Carbonation –

Binding CO₂ permanently into products

4th Report of the Thematic Working Group on:

CO₂ capture and utilization

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About the CCUS Projects Network

The CCUS Projects Network comprises and supports major industrial projects under way across Europe in the field of carbon capture and storage (CCS) and carbon capture and utilisation (CCU). Our Network aims to speed up delivery of these technologies, which the European Commission recognises as crucial to achieving 2050 climate targets. By sharing knowledge and learning from each other, our project members will drive forward the delivery and deployment of CCS and CCU, enabling Europe’s member states to reduce emissions from industry, electricity, transport and heat.

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Executive summary

The present report depicts the state of the art of CO₂-carbonation process related to CCU. The aim of the report is to illustrate the potential to produce building materials like cement or concrete while permanently storing CO₂ in it. The report gives an introduction about the concepts as well as an overview of specific companies and projects in the field of CO₂-carbonation.

The production of cement, the binding element in concrete, is responsible for approximately 8% of the total global carbon dioxide emissions per year. Concrete is one of the most utilized resources on earth, with an estimated 26 billion tons produced annually worldwide. The share of the worldwide production volume of 4.1 billion tons of cement for Europe is only approx. 2%. The production is not expected to slow down significantly for at least two more decades. In order to achieve the climate goals formulated in the Paris Agreement, the cement industry is striving to find ways to significantly reduce emissions. To tackle this goal, it is important to understand which processes are responsible for the CO₂-emissions of cement production, as the largest part of the emissions is caused due to the process itself – two thirds of the emissions are process-related and one third fuel-related. The reduction of fuel-related emissions through use of alternative raw materials is a pathway to cut CO₂-emissions on this end. Promising options are the use of hydrogen as fuel or the electricity-based clinker production. However, changing the energy supply for running the processes is not sufficient to make the cement industry climate neutral. The process related emissions of the cement industry are considered as unavoidable, however, there are pathways to reduce them, such as clinker-efficient cements. Furthermore, CCS and CCU are options that need to be considered. In the area of CCU, CO₂-carbonation is particularly interesting in the cement industry, as not only CO₂ is bound in a product, but also Portland cement – the type of cement that is used the most - can be replaced.

Carbonation is a natural process that stores CO₂ permanently. The process is a reaction of CO₂ with calcium or magnesium and iron. While the natural process to form carbonates takes many years, CO₂-carbonation as technology pathway accelerates the carbonation process and cuts down the reaction time to minutes. CO₂-carbonation, also called CO₂-mineralisation, is in respect to CCU a concept that has attracted a lot of attention in science, business and politics in recent years. In contrast to most other CCU processes, the reaction itself is exothermic, thus there is no need to have a reaction partner that brings in the energy for the process.

CO₂-carbonation processes offer promising potential in many respects. On the one hand, CO₂ is converted into carbonates during the process and thus permanently stored, and products of the construction industry, such as cement and concrete, can be manufactured with a lower CO₂ footprint compared to the current state. The research and market entry and expansion of the above-mentioned processes are promising. Nevertheless, it is difficult to gain a foothold, especially in a "conservative" market such as the cement and concrete industry, towards new technologies. But still, there are some breakthroughs from some forerunner companies:

1 Climate protection in the concrete and cement industry, E. Bellmann, WWF, 2019

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The company **Carbon8 Systems** from the UK treats industrial wastes that contain calcium or magnesium with CO$_2$ to produce carbonates that can be used as lightweight aggregate, fertiliser, ready mix concrete, green roofing, or other building materials. In England, Carbon8 has installed three plants. The biggest plant is in Brandon, Suffolk, where Carbon8 produces aggregates with a capacity of 30,000 tonnes of APCr (Air Pollution Control residues - hazardous waste from municipal solid waste incineration) per year. Also a commercial contract was set up with the Vicat Group in 2020, where a cement plant in France is equipped with a Carbon8 container.

The German company HeidelbergCement is active in several R&D investigations to explore the potential of CO$_2$-carbonation. First outcomes of projects funded by the German Ministry of Education and Research (BMBF) show which minerals are most likely suitable for CO$_2$-carbonation in an economical way.

