capture is removed from the CCS chain the resulting CS (carbon storage) process may be cost-competitive with methods that involve underground storage of CO<sub>2</sub>, as there is no need for post-storage CO<sub>2</sub> monitoring. This is particularly urgent since the costs for the capture step alone typically exceed what economically viable CCS may cost. This makes "conventional" CCS economically unattractive irrespective of public acceptance and other non-technical problems. Also the current low "cost" of CO<sub>2</sub> emissions under the European Emissions Trading Scheme (ETS) presents an obstacle for CCS.

In this text the current status of knowledge with respect to Finnish mineral resources and their possible use is reported and updated. The carbonation technology itself is not addressed in detail, but for the purpose of the Finnish CCSP project, the Meri-Pori coal-fired power plant and also application at Nordkalk's lime kiln at Parainen are discussed as case

<sup>3</sup> For Singapore this implies a Tekes co-funded project (2010-2013).

<sup>4</sup> This was also one of the conclusions of the Finnish (Tekes-funded) programme CLIMTECH (1999-2002).

<sup>5</sup> According to T. Katz, BASF Germany that market "only exists in the mind of politicians" [20]

studies. Export of mineral to countries that are less fortunate when it comes to this CCS option is not considered here but should be kept open as a future option.

## 2. CO<sub>2</sub> mineral sequestration technology

Recently Deliverable 503 (Assessment of options and a most feasible design of serpentinite carbonation applied to a lime kiln) [23] gave an assessment and comparison of a total of ~ 35 different process routes, of which ~1/3 appeared capable of operating on a CO<sub>2</sub>-containing gas, not requiring CO<sub>2</sub> pre-separation. For most of these a magnesium-based material is carbonated. Although the study was partly focussing on lime kiln application it applies likewise to other large CO<sub>2</sub> producing point sources. Four routes were recommended for consideration by Nordkalk:

- An Mg-silicate process route under development at Nottingham University (UK) [16]
- The ÅA serpentinite dry/wet/dry carbonation route via MgSO<sub>4</sub> and Mg(OH)<sub>2</sub> [24-28]
- The Aalto/ÅA “slag2pcc” route for PCC production from steelmaking slags<sup>6</sup>
- The air pollution control (APC) residue gas/solid from Rome (IT), for which operation in a fluidised bed may be considered [29]

At this point the ÅA route seems preferable over the Nottingham route from an energy efficiency and reaction kinetics point of view, while the other two listed deal with calcium-based industrial process residues that won't be able to offer necessary large-scale CO<sub>2</sub> sequestration capacity.

Recently, ÅA reported two studies on the application of the ÅA route in Finland:

- the first involves the application of the process at Nordkalk, Parainen, at a scale of just several 100 kg/h [30]<sup>7</sup>, using waste heat from the kiln process for the pre-treatment of rock (i.e. production of Mg/Ca hydroxides);
- the other study<sup>8</sup> involved the use of magnesium silicate rock from south-west Finland for the purpose of mineralisation of CO<sub>2</sub> from the Meri-Pori power plant, for example using mineral resources located at Vammala, located ~ 80 km to the east of Meri-Pori [31]. In the study also the co-fixation of CO<sub>2</sub> and SO<sub>2</sub> using Mg(OH)<sub>2</sub> is addressed which, if successful, may remove the need for separate flue gas desulphurisation (FGD) units when operating CO<sub>2</sub> mineralisation on coal-fired power plant flue gas directly. The mineral resources assessment<sup>9</sup> will be summarised below.

## 3. Mineral resources in Finland – earlier assessments

Many active mines in Finland are located in areas with rich magnesium silicate deposits, as reported in a first study on CO<sub>2</sub> mineralisation in Finland by Kohlmann [33]. Most of this is found in northern and central Finland, at quite large distances from large CO<sub>2</sub> point sources in the south of the country. Nickel mines were already then (2000) identified as sites where suitable magnesium silicates would be available, with the nickel mine at Hitura (Nivala) as an interesting case with serpentinite volume estimated (in 2001) at 95·10<sup>6</sup> m<sup>3</sup>, or (with ~3000 kg/m<sup>3</sup> density) ~ 285 Mt [34].

The Finnish resources have been widely mentioned in project reporting and quite a few publications; for example (quoting [35] from 2007):

*Finnish bedrock consists locally of rock types that contain large amounts of magnesium- and calcium silicates. However, calcium silicates with a significant content of calcium, such as*

<sup>6</sup> Scale-up of this is part of Cleen CCSP project Task 5.2 as well. For a good and pure PCC (precipitated calcium carbonate) it would require pure (pre-separated) CO<sub>2</sub>, however.

