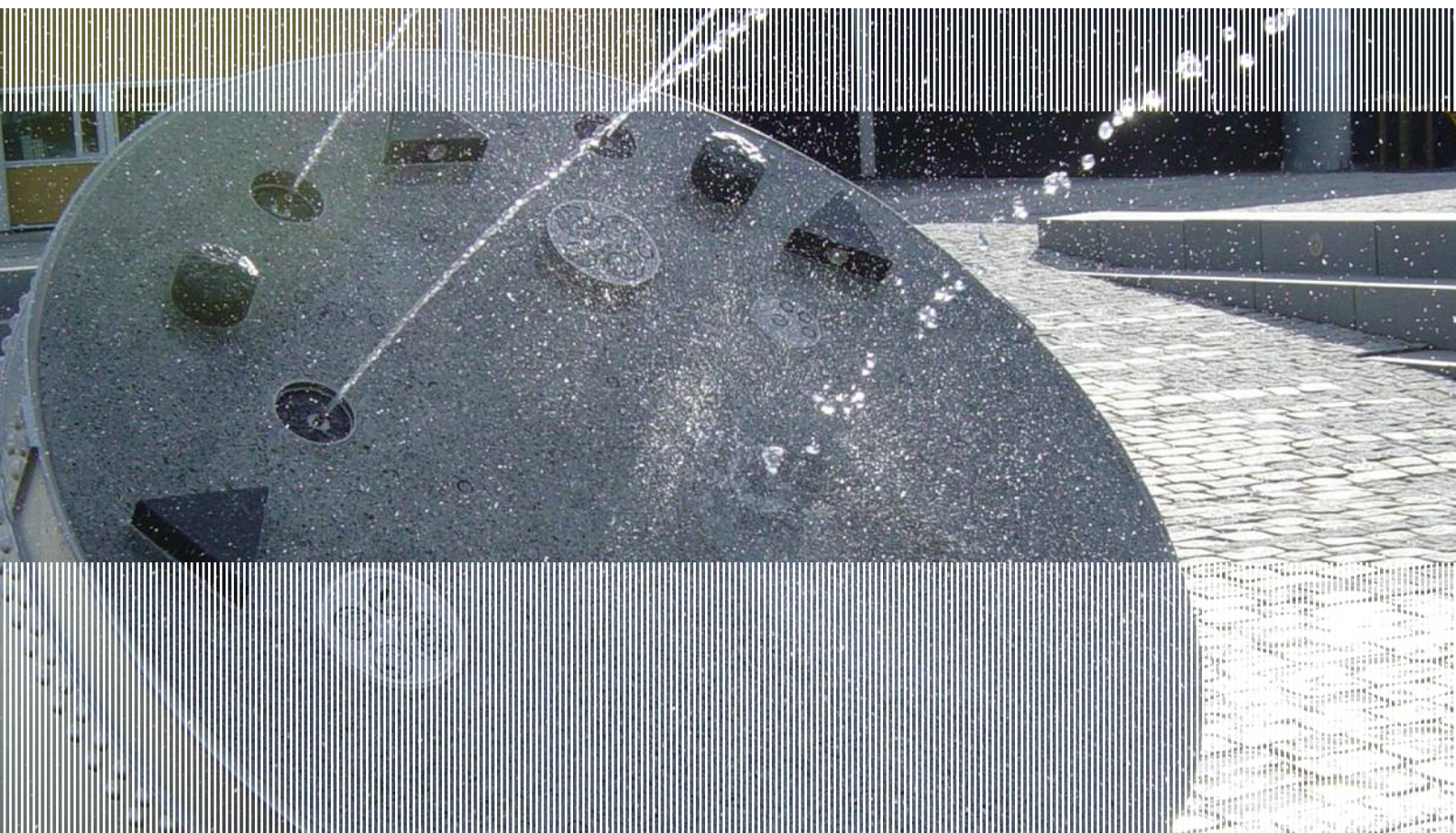


SINTEF Building and Infrastructure Harald Justnes

Pozzolana from minerals – State of the art

COIN Project report 16 - 2009



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COIN P1 Advanced cementing materials and admixtures

SP 1.4F Alternative pozzolans

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Preface

This study has been carried out within COIN - Concrete Innovation Centre - one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see www.coinweb.no

Tor Arne Hammer
Centre Manager

Summary

The objective of this state-of-the-art report (STAR) is to review work done to make pozzolana from natural occurring minerals by *chemical* treatment, and also outline principle possibilities of doing so. It does not include pozzolana by *thermal* treatment as for e.g. clays.

Based on the theory of acidity of oxides a general principle for preparing pozzolana from a mineral has been forwarded; *to present the basic oxide part of a "neutral" mineral for a more acidic chemical than its acidic oxide counterpart*. Thus, the present STAR has reviewed the possibility of making pozzolana for cement and concrete by treatment with weak and strong acids.

The most feasible minerals seem to be olivine and serpentine, both widely available in the Earths crust, and also with large deposits in Norway.

The more seldom mineral Anorthite, but with a good deposit in Norway, is deemed less suitable since the pozzolana produced by strong acid attack retain the shape of the original mineral, unlike Olivine that falls apart to a fine powder. Thus, the relatively coarse grain pozzolana from Anorthite will react chemically, but there will be no physical effect of improved particle packing as for conventional silica fume and possibly by pozzolana from Olivine. The pozzolana from Anorthite also contains fine pores that will suck water and reduce workability of concrete mixes containing it.

A new process is starting up for production of magnesium chloride in Porsgrunn, Norway, by SilMag Technology treating Olivine with hydrochloric acid. However, before the silica residue can be used as a pozzolana for reinforced concrete, the remaining chloride content must be reduced to an acceptable level.

However, Olivine can also react with the weak carbonic acid (CO_2 in water) and form a mixture of magnesium carbonate and silica. This will solve the potential problem of chloride contamination. It may not be necessary to separate the two components for concrete applications as magnesium carbonate could act as excellent filler and the silica as pozzolana.

