STP 1432

Masonry: Opportunities for the 21st Century

Diane Throop, Richard E. Klingner, editors

ASTM Stock Number: STP1432

ASTM International
100 Barr Harbor Drive
PO Box C700
West Conshohocken, PA 19428-2959

Printed in the U. S. A.

Contents

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Investigation of the Rheology and Microstructure of Hydrated Lime and Sand for Mortars

REFERENCE: Abell, A. B., and Nichols, J. M., "**Investigation of the Rheology and Microstructure of Hydrated Lime and Sand for Mortars,**" *Masonry: Opportunities for the 21st Century, ASTM STP 1432*, D. Throop and R.E. Klinger, Eds., ASTM International, West Conshohocken, PA, 2003.

ABSTRACT: This paper presents the investigation and characterization of Type S hydrated lime in aged solutions with sand and with subsequent addition of Portland cement. The plastic mortar workability and flow as prescribed by ASTM Standards C207 and C270, the rheological properties, the microstructure of the lime-sand slurries, and the hardened microstructure and properties as prescribed by ASTM Standard C109/C 109Mhave been analyzed to identify the optimal relation of lime hydration product form to sand and the implications to selection of materials or manufacture of a hydrated lime type for constructability and performance.

KEYWORDS: lime, sand, workability, mortar, electron microscopy, morphology

Introduction

The importance of hydrated lime to the workability and water-tightness of mortars is well recognized. The water retention required of lime mortars is specified in ASTM Standard C207 and discussed in relationship to the selection of mortars in the Appendixes of ASTM Standard C270. The ability of a mortar to withstand repeated stresses without rupture of bond and heal autogenously is attributed to plastic flow, creep, and moduli of elasticity; all directly influenced by the presence of lime [1]. The process of carbonation, which can cause irreversible drying shrinkage and reduced corrosion resistance at surfaces, is beneficial by effectively closing off the access of moisture into hardened mortar by forming calcium carbonate crystals ($CaCO_3$ or $C\overline{C}$) that aid dimensional stability upon wetting and drying and is a chemical process directly involving lime hydration products of calcium hydroxide ($Ca(OH)_2$ or CH) [2]. The increase in strength with time after compaction of crushed aggregate materials treated with calcium hydroxide for base courses of Portland cement concrete pavements has been attributed to good interfacial bond from the carbonation products by scanning electron microscopy

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(SEM) studies [3]. The microscopy showed that there is good attachment of cement with carbonate (limestone) aggregates.

Typically, scanning electron microscopy is used to examine the hardened state of cement and mortar materials. These non-conducting materials must be dried and coated with a conductive material such as gold or carbon in order to be examined using the electron beam. The drying of hydrating materials can cause damage to the microstructure as water is removed from clay-like layers, and effectively freezes the form of hydration products, which may change with further hydration, and consumption of available water. Environmental scanning electron microscopy (ESEM), which is a relatively recent advance in the technology, allows observation of a wet specimen in a microenvironment at high magnifications without disturbing the development of the microstructure. Lange, Sujata, and Jennings [4] observed dissolution and precipitation processes in cement paste by examining wet pastes and by the addition of water to Portland cement within the specimen chamber of the microscope. They also examined the microstructure as the water was removed from the microenvironment and the resulting drying, cracking, and shrinkage of the microstructure.

The types of lime for masonry purposes are supplied as hydrated lime in dry form, with and without air entraining additives, or as a putty that is fully slaked and screened. The crystalline shape of the hydrated lime is variable, particularly with respect to aging, as shown by Rodiquez-Navarro, et al. [5]. Their study found from X-ray diffraction, nitrogen adsorption, and scanning electron microscopy that there was a size reduction and morphological or shape change between fresh and 14-month-old aged lime putties. The traditional use of aged or slaked lime to improve workability and water-tightness is based on experience, as evident by an ancient Roman law requiring lime to be slaked and stored under water three years before its use [6]. But the science underlying the material behavior is still not well understood, although the increase in surface area by the crystal size reduction has been suggested as a reason for the quality improvement [5] and rapid carbonation of lime mortars [7]. The benefit of adding the sand to a lime putty for a period prior to mixing with cement is also based on experience[3] [1][9]. Modern construction practices using the commercial forms of hydrated lime preclude the use of these aging techniques.

