

LIME AS A NATURAL CARBON SINK

Examples of mineral carbonation in lime applications



TABLE OF CONTENT

INTRODUCTION	3
LIME AND ITS APPLICATIONS	4
THE LIFECYCLE OF LIME	6
EXPLORING THE BENEFITS OF CARBONATION	8
EXAMPLES OF CARBONATION IN APPLICATIONS OF LIME	11
CONCLUSION	14
ANNEXES	15
Steel	
Lime mortars	
Hemp lime	
Drinking water	
Flue gas treatment	
Pulp and paper	
Aluminium	
DEFINITIONS	30
ABOUT EULA	32

INTRODUCTION

Each year over 20 million tonnes of lime, in various forms, are produced in Europe. As an abundant and multifunctional material, lime is required for many processes, from producing iron and steel to providing society with clean drinking water. It acts as a purifying agent and captures pollution in the most extreme industrial environments, while it is also useful for processing food and enhancing soils. Lime is therefore essential for society.

The production of lime involves heating limestone (CaCO_3) to transform it into high purity quicklime (CaO), releasing carbon dioxide (CO_2) as part of the chemical reaction – called ‘process CO_2 ’. This means lime production is inherently a carbon-intensive process. The European lime sector (represented by the European Lime Association – EuLA) acknowledges it has an important role to play in the European Union’s ambition to become carbon neutral by 2050 and is fully committed to the Green Deal objectives [1].

The lime sector is contributing to this transition by shifting towards lower carbon fuels and by increasing the energy efficiency of production processes. This will reduce emissions from fuel combustion. However, fuel emissions account for less than a third of the total amount of CO_2 released during production. The remaining CO_2 emissions are process CO_2 which cannot be avoided. Carbon capture and utilisation or storage

are necessary to eventually make lime production carbon neutral by addressing CO_2 emissions at source. These technologies are still in development and currently not commercially viable.

And yet, there is an important property of lime that is still to be fully documented or implemented in calculating the carbon footprint of the lime sector. Lime captures ambient CO_2 as it reverts to limestone, a natural process known as carbonation (or mineralisation by carbonation).

The extent to which this happens in practice depends on how lime is used. Studies show that in applications like purifying drinking water, the carbonation rate amounts to 100 %, meaning the full amount of process CO_2 generated during lime production, is captured when this lime is used to produce drinking water. This CO_2 is permanently captured and is not released to the atmosphere as the lime has reverted to limestone – CaCO_3 .

In this document, we, EuLA, present the results of a literature review by Politecnico di Milano (PoliMI), that considered the available data on carbonation rates in various uses of lime. Their findings show that on average 33% of the amount of process CO_2 emitted during the production of lime is captured via carbonation.



LIME AND ITS APPLICATIONS

An essential enabler

Lime is one of those usually unseen products that has a profound effect on our daily lives. It is used in numerous industrial processes including steel manufacturing, building/construction, food industry, agriculture, and many environmental applications to name just a few. It has been used all throughout history, such as when the Romans used lime mortar to build their empire. Today its versatile and unique characteristics help the construction and manufacturing industries optimise their products and it plays an important role in farming, food production and water treatment.

Lime is often used as a mortar in construction, taking advantage of its workability when wet and its natural carbonation and hardening back into limestone as it sets. This process is especially valuable in the restoration of heritage buildings. Modern forms of mortars mix lime with other compounds that accelerate binding. Similarly, a combination of lime and the woody core of hemp plants is used to form hemp lime.

In many modern applications industrial lime is used as a basic or alkaline compound to neutralise acidity or sequester acidic impurities. This is most notably the case in the iron and steel industry, where lime binds to acidic elements during the smelting process to remove impurities by forming slag. Lime was used to tackle acid rain at the end of the last century and it is still used to clean acids from the flue gas of industrial and power plants. During aluminium production lime is used in a caustic mixture to dissolve bauxite (aluminium ore).

Lime is used to purify and soften drinking water and to treat wastewater and sludge. For some applications, lime is suspended in water and combined with CO₂ to manufacture different forms of so called Precipitated Calcium Carbonate (PCC), essentially purified limestone. This is used as a pigment or filler in materials such as paper and paint.



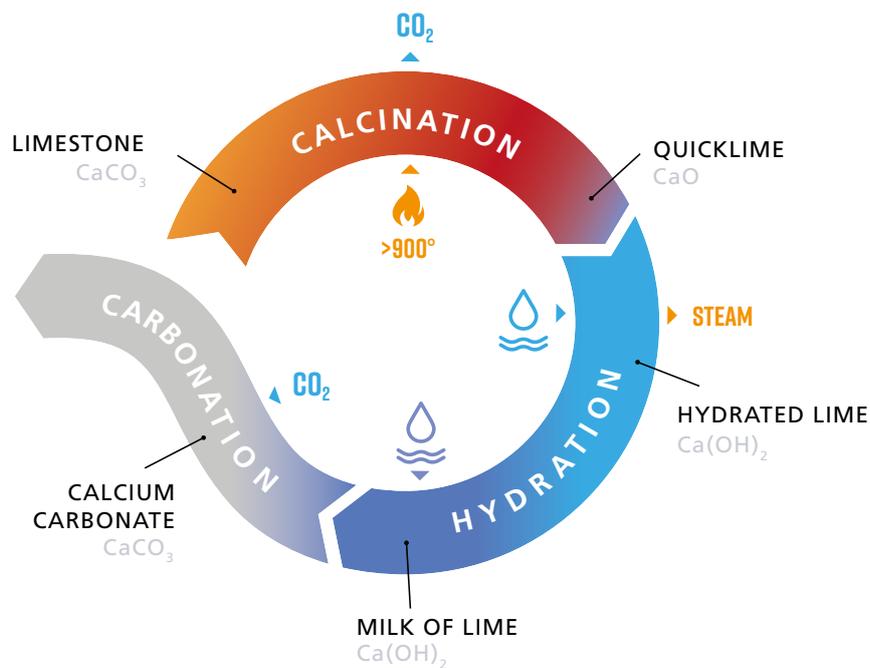


THE LIFECYCLE OF LIME

Lime product stages

The lime cycle is central to the many applications of lime. It allows us to convert the limestone we quarry as a basic resource, into a diverse family of products including

quicklime, hydrated lime and its suspension in water - milk of lime. Each of these products are used in a variety of different ways.