An interesting aspect is to see the sequestering of CO_2 by Olivine in connection with the cement industry. A cement factory has a flue gas relatively rich in CO_2 (about 20 vol%). If olivine or serpentine is used to capture some of this, the resulting residue of magnesium carbonate and silica could be interground with clinker to form blended cement with a filler part (magnesium carbonate) and a pozzolana part (silica). Thus, it would enable a double principal CO_2 reduction from a cement plant. An alternative to make a blended cement (requires drying), is to deliver the resulting slurry to a ready mix concrete producer or a precast concrete element fabric.

It is recommended that COIN cooperates with the new CO_2 absorption laboratory to be built at SINTEF/NTNU to make a combined CO_2 sequestering and pozzolana/filler production.

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1 Introduction

1.1 Principal objectives and scope

The objective of this state-of-the-art report (STAR) is to review work done to make pozzolana from natural occurring minerals by *chemical* treatment, and also outline principle possibilities of doing so.

Thus, the STAR does not include pozzolana by *thermal* treatment as reviewed for e.g. clays by Østnor (2007).

This STAR is the one described in the COIN Project 1 CTR form 1.4f of 2009.

1.2 Theory of oxide acidity and mineral formation

Natural occurring minerals are most often oxides, and this STAR is limited to those. Oxides can be grouped into basic, amphoteric and acidic going from the left to the right in the periodic table. An example of a basic oxide is calcium oxide, CaO, which will spontaneously react with water to calcium hydroxide with high equilibrium pH (12.5);



An example of an acidic oxide can be sulphur trioxide, SO₃, which will react spontaneously with water to sulphuric acid of very low pH;



Most natural occurring minerals are more or less neutral combination of a basic and an acidic oxide. For instance by combining calcium oxide and sulphur trioxide, one will get gypsum;



Another acidic oxide that is not as obvious since it does not form a strong acid with water, is silicon dioxide (SiO₂). A combination of calcium oxide and silicon dioxide will give the natural occurring mineral Wollastonite;

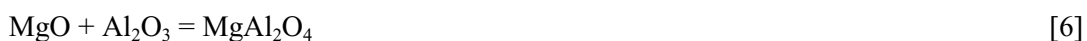


“Natural occurring” mineral usually means that it does not react with water, nor dissolve in it, within reasonable observable time (except for in extremely arid regions).

An amphoteric oxide is an oxide that is both acidic and basic and that can react with both bases and acid depending on their relative strength. The most relevant amphoteric oxide is aluminium oxide, Al₂O₃, that will behave as a base in reaction with acidic silicon dioxide and form natural occurring Mullite;



or behave as an acid in reaction with the more basic oxide magnesium oxide, MgO, to form natural occurring Spinel;



Pozzolana in the context of concrete technology is actually acidic oxides that will react with the excess basic calcium hydroxide formed during hydration of cement and form “neutral” hydrates. The speed of reaction depends on the specific surface of the pozzolana and whether it is crystalline or amorphous. A well known example is silica fume produced in ferro-silicon smelters as condensed gas. It is close to pure SiO₂ (85-95%), has high specific surface (typically 22 m²/g by BET) and it is amorphous. Thus, it is very reactive and form hydraulic binder in reaction with calcium hydroxide as recently reviewed by Justnes (2007). Justnes (1992) found the empirical formula to be



when related to dimeric silicate units. However, the polysilicate anion is actually a mix of dimers, pentamers and octamers with an average polysilicate unit length of maybe 3-4 depending on reaction conditions.

Generally speaking, only silicate, aluminate and aluminosilicates are relevant as pozzolana for concrete, since they will be reactive towards calcium hydroxide from cement hydration.

The preceding brings us to a general principle for preparing pozzolana from a mineral; *to present the basic oxide part of a “neutral” mineral for a more acidic chemical than its acidic oxide counterpart.*

The basic oxide may then dissolve or precipitate, but nevertheless it will usually be a residue of an acidic oxide, may be hydrolyzed, that will act as a pozzolana in concrete.

It is of course not only the “acidity” that determines whether the reaction will go or not, but the stability of the reaction products relative to the reactants, or in thermodynamically terms the Gibb’s free energy of the overall reaction.

2 Minerals suitable for chemical pozzolana production

2.1 Introduction

There may be a number of minerals suitable for chemical treatment to form pozzolana for concrete, but they are only of interest if they are sufficiently abundant to play a commercial role in concrete technology. This chapter is divided according to the mineral, not the chemical treatment.

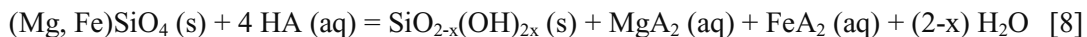
2.2 Olivine

2.2.1 General information

The mineral **Olivine** (when gem-quality also called **peridot**) is a magnesium iron silicate with the formula $(\text{Mg,Fe})_2\text{SiO}_4$. It is one of the most common minerals on Earth. The ratio of magnesium and iron varies between the two end members of the solid solution series: Forsterite (Mg-end member) and Fayalite (Fe-end member). Compositions of olivine are commonly expressed as molar percentages of Forsterite (Fo) and Fayalite (Fa) (e.g., $\text{Fo}_{70}\text{Fa}_{30}$). Forsterite has an unusually high melting temperature at atmospheric pressure, almost 1900°C, but the melting temperature of Fayalite is much lower (about 1200°C). The melting temperature varies smoothly between the two end members, as do other properties. Olivine incorporates only minor amounts of elements other than oxygen, silicon, magnesium, and iron. Manganese and nickel commonly are the additional elements present in highest concentrations. Olivine gives its name to the group of minerals with a related structure (the **olivine group**) which includes Tephroite (Mn_2SiO_4), Monticellite (CaMgSiO_4), and Kirschsteinite (CaFeSiO_4), which then could be candidates for analogues reactions, albeit less abundant than Olivine. However, Olivine seems to have excess basic oxide since it is weakly basic by nature.

