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THE CALCINATION OF LIMESTONE – STUDIES ON THE PAST, THE PRESENCE AND THE FUTURE OF A CRUCIAL INDUSTRIAL PROCESS

S. Felder-Casagrande[1], *H. G. Wiedemann*[2] *and A. Reller*[3]

[1]Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich,
[2]Mettler-Toledo AG, CH-8606 Greifensee, Switzerland
[3]Inorganic and Applied Chemistry Institute, University of Hamburg, Martin-Luther-King Platz 6, 20146 Hamburg, Germany

Abstract

The calcination of limestone is one of the oldest technical processes and it is still of actual interest. Very early calcitic mortars from Turkey have been investigated and compared with materials of other early civilisations i.e. with Egyptian mortars containing gypsum as well as medieval dolomite-based mortars from alpine regions. Contemporary calcination procedures, in particular the cement production, range among the most important global industrial processes causing non neglectable environmental problems. Sustainable, solar energy assisted calcination technologies and the conversion of product CO_2 into useful commodities are discussed.

Keywords: antique mortar, calcination, dolomite mortars, limestone, "solar cement"

Introduction

The calcination of limestone, i.e. the production of mortar or concrete, is one of the earliest technical processes human civilisations learned to perform under controlled conditions [1]. The production of mortar is accompanied by a CO_2 cycle, i.e. the re-carbonation occurs by immobilising atmospheric CO_2. This reaction leads to fixation of actual CO_2 and enables ^{14}C dating measurements of antique mortars [2]. Nowadays, the enormous CO_2 release during cement production including firing of $CaCO_3$ stands for an actual problem.

In early civilisations the technology and the materials used were determined by local conditions and the regional skills. Following the development of the calcination till nowadays interesting information about civilisations and their living conditions can be discovered. Contemporary calcination procedures, in particular the cement production, range among the most important global industrial processes. Therefore it became an important factor for air pollution in particular the CO_2 problem. To improve this situation, research is entering to the field of solar technology so in future, the calcination of limestone may be performed in solar reactors.

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Experimental

Decomposition processes were investigated using a Mettler Thermosystem 8000/TG850 coupled to a simultaneously measuring Balzers MS-Cube^{TM} (MSC 200) as well as a Netzsch STA 409 thermoanalyzer coupled to a simultaneously measuring Balzers QMG 511 mass spectrometer. The morphological characterisation of parent, intermediate and product phases were studied in a Philips SEM 515 scanning electron microscope.

Results and discussion

Ancient mortars from Turkey and Egypt

Mortar from a cult building constructed during the Aceramic Neolithic at Nevali Çori in Turkey [3] was investigated. The settlement is located on a plateau surrounded by limestone hills. Mortars found in the terrazzo floor and remaining pieces of the wall consist of pure chalk. This is a soft, fine-grained, fossilierous form of calcium carbonate. The chalk includes calcareous nanofossils, so-called *Coccoliths* (Fig. 1a), that allow the age determination of the geological source [4]. For our sample the presence of *Discoaster saipanensis* (Fig. lb) together with *Istmolithus recurvus* restricts the age to some 40–37 million years.

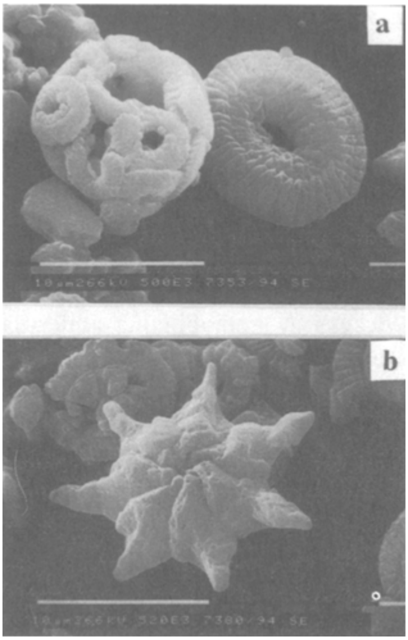

Fig. 1 SEM images of a) *Coccosphere* and outer (distal) side of a single *Coccolith*, i.e. calcareous nanofossiles included in geological chalk; b) Star-shaped species named *Discoaster saipanensis* having an age of 40–37 million years

The ^{14}C dating measurements of mortar from the floor yield an age of 22600 years. On one side this result proofs that this mortar was burned, but the age is about double of the historic determined period of 10000 years. The problems of age determination of mortars are mainly two: first the sample is easily contaminated by unprocessed additive calcite splits. The other problem is an incomplete calcination caused by imperfect manufacturing. As result particles with a "geological heart" coated with processed calcium carbonate are present. Therefore the ^{14}C content is too small and the sample seems too old [5].