Process CO₂

Producing lime is a carbon intensive process due to the release of CO₂ from the limestone, called 'process CO₂'. Burning fuel to generate the required heat also emits CO₂, called 'combustion CO₂'. Generally, process CO₂ accounts for more than two thirds of CO₂ emissions from the European lime sector, whereas combustion CO₂ makes up less than a third. While the emission of combustion CO₂ can be reduced as much as possible by moving towards more CO₂ neutral energy sources, this cannot be done for process emissions, as these are an inherent part of the chemical reaction which produces lime.

Lime as a natural carbon sink

Lime naturally reverts to limestone by capturing ambient CO₂. This is called carbonation (or mineralisation by carbonation) and is essential to many uses of lime. For example, mortars containing lime capture CO₂ from the atmosphere, which reacts with the lime to produce calcium carbonate crystals. This is why lime mortars harden over time. Pure

lime is often called air lime in opposition to hydraulic lime that sets in water. The calcium carbonate crystals are larger than the lime and they form in available spaces, such as cracks, and grow, thereby sealing the cracks. This 'self-healing' characteristic reduces water penetration and increases the durability of mortars.

Carbonation rate

The carbonation rate of an application describes the amount of CO₂ that is captured as a percentage of the process CO₂ emitted during the manufacturing process. Drinking water treatment (water softening) for example has a carbonation rate of 100%. In this application, lime is purposefully exposed to CO₂ in order to precipitate as calcium carbonate. As all the lime present in the water is precipitated, it captures an amount of CO₂ equal to the process CO₂ emitted during its manufacturing. In steel production, lime is used to remove impurities, which are not CO₂, and so this application has a lower carbonation rate that occurs after the steelmaking process itself.



EXPLORING THE BENEFITS OF CARBONATION

A lot of studies have been conducted and published in the recent past on permanent CO₂ capture thanks to lime properties. To accurately assess the carbon footprint of the lime sector, we need to account for the amount of CO₂ that is captured by lime when it is used in different applications. This requires data on the carbonation rate for all major uses of lime and their respective shares of the total lime sector.

To address this knowledge gap, in 2018, EuLA commissioned Politecnico di Milano (PoliMi) to conduct a literature review of peer-reviewed research on carbonation of lime [2]. PoliMi assessed the natural and enhanced carbonation (see later) in various lime applications, considering the quantity

and reliability of the available information and data.

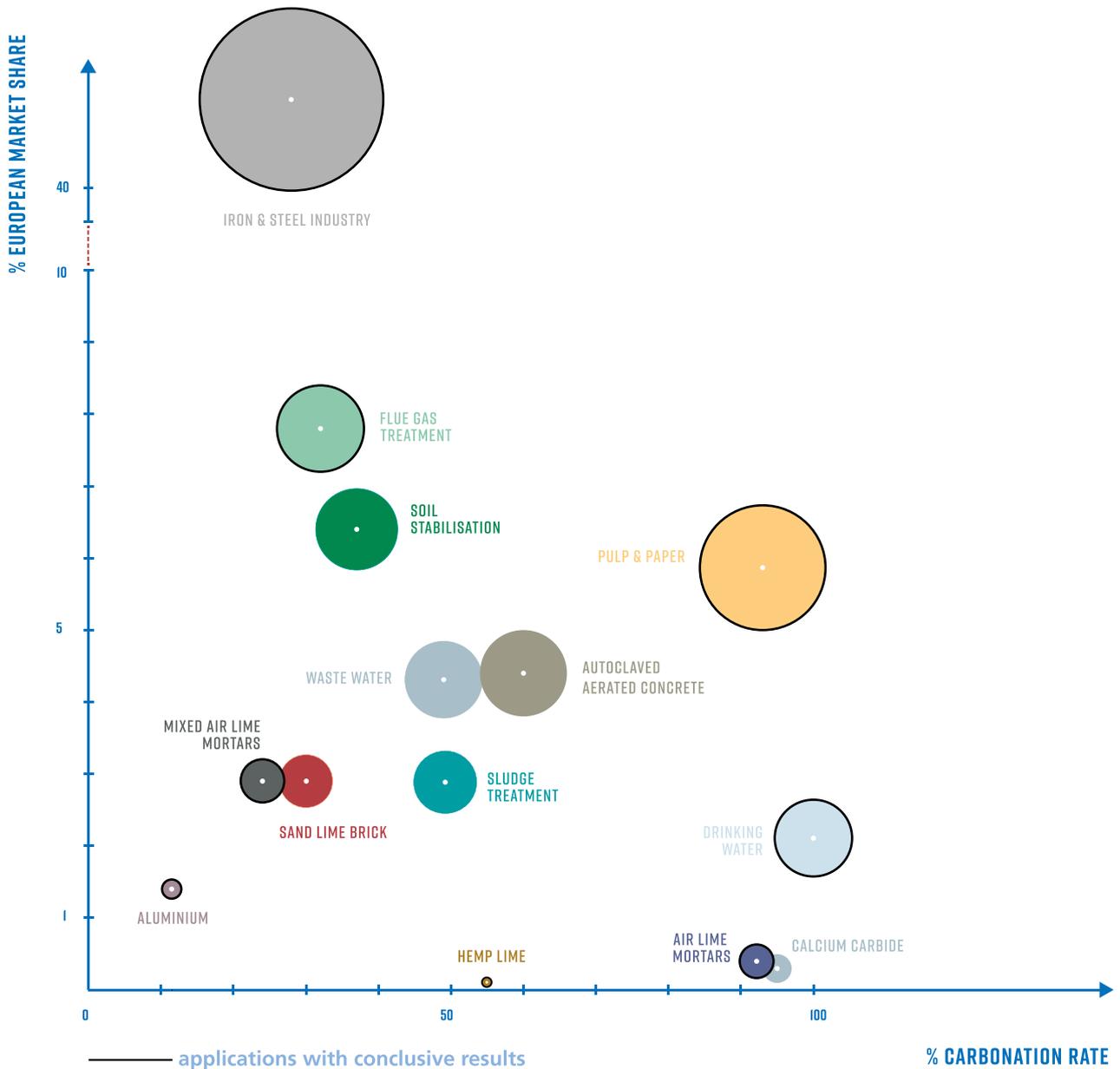
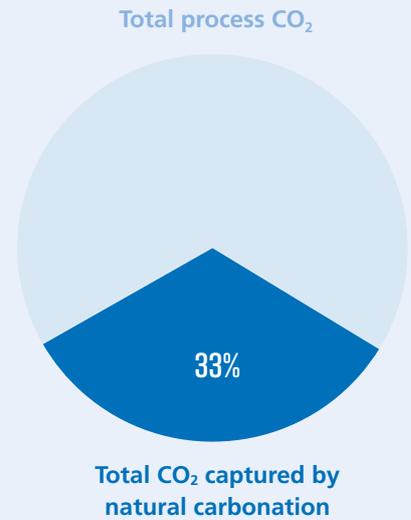
What do we know for certain?