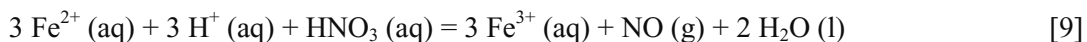
2.2.2 Reaction with strong acids

Olivine is an abundant mineral in Norway, and several deposits are mined in for various applications. Olivine has a pH of about 10, and can be decomposed into magnesium and ferrous salts along with finely divided silica by any acid as outlined in equation 8 according to Justnes and Østnor (2001) for olivine with assumed $\text{Mg/Fe} = 1/1$, but usually the Fe content is much lower than the magnesium content.



where A = the anion of monoprotic acid (e.g. Cl^- for hydrochloric acid or CH_3COO^- for acetic acid), (s) means solid, (aq) means dissolved in water and x is the degree of protonation of the resulting silica with $0 < x < 2$.

It should be noted that the only acid NOT recommended is nitric acid, HNO_3 , since the content of divalent iron may lead to formation of NO_x as exemplified in Eq. 9;



The process of producing silica from Olivine was already patented in 1979 by Gjelsvik and Torgersen suggesting hydrochloric acid (HCl) to be used to synthesise amorphous silica. HCl is probably the cheapest acid and available in large amounts as waste acid (e.g. paper pulp industry). In addition, the resulting magnesium chloride lye will probably be valuable as a raw material for magnesium metal production, after removal of iron by precipitation, for instance by adding magnesium hydroxide. This process would also eliminate the carbon dioxide generated from the production of magnesium chloride, by hydrochloric treatment of

Magnesite, MgCO_3 , or Dolomite, $\text{CaMg}(\text{CO}_3)_2$. Such an industrial use of olivine for magnesium chloride production would generate a large amount of finely divided silica. Although fine silica probably could be used as a catalyst carrier, concrete production is the only industry large enough to handle the vast possible amounts of silica produced according to Justnes and Østnor (2001).

Justnes and Østnor (2001) used fine waste olivine after nickel recovery from the mining industry “Nikkel og Olivin” in Ballangen, Norway (the mine is now closed, but a lot of fine waste olivine is still available in the area). They produced silica synthesised from olivine (denoted OS) by dispersing finely divided olivine in water, adding hydrochloric acid to decompose the olivine followed by settling, decanting and washing repeatedly. Three batches were made during this initial study (i.e. not optimized reaction conditions) as follows:

The first batch (OS1) was initially made by dispersing 100 g olivine residue in 150 ml water, adding 250 ml 37% HCl (excess hydrochloric acid) and stirring for 24 hours at 20°C. The solution was decanted and 200 ml, 6 M HCl added. The solution was heated to 50°C for 2 hours, allowed to settle, decanted and excess water was added before it was left to settle for 72 hours. It was further washed 3 times before filtering. Finally, the OS was dried at 105°C to remove adsorbed water.

The second (OS2) and third (OS3) batches were made by dispersing 200 g olivine residue in 300 ml water, adding 500 ml 37% HCl (excess hydrochloric acid) and stirring for 4 hours, at 70°C. The slurry was allowed to settle, decanted and washed with excess water four times before filtering. The amount processed was about 37 g of amorphous silica or about 18 % of the olivine processed. The low yield might be caused by too high acid dosage which might have dissolved part of the silica. The specific surfaces of OS2 and OS3 according to BET were 101 and 115 m^2/g , respectively, after drying at 105°C. In an attempt to reduce the specific surface, 100 g of batch OS3 was dried for 4 hours at 400°C (denoted OS3D) and allowed to cool to the next day. The weight loss was about 2 % and the specific surface reduced to 90 m^2/g indicating that some protonated silica had condensed;



Silica fume (denoted E8) was obtained from a Norwegian ferrosilicon plant and used as reference for the pozzolanic activity test by Justnes and Østnor (2001). The composition was 93.0 % SiO_2 , 2.1 % Fe_2O_3 , 1.2 % MgO , 1.0 % CaO , 1.0 % C , 0.56 % K_2O , 0.42 % SO_3 , 0.30 % Na_2O , 0.29 % Al_2O_3 and 0.11 % H_2O . The BET specific surface area was 22 m^2/g .

The recipes and flow values for the mortars tested by Justnes and Østnor (2001) are reproduced in Table 1 and the flexural and compressive strength after 2 and 28 days are listed in Table 2. The concept of equal flow was used and adjusted by a naphthalene sulphonate- formaldehyde condensate based super-plasticizer (SP).

Table 1 Recipes of mortars with different amorphous silica types (Justnes and Østnor, 2001).

Silica type	None	E8	OS2	OS3D
Recipe (g):				
Cement	450.0	418.5	418.5	418.5
Silica	-	31.5	31.5	31.5
Water	225.0	225.0	225.0	225.0
SP	-	2.8	9.7	6.8
Sand (RC)	1,350.0	1,350.0	1,350.0	1,350.0
Flow (mm)	175	174	180	175

Table 2 Flexural (f) and compressive (c) strength (MPa) of cement mortars with different types of silica (\pm standard deviations) after Justnes and Østnor (2001).

Curing	None		E8		OS2		OS3D	
	f	c	f	c	f	c	f	c
2 days	5.6 ± 0.2	31.5 ± 0.6	6.4 ± 0.4	36.3 ± 1.0	5.8 ± 0.1	35.9 ± 0.2	5.6 ± 0.3	32.9 ± 0.2
28 days	8.3 ± 0.3	55.8 ± 1.0	9.5 ± 0.5	67.4 ± 1.7	8.6 ± 0.6	67.7 ± 0.5	9.4 ± 0.4	68.2 ± 0.5

Justnes and Østnor (2001) also made a pozzolanic activity test based on calcium hydroxide consumption: Lime and silica mixtures with molar Ca/Si ratio of 1.2 were made by using artificial pore water (i.e. pH = 13.5 and molar KOH/NaOH = 2) as mixing water. The recipes of the three mixes are given in Table 3. All lime-silica mixes were sealed cured at 20°C in small glasses. At the time periods of 1, 4, 7, 28 and 180 days, the curing of a sample was stopped by grinding and dispersion in excess ethanol. This was followed by filtering and drying at 105°C. The dried powders were all subjected to thermal analysis by DTA/TG to determine the consumed amount of calcium hydroxide by the pozzolanic reaction. The results are replotted in Fig. 1.

