Characterization of a Marl-Type Cement Raw Meal as CO₂ Sorbent for Calcium Looping

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ABSTRACT: The use of cement raw meals as sorbent precursors for CO₂ capture can reinforce the synergies between the cement production process and calcium looping CO₂ capture technology. In this work, we measure the CO₂-carrying capacity of different calcined samples of a particular marl, which were obtained under very different calcination conditions and setups (thermogravimetric analyzer, drop tube furnace, and industrial calciner). We find that the reactivity toward CO₂ of these calcined materials displays a strong sensitivity to the calcination conditions, in particular to calcination time. A pronounced competition between the belite (Ca₂SiO₄) formation reaction and the formation of free CaO needed for CO₂ capture is detected. As the calcination of the raw meals approaches flash conditions (i.e., >90% calcination conversion in less than 10 s), the belite formation is shown to be minimized, leading to sorbents with CO₂-carrying capacities of approximately 0.4 mol CO₂/mol CaO.

INTRODUCTION

The cement industry is responsible for 5% of global CO₂ emissions when only the decomposition of CaCO₃ in the process is taken into account. Therefore, those emissions can only be avoided by CO₂ capture and storage technologies, niche uses of CO₂ involving recarbonation of the cement materials, or passive carbonation of the global inventory of cement-made materials that has been reported to offset 43% of the current emissions.

The postcombustion CO₂ capture technology, calcium looping (CaL), has been developed over the last decade up to 2 MW scale. The CaL process is based on the reaction of CaO with CO₂ to form CaCO₃, which subsequently is decomposed again to CaO in an oxy-fuel-fired calciner. The synergies between the CaL technology and the cement sector have been recognized almost from the beginning of the CaL development. There are different possibilities to apply this technology to the cement sector for which the integration level with the cement plant will be different. The highest level of integration can be achieved if the source of CO₂ for the CaL systems is the cement raw meal itself, instead of limestone. However, taking advantage of the fact that a typical raw meal contains approximately 80 wt % of CaCO₃, this configuration, the precalciner of the cement plant is switched to oxy-fuel combustion mode and hence it is used as the calciner of a CaL system. In the carbonator, only the CO₂ from the additional fuel combustion and residual calcination of the sorbent in the rotary kiln is captured. Although the inert materials present in the raw meal will affect the energy balance in the CaL, by increasing the heat requirements in the calciner, it is well understood that the large makeup will compensate the energy penalties by increasing the average activity of the sorbent.

The use of calcined raw meals as potential CO₂ sorbents in CaL was only recently investigated at the particle level in thermogravimetric analyzers (TGAs), looking for the kinetic information needed for the design of the reactors in the system: mainly the carbonation kinetics and the CO₂ carrying capacity of the free CaO present in the calcined raw meal. It was concluded from these studies that the formation of belite (Ca₂SiO₄) could greatly affect the CaO activity over multiple cycles at typical calcination conditions (i.e., temperatures above 900 °C and high CO₂ concentrations). Raw meals with low aggregation levels between Ca compounds and Si compounds (i.e., raw meals mixed by comilling the lime-rich and clay-rich fractions) can be used as effective CO₂ sorbents, whereas high aggregation levels of Ca–Si, as in natural marl minerals, yield highly deactivated sorbents of modest use for CO₂ capture. This is in principle a negative result regarding the viability of highly integrated CaL configurations in many existing cement plants, which use the marl-type raw meals (i.e., with a high aggregation level of Ca–Si in the raw meal). The utilization of such raw meals in clinker production is preferred because the milling and mixing operations in the clinker process are greatly facilitated. It is therefore important to better understand if the results from these initial studies in TGAs are sufficiently significant and general regarding the calcination conditions. One of the key
In the commercial flash calciners that are widely applied in modern cement plants, shorter calcination times (i.e., with gas residence times on the order of 10 s) are common. These conditions are not reproducible in laboratory-scale TGAs. Therefore, the present work explores the CO$_2$ reactivity and carrying capacity of a typical marl-type raw meal calcined under flash calcination conditions with typical air and oxy-fuel fired combustion atmospheres, confirming that the calcination time is a critical variable to determine the activity toward CO$_2$ capture in the marl-type calcined raw meals.