For eight applications, there is conclusive scientific information about the rate of carbonation. These are referred to as the 'conclusive applications'. They include the largest and second largest uses of lime: the iron and steel manufacturing and flue gas treatment. Together the eight applications capture 23% of the total process CO₂ emissions of European lime production. For six other common applications there are fewer data available, but they suggest the capture of an additional 10% of the European lime process CO₂ emissions.

The natural carbonation rate of the European lime sector could be on average 33% of the process CO₂ emissions initially generated by the production of lime.

Natural carbonation of lime captures on average 33% of the amount of process CO₂ emitted during production

The graph below shows the amount of CO₂ captured by natural carbonation. For each application, the area of the circle represents the amount of CO₂ captured, as a percentage of total process CO₂ emitted during production of lime for the European market.



Enhancing carbonation

Carbonation happens naturally as a result of the lime in use. In some cases it is possible to adjust how the lime is used in order to maximise the carbonation rate. This is often best achieved by maximising the contact between the lime and the CO₂, both in terms of surface area, CO₂ concentration, pressure, and time. Other options include: improving the process efficiency, adjusting the ratio of lime to reactants or minimising impurities and controlling the relative humidity, acidity and temperature of the reaction.

PoliMI has collected information that demonstrates a combined carbonation potential of around 40% of process CO₂ emissions when applying natural and enhanced carbonation techniques.

Carbonation timeframe

When lime is used in flue gas treatment, to treat drinking water or in the production of pulp and paper, carbonation occurs instantaneously. In the iron and steel industry, carbonation occurs during the open-air storage of slags, typically lasting between 3 and 6 months. Lime used in various construction materials, such as mortars and hemp lime, will carbonate gradually during the lifetime of the building.

While large differences exist in the carbonation timescales for different applications, most of the carbonation reactions occur within the first year.

Carbonation is permanent

CO₂ capture via carbonation is permanent, as a large amount of heat energy is required to release it again. In other words, without remanufacturing into lime, the CO₂ remains permanently locked-up.

Lime can therefore truly be considered as a permanent carbon sink.



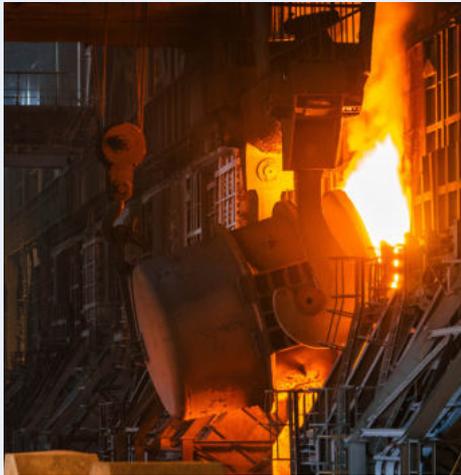


EXAMPLES OF CARBONATION IN APPLICATIONS OF LIME

On the next page we present examples of lime applications where conclusive data on carbonation is available. A more detailed assessment was made by PoliMi [2]. The annexes included at the end of this brochure provide additional information from their work. The following pages describe the role lime plays in each of these conclusive applications and indicate when and how natural carbonation takes place. For each application we provide the following data:

- **Carbonation rate:** the CO₂ captured during use, expressed as a percentage of the process CO₂ emitted during the manufacturing of lime for that application.
- **Enhanced carbonation rate:** indicating the carbonation rate(s) that can be achieved by implementing additional measures aimed specifically at maximising carbonation.
- **Relevant publications:** the number of publications that contain credible data for an application, compared to the total number of publications assessed for that application.

STEELMAKING



Use: lime neutralises acid-forming elements, removes impurities, enables foamy slag in EAFs, and protects refractories
Natural carbonation: occurs during open air storage of steel slag over 3-6 months
Carbonation rate: 5 - 28%
Enhanced carbonation rate: 39 – 56%
Relevant publications: 55 out of 72 assessed

HEMP LIME



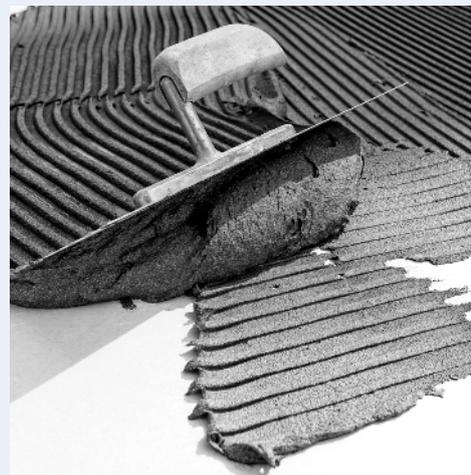
Use: Air lime mixed with hemp shiv to create bricks or cast walls, which harden by carbonation
Natural carbonation: during lifetime of the building
Carbonation rate: 55%
Enhanced carbonation rate: 65%
Relevant publications: 9 out of 15 assessed

AIR LIME MORTARS



Use: air lime mixed with aggregates to create a mortar, which hardens by carbonation to become limestone
Natural carbonation: during lifetime of the building
Carbonation rate: 80% – instead of to as the others 92%
Enhanced carbonation rate: 92%
Relevant publications: 21 out of 100 assessed

MIXED AIR-LIME MORTARS



Use: Air lime mixed with a co-binder and aggregates. The hydrated lime will set by carbonation to limestone, while the co-binder sets in another reaction, often by hydration
Natural carbonation: during lifetime of the building
Carbonation rate: 20 - 23%
Enhanced carbonation rate: 23%
Relevant publications: 27 out of 90 assessed

DRINKING WATER



Use: hydrated lime precipitates calcium, removes impurities and regulates acidity
Natural carbonation: CO₂ is dissolved in water in the form of bicarbonates and gets precipitated with the calcium
Carbonation rate: 100%
Enhanced carbonation rate: 100%
Relevant publications: 2 out of 14 assessed

