



NOVEL TECHNIQUES IN A STUDY OF THE MECHANISM OF DEDOLIMITISATION IN ALKALI-CARBONATE REACTION

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ABSTRACT

This study aimed to understand the mechanism of the Alkali-Carbonate Reaction (ACR), through the application of the surface sensitive techniques X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). The behaviour of a single dolomite crystal in an alkaline environment, simulating concrete conditions, was studied to investigate the expansive nature of the dedolimitisation process. The combination of microscopic and spectroscopic techniques enabled the identification of the (Mg/Fe)-Ca ion exchange in the crystal lattice and of the preferential nucleation sites at the dolomite surface.

The experimental results show that the transformation of dolomite to calcite and brucite initially occurs along cleavage or defect planes within the crystal lattice. Once established however, nucleation sites initiate further reaction involving the deposition of Mg and Ca phases. From the chemically unbalanced system, dedolimitisation products are further altered, suggesting that the ACR-mechanism in the dynamic concrete environment involves sequential reactions, from dissolution through precipitation to hydration.

The results indicate that several processes may contribute to expansion, including the formation of brucite, the uptake of water and the formation of Fe-rich phases from ferroan dolomite. Furthermore, it appears that expansive forces can be attributed to the presence of large reactive surface areas in dolomite grains for nucleation and growth of new deposits.

Keywords: acr, dedolimitisation, surface techniques, nucleation, surface energy.

INTRODUCTION

The alkali-carbonate reaction (ACR) occurs in concrete containing dolomitic limestone aggregates, making them susceptible to expansion in high pH environments (Gillott 1995). In view of the practical problems expansion causes, the expensive repair work and its controversial chemical mechanism, a great deal of scientific research has been devoted to the problem at the international level. The mineralogical and chemical changes detected in ACR-affected aggregates include the transformation of dolomite to calcite, brucite and alkali carbonates or hydrated alkali-carbonates. However such processes of dedolomitisation were generally thought to be volume-reducing from lattice cell calculations. Large amounts of secondary calcite have been identified on the cement side of the transition zone (Carles-Gibergues et al. 1989), suggesting that the precipitation of calcite as a dedolomitisation product may occur some distance from the reaction site, probably as a result of a dissolution-diffusion precipitation mechanism. At the same time, the aggregate side of the transition zone was found to be enriched in the Mg phase-brucite, which unlike calcite, is insoluble at high pH. These observations have been confirmed by microscopic studies of aggregate particles extracted from field concrete samples (Hewlett 1998, St John *et. al* 1998, Radonjic 1998).

The present study was carried out to investigate the mechanism of the dedolomitisation reaction by observing changes in the microstructure using Environmental Scanning Electron Microscopy (ESEM) together with Atomic Force Microscopy (AFM) and the surface analytical technique X-ray Photoelectron Spectroscopy (XPS). The advantage of XPS is that it can detect chemical changes of elements within the top few atomic layers of the surface of the sample; eg the chemical transition of $MgCO_3$ to $Mg(OH)_2$ may be observed based on a difference in their binding energies. Particular emphasis was placed on defining the origin and nature of ACR expansive forces and their association with the chemical reactions involved (Hochella 1990, Radonjic 1998).

EXPERIMENTAL PROCEDURE

To monitor changes at the surface of a single dolomite crystal, measurements were carried out prior to and during exposure to an alkaline solution. Experiments were devised to observe the dolomite surface without alteration from sample preparation processes, and to acquire images of newly formed phases 'in-situ'.

Single dolomite crystals of almost perfect rhombic structure and measuring approximately 3mm by 2.5mm were used, as indicated in Table 1. The crystals were obtained from Richard Tayler Minerals, Cobham, Surrey, UK. Scanning electron micrographs were recorded from the as-received mineral surface using a Hitachi 2300 Scanning Electron Microscope (SEM). Examination of the same surface after exposure to 1N NaOH for 3 months at room temperature was carried out using a Philips Environmental Scanning Microscope (ESEM) at English China Clays International, St Austell, Cornwall, UK. For atomic force measurements, a Digital Instruments Nanoscope 3 Atomic Force Microscope was used in contact mode before, and tap mode at the end of three weeks exposure to 3N NaOH solution. A VG ESCASCOPE instrument was used for all the XPS measurements.