**EXPERIMENTAL SECTION**

**Materials.** The marl-type raw meal used in this work (the same material used as RM1 in ref 24) has a chemical composition as shown in Table 1. The average particle size is 9 μm (i.e., $d_{50}$) measured by a Beckman-Coulter LS 13320 laser diffraction particle size analyzer.

**Experimental Setup and Methods.** The raw meal was calcined in an entrained flow (EF) reactor setup at IFK’s BTS-VR facility, which was operated to simulate the flash calcination of the raw meal in conditions similar to industrial flash calciners. The calcined samples from an industrial cement plant using the same raw meal were also tested and the results are discussed below. A schematic of IFK’s BTS-VR setup is shown in Figure 1. The cylindrical, electrically heated furnace of this facility is 2.5 m in height and 200 mm in diameter. The heating system is divided into 5 sections, which can be individually controlled to a given wall temperature. By means of a temperature-controlled sampling probe, solids and gases can be sampled at various points along the reactor height. The cooling of the probe allows for a rapid quenching of the sampled gas and material once they enter the probe. Furthermore, access ports positioned at the top and bottom (axial access) and at 0.5 and 1.5 m (radial access) from the top of the furnace allow for a determination of axial and radial temperature profiles within the furnace.

The raw meal was calcined under different atmospheres in this setup. The first one (air-fired) corresponds to the typical conditions of precalciners in cement plants (i.e., 20 vol % CO$_2$, 3 vol % O$_2$, and balance N$_2$). The second condition (oxy-fired) corresponds to the conditions of an oxy-fuel fired CaL calciner (i.e., 80 vol % CO$_2$, 3 vol % O$_2$, and balance N$_2$). The experimental procedure in this facility started with an average axial temperature profile inside the reactor before the raw meal injection of 880 °C for the air-fired calcination and 960 °C for the oxy-fuel-fired calcination. These temperatures were chosen to ensure a residence time sufficient to achieve a calcination efficiency of approximately 90% for both cases. The raw meal was fed by a gravimetrically controlled screw feeder at a feeding rate of 1 kg/h and injected into the reactor using a circular injection pipe. Additional gases were injected via two annuli to adjust the gas atmosphere as well as the residence time. The carrier gas was preheated to 650 °C, whereas the primary and secondary gases were preheated to 550 °C using electric gas heaters. A total gas flow of 10.5 m$^3$/h (STP) was used in both cases. On that basis, an average particle residence time in the reactor of approximate 6.2 s can be estimated. Samples of the calcined raw meal presented in this study were taken at the reactor outlet (2.5 m) using the cooled sampling probe.

The calciner that provided industrially calcined raw meal samples is located in a Heidelberg cement plant in Arrigorriaga (Spain). As in other cement plants, in this facility, the raw meal is precalcined in an entrained flow (flash) calciner before entering the clinker kiln. In this plant, the average temperature in this calciner is approximately 900 °C and the average CO$_2$ concentration is approximately 20 vol %. The calcined samples from the inlet of the kiln were extracted and rapidly cooled down to minimize solid–solid reactions.

The calcination efficiency of the samples was checked through the analysis of the initial carbon content of the samples by using a LECO C/S 230 analyzer. Table 2 shows the carbon weight fractions ($w_C$) of the fresh and calcined samples measured by the analyzer, the calcination degree estimated by $(1 - w_{C,\text{sample}}/w_{C,\text{fresh}})$ and the calcination conditions. Here, $w_{C,\text{fresh}}$ is the carbon weight fraction of the fresh raw meal (i.e., 0.1). As seen, the calcination degree (0.88) is similar in the oxy-fired and air-fired calcination conditions, as the higher concentration of CO$_2$ in the latter is compensated with higher calcination temperatures, which were increased to achieve similar calcination efficiencies. This value for the air-fired

Table 1. Chemical Composition Measured by XRF

| Comp.         | CaO (wt %) | Al$_2$O$_3$ (wt %) | SiO$_2$ (wt %) | Fe$_2$O$_3$ (wt %) | K$_2$O (wt %) | MgO (wt %) | TiO$_2$ (wt %) | SO$_3$ (wt %) | LOI$^*$ (wt %) |
|---------------|------------|---------------------|----------------|---------------------|---------------|-------------|----------------|---------------|---------------|
|               | 42.7       | 4.1                 | 13.4           | 1.9                 | 0.9           | 0.7         | 0.2            | 1.0           | 35.0          |

$^*$Loss On Ignition.