Nichols [10] completed a systematic investigation of pressed clay masonry shear walls subjected to dynamic loads. This research used a 1:1:6 mortar that had been used in repairs to the Catholic cathedrals after the 1989 Newcastle earthquake (M5.5). The masons had observed that this mortar provided improved workability when the lime component was delivered in the form of a putty. The laboratory work investigated a number of alternative methods for combining the lime, and, and cement. The masons observed improve workability with a sand-lime mix that had been allowed to stand overnight compared to dry lime mixes and lime putty mixes that had not.

If the enhancements attributed to the aging techniques can be characterized through understanding the microstructural relation of the lime to the sand in the wet state and the relationship of the lime-sand slurry to the cement hydration process, the lime could be

[3] Personal communications with masons.

supplied in a form tailored for the desired fresh and hardened masonry properties. This work studies the effects of aging lime putty and lime-sand slurries on the workability, microstructure and strength of Portland cement mortars using standard test methods and microscopy.

Experimental Procedure and Technique

The effect of aging lime-sand slurries on calcium hydroxide crystal size and shape, fresh mortar rheology and plastic flow, and compressive strength were of particular interest in this investigation. Lime-sand slurries and a lime putty were observed using an ESEM in the wet state and with removal of water. The addition of Portland cement to the sample surface was also observed in wet and dry states. Mortars made with Portland cement and the lime-sand-slurries were tested for rheological properties and flow, and formed into 2-in cube specimens for compressive strength testing. The mortars were also used in a brick prism for examination of the hardened microstructure.

Materials

Type S lime — special hydrated lime for masonry purposes — is the most commonly used form of hydrated lime in masonry mortars, particularly because it is able to develop high, earlier plasticity and higher water retentivity than normal hydrated lime (Type N). In addition Type S lime is allowed to have a maximum of 8% unhydrated oxides as by Standard Specification for Hydrated Lime for Masonry Purposes, ASTM C207, which does not limit the unhydrated oxide content for Type N lime. The hydrated lime used in this study was Type S hydrated lime (Standard Specification for Hydrated Lime for Masonry Purposes, ASTM C207). Type I Portland cement (Standard Specification for Portland Cement, ASTM C150) and masonry sand (Standard Specification for Aggregate for Masonry Mortar, ASTM C144) were used in the mortars.

A lime putty was formed by adding sufficient water to fully liquify the hydrated lime, and was aged for a minimum of one week before use in lime-sand slurries and mortars for this study. The putty had a specific gravity of 1.3. The proportions of the mortar components by weight were 1 part hydrated lime/lime putty to 1 part Portland cement to 6 parts masonry sand. The equivalent laboratory volume ratio is 2:1:4.5, which classifies as sand-rich Type O Cement-Lime mortar. Three mortars were constructed and designated Putty — made with the lime putty, 1 Hour — made when the lime-sand slurry was 1 hour old, and 4 Hour—made when the lime-sand slurry was 4 hours old. The lime, cement, and sand were mixed for 30 seconds when 1 part by volume of water was added and mixed for 30 seconds. Additional water was added to the lime-sand slurries until the point at which the sand grains could just easily flow past each other and mixed for 3 additional minutes. When the slurries mortars were mixed, the additional water was added until the coated sand particles formed a cohesive mass with the masonry paste and the sand grains could just easily flow past each other. The specific w/s ratios were not determined, as water was added for the desired workability.

A prism was constructed using bricks with IRA of 17.2 g/ 30 in^2 with a standard deviation of 0.34 g/30 in^2 and a bed with each mortar covering a third of the brick. The

prism was constructed to examine the resulting hardened microstructure upon water removal by brick absorption.

Rheology

Viscosity measurements were taken following Test Method A of Standard Tests Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer, ASTM D2196 for the Putty, 1 Hour and 4 Hour lime-sand slurries, and the lime putty. A Brookfield Viscometer Model LVF was used with a #4 spindle and rotational speed of 12 RPM having a scale factor of 500. The apparent viscosities after 8 minutes (for stabilization) are presented in Table 1. The viscosities can be referenced to those of water: 1 mPa·s, and glycerine: 1500 mPa·s. The 4 Hour lime-sand slurry has a distinctly lower viscosity than the 1 Hour and Putty mixes. Hydration of Portland cement produces an increase in viscosity, which suggests that the lime hydration products are not mechanically interlocking and resisting the flow. The putty without addition of sand shows the influence of sand particle suspension with minimal adhesion of lime hydration products on the surface of the particles (no aging time with addition of sand) by an increase of 8190 mPa·s. The increase in viscosity of the Putty mix with respect to the 1 Hour mix could be attributed to the presence of early age hydration products having large surface areas.

