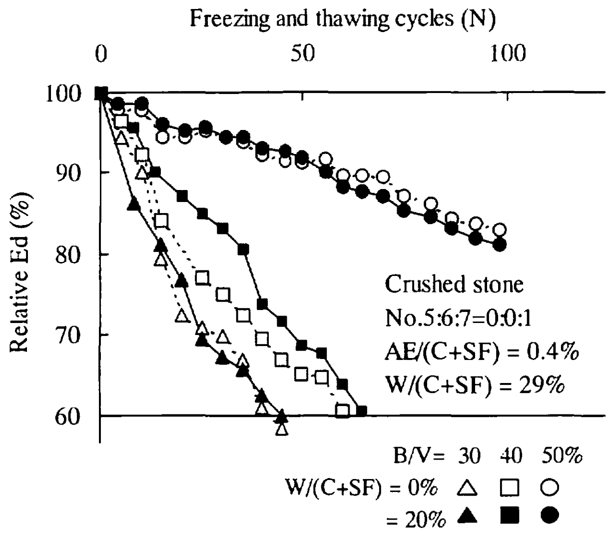

Fig.5. Results of freezing and thawing test of porous concrete with AE agent

Sulfate-Resistance of Lime-Pozzolan-Cement Grouts

by E.-E. Toumbakari and D. A. Van Gemert

Synopsis:

One of the major concerns during application of cementitious grouts inside historic masonry is the possible presence of gypsum, which may lead to the creation of ettringite and the subsequent damage of the masonry. The design concept of the presented hydraulic grouts is based on the reduction of the portland cement content to the 30%-wt of the total binder mass, in favour of appropriately proportioned mixtures of hydrated lime and natural and artificial (silica fume) pozzolans. The behaviour of the system lime-pozzolan-portland cement in the presence of gypsum is investigated. A series of mortar specimens are made, in which a part of the sand is replaced by gypsum. The various grouts are used as binders. The evolution of the length change and the modulus of elasticity are followed for 730 days. A very big expansion is recorded in the lime-natural pozzolan-portland cement mortars, which may be considered as non-sulfate resistant. On the contrary, the substitution of a part of the natural pozzolan (10%-wt of the pozzolan) by an equal in weight amount of silica fume leads to a drastic reduction of the recorded expansions.

Keywords: cement; durability; lime; pozzolan; silica fume; sulfate

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INTRODUCTION

The use of hydraulic binders for the repair and strengthening of historic masonry is nowadays considered necessary because air-hardening binders such as hydrated lime -which could be considered as an alternative- do not permit the development of strength in a period of time meaningful from a structural point of view. However, one major issue in the design of the repair materials is the replacement of portland cement with combinations of other inorganic materials. In fact, cement or cement-polymer materials have the advantage of developing high strengths in a short period of time. Nevertheless, damages and durability failures may, and have, been induced due to incompatible pore systems and mechanical properties, as well as interactions with compounds, such as sulfate, present inside the masonry mass. The development of ternary systems containing lime, natural pozzolans and cement in limited quantities presents an attractive alternative (1).

The available bibliographical references in the conservation sector regarding sulfate attack concern mortars rather than grouts. Studies on the behaviour of hydrated lime mortars with different contents of hydraulic components against sulfate attack simulated through gypsum addition inside the mortar (2) confirm the occurrence of expansive processes associated to the development of ettringite. The measured expansion of 40 x 40 x 160 mm specimens ranges between 1.5-4 mm/m within 28 days. Only when the hydrated lime mortars are carbonated, no expansion due to sulfate attack takes place. The authors recommend the addition of granulated blast furnace slag-cement and pozzolanic or latent hydraulic materials, such as Rheinisch Trass and blast furnace slag respectively, for the improvement of the sulfate resistance of the mortars used for restoration. Similar are the conclusions of Mehr (3). In the absence of admixtures, the expansion of 40 x 40 x 160 mm specimens of portland cement mortars containing 15 %-wt gypsum and cured at 20 °C in water ranged from 6-10 mm/m in 1000 days depending on the fineness of the cement. The expansion of blast furnace slag cement under the same conditions reached 11 mm/m in 90 days. In order to limit expansion to 3mm/m, it is necessary to substitute 70 %-wt of cement by Rheinisch Trass or 15 %-wt by silica fume. The replacement levels in the case of blast furnace slag cement (with 70 %-wt blast furnace slag content) are 40 %-wt and 5 %-wt respectively. The expansion processes are affected by the presence of calcium carbonate and the environmental temperature as well. Mortars prepared with gypsum, calcium carbonate and the aforementioned binders proved unable to withstand sulfate attack at 2 °C (3). Expansion reached 10mm/m in certain cases. The presence of ettringite was observed in all cases, whereas thaumasite was identified only in the mortars containing silica fume. Excessive expansions up to 16mm/m were also observed in mortars prepared with commercial ordinary portland cement and blast furnace slag cement in the presence of gypsum and calcium carbonate.

