



DEVELOPMENT OF A SYNTHETIC LIMESTONE FOR MASONRY APPLICATIONS

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ABSTRACT

This study was inspired by recent findings that some of the blocks in the pyramids of Egypt are synthetic made by combining diatomaceous earth, DE, with limestone aggregate and activated by lime. As a feasibility study this work reports on the development of a NaOH-activated masonry material in which the Si in the cementing phase comes D . Initial attempts at a NaOH/DE based material using sand as an aggregate achieved strengths of 45 MPa, but were soluble in water. After curing at 90 °C for 6 - 48 h, formulae containing small quantities of metakaolin and quicklime achieved compressive strengths on the order of 20±5 MPa; curing at 90 °C for a week increased the average strength of one of the formulae to 35 MPa, suggesting that the strengths of all formulae will increase with time. The slight alteration of the formulae by adding metakaolin and/or quicklime lowered the compressive strengths, but dramatically enhanced the water solubility resistance of this mortar when compared to compositions that did not contain them. X-ray diffraction spectra of the various cement pastes were featureless, indicating that the cementing phase is fully amorphous. The absence of C-S-H suggests that the cementing phase that forms here is unlike that formed in ordinary Portland cement.

KEYWORDS: Alkali-Activation, Diatomaceous Earth, mortar, Pyramids

INTRODUCTION

A theory proposed by Davidovits in the early 1980s claimed that the limestone blocks making up the bulk of the pyramids of Egypt were not, as was commonly held, carved and hoisted into place; rather, they were made of a concrete-like material containing a limestone aggregate held together by what he called “geopolymers” [1, 2]. This synthetic limestone would have been formed by the disaggregation of Egyptian limestone in a solution made highly alkaline through use of lime, natron, and/or plant ash, and mixed with naturally occurring clays, so as to create an amorphous, quasi-zeolitic binder.

Analysis of inner and outer casing stones from the Great Pyramid of Khufu showed, however, that they were in fact held together by a cementing phase formed of amorphous Si and Ca/Mg-

silicates [3]. In other words, the cementing phase did not contain Na or Al. The conspicuous absence of these elements eliminated the use of clay as a possible reactant in the binder, leaving only diatomaceous earth (DE, see below) as the source of Si.

The geopolymers developed by Davidovits have been the subject of much interest in recent years, and are reported to have strengths comparable to those of OPC-based concretes [4], high thermal stabilities [5], and the ability to encapsulate toxic waste, either through immobilization in the cementing phase or through chemical incorporation into the structure [4, 5]. These geopolymers also have a much smaller carbon footprint than OPC.[6] During the calcination of CaCO_3 to form CaO, roughly one ton of CO_2 is produced for each ton of OPC (half of the CO_2 is produced, the other half through the consumption of fuel to attain the high temperatures needed for calcination. Thus, even with an ideal fuel that did not produce greenhouse gases during combustion, a ton of OPC would still create roughly a half-ton of CO_2 . In total, the cement industry is the third largest producer of greenhouse gases, representing 5 – 10 % of global production and consuming nearly 5% of global industrial electricity [7, 8]. ‘Geopolymers,’ on the other hand, do not rely on the calcination of CaCO_3 and thus produce less CO_2 .

These properties have led to the use of geopolymers as a replacement for structural concrete, foundry equipment, or quick-setting runways for aircraft [9]. To date, many geopolymers have been synthesized starting with a host of materials, including fly ash[10] and naturally occurring clays such as metakaolin[11].

Diatomaceous earth (DE) is a naturally occurring mineral made up from the exoskeletons of unicellular marine or freshwater algae.[12] With time, large and pure deposits of amorphous silica can form. DE has a number of advantages over Al-containing metakaolin clays, in that it is cheaper and does not require high-temperature processing to render it reactive. The use of Si in geopolymers has previously been limited to the use of silica fume and soluble silicates.[5-10]

The purpose of this paper is to show that it is possible to fabricate masonry materials wherein the cementing phase is alkali/DE-based and the aggregate is a fine limestone. Although these formulae do contain Na, they are a first step on the path of duplicating the technology with which we believe the ancient Egyptians constructed the pyramids. Further, efforts to render the concrete resistant to dissolution in water are reported.