TABLE 1—*Viscosity of Lime-Sand Slurries and Lime Putty*

Slurry Type	Viscosity (mPa·s)
1 h	15500
4 h	11100
Putty	14300
Putty (no sand)	6110

Mortar Flow

Flow was determined for each mortar made from the lime-sand slurries in accordance with Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, ASTM C109/C 109M by dropping the table 25 times. The resulting measurements are presented in Table 2. The flows are less than those anticipated for field mortars due to the criteria for the addition of water to the point where the sand grains would flow past each other. The 4 Hour mortar formed plastic cracks on top of the molded shape as it was dropped and also had surface bleed water.

Table 2 – *Flow of Mortars*

Slurry Type	Flow %
1 Hour	52
4 Hour	62
Putty	78

Compressive Strength

Compressive strength of 2-in. cube specimens was determined following Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, ASTM C109. Two test specimens of each mortar mix were molded and moist cured for 7 days prior to testing. Results of the tests are reported in Table 3.

TABLE 3 —*Mortar Compressive Strengths*

Slurry Type	7 day Compressive Strength (psi)
1 h	620
4 h	808
Putty	774

Microstructural Characterization

Of particular interest to the workability of lime-sand slurry mortars is the influence of aging of the lime-sand slurry. As this material is composed of saturated lime water, lime hydration products and sand, optical microscopy can show little beyond the surface, while scanning electron microscopy requires the removal or freezing of the water. With the use of an environmental stage, the pressure can be elevated while still allowing sufficient pressure in the electron gun for the secondary-electrons to be detected[8]. A Philips XL30 ESEM-FEG scanning electron microscope was used with water vapor pressure and a cooling stage in this study. A 0.5 mm gaseous secondary electron detector (GSED) was used with a 20kV electron beam. With the stage chilled to 3° C and pressure of 6.4 torr, the sample experienced 100% relative humidity. As the pressure was reduced, the relative humidity dropped and water was removed from the chamber and specimen. The sample chamber with cooling stage (two water lines and serial cable), sample container, and GSED (above the sample) can be seen in Figure 1.

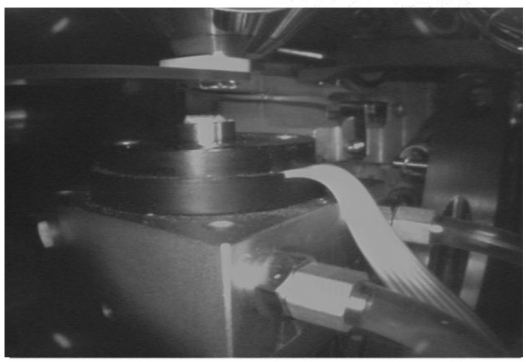


Figure 1 – *ESEM Sample Chamber*

The wet mode observation of all the lime-sand slurries and the lime putty revealed very little in the way of surface features. The surface tension of the lime solution

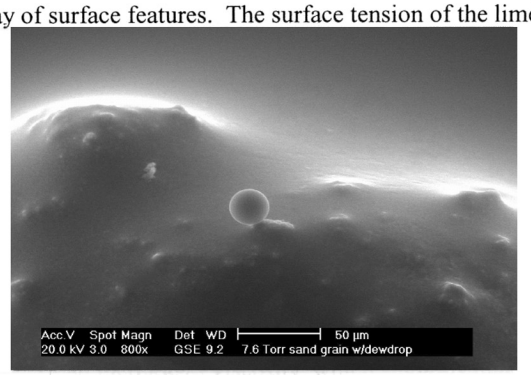


Figure 2 – *ESEM Wet Mode Feature: Water Droplet, Sand Grains, and Crystals*

remained fairly featureless with relief provided by sand grains and hydration products. Figure 2, from a preliminary investigation of a week old lime-sand slurry, shows the contrast between a water droplet that has formed with an increase in vapor pressure compared to the sea-like expanse with edges of elevated hydration crystals in relief (bright).

