

Separation of reaction products from ex-situ mineral carbonation and utilization as a substitute in cement, paper, and rubber applications

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ABSTRACT

Ex-situ mineral carbonation, a CCU process, is one possible approach for the decarbonisation of emission-intensive industry with hard-to-abate process emissions like the cement industry. The chemical reaction ensures long-term binding of carbon dioxide in minerals with the effect of storing otherwise emitted CO₂ long term. As a major hurdle for CCU processes is often their economic viability, to create incentives for the usage of this process, these carbonated mineral products must become marketable. A separation approach for the reaction products of this process and possible utilization paths are presented. The separation results in three different fractions, each enriched in either the reaction products amorphous silica or magnesium/calcium silicate or unreacted peridotite. The fractions enriched with reaction products are tested as supplementary cementitious material in cement or as a filler in rubber and paper. The application tests show promising results, comparable or even better than the conventional product. Additionally, based on the laboratory explorations, we present initial economic and environmental investigations showing potential carbon footprint reductions of up to 27% for blended cement with a total global reduction potential of 681 Mt_{CO_{2e}}/a. Also, potential carbon footprint reductions of 52% can be achieved by using carbonation products as fillers in rubber and 197% in paper, respectively. While the costs for the utilization of carbonated minerals have been calculated to be higher than for the conventional products, CO₂ emission certificates could ensure the same price for cement and even lower costs for the substitution of fillers in paper and rubber.

1. Introduction

The greenhouse gas emissions of the energy-intensive industry, especially the cement and steel industry and the increasing amount of CO₂ in the atmosphere lead to negative effects of global warming in the environment. To achieve the targets of the Paris agreement [1], by means of keeping the global average temperature increase below 2 K above pre-industrial levels, it is no longer sufficient to reduce the carbon dioxide emissions, but negative emissions must be generated. This results in the necessity to find certain pathways to reduce the emissions or to store the CO₂ of the process inherent emissions of the energy-intensive industry in particular. Possible approaches are carbon

capture and storage (CCS) with already some plants operating on a large scale [2] and carbon capture and utilization (CCU) where huge efforts are undertaken globally in research [3,4]. An important additional step in comparison to CCS is the utilization of the carbonated products making it theoretically possible to obtain negative emissions by substituting conventional products. One approach of CCU is the mineral sequestration of carbon dioxide, a chemical process in which CO₂ reacts with alkaline earth metal oxides by forming carbonates [5,6]. Due to the availability as feed material, magnesium and calcium silicates are commonly used for the process, which can be chemically described by formula 1, where Me represents magnesium (Mg) or calcium (Ca) [7,8]:

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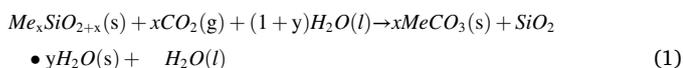
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This carbonation reaction in an aqueous solution generates carbonates with the bound carbon dioxide as well as hydrated amorphous silica. To enhance the reaction degree of this naturally occurring reaction, the kinetics, pressure and temperature are adapted and specific chemicals are added as catalysts. [9–11].

Previous research over the last 20 years mainly aimed at achieving maximum carbonation degree by investigating the manifold sub-processes on a laboratory scale and using the carbonated material as a pozzolanic cement substitute [3,12–19]. While substantial economic potential for using carbonated materials have been reported for multiple fields on application (e.g., supplementary cementitious materials, fillers for paper as well as rubber industry, or as pigments) [20–22], experimental work on separation and application of these products remain scarce. To this end, based on our initial work on separating carbonation products [23], we describe a demonstration-scale direct aqueous carbonation process (i.e., batch process in 1000 L autoclave with a capacity of up to 0.6 $t_{\text{mineral,carbonated/day}}$ – approximately 1/1000 of fullscale operation), to enable the establishment of a future continuous process. Here the reaction products, which are present in the particle size range of a few micrometers, are separated from each other and the unreacted initial material to obtain better product properties and to improve the subsequent use. We evaluate the separated products regarding their utilization potential as cement replacement and as a filler in paper and rubber production. Additionally, we here investigate the costs and carbon footprint of a potential large-scale process and compare them to conventional products which we aim to substitute (i.e.,

cement, filler in paper and rubber).

2. Materials and methods

2.1. Overview of experimental setup of the demonstration-scale process

The demonstration-scale process (see Fig. 1) investigated is a direct aqueous carbonation process operated as a batch process. The process consists of the three main process units: carbonation, separation, and application, with different sub-process units like the pre-treatment of the feed material for the carbonation using milling, classification, and post-treatment. Post-treatment is mainly the filtration of the carbonation slurry with a filter press and the characterization of the obtained solids by various analytical methods, followed by deagglomeration by attrition. The fine particle size fractions of the separated solids are used for application tests and the coarse fraction, the unreacted solids are fed back into the carbonation process with a bypass to get unreactive material out of the system.

2.2. Feed material and parameters for carbonation

Two different feed materials are carbonated in the 1000 L autoclave, one primary (i.e., peridotite) and one secondary raw material (i.e., slag from ferrochrome production). The peridotite (commonly named olivine due to its main component) is an ultramafic rock, which is rich in reactive magnesium silicate. The peridotite selected for the carbonation originates from Norway, the largest producer of olivine-bearing rocks with around one-third of the annual global production of 7800 to 9000 ktpa [24]. The peridotite consists mainly (~80%) of forsterite (Mg_2SiO_4)

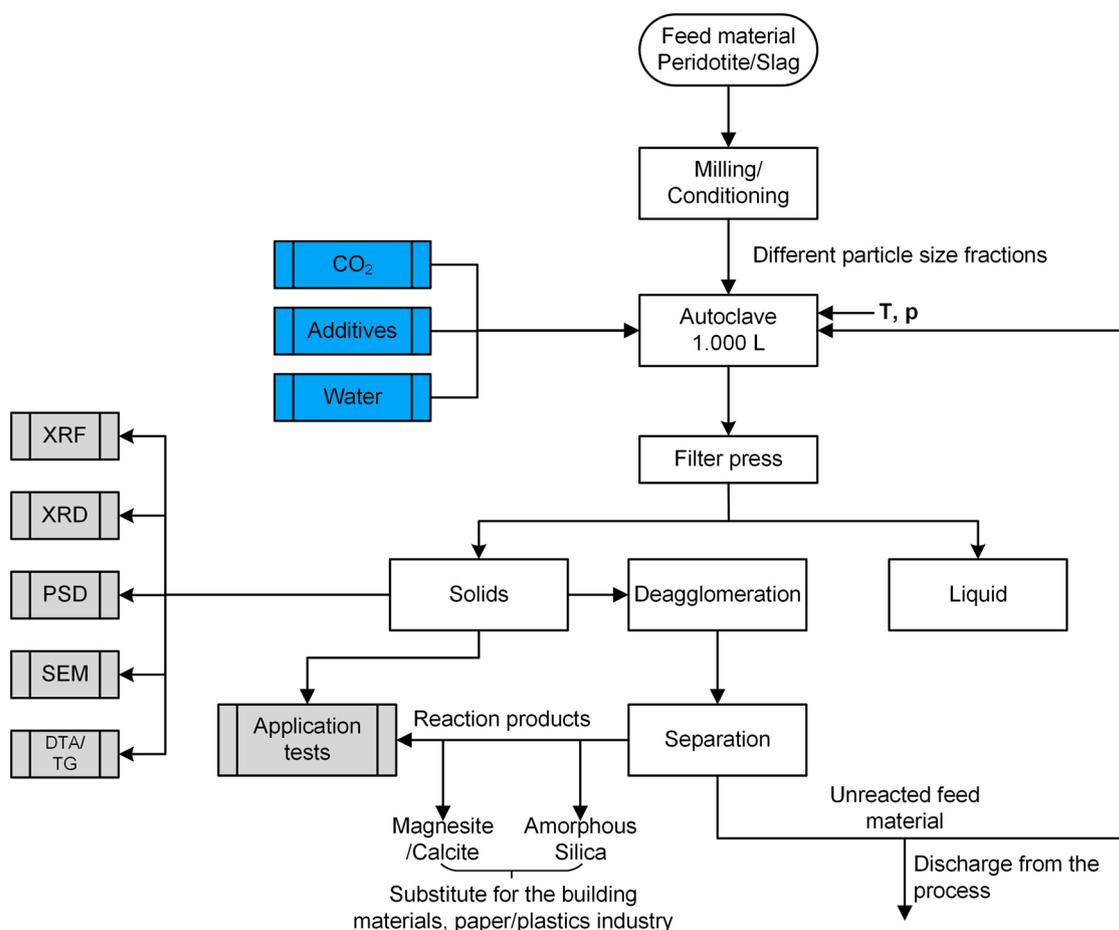


Fig. 1. Flowsheet of the demonstration-scale process, including pre-treatment, post-treatment, and application. Adapted from Kremer et al. [23].

and enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) with minor contents of clinocllore ($(\text{Mg}, \text{Fe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$) and lizardite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), resulting in an olivine content of more than 80%. Due to previous results, the peridotite was pretreated by milling in a vertical roller mill (Loesche GmbH, Duesseldorf, Germany) to a maximum particle size of 20 μm with a d50 of 7.5 μm . The secondary raw material is a slag from the production of ferrochrome, a byproduct that is currently stabilized and landfilled. The main phases of the slag from the ferrochrome production are merwinite, belite, bredigite, spinel with minor contents of periclase and calcite. Both of the investigated feed materials have a theoretical potential CO₂ uptake of approximately 480 $\text{kg}_{\text{CO}_2}/\text{t}_{\text{feed}}$, as is visible in Table 1. The slag was milled below 63 μm with a d50 of 18 μm .