EXPERIMENTAL PROCEDURE

The reactants used for the masonry materials were: NaOH pellets (Alfa Aesar, Ward Hill, MA), DE (PermaGuard, Inc., Albuquerque, NM), quicklime (Graymont, Inc., Bellefonte, PA), and metakaolin (Concrete Countertop Institute, Raleigh, NC.) Limestone (OldCastle Stone Products, Charlotte, NC, 91% CaCO_3 equivalent; 92 vol.% pass through 20 mesh) was used as aggregate. The samples were cured in 5 cm x 10 cm cylindrical molds (Jatco Industries, Union City, CA.) A set of initial exploratory samples were formulated using only NaOH, DE, and sand.

All samples were manufactured in the same manner: the NaOH pellets were first dissolved in water to make an activating solution. In a separate beaker, water was added to the ground lime and stirred to form a white paste. The DE and metakaolin powders were dry-mixed in a plastic container and the activating solution was then added. (For the exploratory samples, DE was added to the NaOH solution, which initiated an exothermic reaction the result of which was a brown syrup to which aggregate was added. Samples were then molded as described below.)

Although the viscosity initially rapidly increased, as the exothermic dissolution of the powders continued, the viscosity fell; the end result was a thick, brown syrup. After stirring for ≈ 120 s, the lime slurry was mixed into the syrup, which further lowered the viscosity. Finally, after mixing for another ≈ 60 s, the limestone aggregate was added to form the concrete and mixed with a paint mixer for another ≈ 120 s. In general, the addition of the lime slurry reduced the viscosity of the cement; addition of metakaolin or reduction of NaOH increased it.

The mixture was packed into molds, sealed with plastic wrap, and left standing for ≈ 1 h at room temperature, before being placed in an oven (Fisher Model 215G, Pittsburgh, PA) for heat treatment at different times and temperatures.

Three samples were compression tested 1 d after heat treatment. To explore the solubility of the samples, three samples of a given composition were removed from the molds after 1 d, soaked in water for 3 d, and allowed to dry for 1 d, before compression testing. Two sample batches were left soaking in water for longer periods of time (1, 3 and 6 months.)

Four different formulae, plus the exploratory formula, were made (Table 1.) Formula A contained lime; B contained lime and a lower amount of NaOH; C contained both lime and metakaolin; and D was similar to the third but had less NaOH.

Table 1: Composition (g) of formulae investigated

Formula Name	Exploratory (g)	A (g)	B (g)	C (g)	D (g)
Diatomaceous Earth	60	105	105	105	105
NaOH	36	63.5	50	63.5	50
Metakaolin	0	0	0	25	25
Lime	0	24.5	24.5	24.5	24.5
Limestone	171.6	650	650	650	650
Water	270	140	140	140	140
Sand	216	0	0	0	0

Mechanical properties in the form of compressive strength were determined (Instron 5700, Norwood, MA) in accordance with ASTM standard C39. When needed, the samples were ground to ensure parallelism.

A scanning electron microscope, (SEM; Zeiss Supra 50VP, Thornwood, NY) with an electron energy dispersive spectrometer, (EDS; Oxford Inca X-Sight, Oxfordshire, UK), was used for elemental analysis of the various microstructures. For SEM analysis, samples were mounted, ground, and then polished with diamond solution. Image analysis was performed on the SEM micrographs using ImageJ software developed by the national institutes of health.

Powders for x-ray diffraction (XRD; Siemens D500, Karlsruhe, Germany) experiments were obtained by drilling into the bulk of the samples and run with a Cu $K\alpha$ source, $\lambda = 0.154$ nm, step size of 0.02° , and dwell time of 0.5 s.

