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ON THE CONSERVATION OF GUADALAJARA, MEXICO BUILDING STONES WITH A NEW ALUMINOSILICATE COMPOUND

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Abstract

A procedure to understand and consolidate the volcanic tuff used in ancient churches and other historical buildings in Guadalajara is proposed. Initially, the deterioration mechanism of the local tuff was determined through textural, morphological and structural characterization. The techniques employed were, among others, ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR), infrared spectroscopy (FT-IR ATR), X-ray powder diffraction (XRD), nitrogen adsorption-desorption, scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA) and compressive strength tests. According to these results, different consolidating materials could be proposed.

Inorganic polymeric materials based on silicon and aluminum were developed and tested as consolidation materials for this type of stone. A complete structural and textural study on the properties of the stone consolidated with those polymers was performed in order to establish the interaction of the new material with the stone and measure the improvement in the stone properties.

The performance of the new material was compared with tuffs consolidated with the currently used siloxane based materials. The aluminosilicate showed better consolidation features for white tuffs which have a high amount of silicon in their composition, while the silicate was the best choice for tuffs with a high amount of aluminum.

Keywords: consolidation, volcanic tuff, aluminosilicates

1. Introduction

Among the principal procedures of conservation that are held in stone materials, is the consolidation process, which is performed to restore the structural stability and improve the mechanical resistance that has been affected by different deterioration processes, such as atmospheric contamination, salts crystallization, humidity, biodeterioration or anthropogenic factors.

Some inorganic consolidants, used in stone conservation, are the barium hydroxide, silicates and alcoxysilanes. More recently consolidants based on silica and calcium hydroxide nanoparticles were also used (Price 2006; Dei et al. 2006). Organic consolidants like the epoxy resins have been also used in Mexico, natural products such as the mucilage of cactus have also been employed (Pérez 2008).

Guadalajara City, Mexico has many historic buildings constructed mainly with volcanic tuff, and therefore it is mandatory to study and develop a stone consolidant that could improve the stability of the local building stones.

2. Geological setting

The tuff is a very abundant material in Mexico. The Sierra Madre Occidental (west main mountain chain) is a geological province that is characterized by being mainly formed of tuffs, as a result of a long explosive volcanism period during the Cenozoic age (figure 1) (Morán 2011).

Figure 1. The location of the Sierra Madre Occidental and Guadalajara, Jalisco in Mexico.

Rhyolites, tuffs and breccias form the nucleus of the Sierra Madre Occidental. The main type of rhyolite found is fluidal which is intercalated with tuffs of the same composition. These rocks have a light yellow color, are compact and fractured. The mountain chain has wide eruptive bodies whose deposition order is the following: andesites, traquites, rhyolites and basalts, all of these rocks are Cenozoic and are deposited on top of Mesozoic rocks (López 1983).

The modern volcanic formation dominates the region of Jalisco and Tepic, in the geologic map of the state of Jalisco there is a wide distribution of intrusive and extrusive igneous rocks. The repeatedly volcanic eruptions near the Nevado and Colima peaks during a large period of time, justifies the lava flows and layers of tuff and ashes that are extended up until the Guadalajara Valley (Aguilera 1896).

3. Experimental

3.1 Samples

During 2006, restoration procedures were held at the Santa Mónica Church, a XVII century church, located in the downtown of Guadalajara (figure 2). The church was built with yellow and white tuff. The types of degradation present were salt efflorescence, erosion, exfoliation, biological deterioration and also thermal expansion at the top of the building and anthropological factors such as loss of material due to collisions with the public transport (Jáuregui 2008).