Table 3: Recipes used for the pozzolanic activity tests

Silica type	OS1	E8	OS3D
Silica (g)	8.6	20	10
Ca(OH) ₂ (g)	12.9	30	15
Pore water (g)	25	45	50
water/solid-ratio	1.2	0.90	2.0
molar Ca/Si-ratio	1.2	1.2	1.2

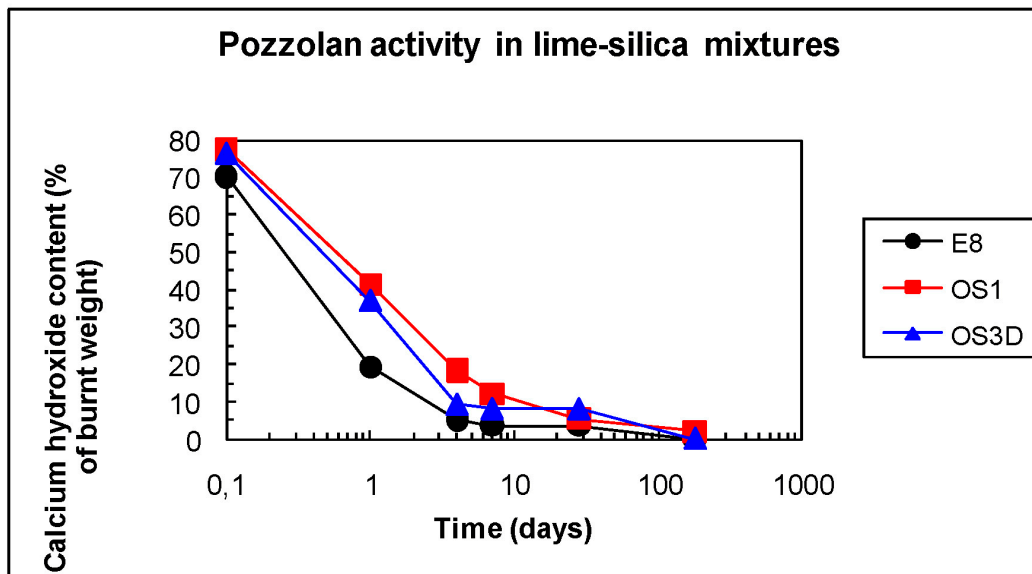


Fig. 1 Calcium hydroxide content decline as function of time in lime - silica mixtures as determined by DTA/TG.

Justnes and Østnor (2001) concluded that:

1. It is possible to obtain amorphous, off-white, free flowing silica with a typical specific surface of 100 m²/g by decomposing the basic mineral olivine, (Mg, Fe)SiO₄, with an acid and separating the silica from the lye by filtering or decanting.
2. Amorphous silica from olivine has a pozzolanic activity comparable to silica fume starting at 4 days and continuing afterwards.
3. The compressive strength improvement at 2 and 28 days when ordinary Portland cement is replaced with silica is comparable for silica obtained from Olivine and ordinary silica fume from ferro-silicon manufacturer.

The above process is now intended to be used by the company SilMag Technology (www.Silmagtechnology.com), a 50/50 joint venture of Hydro and AMG (Advanced Metallurgy Group). The plan is to make a factory at Herøya, Porsgrunn, Norway, with an annual production capacity of 30,000 ton both of magnesium chloride and silica. The magnesium chloride is intended used in magnesium metal production, while the primary intended use of silica is replacement of active carbon as filler in car tyres according to the magazine “Prosessindustrien” (eng. The Process Industry). The potential use of the silica as pozzolana in concrete is not mentioned, but one of the challenges for such an application is of course to make it sufficiently low in chlorides for application in reinforced concrete. A pilot plant producing about 1 ton silica per week is expected to be working from autumn 2009, while the decision to actually make a full scale factory is likely to be made late 2010 (potential contact; Manager Per Bjørn Engseth at per.bjorn.engseth@hydro.com).

2.2.3 Reaction with weak acids

Olivine can be made reactive with weak acids, in particular if the resulting magnesium salt of the acid is stable (one indication is if the magnesium salt precipitates). One example of an important weak acidic oxide is CO₂, which partly will form carbonic acid when dissolved in water;



A worldwide search is on for cheap processes to sequester CO₂ by mineral reactions. Removal of CO₂ by reactions with olivine is an attractive option, because it is widely available and reacts easily with the (acid) CO₂ from the atmosphere. When olivine is crushed, it weathers completely within a few years, depending on the grain size (Schuiling, R.D. and Krijgsman, P., 2006). All the CO₂ that is produced by burning 1 liter of oil can be sequestered by less than 1 liter of olivine. The reaction is exothermic but slow. In order to recover the heat produced by the reaction to produce electricity, a large volume of olivine must be thermally well isolated. Then it can produce power, while at the same time removing CO₂. The end-products of the reaction are silicon dioxide, magnesium carbonate and small amounts of iron oxide (Goldberg et al, 2001).

However, the objective of this STAR is to produce a pozzolan and not to generally sequester CO₂, so it has to be done in a closed process rather than spread crushed Olivine on the fields etc.

For example, research at the Albany Research Center (O’Connor, 1998, O’Connor et al, 2000) has focused upon the direct carbonation of olivine. When the program first started, it took 24 hours to reach 40-50% carbonation of olivine. The reaction required temperatures of 150-250°C, pressures of 85-125 bar, and mineral particles in the 75-100 micron size range. Careful control of solution chemistry yielded olivine conversions of 90% in 24 hrs and 83% within 6 hours. The most recent results show that further modifications of the same basic reaction can achieve 65% conversion in 1 hour and 83% conversion in 3 hours.

Note that magnesium carbonate is very stable and sparingly soluble (might help the reaction to proceed) with a solubility of 0.6 g/litre (7 mM). Thus, the reaction product will probably be an intimate mixture of magnesium carbonate and amorphous silicate or protonated silica. However, it may not be necessary to separate the two components for concrete applications as magnesium carbonate could act as excellent filler. A picture from a presentation by O'Connor et al (2001) is reproduced in Fig. 2 showing indeed very small particles of free magnesium carbonate (about 5µm) and silica (about 3 µm). The chemical compositions in the analysis points marked 1-4 in Fig. 2 are listed in Table 4.