<sup>7</sup> A pre-study for Cleen CCSP project year 2

<sup>8</sup> Funded by KH Renlund Foundation (2010)

<sup>9</sup> By ÅA prof. O. Eklund and M. Mäkelä – see [32]

wollastonite, are both rare and expensive (Teir et al., 2005)<sup>10</sup>. The most interesting rocks for CCS purposes are serpentinites, because they consist mainly of serpentine which may contain about 40% MgO. Millions of tons of in situ and mined (tailings containing) serpentine minerals are present, particularly in central Finland. To bind ~ 11 Mt CO<sub>2</sub>/a<sup>11</sup> by carbonation of serpentine, ~ 25 Mt/a minerals would be required. Accordingly, it is estimated that the serpentinites in eastern Finland alone could be sufficient for 200-300 years of CCS processing are situated especially in those ultramafic rock units which have already been mined for industrial minerals and metals, such as talc, soapstone, chromium and nickel, all contain considerable amounts of minerals and rocks potentially suitable for sequestration of CO<sub>2</sub>. These rocks are being constantly stockpiled or dammed as tailings for later use in industry - see Figure 1. Currently available resources of hoisted serpentine / serpentinite (33-39% MgO) at Finnish Ni, Cr and talc mines are ~ 29 Mt (Aatos et al., 2006)<sup>12</sup>.

The Figure 1 referred to in the quoted text is given below as Fig. 1 (left); that also indicates proximity to CO<sub>2</sub> sources. For comparison a (more recent) mapping of large-scale CO<sub>2</sub> sources is given as well (right).

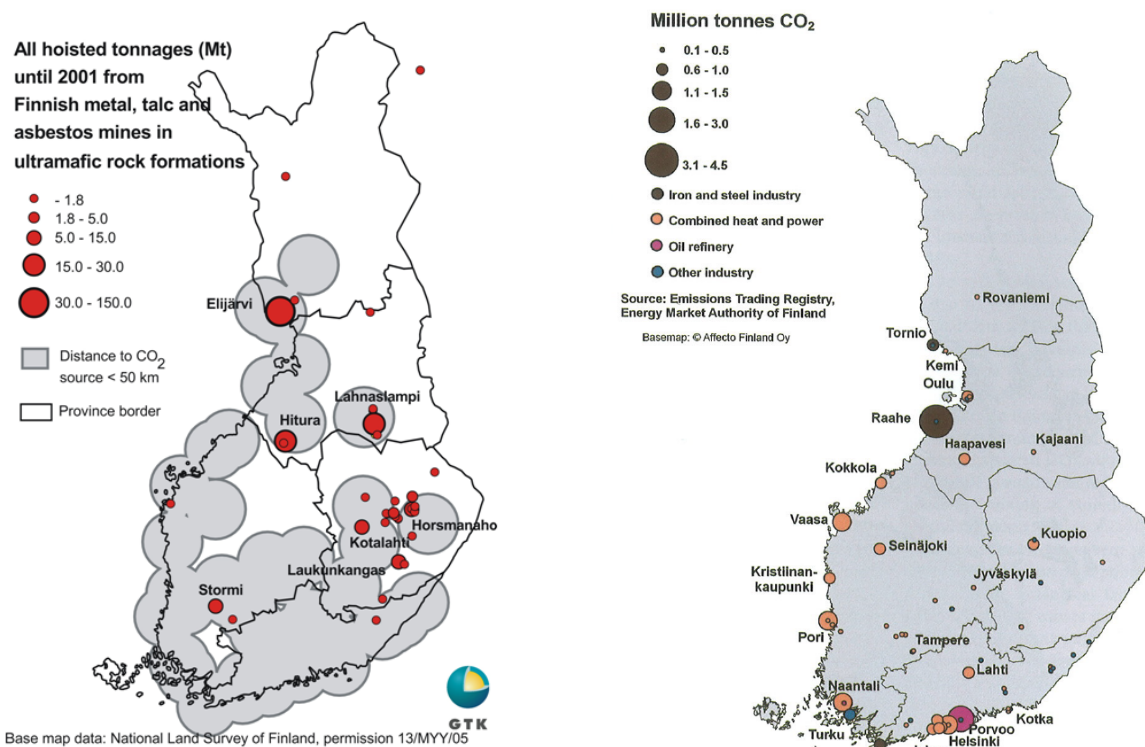


Fig. 1 Possible resources of serpentine in Finland until 2001 (left) [6]; CO<sub>2</sub> emission sites as of 2008 (right) [8].

More recently [36], the capacity of Hitura was estimated at a much larger  $390 \cdot 10^6 \text{ m}^3$ , or (again with  $\sim 3000 \text{ kg/m}^3$ )  $\sim 1170 \text{ Mt}$ . The MgO content of the serpentinite (rock mainly composed of serpentine mineral,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) is  $\sim 35 - 40\%$ -wt, enabling 1 t of rock to bind  $\sim 1/3 \text{ t}$  of CO<sub>2</sub>. Thus, the Hitura site rock material would be able to bind  $\sim 400 \text{ Mt CO}_2$ .