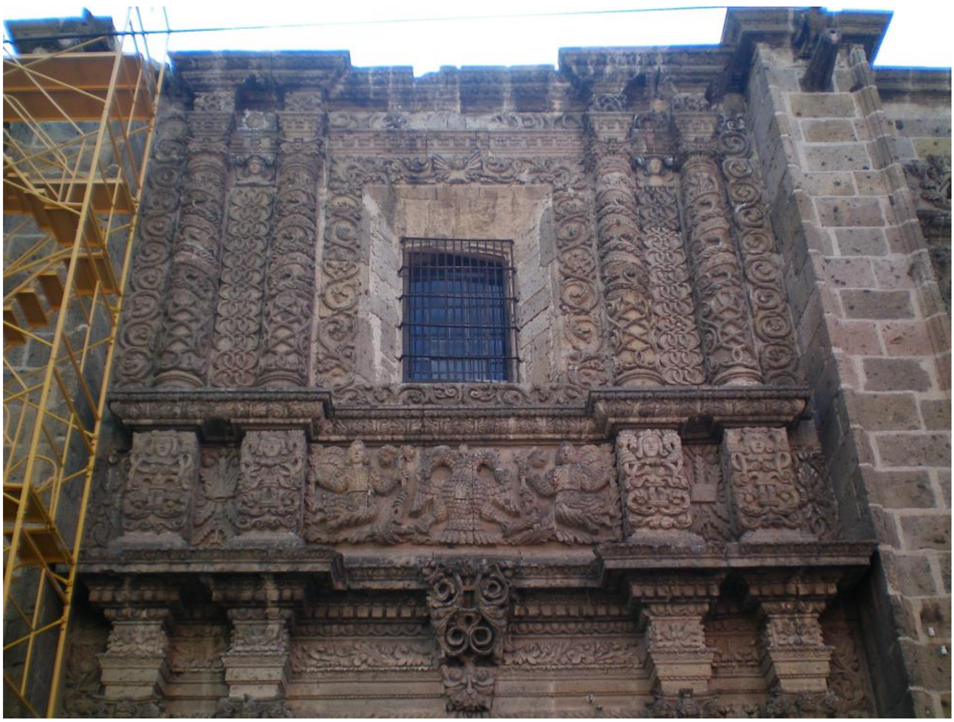

Figure 2. Detail of the façade of the Santa Mónica church in Guadalajara, Jalisco, Mexico.

Different rocks that showed advanced deterioration were removed and replaced with new tuffs, which were obtained from the original quarry used for the building. For this study, desalinized samples of weathered white and yellow tuffs, were used and compared with samples from the fresh stones.

3.2 Analytic methods

First, the deterioration mechanism of the local tuff was determined through textural, morphological and structural characterization. The techniques employed were, among others, ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR), infrared spectroscopy (FT-IR ATR), X-ray powder diffraction (XRD) and the identification of the minerals was performed conventionally comparing with the JCPDS files, adsorption-desorption nitrogen, scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA), porosity, colorimetric measurements and compressive strength tests were also performed. Further details regarding the methodology are reported in Pérez 2012.

After the understanding of the material's transformation as time went on, an aluminosilicate compound was proposed for the consolidation of this type of tuff, and was synthesized by the sol-gel method.

The stone samples were cut into probes of 5X2.5X2.5 cm and afterwards were consolidated through a cellulose compress soaked with the consolidant; another set of probes was consolidated trough the same method with the commercial silicate consolidant KSE® from Remmers. The probes were kept in an accelerated aging chamber for five months, which is equivalent to six real years, in order to test the stability of the consolidated stones. The evaluation of the consolidated stones was made with the same techniques employed for the characterization of the untreated stones for comparison. In this work the most outstanding results of the research are presented.

4. Results and discussion

4.1 Deterioration of the local tuff

In all samples, either fresh or weathered stones, two crystalline phases were identified by XRD, sanidine ($K_{0.65}Na_{0.35}AlSi_3O_8$, JCPDS 01-083-1657) which is an alkaline mineral feldspar and low trydimite (SiO_2, JCPDS 00-042-1401). These compounds are generally present in volcanic rocks. In the case of the altered yellow tuff, a third phase was identified, which corresponds to a potassium hydrated aluminosilicate (philipsite, $K_{10.32}(Si_{21.7}Al_{10.3}O_{64})(H_2O)_{24.32}$, JCPDS 01-086-1110).

These phases were also observed in the petrographic studies where the silicon dioxide matrix is present with crystals of sanidine and other alkali feldspar, also lithic materials were present which are characteristic of volcanic explosions (figure 3). In the altered tuff an increase of iron oxides was evident, which was in agreement with the colorimetric measurements.