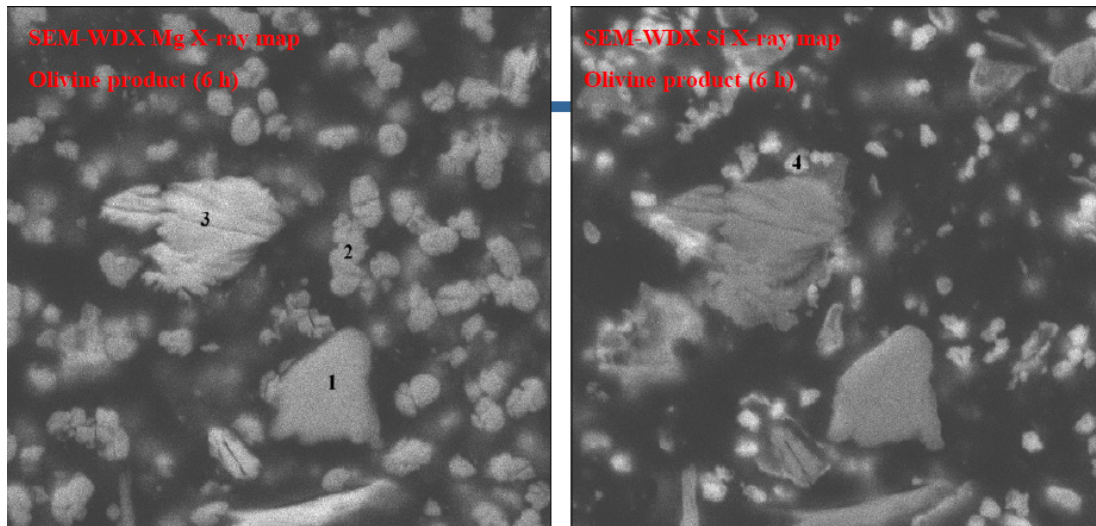


Fig. 2 Magnesium (left) and silicon (right) x-ray mapping of olivine treated with CO₂ for 6 h in aqueous suspensions (O'Connor et al, 2001)

Table 4 Chemical element compositions (atomic %) of particles numbered 1-4 in Fig. 2

Point	C	Mg	Si	Mg/Si
1	3	20	13	1.5
2	26	17	1	17
3	3	25	12	2.1
4	6	1	26	0.04

The reason why Olivine apparently falls so easily apart under influence of acid (unlike Anorthite in section 2.4.2 that retains its shape) might be that it is a nesosilicate with individual SiO₄⁴⁻ tetrahedra so there is no Si-O-Si bonds to be broken in a three dimensional silica network. The crystal structure of Olivine is shown in Fig. 3.

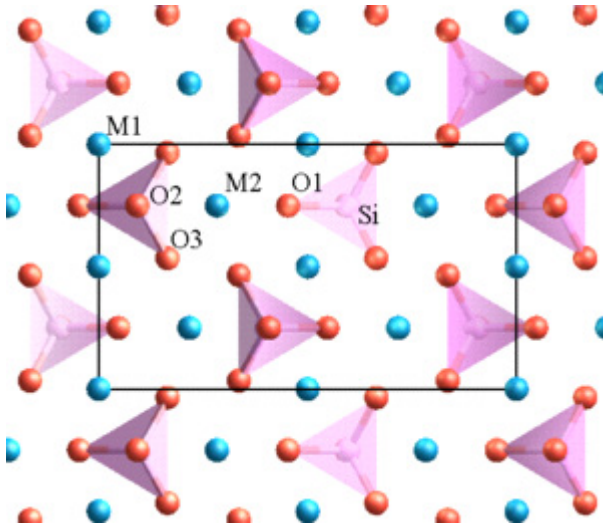


Fig. 4 The crystal structure of Olivine where silicon (pink) and oxygen (red) is bound in individual SiO_4^{4-} tetrahedra and the charge balanced by divalent metal ions (blue) of magnesium or iron. The black frame indicates the unit cell with a view along the a -axis.

2.3 Serpentine

2.3.1 General information

The **serpentine group** describes a group of common rock-forming hydrous magnesium iron phyllosilicate $(\text{Mg, Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ minerals; they may contain minor amounts of other elements including chromium, manganese, cobalt and nickel. In mineralogy and gemmology, serpentine may refer to any of 20 varieties belonging to the serpentine group. Owing to blends, these varieties are not always easy to individualize, and distinctions are not usually made. There are three important mineral polymorphs of serpentine: Antigorite, Chrysotile and Lizardite.

Most serpentines are opaque to translucent, light (specific gravity between 2.2–2.9), soft (hardness 2.5–4), infusible and *susceptible to acids*. All are microcrystalline and massive in habit, never being found as single crystals. Lustre may be vitreous, greasy or silky. Colours range from white to grey, yellow to green, and brown to black, and are often splotchy or veined. Many are intergrown with other minerals, such as calcite and dolomite. Occurrence is worldwide; New Caledonia, Canada (Quebec), USA (northern California), Afghanistan, Cornwall, China, Asia, France, *Norway* and Italy are notable localities.

Rock composed primarily of these minerals is called serpentinite. Serpentines find use in industry for a number of purposes, such as railway ballasts, building materials, and the asbestiform types find use as thermal and electrical insulation (Chrysotile asbestos). Note that the asbestos content can be released to the air when serpentine is excavated, or if it is used as a road surface, forming a long term health hazard by breathing. Asbestos from serpentine can also appear at low levels in water supplies through normal weathering processes, but there is as yet no identified health hazard associated with use or ingestion. In its natural state, some forms of serpentine react with carbon dioxide and release oxygen into the atmosphere.

2.3.2 Reaction with strong acids

In the process development area, the team at Albany Research Center (ARC) has completed a feasibility study of a process originally proposed by Los Alamos National Laboratory (Lackner et al, 1995, Butt et al, 1997). This process uses HCl solution reacting with

serpentine to produce $\text{Mg}(\text{OH})_2$ which is subsequently used to sequester CO_2 . Although the study found the process energy intensive and inappropriate for CO_2 sequestration, the analyses of individual steps were useful for developing new processes. Los Alamos National Laboratory is currently pursuing reaction mechanisms that may allow elimination of the heat treatment step for serpentine.

