Rationalist architecture in rural villages: petro-morphological characterization of natural asbestos fibers in decorative plasters used for artificial stones

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At the beginning of the twentieth century, artificial stones became commonly used as structural building materials, masonry materials, and architectural decorative elements. The main purpose of this work was to characterize the building materials used in a historical building in Codigoro, a small town near Ferrara, northeastern Italy. This building was constructed according to the Italian rationalist rules for monumental architecture and is an example of the rationalist architecture found in rural villages, which uses innovative materials and decorations including artificial stone. The samples analyzed in this work were imitation natural stone, such as “fake travertine” and “fake Ceppo di Grè”, composed of reinforced concrete slabs coated with white mortar. Asbestos minerals have been observed in the fillers in these materials. Petrographic, mineralogical, and chemical characterization of samples of artificial stones and concrete was performed with optical transmitted light microscopy, scanning electron microscopy-energy dispersive spectroscopy, and X-ray diffraction analyses. The results revealed chemical and biological degradation in almost all the artificial stones examined and enabled identification of the presence of calcite, iron oxychloride complexes, and asbestos lizardites used as fillers in two of the analyzed samples. This study aimed to describe a general investigation methodology used to examine the artificial stone façades of the Ex Casa del Fascio of Codigoro, whose architecture is particularly representative of the rationalist architecture in rural villages. The results highlight the relevance of compatible and suitable conservation measures that should be monitored during all restoration interventions to minimize post-degradation fracturing and transformation into elements harmful to human health and the environment.

Introduction

During the nineteenth century, the process of construction rationalization, together with its economic implications, led to the introduction of new construction systems as well as new industrial materials, which were sometimes used in conjunction with, or as substitutes for, traditional materials. Artificial stone appeared in the early nineteenth century and represents a link between traditional stone construction and the newer reinforced concrete technique (Bertolazzi, 2013). The use of artificial stone, together with unconventional materials (iron, glass, or concrete), spread throughout European architecture from the end of the nineteenth century. Artificial stone was broadly present at the beginning of the twentieth century in social and economic contexts, as an expression of the middle-class cultural evolution, which enabled building prestigious buildings inexpensively by using modern hydraulic binders (cements) for the decorative elements. The term “artificial stone” describes materials obtained by mixing sand, gravel, and water with lime, Portland cement, or plaster to produce a material resembling stone (Pecchioni et al., 2005; Stefanidou et al, 2015). This material provided an economical alternative to natural lithic ornamental luxury materials, owing to the reuse of waste material (Mazzeo, 2018). After the invention of Portland cement in the United Kingdom at the end of the nineteenth century, the use of artificial stone became widespread, and residential and industrial architecture (Pecchioni et al., 2005; Fatiguso et al, 2013) were transformed with the development of the Art Nouveau style in Europe. These materials provided high aesthetic value and allowed for decorative elements to be used in public and industrial architecture, as well as in the residential sector (Mazzeo, 2018). This artificial building material could be mass-produced enabled high reproducibility in short time periods, with low environmental and economic costs; ornamental elements with properties similar to those of specific stones could be created in the desired shapes and sizes. The construction techniques used for artificial stone
decorations and their use in the cultural heritage were well described in many European architecture magazines, as indicated by Baldazzi, 2012. The production of artificial stones in Italy first appeared in 1881 at the Industrial Expo in Milan (Sandrolini et al., 2011).

At the beginning of the twentieth century, the production of artificial stone became well known, and many production methods were issued in Italy. Several patents in this period describe the use of asbestos fillers to improve the physical-mechanical features, processability, and durability of cement decorative elements, such as the GB 277884 patent (1927) for mold improvement in the construction of artificial stone blocks. Artificial stone was used throughout Italy (Biscontin and Driussi, 2006; Rocchi, 2012), and studies of materials from different areas in Italy have revealed that the mixture was often packed and modified according to the desired prototype (Michelacci, 2000; Di Biase et al., 2008; Dameri, 2012; Monica and Bergamaschi 2019). As a result, unconventional and cost-effective materials (some of which have recently been identified as harmful materials) were used to create the decorative elements of buildings.