Researches on the microstructural characterisation and mechanical properties of ternary compositions used as injection grouts for masonry repair are already presented elsewhere (4, 5, 6). The studied compositions were designed so as to contain a limited portland cement quantity (30 %-wt of the total binder content) and an appropriate combination of lime and natural pozzolan (with or without silica fume). Thus, strength development relies mainly on the cement hydration for the first 28 days and on the pozzolanic reaction afterwards. The limited use of cement automatically limits the calcium aluminate, gypsum and soluble alkali content of the mixture, which are known to be among the main causes for durability failures in masonry. This approach permitted the development of binders that address both mechanical and durability requirements. At a second stage, research focused on the durability performance of the developed grouts against sulfates. Indeed, sulfate attack originating from sulfate that may be found inside or on the surface of a masonry wall is an important factor of concern in historic masonry walls (7). In this paper, the results of studies on sulfate attack are discussed.

MATERIALS

Portland cement CEM I L/A 42.5 HSR (according to the European Norm EN 206-1) with low C_3A content, hydrated lime with a BET specific surface equal to 13.32 m^2/g, the natural pozzolan Rheinisch Trass and Silica Fume in slurry were used. The chemical analyses of the materials and the mineralogical analysis of the cement are presented in Table 1. The gypsum was a commercially available construction type gypsum, according to DIN 1168 (1986). The Rheinisch Trass was always sieved at the 80 microns sieve before use. The mixture proportions of the grouts are presented in Table 2. The W/S (water/solid ratio) was 0.85 to achieve penetrability at voids smaller than

0.3mm. To increase fluidity, a sulfonated naphthalene formaldehyde-based superplasticizer was used.

EXPERIMENTAL PROCEDURES

Mixing Procedures

The grouts without silica fume were prepared by using a mechanical mixer at 2400 revolutions per minute. All the materials were first mixed dry and then water and superplasticizer were added. The grouts containing silica fume were prepared with a mixing procedure, which combines an ultrasonic dispersion at 28 kHz and a mechanical stirring at 300-rpm (ultrasonic mixing). In this procedure, the materials were introduced to the water in a sequential way: the fines were mixed first and then cement was added. The differentiation in mixing procedures is necessary to keep the water to solids ratio constant (8).

Preparation of specimens for sulfate attack

It is known that norms appropriate for use in dilute cementitious systems (as our grouts) do not exist. The use of norms destined to portland cement mortars was therefore inevitable. Sulfate attack occurring inside masonry walls was considered to be better described by the provisions of Norm ASTM C 452-89 for potential expansion of portland cement mortars exposed to sulfate than the other norms involving sulfate attack, e.g. Norm ASTM C 1012-89. Thus, the first was basically used with certain adaptations. It was decided to work with mortars made of sand and the grout as binder and not with pure grouts. A constant gypsum quantity replaced an equal in weight part of the sand. This set-up was considered to simulate quite well the situation of a grout that encounters sulfate in the form of gypsum inside a wall.