The Australian start-up Mineral Carbonation International (MCI) gained a lot of attention recently. In October 2021, MCI won the first prize out of 2700 competitors in a start-up competition for climate solutions at COP26 in Glasgow. Furthermore, the cleantech company was awarded with a 14.6 million USD grant by the Federal Government through the Ministry of Energy and Emissions Reduction in June 2021. In June 2021 as well, the Japanese ITOCHU Corporation invested 14.6 million USD as well.\(^2\) MCI’s stated goal is to scale the technology to capture and store 1 billion tonnes of CO$_2$ by 2040 in construction and industrial products for the circular economy. Following MCI’s recent grants, the investment will significantly advance MCI’s company growth with plans to be a global leader in removing CO$_2$-emissions from hard to abate industry sectors like steel, cement, mining and manufacturing.

Another important step for CO$_2$-carbonation was made by the German limestone producer Schäfer-Kalk GmbH. Schäfer-Kalk went to the European Court of Justice (ECJ) with regards the scope of the EU ETS. The outcome to the case showed, that the CO$_2$ emissions saved or bound in the products can be credited in the EU ETS. Since 2017, the ruling by the European Court of Justice has been legally binding, which allows the German company not to have to account for the CO$_2$ used for precipitated calcium carbonate in the lime industry via certificates. That might lead to a major advantage of CO$_2$-carbonation in general, if applied to other cases as well.

In general, CO$_2$-carbonation is a promising approach to use CO$_2$ for the production of products and to store the CO$_2$ for very long periods of time. As discussed, there have been initial commercial successes, but the extent to which it can be implemented on a widespread basis remains to be investigated.

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\(^2\) MCI-Website, visited on December 2\(^{nd}\), 2021, https://www.mineralcarbonation.com/

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Carbonation – Binding CO$_2$ permanently into products

1 Introduction

The production of cement, the binding element in concrete, is responsible for approximately 8% of the total global carbon dioxide emissions per year. Concrete is one of the most utilized resources on earth, with an estimated 26 billion tons produced annually worldwide. The share of the worldwide production volume of 4.1 billion tons of cement for Europe is only approx. 2%. The production is not expected to slow down significantly for at least two more decades. In order to achieve the climate goals formulated in the Paris Agreement, the cement industry is striving to find ways to significantly reduce emissions. To tackle this goal, it is important to understand which processes are responsible for the CO$_2$-emissions of cement production, as the largest part of the emissions is caused due to the process itself – two thirds of the emissions are process-related and one third fuel-related. The reduction of fuel-related emissions through use of alternative raw materials is a pathway to cut CO$_2$-emissions on this end. Promising options are the use of hydrogen as fuel or the electricity-based clinker production. However, changing the energy supply for running the processes is not sufficient to make the cement industry climate neutral. The process related emissions of the cement industry are considered as unavoidable, however, there are pathways to deal with them. For example, the reduction of process-related emissions can be reached through clinker-efficient cements. Furthermore, CCS and CCU are options that need to be considered. In the area of CCU, CO$_2$ carbonation is particularly interesting in the cement industry, as not only CO$_2$ is bound in a product, but also Portland cement – the type of cement that is used the most – can be replaced.

In the present report, CO$_2$-carbonation processes that belong to CCU-technologies where the goal is to bind CO$_2$ permanently in products are described and discussed. Carbonation is a natural process that stores CO$_2$ permanently. The process is a reaction of CO$_2$ with calcium or magnesium and iron. In other words, oxides, hydroxides and silicates react with CO$_2$ to form carbonates. Calcium and magnesium compounds are in basic and ultrabasic rocks like basalt, dunite (olivine) and serpentine. This natural process takes many years to form carbonates. CO$_2$-carbonation as technology pathway accelerates the carbonation process and cuts down the reaction time to minutes. CO$_2$ carbonation, also called CO$_2$ mineralisation, is in respect to CCU a concept that has attracted a lot of attention in science, business and politics in recent years. In contrast to most other CCU processes, the reaction itself is exothermic, thus there is no need to have a reaction partner that brings in the energy for the reaction.