RESULTS AND DISCUSSION

After removal from the plastic molds, the samples had a beige color; most samples also had a glossy surface and were (aside from formula D, see below) crack free. The exploratory formula looked remarkably like natural sandstone but dissolved within minutes of being submerged in water. When the other four formulae were submerged for 3 d, however, the pH of the water increased to around 12 within the first 2 h of submersion, and a white precipitate settled to the bottom of the container after 3 d, but the samples remained intact.

Even after 48 h at 90 °C, none of the samples lost more than 0.5 wt.%, therefore, almost all of the water remains bound in the cementing phase. Sample shrinkage was minimal; all samples had to be cut out of the molds.

During the optimization of the exploratory formula, some general trends were observed: Too much NaOH led to a violent reaction, the result of which was a brown syrup that did not harden; too little while decreased workability and inhibited the reaction; too much water created an overly fluid material that did not harden; finally, too much DE (or too much aggregate) raised the viscosity of the system to a point that resulted in serious workability issues. After the concentrations of these various reactants were optimized, the strength of the exploratory samples reached 45 ± 5 MPa when heated at 60 °C for 6 h. Unfortunately, these samples had no strength after even an hour submerged in water.

Longer curing times had no effect on solubility; neither did raising the temperature from 60 to 90 °C. Samples that were not cured in the oven, rather, we left to sit at ambient conditions, still dissolved in water, however, did not harden completely and achieved strengths on the order of 20 MPa, showing plastic behavior.

With the possible exception of formula D, after 24 h of curing the difference in strength between the various compositions was small and hovered around 20 MPa (fig. 1). For example, after curing for 48 h at 90 °C, the ultimate compressive strengths of formula A were 25 ± 5 MPa; for formula B the maximum strengths observed were 20 ± 4 MPa. The combined additions of lime and metakaolin clay in formula C resulted in samples with a strength of 18 ± 2 MPa after curing for 6 h at 90 °C and 22 ± 4 MPa after a 24 h cure (fig. 1.) Longer curing times, on the other hand, had a significant effect on strength. For example, the average compressive strength of the 3 samples of formula C left to cure at 90 °C for a week (168 h), was $\approx 36\pm 3$ MPa.

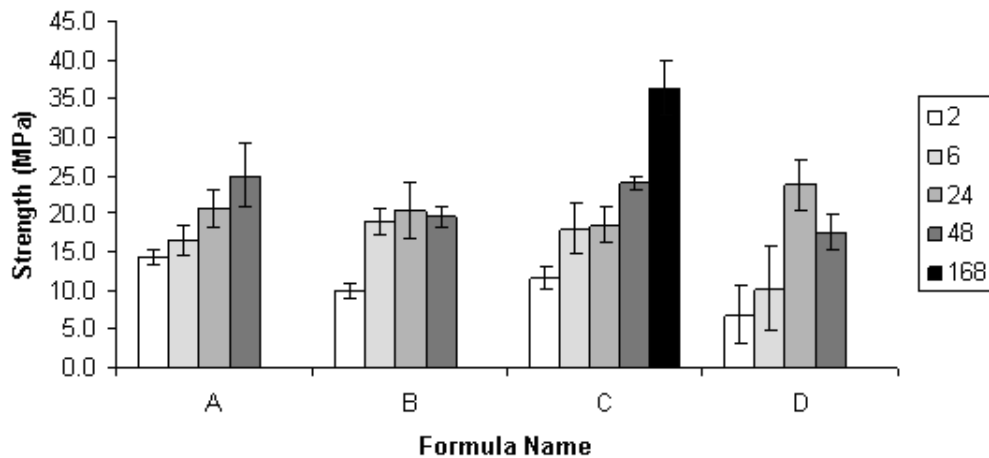


Figure 1: Strength of formulae heat treated at 2, 6, 24, or 48 hours at 90 °C and formula C cured for 168 h before soaking in water. 3 samples of each formula were tested.