2.3.3 Reaction with weak acids

There is approximately an order of magnitude more serpentine than olivine available. Consequently, finding a way to use serpentine to scrub CO_2 will have greater practical impact than using olivine. Both minerals are valuable feedstocks and progress has been made in direct carbonation using serpentine. Tests conducted at Los Alamos National Laboratory achieved initially only 25% conversion using CO_2 on 100 μm serpentine particles, even at a very high pressure of 340 bars. Independently, researchers at ARC developed a successful carbonation process for serpentine that utilized mineral heat pretreatment and carbonation in aqueous carbonic acid solution. A literature review indicated that weak carbonic acid treatments had also been suggested for Mg extraction (Drăgulescu et al, 1972). Carbonation tests performed at ARC employing heat pretreated serpentine have resulted in up to 83 % conversion in 30 minutes at 115 bars (O'Connor et al, 2000).

The high pressure requirement of *direct carbonation* reaction will lead to high process costs. The ACR team therefore modified the solution chemistry to allow the reaction to proceed at a lower pressure and temperature. The research is guided by the idea that the concentration of HCO_3^- in the solution is critical to the reaction rate. The high CO_2 pressure will lead to increased CO_2 absorption in the solution and thus enhanced HCO_3^- concentration. Adding bicarbonate such as sodium bicarbonate in the solution will significantly increase the HCO_3^- concentration even at a relatively low CO_2 pressure. Indeed, by increasing the sodium bicarbonate concentration, the carbonation reaction of serpentine can reach 62% completion under 50 bars (Goldman et al, 2001). However, even small magnesium carbonate particles (about 2 μm) is obtained as shown in Fig. 5 (O'Connor et al., 2001), small silica particles seems fewer and far between as compared to olivine in Fig. 3.

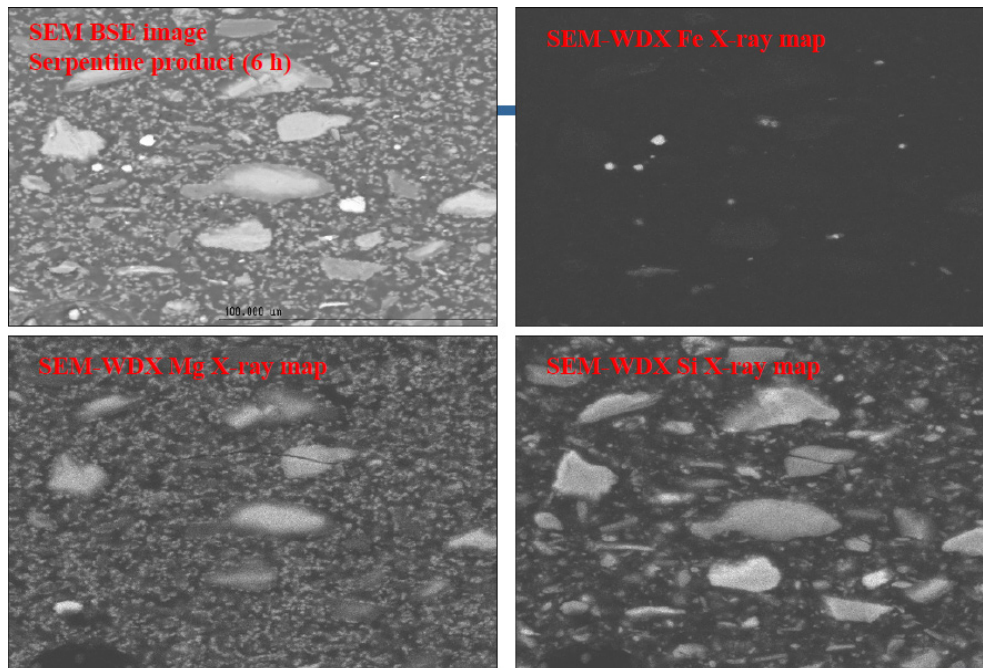


Fig. 5 Backscattered electron image (upper left) and X-ray mapping of iron (upper right), magnesium (lower left) and silicon (lower right) of serpentine treated with CO_2 for 6 h in aqueous suspensions (O'Connor et al, 2001)

The reason for perhaps more difficult breakdown of the silica part of Serpentine than for Olivine, is that Serpentine is a phyllosilicate with parallel sheets of silica tetrahedra of composition $\text{Si/O} = 2/5$.

2.4 Anorthite

2.4.1 General information

There is a general word confusion between Anorthosite and Anorthite, particularly in the technological press, so to sort this out;

2.4.1.1 *Anorthosite*

Anorthosite is a phaneritic, intrusive igneous rock characterized by a predominance of plagioclase feldspar (90–100%), and a minimal mafic component (0–10%). Pyroxene, ilmenite, magnetite, and olivine are the mafic minerals most commonly present.

Anorthosite can be divided into two types: Proterozoic Anorthosite (also known as massif or massif-type anorthosite) and Archean Anorthosite. These two types of Anorthosite have different modes of occurrence, appear to be restricted to different periods in Earth's history, and are thought to have had different origins.

Since they are primarily composed of plagioclase feldspar, most of Proterozoic Anorthosites appear, in outcrop, to be grey or bluish. Individual plagioclase crystals may be black, white, blue, or grey, and may exhibit an iridescence known as labradorescence on fresh surfaces. The feldspar variety Labradorite is commonly present in Anorthosites. Mineralogically, Labradorite is a compositional term for any calcium-rich plagioclase feldspar containing between 50–70 molecular percent Anorthite (An 50–70), regardless of whether it shows labradorescence or not. The mafic mineral in Proterozoic Anorthosite may be Clinopyroxene, Orthopyroxene, Olivine, or, more rarely, Amphibole. Oxides, such as Magnetite or Ilmenite, are also common. Most Anorthosite plutons are very coarse grained; that is, the individual plagioclase crystals and the accompanying mafic mineral are more than a few centimeters long. Less commonly, plagioclase crystals are megacrystic, or larger than one meter long. However, most Proterozoic Anorthosites are deformed, and such large plagioclase crystals have recrystallized to form smaller crystals, leaving only the outline of the larger crystals behind.