In this report, the concept of CO$_2$-carbonation is described, and the most relevant stakeholders are introduced. Furthermore, a first prediction on how CO$_2$-carbonation can help to reduce the CO$_2$-emissions of the cement and construction industry is made.

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3 Climate protection in the concrete and cement industry, E. Bellmann, WWF, 2019

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1.1 Objective and scope

The present report focuses predominantly on CO₂-carbonation in respect to CCU. Within the report, the idea behind the concept will be described. Furthermore, the state of the art is described, and selected examples of companies and projects are presented.

The answers for the following questions shall help to understand and exploit the potential of CO₂-carbonation to reduce GHG-emission of the cement industry:

- What is CO₂-carbonation and what kind of processes are investigated?
- What is the difference between CO₂-carbonation and other CCU-processes?
- What is the state-of-the-art of CO₂-carbonation?
- What can be expected in the future from CO₂-carbonation?

Since CO₂-carbonation and CCS have more thematic overlap than other CCU-pathways and CCS, learning more about CO₂-carbonation can be of benefit for the members of the European CCUS Projects Network. Since most members of the network are CCS experts, the aim here is to show what is behind the topic and which synergy effects can be used.

1.2 Report structure

This report consists of the following main sections:

1. Introduction: Cement and concrete production

   Within the 1st chapter, the situation of the cement and concrete industry into the context of GHG-emission goals are described.

2. CO₂-Carbonation

   The 2nd chapter includes a description of the different technological CO₂-carbonation pathways.

3. Key stakeholders

   The 3rd chapter depicts the activities of the key stakeholders in the field of CO₂-carbonation.

4. Conclusion

   The most important massages of the report are summarized and discussed in the conclusion.
2 CO₂-carbonation concepts and processes

CO₂ can be bound with silicates and oxidic minerals into inorganic carbonates, which in turn can be used to produce building materials such as cement and thus also as a binder to produce concrete. As indicated in the introduction, the process behind it is called CO₂-carbonation and it occurs also naturally. The reaction time of the natural process lasts years, while new technology pathways show that the process can be accelerated to reaction times of minutes. Silicates and oxidic minerals can be found in various sources like industrial wastes such as contaminated soil, fly ashes or slag from steel making as well as basic and ultrabasic rocks like basalt, dunite (olivine) and serpentinite. Cement residues or crushed concrete can also be considered as a source of minerals. The recycling concept plays a major role here.

The three main carbonation reactions are the following:

- \[ \text{CO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \] (Carbonation of sodium hydroxide)
- \[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2 \text{NaHCO}_3 \] (Carbonation of sodium carbonate)
- \[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \] (Carbonation of calcium oxide)

The minerals are brought into contact with highly concentrated CO₂ in a reactor. All three reactions are exothermic, that means that energy is set free during the process. In other words, for the reaction itself, no further energy input is needed. This is a huge difference in comparison to most other CCU pathways, at least for bulk chemicals or fuels, where CO₂ needs a reaction partner that comes with a much higher energy content, such as hydrogen, to synthesise valuable products. Nevertheless, the supply of CO₂ (capture process) and the preconditioning of the minerals for the carbonation process like tumbling or grinding, are energy-intensive process steps. E.g. olivine reacts with CO₂ at high pressure and temperature (and therefore very fast). The reaction of minerals from industrial wastes with CO₂ is less energy intensive as the reaction happens at atmospheric pressure and no increased temperature is needed.

The process can be an opportunity for the construction industry, as it offers a promising way to use CO₂ as a material and lock it permanently in inorganic carbonates, which in turn can be used for building materials such as cement and thus also as a binding agent for the production of concrete. The reaction to inorganic carbonates seems like a sustainable sink of CO₂, as the carbonates formed remain stable over geological periods.

