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A STUDY OF NOVEL LIME BASED MORTARS CONSISTING OF LIME, OYSTER SHELL LIME, CLAY, SUGAR, SAND AND RICE USING FOCUSED ION BEAM MICROSCOPY, RAMAN SPECTROSCOPY AND MECHANICAL TESTING

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Abstract

A number of novel lime mortars consisting of either lime or oyster shell lime and combinations of clay, sugar, sand and rice as additives have been studied. Compression tests indicated failure stresses in the range 14.7 to 29.4 MPa. Focused ion beam imaging and Raman spectroscopy have been used to determine the crystal microstructure and chemical composition of the samples. Raman spectroscopy identified the presence of carbonate groups and amorphous carbon, which was thought to originate from the organic components in the mixes. Examination of the microstructure revealed similarities to structures observed in historic mortars.

Keywords: Lime, Mortar, Raman, FIB

Introduction

A partnership set up between the National Yunlin University of Science & Technology and the Interface Analysis Centre, University of Bristol has focused on the study of a number of novel mortars consisting of either lime or oyster shell lime mixed with various additives including clay, sugar, rice and sand. The compositions and ratios used are based on historic records of traditional mortars used in past centuries in Taiwan.

Lime is a readily available material with a proven track record in building, and is classed as an 'environmentally-friendly' binder (Pritchett, 2003). This is predominantly due to the lower temperatures required in its manufacture compared to ordinary Portland cement and the concomitant reduced energy consumption and carbon dioxide emissions. It also has the ability to adsorb carbon dioxide from the atmosphere during the process of curing.

Lime exhibits important chemical properties and has a history of being used in combination with a range of different additives. Records show that many historic buildings throughout the world were built using lime mortars with additives such as clay, sand, sugar, rice and hemp (Holmes and Wingate, 2002). It is unknown whether these materials were added to enhance the properties of the mortar or as a convenient route for disposal.

This paper describes the initial results obtained from the analysis of three mortars designs based on Taiwanese historic records. Mechanical properties were

obtained by compressive testing. The chemical composition of the mortars was determined using micro-Raman spectroscopy which identified the constituent phases calcium carbonate and amorphous carbon. Focused ion beam imaging was used to determine the microstructure of representative regions within the sample.

Experimental

Sample Preparation

The origin of the components used in the preparation of the mortars was as follows.

- Lime - The lime was manufactured from limestone quarried in Taiwan. The composition of the limestone was 87 - 95% calcium carbonate, 3 - 8% magnesium carbonate with other minerals in much smaller quantities including SiO_2. The natural mineral limestone was burnt to form oxides prior to slaking.
- Oyster shell lime - Oyster shell was burnt to produce lime. The resulting composition of the slaked lime was approximately 90% calcium hydroxide and 10% magnesium hydroxide.
- Sugar - Sugar was added in the form of the black, highly viscous residue remaining from the purification of cane sugar commonly known as molasses.
- Rice - Glutinous rice in jelly-like form similar to that used by the Chinese to make bamboo rice was added.
- Clay - Finely divided clay particles prepared in the traditional way by washing several times in water. Energy dispersive x-ray analysis indicated the presence of silicon, aluminium, potassium, iron, calcium, magnesium and titanium. This analysis was almost identical to that from a Devonshire clay used in the UK for cob block manufacture.
- Sand - The sand used conformed to the China National Standard A2261 and ASTM C778 (OTTAWA standard sand). A typical particle size was 850μm and it consisted of almost pure quartz.

Samples were prepared by intimately mixing the mortar components as indicated in Table 1. The minimum quantity of water required to provide a consistency necessary to allow effective filling of a mould was then added. Samples measuring 50x50x50 mm were cast and allowed to harden before removal from the mould. Curing was carried out under controlled conditions at 23?C, 50% relative humidity and 20% carbon dioxide.