Smaller amounts of Anorthosite were emplaced during the Archean eon (ca 3,800-2,400 Ma), although most have been dated between 3,200 and 2,800 Ma. They are distinct texturally and mineralogically from Proterozoic Anorthosite bodies. Their most characteristic feature is the presence of equant megacrysts of plagioclase surrounded by a fine-grained mafic groundmass.

The composition of plagioclase feldspar in Proterozoic Anorthosites is most commonly between An_{40} and An_{60} (40-60% anorthite). This compositional range is intermediate, and is one of the characteristics which distinguish Proterozoic Anorthosites from Archean anorthosites. Mafic minerals in Proterozoic Anorthosites have a wide range of composition, but are not generally highly magnesian.

The primary economic value of Anorthosite bodies is the titanium-bearing oxide Ilmenite. However, some Proterozoic Anorthosite bodies have large amounts of Labradorite, which is quarried for its value as both a gemstone and a building material. Archean Anorthosites, because they are calcium-rich, have large amounts of aluminum substituting for silicon; a few of these bodies are mined as ores of aluminum.

2.4.1.2 Anorthite

Anorthite is a compositional variety of plagioclase feldspar. Plagioclase is an abundant mineral in the Earth's crust. The formula of pure Anorthite is $\text{CaAl}_2\text{Si}_2\text{O}_8$. Anorthite is the calcium-rich end member of plagioclase solid solution series, the other end member being Albite, $\text{NaAlSi}_3\text{O}_8$. Anorthite also refers to plagioclase compositions with > 90 molecular percent of the anorthite end member. Anorthite is a rare compositional variety of plagioclase occurring in mafic igneous rocks. It also occurs in granulite facies metamorphic rocks, in metamorphosed carbonate rocks and corundum deposits. Its type localities are Monte Somma and Valle di Fassa, Italy, but there is a huge pure deposit at Gudvangen, Norway.

2.4.2 Reaction with strong acids

Jahren and Lindbak (1998) reviewed most of the work done at SINTEF and NGU (Norwegian Geological Survey) on a pozzolan (traded marketed under the name "Sican") produced by treatment of Anorthite from Gudvangen with hydrochloric acid to form a flocculant for sludge treatment rich in aluminum chloride and a silica residue. In Norway, the rock is found in one location, as a massive homogenous rock in an area of some square kilometres (several hundred million ton deposit), close to an ice free fjord that ease transportation. Its chemical composition is 50.2% SiO_2 , 31.7% Al_2O_3 , 15.3% CaO , 2.6% Na_2O , 0.7% Fe_2O_3 and 0.2% MgO . There are also large deposits of Anorthite in Canada.

Jahren and Lindbak (1998) summarized properties of the pozzolan from anorthite as follows: The pozzolan had the same grain size as the original rock grain before processing. The pozzolan should be ground before being used in concrete or cement as the chosen grain size will influence the properties of the final product. The particles consisted of 80-90% amorphous SiO_2 depending on the time in the leaching reactor. Unreacted mineral might occur in the centre of some of the larger grains. After leaching the metals, the SiO_2 was left with an unstable, amorphous structure with minute channels in the particles. Even in the coarse particles, the total surface area was considerable, typically with a specific surface area of $57\text{m}^2/\text{g}$ according to N_2 adsorption (BET) where more than 2/3 of the pores were less than 4 nm in diameter (porosity 9.7 vol%). Bulk density of non-ground pozzolana was $1,620\text{ kg/m}^3$, which was reduced to about 600 kg/m^3 upon grinding. The original pozzolana before grinding was very white, but upon grinding in a roller mill the iron balls might reduce the whiteness. However, whiteness can be improved by magnetic separation; typically a whiteness of 80-82% after grinding can be improved to 91-94% after magnetic separation. Some results for mortar testing with 10% pozzolana are given in Table 5.

The reason why Anorthite retains its original grain size after acid leaching, as indicated in Fig. 6, is that it is a tectosilicate, meaning that it is a "framework silicate" where silicon and aluminium tetrahedra are bridged to neighbouring tetrahedra via oxygen in three dimensions. Thus, these bridging bonds have to be broken for the structure to collapse. Such bond are more easily broken by strong bases rather than by acids.

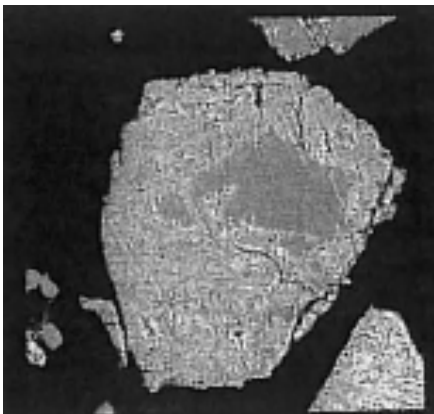


Fig. 6 A scanning electron image of a pozzolana particle derived from Anorthite showing the original grain with an area of non-leached mineral appearing more grey than the rest (Jahren and Linbak, 1998)

Table 5 Mortar tests where 10% cement was replaced by pozzolana from Anorthite (Jahren and Lindbak, 1998)

<u>Recipe (parts):</u>		
Cement	1.00	0.90
Pozzolana	0.00	0.10
Water	0.45	0.45
RC-sand (DIN 1164)	3.00	3.00
Super-plasticizer (Mighty 150)	0.0036	0.0058
Slump (mm)	35	25
Max hydration heat (°C)	43.5	39.5
at time after water addition (h)	11.15	11.30
<u>Flexural strength (MPa) after</u>		
1 day	4.6	3.3
7 days	7.5	7.4
28 days	8.7	9.7
<u>Compressive strength (MPa) after</u>		
1 day	23.1	16.0
7 days	47.6	50.3
28 days	67.6	76.0

The lower slump in spite of higher super-plasticizer dosage for the 10% cement replacement with pozzolana from Anorthite seen in Table 4 might be due to the porous grains with fine pores sucking water from the mix. The pozzolana grains are probably too coarse to make a stable slurry as silica fume, but the problem may be omitted by saturating the grains with water first. In this way they may even serve as internal curing agents after cement setting.