Lime Putty

The lime putty showed very similar features in wet mode, without the relief provided

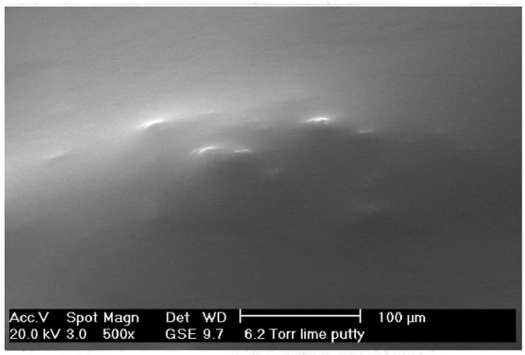
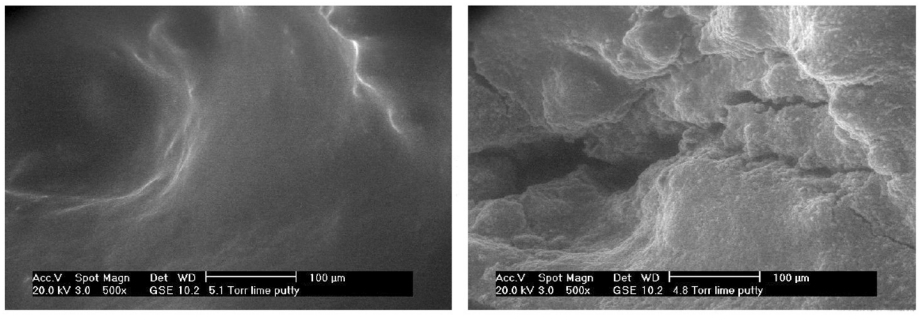


Figure 3 – *Lime Putty (wet mode)*

by presence of sand grains (Figure 3). Objects under the surface of the lime solution were difficult to distinguish because of the scattering of electrons, but faint cracks and hydration product close to the surface were visible. As the water vapor pressure was reduced, the sharpness of the features increased. Figure 4 shows the pressure reduction from 6.4 torr (100% RH) at 5.1 torr (a) to 4.8 torr (b).

Closer inspection of the smooth structure of the dried hydration products (Figure 5) shows that the individual crystals of calcium hydroxide are thin hexagonal plates varying in size from 0.1 µm to 1 µm.



a) 5.1 torr b) 4.8 torr

Figure 4 – *Lime Putty Drying*

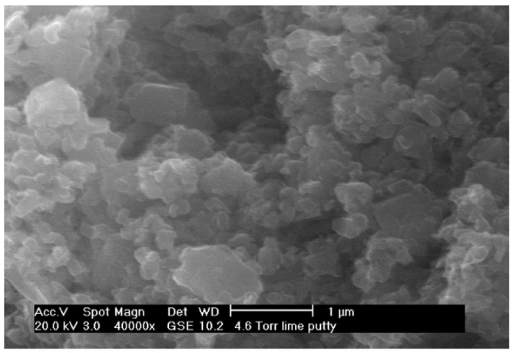
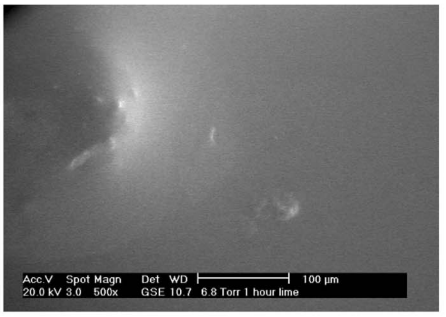


Figure 5 – *Calcium Hydroxide from Lime Putty*

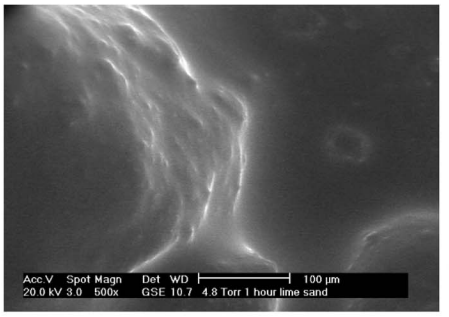
1 Hour Lime-Sand Slurry

Relatively few surface features were found in wet mode for the 1 Hour lime-sand slurry, and were due again to elevation of sand grains and hydration products. Figure 6 shows the drying evolution at a sand grain. Figure 6b reveals the edge of a large hydration cluster to the right of the sain grain. This cluster and the smaller ones near it appear to be of generally hexagonal shape built up of layers. In general, the smooth coating of the sand grains appears very similar to the dried lime putty.