The ^{29}Si MAS-NMR spectra shows a broad signal at -99 ppm for all samples, this signal can be assigned to Q^1, Q^2 or Q^3 units (Mackenzie 2002) present in silicate minerals. The signal at -112 ppm corresponds to tetrahedral silicon (Q^4) belonging to trydimite. The ratios between both signals were calculated from integration of corresponding peaks.

In the white tuff there was an increase in Q^4 units for the altered rock in accordance to the devitrifying process of the rock, while for the yellow tuff there is a slight decrease in this signal which can be attributed to the presence of silanol species at the chemical shift of -101 ppm (Zhao et al. 1997).

All the nitrogen adsorption-desorption isotherms were type IIb with hysteresis loops type H3, according to the IUPAC classification (Rouquérol et al. 1999), which indicates a mesoporous material possessing rigid aggregates laminar type in long, thin pores.

From the various analyses it was concluded that the yellow tuff is more susceptible to alteration processes in comparison to the white tuff. A proposed degradation process involves the presence of aluminum atoms which increases the degree of hydration of the rock surface, promoting the hydrolysis of the silicon in the framework causing condensation reactions, being the yellow tuff more altered.

Therefore the proposed consolidant must interact with the hydrolized aluminosilicate structure in order to achieve an efficient restoring of the rock. According to the NMR results, the most compatible material for the white tuff would be an aluminosilicate and for the yellow tuff, the most compatible material would be a silicate in order to equilibrate the Al-Si composition.

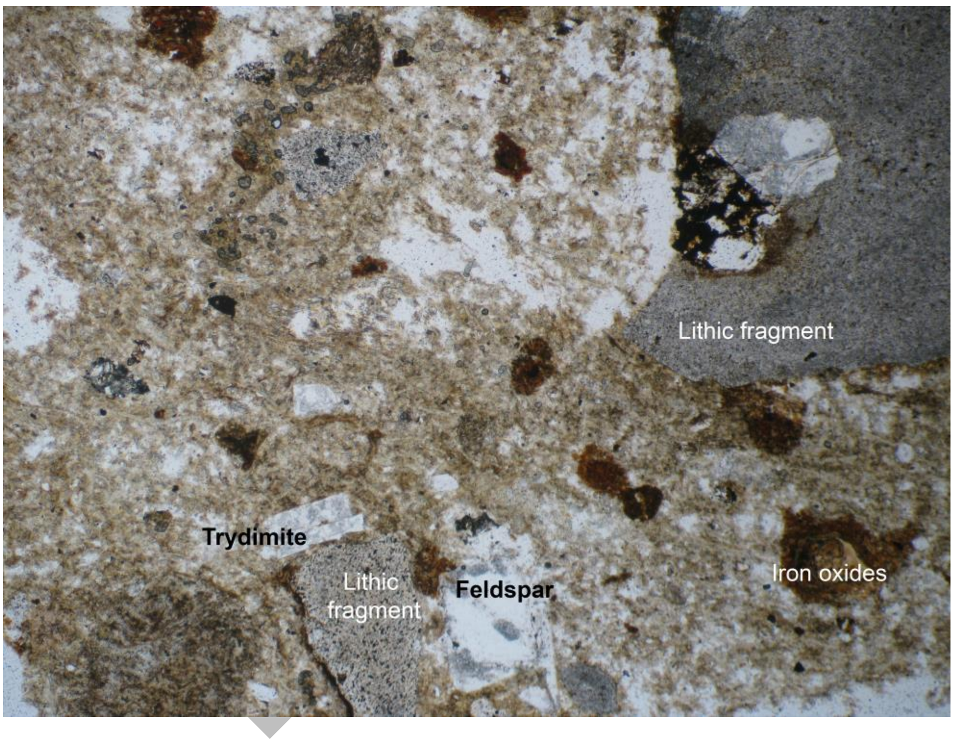

Figure 3. Petrographic images of the altered yellow tuff.