<sup>10</sup> Teir, S, Eloneva, S, Zevenhoven, R. Production of precipitated calcium carbonate from calcium silicates and carbon dioxide Energy Conv. & Manage. 2005; 46: 2954-2979.

<sup>11</sup> At the time of writing, Finland's "excess" CO<sub>2</sub> emission level with respect to the Kyoto Protocol target.

<sup>12</sup> Reference [6]; see also [7].

Typical to many other locations worldwide, Finland's resources of suitable mineral are large, yet also concentrated, and rocks located at a single or a few sites like Hitura will be sufficient for sequestration of hundreds of Mt of CO<sub>2</sub>, operating for several decades<sup>13</sup>.

A map of Finland (2001) that indicates the presence and location of ultramafic rocks is given in Fig. 2, indicating also the locations of Hitura, Vammala and Suomusjärvi, and the Outokumpu-Kainuu belt. The latter was quoted to have a CO<sub>2</sub> fixation capacity of the order of 2-3 Gt [2,6]. The ☆ sites the Meri-Pori power plant (an earlier cornerstone of the Clean CCSP project) to be addressed below.

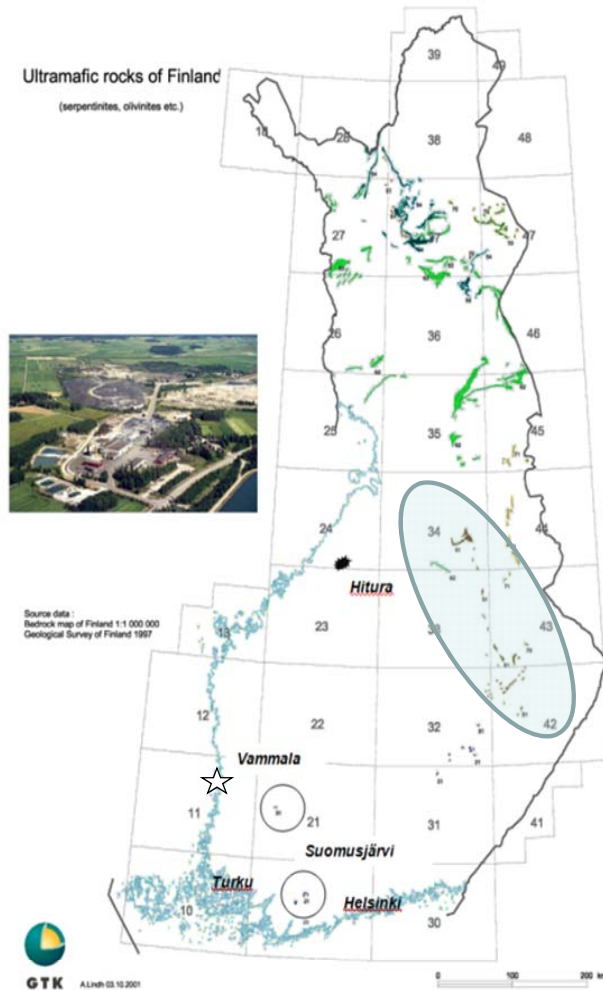


Fig. 2  
The location of ultramafic rock in Finland.

Also shown: a photo of the nickel mine at Hitura and its location, ultramafic rock findings in southern Finland at Vammala and Suomusjärvi, and (oval circle) the Outokumpu-Kainuu belt.

#### 4. Mineral resources in Finland – recent assessments

Finland has large amounts of serpentinite available in the centre and north of the country. Based on data on mineral resources exploitation operations for Finland, a total value of 33.4 Mt of suitable material was recently reported for year 2010 [2] (significantly less than the numbers for Norway (70.2 Mt) and Sweden (50.8 Mt) for year 2009).

The suitability of any given mining site as a source of mineral for carbonation depends on the magnesium (and calcium) content(s) of the rock. In addition, the distance from the power plant and total amount of rock, as well as possible nearby sources of waste heat are of

<sup>13</sup> Likewise, for the Bragança serpentinite deposit in Portugal has a capacity for 260 Gt, corresponding to ~3500 years of current annual Portuguese fossil-fuel derived CO<sub>2</sub> emissions [13].

importance. Many mines in relative proximity to Meri-Pori, for example, are in operation or have previously been in operation producing large amounts of serpentinite as mine tailings and overburden.

Thus, a study was conducted in 2010/2011 that focussed on identifying mineral resources suitable for CO<sub>2</sub> mineralisation located in south/south-west Finland [32]. Table 2 presents a shortlist of sites with their respective rock compositions. (Hitura material is included in the Table for comparison.)