TABLE 1: Samples of Single Minerals Used in this Study and the Purpose of their Use

| Sample No. | Minerals | Origin and supply | Description and sample conditioning | Purpose and experiments |
|------------|----------|--------------------------------------|---|--|
| MR01 | Dolomite | Spain, R. Taylor minerals | Single crystal, brown-black colour due to Fe, Mn impurities, 3mm long, 2mm wide, perfect rhombic structure and cleavage. | Sample was used as a standard for XPS, ESEM EDX. |
| MR02 | Dolomite | Spain, R. Taylor minerals | Single crystal, Fe-rich, silicate inclusions, 3.5 by 2.5mm, rhombic, one fractured corner with a quartz inclusion. Treated with 15ml 1N NaOH solution at room T for 3months in a sealed PVC bottle, no coating or drying was required. | To detect the dedolomitisation reaction with the formation of calcite and brucite, by ESEM EDX. |
| MR03 | Dolomite | Spain, R. Taylor minerals | Single crystal, 4mm by 3mm, the same composition as MR02, ultrasonically washed in pure water prior to analysis. The sample was then immersed in 5ml 3N NaOH for 3weeks, at room T in a sealed PVC bottle. After removal from solution, sample was thoroughly washed in pure water before the second analysis of the surface. | Crystal structure and changes at atomic level, observation of dissolution of the dolomite crystal and nucleation of brucite crystalites, by AFM. |
| MR04 | Brucite | The NHM London, origin from Zimbabwe | Fine, plate-like colourless crystals, 2-3mm in diameter easily cleaved into thin fragments. SEM samples were Au coated; XPS and ESEM samples as received. | Samples used as standards for ESEM, EDX and XPS calibration. |
| | Brucite | The NHM London, Zimbabwe. | A thin plate (1cm ²) removed from a cluster of brucite crystals and immersed in 1N NaOH for several weeks at room T, on removal from solution rinsed with pure water, dried at room T before XPS spectrum was acquired. | Examination of changes induced by alkaline solution, using ESEM and XPS techniques. |

* Single dolomite crystal containing chemical impurities was used as a standard to simulate dolomite in Kingston aggregate, where the dolomite fraction is known to contain Fe/Mn impurities.

RESULTS

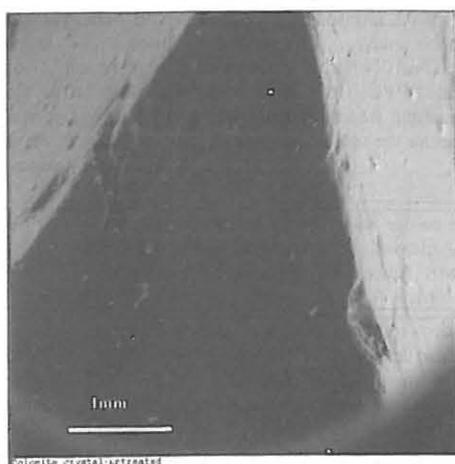
Reactions at Mineral Interfaces

In this study some of the challenging phenomena in concrete mineralogy were resolved by applying the techniques of mineral surface science. These include description and characterisation of surfaces and their interactions at a molecular or atomic level and quantitative elemental analysis under various conditions. Crystals were always assumed to have a perfect structure, with atoms permanently appointed in the lattice until in the 1920s, when Griffith introduced the concept of imperfections, weakness-planes and cracks in solids in a form of theory relating flaws to mechanical properties. These point defects can be in the form of vacancies or interstitial impurities, or may take the form of impurity

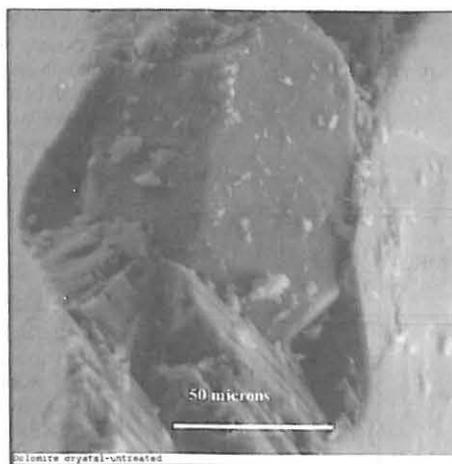
atoms, which can occupy a regular lattice space or an interstitial impurity, depending on the thermodynamics of the chemical state. More influential though are the line defects, represented by the dislocation or disruption of the crystal lattice, stacking faults, twin boundaries, grain boundaries and free surfaces (Cotterill 1986).