As it is known for Egyptian mortars the dominant component used in this culture is gypsum $CaSO_4 \cdot 2H_2O$. Pure calcite is found only rarely and mixtures of both are encountered sometimes. Again the use of these materials represent the geological reality of the region. All samples investigated in this work originated from the Cheops and Chephren pyramids as well as from the Sphinx (Giza). They contain both gypsum and calcite. By TG-MS (Fig. 2) the proportion of both components can be determined. The first step refers to the water loss of gypsum. At higher temperature the decomposition of calcite accompanied by CO_2 release can be observed. Further analytical methods revealed the presence of quartz, an additive admixed in form of sand. Some samples show an extensive content of sodium chloride. Salt has a negative influence on the quality of the mortar, therefore it is unlikely an additive. A possible explanation is the saltification of monuments, probably a consequence of the modern modification of the water equilibrium in the Nil-Valley. In conclusion the ability to manufacture limestone by a calcination process was known by the Egyptians as well although natural resources were scarce and the culture developed the use of an alternative, abundant material, gypsum.

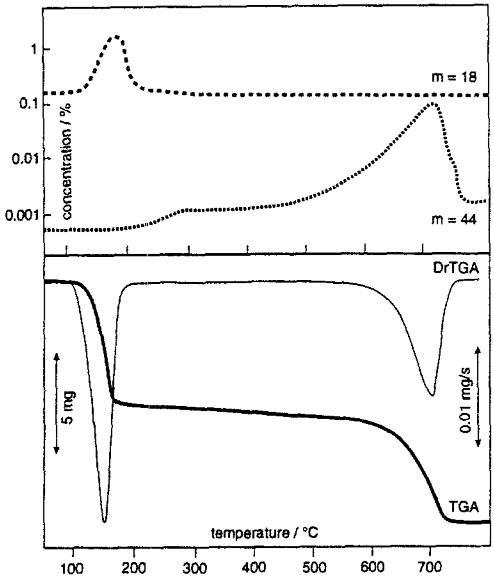

Fig. 2 TG-MS measurement of an Egyptian mortar (Sphinx) containing a mixture of gypsum and calcite

Medieval alpine mortar

The medieval mortars and calcination kilns investigated were found in the Binn valley, an alpine region dominated by dolomite rock. The analysis revealed for all samples calcite mortar. This was surprising because in this region nature offers no geological source for limestone. If we follow the idea that craftsmen prefer to use local materials, then we would expect dolomite mortars. Dolomite is a double carbonate $CaMg(CO_3)_2$ containing magnesium, which is not present in calcite. If at all, only poor historic documentation about mortar preparation in alpine region is known till now. Therefore the question arose what kind of modification to the cal-

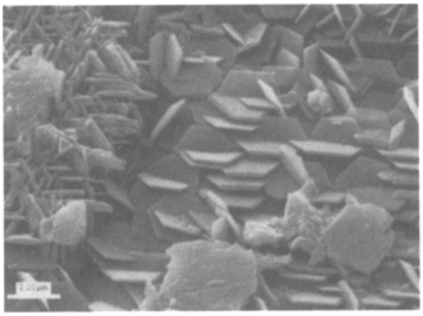

Fig. 3 SEM image of the blue residue found in dolomite calcination kilns, showing the hexagonal shape of brucite crystals ($Mg(OH)_2$)

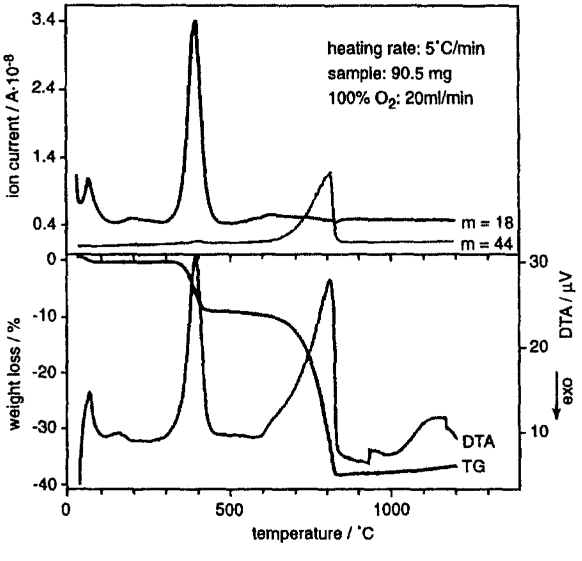

Fig. 4 TG-MS measurement of the blue calcination residue containing brucite and calcite

cination process was developed by alpine civilisations to make use of dolomite as starting material.