Asbestos is a general commercial-industrial term used to describe a group of naturally occurring silicate minerals of fibrous or asbestos-form habit. These minerals can be divided into two groups: (i) serpentine, which includes only the asbestos chrysotile polymorph, and (ii) amphibole, which includes the actinolite, tremolite, anthophyllite, crocidolite (rhebeckite), and amosite (cumminingtonite-grunerite) asbestos varieties. The other serpentine polymorphs (i.e., lizardite and antigorite) and other amphiboles (i.e., fluoro-edenite) or zeolites (i.e., erionite) are not regulated and therefore are termed “asbestos.” Because of their exceptional attributes (high tensile strength, flexibility, and chemical and heat resistance), asbestos minerals have been used since ancient times as raw materials to produce a large variety of materials and objects. The inherent properties of asbestos fibers appear to contribute to the toxicity of these mineral particles when they are lodged inside the human respiratory system (Stanton et al., 1981; Mossman et al., 1990; Wylie et al., 1993; Nolan et al., 2001; Constantopoulos, 2008; Harper 2008; Murray and Nelson, 2008; Baumann and Ambrosi, 2013; Bloise et al., 2016; Pollastri et al., 2016; Turci et al., 2016; Bloise et al., 2020). Ophiolitic rocks may contain various amounts of asbestos minerals (e.g., Skarpelis and Dabitzias, 1987; Ross and Nolan, 2003; Skarpelis, 2006; Rigopoulos et al., 2008; Punturo et al., 2015), among which chrysotile is usually the most common. Chrysotile can be found in many types of serpentinitized ultrabasic rock, either as alteration product of olivine and/or orthopyroxene, or as veins cutting the rock. Among ophiolitic rocks, metabasite may also contain considerable amounts of amphibole asbestos fibers, principally actinolite or tremolite, which represent the transformation products of clinopyroxene (e.g., Tsikouras et al., 2005; Rigopoulos et al., 2006). Asbestos fibers are thin, needle-like crystals that may vary widely in diameter from millimeters to micrometers. The biologically important “critical” fibers are those with the following shape criteria: length ≥ 5 μm, diameter (width) ≤ 3 μm, and length to diameter ratio (aspect ratio) ≥ 3:1 (World Health Organization, 1986; National Institute for Occupational Safety and Health, 2008; International Agency for Research on Cancer, 2009). Asbestos minerals in the ophiolitic rocks used as aggregates for road construction, railway ballast, concrete, and other applications are particularly dangerous for public health, because fibers of the sizes described above may be released into the air during in-service deterioration of aggregates and may be inhaled into the lungs, thus causing serious health problems (Bloise et al., 2016; Punturo et al., 2019).

Italian monumental rationalist architecture has recently become a subject of particular interest in the study of its constituent materials (Fiorentino et al., 2015). Codigoro and Tresigallo, two small towns near Ferrara in northeastern Italy, have well-known examples of the Italian monumental architecture from the twentieth century and of rationalist architecture (Caprotti, 2007), which widely used artificial stone. Moreover, these two municipalities have examples of Italian architecture in the fascist period (Viganò, 1971; Baldazzi, 2012). On May 20th and 29th 2012, both these towns, as well as Ferrara and most parts of the Emilia Romagna region, were affected by two seismic events that damaged buildings in the historic centers and rural areas (Courard et al., 2012; Freire-Lista et al., 2019). This work was part of a reconstruction and post-seismic restoration project involving several historic rationalist architectural buildings damaged by these earthquakes. Our focus was on the Ex Casa del Fascio of Codigoro. According to Tamiozzo (2009), the ability to distinguish between original building materials and those used after restoration is fundamental for making effective and respectful choices to ensure effective intervention. Accordingly, with a suitable stability plan for damaged historical buildings in place, we performed a chemical and micro-structural investigation on the construction materials (and artificial stones) used in rationalist buildings. As suggested by Varas-Muriel et al. (2015), mineralogical and petrographic characterization of the materials used in buildings is a helpful tool to identify the best and most cost-effective strategies for removing or reducing degradation agents, as well as for predicting behavior over time, in the presence of agents of material degradation.

Many analyses were performed to understand the probable degradation resulting from reusing building elements and materials and to investigate the presence of asbestos minerals. This particular study was justified because, in the period of rationalist architecture, some artificial stone materials were produced from products potentially containing materials with harmful health effects (Bloise et al., 2016). Determining the presence of asbestos mineral phases is important because they pose health risks.

Materials and Methods

According to well established methodological procedures (Binda et al., 2000; McCann and Forde, 2001; Schuller, 2003; Warkea, 2003), an investigation system to support the study of artificial stone façade components should be based on preliminary analysis using historical research, geometry surveys, and visual assessment. The diagnostic process may involve onsite destructive/non-destructive and laboratory tests (Sandrolini, 2005; Bartz, 2012).