The Norwegian cement producer Norcem made internal trial testing of making a blended cement in 1992 by intergrinding 10% replacement of their high strength clinker at that time by the pozzolana from Anorthite. The composition per m³ concrete was 415 kg cement, 186 kg water (w/c = 0.448), 796 kg 0-8 mm sand, 669 kg 8-11 mm gravel and 344 kg 11-16 mm gravel. The compressive strengths after 1, 2, 7 and 28 days were 25.1, 38.1, 52.5 and 69.8 MPa, respectively, for the pure cement and 21.4, 33.9, 57.9 and 80.0 MPa, respectively, for the cement with 10% interground pozzolana.

It is important to note that even though the pozzolana from Anorthite has reactivity comparable to silica fume (i.e. chemical effect), its grain size makes the particle packing less optimal compared to silica fume, and the permeability is thus not as much reduced. However, this does not apply to the pozzolana made from Olivine as this mineral is totally disintegrated and the particles does not retain the original grain shape as the mineral after leaching with strong acid.

2.4.3 Reaction with weak acids

Nordic Mining AS (www.nordicmining.com, or contact post@nordicmining.com) has made a cooperation agreement with the Norwegian oil company Statoil in using Anorthosite from Gudvangen as a mean to sequester CO₂ and at the same time produce calcium carbonate, alumina and silica according to the technical magazine "Prosessindustrien". Trial tests are carried out at the Norwegian research institution IFE (Institute for Energy technology), who also have tested sequestering of CO₂ by the minerals Olivine and Eclogite.

According to "Prosessindustrien", 2.5 million ton Anorthite can consume 275,000 ton CO₂ to form 750,000 ton alumina, 600,000 ton calcium carbonate and 1.5 million ton silica. The

deposit of pure Anorthosite at Gudvangen is estimated to 500 million ton, while mining 3-5 million ton annually is realistic. The economy in this project depends on the quota price of CO₂ that lately has plunged due to the recent global financial crisis.

Another process plant sequestering CO₂ is planned in Kaustinen, mid-Finland, by the company Keliber Oy (part of Nordic Mining). This process will in addition result in valuable products such as lithium carbonate and Tantalum (Ta), and is planned to start in 2011 after an investment of 300-400 MNOK.

3 Further research

An interesting aspect is to see the sequestering of CO₂ by minerals in connection with the cement industry. A cement factory has a flue gas relatively rich in CO₂ (about 20 vol%). If olivine or serpentine is used to capture some of this, the resulting residue of magnesium carbonate and silica could be interground with clinker to blended cement with a filler part (magnesium carbonate) and a pozzolana part (silica). Thus, it would enable a double principal CO₂ reduction from a cement plant. An alternative to make a blended cement (requires drying), is to deliver the resulting slurry to a ready mix concrete producer or a precast concrete element fabric.

Another interesting aspect is that recently ESFRI (European Strategy Forum on Research Infrastructure) has decided that SINTEF/NTNU should coordinate the building of 15 European labs for CO₂-handling research for 81 M€ in Norway, Germany, France, Switzerland, Netherlands, Hungary, Poland, Croatia and Denmark in accordance with their application with the acronym ECCSEL.

5 of the labs for 23 M€ will be built and placed at SINTEF/NTNU in Trondheim and are planned to run from 2010-2020;

1. Lab for absorption of CO₂ (removal of CO₂ from exhaust gases by chemicals) for 8 M€
2. Material and process technology lab for 4 M€
3. Combustion technology lab for 4 M€
4. CO₂ storage technology lab for 4 M€
5. Lab for CO₂ removal from gas mixes by freezing for 3 M€

The labs will be available for researches from the whole EU/EEC. The consortium has to raise some of the money from their local authorities or through the EU framework program, so the construction is not final before this is done. More information can be found at the homepage www.ntnu.no/eccsel.

Contact at SINTEF is Nils A. Røkke at nils.a.rokke@sintef.no.

Thus, it is suggested that COIN seek cooperation with laboratory 1 in the above list to make a pozzolana from Olivine or Serpentine. They get a material for CO₂ sequestering and COIN get a new pozzolana for testing in blended cement or concrete.

Due to the chloride problem with hydrochloric acid treatment as in the SilMag process, CO₂ sequestering seems like a better option to pursuit.

4 Conclusions

The present state of the art report has reviewed the possibility of making pozzolana for cement and concrete by treatment with weak and strong acids.

The most feasible minerals seem to be olivine and serpentine, both widely available in the Earths crust, and also with large deposits in Norway.

The more seldom mineral Anorthosite, but with a good deposit in Norway, is deemed less suitable since the pozzolana produced by strong acid attack retain the shape of the original mineral, unlike Olivine that falls apart to a fine powder. Thus, the relatively coarse grain pozzolana from Anorthite will react chemically, but there will be no physical effect of improved particle packing as for conventional silica fume and possibly by pozzolana from Olivine. The pozzolana from Anorthite also contains fine pores that will suck water and reduce workability of concrete mixes containing it.

A new process is starting up for production of magnesium chloride in Porsgrunn, Norway, by SilMag Technology treating Olivine with hydrochloric acid. However, before the silica residue can be used as a pozzolana for reinforced concrete, the remaining chloride content must be reduced to an acceptable level.

However, Olivine can also react with the weak carbonic acid (CO_2 in water) and form a mixture of magnesium carbonate and silica. This will solve the potential problem of chloride contamination. It may not be necessary to separate the two components for concrete applications as magnesium carbonate could act as excellent filler and the silica as pozzolana.

An interesting aspect is to see the sequestering of CO_2 by Olivine in connection with the cement industry. A cement factory has a flue gas relatively rich in CO_2 (about 20 vol%). If olivine or serpentine is used to capture some of this, the resulting residue of magnesium carbonate and silica could be interground with clinker to form blended cement with a filler part (magnesium carbonate) and a pozzolana part (silica). Thus, it would enable a double principal CO_2 reduction from a cement plant. An alternative to make a blended cement (requires drying), is to deliver the resulting slurry to a ready mix concrete producer or a precast concrete element fabric.

It is recommended that COIN cooperates with the new CO_2 absorption laboratory to be built at SINTEF/NTNU to make a combined CO_2 sequestering and pozzolana/filler production.

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