The carbonation process is based on previous studies in lab-scale in a 1.5 L and 10 L autoclave (Type 3E Büchi Kiloclave, Büchi AG, Uster, Switzerland) [9,10]. Due to the size and specifications of the reactor, some changes had to be made. The pressure was limited to a maximum of 40 bar due to the bursting discs and the heating and cooling rates were much slower due to the increased ratio of solution volume to reactor wall. The process conditions are as listed in Table 2.

First, as a preconditioning treatment, 100 kg of ground material was added to 750 L of water in a stirred tank for each carbonation test. In this tank the additives sodium bicarbonate (37.5 kg), ascorbic acid (5.4 kg), and oxalic acid (1.2 kg) were added. After stirring this feed solution, it was pumped to the 1.000 L batch autoclave. The stirrer was started at around 500 1/min and pure CO₂ was injected to a stable initial pressure of 17.5 bar. The reactor was heated up to 175 °C, which was accompanied by a pressure increase to about 30 bar. After a reaction time of 4 h, the reactor was cooled down to 95 °C before releasing the remaining pressure (total dead time of reactor ~2 h), followed by filtration of the solution in a filter press to obtain the solids as a filter cake and the filtrate. Three carbonation tests were carried out per material according to this procedure.

2.3. Separation process

Separation tests were carried out with a classifying centrifuge. The high-performance centrifuges of the *Heinkel Drying and Separation Group* are commonly used for classifying fine and ultra-fine particles down to nanoparticles as well as for decanting in the chemical, fine chemical, pharmaceutical, and food industries. A particular advantage over decanters, which was also decisive for the selection of this machine, is the very fine (1 μm) and precise separation cut, whereas the throughput is significantly lower in comparison. Classifying centrifuges are usually operated in batch mode, but fully automatically, whereas a test machine with manual loading and product removal was used for the following tests. Decisive parameters for calculating the speed and feed quantity to achieve the desired separation cut are the temperature, solids concentration, density, and size of the particles contained, the specific weight difference between liquid and solid, as well as the desired throughput rate. [25].

2.4. Application tests

2.4.1. Description of experiments for cement

For application in cement production, two characteristics are of importance: the material needs to be compatible with the hydrating cement and, ideally, it should be reactive either as a semi-hydraulic or pozzolanic material to facilitate higher clinker substitution rates. The compatibility and reactivity can be directly assessed by evaluating the

Table 1
Elemental composition of investigated feed material.

| Oxides [%] | CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | Cr ₂ O ₃ | MgO | NiO | Others | Potential CO ₂ uptake |
|------------|------|------------------|--------------------------------|--------------------------------|--------------------------------|------|-----|--------|------------------------------------------------------|
| Peridotite | 0.2 | 48.6 | 0.5 | 7.8 | 0.0 | 41.1 | 1.2 | 0.6 | 493 $\text{kg}_{\text{CO}_2}/\text{t}_{\text{feed}}$ |
| Slag | 43.9 | 32.7 | 6.3 | 0.2 | 4.7 | 11.6 | 0.0 | 0.6 | 472 $\text{kg}_{\text{CO}_2}/\text{t}_{\text{feed}}$ |

Table 2
Process conditions.

| Reactor: | 1000 L |
|------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| Temperature: | 175 °C |
| Initial pressure (before heating): | $p_0 = 17.5$ bar |
| Reaction pressure (after heating): | $p_1 = \sim 30$ bar |
| Stirring speed: | ~ 500 1/min |
| Heating rate: | 2,5 K/min |
| Cooling rate: | ~ 1 K/min until < 100 °C |
| Time at max. T.: | 240 min |
| s/L ratio: | 1: 7.5 |
| Additives: | 0.64 M NaHCO ₃ 0.04 C ₂ H ₂ O ₄ 0.01 M C ₆ H ₈ O ₆ |
| pH of solution: | 8 – 8.5 |

impact of the material on strength development of cement. This was done assuming two scenarios – utilization of the carbonation products as inert filler at substitution rate of 5% (minor cement constituent according to EN 197–1 [26]) and at substitution rate of 20% according to main cement constituent. For both scenarios, the same cement – industrially produced CEMI 42.5 R (HeidelbergCement, Germany) – was used. To achieve a homogenous mix of the cement with the material investigated, the blend was homogenized in a laboratory planetary ball mill. The strength was assessed in the so-called micromortars. The mortars were prepared by mixing cement, sand (and de-ionized water in weight proportions of 2:1:0.5, i.e., a water – binder ratio of $w/b = 0.5$). The sand used was composed of quartz grains which had maximum diameter of 0.4 mm. The samples were mixed and vibrated as prescribed in EN 196–1 [27]. Mortar cubes with edge length of 20 mm were cast, stored sealed for the first 16 h, demoulded and cured at 20 °C and RH of 95% until testing. The compressive strength was determined on 7 mortar cubes for each testing age in a way similar to EN 196–1, but with a loading rate of 0.4 kN/s which corresponds to the loading rate of EN 196–1 when expressed in MPa/s. [27].

2.4.2. Description of experiments for paper

For applications in the production of paper, the optical properties of the substitutes are the key parameters and the fixation of the pigments in a sheet of paper needs to be investigated. The optical properties of the pure minerals have been tested by pressing tablets for optical testing of pigments according to the Zellcheming code of practice ZM V/27.5/90 and subsequently measuring the color of these tablets (EN ISO 11664–4) and the brightness value R_{457} (ISO 24 69). To evaluate the retention of the pigments in the paper, laboratory handsheets have been produced with the Rapid-Köthen device (ISO 52 69–2) based on northern bleached softwood kraft pulp fibers from Mercer, Stendal. The minerals have been added in different concentrations and with different dosages of Nalkat 61001 as a fixing agent. The basis weight of the handsheets manufactured was in the range of 60 g/m^2 to 160 g/m^2 . These handsheets have been evaluated by measuring the amount of retained filler material as ash content and the optical properties of the handsheets (EN ISO 11664–4; ISO 24 69). [28] For the application in paper we investigated the use of carbonation products as the sole filler, replacing 100% of the conventional filler (i.e., calcium carbonate (CaCO₃)).

2.4.3. Description of experiments for rubber

The possible applications of the carbonated and separated reaction products of the carbonated peridotite (C-P) and the carbonated slag (C-S) as fillers in the field of polymers are broad. Due to the large

proportion of rubber in polymer products by mass, the carbonation products were tested in rubber applications. Therefore styrene-butadiene (SBR) rubber compounds were produced. SBR was selected because the polymer is an important rubber that is used in large quantities [29]. The recipe shown in Table 3 was used. The added compound proportions are given in parts per hundred rubber (phr). Consequently, the amount of all added compounding components is related to 100 parts of the polymer. To test the usage of separated carbonation products, we replaced up to 50% of the conventional filler carbon black.

The compounds were produced in an internal mixer 350 E (Bra-bender GmbH & Co. G, Duisburg) at a rotor speed of 50 rpm and a mixing chamber temperature of 50 °C. The filling factor of the mixing chamber was 75%. First of all the polymer was fed into the mixing chamber. After a mixing time of approximately 20 s, the non-crosslinking chemicals were added and mixed for five minutes. Subsequently, the crosslinking system was added. All recipe components were mixed for one minute. The compound leaves the mixing chamber as a shapeless mass. To form a band of rubber for further processing, a rolling mill type RC-WW 150/330 with adjustable gap width from Rubicon Gummitechnik und Maschinenbau GmbH, Halle, Germany, was used. Three different compounds were produced. The compound which is named “reference” contains no carbonated mineral filler. To investigate the carbonated mineral fillers two further compounds were produced, one compound for each filler. The amount of added carbonated mineral filler was 30 phr.

The crosslinking behavior of the non-vulcanized compounds was characterized using the rubber process analyzer (RPA 2000, Alpha Technologies, Schwabach, Germany). The measurements were carried out following DIN 53529 at 170 °C [30]. Among other parameters, the t_{90} -time was determined and evaluated. This is the time required to achieve 90% cross-linking of the rubber samples. For further investigations of the compounds, plate-shaped test specimens of the size $84 \times 84 \times 2 \text{ mm}^3$ were produced. For the vulcanization of the mixture, a pressing plant of the type KV247.01 from RUCKS Maschinenbau GmbH, Glauchau, Germany, was used. The required press time agreed with the t_{90} -time. The press temperature was 170 °C at a pressure of 220 bar. S2 tensile bars were taken from the produced test plates and tensile tests were carried out at a test speed of 200 mm/min following ISO 37 [31]. Furthermore, the S2 tensile bars were used to analyze the temperature-dependent mechanical behavior (storage modulus) as well as the occurring glass transition temperature using the dynamic mechanical analysis. The test parameters used for the dynamic mechanical analysis can be found in Table 4. The initial forces for the tests were determined by carrying out preliminary tests at -40 °C , as these are lower and thus ensure that the maximum force of 18 N is not reached.