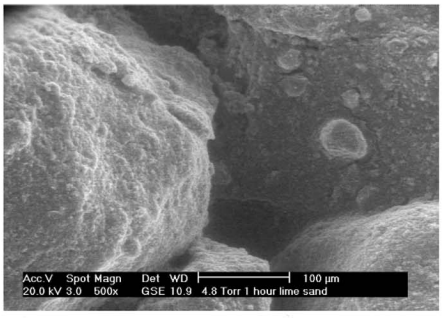
An interesting feature for the dried slurry appeared several times at the top surface of a sand grain of a dark flat crystal formation (Figure 7a). The darkness suggests that the formation is sufficiently thin to suppress secondary-electron effects. Higher magnification shows that the crystals are plate-like and thin, 1 µm or less, and intergrown. The very small hexagonal crystals are randomly forming the classic irregular "rosettes" of monosulfoaluminate in hydrated Portland cement. There also appears to be no adhesion of the bulk lime hydration product on the sand grains where these features are. The lime hydration product that is nearest to the bare area is less dense and level in appearance. These formations could be a result of the surface tension of the lime solution receding as water is removed by lowering the vapor pressure, stunting the crystal growth.



a) 6.8 torr

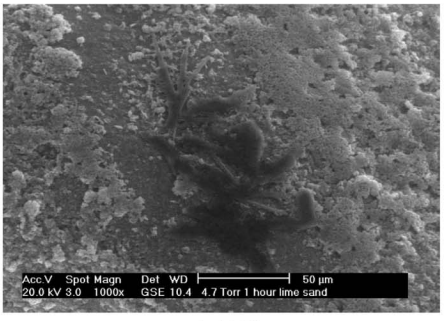


b) 4.8 torr

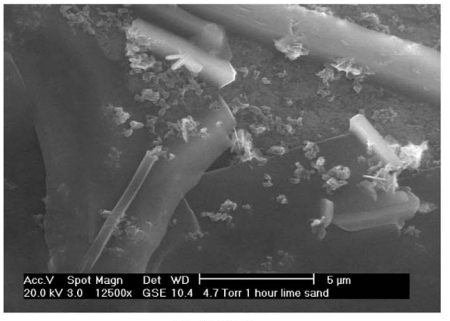


c) dried

Figure 6 – *1 Hour Lime-Sand Slurry Drying*



a) 1000x



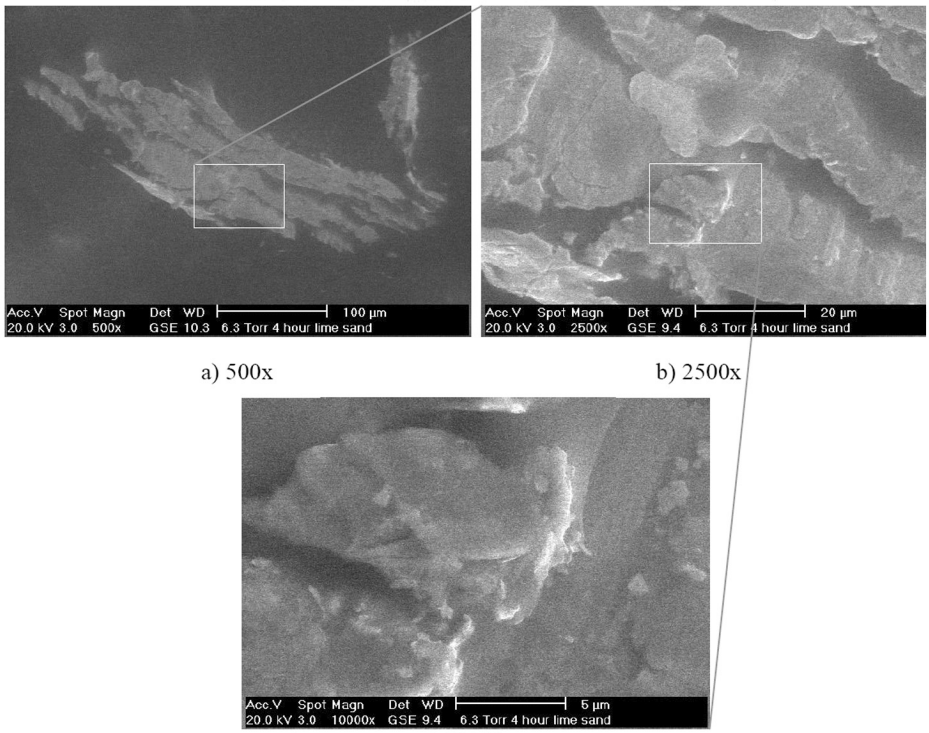
b) 12500x

Figure 7 – *Flat Crystal Formation in Dried 1 Hour*

4 Hour Lime-Sand Slurry

Somewhat more surface features were found in wet mode for the 4 Hour lime-sand slurry due to elevation of sand grains and hydration product. There was an increase in identifiable small hydration clusters on the sand grains and subsurface features. Figure

8a shows a lamellar feature on the scale of a sand grain not seen on the 1 Hour lime-sand slurry in wet mode. Higher magnifications (b & c) suggest that the submerged crystals are of similar form to the intergrown crystals seen in the dried 1 Hour lime-sand slurry (Figure 7b) but are of much greater