TABLE 5 —THE COMPRESSIVE STRENGTH, σ_c (Mpa), FOR CONCRETE WITH 0.00 AND 3.86% CN AS A FUNCTION OF CURING TIME (DAYS)

Curing time (days)	σ_c (MPa) without CN	σ_c (MPa) with 3.86 % CN
1	14.3±0.1	14.2±0.1
3	22.0±0.3	26.7±0.6
7	33.0±0.6	35.4±0.3
28	49.8±0.5	47.3±0.0
90	53.7±0.7	52.1±0.9
497	47.4[1]	54.4[1]

[1]Measured on only one cube instead of the usual three.

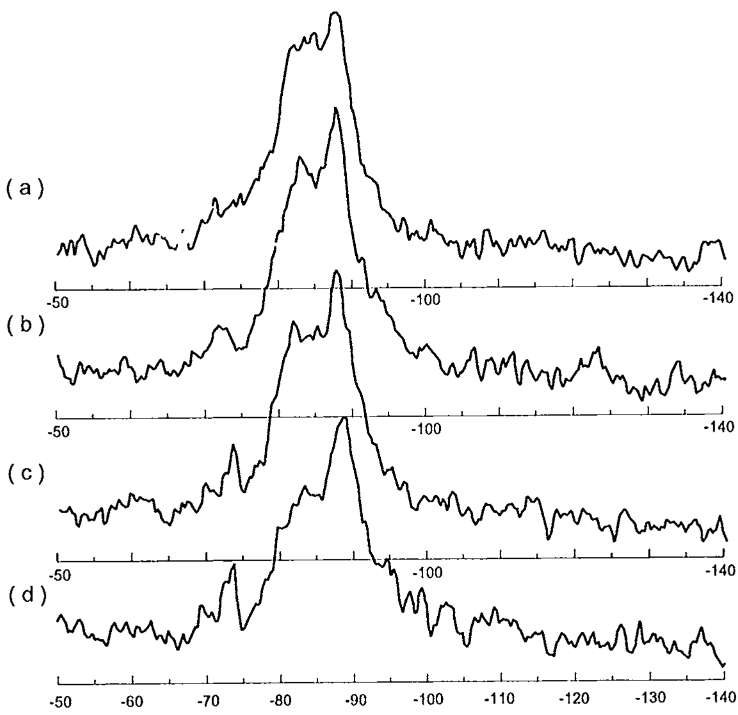

Fig. 1—Solid state[29] Si MAS NMR spectra of cements pastes with w/c =0.50 and based on (a) OPC + 0.00% CN, (b) OPC + 5.26% CN, (c) SRPC + 0.00% CN and (d) SRPC + 5.86% CN

