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Citation: Pesce, Giovanni, Ball, Richard, Grant, Robert, Yeandel, Stephen and Parker, Stephen (2015) Atomistic modelling for the construction industry. In: 35th Cement and Concrete Science Conference (CCSC35), 26-28 August 2015, Aberdeen.

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**Pesce, G., Ball, R., Grant, R., Yeandel, S. and Parker, S. (2015)
Atomistic modelling for the construction industry. In: 35th
Cement and Concrete Science Conference (CCSC35), 2015-08-26
- 2015-08-28, Scotland.**

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Atomistic modelling for the construction industry

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SUMMARY - Advances in computing power now make atomistic modelling a viable approach for the study of complex chemical processes in a number of applications including construction. We aim to apply these methods to processes such as the carbonation of lime mortars. The current research highlights the potential for studying construction materials using atomistic modelling. Computational models of different oxide structures simulating products of the thermal decomposition of dolomite support the view of some authors that suggest formation of phase separated calcium and magnesium minerals.

KEYWORDS - Atomistic modelling, Dolomitic lime, Carbonation.

1. INTRODUCTION - Lime is of traditional importance for construction, especially in the new-build sector as it is an essential component in many emerging low carbon building technologies. Starting from the 19th century it was largely replaced by cement because of the faster set and improved mechanical properties (Bleazard 2003). However, lime has many advantages over cement such as its higher permeability to water vapour and its self-healing and mild antiseptic properties. Currently the use of lime in the construction industry is limited by the relatively slow carbonation time especially when used as thick layers of mortar and render. Our aim is to develop models based on a combined atomistic modelling and applied research approach. This is achieved by an integrated approach using experimental data from manufactured samples to inform atomistic models which in turn guide development of materials with optimised performance. An understanding of the underlying science and an appreciation of the limitations of the technology will allow for more efficient and increased use of lime as a 'green' construction material. Ultimately the computational objective is to develop and refine potential models to conduct atomistic studies of, for example, the process of carbonation. Potential based methods allow relatively largescale simulations to determine bulk properties or investigate surfaces such as those shown in fig.1. Models such as partially carbonated portlandite (fig. 1a) and fully carbonated brucite (fig. 1b) can then be tested to determine whether carbonation energies and resultant structures reproduce experimental results. In the first instance however we need to know whether the bulk mineral consists of pure minerals or is mixed phase and therefore we use results from an experimental study of the decomposition process of dolomite, simulating the lime burning process, to validate a computational model.

2. EXPERIMENTAL METHODS

2.1. Experimental data - Naturally occurring dolomite has been used for centuries for the production of lime. Its enhanced performance compared to pure calcic lime is widely documented (Allen *et al.* 2003, Beruto *et al.*, 2003a and b). Dolomite decomposition was studied on samples of 26.1 ± 0.1 mg using a thermo-balance SETARAM model TGA 92 1750 with a 1600°C module in a dynamic regime, with a heating rate of 5°C/min. During the decomposition, air was fluxed inside the furnace to optimize the heat distribution and promote CO₂ removal from the crucible. Samples were prepared by firstly crushing the stone with a hammer and, then, the fragments obtained were finely powdered using a ceramic mortar and pestle. Particles between 60 and 125µm were used for the TG-DTA and XRD

analyses. XRD spectra were obtained using a Bruker D8-Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation, 2θ with a step of 0.016° and step time of 269s between 10° and 70° .

2.2. Computation – Computational methods allow the study of materials and conditions that cannot be treated theoretically, and even if they do not exist. Thus simulation can be used to help explain why materials are, or are not seen experimentally. To this end we have performed quantum calculations at the DFT level of description. These calculations explicitly include electrons meaning that they are in principle more accurate than potential based methods and can be used later to refine or derive potential models. Calculations were performed for the carbonate materials calcite, magnesite and dolomite and for oxides lime and periclase in addition to two mixed phase oxides. The mixed phase structures were alternating layers based on projections of a lime unit cell in $\{100\}$ and $\{111\}$ Miller indices. Plane-wave based DFT implemented in the VASP code (Kresse, 1994, 1996, 1999) using the PBE correlation-exchange functional (Perdew, 1997) were used to obtain energies for the different minerals which were in turn used to determine the formation energies of the mixed phase structures. For the cubic oxide unit cells a $4 \times 4 \times 4$ k-mesh was required to ensure accuracy while due to the anisotropic unit cell of the carbonates at $4 \times 4 \times 1$ k-mesh was sufficient and for all calculations the plane wave cut off was 500eV. Convergence was 10^{-6} eV for electronic steps and 10^{-2} eV/Å for ions.