Table 1: Composition and mechanical strengths of mortars

Sample	Composition	Ratio	Strength (MPa)	Age (days)
A	Lime : Clay: Sugar: Rice	72:6:1:2	15.56	28
B	Oyster Shell Powder (Lime): Clay : Sugar : Rice	72:6:1:2	29.4	35
C	Lime : Clay : Sand : Sugar : Rice	72:6:12:1:2	14.7	28

Mechanical Testing of Samples

Samples were tested in compression at the National Yunlin University of Science & Technology, Taiwan with a loading rate of 0.4kNsec^{-1}. For each sample, A, B and C, sets of 3 samples were compressed and an average strength calculated. This was repeated at regular intervals of 4 to 7 days, until no significant increase in average strength with time was observed. The maximum strength evolved for each sample type and the corresponding age of the sample when tested is reported in Table 1.

Raman Spectroscopy

Materials were characterised using a Ramascope spectrometer model 2000 manufactured by Renishaw, Gloucestershire, UK. A He/Cd ion laser (wavelength 325.0 nm) was used to illuminate an area of approximately 4 μm in diameter through an optical microscope. The laser power at the specimen surface was of the order of 4mW. Prior to the analysis, the spectrometer was calibrated using monocrystalline silicon and diamond standards. Peak fitting of Raman spectra was performed using GRAMS32 software.

Focused Ion Beam Microscopy

An FEI FIB201 ion beam instrument was used for high-resolution imaging of the samples. A gallium ion beam of 30KeV energy and 7 nm diameter was focused onto the samples using beam currents in the range 5 and 75 pA. A platinum organometallic gas injector was used for ion-assisted deposition of platinum over selected regions of the sample to avoid electrical charging effects produced under ion bombardment. Secondary electrons, excited by the ion beam, were captured using a channel electron multiplier.

Analytical Methods

The chemical composition of each sample was determined using micro-Raman spectroscopy. The morphology was obtained from secondary electron images obtained using a Focused Ion Beam (FIB) imaging system. Figures 1, 2 and 3 show these images with Raman spectra recorded from the regions identified. This was

achieved by imaging the samples in the FEI FIB2000 instrument and subsequently identifying the same area under the optical microscope to record the Raman spectrum.

Results

Mortar formed from Lime, Clay, Sugar and Rice – Sample A

The mix designs of the mortars studied are given in Table 1. Compression testing of sample A showed a high strength of 15.56 MPa. This value is significantly higher than that obtained in a typical mix design used in construction today. For example a compressive strength of 6.2 MPa developed after 370 days in a mortar prepared with a 1:1 by volume mixture of 3.5 NHL hydraulic lime/sand mixture (Allen et al., 2003). These strengths can be compared on the basis that both mortars reached a state of equilibrium after which no increase in strength was observed.

FIB images recorded from sample A, identified in Table 1, are shown in Figure 1. A number of different crystal features are observed. Figure 1a shows a surface covered with islands of different morphology and the same area at higher magnification is shown in Figure 1b. However at very high magnification, Figure 1c, various structures resembling angular calcium carbonate crystals are observed.