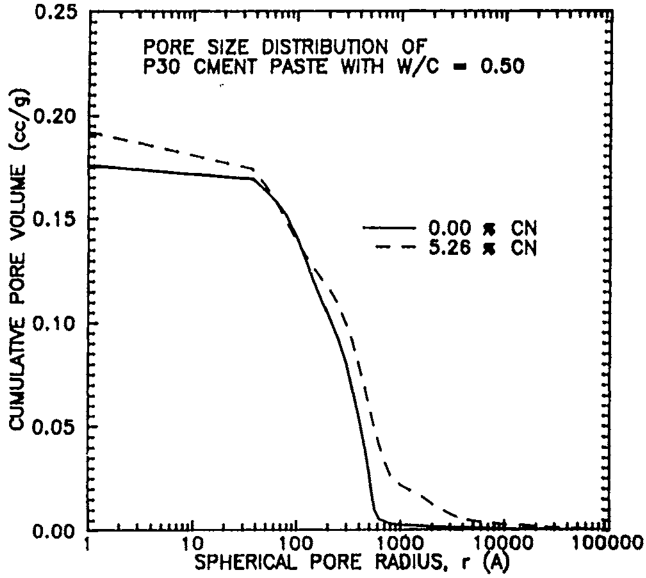

Fig. 2—Pore size distribution of OPC pastes (w/c = 0.50) with 0.00 and 5.26% CN

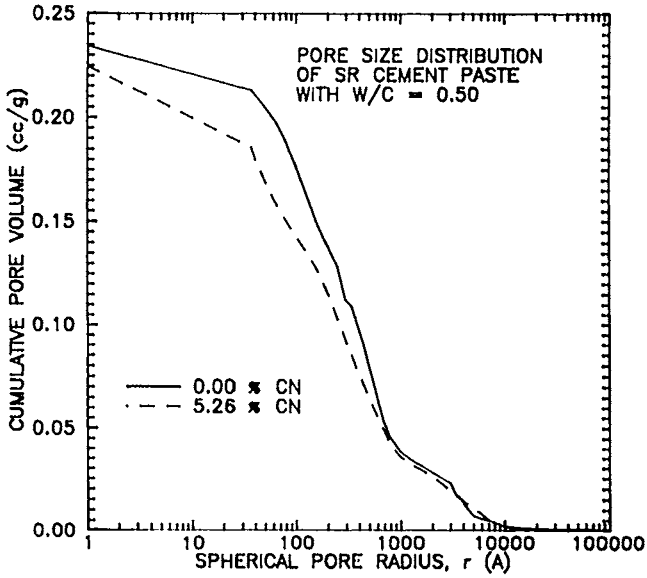

Fig. 3—Pore size distribution of SRPC pastes (w/c = 0.50) with 0.00 and 5.26% CN

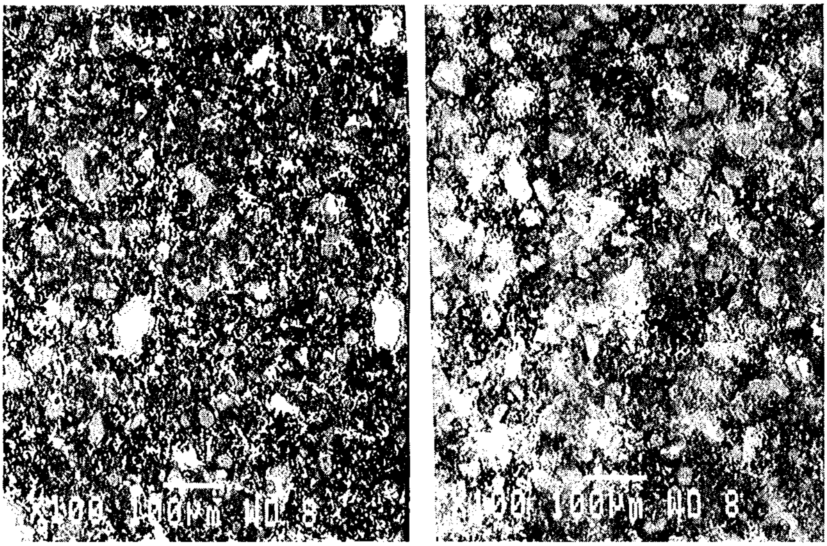

Fig. 4—BEI (100x) of mature SRPC paste (w/c = 0.50) with (right) and without (left) 5.26% CN

