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## ATOMISTIC MODELLING FOR LOW-CARBON CEMENT AND CONCRETE TECHNOLOGIES

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**ABSTRACT:** In recent years, a number of theoretical methods and computational techniques have been applied to construction materials to investigate processes such as water transport in nano-pores and hydration processes in cement. This approach has proved to be extremely useful and beneficial to understanding the chemical and physical processes. These methods and techniques are generally referred to as “atomistic modelling”. The main limitation to a more widespread use of atomistic modelling has been the computing power. However, recent advances in the speed at which computers can now process data make these methods and techniques a viable approach for the study of complex chemical processes in construction materials. This contribution seeks to highlight the potential of atomistic modelling applied to the development of low carbon building materials. In our research we investigated different processes involved in the production and use of lime by combining atomistic modelling and applied research. Experimental data from manufactured samples were used to inform atomistic models which, in turn, can guide the development of materials with optimised performance.

**Keywords:** atomistic modelling, carbonation, decomposition, lime, Raman spectroscopy.

## INTRODUCTION

Recent advances in computing power make atomistic modelling a viable approach for the study of chemical processes in a variety of applications of interest to the construction industry. Atomistic modelling has nowadays the potential to elucidate fundamental reaction mechanisms in some of the most complex construction materials<sup>[1,2]</sup> and can also provide an essential insight into the physical and chemical behavior of newly developed low-carbon materials. This abstract contains a concise description of the integrated approach used to investigate some fundamental processes involved in the production and use of lime.

Lime is a material that has been used for centuries in the construction industry<sup>[3]</sup>. It is produced at temperatures lower than Portland cement<sup>[4,5]</sup> and re-adsorbs part of the CO<sub>2</sub> released during hardening. Furthermore, lime is widely recognized for its superior permeability<sup>[6]</sup>, flexibility and self-healing properties compared to cement<sup>[7]</sup>, and it is commonly accepted that in terms of vapor permeability and flexibility lime has distinct advantages compared to Portland cement.

In this long abstract, our research on experimentally verified atomistic modeling of lime is described using as examples two fundamental processes involved in the production and use of lime: decomposition of carbonates and carbonation of hydrous materials.

## CARBONATE DECOMPOSITION

Oxide formation is the initial step of the lime manufacturing processes. Thermal decomposition of simple carbonates such as calcium carbonate (CaCO<sub>3</sub>), has been widely investigated in the past decades<sup>[8]</sup>. However, decomposition of carbonates containing mixed cations, such as dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) is still debated<sup>[9]</sup>. These carbonates are relevant to a number of industries since magnesium limestone and dolomite are used in a number of industrial applications such as magnesia production and for the production of Dolomitic Lime (DL)<sup>[10]</sup>. Our research combined experimental and computational methods to investigate possible formation of mixed oxide phases at the end of the decomposition process that could explain some of the unique properties of DL<sup>[2]</sup>.

Experimentally, decomposition of dolomite was investigated using a natural dolomite sourced from a quarry near the city of Genoa (Italy, southern Europe). Material characterization was carried out by X-ray diffraction analysis (XRD), Raman spectroscopy and thermal analyses (TG-DTA). Atomistic modelling calculations were performed using VASP at the DFT level of description using PBE exchange-correlation functionals with a correction for van der Waals (vdW) forces. Single unit cells of carbonates (calcite, magnesite and dolomite), oxides (and elements) were studied together with 2×2×2 supercells of oxides using 4×4×1, 4×4×4 and 2×2×2 k-point meshes respectively, maintaining similar k-point densities. Modeling allowed simulating Raman activity of different phases that was obtained by calculating the polarizability for the vibrational modes (details of these calculations are given in [2]). Experimental Raman spectra of the products obtained at the end of the decomposition process were compared with simulated spectra to investigate the composition of reaction products. Simulations considered three potential mixed phase configurations: alternating bilayers (model 1) and monolayers (model 2) in the {100} plane, and alternating monolayers in the {111} plane (model 3). Models also considered low concentration defects to approximate infinite

dilution required for estimating the phase diagram for supercells containing 32 formula units of CaO replacing one Ca with Mg and vice versa.

Overall, computational results confirm the experimental work that suggests formation of only pure phases and, therefore, rules out formation of mixed phase oxides. Simulations, however predict an upper bound for bulk and surface substitution defect concentrations. The calculations show that the pure oxide minerals are significantly favored over all of the proposed mixed phase configurations. Raman spectra for the mixed phase oxides (model 1 and 3) confirm that these mixed phases do not exist in the experimental sample since the decomposed dolomite was found to be non-Raman active (this data is consistent with the lack of activity in pure bulk CaO and MgO). Another simulated structure (model 2), despite being non-Raman active, has a structure with the highest predicted mixing energy of the candidate structures. This result is consistent with the physical intuition where we expect strain between different mineral layers the concentration of which is maximised in model 2).