Figure 1. Schematic of the entrained flow reactor BTS-VR of IFK.
sample obtained at BTS-VR was also compared to the gas composition sampled at the reactor outlet mass balances, yielding a good agreement. The carbon content in the sample from the industrial calciner is almost 2.8 times higher than that from the flash calcination tests at BTS-VR, indicating a lower calcination degree in the industrial calciner (0.66 or a molar fraction of CaCO3 of 0.28).

In addition to the analysis of the carbon content, all calcined raw meal samples were also analyzed for their maximum CO2-carrying capacity by a TGA. Furthermore, the X-ray diffraction (XRD) patterns of the samples were determined by using a Siemens D5000 X-ray diffractometer.

The homemade TGA and the experimental procedure to determine the CO2-carrying capacities were described in detail elsewhere.32,33 The sample is placed in a platinum basket suspended inside a mullite tube of 2.54 × 10−2 m OD. The mullite tube was surrounded by two electrical ovens controlled independently by two temperature controllers. The bottom oven was used as a gas preheater, whereas the upper oven was used to set the sample temperature. The sample temperature was measured by a thermocouple located 5 mm below the sample. The reactant gases were fed to the bottom of the tube and the flow rates were controlled by mass-flow controllers. The sample weight, temperatures, and gas flows were continuously recorded on a computer during the analysis.

The determination of the maximum CO2-carrying capacity was performed using initial sample weights of approximately 15 mg to use a representative and sufficiently large sample mass without the extensive effects caused by limited gas diffusion within the sample batch in the TGA system. As this weight is still larger than the weight needed to avoid diffusion resistance (i.e., approximately 3 mg34), the carbonation times were increased to ensure a good reading of the asymptotic value of the maximum CO2-carrying capacity. In the used TGA system, this time is approximately 10 min at a gas velocity of 0.06 m/s. Therefore, the conversion at 10 min was adopted from this point as the CO2-carrying capacity of each material. At the beginning of the test, the sample was heated up from room temperature to 650 °C in an air atmosphere. Once the temperature was stabilized, a mixture of 10 vol % CO2 in air was fed to the sample during 10 min. Then, the atmosphere was changed back to the air without CO2 and the temperature was increased to 900 °C. This temperature was maintained for 1 min to ensure the complete calcination of the sample. Blank tests were carried out to correct the buoyancy effect of the basket in the TGA system.

Figure 2 shows an example of the weight and temperature changes as a function of time when the described procedure was applied to the samples. When the samples contain a certain amount of CaCO3 at the beginning of the analysis, an unavoidable calcination will occur during the heat-up to 650 °C in air. Once the gas mixture containing CO2 is fed, CaO reacts with CO2 and the weight increases sharply. During the calcination (see Figure 2), which is initiated with the change in the gas mixture back to air, the evolution of the sample weight is self-explanatory.

From the changes in the weight measured in the TGA and the chemical composition of the raw meal, the initial molar fraction of CaCO3 and the maximum carrying capacity of the sample can be calculated.

Finally, the X-ray diffraction analysis was carried out over the samples from BTS-VR and the industrial plant. The diffraction data were collected by step scanning using a step size of 0.02°, a scan step time of 4 s, and a scan range of 2θ of 5–60°.

### RESULTS AND DISCUSSION

As noted in a recent study,32 marl-type raw meals yield CO2-carrying capacities lower than expected: \( X_{\text{CO2}} < 0.25 \) when an equivalent limestone would give \( X_{\text{CO2}} \sim 0.70 \) under the same conditions. This is due to the rapid formation of belite, facilitated by the intimate mixing of Ca and Si atoms in marls. The main target of the experiments carried out in this work has been to elucidate if reducing the calcination times to the range (a few seconds) could possibly allow detection of a significant improvement in the CO2-carrying capacities of the calcined raw meals.