Furthermore, sodium carbonate, for example, belongs also to the group of inorganic carbonates (soda, fluxing agent in the glass industry, flotation and desulphurisation agent in iron and steel production, pulping and bleaching agent in the paper industry, tanning agent in leather production). Calcium carbonate (limestone) or potassium carbonate are used, for example, in pharmaceutical products. Production with CO₂ is already used today, but high demands are placed on the CO₂ purity due to the process itself.
3 Key stakeholders

In the following chapter, selected organisations are mentioned that have achieved success in the field of CO₂ carbonization and contribute to advancing the issue and the processes for various reasons. The list does not claim to be exhaustive; it is merely intended to provide an overview of the various areas and activities of CO-carbonization.

3.1 Carbon8 Systems

The company Carbon8 Systems from the UK treats industrial wastes, such as contaminated soil, slag from steel making, galigu from soap making, North Sea drill cuttings, cement kiln residues, water treatment sludges, (silt) sand, quicklime, quarry residues, ash, cement kiln dust or mining tailings that contain calcium or magnesium with CO₂ to produce carbonates that can be used as lightweight aggregate, fertiliser, ready mix concrete, green roofing, or other building materials. The patented process (WO 2007/096671 A1) Accelerated Carbonation Technology (ACT) offers a fast and, according to Carbon8, cheap way to process wastes and natural minerals. Carbonation takes place during a 15-minute process. Over 120 residue types were already tested, and mix designs developed. During the process, the reactants are carbonated by the process steps tumbling (rolling the material) and adding moisture and carbon dioxide. During the treatment, the reactive components of the medium to be carbonated are mechanically activated by thorough mixing. The reaction products are then removed to expose a new reactive surface.

According to Carbon8, three plants are installed in England. In Brandon, Suffolk, Carbon8 produces aggregates with a capacity of 30,000 tonnes of APCr (Air Pollution Control residues - hazardous waste from municipal solid waste incineration) per year. Another plant exists in Avonmouth near Bristol. Information on where the third plant is located could not be found. Also a commercial contract was set up with the Vicat Group in 2020. Here, a cement plant in France is equipped with a Carbon8 container. Furthermore, a plant is planned in Duiven near Rotterdam, NL. At the site, 100 tonnes of a building product will be produced in a pilot project for validation and use, with the possibility of using more CO₂ from the plant in the future. In Duiven, a so-called CO₂ntainer from Carbon8 Systems will use the CO₂ from the flue gases of an energy-from-waste (EfW) plant that would normally be emitted into the atmosphere.4,5

According to Carbon8, the products do not receive approval in Germany because some of the ingredients are classified as questionable by the German authorities in terms of their environmental compatibility. It is not known which ingredients are involved. Furthermore, it is not known whether the reasons for rejection concern the environmental impact, such as release rates or fly ash, or whether the building material does not meet the required quality. According to Deutsches Institut für Bautechnik, which is responsible for approvals of new types of building materials in the cement/concrete sector, no approval of Carbon8 has been applied for.

4 Carbon8 Systems Website, visited on December the 1st, 2021
5 Presentation by Dr. Paula Carrie, CCUS Projects Network meeting on 29th of November 2021

This project is financed by the European Commission under service contract No ENER/C2/2017-65/SI2.793333.
3.2 Mineral Carbonation International (MCi)

The company Mineral Carbonation International (MCi) from Canberra, Australia, is currently generating a lot of attention. The start-up has built a demonstration plant in Newcastle, which is rated at a technology readiness level (TRL) of 6. The company uses alkaline waste containing calcium or magnesium, which is processed through grinding, theming and a slurry process, with CO₂ captured and used from Orica’s ammonia plant. The CO₂ is blown through the industrial waste in a continuous reactor system. This produces products such as silica, carbonates and metal oxides that can be used in the construction industry. MCi’s stated goal is to scale the technology to capture and store 1 billion tonnes of CO₂ by 2040 in construction and industrial products for the circular economy.

In October 2021, MCi won the first prize out of 2700 competitors in a start-up competition for climate solutions at COP26 in Glasgow.

The cleantech company was awarded with a 14.6 Million Dollar grant by the Australian Federal Government through the Ministry of Energy and Emissions Reduction in June 2021. Furthermore, the company seeks for investors and has secured its first major cornerstone: In June 2021, the Japanese company ITOCHU Corporation invested 14.6 Million Dollar as well.⁶

3.3 HeidelbergCement

The German company HeidelbergCement is active in several R&D investigations to explore the potential of CO₂-carbonation. The German Ministry of Education and Research (BMBF) funded CO₂MIN and C²inCO₂ projects are worth mentioning here.