Three samples of formula C were also cured at 90 °C for 2, 6, 24, or 48 h and subsequently left to cure at room temperature for an additional month. The average strengths after the month of curing depended on the initial curing times. Samples initially cured for 2 h increased in strength by ≈ 55 % (to $\approx 20\pm 3$ MPa); samples cured for 6 or 48 h increased in strength by ≈ 25 % (to ≈ 27 MPa.) Why those cured for 24 h showed no increase in strength is not clear. Since the latter numbers are small, and within the experimental scatter of the results, it appears that curing at

room temperature only enhanced the strengths of the samples that were heat treated for the shortest time. When taken together with the results of the samples cured for a week (fig. 1), it is clear that temperature and time are interchangeable; annealing at higher temperature or holding at lower temperature for longer times increase the strength. This is an important conclusion because it is reasonable to assume that if these formulae are used as masonry materials they should, over time, become stronger.

The addition of metakaolin together with less NaOH in formula D resulted in an increase in cement viscosity that led to poor mixing, which may partially explain why this composition was weaker than the others. While the strengths for short curing periods were low, they increased to levels similar to the other formulae with longer curing times (fig. 1.)

The strength results after soaking in water for 3 d (fig. 2) were statistically indistinguishable from those that were not soaked (fig. 1.) It thus appears that the samples were water resistant for that time period, which contrasts with the exploratory samples. Apparently the presence of Ca^{2+} ions in solution greatly enhanced the dissolution resistance of the cementing phase. If the presence of Al^{3+} ions further enhances the dissolution resistance is unclear.

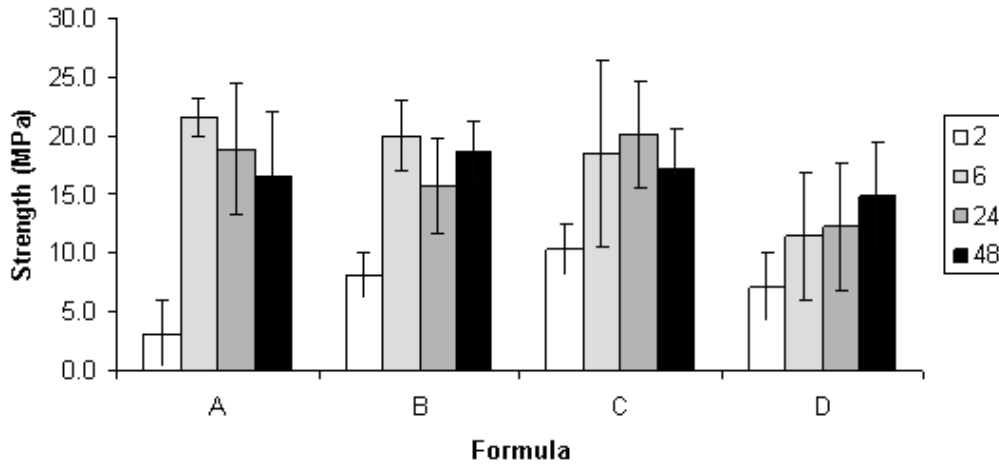


Figure 2: Strength of formulae treated at 90 °C for 2, 6, 24, or 48 h and soaked in water for 3 d.

As noted above, specimens of formula C that had been cured at 90 °C for 6 h were submerged in water for 1, 3, and 6 months. After soaking, the samples were removed, allowed to dry for 1 d, and then compression tested. After a $\approx 25\%$ drop in strength after the first month of soaking, longer soaking times caused little further degradation (fig. 3). At this time it is not clear whether this plateau represents a true steady state or simply reflects a balance between longer curing times that would enhance the strengths and dissolution that would reduce them. More work is needed, especially in an open system, with flowing water, to further explore the water resistance of the compositions tested herein.

Even after 6 months of soaking, the pH of the water did not rise higher than it had risen after the first hour; however, longer soaking resulted in a larger quantity of the white precipitate that x-ray diffraction revealed to be sodium carbonate, Na_2CO_3 .