FLUE-GAS TREATMENT



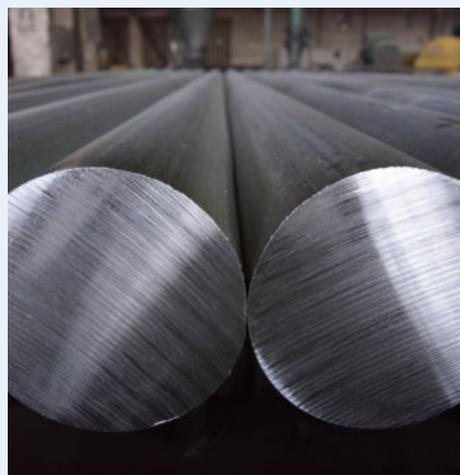
Use: hydrated lime reacts with acid gases from industrial plant emissions
Natural carbonation: free lime reacts with CO₂ in emission gasses
Carbonation rate: 32%
Enhanced carbonation rate: 59 – 64%
Relevant publications: 23 out of 39 assessed

PULP AND PAPER



Use: hydrated lime is precipitated into different forms of calcium carbonate
Natural carbonation: CO₂ is added during the process to induce precipitation
Carbonation rate: 93%
Enhanced carbonation rate: 100%
Relevant publications: 26 out of 41 assessed

ALUMINIUM



Use: quicklime or hydrated lime is used in a mixture to dissolve bauxite
Natural carbonation: free lime reacts with atmospheric CO₂ during storage of residue
Carbonation rate: 12%
Enhanced carbonation rate: 12%
Relevant publications: 13 out of 52 assessed

CONCLUSION

On average 33% of the amount of all process CO₂ emitted during production of lime in Europe is captured through carbonation during use and by using specific techniques this could even be 40%.

It is important to note that this carbonation mostly occurs within the first year.

As this CO₂ is permanently captured, this should be considered when calculating the sector's carbon footprint.

Clearly defining and accounting for the role of lime in CO₂ removal and permanent storage will allow the European lime sector to be a strong partner in a shared ambition

for a carbon neutral Europe, while remaining competitive within a global market.

EuLA is fully committed to the vision of a carbon neutral Europe by 2050, realising it will require both technological innovations and a robust regulatory framework. We believe a proper accounting of the carbonation occurring through widespread uses of lime is an integral part of this framework.

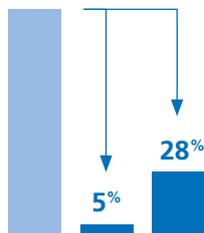
EuLA is developing research topics to generate additional data on natural and enhanced carbonation for those applications where the currently available data or scientific research do not lend themselves to robust conclusions. This will allow even more detailed accounting of carbonation resulting from the use of lime.

REFERENCES

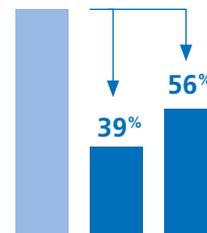
1. EC. 2019. Communication by the Commission on the green deal. COM(2019) 640 final. Brussels. https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal/actions-being-taken-eu_en
2. Grosso M., Biganzoli L., Campo F. P., Pantini S., Tua C. 2020. Literature review on the assessment of the carbonation potential of lime in different markets and beyond. Report prepared by Assessment on Waste and Resources (AWARE) Research Group at Politecnico di Milano (PoliMI), for the European Lime Association (EuLA). Pp. 333.
 - Campo F. P., Tua C., Biganzoli L., Pantini S., Grosso M. 2021. Natural and enhanced carbonation of lime in its different applications: A review. Submitted in Environmental Technology Journal.



ANNEXES



NATURAL CARBONATION RATE
GRADUAL INCREASE OVER TIME



ENHANCED CARBONATION RATE
GRADUAL INCREASE OVER TIME

Natural carbonation rate from 5-28% (<1 year) during storage of steel slag
Enhanced carbonation rate from 39% to 56% (< 5 years) during storage of steel slag

FACTORS THAT INFLUENCE CARBONATION RATE

Natural carbonation of lime in steel-making is affected by

- Exposed surface area of steel slag piles
- Low pile porosity prevents contact with CO₂

Enhanced carbonation rate is affected by

- Composition of the steel slags
- Particle size and surface area in contact with CO₂

Use of lime in iron and steel production

The presence of calcium compounds in the steel slag is a consequence of the use of lime (CaO) or limestone (CaCO₃) during the iron and steel making processes. Lime is used in the hot metal desulphurisation processes as well as in the Basic Oxygen Furnace (BOF) and Electric Arc Furnace (EAF) processes. It acts as a fluxing agent to create an alkaline slag that can protect the refractories, neutralise acid-forming elements and remove sulphur, phosphorous, silica and alumina inclusions.

Lime is also used in a broad variety of secondary metallurgical processes for the removal of additional impurities and to prevent the reabsorption of impurities from the slag. In addition, it can be used together with other materials, such as fluorspar, to form a synthetic slag, which is used as a flux to remove additional sulphur during the steel refining process.

In the pig iron production process, lime is used far less often. Here it is mixed with limestone in a proportion of 1:6, mainly in the sintering process.

Carbonation process

Natural carbonation occurs during the open-air storage of steel slag, as the hydrated lime $\text{Ca}(\text{OH})_2$ in the slag reacts with the atmospheric CO_2 . $\text{Ca}(\text{OH})_2$ is the result of the complete hydration of free CaO remaining in the slag.

This hydration is required for recycling slag as a construction material and takes place through open-air exposure of slag piles, usually for 3-6 months. In iron slag carbonation is considered negligible even after 100 years.

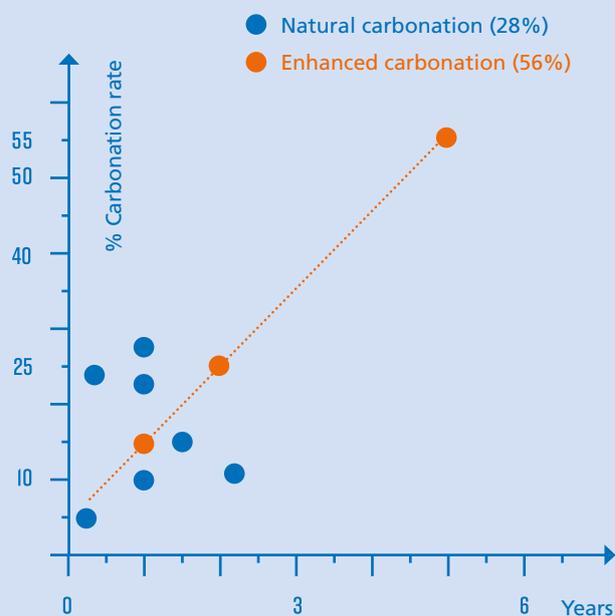
Carbonation timeframe

The carbonation over time of lime in steel slag follows the equation below.