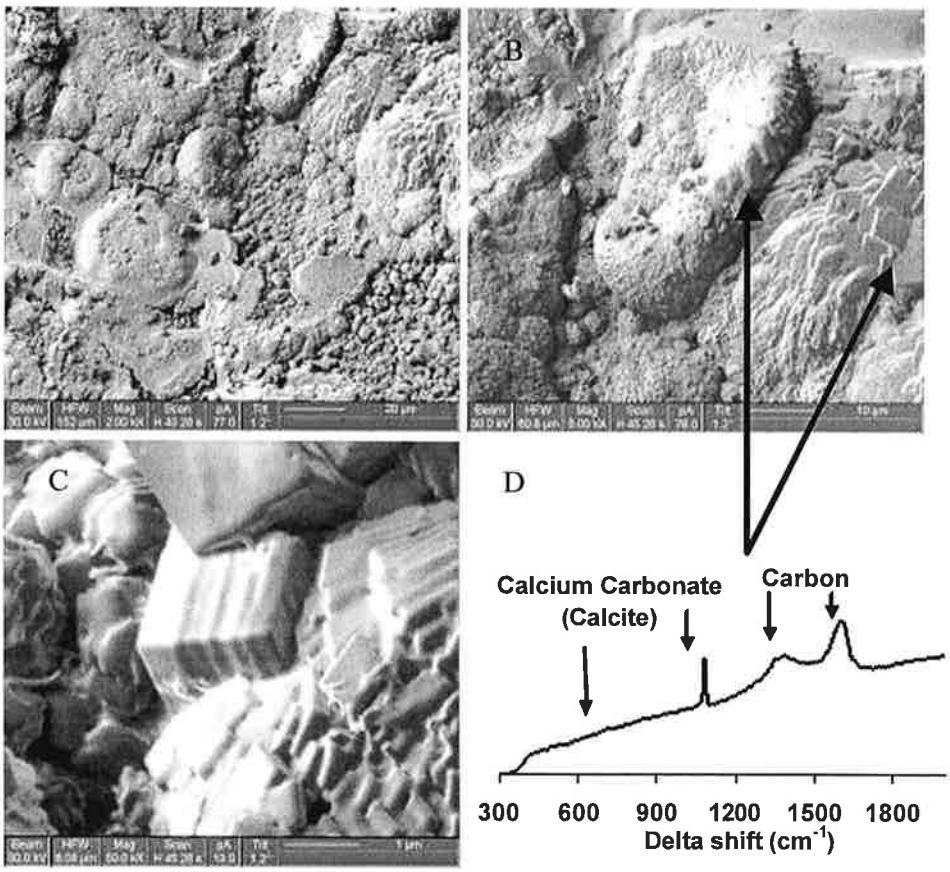

Figure 1: a), b) and c) Ion beam stimulated electron images obtained from sample A consisting of lime clay, sugar and rice. d) A typical Raman spectrum obtained from the areas indicated on image b.

Figure 1d shows a typical Raman spectrum acquired from representative areas shown in Figure 1b. The spectrum contains a strong band located at 1085 cm-1 (?$_1$) and a weak band located at 707 cm-1 (?$_4$) (Martinez-Ramirez et al., 2003), (Kwon et al., 2004) and (Zoppi et al., 2002). These bands are attributed to the calcite form of calcium carbonate. The presence of calcite is due to the reaction of calcium hydroxide and carbonic acid formed from the dissolution of atmospheric carbon dioxide into water within the matrix material. In addition to those assigned to calcium carbonate, two broad bands located at 1333 and 1591 cm-1 were also identified. These bands, Figure 1d, are characteristic of amorphous carbon, (Knight & White, 1985). The presence of carbon bands in the spectrum is almost certainly generated by the organic components of the mortar, sugar and rice.