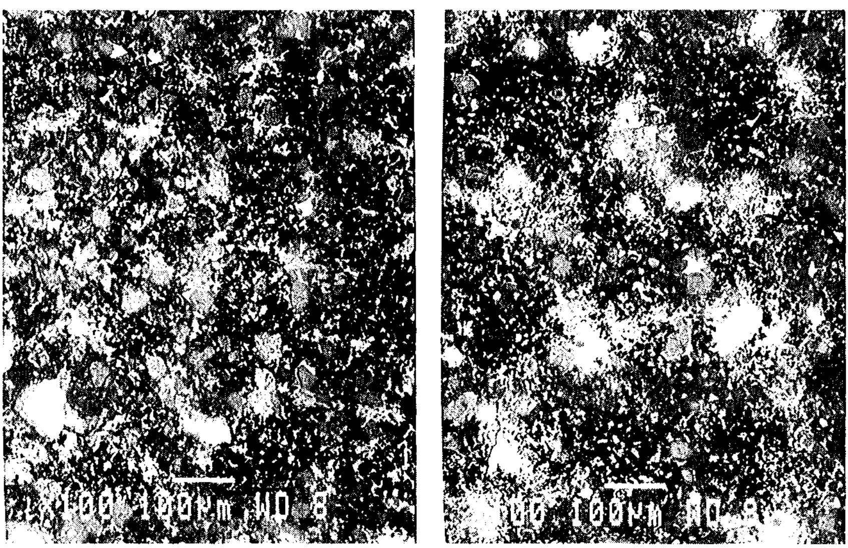

Fig. 5—BEI (100x) of mature OPC paste (w/c = 0.50) with (right) and without (left) 5.26% CN

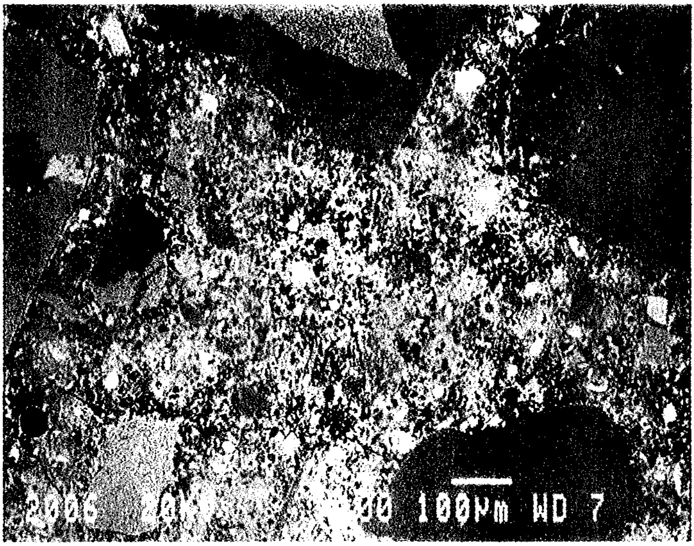

Fig. 6—BEI (100%) of mature HSPC concrete (w/c=0.57) without CN

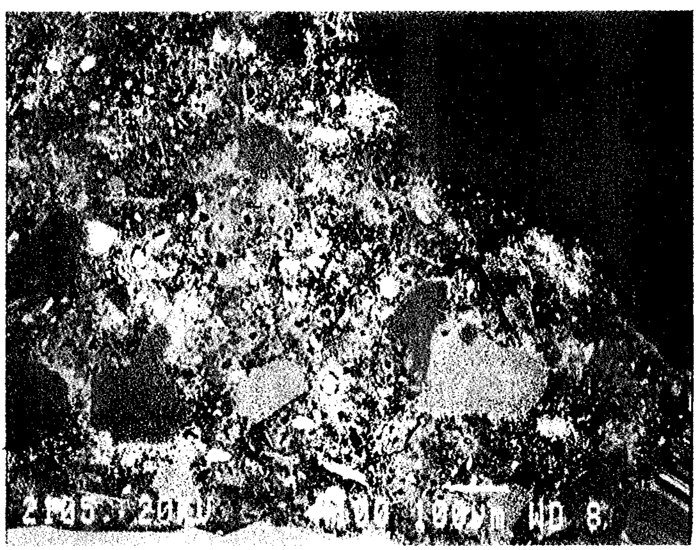

Fig. 7—BEI (100%) of mature HSPC concrete (w/c=0.57) with 3.86% CN

SP 173-34

A Historical Review of the Development of Chemical and Mineral Admixtures for Use in Stucco Plaster and Terrazzo Floor

by M. Collepardi

Synopsis: When the historical buildings of the Republic of Venice were erected all the construction materials and the corresponding techniques were always carefully selected. Even at that time architects were aware of the importance of the durability of buildings in a very hostile environment such as that existing in Venice characterized by permanent humid air and capillary rise of salty water from the foundations.