Carbonation rate

- For the first 5 years:
= $0.0085\sqrt{\text{number of days}}$
- After the first 5 years: 39%

According to the equation, the minimum enhanced carbonation rate of 39% is reached after 5 years. The value is slightly overestimated, considering that 2/3 of the free lime in steel slag reacts within the first 5 years. Whereas carbonation of calcium silicates and calcium aluminates takes more than 5 years, reaching a final carbonation degree of only 1/3. Thus, 39% can be considered as a theoretical maximum natural carbonation rate, usually reached after more than 5 years. Since the surface of the slag pile is less porous once carbonated, the CO_2 diffusion decreases over time.



Steel slag

Literature assessed: 72

Publications with relevant and reliable information and data: 34

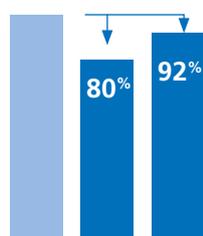
Iron slag

Literature assessed: 72

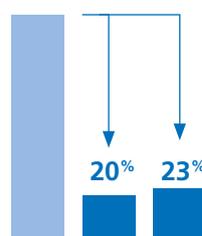
Publications with relevant and reliable information and data: 21



LIME MORTARS



AIR LIME MORTAR
GRADUAL INCREASE OVER TIME



MIXED AIR LIME MORTAR
GRADUAL INCREASE OVER TIME

NATURAL CARBONATION RATE

Natural carbonation rate is affected by depth of the mortar

Lime is expected to carbonate from 0 to 191 mm below the mortar surface over 100 years

Use of lime as mortar

Lime mortars have been used since ancient times.

Air lime mortars are made of hydrated lime ($\text{Ca}(\text{OH})_2$).

Mixed air lime mortars are a mix of lime and other compounds to accelerate binding, e.g. Portland cement.

Carbonation process

Air lime mortars harden as a result of their exposure to atmospheric CO_2 , forming calcium carbonate (CaCO_3). Thus, carbonation is part of the hardening and self healing process of air lime mortars.

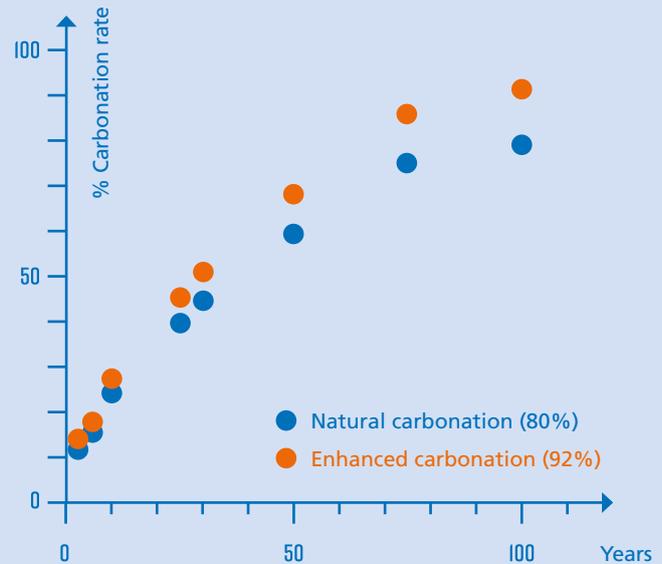
In **mixed air lime mortars** the hydrated lime will set by carbonation to limestone, while the co-binder sets in another reaction, often by hydration

Carbonation timeframe for air lime mortars

Natural carbonation rate over time for air lime mortars follows the assumed equation:

$$[CR=NCR \cdot K \cdot \sqrt{t}/depth]$$

- **CR** = carbonation rate (%)
- **NCR** = natural carbonation rate (80-92%)
- **t** = time expressed in days
- **K** = the carbonation constant equal to $1 \text{ mm}/\sqrt{\text{day}}$
- **depth** = the application thickness that carbonates after 100 years (191 mm)



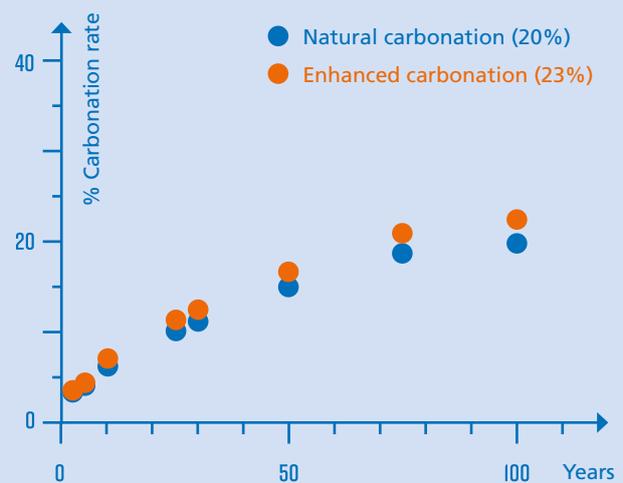
Carbonation timeframe for mixed air lime mortars

Natural carbonation in mixed air lime mortars is affected by the substitution rate of Portland cement, which reduces porosity. This in turn decreases the carbonation rate to one quarter of air lime mortars.

Assumed equation:

$$[CR=NCR \cdot K \cdot \sqrt{t}/depth]$$

- **CR** = carbonation rate (%)
- **NCR** = natural carbonation rate (80-92%)
- **t** = time expressed in days
- **K** = the carbonation constant equal to $1 \text{ mm}/\sqrt{\text{day}}$
- **depth** = the application thickness that carbonates after 100 years (191 mm)



Air lime mortar

Literature assessed: 100

Publications with relevant and reliable information and data: 21

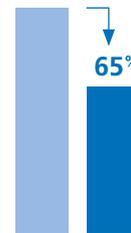
Mixed air lime mortar

Literature assessed: 90

Publications with relevant and reliable information and data: 27



NATURAL CARBONATION RATE
GRADUAL INCREASE OVER TIME



ENHANCED CARBONATION RATE
GRADUAL INCREASE OVER TIME

Carbonation rate is affected by

- Binder composition
- Contact with CO₂

Use of hemp lime as construction material

Hemp lime construction materials are mainly used in France and the United Kingdom, where most publications originate from. Hemp lime material is made with hemp shiv, the chopped

woody core of the stalks of the hemp plant. This is mixed with an air lime binder with pozzolanic cementitious or hydraulic lime additives and in some cases surfactants.