Table 3

Used recipe (* the reference is produced with 0 phr of the carbonated fillers).

| Recipe Ingredient | Trade name | Producer, Location | Ratio [phr] |
|---------------------------|----------------------------|------------------------------------------------------------|-------------|
| Polymer | Ker 1502 | Avokal GmbH, Wuppertal, Germany | 100 |
| Filler | Sterling SO (carbon black) | Cabot GmbH, Rheinfelden, Germany | 30 |
| | C-P / C-S | RWTH Aachen University, Unit of Mineral Processing | 0 * /30 |
| Processing aid | Stearic acid | Emery Oleochemicals GmbH, Düsseldorf, Germany | 1 |
| Vulcanization activator | Zinkoxyd aktiv | Lanxess Deutschland GmbH, Köln, Germany | 4 |
| Crosslinking agent | Sulphar | Solvay & Barium Strontium GmbH & Co. KG, Hannover, Germany | 3 |
| Vulcanisation accelerator | Rhenogran MBT-80 | Lanxess Deutschland GmbH, Köln, Germany | 0.5 |
| | Rhenogran CBS-80 | Lanxess Deutschland GmbH, Köln, Germany | 1 |

Table 4

Process parameters for the dynamic-mechanical analysis.

| Load type | [-] | Tensile |
|----------------------------------------|----------|--------------|
| Investigated temperature range | [°C] | -60 bis + 60 |
| Heating rate | [°C/min] | 2 |
| Frequency | Hz | 1 |
| Amplitude | [µm] | 45 |
| Initial load – reference | [N] | 0.7599 |
| Initial load – Compound containing C-P | [N] | 0.9111 |
| Initial load – Compound containing C-S | [N] | 0.7251 |

2.4.4. Methods of characterization

2.4.4.1. XRF characterization and loss on ignition determination. To determine the loss on ignition (L.O.I.) values of both the input and output materials of all carbonation trials presented in this study, 2 g of each sample is annealed for 2 h at 1050 °C and balanced after cooling. Especially with regard to the samples having passed the autoclave treatment, the L.O.I. may provide additional information about the carbonation success.

To prepare glass disks for the subsequent chemical analysis via X-ray fluorescence (XRF), 1 g of each sample is transferred to a platinum crucible and fused by a Claisse LeNeo fusion instrument by Malvern PANalytical B.V. (Eindhoven, Netherlands). Eventually, the received glass disks are analyzed via XRF utilizing a PW2404 device by Malvern PANalytical B.V. (Eindhoven, Netherlands) to obtain the chemical composition.

2.4.4.2. XRD characterization. To analyze the present mineral phases of the input materials as well as the carbonation products, X-ray diffraction (XRD) technique was conducted in Bragg–Brentano geometry employing a Bruker D8 Advance device by Bruker AXS (Karlsruhe, Germany) equipped with LynxEye detector, CuK α tube, and nickel filter. The chosen measuring range from 5° to 90° 2 θ was scanned in 0.02° steps at a rate of 2 s per step. As this study also aims at a quantitative comparison of the present and formed mineral phases respectively, a subsequent semiquantitative evaluation of the mineral phase composition was executed.

2.4.4.3. TG/DTA determination. Thermal gravimetric and differential thermal analysis were performed using STA 449 F3 Jupiter® and Proteus Thermal Analysis 8.0.2 software by NETZSCH-Gerätebau GmbH, Selb, Germany. Analysis runs were carried out using Al₂O₃ crucibles, in a temperature range from 23 °C to 1000 °C with a heating rate of 10 K/min, and were performed under argon with a gas flow of 50 ml/min each.

2.4.4.4. Scanning Electron Microscopy (SEM). The documentation of the input materials' initial state, examination of the products' microstructure for any abnormalities due to the varied experimental parameters and visual validation of further chemical and mineralogical analysis steps, Scanning Electron Microscopy (SEM) was carried out by a ZEISS GeminiSEM500 by Carl Zeiss AG (Oberkochen, Germany). Additionally, Energy Dispersive X-ray Spectroscopy (EDS) was carried out by an X-Max 80 detector and AZtec software by Oxford Instruments (Oxon, England) to reveal local chemical variations and to selectively analyze the elemental composition of the formed products.

3. Results and discussion

3.1. Evaluation of carbonation process

In the large-scale tests in the 1000 L reactor, carbonation levels of 23% on average were achieved for the peridotite and 46% for the slag, corresponding to 113.5 and 192 kgCO₂/t_{Feed}, respectively. In a lab-scale

autoclave with optimised parameters that could not be transferred to the large-scale reactor, a carbonation degree of 60% could be obtained for the peridotite [19]. Although the theoretical carbonation potential for peridotite is higher than for the slag from ferrochrome production, more CO₂ is stored in the slag under the same conditions. This may be due to the better solubility of the Ca²⁺ ions compared to the Mg²⁺ ions, as well as the possible presence of free lime in the slag.

Previous studies showed different specific particle sizes for the reaction products magnesite (<25 µm) and amorphous silica (~20 nm) [32,33]. In the context of the project carried out, typical particle sizes of 2 – 5 µm for magnesite/calcite and about 100 – 200 nm for amorphous silica were found to form independently of the particle size of the feed material [23].

As can be seen in Fig. 2, the particles are different after the large-scale tests with peridotite. Although the same mineral phases and the magnesite in its rhombic crystal structure are present in the reaction products, no clear spherical silica particles are visible on the surface. Instead, as confirmed by EDX measurements, the amorphous silica lies as a fissured layer on the surface of the unreacted peridotite. Partially spherical particles are enclosed in this fissured layer. This change in the structure of the reaction products could be a consequence of the process-related change or slowdown in cooling in the 1000 L autoclave.

In the carbonated slag (see Fig. 3), no clear calcium carbonate crystals are visible, as both the carbonates and the unreacted slag are almost completely covered by spherical amorphous silica particles.

The enrichment of the products from the carbonation of peridotite, as well as the separation of the unreacted peridotite components, is based on different chemical, physical and mineralogical properties of the components. The following particle sizes and shapes of the three main components are to be expected:

- Unreacted portions of the peridotite or slag: depending on the particle size of the feed material < 63 or < 20 µm, crystal form rhombohedral, but due to grinding and good fissility as well as brittle and conchoidal fracture, high diversity in particle form follows
- Magnesite/ Calcite: 2 – 5 µm, rhombohedral crystals
- Silica: < 1 µm, spherical, amorphous particles or fissured layer on the unreacted peridotite

There are density differences in the individual minerals from 2.65 g/cm³ for the silica to 3.0 g/cm³ for magnesite, 2.7 g/cm³ for calcite, and 3.3 g/cm³ for the peridotite used. Nevertheless, most common separation methods such as density or magnetic separation cannot be used because the very small particle size of the mineral phases to be separated

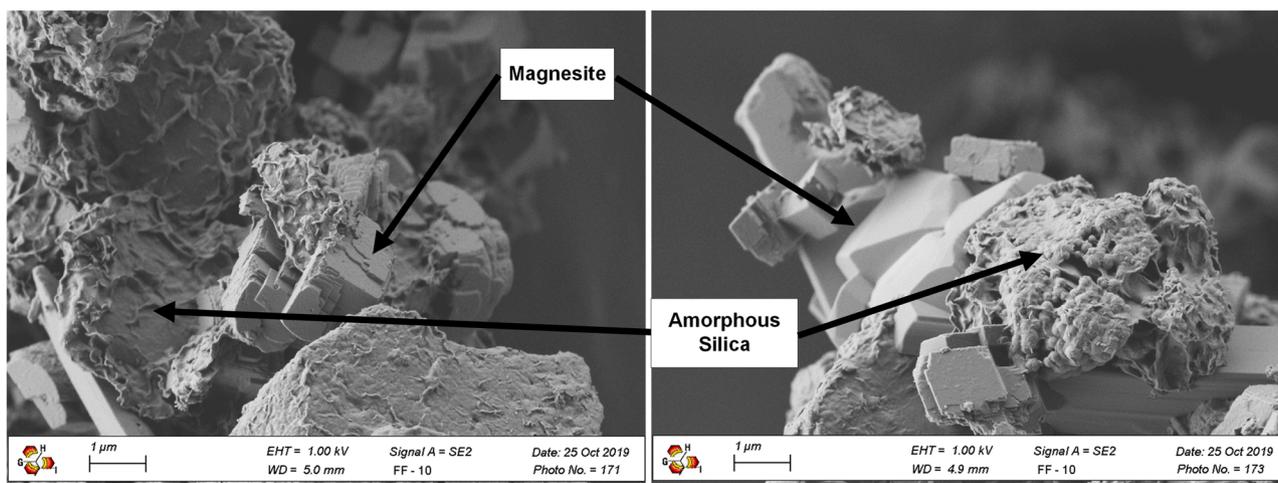


Fig. 2. SEM image of the carbonated peridotite. The reaction products, magnesite crystals, and spherical amorphous silica particles form on the surface of the unreacted peridotite (magnified by 10,000).