Microscopic Observations

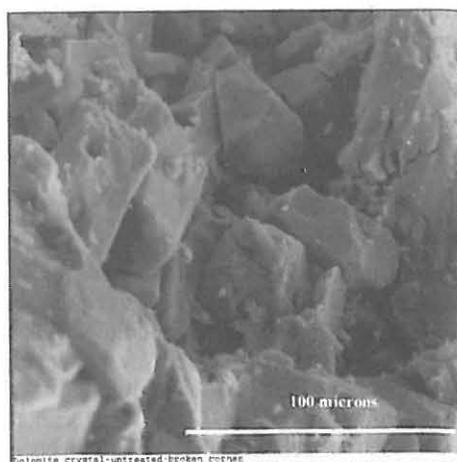
Prior to immersion in a NaOH solution, the single dolomite crystal was characterised in the SEM. Figure 1.a presents the surface observed. One of the corners of the crystal was fractured for observation of the behaviour of an unaltered fracture surface in alkaline solution. Quartz inclusions and some silicates were observed as shown in Figure 1.b,c. It was concluded that the sample was a non-stoichiometric dolomite in which the Ca/Mg ratio was not unity is not 50/50wt%. This can be seen in EDX spectrum, Figure 1.d, acquired from an unaltered dolomite.



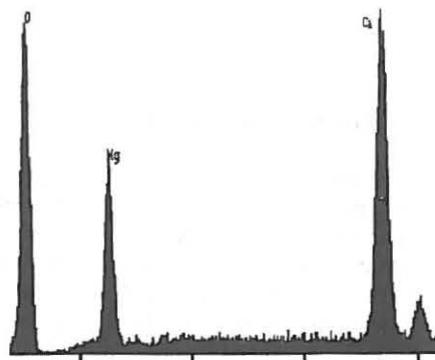
a) SEM micrograph reveals rhombic shape.



b) Quartz grain inclusion within dolomite.



c) Fractured corner of dolomite crystal.



d) EDX spectrum of untreated dolomite.

Figure 1: SEM characteristics of dolomite crystal prior to immersion in NaOH solution.

After removal from a 1N NaOH solution the sample was rinsed in pure water several times and immediately placed in the ESEM chamber for analysis, to avoid phase changes due to drying and migration of pore solutions. The growth of uniform crystals with preferred orientation was observed at the surface, as shown in Figures 2a-c. Images were also acquired at higher magnification to clarify the direction of crystal growth and its relation with the dolomite substrate. There was no indication of any induced physical changes such as micro-cracks and larger crystals growing along defined lines were surrounded by underlying patches of fine plate-like crystals (Figure 2b).

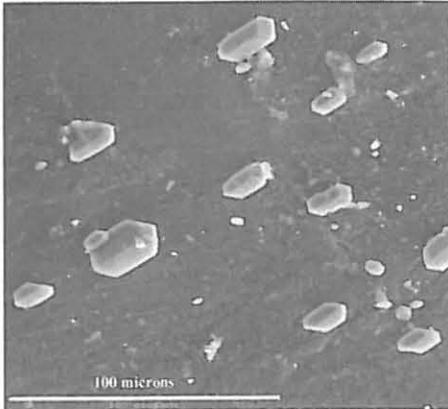


Figure 2a: Oriented epitaxial growth of calcite at the surface of dolomite crystal.

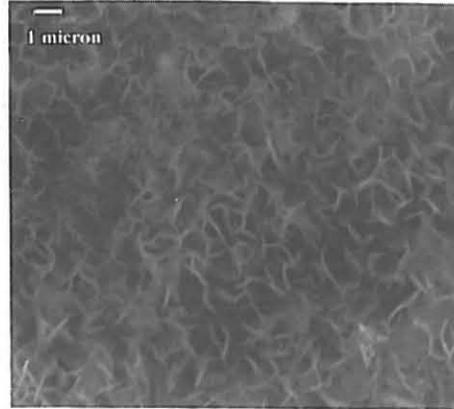


Figure 2b: Precipitation of underlying brucite crystals with large surface area.