Carbonation process

The air lime binder is hydrated lime (Ca(OH)₂). During the use phase of the hemp lime construction material, the hydrated lime carbonates

by reacting with atmospheric CO₂ forming calcium carbonate (CaCO₃). The literature review shows the natural carbonation rate is 55%.

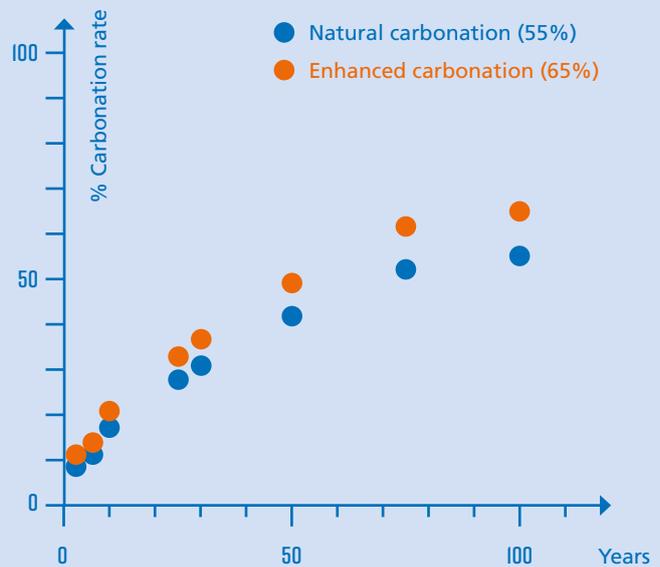
Carbonation timeframe

This occurs to a depth of 50 mm, where lime is fully carbonated after 91 days. Thus, the carbonation constant which measures the advance of carbonation depth over time is equal to 5.24 mm/ $\sqrt{\text{day}}$ given by the ratio of 50 mm over the square root of 91 days.

Natural carbonation rate in time for hemp lime follows the assumed equation:

$$[CR = NCR \cdot K \sqrt{t} / \text{depth}]$$

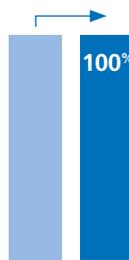
- **CR** = the carbonation rate (%)
- **NCR** = the natural carbonation rate (55%)
- **T** = time expressed in days
- **K** = the carbonation constant equal to 5.24 mm $\sqrt{\text{day}}$
- **Depth** = 1001 mm, the application thickness which carbonates after 100 years



Hemp lime

Literature assessed: 15

Publications with relevant and reliable information and data: 9



NATURAL CARBONATION RATE
INSTANTANEOUS

Carbonation rate is affected by

- Low solubility of calcium carbonate and magnesium hydroxide
- Addition of coagulants and flocculating agents to accelerate the process
- Addition of inert fine particles, such as sand or previously precipitated CaCO_3 , to act as nucleation centres, increasing the reaction speed

Use of lime in treating drinking water

Lime is used in the drinking water sector for many applications such as softening, pH adjustment, acid neutralisation, metals removal, alkalinity adjustment or removal of fluoride,

phosphate, sulphate and nitrogen. One of the main applications is water softening, which aims to reduce the hardness of raw water (i.e. calcium and magnesium bicarbonates), reduce alkalinity and remove silica to avoid undesirable effects of scaling.

Carbonation process

The hard water is softened by using hydrated lime (Ca(OH)_2) to precipitate the dissolved calcium and magnesium as insoluble calcium carbonate and magnesium hydroxide, respec-

tively. After sedimentation or settling these insoluble compounds are removed by filtration. Lime used in water softening is considered fully carbonated, because CaO and Ca(OH)_2 are absent in the obtained by-product containing calcium in the form of carbonate (CaCO_3)

Carbonation timeframe

The natural carbonation rate in time for drinking water is not reported in the assessed literature. It is presumably instantaneous, meaning that

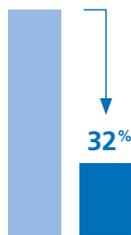
100% of the amount of process emissions are absorbed during the use phase for the drinking water application.

Drinking water

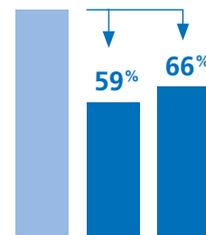
Literature assessed: 14

Publications with relevant and reliable information and data: 2

FLUE GAS TREATMENT



NATURAL CARBONATION RATE
INSTANTANEOUS



ENHANCED CARBONATION RATE
INSTANTANEOUS

Carbonation rate is affected by

- Flue Gas characteristics (composition, temperature...)
- The formation of an outer layer of calcium compounds, characterized by low porosity, which inhibits CO₂ diffusion
- The flue gas treatment process impacts the carbonation rate: suboptimal design can lead to a higher specific dosage for acid removal (higher stoichiometric ratio), this increases the potential reaction with the CO₂ from flue gas and thus the natural carbonation

Carbonation rate is affected by

- Temperature:
 - 20-30°C for aqueous-based carbonation
 - above 350°C for gas-solid carbonation
- L/S ratio for aqueous base carbonation
 - 0.2-0.3 L/S ratio for optimal carbonation
- Presence of SO₂
 - SO₂ will clog pores in the Air Pollution Control Residue and reduce carbonation

Use of lime in flue gas treatment

Lime is used for removing the acid gases (HCl, SO_x, HF) contained in flue gases generated from combustion plants: fossil fuel power plants, biomass combustion and waste incineration facilities. A flue gas treatment process can be semi-dry or dry, depending on the form of lime used.

In (semi-)wet processes, lime is supplied as an aqueous solution or suspension, i.e. as milk

of lime or as lime slurry (Ca(OH)₂). During the reaction with the flue gas in wet processes, the reaction produces a slurry to be treated. While in semi-wet processes, the water evaporates and the reaction products are dry. In (semi)-dry processes, hydrated lime (Ca(OH)₂) powder is directly supplied as sorbent. For both processes the reaction products are separated in a conventional dedusting unit (typically a baghouse filter).

Carbonation process

During the flue gas treatment, lime reacts with HCl, HF and SO_x but also with CO₂, forming calcium carbonate.