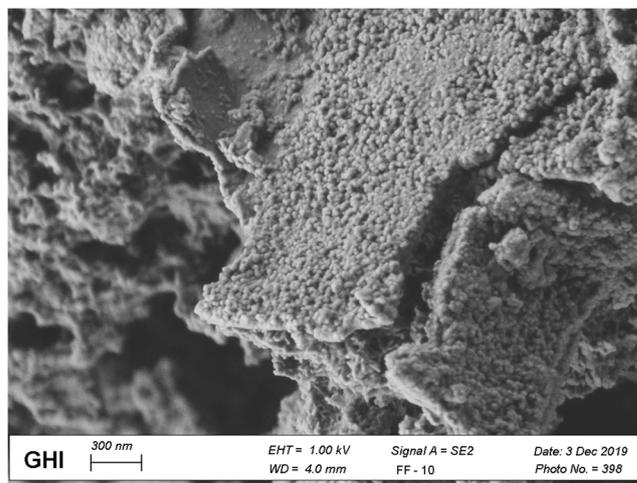


Fig. 3. Carbonated slag from the large-scale test (magnified by x30,000) with an initial particle size of < 63 µm.

of < 5 µm are below the feasibility limit or the differences within the dispersed mixture of substances are too small concerning these properties. [23].

3.2. Separation of carbonation products

Kremer et al. [23] investigated different processing approaches like flotation and flocculation based on the chemical and physical properties of the reaction products. The best results, however, were achieved by classification through sieving at 5 µm, obtaining a mixed carbonation product enriched with carbonate and amorphous silica. To further reduce the separation particle size from the previously investigated minimum of 5–1 µm for C-P and 2 µm for C-S and to increase the possible throughput, a classification centrifuge was selected for the separation. This novel approach of separating the different phases is supposed to lead to better utilization possibilities and thus significantly accelerate the path towards negative emissions.

The classification with the classification centrifuge was carried out in two stages at a defined speed and volume flow to realize both separation cuts. The separation cuts and the principle of the classification process can be seen in Fig. 4. As sample preparation, both the carbonated peridotite and the carbonated slag samples from the large-scale tests were attrited for 4 h (~8.5 kg per batch). These samples were available

| Target fraction C-P | Target fraction C-S | Expected composition |
|----------------------|-----------------------|-----------------------------------------------------|
| < 1 μm | < 2 μm | Mostly microsilica |
| 1 – 5 μm | 2 – 11 μm | Mostly Magnesite / Calcite |
| 5 – 20 μm | 11 – 63 μm | Mixture of unreacted material and reaction products |

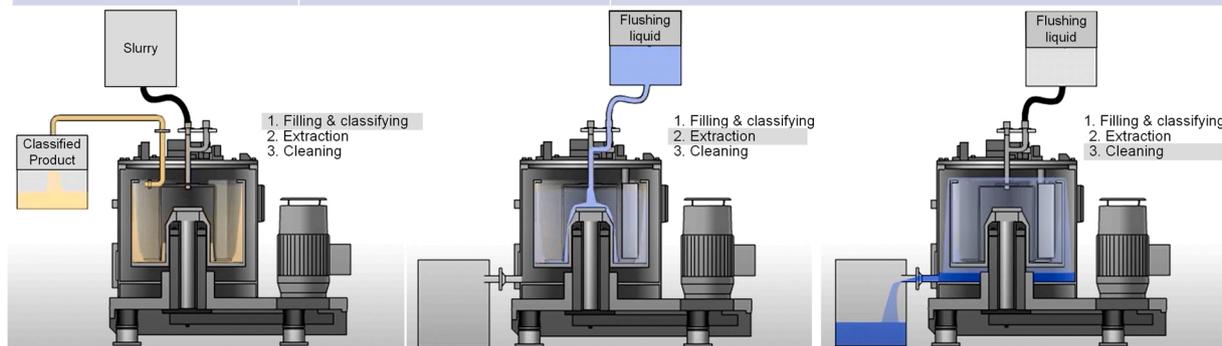


Fig. 4. Principle of the classification process with a classification centrifuge [34].

as filter cakes after the large-scale tests. The solids content during attrition was about 70 – 75% and the speed of the attrition cell was about 1100 1/min. After attrition, water was added to the suspension to reduce the solids content to about 50%. For the first stage of classification to separate the unreacted material, the speed was adjusted. The suspension was pumped into the centrifuge using a diaphragm pump with a defined volume flow. The coarse material remains in the drum depending on the separation particle size and the fine material overflows as a suspension and is collected. After the entire feed suspension has been fed in, the centrifuge can be switched off and the bowl cleaned manually, i.e., the dewatered coarse material can be recovered.

The fines, which are present as a suspension, can be classified in the next stage at a different speed and feed volume flow (see Table 5). In this way, the medium-size product can be removed from the machine again as a filter cake. The fine product is present as a suspension. The three respective particle size fractions are thus present as filter cake or as suspension and must be dried and divided for analysis.

The consistency of the fine fractions from both the C-P and the C-S was very viscous and, after subsequent drying, very hard, indicating the accumulation of amorphous SiO₂ as pozzolanic material (Fig. 5).

3.3. Characterization of the separated products

The analyses of the classification products (Table 6) each showed a significantly higher loss on ignition for the medium particle size fraction than for the non-separated carbonated mixed product, which confirms the enrichment of the carbonate-containing phases. Thus, the loss on ignition of the C-P 1 – 5 μm is 23.9%, compared to 11.2% in the mixed product before separation. In the fine fraction, the SiO₂ content is enriched and the MgO content is lowered, whereas the CaO content in the carbonated slag is higher. In addition, a higher loss on ignition is visible, which indicates a high carbonate content. Due to the high SiO₂ content in the feed material, it can be assumed that a large part of the silicon in the coarse fractions is bound crystalline in the unreacted material. However, the qualitative XRD of the fractions C-S < 2 μm and C-S 2 – 11 μm showed only calcite phases in which no SiO₂ is bound,

Table 5
Process parameters of the classification centrifuge.

| Cut-off | C-P | | C-S | |
|--------------------------|-----------------|-----------------|------------------|-----------------|
| | 5 μm | 1 μm | 11 μm | 2 μm |
| Rotational speed [1/min] | 1200 | 3600 | 450 | 2500 |
| Volume flow rate [L/h] | 650 | 150 | 360 | 350 |

which is why it can be assumed that the contained silica is amorphous, confirming a successful separation.

However, the yield (mass percentage) in the two fine fractions < 11 μm (added ~11%) is low, which can also be seen in the still high loss on ignition in the coarse fraction. The successful separation in terms of purity of the individual fractions could be confirmed utilizing a classifying centrifuge, but the poor yield and the lack of depletion in the coarse fraction, as well as SEM images show that the deagglomeration does not yet provide satisfactory results. As the parameter study of Kremer et al. [19] shows, by adjusting reaction parameters and addition of seed crystals, the carbonation degree of peridotite can be increased by the factor 2.6. Due to the limitations of the available large reactor, which was mainly needed to obtain sufficient material for separation and application tests, no comparable result could be achieved here, which is reflected in the yield. With this factor for the optimised carbonation, the yield of reaction products after separation can also be expected to be higher (~7.5% for fraction <1 μm and ~19% for fraction 1 – 5 μm).

3.4. Application tests

The separated products were used for application tests as substitutes for cement, as alkaline activators, or as fillers in concrete or mortar, as well as in paper and rubber. The focus was on cement due to the high CO₂ emissions within the production. The substitution of emission-intensive substances is intended to achieve the goal of negative CO₂ emissions, which are necessary to reach the goals of the Paris Climate Agreement. Also due to the high durability of cementitious products and the large mass and correspondingly large potential for carbonation, cement is the most important application example here. Nevertheless, the carbonated separation products should also be tested in other areas where they can reduce CO₂ emissions by substituting the common fillers. For the application tests, the coarse fraction of C-P (>5 μm) and C-S (>11 μm) was ignored in each case, as these are to be returned to carbonation as unreacted material. The middle, carbonate-rich fraction, which is enriched in bound CO₂, was tested as an alternative filler for paper and rubber as well as for cement. The respective fine fraction of both carbonated materials was tested as a possible pozzolanic material for cement only.

3.5. Cement

In 2020, more than 35 million tonnes of cement were produced in Germany. On average, the cements contained 70% of Portland clinker and 30% of the so-called supplementary cementitious materials such as ground granulated blast furnace slag, fly ash, limestone, natural

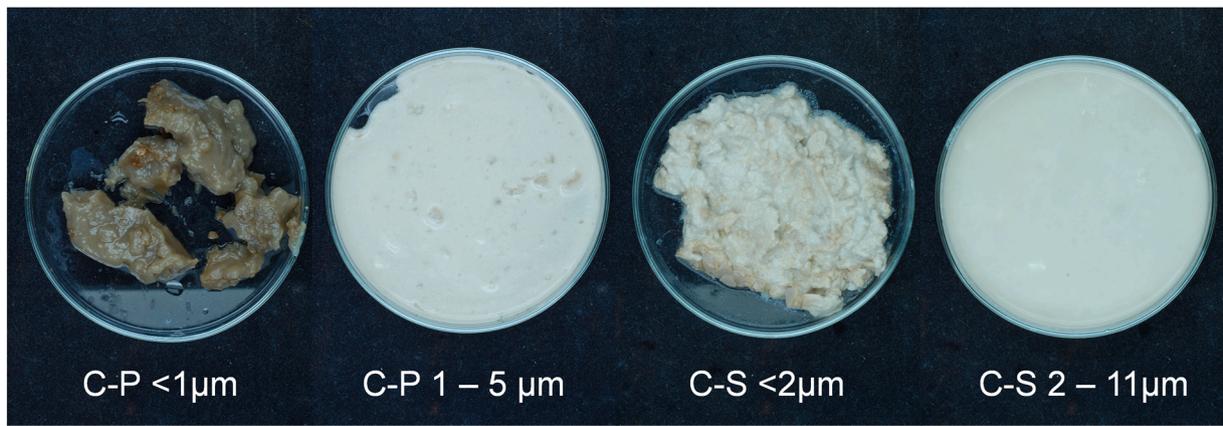


Fig. 5. Separation products after treatment with a classification centrifuge.