3. RESULTS AND DISCUSSION

3.1. Experimental results - Results of thermal analyses demonstrate that under the experimental conditions of these tests, the decomposition process of dolomite starts at 600°C and follows a two-stage route. The end of the first stage and the beginning of the second was detectable by both TG and DTA at 778°C . Total weight loss calculated for the sample at 850°C was approximately 41.26%. It is interesting to note that existence of a two-stage process has been associated to a specific threshold in the p_{CO_2} (Rodriguez-Navarro *et al.*, 2012). Analysis using XRD of partly-decomposed dolomite shows that the transition from dolomite to lime and periclase, is a complex process. At 778°C the intensity of the main dolomite peaks is reduced and some of the smallest peaks disappeared. Calcite, instead appears and is represented by a relatively broad peak at a 2θ value of approximately 29.5° other than other smaller peaks. At 850°C , only peaks of lime and periclase can be identified. Overall, these results support the formation of an intermediate phase of magnesium-calcite prior to formation of pure oxides at higher temperatures.

3.2. Computation - The calculations give minimised energies for the systems from which the formation energies of the mixed phase materials can be readily determined. 50% mixed phase systems are compared with the equivalent energy of pure minerals. For dolomite the formation energy from calcite and dolomite was found to be -1.8kJmol^{-1} , indicating its relative stability, albeit slightly less than the experimental value of -5.7kJmol^{-1} . In contrast the mixed phase oxides considered were significantly less stable than the pure oxides

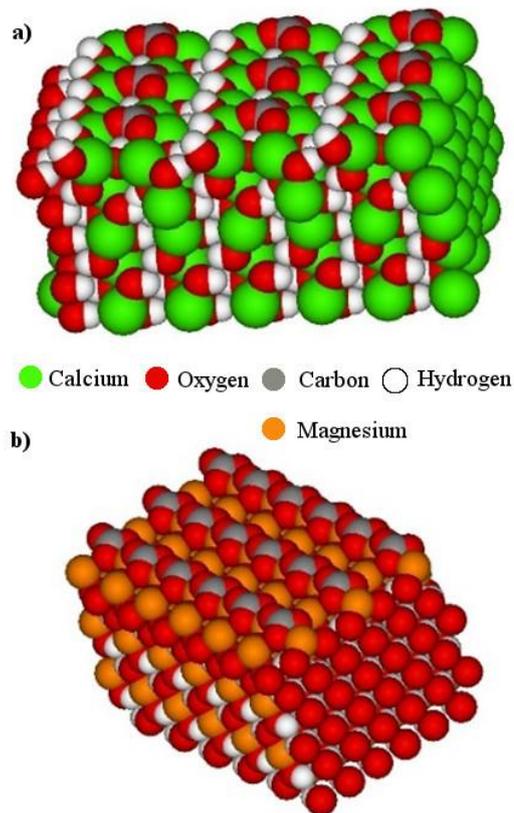


Figure 1 - Surface models of a) portlandite 50% carbonated and b) brucite 100% carbonated

having formation energies of 160kJmol^{-1} for the {100} layered structure and 300kJmol^{-1} for the {111}. These calculations provide further evidence to support experimental analysis that the oxides obtained from the decomposition of dolomite phase separated.

4. CONCLUSIONS

Experimental characterisation of dolomitic lime samples during the thermal decomposition process has demonstrated phase separation of calcium and magnesium. Atomistic models developed to study the behaviour of lime have been shown to be in agreement by predicting phase separation of two mixed-phase structures. This result is of key importance in the development of both understanding the nature of dolomitic lime and the decomposition process because it rules out some of the possible phases which are difficult to detect using traditional analytical techniques.

6. ACKNOWLEDGEMENTS

The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support through project EP/K025597/1. Access to ARCHER was provided via our membership of the Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202).

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