Development and evaluation of a lime-metakaolin grout

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Abstract

Fluid, lime-based grouts for the conservation of historic buildings have been mentioned infrequently in the literature, and with relatively few details of the experimentation that led to their formulation, evaluation and use. For non-hydraulic limes, the fundamental dilemma is, of course, that limes cure by carbonation, and cavities to be grouted are places in walls where little or no air is available. Our work has therefore focused on the use of pozzolanic admixtures, and in particular on dehydroxylated clay. The paper describes the technical challenges associated with the development of a lime-metakaolin grout, created as part of an engineered “port” anchor system for structural stabilization in multiple lifts. Among these challenges are the competing requirements of fluidity, control of water, and the incorporation of aggregates to minimize shrinkage. The first large-scale use of the low-strength grout was in the fall of 2012, in the northeastern United States. Study of the lime-metakaolin formulation is on-going, with the potential to create a range of conservation materials, including crack fillers and repair mortars.

Keywords: lime-pozzolan; grout; metakaolin; lime-metakaolin

1. Introduction

This paper describes the development and evaluation of a low-strength pourable/pumpable grout. The material is one component of a structural repair system that utilizes a stainless steel anchor that spans across voids in a masonry wall. The anchor provides an integral “port” through which voids can be inspected, cleaned, pre-wetted, and then grouted. Anchors are produced in a wide variety of configurations and lengths, to suit geometry, loading, and grouting conditions.

The grout is based on a blend of lime and metakaolin, a dehydroxylated white clay. Dehydroxylation is the thermally-induced loss of what is often called chemically bound water. It is typically carried out at temperatures of 500-650 degrees C, and results in the development of pozzolanic reactivity as the aluminosilicate structure becomes amorphous or weakly crystalline (Fernandez et al. 2011). This ability to react with calcium hydroxide is lost at higher calcining temperatures, as other phases, including mullite and glassy silica, develop.

Metakaolin, or HRM (for high reactivity metakaolin), is an updated version of an ancient construction material. In his discussion of volcanic ash ("pozzolana"), the Roman writer Vitruvius noted that volcanic ash was not available in some places, adding that “if to river or sea sand, potsherds ground and passed through a sieve, be added, the mortar will be better for use” (Vitruvius Pollio, trans. Gwilt 1826).

Basic scientific studies on the calcining of kaolinite were done in 1933-49, as part of a larger research project undertaken by the U.S. Bureau of Reclamation, in conjunction with the construction of a number of concrete dams (Mielenz et al. 1950). Metakaolin—derived from China clay (kaolinite)--is described as a Class N calcined natural pozzolan in ASTM C618, a document first published in 1968 (ASTM 2008). It should be noted that there were no Class N pozzolans produced in the United States at that time (Cain 1994). That situation was to change in 1993-4, when an important investigation evaluated an HRM marketed in North America as a concrete admixture, and reported excellent results in terms of physical properties. In those tests, HRM seemed comparable to silica fume, which had appeared on the scene in the 1980’s (Marsh 1994).

Like fly ash (accepted in the concrete industry in the late 1940's), metakaolin can be added to portland cement concretes as a densifier and to increase strength, often with some reduction in the required amount of cement. But it is specifically its ability to enhance the setting of hydrated lime that should be of interest in the historic building preservation community.

The earliest reports of experimentation with metakaolin in conservation seem to have been in the 1990's (Bosc et al. 1993). Following the availability of a product manufactured in the U.K., there was some discussion of it among practitioners (Asp 2001), but most developmental research on lime-based grouts continued to be pursued with other reactive admixtures, such as brick dust and volcanic pozzolana itself (Griffin 2004). The most recent literature review on the subject of injection grouts for the conservation of historic buildings make only slight mention of metakaolin (Bicer-Simsir et al. 2009). At the present time, it appears that the only active research is in Spain (Sepulcre-Aguilar and Hernandez-Olivares 2010), along with our own work in the United States.