Due to the short contact time between the lime sorbent and the pollutant gas, typically in the range of a few seconds, and the kinetic limits of the chemical reactions, lime is supplied in excess to the anticipated acid gases, commonly to a stoichiometric ratio of 1.3 to 2.5. As a result, the solid residues generated by the process, referred to as Air

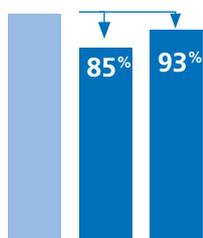
Pollution Control Residues (APCR), contain some amounts of free lime available for carbonation.

Enhanced carbonation of APCR has been largely proposed as a technology to improve their chemical stability and their leaching behaviour before their final disposal or recycling. Furthermore, enhanced carbonation of APCR allows for a contextual CO₂ sequestration directly at a CO₂ point source emission where these residues are generated.

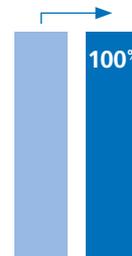
Flue gas treatment

Literature assessed: 39

Publications with relevant and reliable information and data: 23



NATURAL CARBONATION RATE
INSTANTANEOUS



ENHANCED CARBONATION RATE
INSTANTANEOUS

Carbonation rate is affected by

- The rate of dissolution of calcium hydroxide in the slurry.
- Pressurisation of the carbonation reaction
- Use of specific additives

Use of lime in pulp and paper production

Precipitated Calcium Carbonate (PCC) is largely used as a coating pigment or filler in pulp and paper but also in other industrial applications. PCC is produced chemically by combining carbon dioxide (CO₂) with lime (CaO) under controlled operating conditions. Hydrated lime slurry is put in contact with flue gases containing CO₂, leading to re-carbonation of the lime. Thus, calcium carbonate reforms, and being insoluble in water, it precipitates. Separation of impurities from the

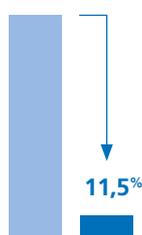
lime slurry is used to ensure high purity PCC.

The precipitation can produce each of the three crystalline forms (calcite, aragonite, and vaterite) depending on the reaction conditions. PCC characteristics can be tailored by regulating: the temperature, the CO₂ concentration and flow rate, the stirring rate, the particle size, the concentration of the hydrated lime slurry and the use of additives.

Pulp and paper

Literature assessed: 52

Publications with relevant and reliable information and data: 13



NATURAL CARBONATION RATE

TIMEFRAME NOT REPORTED IN THE ASSESSED LITERATURE

Natural carbonation is affected by

- Red mud composition
- Exposure time since dissolution of Ca-bearing minerals typically present in the red mud
- The amount of stirring during storage of red mud and consequently the number of surfaces exposed to atmospheric CO₂

Use of lime in aluminium production

Lime is used in the Bayer process, the principal means of refining bauxite ore for alumina extraction. During the Bayer process, bauxite is digested in a caustic liquor including lime. This process produces two output streams: a liquor rich with alumina that is used for subsequent aluminium production and a solid residue, called red mud, for disposal.

This waste residue is an alkaline slurry with a water content of about 50-70% and a pH generally above 13. Current red mud disposal consists of dry stacking for thickening until it reaches a solid content of at least 48-55%. The thickened red mud is then stored in such a way that it consolidates and dries out.

Carbonation process

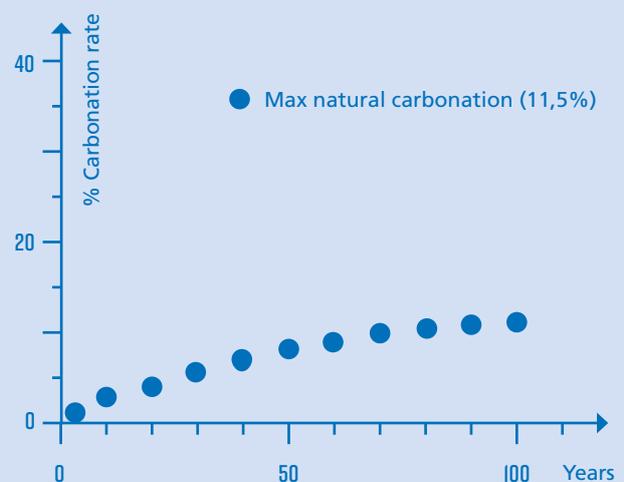
The natural carbonation of red mud involves both pore water carbonation and solid phase reactions of tri-calcium aluminate (TCA) dissolution and calcite precipitation.

To neutralise the mud, reducing its pH, different

neutralisation methods are proposed by means of seawater or technologies that use artificial Ca and Mg rich brines. Another neutralisation is based on CO₂, i.e. a carbonation under enhanced conditions.

Carbonation timeframe

The timeframe for natural carbonation is not reported in the assessed literature. Carbonation occurring over a period of 100 years is considered as the worst case scenario. This graph provides an estimated representation of this scenario.



Aluminium production

Literature assessed: 41

Publications with relevant and reliable information and data: 26

DEFINITIONS

AIR LIME MORTARS

In most building material applications, including mortars, renders and plasters, the calcium hydroxide, known as hydrated lime or slaked lime is used. It hardens slowly by reacting with carbon dioxide of the atmosphere to form back calcium carbonate, a reaction known as carbonation. Lime which does this, is known as “air lime” because it reacts only with air.

CALCINATION

Refers to the heating of limestone or other rocks composed mainly of calcium carbonate (CaCO_3) to produce quicklime or burnt lime, i.e. calcium oxide (CaO). During the thermal decomposition (calcination) of CaCO_3 two product are produced: CaO and CO_2 .

CARBON SINK

Refers to natural systems that absorb and store carbon dioxide from the atmosphere.

CARBONATED LIME

The part of lime which has been transformed to CaCO_3 (carbonates) through reaction with carbon dioxide (CO_2).

CARBONATION CONSTANT (K)

Parameter of the equation which expresses the progression of the carbonation by its depth related to time (t) for construction materials: carbonation depth = $K\sqrt{t}$.

CARBONATION DEPTH

The distance from the surface of lime to where the lime is low or not carbonated. It is measured through the phenolphthalein solution test and is expressed in mm.

CARBONATION RATE

The percentage ratio between the amount of CO_2 absorbed during carbonation and the amount of process CO_2 emitted during calcination.