The molar conversion of CaO vs time during the carbonation test in the TGA system (discounting the initial content of CaCO3 in all samples) is shown in Figure 3, left for all calcined samples. Moreover, four carbonation tests were carried out over the fresh raw meal calcined in the TGA (without previous flash calcination) for comparison purposes (Figure 3, right).

Comparing the maximum carrying capacity of the oxy-fired (BTS-VR) and air-fired (BTS-VR) samples, the decrease of 0.05 cm3 can likely be attributed to the difference in the calcination temperature between the two conditions. The highest CO2-carrying capacity of the calcined samples was found for the sample calcined in the air-fired conditions (empty circles). The maximum carrying capacity was 0.42, which is close to the maximum carrying capacity measured in a TGA test when the fresh raw meal was calcined in air during 1 min at 900 °C and the calcination of the CaCO3 contained in the sample was avoided during the heating of the sample up to the calcination.

| sample                  | \( \omega_{\text{C}} \) (wt %) | calcination conditions | calcination degree |
|-------------------------|-------------------------------|------------------------|-------------------|
| oxy-fired (BTS-VR)      | 1.2 ± 0.3                     | 960 °C, \( t_{\text{CO2}} = 0.8 \) | 0.88              |
| air-fired (BTS-VR)      | 1.2 ± 0.3                     | 880 °C, \( t_{\text{CO2}} = 0.2 \) | 0.88              |
| industrial calciner     | 3.4 ± 0.1                     | 900 °C, \( t_{\text{CO2}} \sim 0.2 \) | 0.66              |

Figure 2. Example of the evolution of the weight and temperature signals during a typical test in the TGA.
temperature i.e., by heating in 100 vol % CO₂, the calcination and the heating is uncoupled (UHC) (Figure 3, right, empty circles). This outcome seems to indicate that despite differences in the times of heating between an EF reactor (i.e., seconds) and the TGA (i.e., minutes), it may be possible to simulate the EF results in a TGA if the heating and the calcination can be uncoupled. If the same TGA test was carried out at 800 °C, the maximum carrying capacity measured was 0.64, which is similar to the maximum average carrying capacity of CaO from limestone (i.e., 0.7). Therefore, the calcination temperature has a strong effect on the reaction rate of the belite formation from CaO in the raw meals. When the test was carried out at 900 °C, enabling simultaneous calcination and heating (i.e., coupled heating and calcination noted in the Figure 3 as (CHC-900)), the maximum carrying capacity achieved was only \( X_1 = 0.23 \). Thus, taking into

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**Figure 3.** Left: molar conversion of CaO of the calcined samples vs time during the carbonation test in the TGA system (empty symbols: air-fired conditions; black circles oxy-fired conditions). Right: molar conversion of CaO vs time of the raw meal calcined in the TGA after different calcination histories (UHC: uncoupled heating and calcination; CHC: coupled heating and calcination; empty symbols: \( ν_{CO₂} = 0 \); black symbol: \( ν_{CO₂} = 0.7 \)).

**Figure 4.** XRD spectra of the raw meal samples calcined in an industrial calciner and the BTS-VR calciner.
account the fact that the thermal history was the same as in the UHC-900 test, it is clear that the extended calcination time causes a sharp increase in the belite formation from CaO at these high temperatures. Moreover, it can be calculated that this is the maximum carrying capacity that can be achieved, assuming that all SiO₂ reacts to form Ca₃SiO₅ and the remaining free CaO can reach a carrying capacity of 0.7 (similar to the calcined limestone).

When comparing the results from the calcination in CO₂-rich oxy-fuel atmospheres, the maximum carrying capacity of the oxy-fuel calcined samples from BTS-VR (i.e., X₁ = 0.37) is higher than the maximum carrying capacity measured for the samples calcined in the TGA in oxy-fuel conditions (Figure 3 right, black circles, with X₁ = 0.23). This outcome is again a consequence of the unavoidable long time required to calcine the sample in the TGA setup, which is due to the relatively slow heating rate of the sample. Indeed, for the calcination test in the TGA in a CO₂-rich atmosphere (UHC-930) and the test with coupled heating and calcination (CHC-900), the maximum carrying capacity measured is similar (X₁ = 0.23) because, in both cases, there is sufficient time to fully convert the available silica in the marl-type raw meal sample to belite. Thus, when the calcination temperature is higher than 900 °C, the TG apparatus is unable to simulate the results from flash calciner reactors and can yield misleadingly low values of CO₂-carrying capacities for the marl-type calcined raw meals.