The project “CO₂MIN - CO₂ capturing through mineral raw materials - generation of marketable products with simultaneous sequestration of CO₂ from the cement industry” was running from 2017 to 2020. The aim of the CO₂MIN project was to find and characterise a possible feedstock for CO₂-mineralisation. The goal was to determine the optimal conditions for the maximum degree of carbonation of magnesium silicates and to evaluate applications of the product in the cement industry. Among others, the mineral olivine was evaluated, which occurs in many parts of Europe and Asia and is well suited for carbon dioxide binding. In Germany, only small amounts of mangesia-rich phases were found in basalt samples. This was the reason why other minerals went into the focus for Germany like secondary resources such as steel slags, fly ashes and filter ashes that show potential for CO₂ carbonation due to their high CaO content.⁷, ⁸ In CO₂MIN, primary input materials for the mineralisation were evaluated.

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⁶ MCi-Website, visited on December 2nd, 2021, https://www.mineralcarbonation.com/
⁷ Kelemen et al.

This project is financed by the European Commission under service contract No ENER/C2/2017-65/SI2.793333.
In the project “C\textsuperscript{2}in\textsubscript{CO}\textsubscript{2} - Calcium Carbonation for industrial use of CO\textsubscript{2}” secondary input material will be evaluated. C\textsuperscript{2}in\textsubscript{CO}\textsubscript{2} started in 2020. The main goal of the project is also to produce building materials with CO\textsubscript{2}. The basic idea is to exploit the carbonation reaction to which concretes are naturally exposed during their life cycle. Doing so, CO\textsubscript{2} can be firmly re-integrated as calcium carbonate in recycled concrete components. The hardened cement paste, which is a central component of concrete along with sand and gravel, plays a decisive role. The calcium present in this "RCP" (Recycled Concrete Paste) can bind CO\textsubscript{2} again. The basic prerequisite for this, however, is a proper separation of these concrete components in order to have the RCP as quantitatively and purely as possible as well as in powder form with a high surface area. Under these conditions, calcium and CO\textsubscript{2} can again form a stable, permanent bond. This "carbonated" continuously reinforced concrete pavements (cRCP) can then be reused as a cement constituent. The main task and innovation are the development of a process technology for the quantitative separation of the recycled concrete constituents with a focus on RCP as well as the development of a related process technology for the carbonation of this material. In addition, the properties of cements produced with this material, and ultimately of the resulting concretes, are largely uncharted territory.\textsuperscript{9}

CaO in concrete spontaneously binds CO\textsubscript{2} when in contact with air. Figure 1 depicts the process steps to produce concrete as well its life cycle. About 80\% of CaO remains available for CO\textsubscript{2} reduction in the demolished concrete phase. Thus, the recycling sand and aggregates as well recycled concrete paste represent a high potential for binding CO\textsubscript{2} and the creation of new products. The emissions from clinker production are used as a CO\textsubscript{2}-source.


This project is financed by the European Commission under service contract No ENER/C2/2017-65/SI2.793333.
Until 2022, the project will evaluate advanced concrete recycling, forced carbonation of concrete and novel concrete products with the resulting materials to demonstrate industrial scale applicability accompanied by a life cycle assessment (LCA).

3.4 Schäfer-Kalk

CCU processes are in general not applicable to save CO₂-certificates within the EU Emission Trade System (ETS). However, there is one exception.