Table 6
XRF characterization of the separation products (*carbonated material before classification).

| Component [%] | C-P | | | C-S | | | |
|--------------------------------|------------------|--------|----------|------------------|--------|-----------|---------|
| | P ₀ * | < 1 µm | 1 – 5 µm | S ₀ * | < 2 µm | 2 – 11 µm | > 11 µm |
| Yield | 100 | 2.9 | 7.3 | 100 | 3.7 | 7.7 | 88.6 |
| SiO ₂ | 41.1 | 44.9 | 33.4 | 42.1 | 24.8 | 30.6 | 18.7 |
| MgO | 37.4 | 5.2 | 33.7 | 38.4 | 9.1 | 2.7 | 5.4 |
| CaO | 0.7 | 0.9 | 1.4 | 0.7 | 35.6 | 37.0 | 36.7 |
| Fe ₂ O ₃ | 6.1 | 13.5 | 5.5 | 6.4 | 0.2 | 0.5 | 0.0 |
| Al ₂ O ₃ | 0.5 | 0.2 | 0.5 | 0.5 | 4.9 | 0.2 | 1.9 |
| Cr ₂ O ₃ | 0.3 | 0.1 | 0.2 | 0.4 | 3.6 | 0.9 | 1.1 |
| Na ₂ O | 1.7 | 2.6 | 0.8 | 0.4 | 0.9 | 0.8 | 1.4 |
| Others | 1.0 | 6.7 | 0.6 | 0.8 | 0.5 | 1.3 | 0.4 |
| L.O.I. | 11.2 | 26.0 | 23.9 | 10.3 | 20.4 | 26.0 | 34.5 |

pozzolans and others. These materials not only reduce the overall CO₂ intensity of cement, but, when reactive, also contribute to an improved performance of resulting concrete such as durability. [35] However, volumes of the most widely supplementary cementitious materials – blast furnace slag and fly ash – are declining as the respective industries decarbonize. This, together with the ambition of cement industry to further lower the clinker content in cements opens up utilization potential of new supplementary cementitious materials of yearly volumes of several million tonnes only in Germany.

3.6. Requirements for the substitute

Requirements on cement constituent result from requirements on durable and environmentally compatible reinforced concrete. Any substitute material needs to be compatible with the key constituents of reinforced concrete, i.e., cement, aggregates and steel. In practical terms, it translates to low content of chloride, sulfate and alkali required in order to prevent issues with steel passivation, concrete integrity including the detrimental effects of alkali-silica reaction. Additionally, concrete needs to have limited content of heavy metals to quarantine health and safety, prevent their leaching to the environmental and to enable recyclability of the concrete at the end of its service life. Ideally,

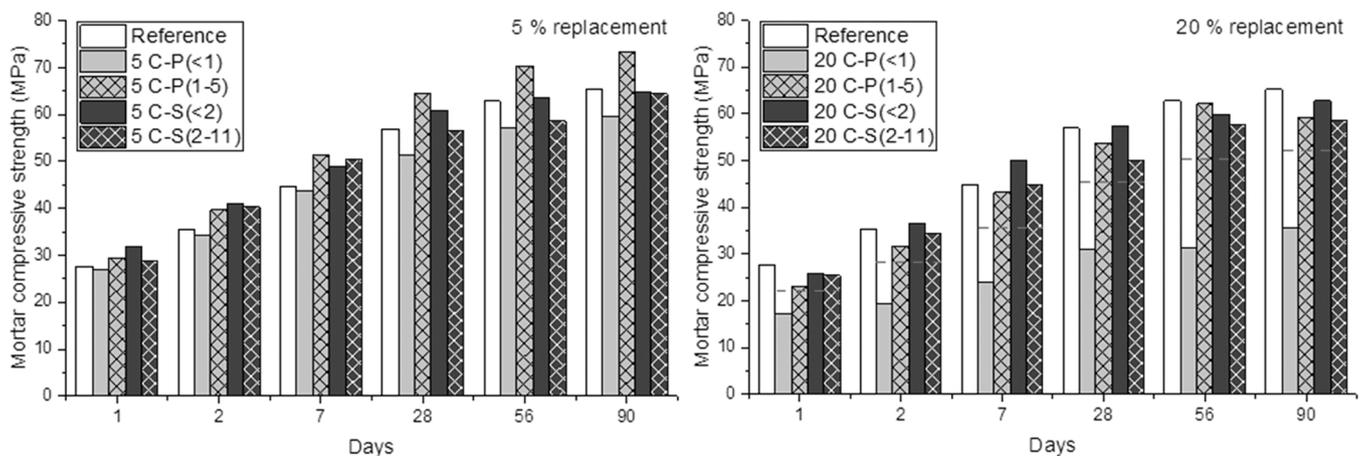


Fig. 6. Strength development of cements containing 5% (left) or 20% (right) of the materials assessed. C-P represents the carbonated peridotite and C-S the carbonated slag. The red dashed lines in the right figure correspond to the dilution factor, i.e., to 80% of the reference strength at a given age.

the substitute material should be reactive, i.e., should participate in the hydration reaction of cement to reduce the final porosity in concrete finally improving its technical as well as environmental performance.

3.7. Performance of the substitute

Cement strength development is a straightforward way to evaluate the compatibility of the substitute material with cement and to assess its reactivity. Fig. 6 shows strength development of mortars made of cement with 5% and 20% substitution level compared to the reference, which is the neat industrial CEM I 42.5 R cement. Traditionally and in accordance with standards, the strength after 2 and 28 days are the key properties ultimately determining the strength class of the cement (42.5 R in the case of the reference).

At 5% substitution level, all materials are tested but the fine carbonated peridotite show compatibility with the hydrating cement. Early age hydration kinetics is accelerated due to the so-called filler effect which promotes clinker reaction as the fine substitute materials fill the gaps between the cement grains and additionally provide extra surfaces for hydrates growth. The significantly higher strength of the cement with the coarser fraction of carbonated peridotite at later ages points to active contribution of this material to strength gain, i.e. to reactivity. On the other hand, the addition of fine carbonated peridotite measurably reduces cement strength pointing to incompatibility of this material with cement. This could be caused by an increase in concentration of components retarding cement hydration such as nickel. This is likely caused by the high NiO content in this fraction (NiO content 4.33%) retarding cement hydration and thus lowering the compressive strength.

At 20% substitution level, the fine carbonated peridotite lowers the compressive strength well below the dilution factor confirming the aforementioned incompatibility of this material with cement. The remaining three materials improve the compressive strength when compared to the dilution factor at all ages. The achieved strengths are close to the reference cement implying that the materials are highly reactive. The strength gain development resembles findings made for carbonated cement paste, showing the potential for carbonated material as substitute of cement [36]. There, the alumina-silica gel formed up to carbonation was highly pozzolanic, contributing to the compressive strength development already at one day. The later age contribution was however lower compared to common pozzolans such as e.g. fly ash, which was contributed to the low overall content of the gel in the material. [37] For materials investigated here, the content of reactive silica is also low due to the limited carbonation levels achieved and due to the imperfect separation.

Content of critical constituents such as chloride, sulfate or alkalis is at a common level for all materials. The nickel and chrome contents of the fine carbonated peridotite and coarse carbonated slag, respectively, are high.

3.8. Evaluation of the potential for substitution

Fine carbonated peridotite is not suitable for cement production as it is not adversely impacting strength development even at low substitution levels. Most likely, this is attributed to the elevated content of nickel in this material.

The remaining materials are potentially suitable supplementary cementitious materials. The strengths achieved at 20% replacement level are consistent with common cements produced in Germany. More detailed study including an assessment of impact on concrete durability would be needed for quantitative evaluation of the application potential. Additionally, as these materials are not part of currently allowed cement constituent in EN 197-1 [26], technical approvals of the respective cements would be needed prior to their large-scale deployment. Further, the contribution of the materials assessed to the overall heavy metal content of concrete as well as the leachability of these heavy metals need

to be assessed in detail and considered before the final application.

3.9. Paper

The Paper industry in Germany used about 2.3 million tonnes of fillers and pigments in 2020. CaCO₃ has by far the highest share of filler materials for paper applications. CaCO₃ is used for increased optical properties, smooth, bright, and sometimes glossy surfaces, and in some cases just for increasing the specific weight of the paper at a lower cost than with fibers and without too much loss of optical properties.