The molar CO₂-carrying capacity of 0.37, which was reached for the marl-type raw meal sample calcined under oxy-fuel conditions allows for 0.19 g CO₂ to be absorbed per gram of the calcined sorbent. This outcome is in the same range as the typical CO₂-carrying capacities of CaO obtained from the pure CaCO₃ calcination with a molar CaO conversion of 0.24. Such a CO₂-carrying capacity would allow for high CO₂ capture efficiencies in standard CaL systems.35 Taking into account the fact that in a CaL system for a cement plant, the sorbent would be the freshly calcined raw meal (i.e., sorbent), this means that the fact that in a CaL system for a cement plant, the sorbent would be the freshly calcined raw meal (i.e., sorbent), this means that this raw meal can be a suitable sorbent as long as the sorbent calcination is rapid (i.e., flash calcination).

Finally, the maximum carrying capacity of the industrially calcined sample was X₁ = 0.20. This is consistent with a very high conversion of CaO to belite. In this sample, all available silica in the original marl must have consumed CaO when forming belite and/or potentially other compounds may have reacted with active CaO, as the carrying capacity is slightly lower than the maximum carrying capacity in the case of full conversion to belite (X₁ = 0.23). This result is also in contrast with the higher value of X₁ obtained in the flash calciner of IFK under more controlled (air-fired and oxy-fuel-fired) conditions.

To support the previous discussion, XRD analyses were carried out for 3 different calcined raw meal samples (see Figure 4).

As seen in the samples from BTS-VR, CaO, SiO₂, CaCO₃, and Ca₃SiO₅ can be identified. However, in the sample from the industrial calciner, CaCO₃, CaO, SiO₂, Ca₃SiO₅ and Ca₃SiO₉, as well as signals of the minor compounds with a lower Ca/Si ratio, such as Ca₃Si₂O₇, CaSiO₃, Ca₁₃Al₂O₆, Ca₉(Al₂O₁₉), and CaSi, were found. Therefore, the hypothesis with respect to the presence of other Ca–Si and Ca–Al compounds, which are able to consume active CaO in addition to belite, is confirmed and can explain the very low CO₂-carrying capacity observed in the sample from the industrial calciner.

From a practical point of view, the low CO₂-carrying capacity displayed by the sample from the air-fired industrial calciner, despite its favorable nominal calcination conditions (average temperature: 900 °C), is an indication that the temperature profile and/or the residence times of the solids in the calciner of the plant are higher than those in the laboratory-scale entrained flow reactor BTS-VR at IFK. Unfortunately, we do not have detailed information to elucidate this issue at this point in more detail, but it becomes clear that the calciner design will be a critical element for the successful integration of a CaL system to cement plants using marl-type raw meals. In such facilities, flash calcination conditions with an accurate temperature control and short particle residence times need to be ensured to keep a raw meal-based sorbent active for CO₂ sorption.

### CONCLUSIONS

Marl-type raw meals can retain sufficient CO₂-carrying capacities and can be used as effective CO₂-capturing sorbents in the CaL systems when the calcination is carried out under flash calcination conditions (i.e., short calcination times of less than 10 s at temperatures up to 960 °C). When the calcination temperature is higher than 900 °C, the TGA systems are unable to simulate the results from flash calciner reactors and can yield misleadingly low values of CO₂-carrying capacities of the marl-type calcined raw meals. At longer calcination times and high temperatures over 900 °C, the formation of belite (and maybe other Ca–Si or Ca–Al compounds) will consume CaO and make a large fraction of the free CaO unavailable for carbonation. Hence, this will severely reduce a material’s CO₂ capture capacity. Therefore, the calciner design turns into a critical element for the successful implementation of a CaL system that uses the marl-type cement raw meal as a sorbent. In such systems, great care needs to be put into ensuring flash calcination conditions of the raw meal with an accurate temperature control and short particle residence times.

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**Notes**

The authors declare no competing financial interest.

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