thickness. Upon drying of the 4 Hour lime-sand slurry, the separations between the lamellæ in wet mode are actually the edges of overlapping sheets of hydration product (Figure 9), which appear bright because of the edge effect of the secondary-electrons. It is not clear if this feature was uniformly distributed within the 4 Hour lime-sand slurry, as the sample container was less than 1 cm in diameter, but it is possible that sliding of these sheets against each other contributes to the workability of this aged slurry and lower viscosity.



a) 500x b) 2500x

c) 10000x

Figure 8 – *4 Hour Lime-Sand Slurry Lamellar Feature (wet mode)*

The dried bulk hydration product on the sand grains had similar topology to that of the 1 Hour lime-sand slurry, but was more porous, delicate, and stratified. Shrinkage cracks were not in evidence between grains, but there was a separation, almost plastic-like, of the porous sheets (Figure 10). The increase in surface area could easily contribute to water retentivity by capillary effects, to the bond by interlocking in the masonry unit surface, and to self healing by dissolution and precipitation upon wetting to fill cracks.

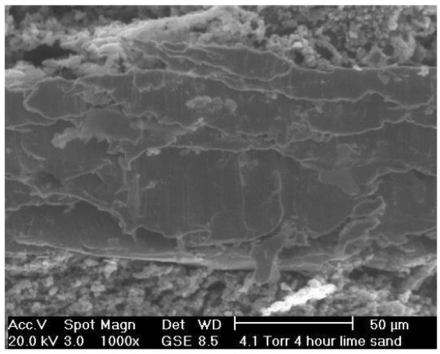


Figure 9 – *Dried 4 Hour Lime-Sand Slurry Lamellar*

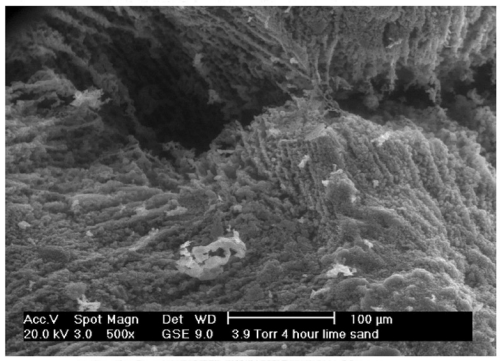


Figure 10 – *Dried 4 Hour Lime-Sand Slurry*

Addition of Portland Cement – Portland cement grains were added on the surface of a sample of 4 Hour lime-sand slurry. In wet mode, the grains are evident as their surfaces begin to dissolve in the saturated lime solution (Figure 11). As there is no evidence of hydration products with the Portland cement until the concentration of dissolved ions is large enough, the sample was only left in the microscope chamber for about 15 minutes