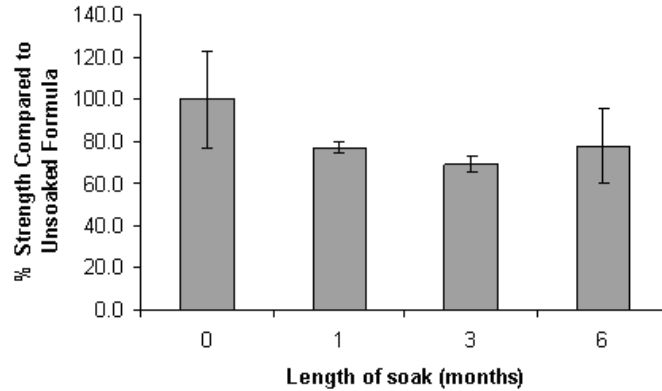


Figure 3: Results of long term soaking, based on samples of Formula C heat treated for 6 h at 90 °C prior to soaking.

Select specimens of each formula that had been cured for 6 h and fractured during compression testing were investigated in the SEM (fig. 4). At low magnifications, aggregate particles, the cementing phase, and pores were easily observed on polished specimens (fig. 4a.) In backscatter electron (BSE) mode, the difference between aggregate and cementing phase became more pronounced, and it became possible to observe cracks (fig. 4b.)

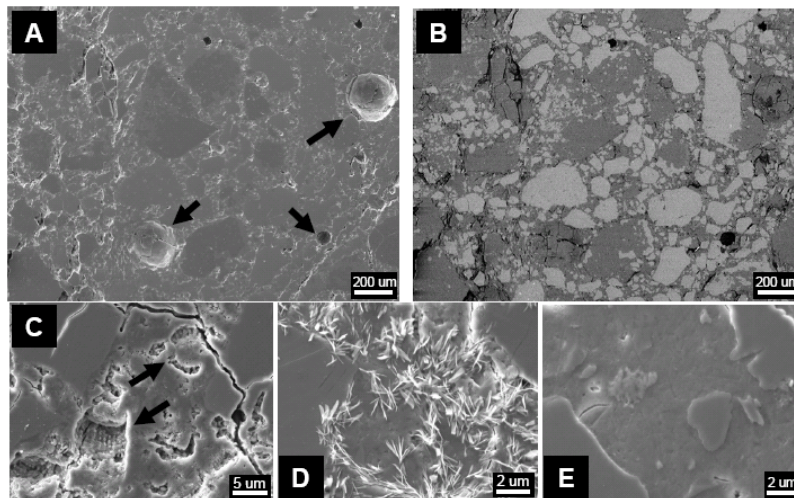


Figure 4: SEM imagery. a) Typical polished surface, with visible aggregates and pores (arrows). b) BSE image with more clearly defined aggregate (light color) and cracks. c) Undissolved diatoms (arrows) found in formula D. d) Grass-like structures found on the surface of formulae C and D. e) High-magnification image of pure cement, showing a lack of the extensive cracking seen in the exploratory formula.

Formula D contained numerous undissolved diatoms (fig. 4c); none were observed in other formulae. This is an important observation that attests to the ease by which the DE dissolves in alkali solutions. Given that the dissolution of Si is the key step in the formation these alkali activated fine aggregate concretes, this bodes well for future formulations. It also confirms

the extent of knowledge available to the ancient Egyptians and the viability of reconstituting limestone with DE.

The two formulae containing Al showed the presence of thin, grass-like structures on the sample surface (fig. 4d.) Although they were too thin for EDS measurement, they appeared to be a Na-based salt, as Na is known to leach out of the sample and react with the local environment.[1] Image analysis of two backscattered SEM micrographs per formula (not shown) showed that at $\approx 40\pm 5$ vol. %, the average aggregate content is in agreement with the amount of aggregate added during formulation. The possibility of using larger amounts of limestone aggregate is being investigated, as it is estimated that reconstituted limestone made by the ancient Egyptians was > 75 vol. % limestone aggregate.