To qualify the mixtures and assess the decay, we characterized the materials through laboratory analyses. Preliminary macroscopic observation of all samples was fundamental to support the interpretation of the results obtained from onsite non-destructive tests.

Petrographic and mineralogical characterization of the binders, aggregates, and microstructural and morphological observations was performed on samples from the ground floor of the external façade of the Ex Casa del Fascio building in Codigoro (near the city of Ferrara). This building is a typical example of rationalist architecture in rural September 2020
areas. Its ground floor is clad with artificial stone slabs, used as decorative stones, built above a reinforced concrete base. These slabs were severely damaged because of dilation phenomena caused by the highly corroded reinforcements. To fix this damage, several restoration operations were performed before 1992; these interventions were performed with mortar mixes containing fibrous fillers, whereas the most recent restoration operations used mortars without fillers.

Monumental balconies overlooking the main entrance are a typical

Figure 1. The Ex Casa del Fascio building façade, Codigoro, near to Ferrara, northeastern Italy.

Figure 2. “Fake travertine” sample CO1. This artificial stone is present in the ground floor of the Ex Casa del Fascio building and is composed by 3 different layers: layer A (the inner), layer B (above layer A) and layer C the most superficial.
element with high symbolic value in public buildings built during the rational and neoclassical architecture periods. The Ex Casa del Fascio building follows that architectural rule. The monumental colonnade balcony in artificial stone imitating marble is one of the most relevant elements of this building (Fig. 1).

**Sampling**

Samples were collected at different locations from the ground level up, and differences among the types of artificial stone decorative elements and exposure to rainwater were considered.

Although well established diagnostic procedures and techniques exist for natural stone, for artificial stone components, the diagnostic process should be carefully planned to consider specific features such as mixtures, installation and connection methods, and the mechanisms of interaction with reinforcement and support materials.

For “fake travertine” artificial stone, CO1, the sampling was mainly performed on the ground floor slabs in the areas near fractures where the reinforcement bars of the basement concrete produced expansion phenomena due to weathering (Fig. 2).

Samples of “fake Ceppo di Grè” artificial stone, CO2, CO4, and CO7, were collected from the inner parts of the pillars (Fig. 3). The artificial stone materials used for building the monumental colonnade balcony has been covered by successive layers of a mixture of gray cement and lime; for this reason the materials below this strata were sampled as CO6 (Fig. 4).

Sample CO3 came from the replacement materials used to infill cracks, which was easily recognizable because of the dark gray color, relief with respect to the surfaces of the slabs, and thin appearance (Fig. 5).

Details of collected samples are listed on Table 1.

**Chemical and Mineralogical Characterization**

A petrographic study of the samples was performed to determine the composition and granulometry of the aggregate and to verify the potential presence of asbestos minerals used as fillers. Petrographic observations and measurements were performed with optical trans-
mitted light microscopy (OTLM) with an OPLOPTIKA B510 POL-AOS and a stereomicroscope SZ6745TR. Both microscopes were equipped with a MOTICAM 2500 5.0 M pixel webcam operated by Motic Images Plus 2.0 ML software. Microscopic observations were performed on polished thin sections of whole rock samples prepared according to the standard procedures established for Cultural Heritage (UNI 11176:2006, 2006; Di Biase et al., 2008; Tamiozzo, 2009; Fatiguso et al., 2013). Scanning electron microscopy (SEM) observations on thin sections and fragments of samples were performed with a model ZEISS EVO MA 15, coupled with an energy dispersive X-ray spectroscopy (EDS) system (Aztec Oxford apparatus, SDD detector, WD 8.5 mm, EHT 20 kV), with an LaB6 filament as the electron source, and used for microstructural characterization and qualitative determination of chemical composition. SEM images in back-scattered detector imaging mode were used to study the morphological and topographical features of the samples. SEM imaging is an efficient tool used to determine the chemistry of amphibole fibers/particles (diameter > 3 μm). By extension, the combination of polarized light microscopy and SEM coupled to EDS analyses enabled efficient identification of amphibole fragments and/or fibers larger than 3 μm. Additionally, the qualitative EDS analyses indicated extensive variations in textures, morphologies, crystal growth patterns, habits, and crystal structures.