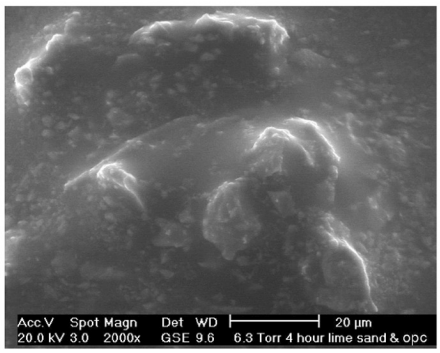


Figure 11 – *4 Hour Lime-Sand Slurry with Cement*

before the water vapor pressure was reduced. The dried structure of the lime hydration products is much like that of the 4 Hour lime-sand slurry, but with the addition of calcium silicate hydrate (C-S-H) needles and larger calcium hydroxide grains as identified in Figure 12.

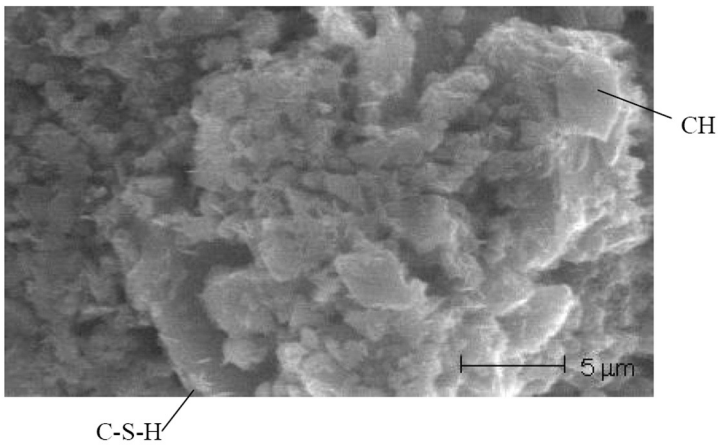


Figure 12 – *Dried 4 Hour Lime-Sand Slurry with*

Mortar Microstructure

The microstructure of the hardened mortar was examined using an optical microscope at a magnification of 30 times. The brick prism had been cut with a water-lubricated saw to expose the center of each mortar in the bed at 7 days. The cut surfaces showed a predominance of white calcium hydration product. The Putty mortar showed blocky crystal formation on the sand grain surfaces, gaps at the interfaces with grains, and pull-outs where grains had been. The 1 Hour mortar showed cracks around grains and single plate crystals in pull-outs and voids. There were more deep pull-outs and voids, and very little crystallization on the grains themselves. The 4 Hour mortar had crystal formations in the pull-outs, with little crystallization on the sand grains.

The observations suggest that the Putty and 1 Hour mortars experienced more shrinkage than the 4 Hour mortar. The crystal formation on the grains of the Putty could be an indication of interface adhesion contributing to a higher compressive strength.

Implications to Selection or Specification of Masonry Materials`

The differences in morphological characteristics of the 1 Hour and 4 Hour lime-sand slurry were most evident in the dried state observed with ESEM. Although wet mode observation of the 4 Hour lime-sand slurry showed a large thick flat crystal feature as opposed to the small thin flat crystal features on the surface of sand grains in the 1 Hour lime-sand slurry, the major difference was in the density and thickness of the bulk lime hydration product, and its form at grain to grain interfaces. The increase in surface features and the reduction of the size of these features in the 4 Hour lime-sand slurry

when Portland cement was introduced to the mortar could play a key role in the saturation of dissolved ions in solution to a concentration initiating precipitation of C-S-H, which is implicated in the strength of cement based materials due to its proportion in the cement hydration products and the high surface area interlocking. When sufficient thickness of hydration product has formed around a cement grain to prevent all of it from dissolving into solution indicating that sufficient water is available for continued hydration, higher strength is expected as well[2]. Increased amounts of calcium hydroxide crystals in the thicker coating may contribute to a decrease in strength if the crystals were oriented preferentially, like at aggregate interfaces in cement-based materials, but there is no distinct orientation in the 4 Hour lime-sand slurries. There does not appear to be a significant difference in the amount of large calcium hydroxide crystals oriented with their hexagonal surfaces parallel to sand grains in the 1 Hour and 4 Hour lime-sand slurries.