2. Grout formulation

The grout binder is based on a lime-pozzolan blend previously developed by one of the authors (Thomson 2003; Tanner et al. 2011). The lime is a dolomitic hydrate conforming to ASTM C207, Type S (ASTM 2006). Dolomitic hydrates, essentially equimolar mixtures of portlandite and brucite, have a long history of use in the United States. With prolonged slaking, they were particularly used for plastering, because of their plasticity. By about 1910, the demand for shorter slaking times (to suit faster methods of construction) and for dry hydrates (for blending with portland cement) exposed a serious issue: slow hydration of the magnesium oxide in dolomitic quicklime. This, in turn, led to the development of the Corson pressure hydrator in 1937, in Pennsylvania. By 1980, nearly all of the lime used for construction in the US was in the form of dry hydrate, and roughly 80% of that was dolomitic (Schork 2012a).

Our first tests, done on samples of a not-yet finalized mix design, suggested that the two-component binder (i.e., only lime and metakaolin) was setting too slowly for the intended purpose. The experimental addition of small amounts of portland cement was an obvious route to the development of satisfactory early strength.

One of the set-related requirements of a grout is the support of successive lifts in a practical timeframe. Based on discussions with grouting contractors and on our own experience, it was considered reasonable to allow for a single 1-meter lift to be installed every work day. Because of the scale of use, restraining against fluid pressures is critical. Each lift could exert up to 19 kPa of lateral fluid pressure at the bottom.

The port anchor system provides that restraint, with vertical spacing of the anchors at 1 meter, but a three-lift column of grout, if still entirely in the liquid state, creates forces that are near the reasonable load limit of the anchors. Thus, some solidification of the first lift is necessary at 48 hours. With a safety factor of 4, the 48-hour strength requirement was calculated as 0.23 mPa (33 psi).

Cubes of a cement-modified mix were unmolded for testing at 48-hours. With each loading increment, the material relaxed noticeably, confirming that it was still in a semi-plastic state. Further study was done with digital micrometers to measure transverse (Poisson) strain as the axial load was applied. From this data set, a working strength of the grout was determined to be 0.70 mPa (102 psi). Transverse strain at that point was measured at about 0.05%, just less than the measured shrinkage at 28 days (see "Laboratory evaluation", below). These effects roughly cancel each other, so that the first lift can carry two additional lifts at the start of day three without additionally loading the restraint system.

The current version of the grout has a portland cement content at less than 4% by weight of the total dry powder. As this is less than 14% of the binder weight, the formulation easily complies with the designation of "PHLc" in ASTM C1707, which sets an upper limit of 20% (ASTM 2009a). In volumetric terms, the binder is equivalent to 1 part white portland cement and roughly 13 parts of the pozzolanic hydraulic lime.

The formulation is made flowable by the addition of a superplasticizer. These admixtures, also called high range water reducers, were introduced in the concrete industry in about 1980. (Conventional lignosulphonate water reducers have been in use since the 1930's.) The benefit of superplasticizers lies in the ability to dramatically increase fluidity while maintaining a low water/cement ratio. This, in turn, prevents the segregation of constituents that would occur if fluidity is instead enhanced by the addition of larger amounts of water.

Although developed for use in cement-based systems, superplasticizers can work in the presence of substantial amounts of hydrated lime by adjusting the concentration (Jerome et al. 2003). Two of the authors have had substantial experience with them (in liquid form) for the modification of cement-lime blends since the mid-1990's.

For the new grout, we are using a polycarboxylate powder. As this type of superplasticizer can be pre-blended with the other dry constituents, the grout only requires mixing with water in the field.

Aggregate in a grout is desirable to limit shrinkage, but is always somewhat problematic. The maximum particle diameter controls the ability to inject into narrow openings or to pump through narrow tubes. Aggregates will increase grout viscosity; this is particularly true with angular sands. For low viscosity grouts, there is (as noted earlier) the additional problem of segregation.

The selected aggregate is a highly rounded, fine quartz sand (Figure 1), with more than 97% passing a No. 50 (300 micron) screen. More than 82% of the particles are in the range of 75 to 200 microns. As the sand has been washed for use, there are no particles smaller than 50 microns.