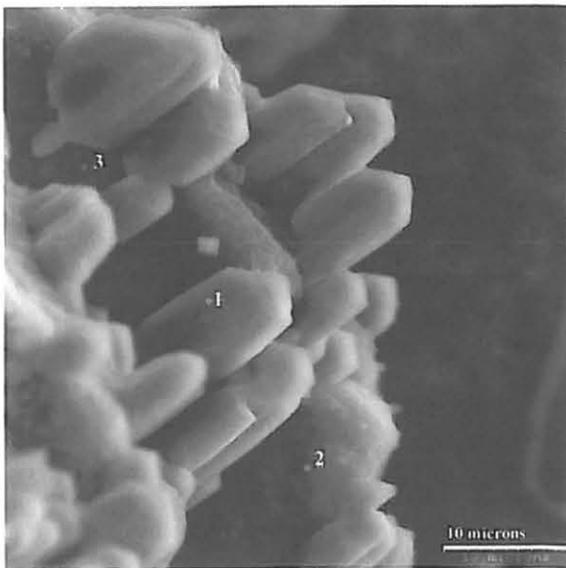


Figure 2c: Calcite growth from a fractured dolomite corner.

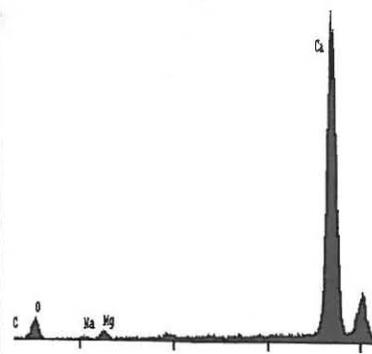


Figure 2d: EDX of calcite.

Figure 2: Single dolomite crystal after immersion in NaOH solution.

A further set of images was obtained from the fractured corner of dolomite Figure 2c. Unlike the cleavage plane this surface allowed access of solution species to all of the structural layers containing Ca^{2+} , Mg^{2+} and CO_3^{2-} groups. Secondary crystals (point 1, Figure 2c) were observed to be growing from the dolomite substrate and as witnessed previously on the dolomite cleavage plane surface, areas between these calcite crystals were covered with a mat of fine perpendicularly growing brucite crystals (point 3) in Figure 2c.

Surface Characterisation

The resolution of the electron microscope was not high enough to observe changes at the sub-micron level. It was therefore decided to use Atomic Force Microscopy (AFM), to characterise the crystal surface on an atomic scale, giving more detailed information on the nucleation sites and the direction of preferred growth of the calcite crystals. A dolomite crystal identical to that used in the ESEM study (Table 1) was ultrasonically washed with pure water for 3 minutes and thoroughly rinsed several times with pure water to obtain a surface free of any particles and impurities. After drying the crystal was examined in the AFM.

The sample was then immersed in 5ml 3N NaOH solution and placed in a sealed plastic container at room temperature for 3 weeks. After removal from the solution the sample was rinsed several times with pure water and examined under the AFM as soon as the surface had dried. The aim was to observe the area examined before the treatment, within a 20 by 40 μm field.