Table 2. Composition (as oxides) of the Finnish rock considered in [32] for mineralisation

Location	MgO %-wt	CaO %-wt	*Fe <sub>2</sub> O <sub>3</sub> %-wt	SiO <sub>2</sub> %-wt	Al <sub>2</sub> O <sub>3</sub> %-wt	Other %-wt
Suomusjärvi	16.2	8.6	11.4	47.6	10	6.2
Hyvinkää / Mäntsälä**	9.8	11.4	13.2	45.9	13.6	6.1
Lammi / Asikkala**	4.9	6.8	8.0	58.0	15.6	6.7
Kaipola / Kuhmoinen**	7.2	7.5	7.7	55.2	14.9	7.5
Vammala	14.5	5.6	12.5	49.5	8.8	9.1
Hitura	38.1	0.5	14.8	32.6	0.4	13.6

\* Calculated, presumably a mixture of FeO and Fe<sub>2</sub>O<sub>3</sub>, partly (?) Fe<sub>3</sub>O<sub>4</sub>. \*\* Not a mining site

The Suomusjärvi and Vammala rock and, for comparison with a “better” material, the Hitura nickel mine mining tailings offer potential for CCS application at Meri-Pori and Nordkalk. (See Fig. 2.) The other southern-Finland rock types (Hyvinkää, Lammi and Kaipola) won't be further addressed here - see [32]. For the samples as tested, i.e. assessing suitability for the production of Mg(OH)<sub>2</sub>, chemical composition is given in Table 3.

Table 3. Composition (as oxides) of the Finnish rocks for mineralisation as tested

Working names	MgO %-wt	CaO %-wt	*Fe <sub>2</sub> O <sub>3</sub> %-wt	SiO <sub>2</sub> %-wt	Al <sub>2</sub> O <sub>3</sub> %-wt	Other %-wt
Hitura <sup>#</sup>	36.2	0.5	14.4	24.8	<0.1	24.1
Vammala-1 <sup>‡</sup>	19.2	9.0	15.4	45.0	3.5	7.9
Vammala-2 <sup>‡</sup>	28.0	1.4	18.4	39.3	1.3	11.6
Satakunta <sup>§</sup> olivine	5.5	8.7	15.3	46.9	16.1	7.5
Suomusjärvi-1 <sup>‡</sup>	13.5	7.8	10.9	50.2	10.8	6.8
Suomusjärvi-2 <sup>‡</sup>	20.9	8.3	11.9	44.3	7.0	7.6

# Ref. [37], § Ref [38], ‡ Ref. [32] \* Calculated, presumably a mixture of FeO and Fe<sub>2</sub>O<sub>3</sub>, partly (?) Fe<sub>3</sub>O<sub>4</sub>.

The Stormi ultramafic complex in the Vammala nickel belt is a 1500 m × 600 m × 300 m large volume, with an upper layer of 70 m of serpentinite [39]. This gives a volume of 0.063 km<sup>3</sup> = 63·10<sup>6</sup> m<sup>3</sup> with an assumed density ~ 3000 kg/m<sup>3</sup> this corresponds to ~ 200 Mt material. Given the rock composition with 20 ~ 25%-wt MgO (Table 3), theoretically around 44 ~ 55 Mt of CO<sub>2</sub> could be sequestered with the upper layer minerals.

The Vammala mine is no longer being mined for nickel, but still produces gold. However, nickel deposits are generally found in ultramafic rock formations, whereas gold tends to be present in quartz formations. There is nonetheless the possibility that the overburden from mining contains serpentinite material. Another option is to reconsider nickel mining in the light of new uses for the mine tailings, or to mine for serpentine without specific regard for nickel altogether. It does however appear that Belvedere Resources, the company operating in Hitura were, at least in 2008, exploring the possibility to start mining nickel in Vammala again [38].

Only a few kilometres south-east of Pori, in the region around Nakkila and Harjavalta, the Satakunta olivine deposits can be found [41]. Historically nickel has been mined in Harjavalta, but presently the only mining activity in the region is copper mining [42]. The chemical composition of olivine favours its use as a source of magnesium due to stoichiometrically higher ratio of Mg to rock, compared to serpentine. Nduagu et al. [38] argued, however, that due to lower surface area and porosity, as well as being harder than serpentine, olivine cannot be used for extracting magnesium according to the method used at ÅA. (This is a topic of ongoing R&D efforts at ÅA.)

Material can also be found in the region around Suomusjärvi, located roughly half-way between Turku and Helsinki. This is at the south end of the Vammala nickel belt [43]. One sample (Suomusjärvi-1) is a side-material from the Salittu quarry where macadam is mined for roadmaking. The other sample (Suomusjärvi-2) is an olivine-hornblendite actually from Nummi-Pusula (~20 km east of Suomusjärvi), containing ~50% olivine (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> [35]. Data on amounts of material is not yet available.

Finally, significant amounts<sup>14</sup> of diopside-type material are produced at the limestone quarry of Nordkalk at Parainen. The composition of this material is given in Table 4 [26]. This material could present Nordkalk with an alternative for silicate rock that would have to be brought to Parainen. The Parainen diopside is not as favourable for carbonation as the Hitura rock due to its low Mg and Ca content; consequently, larger amounts of the Parainen diopside are needed for the carbonation of 1t CO<sub>2</sub>. Details are presented in Section 7.