Compared with OTLM, SEM allows for imaging and identification of smaller fibers, and it can be used to evaluate the morphological and chemical composition of asbestiform minerals. In contrast to OTLM, the ability of SEM to utilize reflected energy for imaging allows fibers adhering to other mineral surfaces to be easily observed. Asbestiform minerals are clearly identifiable, because high magnifications can be obtained (Clinkenbeard et al., 2002).

Morphological and microstructural characterization was performed with SEM analysis to detect the morphology of the particles, to determine the presence of fibers (i.e., asbestos minerals), and to identify the fiber dimensions (diameter and length) and any aggregation (e.g., presence of growth or microfractures). The morphological analysis was conducted through microanalysis to identify the chemical and mineralogical composition of the observed granules.

XRD analyses were performed with a Seifert MZIV automatic powder diffractometer equipped with a graphite monochromator operating.

### Table 1. Details of analyzed samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Samples Classification</th>
<th>Height from ground level (m)</th>
<th>Protection from rain</th>
<th>Original</th>
<th>Restoration</th>
<th>Type of Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO1 (a, b, c)</td>
<td>Fake travertine</td>
<td>0.95 cm – 1.10 m</td>
<td>Sheltered</td>
<td>X</td>
<td></td>
<td>OTLM SEM-EDS</td>
</tr>
<tr>
<td>CO2 (a, b, c, d)</td>
<td>Fake Ceppo di Gré</td>
<td>1.70 – 1.75 m</td>
<td>Partly sheltered</td>
<td>X</td>
<td></td>
<td>OTLM</td>
</tr>
<tr>
<td>CO3 e</td>
<td>Concrete infilling mortar</td>
<td>0.40 – 0.45 m</td>
<td>Partly sheltered</td>
<td></td>
<td>X</td>
<td>OTLM SEM-EDS XRD</td>
</tr>
<tr>
<td>CO4 (a, b)</td>
<td>Fake Ceppo di Gré</td>
<td>1.70 – 1.75 m</td>
<td>Partly sheltered</td>
<td>X</td>
<td></td>
<td>OTLM SEM-EDS</td>
</tr>
<tr>
<td>CO6 (a, b, c)</td>
<td>Fake limestone used in columns</td>
<td>0.20 – 0.25 m</td>
<td>Partly sheltered</td>
<td>X</td>
<td></td>
<td>OTLM SEM-EDS</td>
</tr>
<tr>
<td>CO7 a</td>
<td>Fake Ceppo di Gré</td>
<td>0.30 – 0.35 m</td>
<td>Exposed to the weathering</td>
<td>X</td>
<td></td>
<td>OTLM SEM-EDS</td>
</tr>
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Figure 5. Concrete infilling mortar sample CO3. The Ex casa del Fascio building has been affected by damages caused by the earthquakes in May 2012, but before these events it was been subjected to restore operations not always made following the correct procedures for historical building.

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<td>CO4 (a, b)</td>
<td>Fake Ceppo di Gré</td>
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<td>Partly sheltered</td>
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at 40 kV and 20 mA, using Cu Ka radiation. The XRD data were collected from 5° to 60° 2θ with a counting time of 8 s and step-size of 0.02°. The grinding of samples to perform the diffractometric analyses was performed in an agate mortar and pestle in humid environmental conditions to avoid dispersion of the environment fibers that might be dangerous to human health. XRD analysis was performed on a pulverized sample of replacement cement paste (Clinkenbeard et al., 2002). Although polarized microscopy and XRD are useful for preliminary identification of asbestos mineral phases, given the possible presence of asbestos minerals in these samples, SEM-EDS was considered the most powerful tool for the detailed investigation of fibrous minerals.

**Results**

**Macroscopic Characterization**

“Fake travertine” artificial stone (Fig. 2)

![Figure 6. “Fake travertine” Sample CO1. Thin section micrographs. Layer A, examples of concrete mix with silico-carbonate aggregate a) sharp edge quartz and silicate rocks fragments; b) sharp edge quartz, silicate rocks fragment and carbonate fragments. Layer B, aggregate mainly composed by various lithotypes of carbonate rocks, such as c) light white limestone, low-round foraminifera rocks, d) well-rounded beige micritic pebbles and rare spathic calcite fragments. Reddish color should be due to presence of iron oxides and hydroxides, often deposited inside the binder in contact with the macro and micropores. Layer C stereomicroscope pictures of the outer layer e) spider; f) particular of a black crust.](image-url)
Macroscopic observations of CO1 “fake travertine” artificial stone decoration revealed the presence of three layers.