Figure 1: Fine quartz sand used in PHLc grout at right; a conventional masonry sand at left

3. Laboratory evaluation

Density of the grout in dry powder form is 1.12 g/cc. To prepare all test specimens, laboratory mixing of the grout was done gravimetrically, at 6 parts powder to 1 part water. For field use in the US, where the construction industry is still largely non-metric, this is equivalent to 1 fifty lb bag to 1 gallon of water. Mixing is initially by hand, then with a helical mixing paddle at 1,000 rpm (minimum) for several minutes, until blended and flowable. The fully cured grout specimens have a density of 1.70 g/cc (106 lb/cu ft).

For compressive strength testing, 50 mm cubes were cast and placed in sealed plastic containers for prolonged moist curing. Groups of these were removed and unmolded at 7, 28, 90 and 120 days. Strength data as a function of time is presented in Figure 2, which shows the mean 120-day strength nearly leveling out at 12.89 mPa (1,869 psi). By comparison, most commercial cementitious grouts have 28-day strengths of 34 mPa (4,931 psi) or more.

It should be noted that the 7-day strength, at 3.51 mPa, is only 36% of the 28-day value (9.73 mPa). For cement-based concretes, 7-day strength is typically 65 to 75% of the value at 28 days. The gradual nature of the strength growth curve for the PHLc grout is a reminder of the relatively slow progress of the multi-step lime-metakaolin reaction. X-ray diffraction (XRD) analysis by one of the authors has confirmed that the calcium hydroxide in the PHL is slowly consumed in the first 28 days.