ENHANCED CARBONATION

The process by which the carbonation is fostered under enhanced carbon dioxide concentration, and/or by optimized process parameters such as the temperature, the relative humidity, the surface reactivity area, the pH and others, depending on the reaction matrix in the solid, water or gaseous phase. Thus, the time of carbonation is reduced.

FLUE GAS TREATMENT

Flue gas generated from combustion plants, in particular coal-fired power plants and waste incineration facilities contain significant amount of acid gases (HCl , SO_x , HF). Acid gases removal can be performed by using different alkaline agents, such as lime, limestone, etc. This application is also known as Flue Gas Desulfurisation (FGD); Flue Gas Cleaning (FGC).

HEMP LIME

Is a construction material was originally developed in substitution of wattle and daub infill in timber frame buildings. The components of hemp-lime are hemp shiv, which is the chopped woody core of the stalks of the hemp plant (*Cannabis sativa*), air lime binder with pozzolanic cementitious or hydraulic lime additives and in some cases surfactants.

HYDRATION

Refers to the process of adding water to quicklime to make calcium hydroxide ($\text{Ca}(\text{OH})_2$), the product of the reaction between and water.

LIME

Is a widely used term that refers to both quicklime and slaked lime.

MIXED AIR LIME MORTARS

Today it is common to incorporate a binder such as Portland cement into mortar mixes. This provides a rapid gain of early strength, allowing fast construction progress. Lime (normally hydrated lime) is included in these mixtures to provide better long-term durability and overall performance of the masonry and this is known as mixed air lime mortar applications.

NATURAL CARBONATION

The process by which lime reacts spontaneously with carbon dioxide producing calcium carbonate (CaCO_3) which stores it permanently. The reaction is exothermal and therefore thermodynamically favourable. Depending on the reaction matrix solid, water of gaseous, the CO_2 can come from the atmosphere, from water or from any other source.

PROCESS CO_2

Is the CO_2 released by the decomposition of CaCO_3 in CaO and CO_2 . When referring to process CO_2 the release from fuels combustion is not considered, since this is strongly dependent on the type of energy used.

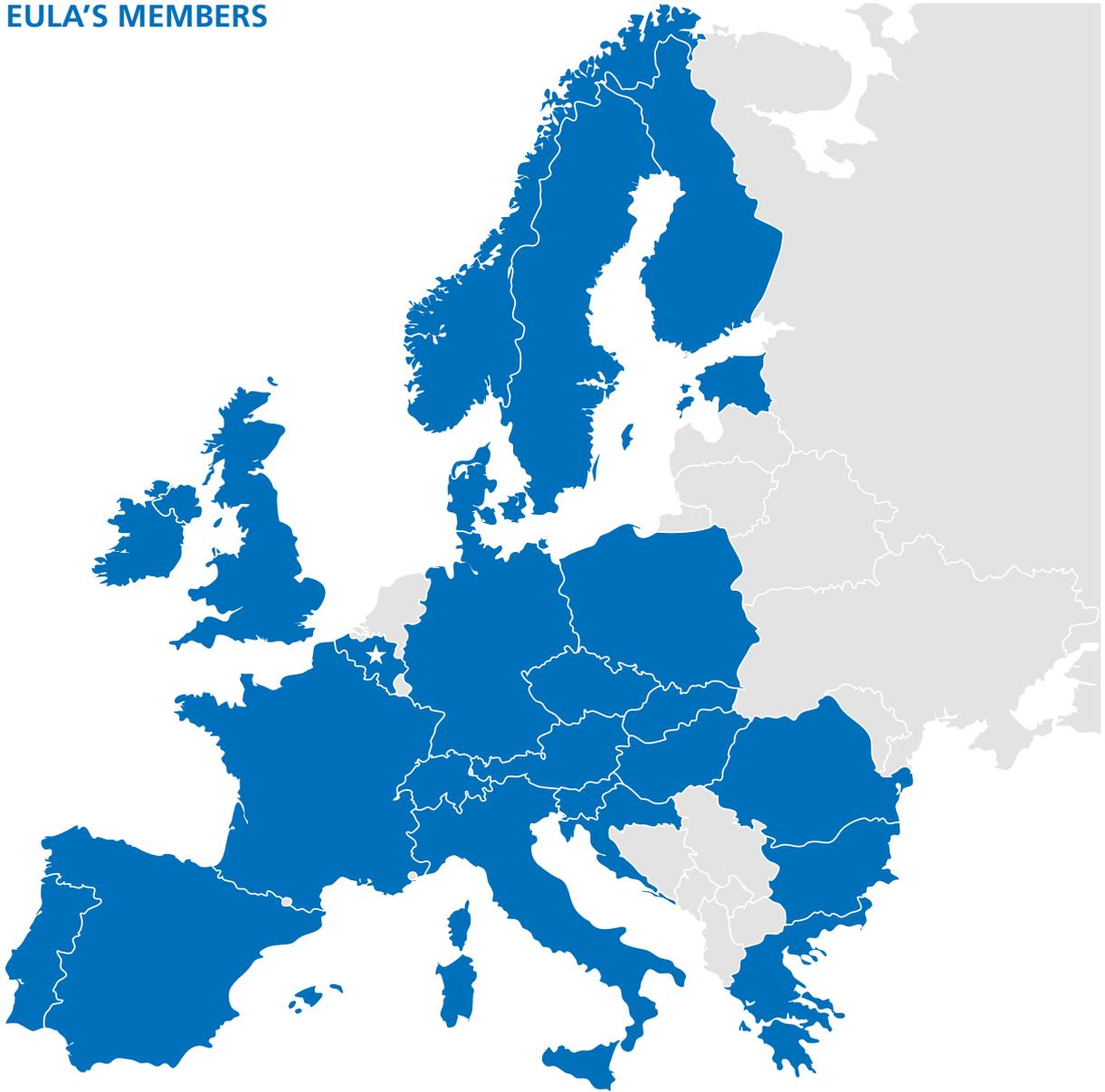
QUICKLIME OR BURNT LIME

Calcium oxide (CaO) is the product of calcination.

SLAKED LIME OR HYDRATED LIME

Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is the product of the reaction between quicklime and water.

EULA'S MEMBERS



The European Lime Association supports realising the vision of the lime sector. It exists to defend the interests of the European lime producers at a European level and support its members to their national objectives driven by a unique voice. EuLA is a member of IMA-Europe (Industrial Minerals Association Europe).



European Lime Association
c/o IMA-Europe
Rue des Deux Eglises, 26
1000 Brussels, Belgium
info@eula.eu | www.eula.eu