3.10. Requirements for the substitute

For all applications in paper the filler and pigment particles need to be in a size range of about 500 nm to 2 µm for pigments and up to about 5 µm for fillers. Filler particles are mixed with the fiber suspension and homogeneously distributed in the paper. For pigment applications, the mineral particles need to be smaller. They are mixed with binders and then coated on the paper surface to achieve higher smoothness, brighter colors, and sometimes higher gloss. While smoothness and gloss can be adjusted by modifying the particle size distribution, the optical properties of the mineral are essential for the optical properties of the resulting coating or paper. For most applications where fillers and pigments are used, target values for brightness (R₄₅₇) between 80 and 100 are demanded. Pure northern bleached softwood kraft pulp has a brightness of about 85–90. In some product areas like newspaper or recycling copy paper lower brightness values are acceptable (60 – 80).

Last but not least it is important that the pigments and fillers can be retained in the paper structure. For conventional minerals, cationic polymers with a high molar mass are used as retention aids.

3.11. Performance of the substitute

For evaluating the performance of the potential substitutes carbonated peridotite and carbonated slag, these materials have been mixed in different concentrations with northern bleached softwood kraft fibres. Then handsheets have been formed on a Rapid-Köthen device with basis weights of about 80 g/m² to 240 g/m². Nalkat 61001 from the NALCO Company has been used as a retention aid in concentrations from 0.03% up to 5%. In all handsheet tests performed the retention of substitute fillers was far too low. While in papers with conventional fillers ash contents from 20% to 40% can be easily achieved, max. 7% of substitute fillers could be retained in the 80 g/m² sheets. The substitute concentration could be raised by producing handsheets with higher basis weight. In sheets with 240 g/m², almost 40% ash content could be achieved by heavily overdosing the substitute fillers in the pulp suspension. An additional effect observed was the adhesion or sticking of the sheets to the carton used for drying the sheets. This adhesion was more pronounced for the peridotite Table 7.

The comparison of the optical properties of the substitute fillers shows that these filler materials will reduce the optical properties of the pure fiber material. This tendency could be confirmed by the handsheet trials, but quantitative examinations were not possible since the retention of the substitutes in the paper web was not high enough.

Table 7
Optical properties of the pure substitutes.

| Optical properties | C-P | C-S | NBSK Fibres |
|--------------------|-------|------|-------------|
| R ₄₅₇ | 64 | 73 | 88 |
| Y | 71 | 76 | 92 |
| L* | 87 | 90 | 97 |
| a* | -0.18 | 0.05 | -1.06 |
| b* | 5.94 | 2.55 | 3.18 |

3.12. Evaluation of the potential for substitution

The tests carried out show that the C-S and C-P investigated can in principle be used as fillers in the paper industry, but there are still problems to be solved. The surface chemistry of these fillers is significantly different from that of the fillers commonly used in the paper industry. This means that the additives for fixing such fillers would have to be adapted. Changing additives in a paper mill always has an impact on the entire process, so that such a change of fixing agents is not entirely trivial. With the additives used in these trials, the retention of the fillers was rather poor and it was not possible to achieve filler contents in the usual range of 20 – 40% for basis weights relevant for graphic paper applications. In principle, however, this should be possible with suitable additives.

The optical characteristics of the fillers tested here are not in the performance range of conventional fillers. They are not bright enough and partly show color casts. In the paper industry, whiteness levels of 60% (newsprint) 80 – 100% (copy and office papers, magazine papers), or even higher are common for graphic papers. For the entire sheet to brighten, the brightness of the fillers should be well above 80%. The carbonation products examined here are below these values. They could therefore be used for lower quality graphic papers, such as newsprint, or in the packaging sector. However, paper manufacturers would probably only use such fillers if significant advantages could be achieved elsewhere.

3.13. Rubber

3.13.1. Requirements for the substitute

Rubber compounds usually consist of the components polymer(s), fillers, plastizisers, cross-linking chemicals and, if required, further chemicals (processing aids, anti-aging agents, special chemicals) [38]. By adding fillers, the rheological, mechanical, and dynamic properties of rubber compounds can be influenced [38]. Fillers are classified into active/reinforcing (500 – 1000 nm) and inactive/non-reinforcing fillers (10 – 100 nm) depending on their particle diameter. Whether a filler has a reinforcing effect also depends on the extensity factor (contact surface) as well as the intensity factor (surface activity) [39]. If reinforcing fillers are introduced into the rubber compound, the rubber-elastic phase is partially replaced by a dispersed inelastic phase [40]. Active fillers consequently increase the viscosity of the rubber compounds and increase the tensile strength. The use of inactive fillers can improve the processability of the rubber compounds. On the other hand, the tensile strength decreases as the amount of filler increases [39]. Both used carbonated mineral fillers belong to the group of reinforcing fillers due to their particle diameter.

If novel fillers are used, it is necessary that they can be easily incorporated into the compound. Furthermore, added fillers should not increase the rubber viscosity so that the maximum power of the internal mixer is reached and the mixing process has to be stopped. In addition, it is essential during the mixing process that the filler can be well divided and distributed in the mixture [41]. The properties of the rubber product must not be worsened by the use of novel fillers and, in the best case, are even improved. In addition, new fillers need to be economically competitive with conventional fillers.

Based on the particle diameter, the used carbonated mineral fillers can be classified as reinforcing fillers. Nevertheless, it is important to notice that the used carbonated mineral filler exceeds the recommended particle diameter.

3.13.2. Performance of the substitute

No irregularities were detected during the production of the rubber compounds with carbonated mineral fillers. Both fillers had good flow properties and were easily incorporated into the mixture after being added to the feeding chute. The torque of the internal mixer also showed no unusual characteristics during the compound production.

After compounding, the rubber compounds have to be further processed to vulcanization by applying heat and pressure. To investigate the vulcanization behaviour, the rubber compounds were analyzed in a rotorless vibration rheometer (Rubber Process Analyser). The aim was to investigate whether the added carbonated mineral filler influences the cross-linking behaviour of the rubber compounds. The t_{90} -times of the rubber compounds can be found in Table 8.

The used carbonated mineral fillers influence the t_{90} -time. The reference sample has a t_{90} -time of 6.13 min. If the filler C-P is added to the mixture, the t_{90} -time required for cross-linking increases slightly. The t_{90} -time of the sample containing the filler C-S is 4.89 min. In general, the carbonated mineral filler used has only a marginal influence on the crosslinking time and it can be assumed that the filler does not negatively influence the crosslinking behavior.

During the tensile tests, the maximum stress and the corresponding elongation were determined (Fig. 7).

If carbonated peridotite is added, there is an average increase in the maximum tension of 17% to 11 MPa. However, the improvement in tensile strength is accompanied by a high standard deviation. This could be a sign that the filler could not be sufficiently well distributed in the compound. Since the tensile tests only allow an indirect conclusion about the distribution in the compound, this should be analyzed additionally, for example with the help of microscopic methods. Should the suspicion be confirmed that the filler is not sufficiently well distributed in the compound, the mixing process could be adapted to realize a more uniform distribution of the filler in the rubber compound. For example, the mixing time could be extended or a higher mixing chamber temperature could be selected to reduce the compound viscosity during processing. The addition of carbonated slag increases this by an average of 12% to 10.6 MPa. The standard deviation corresponds approximately to the standard deviation of the reference sample and is within the typical range.

Similarly, the added carbonated mineral fillers have an effect on the elongation at maximum tension (Fig. 8). By using C-P as a carbonated mineral filler in the compound, the maximum elongation increases from 210% to 248%. This is an increase of 18%. Here, too, it is clear that the measurement results show a high standard deviation. If C-S is added to the compound during compound production, the elongation at maximum tension increases by 26–264%.

Furthermore, the addition of carbonated mineral fillers influence the temperature-dependent mechanical behaviour. Below the glass transition temperature, elastomers harden like glass [39]. Thus, the glass transition temperature marks the end of the possible temperature range of application. The added carbonated mineral fillers do not influence the glass transition temperature, as this is essentially dependent on the polymer used (Table 9).

The analysis of the shear modulus of a viscoelastic solid allows conclusions about the elastic component (storage modulus) and the viscous component (loss modulus) [42]. The storage modulus was investigated in a temperature range from – 60 °C to + 60 °C (Fig. 9).

In the glass transition temperature range, the storage modulus is very high and amounts 1369 MPa for the reference sample. The storage modulus of the sample containing the carbonated mineral filler peridotite is 2052 MPa. The polymer molecules are frozen glass-like in this range [39]. In the subsequent glass transformation range, the storage modulus decreases by several orders of magnitude with increasing test temperature. This is due to the fact that the mobility of the polymer chain segments and thus the elasticity of the samples increases [39]. The curves of the investigated samples do not show any differences within the investigated temperature range. It can be concluded that the use of

Table 8
 t_{90} -time of the produced samples.

| | | Reference | C-P | C-S |
|----------|-------|-----------|------|------|
| t_{90} | [min] | 6.13 | 6.75 | 4.89 |

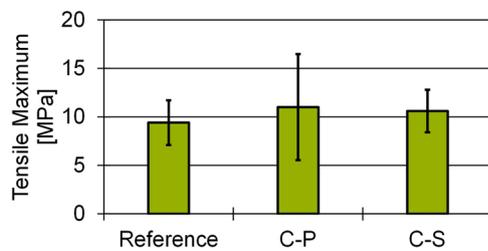


Fig. 7. Tensile Maximum as a function of the added carbonated mineral filler (30 phr / 50% of carbon black filler substituted).