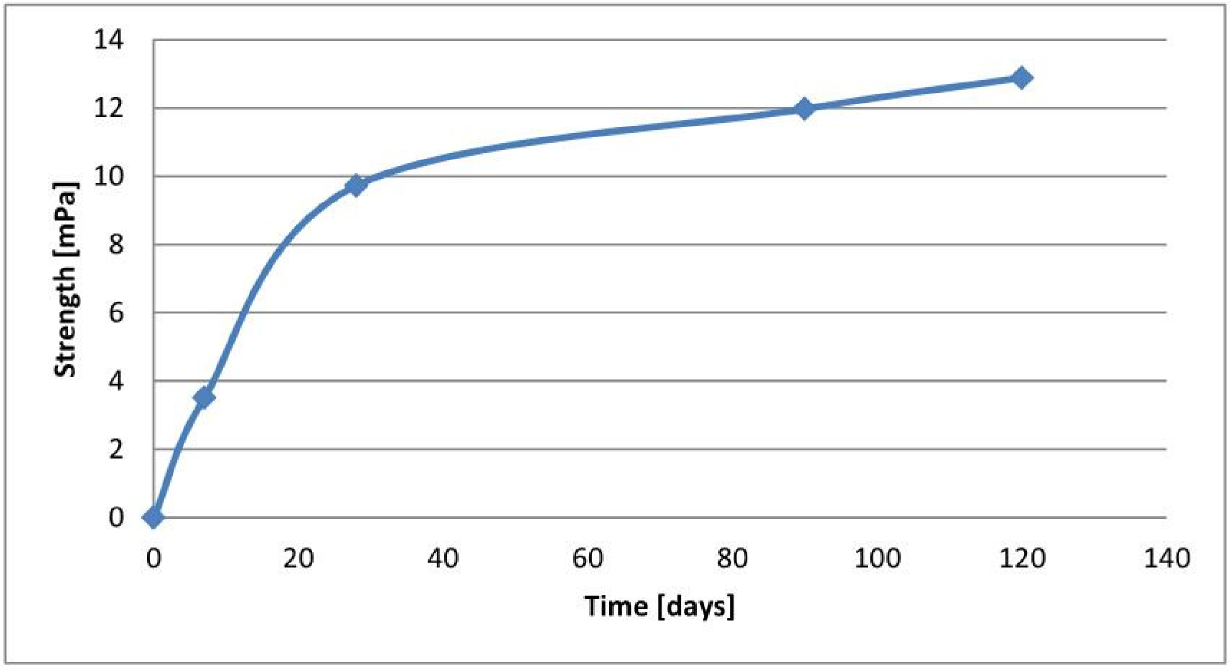

Figure 2: Compressive strength of PHLc grout (in mPa) versus time

Another set of 25 mm cubes was moist-cured for 120 days, to be used to study water absorption and freeze/thaw behavior. The water absorption procedure is a modification of ASTM C97, for stone, with air drying (rather than oven drying) to constant weight (ASTM 2009b). Specimens were fully immersed in water for 48 hours, the dry weights having been recorded at the start of the procedure. At the end of the soaking period, each sample is removed from the water, the surface quickly patted dry, and the wet weight recorded. For each sample, the dry weight is subtracted from the wet weight, to compute the weight of water absorbed. This is divided by the dry weight, and expressed as a percentage. The mean water absorption value for the PHLc grout is 9.6%.

For freeze/thaw evaluation, the procedure is an aggressive modification of ASTM D5860, for mortars (ASTM 1995). Immediately following the 48-hour water absorption test, PHLc cubes, together with cube samples of some commonly-used cement-lime mortar mixes for comparison, were placed in a freezer at 15^0 F for 16 hours. (The mortar cubes were also cured for 120 days.) Thawing is for 8 hours in tap water at room temperature, and the entire process is repeated, with re-weighing at the end of each thaw. (When circumstances require that testing be interrupted, samples are kept in the freezer.)

Individual Y-axis values, plotted for each cycle, are computed as the mean of the wet weight (from all samples in the set) minus the original (that is, intact) mean dry weight, divided by that dry weight, times 100 (see Figure 3). Thus, at the start of the testing program, this value is simply the % water absorption (48 hours), essentially as per C97. As the experiment progresses, some curves actually rise slightly until failure begins, due to imbibition of additional water beyond the amount absorbed in 48 hours. The downward turn of the lines records the progressive crumbling of the samples by cyclical freezing.

As to the number of cycles to failure, our interpretation of durability in this test is related to the performance of Indiana limestone, a widely-used (and durable) American building stone. It fails reproducibly in this test at about 60 cycles. The cement-lime mortars showed dramatic failure, some as early as 10 to 15 cycles. The PHLc grout began to show some losses at 35 cycles, with continuing losses thereafter at a relatively slow pace. The test was ended at 50 cycles.