To consolidate the stones of a small house about 2 m^3 of dolomite mortar is needed. It's weight is about 5.8 t and out of this 1.3 t is magnesium oxide what seems to be lost during the calcination, manufacturing or recarbonation process. This is remarkable and has to be explained.

The answer was found investigating the calcination kilns located in the region. In their interior the kiln left over residues of old calcination processes were harvested. The white blocks found show a layered structure with a centre of compact blue material. By qualitative metal analysis plenty of magnesium was found in the

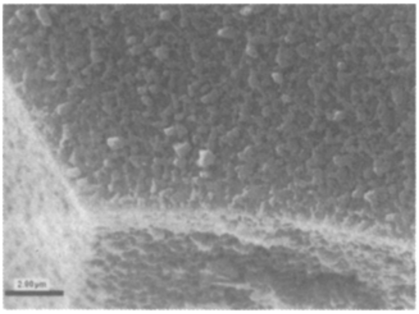

Fig. 5 SEM image of the white surface-near material found in samples of dolomite calcination kilns

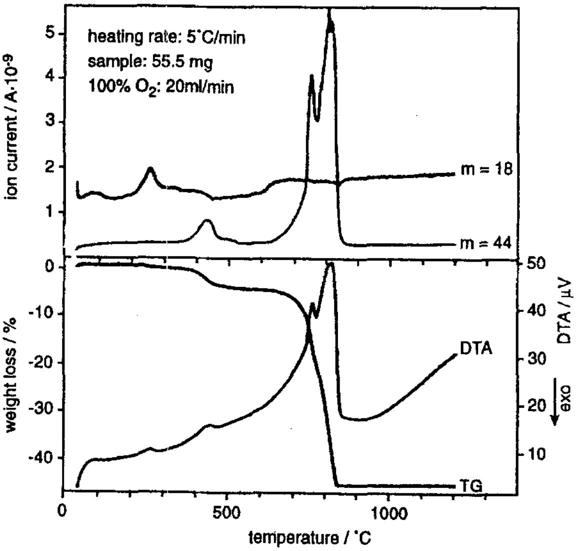

Fig. 6 TG-MS measurement of the white calcination residue containing calcite and small amounts of basic magnesium carbonates

blue part. By X-ray diffraction the blue material was specified as a mixture of calcite ($CaCO_3$) and brucite ($Mg(OH)_2$). SEM pictures (Fig. 3) show the typical hexagonal shape of brucite crystals. By TG-MS measurements in pure oxygen (Fig. 4) the decomposition of both components in the blue mixture are confirmed: the low temperature water loss of brucite and the high temperature CO_2 release of calcite are detected. The white coating is thin, soft and of porous structure (Fig. 5). By X-ray diffraction the white layer was found to be mainly calcite. By TG-MS small amount of gaseous by-products, i.e. water and CO_2 are detected in the temperature range below 500°C (Fig. 6). Most probably, secondary corrosion of surface-near domains leads to the formation of basic magnesium carbonates such as Artinite $Mg_2CO_3(OH)_2 \cdot 3H_2O$, which decomposes in the studied temperature range.

In order to understand the mechanism of the calcination procedure the thermal decomposition of dolomite is important. From earlier investigations we know [6], that at low partial pressure of CO_2 dolomite decomposes in one step to form MgO and CaO. Both oxides are poorly crystalline and highly reactive. A thermal treatment of the mixture in pure CO_2, leads to re-carbonation of the CaO but not of the magnesium oxide. As a consequence dolomite decomposes in two steps with increasing CO_2 partial pressure. Whenever CO_2 is present in small amounts in the atmosphere or generated as the decomposition of dolomite begins, the highly reactive CaO is re-carbonated to $CaCO_3$ and decomposed again causing the second CO_2 evolution.