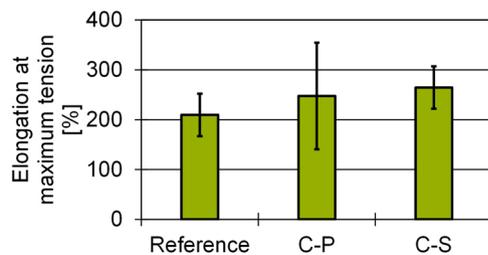


Fig. 8. Elongation at maximum tension as a function of the added carbonation products as filler (30 phr / 50% of carbon black filler substituted).

Table 9

Glass transition temperature as a function of the added carbonated mineral filler.

| Sample Description | Glass Transition Temperature [°C] |
|--------------------|-----------------------------------|
| Reference | -57 |
| C-P | -56 |
| C-S | -57 |

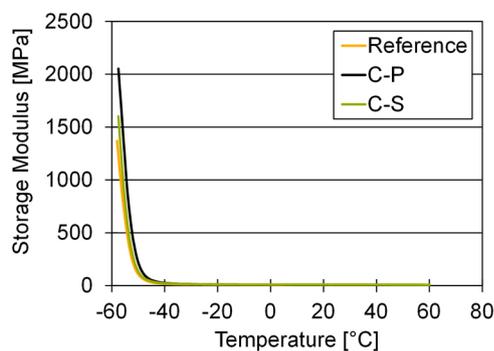


Fig. 9. Storage Modulus as a function of the temperature and the added carbonated mineral filler.

carbonated mineral fillers does not influence the storage modulus and thus the amount of elastic material behaviour.

The tests carried out show only minor differences to the reference material, so the potential for substitution is given. To make a final assessment, however, further tests such as abrasion tests or similar must be carried out.

3.13.3. Preliminary economic and environmental assessment

To assess the economic as well as environmental impacts of the separated product, in-depth life cycle and techno-economic assessments are necessary. To initially grasp the potential of using the separated products in industry we conducted a preliminary assessment of the carbon footprint as well as the production costs of the blended products (i.e., blended cement using carbonated minerals, paper filler and rubber filler) and compared it to their conventional products (i.e., CEM I 42.5 R,

CaCO₃ as paper filler and carbon black as rubber filler). As the economic evaluation as well as the carbon footprint of using CO₂ carbonation products in the cement, paper or rubber industry in the demo-scale does not reflect the expected costs and emissions of a process at scale [20], we here investigate an upscaled model for carbonation and separation, based on our experimental data of the optimized parameters [19]. We used the open-source integrated techno-economic model published by Strunge et al. [20,43] as well as calculations by Ostovari et al. [22], which have been developed closely with the authors of this study in the project 'CO₂Min'. A short description of this approach is shown in the [Supplementary material](#) (Supplementary Note 1).

3.13.4. Model of upscaling-scenario for the process of carbonation and separation

For a process at scale a continuous operation is envisioned, because batch processes have a significantly higher demand for labor, generally leading to continuous processes having lower overall costs [20,44]. Hence, we here also consider a continuous operation for the economic and environmental assessment. The envisioned process is shown in Fig. 10. For simplicity, we only considered the use of olivine-bearing rocks / peridotite as a feedstock for this assessment. Here, mineral is crushed and ground using a cone crusher and a ball mill which is then fed in continuously stirred tank reactors, where the reaction occurs in a slurry. CO₂ is captured using a monoethanolamine (MEA) post-combustion capture from cement production flue gas, which is continuously compressed to the desired pressure and fed into the reactor. After the reaction we use classification equipment which can be used at scale: first, cyclones are used to separate unreacted feed mineral from the slurry. A part of the unreacted material is discharged as unreactive material from the process and the other unreacted material is fed back into the carbonation reactor; second, a share of the product-rich slurry fed to disk centrifuge to separate magnesite and unreacted mineral from the stream; third, the resulting silica-rich solution is added to the residual slurry, producing a desired silica content and the carbonated mineral product is dewatered using solid bowl centrifuges.

3.13.5. Product definition for economic and environmental impact estimations

For the initial economic and environmental assessment performed in this study, we defined 4 products following the application tests presented in this study: blended cement with carbonated mineral as filler (5% carbonated material and 95% conventional clinker, referred to as 'blended cement 5%'); blended cement with carbonated mineral as main cement constituent (20% carbonated material and 80% conventional clinker, referred to as 'blended cement 20%'); paper filler (100% carbonated material as filler); rubber filler (50% carbon black, 50% carbonated material as filler). As a basis for comparison, we use the reference products conventional cement (i.e., CEM I 42.5 R with a clinker content of 100%), CaCO₃ as paper filler and carbon black as rubber filler. Although still work on the development of the products must be conducted, we here assume, that all carbonated mineral products and reference products have the same performance in their respective application.

3.13.6. Environmental impact of carbonated mineral products and their application

For the initial environmental assessment, we only considered the carbon footprint, while acknowledging that future in-depth analyses using other impact categories such as freshwater or metal depletion are needed, which have been reported to be significant for these technologies [45]. For the assessment we used a gate-to-gate approach based on the boundaries shown in Fig. 10, alterations in the use phase or end of life of these products are not assessed. Using the model developed by Strunge et al. [20] as well as assumptions from Ostovari et al. [22], we calculated a carbon footprint of - 277 kg CO₂ equivalent per tonne of product (kgCO_{2e}/t_{product}), meaning more CO_{2e} is stored than CO_{2e} is

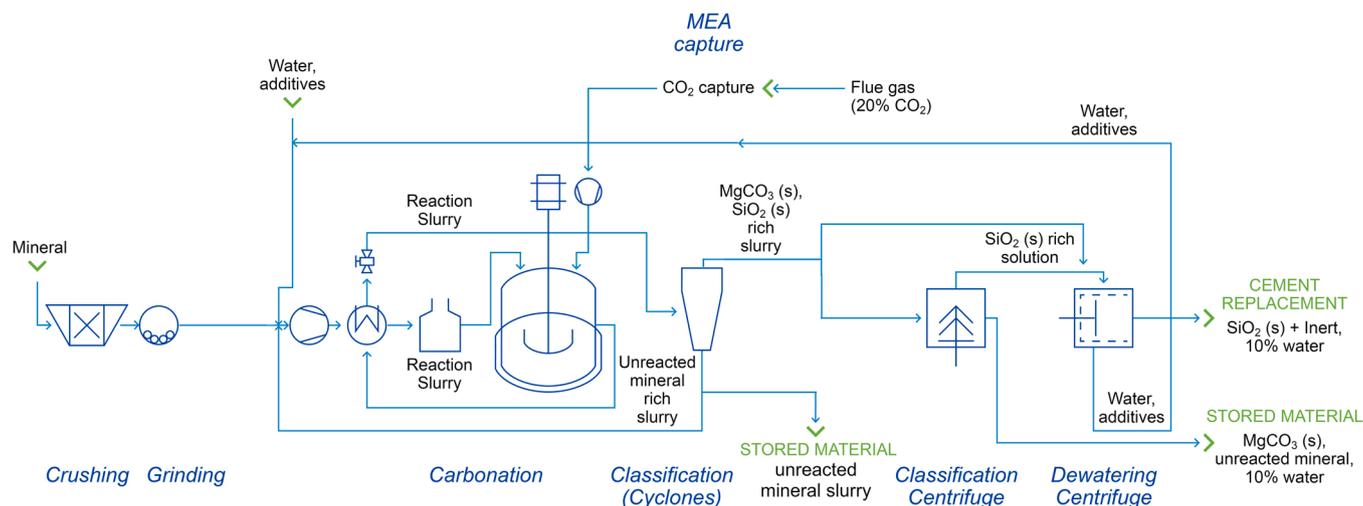


Fig. 10. Modelled large-scale processes for carbonation and separation Modified from Strunge et al. [20].

emitted during the carbonation process, under current conditions for transport and energy. It needs to be pointed out that negative values of these calculations should not be mistaken as negative emissions as defined by the intergovernmental panel on climate change, as here CO₂ is captured from the cement production site and not from the atmosphere [46]. Since the carbon footprint of carbonated minerals has been calculated to be negative, using carbonated minerals as substitutes of conventional products which all have positive carbon footprints will lead to carbon footprint reductions. The results of comparing the carbon footprint of the blended products (i.e., blended cement using carbonated minerals, paper filler and rubber filler) to their reference products show that carbon footprint reductions of 7 – 197% are possible (Table 10). The highest emission reduction potential per tonne of material is to be found in the rubber industry where the rubber filler using carbonated mineral will prevent approximately 3 tonnes of CO_{2e} from being emitted compared to the conventional filler carbon black. As all applications have different market sizes (i.e., 4.1 billion tonnes of cement [47], 422 million tonnes of paper products [48] and 2.7 billion units of tires [49] are estimated to be produced annually), we roughly estimated the CO_{2e} emission reduction potential of using the proposed products. This estimation showed the highest potential for emission reduction through using carbonated mineral products lies in the cement industry, due to it having the biggest market volume among these sectors (Table 10) and can be an indicator to guide future research. But, since for these calculations we assume that carbonated mineral products can be used as

substitutes for all products in a similar matter (i.e., all conventional products have the same properties and same carbon footprint), in-depth life cycle assessments for the variety of products in each field of application will be necessary for accurate estimations of these potentials.