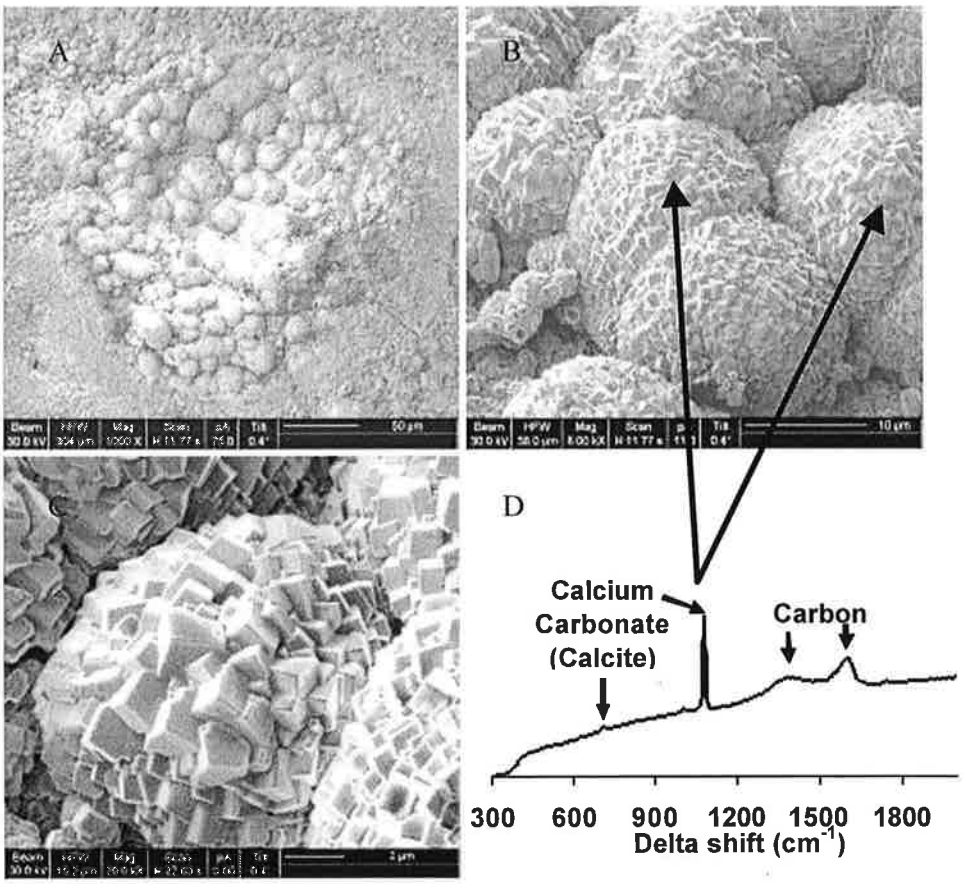

Figure 2: a), b) and c) Ion beam stimulated elctron images obtained from sample B an oyster shell lime, clay, sugar, rice composite. d) A typical Raman spectrum obtained from the areas indicated on image b.

Mortar formed from Oyster Shell Lime, Clay, Sugar and Rice – Sample B

Mechanical testing of this mortar gave exceptionally high compressive strengths in the order of 29.4 MPa. FIB images obtained from the surface of this sample are shown in Figure 2. Spectacular crystal structures are observed which are quite different to those identified in sample A. Spherical agglomerates of angular

calcite crystals are shown under progressively higher magnification in Figures 2(a), (b) and (c) respectively. They appear to have been grown from a central nucleation point. A Raman spectrum obtained from a representative area, shown in figure 2d, identified similar bands to those obtained from sample A, with strong bands associated with the $?_1$ vibration of $[CO_3]^{2-}$.

Mortar formed from Lime, Clay, Sand, Sugar and Rice – Sample C

The main distinguishing feature between sample C and samples A and B is the presence of a sand particulate phase.