The preparation of the specimens was done as follows (9): first, the grouts were mixed as described above. Then, they were introduced in a Hobart mixer together with sand and gypsum, and were mixed for 3 minutes. The gypsum content was always 15 %-weight of the solid part of the grout and was put as a sand replacement, so as to always maintain a binder (grout) to sand + gypsum ratio of 1:3 by weight (Table 2). The dimensions of the specimens were 25 x 25 x 285 mm following Norm ASTM C 490. However, specimens with dimension 40 x 40 x 160 mm were also prepared, in order to compare results with bibliographical data (2,3). Moreover, mortar specimens without gypsum were prepared in the same manner to serve as reference. Curing of the mortars was carried out in 95 % R.H. and 20 °C, and demoulding took place 2 days after preparation. The specimens remained in the room at 95 % R.H. and 20 °C; they were only taken out for measurement and replaced immediately back. The change in length was determined by measuring the change of the distance between two pins (mechanical deformeter Demec) glued on the one surface of the specimens. Moreover, the internal condition of the specimens was assessed through the measurement of the ultrasonic pulse velocity and the subsequent calculation of the dynamic Modulus of Elasticity.

Mechanical Testing

Mechanical test were performed on 40 x 40 x 160 mm specimens of the ternary grouts. Grout 100C was not mechanically tested. The grout specimens were cured at 95 % R.H. and 20 °C. Due to their fluidity and slow strength increase, the specimens were allowed to stay in the moulds for 7 days before demoulding.

RESULTS AND DISCUSSION

Compressive and Flexural Strength

The results are summarised in Table 3. Compressive strength of grouts containing 30 %-wt normal portland cement (base grouts) increased steadily in a practically linear manner. At 60 days, an important difference among the base grouts was measured. It was nevertheless reduced at 90 days. The grout made with a 1:3 lime:pozzolan ratio exhibited the highest compressive strength of all. The flexural strength of the base grouts increased until the 90th day and then slightly decreased until the 180th day.

The improvement of the ternary grouts was done with addition of silica fume. For reasons of dispersion capacity, a limiting value of 10 %-wt of silica fume was set. The results of the mechanical tests confirm the potentiality of multi-blend hydraulic binders. The addition of silica fume increased the compressive strength of the grouts. The maximum was reached by grout 14b-10: 16.2 MPa. It is worth noting that the rate of strength increase of the base compositions remains constant with time, while it seems to slow down or even stop for those with 10 % SF after 90 days of hydration. A reduction in the compressive strength of grout 15b-10 was however observed after 180 days. The addition of silica fume was much more effective as far as the flexural strength of the grouts is concerned. For example, the flexural strength of grout 13b-10 was 40 % higher than grout 13b-0. Flexural strength increased with time until the 90th day. A limited drop between the 90th and 180th day was also observed in some cases. However, the reduction in the flexural strength of the grouts without SF (measured after 180 days) ranged from 8-10 %, for grouts 13b-0 and 14b-0, to 18 %, for grout 15b-0, whereas a decrease of only 3-4 % was observed for grout 13b-10. Grouts 14b-10 and 15b-10 exhibited an increase in flexural strength during this period.

Sulfate resistance of mortars made with the ternary grouts

The results regarding the expansion of the tested mortars are summarised in Figs. 1-3. The results concerning the dynamic Modulus of Elasticity are shown in Figs. 4-6. The mortars bear the same name with the binders (grouts) used for their production.

The major observation regarding the behaviour of mortars without silica fume is the occurrence of a very big expansion ranging between 6.5 mm/m to almost 10 mm/m. As expected, these mortars are not sulfate resistant. It is however of interest to remark that, despite such big measured expansion and corresponding cracks, none of the specimens was destroyed. Continuity of the mass, despite an extensive crack network, was preserved, as it can also be seen from the measurements regarding the Modulus of Elasticity. The trend of the expansion is qualitatively similar in all cases where base grouts were used. Expansion is very rapid until, approximately, the first 90 days of exposure. It continues, with a lower speed though, until the 180th day (120, in the case of mortar 15b-0). After this day, expansion practically ceases, with the exception of mortar 13b-0 (40 x 40 x 160 mm specimen) which has a certain expansion until the 390th day. The behaviour of the mortar made with the pure cement grout was quite different. Expansion remains lower than 1 mm/m until 1 year of exposure. Then, in the case of specimens 25 x 25 x 285 mm (measurements on the 40 x 40 x 160 mm specimens were not available) a sudden expansion increase is recorded, which overpasses the expansion of the silica fume-containing mortars after 730 days.