The EDS results for each of the formulae are summarized in Table 2. Not surprisingly, in all cases oxygen (≈ 70 at.%) was the majority element. This is partially due to the use of oxygen-containing compounds (DE, NaOH, limestone, and metakaolin) and partially because the EDS is unable to detect the H atoms in the physically or chemically trapped water.

Table 2: Representative chemistries of four formulae as determined by EDS

	Na (at.%)	O (at.%)	H (at.%)	Si (at.%)	Ca (at.%)	Al (at.%)
A Theoretical	2.6	54.1	29.0	2.9	11.4	0.0
A Actual	4 \pm 1	48 \pm 1	28 \pm 1	6 \pm 2	13 \pm 1	0.0
B Theoretical	2.1	54.4	28.9	2.9	11.6	0.0
B Actual	3.4 \pm 0.6	47.5 \pm 0.4	32 \pm 1	5 \pm 2	13 \pm 2	0.0
C Theoretical	2.6	54.3	28.4	3.2	11.2	0.4
C Actual	5 \pm 1	47 \pm 2	30 \pm 2	5 \pm 2	11 \pm 1	1.4 \pm 0.4
D Theoretical	2.1	54.6	28.3	3.2	11.4	0.4
D Actual	4.5 \pm 1.6	45 \pm 1	35 \pm 3	3 \pm 2	10 \pm 2	1.4 \pm 0.7

Formulae C and D are consistent in that they contain less than 3 at.% Al, however, there is a relatively high degree of variation. When the elemental analyses of each of the cementing phases in each composition (Table 2) are compared to what would be expected based on the initial reactants used the agreement is good. Note that H, which cannot be detected in EDS, was accounted for by assuming that it balanced the net charge of the cement. Even when standard deviation from averaging 10 points is taken into account, there is a discrepancy between the theoretical and observed elemental compositions; this is likely due to inhomogeneity in the cementing phase as a result of imperfect mixing. For specimens mixed with a tabletop paint mixer, however, the results are not unreasonable.

Though the chemistries varied from sample to sample, depending on initial reactants, elemental mapping by EDS (fig. 5) revealed similar microstructures; a distribution of aggregate particles (limestone, appearing as gray) surrounded by a Si, Al, and Na containing-cement. The elemental map (fig. 5) of a polished sample featured a crack that ran continuously through both the cement and an aggregate particle, suggesting that the failure mode is at least partially intergranular.

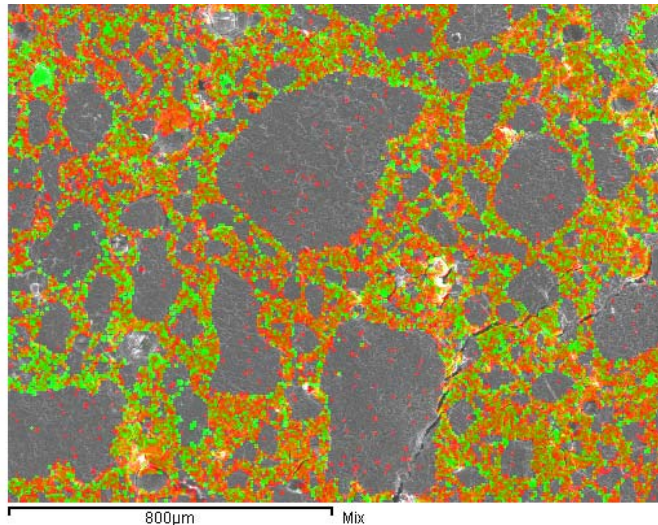


Figure 5: EDS map of formula C. Gray areas are limestone aggregate; red indicates Na; green shows Si. Note intergranular fracture in aggregate (bottom center).