Table 4. Elemental and XRD analysis of the Parainen diopside sample.

Elemental Analysis (%)									Structural Analysis (XRD)
CaO	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Others	
15.6	50.9	0.4	12.2	4.5	4.9	3.1	2.1	6.3	Hedenbergite, Orthoclase, Albite (Calcium), Muscovite, Clinocllore

## 5. Source – sink combinations

Three Finnish source-sink combinations have been considered already in 2002 [34]: the Meri-Pori coal fired power plant + Hitura rock, the Raahe steelworks of Rautaruukki + Hitura rock, and ten pulp and paper factories, respectively.

The pulp and paper facilities produce for a large part “renewable”, i.e. non-fossil fuel derived CO<sub>2</sub>, but those located at (near), for example, Pietarsaari, Kaskinen, Oulu or Kemi are at relatively short (~100 km) distance from a suitable rock deposit. Part of the produced CO<sub>2</sub> will be used to produce PCC and other calcium carbonate.<sup>15</sup>

<sup>14</sup> Nordkalk cannot give produced amount estimates, unfortunately.

<sup>15</sup> See the TKK MSc thesis by Tuulia Raiski (nowadays: Tuulia Lepistö) CO<sub>2</sub> emissions: mineral carbonation and the Finnish pulp and paper industry (2004)

A very promising combination of CO<sub>2</sub> emissions / CO<sub>2</sub> mineralisation capacity would involve the Hitura nickel mine, which explains why serpentinite rock from this site has received most R&D focus from the Finnish resources. The Hitura mine is located around 350 km (in north-east direction) from Meri-Pori, or 500 km from Parainen. Rocks from Hitura, tested at ÅA, have been shown to contain ~ 83% serpentine mineral, which constitutes a MgO content of ~ 36%. The continuous transport cost by pipeline, for pure CO<sub>2</sub>, would amount to less than 5 €/t CO<sub>2</sub>. However, should the transported gas be the total (dried) flue gas, the costs can be expected to rise by a factor of three to five, depending on the CO<sub>2</sub> content [44].

The MgO content in the Stormi-Vammala upper layer serpentinites necessitates the processing of larger amounts of rock (4 ton/ton CO<sub>2</sub> compared to ~3 ton/ton CO<sub>2</sub> for Hitura material). On the other hand, Stormi-Vammala, is significantly closer to Meri-Pori than Hitura is. At a distance of only 75-85 km both pipeline transport costs and capital costs could be kept at a minimum. With an MgO content of 20 – 25 %-wt this would in theory allow for binding ~ 44 - 55% Mt CO<sub>2</sub>, which corresponds to Meri-Pori power plant CO<sub>2</sub> produced during ~20 years.<sup>16</sup>

### 6. Feasibility of the considered deposits for Meri-Pori CO<sub>2</sub>

Figure 3 shows the amount of Hitura mining tailings rock needed to carbonate 1 t CO<sub>2</sub> as a function of Mg extraction, for full and partial (65%) carbonation extent<sup>17</sup>. With Mg(OH)<sub>2</sub> production levels of the order of 65- 70% obtained for the rock processing according to Nduagu et al., the process would require ~ 5 ton rock / ton CO<sub>2</sub> and could sequester 1.2 Mt CO<sub>2</sub>/y for ~150 years with 65% Mg(OH)<sub>2</sub> carbonation. According to Romão et al. [26] – the heat requirements would be ~ 6 GJ/t CO<sub>2</sub> (mainly as 400-450°C heat) which can be reduced somewhat by heat integration. It would be reduced to ~ 4 GJ/t CO<sub>2</sub> if extraction and carbonation levels > 90% can be realised.