3.13.7. Costs of carbonated mineral products and their application

As an initial estimation for the costs, we calculated the production costs using the techno-economic model described in Strunge et al. [20]. Here, we consider the levelized cost of product which include the capital costs, operational costs as well as estimations for expected learning effects during the development of the full-scale process. We here calculated a levelised cost of the product of 119 €/t_{product}. We used these to compare them with the costs of the conventional products for each application. As emitting CO₂ in most sectors is already bound to carbon taxation or certification schemes like the European emission trading system (EU ETS), we included two scenarios one without any carbon tax or emission certificate scheme and one with a certificate price of 50 €/tCO₂. The European supreme court of justice acknowledged that producing precipitated CaCO₃ from CO₂ can be used as means to reduce the number of certificates a producer has to surrender [54]. While the initial ruling did not discuss the carbonation of peridotite, we here assume that it will be acknowledged in the future in a similar way. Hence, for the scenario with emissions certificates, emission reduction with carbonated minerals reduces the number of emission certificates that must be surrendered. The results are shown in Table 11. The calculation showed

Table 10

Results carbon footprint evaluation of carbonated mineral products. Assumptions and detailed results are shown in Tables S1–S2. *The conventional product for cement is CEM I 42.5 R with a clinker content of 100%. **The conventional product for paper filler is CaCO₃. ***The conventional product for rubber filler is carbon black. §Note the carbon footprint has been calculated on a gate-to-gate approach. Negative values mean that more CO₂ is stored than the GHG emissions are emitted during the carbonation process. #Global emission reduction potentials are based on current production volumes of the conventional product and the calculated carbon footprint reduction: ## only clinker is assumed to be replaced (cement has an average clinker content of 73.5% [50]); ### a maximum of 2.5% of filler is assumed in paper products [51]; #### based on the annual production of tires using 29% of filler [52].

| Product | Product description | Carbon footprint of conventional product [kgCO _{2e} /t] | Carbon footprint of product with carbonated mineral [kgCO _{2e} /t] | Carbon footprint reduction | Maximal global CO _{2e} emission reduction potential of product with carbonated mineral [MtCO _{2e} /a] [#] |
|----------------|------------------------------------------------------------------------------|------------------------------------------------------------------|-----------------------------------------------------------------------------|----------------------------|--------------------------------------------------------------------------------------------------------------------------------------|
| Blended cement | 5% carbonated material as filler, 95% conventional clinker | 850 * [50] | 794 | 7% | 170 ## |
| Blended cement | 20% carbonated material as main cement constituent, 80% conventional clinker | 850 * [50] | 625 | 27% | 681 ## |
| Paper filler | 100% carbonated material as filler | 286 ** [48] | -277 § | 197% | 6 #### |
| Rubber filler | 50% carbon black, 50% carbonated material as filler | 5700 *** [53] | 2712 | 52% | 23 #### |

Table 11

Results economic evaluation. Assumptions and detailed results are shown in [Supplementary Table 1 & 3](#). *The conventional product for cement is CEM I 42.5 R with a clinker content of 100%. **The conventional product for paper filler is CaCO₃. ***The conventional product for rubber filler is carbon black.

| Product | Product description | Without consideration of carbon tax or emission certificate | | | With consideration of carbon tax or emission certificate of 50 €/tCO ₂ | | |
|--------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------|-----------------------------------------------|----------------|-----------------------------------------------------------------------------------|-----------------------------------------------|----------------|
| | | Costs of conventional product [€/t] | Cost of product with carbonated mineral [€/t] | Cost reduction | Costs of conventional product [€/t] | Cost of product with carbonated mineral [€/t] | Cost reduction |
| Blended cement 5% | 5% carbonated mineral as filler, 95% conventional clinker | 63[50]* | 65 | -5% | 105 * | 106 | -1% |
| Blended cement 20% | 20% carbonated mineral as main cement constituent, 80% conventional clinker | 63[50]* | 74 | -18% | 105 * | 105 | 0% |
| Paper filler | 100% carbonated material as filler | 100[48]* ** | 118 | -18% | 114 * ** | 104 | 9% |
| Rubber filler | 50% carbon black, 50% carbonated material as filler | 1.100[55]* ** | 609 | 45% | 1385 * ** | 745 | 52% |

that without taking emission certificates into account, only the producing rubber filler might lead to lower costs compared to the reference product, with all other products increasing the costs 5 – 19%. However, with a price for emissions certificates of 50 €/tCO₂, which has been exceeded since summer 2021, the break-even point for the use of carbonated minerals as the main constituent of cement is reached. For applications in paper and rubber this certificate price leads to cost reductions of 8 – 52% compared to the conventional products.

4. Conclusions

Within the framework of this work, the potential of mineral sequestration of CO₂ for the production of possible substitutes was successfully demonstrated. During the separation of the reaction products from the unreacted feedstock or of the reaction products from each other, enrichments of the products, especially of the carbonate phases in the carbonated slag, was achieved. This separation led to strong improvements in application tests compared to untreated carbonated minerals (shown in [Figure S1](#)), but there are still many challenges and potentials that need improvements.

A high purity of the products in terms of the carbonate or amorphous silica content was achieved through classification with a classifying centrifuge. The middle fraction (2 – 11 μm) of the carbonated slag consists of about 80% calcite, up to 15% amorphous silica and small amounts of other phases. However, the recovery of the reaction products in the separation products is still very low. On the one hand, this is due to the reaction conversion of about 23% in the large-scale tests, which could be improved, but especially due to the lack of liberation of the particles to be separated. In SEM images, the surface of the unreacted material is occupied by amorphous silica and magnesite despite deagglomeration by attrition. To improve the separation, the liberation of the particles must be optimised or the precipitation on the reactive surface of the reactant must be prevented by process technology. A continuous process may not prevent precipitation, but additional agglomeration of the particles can be prevented if separation takes place continuously immediately after the reaction to return the unreacted material to the reactor.

We identified a large potential for cement substitutes due to the high CO_{2e} emissions in cement production. In the strength tests as a cement substitute depending on the material used, partially higher compressive strengths could be achieved than with the reference material, which confirms its potential use as a supplementary cementitious material. However, technical approvals for corresponding additives in cement would still be necessary for industrial use, as these materials do not belong to the cement constituents currently approved in EN 197-1 [26]. In addition, the proportions of heavy metals in the concrete and the leachability of these heavy metals must be assessed in detail and considered before final application.

In paper and rubber production, the carbonate-rich fractions of the carbonated separation products could also be successfully incorporated which is reflected in great potentials for utilization in these sectors. In the rubber sector, all the tests carried out were satisfactory and showed no major differences compared to the reference material. However, more extensive tests would have to be carried out to develop a marketable product. The basic incorporation of the fillers has been successful, but there are still challenges with regard to the degree of whiteness and the amount of incorporated filler. In addition, the carbonation product of peridotite in particular is sticky, which can lead to difficulties in paper formation. However, these challenges can be addressed by more extensive investigations, especially tests with further retention agents, so that it can be assumed that it is possible to use the carbonation product in the paper.

Finally, initial assessments of the costs and carbon footprint of producing carbonated materials were carried out, as the potential use of the material is determined by the costs and the potential CO₂ savings. In the production of blended cement, the carbon footprint can be reduced by up to 27% depending on the proportion of carbonated product. In rubber the reduction is 52% and in paper even up to 197%. In terms of mass, however, the reduction potential in cement is by far the greatest, with up to 681 MtCO₂/a that could be saved in the scenario presented.

The costs of substitution - except in rubber - are higher than for conventional products. Considering CO₂ certification at a current certificate price of 50 €/tCO₂, substitution in cement do not bear added costs, in paper and rubber the substitution of fillers might reduce costs by 9% and 52% respectively compared to the usage to conventional fillers (i.e., carbon black and CaCO₃).

Overall, the entire process of sample preparation, carbonation, and separation as well as the subsequent application was successfully carried out for both the selected primary and secondary material. The potential for use as a substitute in various areas of application was demonstrated, but this still needs to be optimised through further research to enable actual use.

Data Availability

The authors declare that the main data supporting the findings of this study are available within the article. Extra data are available in the [supplementary material](#) or from the corresponding author upon request.

CRediT authorship contribution statement

Dario Kremer: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. **Till Strunge:** Methodology, Formal analysis, Investigation, Visualization, Writing – original draft. **Jan Skocek:** Methodology, Formal analysis, Visualization, Writing – original draft. **Schabel:** Methodology, Formal analysis,

Visualization, Writing – original draft. **Melanie Kostka**: Methodology, Formal analysis, Visualization, Writing – original draft. **Christian Hopmann**: Supervision, Writing – review & editing. **Hermann Wotruba**: Supervision, Writing – review & editing, Validation, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflicts of interest

The authors declare no conflict of interest.

Additional Information

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2022.102067](https://doi.org/10.1016/j.jcou.2022.102067).

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