i) Layer A represents the structural element of the decorative slabs and was composed of bar-reinforced well mixed concrete with homogeneous distribution of the aggregate. Thin section observations revealed that the aggregate fraction was mainly composed of a silico-carbonate fraction, with a higher prevalence of silicate than carbonate. The silicate fraction was mainly composed of fragments of mineralogical rocks, such as gneiss, arenaceous-pelitic metamorphosed rocks, and a small amount of ultramafic rock fragments. Quartz, feldspars, a low percentage of micas (muscovite and biotite), and some serpentine crystals were the identified silica mineral phases. Few carbonate rock aggregates were also present (Fig. 6).

ii) Layer B represents the decorative layer, which was obtained by mixing a white cement type with white/pale yellow limestone rock. This decorative layer overlapped the reinforced concrete of layer A. Micrite grains and a low percentage of yellow limestone fragments was detected. OTLM observations indicated that this layer was composed primarily of a carbonate aggregate within a plaster mortar with the typical optical features of a hydraulic binder. The binder aggregate modal ratio was estimated to be approximately 1/3 with a non-homogeneous distribution of aggregate. The aggregate was mainly composed of various lithotypes of carbonate rocks, such as light white limestone, low-round foraminifera rocks, well-rounded beige micritic pebbles, and rare spathic calcite fragments. Reddish areas were present in the mixture, owing to the presence of iron oxides and hydroxides related to steel bar reinforcement alteration phenomena (Fig. 6).

iii) Layer C represents the protection strata subjected to yellowing in the altered areas. Stereomicroscopic observations of the surface revealed strong biological degradation with the presence of nests of insects and fungal hyphae, together with a black crust (Fig. 6) (Randazzo et al., 2015; Chen et al., 2017; Molina et al., 2017).

“Fake Ceppo di Grè” (Fig. 3)

The natural stone material known as Ceppo di Grè is a polygenic conglomerate whose geological name is Ceppo Conglomerate (Vola et al., 2009). It crops out along all foothills of the River Po Valley and as reported by Vola et al., 2009 has been widely used as a decorative stone material in northern Italy. The artificial stone classified here as “fake Ceppo di Grè” faithfully reproduces the Lombard Breccia that crops out in the surroundings of Iseo Lake (Jadoul and Galli, 2008; Muttoni et al., 2010; Berra and Carminati, 2010; Ronchi et al, 2011).

Macroscopic observations of “fake Ceppo di Grè” artificial stones investigated in this work (samples CO2, CO4, and CO7) showed irregular and angular fragments with a prevalence of micritic and microsparitic carbonate rocks. In “fake Ceppo di Grè,” as described for “fake travertine” slabs, regions near the damaged areas showed oxidation affecting the reinforcement bars. Because of the sizes of limestone and dolomite clasts (from 3–5 cm to 100 cm), analysis of these samples focused on the binder. Stereomicroscopic and petrographic microscopic observations of mortars showed the yellowish-gray background of the matrix, with aggregate constituted by sandy fractions. In addition to natural aggregate, some asbestos phases such as fillers (less than 1%) were observed. Thin sections showed a medium aggregate/binder ratio in mortars binding well with mixing. The binder porosity was mainly macroscopic, with low microporosity. Extensive degradation phenomena and carbonation processes corresponded to the weathering of exposed areas. The cement matrix natural aggregate was composed mostly of carbonate aggregates, with a presence of vitrophyric slag and asbestos minerals used as reinforcement fillers. Oxides and hydroxides with black (ilmenite-magnetite) and red blood color were rare (Fig. 7).

Fake limestone used for columns (Fig. 4)

The observation of samples collected from the columns (CO6) showed a tenacious mortar consisting of a white cement with an amorphous structure and a well-classed medium silica sand aggregate enriched in serpentinite. The aggregate was characterized by the prevalence of serpentinite (around 70%) with a minor percentage of micritic limestones, quartz, iron hydroxides, pale yellow vitrophyric slag, and green glass fragments. Degradation phenomena were absent. The aggregate/
binder modal ratio was approximately 1/3, and the mix appeared highly homogeneous (Fig. 8).