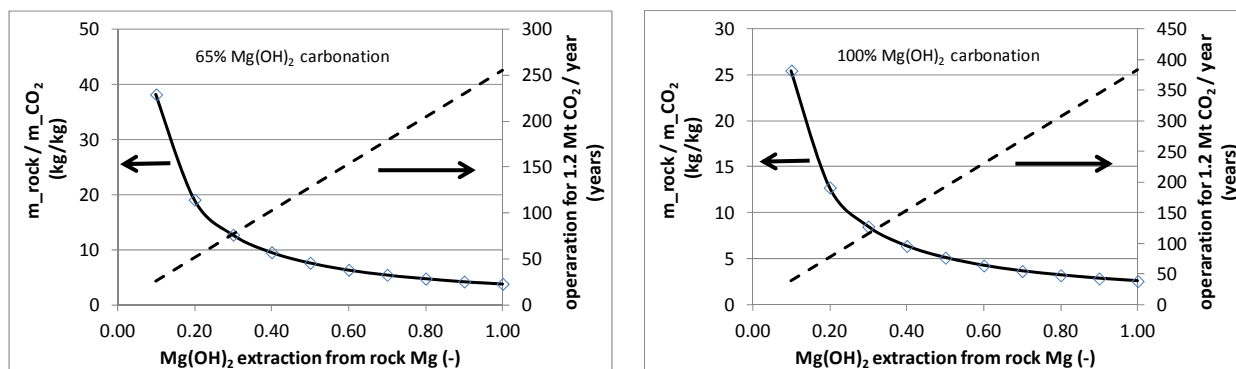


Fig. 3 Rock consumption rate and availability at Hitura depending on extraction of Mg from the rock, for full (left) or partial (right) carbonation of the Mg(OH)<sub>2</sub> produced [31].

The distance of around 350 km from Meri-Pori to the Hitura site would add a few €/t (on-shore pipeline) transport costs to this CCS option [44], making a site like Stormi-Vammala more attractive.

The rock available at Stormi-Vammala has a theoretical capacity to sequester ~50 Mt CO<sub>2</sub>. Figure 4 shows the amount of rock needed to carbonate 1 t CO<sub>2</sub> as a function of Mg extraction, for full and partial (65%) carbonation extent. With Mg(OH)<sub>2</sub> production levels of ~ 25% obtained experimentally for this rock [32] the process would require ~ 12 ton rock / ton

<sup>16</sup> The earlier but cancelled plan of the Fortum/TVO CCS project (2009-2010) to separate and export to the North Sea region an amount of 1.2 Mt /a would saturate these rock resources in ~40 years.

<sup>17</sup> As achieved at ÅA with Mg(OH)<sub>2</sub> carbonation times ~10 minutes [27] while further optimisation is ongoing.



CO<sub>2</sub> and could fix 1.2 Mt/y for < 10 years only, again assuming 65% Mg(OH)<sub>2</sub> carbonation. The heat requirements would be in the range of 4.5 – 20 GJ/t CO<sub>2</sub> depending on whether non-reactive material behaves as inert or not. These values can be reduced somewhat by heat integration but the most urgent need for improvement is the extraction of Mg and producing more Mg(OH)<sub>2</sub> from the rock material. With the current result the contribution of crushing and grinding the rock material will change from a few % to a significant energy penalty.

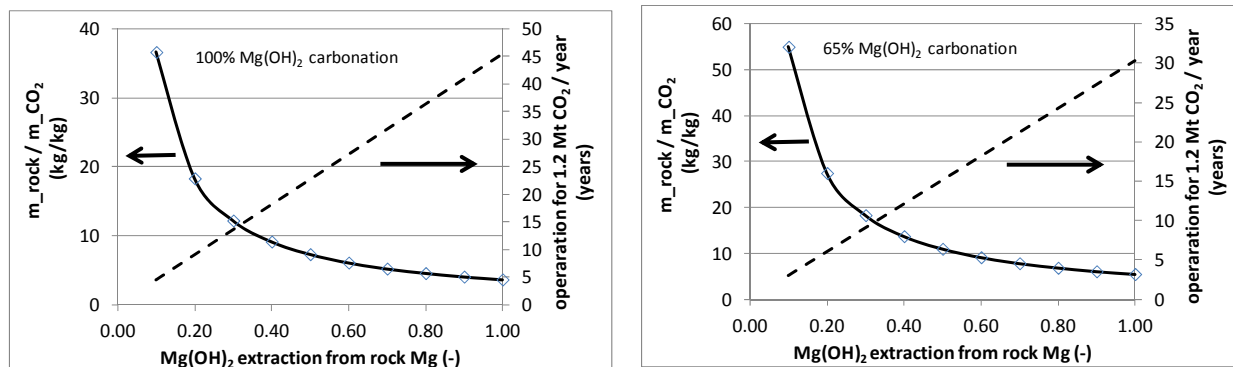


Fig. 4 Rock consumption rate and availability at Stormi-Vammala depending on extraction of Mg from the rock, for full (left) or partial (right) carbonation of the Mg(OH)<sub>2</sub> produced.

A small number of experiments were carried out with olivine from Åheim in Norway, which confirmed (with < 10% of present Mg extracted) the hypothesis that the method developed by Nduagu et al. is not well applicable to olivines. Tests on the Satakunta olivine diabase gave no good results: Mg extraction was a disappointing 15% of the material's Mg content which is already quite low at only 5.5%. Work at ÅÅ is ongoing to further analyse the application of the Mg(OH)<sub>2</sub> production method on minerals like olivine and enstatite, besides serpentine.