The German company Schäfer Kalk GmbH & Co. KG in Hahnstätten captures CO₂ produced in a lime kiln and uses it in another plant for the production of calcium carbonate. Schäfer-Kalk claimed that the CO₂ that was passed on was chemically bound in the calcium carbonate and was not an "emission" because it was not released into the atmosphere. After the German authorities refused to grant an exemption from emissions trading, the company took legal action before the Berlin Administrative Court back in 2013. Due to doubts about the validity of the relevant EU regulation, the Administrative Court suspended the proceedings and referred them to the European Court of Justice (ECJ). The ECJ decided otherwise in a ruling on 19 January 2017, proving the lime producer right. The CO₂ that is transferred to another plant to produce calcium carbonate falls now also under emission trading and allows to deduct its emissions if they are used for the production of precipitated calcium carbonate in another plant, which must not be subject to emission trading. This is an important decision and regulation that could be of great benefit to all CO₂ carbonation processes. As a result, further cases need to be proofed to assess if those are applicable for the ruling as well.

4 Conclusion - The role of CO₂-carbonation in a carbon neutral future

CO₂ carbonation processes offer promising potential in many respects. On the one hand, CO₂ is converted into carbonates during the process and thus permanently stored, and products of the construction industry, such as cement and concrete, can be manufactured with a lower CO₂ footprint compared to the current state. The research and market entry and expansion of the above-mentioned processes are promising. Nevertheless, it is difficult for new technologies to gain a foothold, especially in a "conservative" market such as the cement and concrete industry. In order to be competitive, the products have to be cost-effective and of at least the same quality as conventional building materials. This requires a rethinking of "established" processes and production procedures. Cements with cRCP and concretes produced with it require adjustments in processing, e.g., about fresh concrete properties or in curing. The integration of such new binders into existing or new standards at national or international level is a challenge, especially in terms of the timeframe. The new technology pathways for separation and carbonation require high investments in the plant locations, supplemented by increasing costs for a novel, resource and environmentally friendly products. Increasing the awareness for the need for more climate friendly processes may lead to market acceptance over time, linked with the willingness of enterprises to accept the high investment costs through higher product prices, which is already the case in European pioneer countries such as the Netherlands or Scandinavia. The success of Carbon8 in Great Britain is another example for such a development.

HeidelbergCement stated that it is crucial for a successful implementation of the technology to have a rapid creation of the necessary framework conditions. Market conditions must be politically adapted
to redirect existing material flows and enable sustainable access to concrete demolition. Among other things, this means avoiding “downcycling” of the material or even final disposal in landfills. For example, approx. 80-90% of the construction and demolition waste generated in Germany is recycled, but this happens almost exclusively as so-called “downcycling”. Demolition material is only used as low-value material in road construction, earthworks or for backfilling. The construction waste thus returns to the material cycle predominantly in an inferior function. However, the goal should be high-quality recycling on as large a scale as possible. Therefore, a commitment to careful deconstruction could be considered. Furthermore, public authorities can contribute to evaluating and eventually updating and harmonising outdated regulations and standards. In order to ensure constant market demand and competitiveness, incentives for the use of recycled building materials and CO₂-carbonated materials may be created for customers. CO₂ capture and utilization can be scaled up and made competitive through the creation of CO₂ transport infrastructures and incentive systems.

Following recent CCUS grants, the investment will significantly advance CO₂-carbonation processes and some companies will growth to a point, where the amount of the removed CO₂ emissions from hard to abate industry sectors like steel, cement, mining and manufacturing may become relevant. Furthermore, as the Schäfer-Kalk case showed, a major advantage of CO₂-carbonation can be that the CO₂ emissions saved or bound in the products can be credited in the EU ETS. Since 2017, the ruling by the European Court of Justice has been legally binding, which allows the German company not to have to account for the CO₂ used for precipitated calcium carbonate in the lime industry via certificates. Overall, the CO₂-footprint assessment must take into account that mineralisation also may require energy-intensive processes for preparation, such as grinding and reaction at high temperatures. Nevertheless, this area of CO₂-use is considered to have a very high potential, as cement is the most used material worldwide, but the potential of CO₂-carbonation processes depends on the available and accessible minerals as well of a sufficient CO₂ supply.
5 Glossary of abbreviations and units

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</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>LCA</td>
<td>Life cycle assessment</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Sodium bicarbonate</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>MCi</td>
<td>Mineral Carbonation International</td>
</tr>
<tr>
<td>RCP</td>
<td>Recycled concrete paste</td>
</tr>
<tr>
<td>TRL</td>
<td>Technology readiness level</td>
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