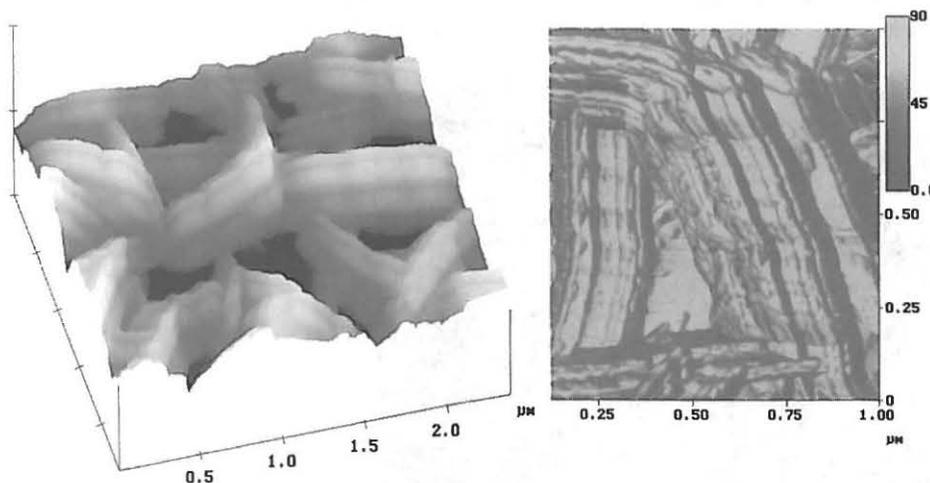


Figure 3a: AFM tap mode image of brucite precipitated at the surface of alkali-treated dolomite crystal.

Figure 3b: AFM phase image shows compositional difference within single brucite (dark and light areas).

Figure 3: AFM characterisation of surface deposits detected on the alkali-treated dolomite crystal, revealing morphology, spatial distribution and compositional differences.

At the outset it was obvious that the secondary phases on the surface were much more un-stable and it proved difficult to obtain images, although the same instrumental settings were used (contact mode AFM). This suggested that the surface was covered with crystals which were poorly-attached to the dolomite surface. It was decided to use the tap mode AFM to carry out imaging. The images thus obtained were stable and revealed that the surface was covered with a network of layered plate-like-crystals growing almost perpendicularly to the surface (Figure 3a). These were identical to the brucite observed under ESEM after 3 months exposure. The AFM imaging that provided the phase information, (resulting in a different shade of a colour image), revealed that the cross section of the plate-like crystals was of a different composition from the side-faces. This partially explained the unstable nature of the crystals if they were covered with thin films of water-rich deposits (Figure 3b).

To be sure that the morphology of phases observed was accurate (suspecting changes such as the contamination of the AFM tip) a further set of images was acquired after a change of tip, and it proved to be effective. These crystals were indeed identical to the brucite observed in the ESEM study, and their formation was apparent after 2-3 weeks of alkaline treatment. None of the original features of untreated dolomite were present the entire dolomite surface was covered with brucite. It was also observed that calcite as a second dedolomitisation product had not precipitated at this stage of the reaction.

Spectroscopic Measurements for Near-Surface Changes

The microscopic morphological observations showing the change on the surface of an alkali treated dolomite crystal may be supported by chemical analysis. Accordingly XPS measurements of the surface were undertaken.

Mineral dolomite - A single dolomite crystal (Table 1) was used to acquire the XPS data before and after the treatment with alkaline solution. Although the main interest lies in the chemical states of Ca, Mg, C, and O, a wide spectrum was obtained from fresh and treated surfaces (400 by 400 μ m), to identify general differences in the composition. As can be observed from Figures 4a-d, the alkaline environment caused a change in the crystal chemistry. These changes can be observed at an early stage by XPS, since the information can be recorded from only a few of the uppermost atomic layers. The wide scan shows the mineralogical changes by the presence of new peaks, but also some of the peaks present in the crystal prior to treatment are no longer observed on the treated surface, Figure 4a. Another important observation is the change in the relative height of the peaks.

Regional XPS scans can revealed more detail and were used to determine chemical shifts. The *C1s* peak height decreased after NaOH treatment and shifted from 290.05 eV to 289.13 eV due to the formation of a second carbonate phase probably CaCO₃ (Figure 4b). Observation of the XPS spectra in the *Mg2p* photoelectron region (Figure 4c) showed a peak shift for the *Mg2p*, leave from 50.59 eV typical for Mg-carbonates to 49.38 eV as in Mg-hydroxide. The same trend was observed for *Ca2p* peak which shifted from 347.62 and 351.34 eV to 346.91 and 350.34 eV (Figure 4c). The position of the *O1s* peak also suggested a change in chemical state, with the treated *O1s* at binding energies in the range typical of the hydroxyl group where the untreated surface showed the *O1s* from the carbonate ion weathered by exposure to atmospheric exposure (Figure 4d).