In particular cementitious materials were adopted in agreement with the empirical rules of the Romans' experience and adapted for the particular Venetian environment. The present paper examines two specific cementitious materials which became very popular throughout the world: the *stucco* plaster and the *terrazzo* concrete.

At the time of the Republic of Venice, chemical admixtures were not available. Therefore, masonry artisans and architects developed a special know-how to manufacture durable materials. This was based on the use of mineral admixtures and natural substances, the invention of innovative binders and the development of special application techniques.

After the advent of portland cement and especially of chemical admixtures, modern *stucco* plaster and *terrazzo* concrete can be produced with different (not necessarily better) properties and at higher rates of productivity. The present paper examines the microstructural aspect, the composition, the performance, and the manufacturing process of the original and modern materials.

Keywords: Admixtures; gypsum; lime; stucco; superplasticizers; terrazzo

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INTRODUCTION

Building materials and techniques used by architects and artisans at the time of the Republic of Venice were substantially based on those described by Vitruvius in his splendid handbook *De Architectura* at the time of the Roman Empire.

However, as Vitruvius says, the Roman art of building was the heritage of the Greek culture. On the other hand, the construction technique know-how, including building materials, came from the Egyptians and Persians through a slow transmission process of the oriental culture (particularly from East Iran) through the Mesopotamian and the Mediterranean civilization.

Even so it should not be surprising that Venice, at the peak of its splendor, returned much of its building experience to oriental countries through a fascinating exchange of culture firstly from East to West, and subsequently from West to East.

The present paper is a sort of tribute to the city of Venice. Neither chemical nor mineral admixtures, as meant today according to ASTM or other modern standard specifications, were available when the historical buildings of the Republic of Venice were erected. Nevertheless, natural substances were used as special additions for mortar mixtures or surface treatments of walls and floors. Even mineral additions were used to modify the time of setting of mortars or to improve the durability performance of the buildings. Moreover, in some cases, the builders also used, deliberately for durability reasons, a new binder, a sort of rough hydraulic lime, anticipating by a few centuries the invention of hydraulic lime which was precursor of the modern portland cement in the 18^{th} century.

The present paper examines two specific cementitious materials, both developed in Venice and widely used in historical buildings: the *stucco* mortar and the *terrazzo* concrete floor. Moreover, these original materials will be compared with the corresponding modern materials, as presently used all over the world.

STUCCO MORTARS

Stucco is a special mortar particularly used to embellish walls and ceilings of buildings in form of decorative frames, high and bas-relief ornaments, sophisticated sculptural works, or artistically finished plasters (Fig. 1).

In general, stucco was made of slaked lime as binder, mixing water, and sand as fine aggregate. In subsequent developments natural sand was replaced by white crushed marble stone particularly on the skin layer of the plaster. Therefore stucco become a special lime-based mortar whose surface, at the end of the hardening process, contained almost exclusively calcium carbonate derived from both the presence of fine aggregates and the carbonation of lime. The final result was the presence of the same substance, $CaCO_3$, in the stucco surface as in the natural marble.

Although these chemical details were unknown at the time of the Romans, Vitruvius used the word *marmatum* to indicate the stucco plastering mortar, deriving this term from the use of crushed marble (*marmor* in Latin) as fine aggregate. At the time of the Republic of Venice the Italian term *marmorino* (marble-like) was used to indicate the special finished stucco layer which, for its special smooth appearance and finished texture, looked as the polished marble (*marmo* in Italian) stone. There are other technical reasons that will be examined later, which justify the close resemblance between *marmorino* stucco on one hand, and natural marble on the other hand: they are based on the microstructure and the performance of these materials, especially in regard to water permeability and moisture absorption properties.

The composition and the application of the stucco changed in the past according to the local traditions and uses in Europe (especially in Italy, France, and UK) or Arabic countries, for instance Morocco. In the present paper, the Venetian stucco, as used in all the territories of the Venice's Republic, will be first examined, and then its subsequent evolution in other countries will be discussed up to the modern available stuccos based mainly on cementitious binder-polymer mixtures.