Concrete infilling mortar (Fig. 5)

Despite the high quality of these artificial stone materials, in “fake travertine” and “fake Ceppo di Gré” types, macroscopic observations revealed the decay process of the reinforced concrete base structures with cracking fragility. The infill materials used for restoration with fibrous minerals were present in restricted and localized areas, with a maximum extension of 10 cm in diameter and thicknesses less than 4 cm. Stereomicroscopic observations of sample CO3, infilling mortar, allowed us to identify fibrous phases that favored macroporosity, which was presumably related to colonization with lithophagous fauna responsible for biodegradation decay. For these samples, thin sections were not made, to avoid the risk of fiber dispersion during the lapping and pol-

Figure 8. Fake limestone sample CO6. This section observations reveal a great Yang et al. (2019) quantity of serpentine mineral phases in the mixture.

Figure 9. “Fake travertine” Layer A. a) Secondary micrograph of the matrix in the concrete substrata showing the iron oxychloride complexes around and inside a vacuolar structure with corresponding the SEM-Energy Dispersion Spectroscopy (EDS) spectra. b) Secondary micrograph showing layered two-dimensional iron oxychloride (FeOCl) husk like structured.
ishing operations. Therefore, the analysis was performed by combining microscopic observations with SEM analysis to confirm the presence of asbestos minerals.

**SEM-EDS Data Analysis**

“*Fake travertine*” artificial stone

Layer A: the corrosion products of reinforcement steel bar were typical layered structures with red and brownish-red color (Fig. 9). This finding was consistent with the iron mobilization from reinforcement steel bars, presumably as a result of capillary action of water, that characterizes the lithological substratum where this edifice was built. These globular clusters were observed in pores of “fake travertine” as well as in the corrosion products of steel reinforcement.

Layer B: the components of the mix design were white cement paste, carbonate aggregate rocks, and yellow pigments, such as iron hydroxides (Fig. 10).

In the samples subjected to SEM observation, EDX analysis revealed iron hydration products with a self-oriented flower shape with an average diameter of 10–12 μm (Fig. 11).

“*Fake Ceppo di Grè*”

Two types of sulfates was recognized: calcium sulfate (Fig. 12) and barium sulfate (Fig. 13). The EDS spectra of these particles demonstrated a high-amount of sulfate in these black points.

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**Figure 10.** “*Fake travertine*” Layer B. Secondary micrograph showing the composition of amorphous white matrix and the corresponding the SEM-Energy Dispersion Spectroscopy (EDS) spectra.

**Figure 11.** “*Fake travertine*” Layer B. a) and b) BSE micrographs showing the iron oxychloride complexes with the self-oriented flower shape with average diameter of 10–12 μm and the corresponding the SEM-Energy Dispersion Spectroscopy (EDS) spectra.
Concrete Infilling Mortar

Because stereomicroscopic observation revealed the presence of fibrous phases, SEM-EDS analysis was performed to better identify the chemical. Fig. 14 shows back scattered images highlighting the presence of various fiber types and confirming the microscopic observations. In these samples, asbestos tailings mainly contained serpentine, including snakesite, antigorite and chrysotile, as well as small amounts of brucite, magnetite, quartz, talc, and chlorite. The main chemical composition of the asbestos tailings was SiO$_2$, MgO, and Fe$_2$O$_3$, with a small amount of Al$_2$O$_3$ and CaO.

Fake Limestone Used for Columns

Thin section observations showed a white cement mortar with amorphous structure and a well-classed medium silica sand aggregate enriched in serpentine. SEM analyses revealed a composition compatible with the presence of tremolite-actinolite amphibole group phases (Fig. 15). SEM analyses also confirmed the use of pale green and white leaded glass (Fig. 16).

XRDP Data Analysis

XRD patterns of sample CO3 (Fig. 17) revealed peaks of lizardite.
(Mg₃Si₂O₅(OH)₄) (2θ at 12° and 24°), a polymorph of the serpentine group minerals.