With this background we can understand that the calcination of dolomite can lead to calcite when the craftsman was able to generate the perfect reaction conditions. But the brucite found in the kiln must be the result of a significant modification in the calcination process. The answer to this problem is water. Only by the addition of water during the firing procedure brucite can be formed according to the following equation.

$$CaMg(CO_3)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaCO_3 + CO_2$$

The calculation of a phase diagram proved (Fig. 7), that at low temperatures and low CO_2 pressures dolomite reacts with water to form brucite and calcite. At higher temperatures periklas (MgO) is formed. This oxide wasn't found in the kilns. This may be an indication that the calcination of dolomite was carried out at low temperatures and the reaction with water to form brucite took place. It is surprising that no recording about the calcination of dolomite is known till now. This must be a technique spread out widely in alpine regions where limestone deposits are rare and dolomite has to be used. Further investigation are still in progress to understand the dolomite calcination completely.

Contemporary problems of the cement production and future sustainable technologies

Contemporary calcination procedures, in particular the cement production, range among the most important global industrial processes. After the industrialization and with the exponential increase of the earth's population, housing con-

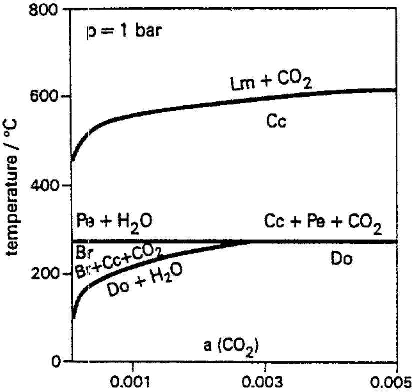

Fig. 7 Calculated phase diagram for dolomite and water. Do: dolomite, Br: brucite, Cc: calcite, Pe: periklas

struction became a large and will be an ever increasing industry. The amount of cement calcined for this purpose is enormous. Therefore the amount of CO_2 released during the firing process ranges among the critical environmental factors responsible for the greenhouse effect. To produce 1 kg of clinker 0.9 to 1.3 kg of CO_2 are emitted by limestone and the fossil fuel used for the process. Summarized over the world this means >1 billion tons of CO_2 release per year.

A crucial innovation for the calcination process must aim at the reduction of pollutant emission and saving of natural energy resources. In order to reach a CO_2 mitigation as well as energy economization in the cement production the use of solar technology has been initiated. A possible engineering solution of the process unit comprises a heliostat field, a solar calcinator and peripheric units (Fig. 8). The

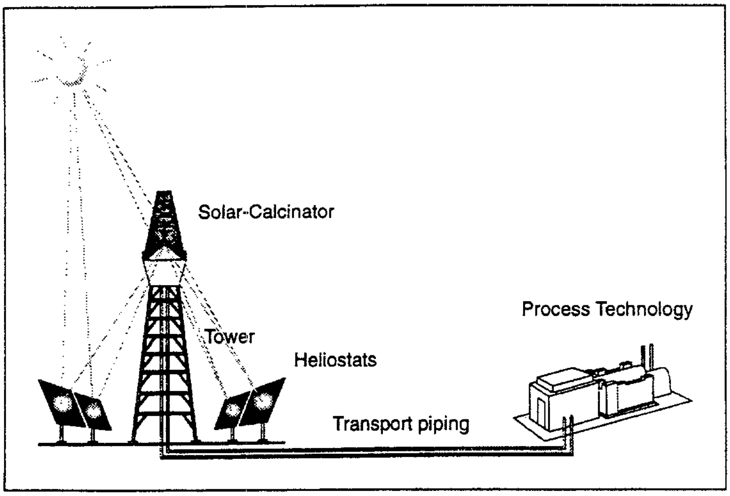

Fig. 8 Scheme of a future cement production via solar energy [8]

decomposition of limestone takes place in a solar cyclone reactor where a powder cloud of calcite particles is passed through the area of highly focused solar radiation [8]. The process efficiency reaches up to 88%. In future secondary processes aim at the catalytic reduction of the gaseous product CO_2 into useful commodities such as methanol. As reducing agent solar hydrogen will be used.

Conclusion

Limestone has been and still remains one of the most important inorganic commodities for the human civilization. But it also plays a crucial role within the global carbon cycle, i.e. as carbon sink or in the biomineralogy of many organisms. Thus, the anthropogenic use and implementation of limestone or its products affords and always afforded skillful technologies. Being aware of the problems connected with the environmental consequences of producing and using enormous amounts of concrete and being aware of the undeniable need of this product for providing socially viable housing in the fast growing agglomerations the search for novel, but sustainable technologies of calcination remains a scientific and industrial challenge.

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