## CARBONATION MECHANISM

Carbonation is the most important reaction occurring during setting of pure (non-hydraulic) lime and is responsible of long term setting of hydraulic lime. It also plays an important role in concrete where carbonation of calcium hydroxide leads to a lower pH leaving rebar susceptible to corrosion. Despite this importance, the reaction mechanism is not yet fully understood. Some authors suggest that carbonation of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) at room temperature in a carbon dioxide ( $\text{CO}_2$ ) rich environment is a solid-state reaction, whereas others suggest that the reaction occurs via a dissolution-and-precipitation mechanism catalysed by the water. Different reaction mechanisms entail different reaction steps and rates that can significantly affect use of the material, and therefore influence setting time and results.

In our research we investigated the formation mechanism of the carbonate ion ( $\text{CO}_3^{2-}$ ; one of the building blocks of carbonates) by study the role of hydroxyl groups ( $\text{OH}^-$ ) produced by the dissolution of  $\text{Ca}(\text{OH})_2$ , during carbonation. For this purpose, a  $\text{Ca}(\text{OH})_2$  containing >99% oxygen-18 ( $^{18}\text{O}$ ) was carbonated in air (containing  $^{16}\text{O}$ ) at  $23^\circ\text{C}$  and  $50\pm 10\%$  relative humidity. Study of the isotopic concentration of the precipitated carbonates after 3 minutes, 1 day, 8 and 137 days allowed  $\text{OH}^-$  ions originating from the hydroxide to be tracked during carbonate precipitation. Raman spectroscopy and Secondary Ion Mass Spectrometry (ToF-SIMS) were used to characterize unreacted and reacted material. Computational procedures were used to validate the Raman spectra of reagents ( $\text{Ca}(^{18}\text{OH})_2$ ) and reaction products ( $\text{CaCO}_3$  containing various amount of  $^{18}\text{O}$ ).

Experimental Raman spectra of the unreacted  $\text{Ca}(^{18}\text{OH})_2$  show a shift in some of the characteristic peaks of  $\text{Ca}(\text{OH})_2$ . In particular, the peak at  $356\text{cm}^{-1}$  is shifted to  $340\text{cm}^{-1}$  and the peak at  $251\text{cm}^{-1}$  is shifted to  $241\text{cm}^{-1}$ . Peaks of the carbonates formed during carbonation suggest the presence of  $^{16}\text{O}$ -calcite containing various amounts of  $^{18}\text{O}$  (other than other phases). Calcite peaks at lower wavenumbers (i.e.  $153$  and  $270\text{cm}^{-1}$ ) are shifted toward lower values compare to the typical peaks reported in the scientific literature for the  $^{16}\text{O}$ -calcite and this suggests that the structure of calcite included some  $^{18}\text{O}$  atoms.

Computational work allowed simulation of Raman spectra for pure  $\text{Ca}(^{18}\text{OH})_2$  and for Calcite containing various amounts of  $^{18}\text{O}$ . This was important for the evaluation of the experimental results. ToF-SIMS results allowed calculation of the  $^{18}\text{O}:^{16}\text{O}$  ratio in

precipitated carbonates. The isotope ratio for the  $\text{Ca}^{18}\text{OH}_2$  sample after 3' carbonation was found to be 0.56, very close to the ratio of 0.5 proposed by Letolle and colleagues in 1990<sup>[11]</sup> who described formation of the carbonate ion by direct reaction of the  $\text{OH}^-$  ions with the  $\text{CO}_2$  dissolved in water. Simulated Raman spectra of calcite with different isotopic composition show peak shifts to higher wave numbers with increasing  $^{18}\text{O}$  content. The best match between simulated and experimental results were observed for the calcite containing two  $^{16}\text{O}$  atoms for every one  $^{18}\text{O}$  atom. This confirms the ToF-SIMS results.

Overall, these results suggest that after 3 minutes from the beginning of carbonation, approximately 1/3 of the oxygen contained in the carbonates originated from the  $\text{Ca}(\text{OH})_2$ . To the best of our knowledge, this is the first independent experimental evidence of the theory proposed by Letolle and colleagues on the formation of the carbonate ion. These results also provide further details of the mechanism suggested by Letolle by establishing that part of the oxygen is generated by the dissolution of  $\text{Ca}(\text{OH})_2$  in water rather than by the dissociation of water molecules.

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