4.2 Evaluation of the consolidated tuff

The aluminosilicate consolidant was designed to react with the water molecules and the hydroxyl groups on the stone's surface, and form afterwards a tridimensional aluminosilicate network. The formation of the xerogel implies also the production of an alcohol, which quickly evaporates and does not remain on the stone. Therefore, this system avoids the accumulation of secondary products which may react later or limit diffusion processes. The inorganic polymeric consolidant can be considered, as an amorphous equivalent of the geological minerals present in the stone, but synthesized as a polymer.

The MAS-NMR technique was determinant to disclose on the structural changes in the consolidated stone, since this spectroscopic technique is sensitive to the chemical ambient of the Si and Al atoms (Mackenzie 2002). From the ^{29}Si NMR intensities ratio, it was evident that the aluminosilicate compound reacted selectively with the white tuff which is the one with a minor proportion of aluminum, and it was inferred that the aluminosilicate was distributed in a homogeneous way at the surface of the deteriorated white tuff, because of the absence of tetrahedral silicon units enriched in aluminum in their second coordination sphere. While the stones consolidated with the commercial silicate, were enriched in tetrahedral silicon based units, mainly the yellow tuff which had been deteriorated by the extraction of this element.

The SEM images of the consolidated stone with the silicate compound after five months in accelerated aging shows that the consolidant forms SiO_2 networks on the surface of the stone, while in the tuff consolidated with the synthesized product it is not possible to distinguish the original from the consolidant (figure 4).

The consolidation of the stones did not change their density, since for the yellow tuff it was of 1.8 g/cm^3, and for the white tuff it was of 1.6 g/cm^3. The physisorption properties of the stone were not altered by any of the consolidants, since they had the same type of isotherm (type II and hysteresis loop type H3), but the pore radius obtained by the BJH method decreased to 1.88 nm, the macroporosity of the stone also decreased in a 74 per cent with the commercial consolidant while with the aluminosilicate consolidant it decreased to 35 per cent.

In the compression tests the stones treated with both consolidants increased their maximum load by two kN, what was interesting was the fact that the rupture pattern on the probes was homogenous in all the probes, no matter the differences due to the heterogeneity of the stones themselves.

Finally in the color measurements, all the stones are in the same color region according to the CIELab system, the commercial product shifts the original color to the green and yellow components, while the aluminosilicate towards the red and yellow components. These changes were of two units with respect to the untreated stone, which is unnoticeable for the naked eye.

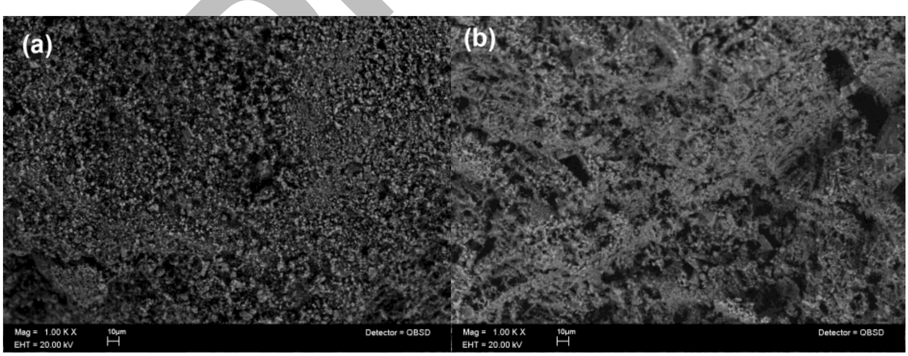

Figure 4. SEM images of the consolidated white tuffs. A) Aluminosilicate compound B) Silicate commercial compound.

5. Conclusions

The synthesized aluminosilicate consolidant is physicochemically compatible with the volcanic tuff, and it does not change the physical appearance of the stone. The consolidation process is irreversible, and the analysis performed on the consolidated stones after six years by accelerated aging did not show further deterioration caused by the treatment, ensuring the midterm stability of the proposed material.

The fact that the aluminosilicate reacted preferably with the white tuff shows the importance of testing and analysing the new conservation materials, in order to have designed materials that will improve the conservation treatments, and besides, by knowing the synthesis method the aim is to redesign the consolidant for other volcanic tuffs in different regions, developing the conservation materials science in the country.

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