The presence of silica fume reduced expansion to 1.5-2 mm/m. This value is above the threshold value of 1 mm/m, nevertheless it seems to stabilize at a lower level than the corresponding cement mortar 100C after practically two years of exposure. The trend of the expansion is similar for all compositions. Expansion is very rapid until, approximately, the first 30-60 days of exposure. It slows down until the 120th day and then it practically remains stable, with the exception – as previously - of mortar 13b-0 (40 x 40 x 160 mm specimen) which has a certain expansion after the 180th day.

The recorded values of expansion were different in the 25 x 25 x 285 mm - and 40 x 40 x 160 mm specimens. However, the difference was not systematic. Indeed, in the case of mortars without silica fume, the biggest expansion is observed with specimen 25 x 25 x 285 mm (in the case of lime:pozzolan 1:3). The drop of the lime content seems to induce a quite similar behaviour, in the case of mortar 14b-0. Finally, the expansion of specimens 40 x 40 x 160 mm is bigger in the case of mortars with a 1:5 lime:pozzolan ratio. In the case of mortars with silica fume, the shorter specimens (40 x 40 x 160 mm) showed systematically the biggest expansion values in comparison to the slender 25 x 25 x 285 mm specimens.

The dynamic Modulus of Elasticity of the specimens containing gypsum is lower than the one of the reference specimens. For example, in the case of the pure cement mortars, the Modulus of Elasticity of the 40 x 40 x 160 mm specimens reaches 31 GPa, whereas the corresponding gypsum-containing specimen drops to 22 GPa. In a similar manner, the Modulus of Elasticity of mortar 13b-0 (with dimensions 25 x 25 x 285 mm) overpasses 20 GPa, whereas the Modulus of Elasticity of the corresponding gypsum-containing specimens drops below 10 GPa at 730 days. The silica fume-containing specimen 13b-10 (with dimensions 25 x 25 x 285 mm) reaches 20 GPa after 730 days. Similar tendencies are observed with all ternary compositions, with or without silica fume. Clearly, the induction of cracks due to the presence of gypsum weakens the mortar mass and results in lower dynamic Moduli of Elasticity than the reference mortars. It is, moreover, interesting to observe that the Moduli of Elasticity of all mortars increase with time until the 90th day despite the ongoing reactions (which are visible through the measured expansion). Then, the Moduli of Elasticity of the silica-fume containing grouts slightly decrease until the 180th-210th day and then practically stabilise, whereas a rather continuing decrease is observed in the case of the ternary grouts without silica fume (which is more pronounced in the case of the slender 25 x 25 x 285 mm specimens).

Those at first sight conflicting results (i.e. ongoing expansion and increase of the dynamic Modulus of Elasticity) may be interpreted as follows: the presence of gypsum results in the creation of expansive phases (probably, ettringite), but the parallely occurring pozzolanic reaction produces new amorphous C-S-H, thus contributing to the increase of the mass stiffness and, eventually, the filling of the induced cracks.

CONCLUSIONS

In the field of masonry repair and strengthening, the requirements that the repair materials should fulfil are twofold: physico-chemical compatibility to the existing fabric and structural efficiency. With the aim to address both issues, ternary compositions in which the cement content was limited as much as possible were developed. Grouts with a limited portland cement content and combinations of lime, natural pozzolans and silica fume can develop sufficiently high mechanical properties, thanks to the initial strength given by the cement and silica fume (when present) contents and the continuation of the pozzolanic reaction for a long period. Studies on durability issues, precisely sulfate attack, have however shown that mortars made with the ternary compositions without silica fume are not sulfate resistant. Natural pozzolans with a normal fineness are not capable of binding the present hydrated lime, so as to limit the reactions producing expansive products. This seems to occur, when ternary blends with silica fume are tested. In this case, the sulfate resistance of those mortars is even better than the sulfate resistance of a pure cement mortar in the long run. It can be concluded, that ternary blends with very fine reactive pozzolans, such as silica fume, may be used in the presence of gypsum. Nevertheless, more research is needed in order to follow up the developing expansive phases and, eventually, to define levels of expansion, that are acceptable in the case of masonry structures.

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