The experimental results showed that Mg(OH)<sub>2</sub> could be produced only from the rock material Suomusjärvi-2, (Nummi-Pusula), at an extraction of ~14% of the ~21%-wt of MgO in the material [32]. This implies that ~ 3 t Mg(OH)<sub>2</sub> can be produced from ~100 t of rock, which is ~10-15× the amount of rock needed compared to a Hitura-type serpentinite and crushing / grinding energy needs become a significant cost factor. Again, more work is needed on extending the capabilities of the Nduagu et al. route to Mg(OH)<sub>2</sub> production from "low quality" (< 20%-wt MgO) type of rock.

## 7. Feasibility of input materials for Nordkalk/Parainen lime kiln CO<sub>2</sub>

A recent study [30] showed that the waste heat available from the Nordkalk lime kiln located at Parainen is enough to process 550 kg/hr of Hitura serpentinite with a capture potential of ~190 kg/hr of CO<sub>2</sub>. 80% of Mg extraction and 90% of Mg(OH)<sub>2</sub> carbonation using the ÅÅ route are assumed. Even though the integration with flue gas allows for an auto-thermal process, a total of 0.71 MJ/kg CO<sub>2</sub> captured is needed, as an electrical input, for materials crushing/grinding and compression of gases.

An alternative would be to use a diopside material that is produced by Nordkalk as by-product from its limestone quarry – see Table 4. Therefore, Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> production from this material using the Nduagu et al. route was attempted at ÅÅ, noting that the expectations were low based on the Mg and Ca content of the rock, and the presence of alkali that would presumably accumulate in the aqueous (ammonium sulphate, AS) solution.

Indeed the results were disappointing, giving an extraction efficiency of 6-10% for Ca and 2-4% for Mg for the solid/solid reaction with AS at 400-500°C. It was concluded that despite the advantage of being readily available it is not a suitable raw material for CO<sub>2</sub> mineralisation.

Compared to Hitura serpentinite, about 6x more solid material must be handled. An option that is currently being evaluated<sup>18</sup> is the processing of the rock to a more suitable form for the ÅA (and other) CO<sub>2</sub> mineralisation route: a low temperature dissolution reaction in an acidic environment may give a serpentine-forming reaction [45] that removes Ca and most of the SiO<sub>2</sub> from the diopside.

## 8. Other issues: energy, operation on flue gas, waste heat

Since CCS is one of the solutions to what is in fact an energy problem, routes that lead to the production of large amounts of CO<sub>2</sub> while producing the power and heat for the CCS process are obviously not viable. The Meri-Pori plant, for example produces 820 g CO<sub>2</sub>/kWh electricity, thus CCS with an electricity consumption of 1/0.82 = 1.22 kWh = 4.39 MJ/kg CO<sub>2</sub> would have a zero net output of both electricity and CO<sub>2</sub>. The use of electricity in CCS processes should be avoided although some power consumption will follow from gas compression and crushing/grinding of solid material. Fortunately, part of the energy input of a CCS processes would be in the form of heat and at ~ 43% thermal efficiency the Meri-Pori plant produces similar amounts of electricity and (waste) heat.

CCS routes based on CO<sub>2</sub> mineralisation appear to be more dependent on heat as energy input than the “conventional” CCS route that involves underground storage of CO<sub>2</sub>, while – as done in the ÅA route – the heat output from the carbonation reaction can be benefitted from<sup>19</sup>. At the same time, CO<sub>2</sub> mineralisation routes that involve electrochemical steps (electrolysis, fuel cells) are very unlikely to have a net CO<sub>2</sub> fixation effect [49].

As presented earlier [26] a quick assessment of energy input requirements for the ÅA route can be made based on the reaction heat  $Q_E$  or  $\Delta H_E$  needed for Mg extraction from rock and the heat  $Q_C$  or  $\Delta H_C$  released by Mg(OH)<sub>2</sub> carbonation. Besides this, crushing/grinding of rock contributes to only a few % of the energy input requirements while process integration and optimisation will result in improvements to the energy efficiency [26].

With Mg extraction conversion  $X_E = X_{Mg(OH)_2prod}$  and Mg(OH)<sub>2</sub> carbonation conversion  $X_C = X_{Mg(OH)_2carb}$  the net heat input requirements is equal to

$$Q \text{ (MJ/kg CO}_2\text{)} = \frac{\Delta H_E}{X_E} - X_C \cdot \Delta H_C$$

with  $\Delta H_E = 234.6$  kJ/mol Mg extracted (value for 480 °C) and  $\Delta H_C = -59.5$  kJ/mol Mg carbonated (value for 550 °C) as in [26]. For serpentinite (rock mainly composed of serpentine) found at Hitura composed of ~84%-wt serpentine, ~13%-wt iron oxides as FeO and ~3%-wt calcium silicates the heat input requirements are given in Table 5 for  $X_E$  and  $X_C$  ranging from 25 to 100% [26].