**Discussion**

The combination of techniques used in this study to characterize the mixtures used to formulate artificial stones highlighted the typical features of each type of artificial stone. OPLM is the most common analytical technique used by geologists for mineralogical and petrographic characterization of materials. Macroscopic observation indicated the presence of a steel bar-reinforced concrete substratum in almost all of the samples; therefore, we hypothesized that pre-packaged slabs based on cement mortar were used. The bar-reinforced concrete substratum was evident only in the “fake travertine” slabs; the artificial stone mixture was found over this layer. OPLM investigation of the artificial stone material revealed the absence of efflorescence that, as suggested by Morillas et al., 2015 and Chen et al., 2017, may be associated with the use of materials with low salt content as aerators. Optical microscopy observations indicated the presence of asbestos minerals in some analyzed samples, but, as suggested by Militello et al. (2019), this technique is considerably limited for identifying asbestos fibers. Therefore, OPLM was coupled with XRD and SEM analyses to investigate the potential presence of asbestiform
minerals in concrete infilling mortars and in fake limestone used for columns. In both types of samples, SEM-EDS data showed high peaks of Mg and Si that may indicate the presence of asbestos at the fibrous elements, but a distinction must be made: in the fake limestone samples, asbestos mineral phases may be associated with weathering processes of ultramafic rock minerals characterizing the aggregate, because lizardite is commonly the main polymorph present in serpentinites (Schwartz et al., 2013). For concrete infilling mortar, the presence of asbestos minerals may be due to the presence of these types of minerals in the starting mixture.

The XRD pattern of a representative sample confirmed the presence of lizardite, one of the three polymorphs of serpentine (Auzende et al., 2004; Votyakov et al., 2005 and Liu et al., 2010; Schwartz et al., 2013; Guillot et al., 2015; Liu et al., 2019), and SEM-EDS analyses characterized the aspect ratios and the textural relationships among the various mineral phases and revealed the presence of different fibrous phases in the studied samples.

SEM-EDS analyses of “fake travertine” samples indicated the presence of iron oxychloride complexes with self-oriented flower shaped markings (Fig. 13). Thus, we hypothesized that iron oxide fibers were present, as reported by Sayed and Polshettiwar (2015), in agreement with iron mobilization from reinforcement steel bars. Oxygen fugacity and pH may influence the corrosion of iron materials, and chloride might be adsorbed or might penetrate easily through the passive film,
thus damaging the integrity and subsequently accelerating the electrochemical reactions.

SEM-EDS analyses of “fake Ceppo di Gré” highlighted unusual peaks of Ba, thus suggesting that Ba hydroxide was added to the mixture to make the concrete harder and therefore resistant to physical and mechanical stress and degradation. The same procedure might have been used for cement, in which barium may be added to help bind and enhance resistance to different types of radiation (Zezulová et al., 2016). Barium cations are a part of the raw mixture and thus can be incorporated into the crystal lattices of alite and belite, and the interstitial phase. Some authors have found neither barium nor ferrite in belite (Juel and Jøns, 2001); only tricalcium aluminate can contain barium in its structure (Katyal et al., 1999). These findings are in accordance with the high SiO₂/calcium in the Ba-rich matrix (spectrum 70–72). Zezulová et al. (2016) have observed that an excessive BaO concentration can inhibit the crystallization of alite or decompose alite in favor of belite and free lime. The free lime then produces an excess of portlandite, which, the crystallization of alite or decompose alite in favor of belite and free lime, justifies the high content of calcium sulfate observed with SEM analyses in this process.

The use of pale green and white leaded glass, as confirmed by SEM analyses, is consistent with the addition of glass fragments to mortar mixtures for aesthetic purposes and with increasing the mortar’s resistance to sunlight.

Conclusions

A combination of different analytical methods were used to characterize the artificial stone materials used in a rationalist architectural building in a rural town near Ferrara in the Emilia Romagna region (northeastern Italy).

Macroscopic observations revealed superficial damage with fractures and cracks, the exposure of degraded and oxidized bar reinforcements, and biological degradation in almost all the artificial stones. OPLM observations showed different compositions of the agglomerate in the various types of artificial stone materials used, thus highlighting the presence of minerals from metamorphosed ultramafic rocks in some samples and filler containing fibrous minerals in other samples. SEM-EDS and XRD analyses confirmed the presence of asbestos mineral phases, particularly lizardite, both in the concrete used for restoring operations and in samples enriched in ultramafic aggregate.

The observed lizardite fibers did not appear to be present at dangerous levels, but potential risks during restoration or collection should be taken into consideration. In this light, mineralogical and petrographic characterization of building materials is a useful tool for investigating the presence of potentially dangerous fillers that required caution during degradation product removal through sandblasting or other methodologies that pulverize the altered surfaces. To prevent effective post-degradation fracturing and transformation into elements harmful for health and the environment, careful monitoring is recommended.

In conclusion, the overall project, besides providing valuable support for the restoration work, enabled studying an eminent artistic product of epochal monumental architecture—a symbol of recent history now deserving renewed attention.

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