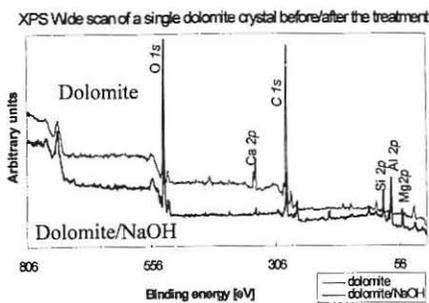


Figure 4a: Wide scan XPS of untreated and alkali-treated surface of the dolomite crystal.

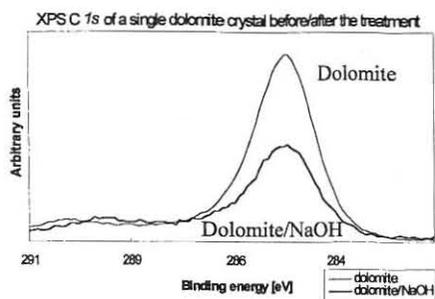


Figure 4b: Regional XPS scan for $C\ 1s$ in dolomite before/after treatment.

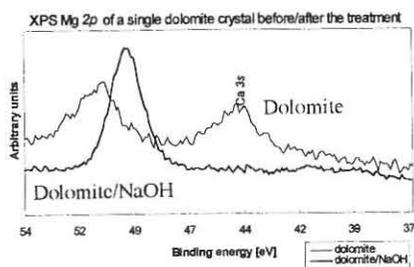


Figure 4c: XPS spectra from $Mg\ 2p$ photoelectron region for untreated (top) and alkali-treated (lower line), reveals chemical shift.

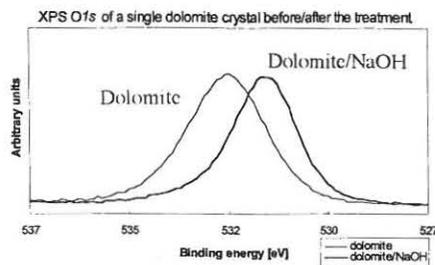


Figure 4d: XPS spectra from $O\ 1s$ photoelectron region for untreated (top) and alkali-treated (lower line), reveals chemical shift.

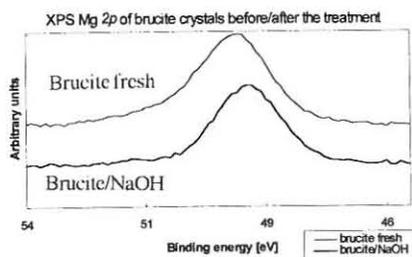


Figure 4e: $Mg\ 2p$ photoelectron spectra from untreated brucite (top line) and alkali-treated (lower line).

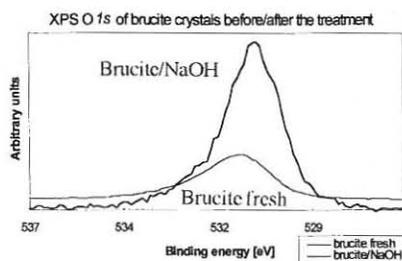


Figure 4f: $O\ 1s$ photoelectron spectra from brucite before (top line) and after the treatment with alkaline solution.

Figure 4: XPS spectra of fresh and alkali-treated surfaces of dolomite and brucite crystals.

Mineral brucite - Brucite in this study is dedolomitisation product. Mineral brucite has a layered crystal structure, in which Mg^{2+} ions are placed between two sheets of OH^- ions which are parallel to the basal plane. Although brucite forms in the alteration process of periclase (MgO), it can be easily transformed to hydromagnesite ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) (Deer *et al.* 1995).

Standard brucite samples were used to acquire XPS spectra before and after alkaline treatment to establish $Mg2p$ binding energy values used to identify the $Mg2p$ photoelectron peak position in the dolomite experiment. A fraction was freshly removed from a cluster of fine plate-like brucite crystals (Table 1) and the $Mg2p$ and $O1s$ peaks identified. The same sample was then exposed to 5ml 1N NaOH solution at room temperature for 3 months. The sample was removed from solution thoroughly washed in pure water and left to dry at room temperature before inserted in the XPS preparation chamber for degassing.