X-ray diffraction patterns (not shown), of the four formulae, as well as samples of each that had been soaked in water for 1 and 3 months showed peaks belonging only to CaCO_3 . A sample of formula C that was left to cure for one week at 90°C , although roughly twice as strong, did not show any difference in its XRD diffractograms when compared to a sample cured for only 2 days. More importantly, none of the samples exhibited the peaks associated with OPC or geopolymers. This absence suggests that Ca is not forming the C-S-H gel typically formed in OPC; rather, it must be incorporated into the structure in another amorphous form.

Furthermore, there was no XRD evidence for Na_2CO_3 in the soaked samples, implying that the white powder observed after soaking formed outside or on the samples' surfaces. It is possible that the fine aggregate concrete contains some amount of soluble material, and after this dissolves away, the remaining material would be unaffected by exposure to water.

These results begin to shed light on the manner in which the synthetic limestones that make up some of the blocks of the Egyptian pyramids were produced. Despite the 2006 paper [3] showing that only some of the stones of the pyramids are cast and that the cementing phase is not a Na-aluminosilicate, Davidovits maintains [16] that the cementing phase the ancient Egyptians used contained Na and Al. At this time over two dozen pyramid samples have been examined; a cementing phase containing Na and/or Al has yet to be found. This work at some level explains why. The ancient Egyptians may have realized that re-agglomerating limestone with Na-containing materials, such as natron and/or plant ash were not as durable as those simply made with DE and lime. Today it is well established that the addition of Ca (and sometimes Al) to amorphous alkali-silicate glasses improve chemical durability in general and water solubility resistance in particular; this is the main reason that CaO is added to window glass for example. [17] Further work in reconstituting a limestone made with nothing but lime, DE, a fine-limestone aggregate, and water, that looks remarkably similar both macro- and microscopically to the ancient re-agglomerated limestone is currently underway.

In the scenario laid out in 2006 [3], the ancient Egyptians must have used a combination of carved and cast blocks since otherwise the amount of lime they would have needed would have

been far beyond their capability. To make lime from limestone, the latter has to be heated to ≈ 900 °C; a difficult and very fuel-intensive operation. To solve this problem the ancient Egyptians compromised and used the cast blocks only where they needed them or could not do without, namely as outer casings and, most probably, the top halves of the pyramids. Recent research has shown [18] that the limestone outer casing of the Bent pyramid of Senefru in Dahshour is a reconstituted limestone that is indeed held together by a combination of amorphous silica and a Ca-silicate binder. That this outer casing has survived four and a half millennia of weathering is not only astounding, but also quite humbling.

SUMMARY AND CONCLUSIONS

A NaOH/DE based masonry material with sand/limestone aggregate was created that reached strengths on the order of 40 MPa, which, however, completely dissolved in water. It is likely that the NaOH and DE combined to make something approaching waterglass, which hardens when heated or exposed to air, yet dissolves in water.

A second material with a cementing phase containing Si or silico-aluminate minerals activated by Ca and/or Na-alkali solutions was then developed in an effort to counteract the dissolution of the exploratory formula. This cementing phase was formulated by mixing DE and metakaolin clay with NaOH and hydrated lime solutions.

To obtain decent mechanical properties the samples were cured for various times at 90 °C. In general, 6 h at that temperature resulted in ultimate compressive stresses of $\approx 20\pm 5$ MPa, irrespective of the small variations in original chemistry. Curing at 90 °C for a week resulted in an increase in strength to ≈ 35 MPa, comparable to common OPC-based concretes. This temperature treatment is apparently interchangeable, to some extent, with time. The addition of hydrated lime to the cement increased the water solubility resistance significantly as compared to samples that did not contain the lime.

When soaked in water, it was shown that there are two things that indicate dissolution at early stages: increasing pH and the appearance of a precipitate identified by XRD to be Na_2CO_3 .

This research represents the first attempt to synthesize a synthetic stone product in the manner used by the ancient Egyptians, following from research performed on samples of the pyramid stones themselves. Development of such a synthetic stone is bound to have numerous applications in the field of masonry.

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