The investigation suggests that the amount of hydration product is more important to the workability and hardened properties of the mortar than the crystal morphology, which is different upon aging as well. Determining a catalyst for crystal shape and size may be of limited use. It would be of greater benefit to provide a sand that is lime-rich, or pre-treated like the crushed aggregate used in highway base courses in Florida[3] which have been exposed to moisture in the air and have hydration products formed on the aggregate before use in a mortar. This could be accomplished in much the same fashion by soaking the materials in lime slurry to a sufficient age, drying, packaging and marketing it as pre-limed masonry sand with "no need" to add additional lime. Material provided in this form may appeal to the time conscious contractor or mason. Future work on manufacturing techniques to reproduce lime-aged sands could provide further insight.

Summary

The effect of aging lime-sand slurries on calcium hydroxide crystal size and shape, fresh mortar rheology and plastic flow, compressive strength and hardened microstructure were investigated with respect to benefits as a result of physical attributes. Lime-sand slurries and a lime putty were observed using an ESEM in the wet state and with removal of water, and the addition of Portland cement to the surface of an aged lime-sand slurry was also observed in wet and dry states. Mortars made with Portland cement and the lime-sand slurries were tested for rheological properties and flow, and compressive strength, in addition to being used in a brick prism to observe the hardened microstructure in 'situ.

The results suggest that the increase in surface area of the lime hydration products resulting from small, lightly packed calcium hydroxide crystals in thick coatings on the aggregates is the primary influence on workability, water retentivity and bond. The aging process contributed more to the thickness and porosity of the coating than it did to changing the crystal formations. One way to incorporate this benefit into a manufacturable masonry material is suggested by pre-liming masonry sand.

Acknowledgments

Graymont Dolime (OH) Inc. and Chemical Lime Company generously supported this research. We thank Anne Werner for providing brick units and IRA characterization, and Scott Robinson of the Image Technology Group for his help with the ESEM at the Beckman Institute for Advanced Science and Technology.

References

[1] Staley, H. R., "A Petrographic Study of the Bond Between Bricks and Mortar," *Transactions of the British Ceramic Society*, Vol. 39, 1939-40, pp. 85–100.

[2] Mindess, S., and Young, J.F., *Concrete*, Englewood Cliffs: Prentice Hall, 1981, p. 498.

[3] Graves, R.E., Eades, J. L, and Smith, L. L., "Calcium Hydroxide Treatment of Construction Aggregates for Improved Cementation Properties," *Innovations and Uses for Lime, ASTMP STP 1135,* D.D. Walker, Jr., T.B. Hardy, D.C. Hoffman, and D.D. Stanley, Eds., ASTM International, West Conshohocken, PA, 1992, pp. 65–77.

[4] Lange, D. A., Sujata, K., and Jennings, H. M., "Observations of Wet Cement Using Electron Microscopy," *Ultramicroscopy*, Vol. 37, 1991, pp. 234–238.

[5] Rodriquez-Navarro, C., Hansen, H., and Ginell, W. S., "Calcium Hydroxide Crystal Evolution upon Aging of Lime Putty," *Journal of the American Ceramic Society,* Vol. 81, No. 11, 1998, pp. 3032–34.

[6] Ashurst, J., "Mortars for Stone Buildings," *Conservation of Buildings and Decorative Arts,* Vol. 2, J. Ashurst, and F.G. Dimes, Eds., London: Butterworths, 1990, pp. 78–96.

[7] Cazalla, O., Rodriquez-Navarro, C., Sebastian, E., Cultron, G., and del la Torre, M.J., "Aging of Lime Putty: Effects on Traditional Lime Mortar Carbonation," *Journal of the American Ceramic Society,* Vol. 83, No. 5, 2000, pp. 1070–76.

[8] Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Romig, A. D., Jr., Lyman, C. E., Fiori, C., and Lifshin, E., *Scanning Electron Microscopy and X-Ray Microanalysis,* 2nd ed., New York: Plenum Press, 1994, pp. 572–574.

[9] Baker, I.O., *Treatise on Masonry Construction, 10th ed.,* New York: Wiley, 1912, pg. 746.

[10] Nichols, J.M., *A Study of the Progressive Degradation of Masonry Shear Walls Subjected to Harmonic Loading*, Doctoral Thesis, University of Newcastle, Newcastle, NSW, 2000.