The $Mg2p$ and $O1s$ photoelectron spectra were then acquired. The results are shown in Figure 4e,f. It can be seen that the alkali-treated brucite gave the $Mg2p$ peak position shifted slightly by 0.2 eV from that of the untreated brucite. The data obtained was used to identify the $Mg2p$ photoelectron peak position observed on the surface of the alkali-treated dolomite crystal. The fact that the brucite phase was first to form was noticed using AFM on a single dolomite crystal (Figures 4c,d). It showed that only after 3 weeks the alkali-treated dolomite surface was covered with sub-micron brucite crystals, characterised by their morphology. No calcite was observed. Although the single dolomite crystal immersion was not representative of dolomite grains in dolomitic limestone where their surfaces are surrounded with a silicate/carbonate matrix, it will give a simplified explanation for dolomite dissolution/transformation susceptibility. The study of a single dolomite crystal immersed in NaOH solution using ESEM revealed the formation of a brucite layer at the surface of the reacted dolomite (Figure 2b). The appearance of calcite and brucite at the surface of an alkali-treated dolomite grain here suggested the formation of both crystal forms. These ESEM images revealed that the brucite had a tendency to grow at an angle of 90° from the dolomite substrate, with fine crystals tightly intersected into a blanket-like surface layer observed in the AFM image (Figure 3a).

Support for the chemical transformation of Mg in dolomite was evident when comparing XPS spectra of brucite from the dolomite surface with those from a brucite standard. It was observed that the $Mg2p$ photoelectron peak from reacted dolomite surface was at a very similar binding energy recorded from the standard brucite crystals treated with alkali. The results suggest that brucite, formed as a result of dedolomitisation in an alkaline environment, would be susceptible to further chemical change by reacting with species from the alkaline solution. This should also be true for Mg and Fe-rich phases formed as a result of the dedolomitisation process and species available in cement pore solutions such as Ca^{2+} and Si^{4+} ions.

CONCLUSION

The results presented here taken with those from other analytical studies and thermodynamic calculations offer a model for the mechanism of the process of ACR centred around the dedolomitisation reaction. The ESEM study of a single dolomite crystal indicated the growth of calcite crystals at the surface of dolomite as the result of dedolomitisation. Initially these crystals form at plane discontinuities or other crystal lattice imperfections. The chemical changes occurring during the dedolomitisation process involve surface reactions and as such would be expected to involve changes in volume

therefore expansion. It was also observed that these changes involve not only the removal of Mg from the dolomitic crystal lattice but also the substitution of Ca in place of Fe.

The ESEM observations however, were insufficient for a complete explanation of the nucleation mechanism, composition and chronology of the precipitation processes. For this reason AFM was used to obtain a more detailed description of the changes after shorter periods of NaOH treatment. From the changes in morphology of the features observed on the crystal surface it was possible to ascertain that the first product in the process of dedolomitisation was brucite. When the ESEM brucite image is compared with the AFM image, it is clear that the formation of CaCO₃ follows that of brucite and that the first stage of the reaction involves the dissolution of dolomite. Brucite is more soluble than calcite, but is readily deposited from NaOH and KOH solution. Although, the immersion of a single dolomite crystal in alkaline solution may not be truly representative of the situation experienced by dolomite grains in dolomitic limestone concrete, where their surfaces are surrounded with a silicate/carbonate matrix, it does provide the opportunity to monitor the dissolution/transformation susceptibility of this material.

An additional and significant observation was obtained using x-ray photoelectron spectroscopy where the investigation of the Mg2p photoelectron spectrum from a reacted dolomite surface was very similar to that recorded from alkali-treated brucite sample (Radonjic 1998). It suggests that brucite formed as a result of dedolomitisation in an alkaline environment would be susceptible to further chemical change by reaction with the solution. Mg and Fe-rich phases formed as a result of the dedolomitisation process would also be expected to undergo further reaction with the alkaline solution together with species present in the cement pore solution including Ca²⁺ and Si⁴⁺ ions. Thus expansive forces would not only be generated by formation of brucite but also through the oxidation of Fe phases, since these minerals grow on the surface and have a large surface area that might hydrate or react with pore solution.

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