Splendor of the Original Venetian Stucco

The materials and the techniques discussed in the present paper are substantially based on the oral tradition of Venetian stucco artisans of the past as described by Fogliata and Sartor (1).

Table 1 shows the individual components of the stucco including binder, aggregate, admixtures and surface treatment products; Fig. 2 schematically shows the composition of the mortar mixtures in each layer (from *A* to *F*) of the stucco plaster. This includes a 20-mm-thick inside mortar and a 5-mm-thick outside *marmorino* coating.

Venice - were used since the 15th century to manufacture durable mortars exposed to the outdoor environments (2). However, there is no documentation to confirm the use of ground glass or iron slag specifically in stucco mortars.

Raw linseed-oil was perhaps the most important natural substance which can be compared to modern chemical admixtures. Unfortunately no specific paper is available, directly from the original users, which could explain the reason why linseed-oil was used particularly in the skin layer of the *marmorino* stucco exposed to exterior humid environments. According to Fogliata and Sartor (2) linseed-oil, at a dosage of about 0.7% by volume of mortar, was used, as a multi-purpose admixture, to improve the plasticity of the mixture, to prolong the time of setting and allow more time for the finishing work, and to reduce the microcracking risk. The last performance seems to be related to the reduction in the open porosity of the skin layer (*F* in Fig. 2). Consequently, the reduction of microcracks promoted by drying shrinkage should be related with the change in the texture of the finished surface caused by the linseed-oil addition. According to the Venetian architect Palladio (3), linseed-oil, as well as nut-oil, improved the watertightness of plasters based on mixtures of slaked lime with natural pozzolan, ground tile or iron slag.

Plaster of Paris (calcium sulphate hemi-hydrate) was used as an accelerating admixture to reduce the time of setting, to accelerate the drying process and to increase early strength, especially in the production of *stuccoforte* (high-strength stucco) for ornamental high-relief work. In this case, the excessive thickness of the stucco would slow down the hardening process in the inner layer by carbonation of lime.

The setting and hardening of the stucco in the presence of plaster of Paris were accelerated, due to the rapid hydration of calcium sulfate hemi-hydrate. The amount of gypsum varied without any specific and strict dosage limit and, in general, some handfuls were used for each mortar bucket as judged by the job execution requirement according to the opinion of the stucco worker. However, gypsum never completely replaced lime as the binder of the original stucco in Venice. This aspect of the subject will be discussed later in regard to the evolution of the stucco technique.

One of the most important key points to explain the success of the stucco plaster, especially when finished with a *marmorino* layer, is the beautiful appearance of its surface texture. To this end, the *marmorino* surface was, in general, treated and protected by brushing a mixture of water, lime, and soap at a liquid consistency. The surface, when dried, was then carefully smoothened by trowel. This treatment should have improved the water resistance of stucco plasters, especially when exposed to exterior environment, due to the hydrophobic character of the skin surface accomplished through the action of long hydrocarbon chains in the soap. When a durable *fresco* paint was required with improved water-resistance characteristics, the colored pigments were dispersed in a soap-water emulsion and then the still fresh (*fresco*), and not yet hardened surface of the *marmorino* skin layer, was decorated. So, by using this technique, the inorganic colored pigments were definitely incorporated into calcite crystals produced by the carbonation of lime and protected by the hydrophobic characteristics of the soap substances. The *fresco* painting technique was very expensive since the decoration had to occur in a limited time range, after finishing and before setting of the *marmorino* surface. In very dry walls and ceiling, not exposed to rain or rising capillary water, plasters were decorated by colored pigments dispersed in turpentine oil and then applied on well-dried and hardened stucco mortars.

For the most important works, the surface of the stucco was polished by using vegetable or animal waxes diluted in turpentine. Due to this final treatment, the surface pores were filled by wax and the appearance became even more brilliant, whereas the underneath colored effects were shining through the upper wax thin layer as it occurs in a polished and naturally speckled marble. The advantage of this stucco technique with respect to marble lining was, of course, the achievement of every irregular and sophisticated form in plastering or decorating walls and ceilings with high- or bas-relief ornaments.