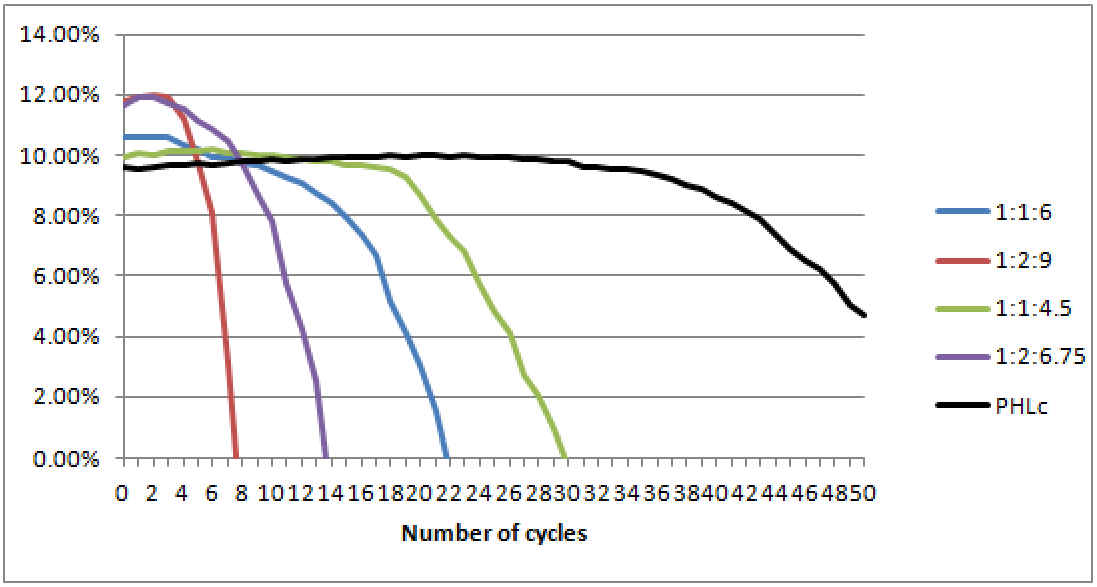

Figure 3: Freeze/thaw performance of PHLc grout versus cement-lime mortars

A number of other parameters have been studied. Chloride ion content, measured as per ASTM C1218, is 0.002% of the total dry weight of the cured grout (ASTM 1999). Evaluation of shrinkage was by a modification of ASTM C1090, which measures negative height change in a cast cylinder of grout over time (ASTM 2010a). Shrinkage at 28 days is 0.06%.

Consistency of the freshly-mixed grout was investigated by two different test methods, with some very curious results. Mean flow cone efflux time, filling the cone within one minute of mixing, was 5 minutes and 33 seconds (ASTM 2010b). For efflux times of greater than 35 seconds, this test method suggests that the consistency would be more reliably studied with a flow table.

Alternatively, if interpreted as per C1090, the measured time would permit characterization of the PHLc grout as "flowable" if the flow table value was between 125 and 145% (ASTM 2007). Dropping the table five times in three seconds, grout flow was off the table, i.e., greater than 156%. That result might permit use of the term "fluid" were it not for the long efflux time. This interesting discrepancy suggests that the grout is somewhat thixotropic, a rheological characteristic that is presumably attributable to the pozzolan.

Water vapor transmission was measured on 28-day moist-cured disks, allowed to air dry at room temperature prior to the creation of dish assemblies (Jacob and Weiss 1989). The measured WVT rate (modified water method) is 1.9 g of water/sq meter/hour (ASTM 2005). This is significantly greater than a value reported recently for white cement mortars (Schork et al. 2012b).

4. Field trials and on-going research

Since September of 2012, five field projects have been undertaken with the PHLc grout. Of these, the largest was the stabilization of the tower of Grace Episcopal Church, a late 19th century structure in New Bedford, Massachusetts. The tower is constructed of stone, with massive brick pilasters at each corner. Over time, the tower had contorted, with buckling and detachment of the brick from the rubble stonework behind it at one corner.

Core drilling revealed a separation of up to 10 cm. In this condition, the pilaster had a fraction of its original strength, as 60 cm of composite masonry had become 20 to 30 cm of brick sliding past 30 to 40 cm of stone. The magnitude of the structural load and the precariousness of the situation argued against disassembly and reconstruction. Installation of stainless steel "port" anchors, followed by injection of the PHLc grout, was instead carried out to bond the corner back together, so that it could again function as a single element.

Laboratory research continues in a number of areas. Additional testing of the grout is underway to assess splitting tensile strength (so-called Brazilian method) and bond strength (with crossed couplets of brick and sandstone).

Initial results on bond strength showed a remarkable level of adhesion. This will be further studied by direct pull-off.

Along with consideration of the (now standard) grout as a water-borne adhesive, there is on-going experimentation with modified formulations for other purposes. One is based on essentially the same binder, but working with a range of masonry sands to prepare low-strength, frost-resistant conservation mortars for pointing and stone repair. Another involves a re-screening of the fine sand to an even finer size, to create a second "conservator-grade" grout for injection into narrower separations, and wiping into the surface of hairline cracks.

References

Asp, M. (2001), Tests of injectable mortars in laboratory and field, in Conservation of Mural Paintings, Lindborg, U., ed., National Heritage Board, Stockholm, ISBN 91-7209-223-8, 39-44

ASTM (1995), D5860-95, Standard test method for evaluation of the effect of water repellent treatments on freeze-thaw resistance of hydraulic cement mortar specimens, ASTM International, 3 pp.

ASTM (1999), C1218-99, Standard test method for water-soluble chloride in mortar and concrete, ASTM International, 3 pp.

ASTM (2005), E96-05, Standard test methods for water vapor transmission of materials, ASTM International, 11 pp.