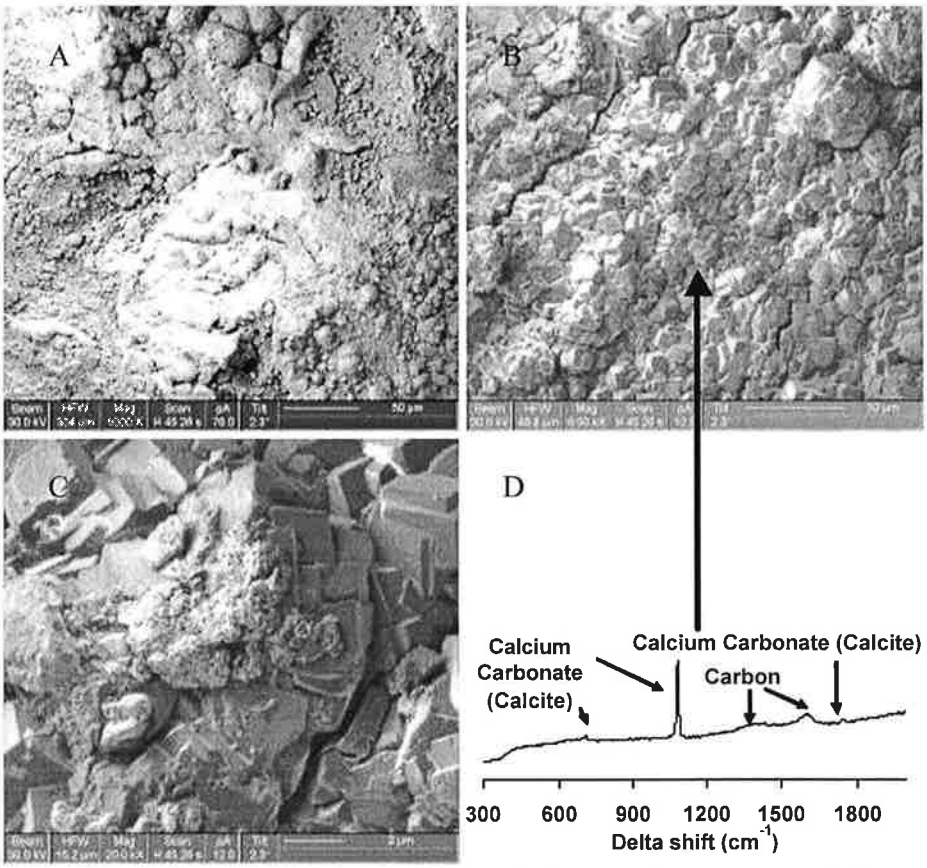

Figure 3: a), b) and c) Ion beam stimulated electron images obtained from sample C consisting of lime, clay, sand, sugar and rice. d) A typical Raman spectrum obtained from area indicated on image b.

A sample of mortar C tested in compression failed at a load of 14.7 MPa. FIB images recorded from the surface of this sample are shown in Figure 3. They reveal a rather different morphology compared to those observed from samples A and B. Far fewer angular calcite crystals are observed when compared to the previous sample B, though the Raman spectrum shown in Figure 3d contains similar bands to those obtained from samples A and B, indicating a similar matrix composition.

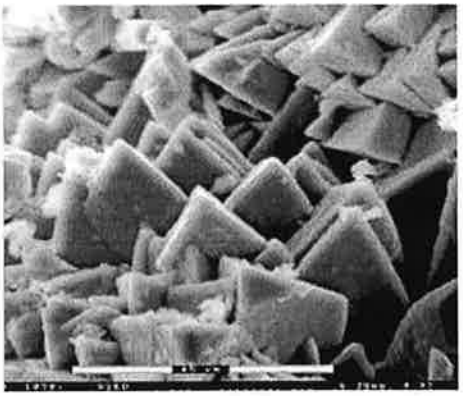

Figure 4 Structure of mortar from Hurst Castle, UK.

Discussion

The use of methods based on focused ion beam technology was found to be invaluable for the determination of the structure of a range of insulating lime mortars with novel additives. Raman spectroscopy was used to identify different chemical structures in the lime matrix. Particularly, the vibrational frequencies characteristic of amorphous carbon, $CaCO_3$ and $Ca(OH)_2$

The structures observed in samples A, B and C, show variable amounts of densely packed calcite crystals with an angular structure. The majority of the crystals observed in all samples were approximately 1 μm in size though some larger crystals 5 μm in size were identified in sample A. The mechanism of formation of these crystals is unknown but the spherical agglomerates observed in sample B, Figure 2, suggested that growth may have initiated around a central nucleation point. The tightly packed network of calcite crystals observed were similar to the crystal networks previously observed in historic mortars. Figure 4 shows the structure of a mortar dating from 1560 obtained from Hurst Castle in the United Kingdom (Radonjic et al, 2001). In this mortar acutely angled densely packed calcite crystals were also observed, albeit of larger dimensions measuring approximately 20 μm.

Lime mortars harden by virtue of a carbonation reaction, the extent of carbonation increases with time until all the calcium hydroxide has been converted into calcium carbonate. An increase in strength as a mortar carbonates is also observed. Old, fully carbonated mortars are known to have significantly higher strengths than those of relatively freshly prepared origin. It is noteworthy that a natural hydraulic lime mortar of classification 3.5 has been observed to reach a maximum strength of approximately 7 MPa after 1 year for a 1:1 lime to sand mix (Allen et al, 2003). This is significantly lower than the strengths observed in the sample mortars of the present study which exhibited strengths of 15.56, 29.4 and 14.7 MPa for samples A, B and C respectively. The densely packed calcite crystals may be at least partly attributable to these remarkably high strengths.

Conclusions

The results indicate that the additives, clay, rice, and sugar, produce the fascinating calcite crystal morphologies and agglomerate features observed in the experimental test mortars. Striking similarities in the form of angular calcite crystals were noted following comparison with 445 year old mortar from Hurst Castle. Further investigations are necessary to identify the mechanisms responsible for the crystallisation processes but the following factors may be important.

- Additives may provide specific nucleation sites for the growth of well defined calcite crystals.
- Additives improve the workability of the mortar by reducing the necessary volume of added water. In this regard the effect of a lime produced from oyster shells may be a consequence of its relative high magnesium content.

Acknowledgements

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