Of course, incomplete Mg extraction would not have a heat penalty (an endothermic reaction that doesn't occur won't give an energy penalty) and thus only the last row of Table 4 would apply. At the same time, if Mg extraction conversion  $X_E \ll 100\%$  then crushing and grinding of what is then mainly inert material will give excessive costs and the material must still be heated to > 400 °C. Also, temperatures > 400 °C give increased thermal decomposition of the AS salt, with an energy penalty that may not benefit Mg extraction.

<sup>18</sup> In cooperation with ÅA Geology / Mineralogy prof. O. Eklund and co-workers

<sup>19</sup> Therefore the higher temperature of the carbonation step in the ÅA route, ~500 °C, compared to the earlier suggested process route from the Albany Research Center (ARC), currently NETL Albany, in the US, results in a better LCA (life cycle assessment) performance of the ÅA route compared to the ARC route [46]. The ARC route is based on one-step carbonation in pressurised aqueous solutions at ~150 bar, ~185 °C [47,48].

Therefore for a case with  $X_E = 0.75$  and  $X_C = 0.75$  the heat input requirements for a Hitura serpentine-type material are  $4.32 < Q < 6.10$  MJ/kg CO<sub>2</sub>, and presumably closer to the higher value. Note that this is heat of  $\sim T = 450$  °C = 723 K.<sup>20</sup>

Table 5. Process energy input requirements (MJ/ kg CO<sub>2</sub>) for Hitura-type serpentine

Mg extraction efficiency	Mg(OH) <sub>2</sub> carbonation efficiency					
	25%	50%	75%	90%	95%	100%
25%	21.33	20.65	20.32	20.11	20.05	19.98
50%	10.66	9.99	9.65	9.45	9.38	9.31
75%	7.11	6.43	6.10	5.89	5.83	5.76
90%	5.92	5.25	4.91	4.71	4.64	4.57
95%	5.61	4.94	4.60	4.40	4.33	4.26
100%	5.33	4.66	4.32	4.12	4.05	3.98

The capture of CO<sub>2</sub> from flue gases that contain oxygen and other problematic species is more complicated than CO<sub>2</sub> (and H<sub>2</sub>S) stripping from natural gas, and is hard to accomplish against an energy penalty lower than 3 – 4 MJ/kg CO<sub>2</sub> captured [50]. This is one main reason why CO<sub>2</sub> mineralisation R&D increasingly focuses on avoiding CO<sub>2</sub> separation and would operate on the CO<sub>2</sub>-containing gas directly.

Energy input requirements for carbon storage by mineralisation would be of the same order as those for only the capture step of “conventional” CCS.<sup>21</sup> In that case a gas with Y%-vol CO<sub>2</sub> must be compressed to a total pressure of  $\sim 20 / (Y/100)$  bar, which is integrated with expansion of a carbonation product gas mixture (in which CO<sub>2</sub> is replaced by H<sub>2</sub>O) at the same  $20 / (Y/100)$  bar, at  $\sim 500$  °C, to atmospheric pressure.

Moreover, the mineralisation of CO<sub>2</sub> from a flue gas may be combined with sulphur capture: Mg(OH)<sub>2</sub> may also react with SO<sub>2</sub> (and SO<sub>3</sub>) present in the flue gas. See [31].

All existing mineralisation processes require significant amounts of energy (usually as heat) in order to achieve sufficient reaction kinetics and/or favourable thermodynamic conditions. Especially those processes, where large amounts of low quality heat are required, could benefit from access to sources of waste heat. Such sources may be low quality steam or flue gas from the very power plant the CO<sub>2</sub> would be extracted from.

In the relative vicinity of Pori (at  $\sim 60$  km to the south), the Olkiluoto nuclear power plant is located, which produces large amounts of waste heat. Presently this waste heat is rejected into the sea as 29500 kg/s of cooling water used to condense low quality steam at a temperature of around 200 °C, from each of the two reactors already in operation. The heat carried off with the cooling water amounts to approximately 1600 MW per reactor. A fraction of that waste heat would be enough to carbonate all the CO<sub>2</sub> emissions from the Meri-Pori power plant [51]. Unit 3 is under construction, for operation in 2014 to generate 2700 MW waste heat besides 1600 MW electricity.

The ÅA mineralisation process requires heat at above 400 °C. But even with a heat source of a lower than required temperature, significant savings could be achieved using a heat pump. This, of course, would require that the mineralisation could be performed close to the heat source.

<sup>20</sup> For surroundings temperature  $T^\circ = 15$  °C = 288 K this corresponds to exergy equal to  $Ex(Q) = (1-T/T^\circ) \cdot Q = 2.6 - 3.7$  MJ/kg. Using the exergy of heat allows for comparing it in calculations with power input requirement P, for which the exergy  $Ex(P) = P$ .

<sup>21</sup> An LCA study on this approach for CO<sub>2</sub> mineralisation applied to natural gas – fired electricity production in Singapore, using the ÅA route with serpentine rock purchased from Australia, and considering both CO<sub>2</sub> capture and operating with the flue gas directly was reported in 2011 [14].

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