ASTM (2006), C207-06, Standard specification for hydrated lime for masonry purposes, ASTM International, 2 pp.

ASTM (2007), C1437-07, Standard test method for flow of hydraulic cement mortar, ASTM International, 2 pp.

ASTM (2008), C618-08a, Coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM International, 3 pp.

ASTM (2009a), C1707-09, Specification for pozzolanic hydraulic lime for structural purposes, ASTM International, 3 pp.

ASTM (2009b), C97-09, Standard test methods for absorption and bulk specific gravity of dimension stone, ASTM International, 3 pp.

ASTM (2010a), C1090-10, Standard test method for measuring changes in height of cylindrical specimens of hydraulic-cement grout, ASTM International, 5 pp.

ASTM (2010b), C939-10, Standard test method for flow of grout for preplaced-aggregate concrete (flow cone method), ASTM International, 3 pp.

Bicer-Simsir, B. Griffin, I., Palazzo-Bertholon, B., and Rainer, L. (2009) Lime-based injection grouts for the conservation of architectural surfaces, Reviews in Conservation, 10, 3-17

Bosc J.L., Chabannet, M., Pera, J., and Auger, F., (1993), Altération des mortiers de ciment placés dans une ambiance aérienne salie: intérêt de l'ajout de metakaolin, in Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress, Thiel, M.-J. (ed.), E. & F.N. Spon, ISBN 0-419-18410-4, 67-74

Cain, C.J. (1994), Mineral admixtures, in Significance of Tests and Properties of Concrete and Concrete-making Materials (STP 169C), Klieger, P., and Lamond, J.F. (eds.), American Society for Testing and Materials, ISBN 0-8031-2053-2, 500-508

Fernandez, R., Martirena, F., and Scrivener, K.L. (2011) The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite, Cement and Concrete Research, 41, 113-122

Griffin, I. (2004) Pozzolanas as additives for grouts: an investigation of their working properties and performance charateristics, Studies in Conservation, 49 (1), 23-34

Jacob, J. and Weiss, N.R. (1989) Laboratory measurement of water vapor transmission rates of masonry mortars and paints, APT Bulletin, 21 (3/4), 62-70

Jerome, P., Weiss, N.R., Risdal-Barnes, M., Crevello, G. and Chusid, J.M. (2003) Conserving the ruins of a Hellenistic farmhouse in Crimea, Ukraine, APT Bulletin, 34 (2/3), 5-14

Marsh, D (1994) An alternative to silica fume?, Concrete Products, November issue

Mielenz, R.C., Witte, L.P. and Glantz, O.J. (1950), Effect of calcination on natural pozzolans, in Symposium on Use of Pozzolanic Materials in Mortars and Concretes (STP 99), Stanton, T.E. and Blanks, R.F. (eds.), American Society for Testing Materials, 43-92

Schork, J. (2012a) Dolomitic lime in the US: history, development and physical characteristics, Journal of Architectural Conservation, 18, 7-25

Schork, J., Weiss, N.R., and Walsh, J.J. (2012b) Comparative laboratory evaluation of conservation mortars, APT Bulletin: Journal of Preservation Technology, 43 (1), 7-14

Sepulcre-Aguilar, A. and Hernandez-Olivares, F. (2010) Assessment of phase formation in lime-based mortars with added metakaolin, Portland cement and sepiolite, for grouting of historic masonry, Cement and Concrete Research, 40, 66-76

Tanner, J.E., Schuller, M.P., Thomson, M.L. and Wo, S., (2011), Validation of a newly developed standard for evaluating mortar for the repair of historic masonry (ASTM C1713-10), in Eleventh North American Masonry Conference

Thomson, M.L. (2003), Pozzolan-lime mortar: limitations of ASTM C593, in Masonry: Opportunities for the 21st Century (STP 1432), Throop, D., and Klingner, R.E. (eds.), ASTM International, ISBN 0-8031-3450-9, 88-94

Vitruvius Pollio, M., trans. by Gwilt, J. (1826), The Architecture of Marcus Vitruvius Pollio, in Ten Books, Priestley and Weale, 413 pp.