Beside the careful selection of the ingredients and their proper mixture proportions, the clue to the success of the stucco, specially with the *marmorino* finishing layer as in all the noble buildings of Venice, was the skilled labor available at that time. In particular, one thing should be mentioned: each of the six layers forming the *marmorino* stucco (Fig. 2), as well as the final surface treatment, required very time-consuming trowel work. Because of this mechanical action, a microstructure as dense as that of natural marble was accomplished particularly in the *marmorino* layer where, as a result of the lime carbonation and the use of marble powder as fine aggregate, low-porosity $CaCO_3$ was the final product.

Decay and Evolution of Stucco

Up to the end of the 18th century, decorated plasters, friezes, and ornaments, all manufactured by original Venetian stucco, played a very important role in the European architectural expression. They were integral and significant part of the whole building system in the Renaissance and the Baroque period as well, especially in the Rococo style.

With the advent of the Neoclassic style in the 19th century, every decoration or ornament, superimposed on the essential architectural substrates of the building, was considered to be useless and having a negative effect because a golden smart frame could divert the attention of the viewer from the picture. This change in the architectural style, related with the parallel change in the philosophical thought on aesthetics as supported by Immanuel Kant (1724-1804), corresponded to the quick decay of the stucco art.

Due to the high cost of the original lime-based stucco, as a work of art of the Venetian stucco-masters, new technologies were developed to manufacture cheaper stucco plasters and ornaments, particularly in the UK where a strong demand for stucco-decorated interior building was growing from the upper middle class. So, in many Neoclassic buildings, gypsum, as binder, completely replaced slaked lime with the following economical benefits:

- no more six-layer stuccos were needed to build up plasters, since gypsum can set and harden very quickly even in the absence of air;
- numerous sophisticated friezes and ornaments could be manufactured, on industrial scale, by casting gypsum mortar at a fluid consistency into few metallic formworks; so, easy and cheap precast gypsum ornaments quickly replaced the in situ high- and bas-relief ornaments made by lime-based stucco;
- no more qualified and expensive stucco workers from the Venice area were required to create decorated plasters and ornaments: local workers could easily replace them.

On the other hand, the performance of the gypsum-based stucco with respect to the original lime-based stucco was definitely inferior in terms of:

- durability in exterior plasters of the walls, due to the intrinsic water solubility of gypsum mortars, which was aggravated by the high water-binder ratio used and therefore the higher porosity of the cementitious matrix;
- aesthetic appearance, due to the loss of the smoothness and brilliancy of the surface when exposed to light; moreover the opacity of the gypsum mortar did not allow the underneath colored effects to shine through the upper layer even when smoothly finished by wax treatments;
- architectural aspects, because of the repeated uses of the same form of ornaments, all based on few casting formworks, to reduce the cost of application.

Subsequent developments of the gypsum-based stuccos, at the beginning of the present century, led to less water-vulnerable materials based on mixtures of plasters of Paris, natural sands, colored pigments, water and natural glues, all of animal origin, as admixtures. Especially fish- and rabbit-glue were used to manufacture more durable gypsum-based stuccos with better finished surface for exposure to humid environments. Nevertheless, these stuccos, known as *pastellone* or *spatolato* in Venice, cannot be compared with the original Venetian lime-based stuccos in terms of either durability or aesthetical effect.

Due to more recent developments, in the second part of this century, revolutionary changes in the composition of stucco led to mixtures of mono-component or bi-component products. Both based on industrially premixed ingredients, these products contain - as predominating or unique binder - a polymer in the form of aqueous emulsion latex based on ethylene-vinyl-acetate (EVA) or equivalent polymers. Inorganic binders, if any, may be present as either lime, $Ca(OH)_2$, or hemihydrate, $CaSO_4 \cdot ½H_2O$, or even white portalnd cement. However they do not necessarily act as a binder, but more frequently they play the role of a very fine filler. In the bi-component form the product is based on two materials: