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Characterization of Artificial Stone Used for Outdoor Monuments and Sculptures in Quebec

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Artificial stone is often employed in sculptural work and architectural details in Quebec, including many monuments that have fallen into disrepair. During this collaborative project between the Canadian Conservation Institute and the Centre de conservation du Québec, 16 samples were taken from 12 sculptures across Quebec and were analyzed by means of stereomicroscopy, scanning electron microscopy/energy dispersive X-ray spectrometry, thin-section petrography and X-ray diffraction. Some aspects of the analysis, for instance the confirmation of the presence of clinker, proved to be challenging due to the restrictions on sample size required in conservation work. The results indicate that more than half of the sculptures analyzed were hydraulic cement-based artificial stone. The remaining sculptures were made of Coade stone, or lime-, gypsum- or dolomite-containing materials. This research provides a limited survey of artificial stones in Quebec and will help guide conservators in selecting proper treatments for these works by allowing identification and better understanding of the materials.

La pierre artificielle est utilisée dans les sculptures et les détails architecturaux au Québec et beaucoup de ces monuments sont maintenant dégradés. Au cours de cette collaboration entre l'Institut canadien de conservation et le Centre de conservation du Québec, 16 échantillons ont été prélevés de 12 sculptures de plusieurs régions du Québec et ceux-ci ont été analysés en utilisant plusieurs méthodes : microscopie optique, microscopie électronique à balayage couplée à la spectrométrie des rayons X, pétrographie de lames minces et diffraction des rayons X. Quelques aspects de l'analyse, tels que la confirmation de la présence de clinker, présentaient un défi puisque les tailles d'échantillons sont restreintes en conservation. Les résultats indiquent que plus de la moitié des sculptures étaient composées d'une pierre artificielle à base de ciment hydraulique. Les autres sculptures étaient composées d'une variété de matériaux à base de pierre Coade, de dolomite, de gypse, ou à base de chaux. Cette recherche donne un aperçu de certains types de pierre artificielle utilisés au Québec et guidera les restaurateurs dans le choix des traitements appropriés pour ces œuvres grâce à une meilleure connaissance des matériaux et de leur identification.

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INTRODUCTION

Artificial stone is used in many applications including the creation of sculptures and architectural details (**Figure 1**). This material is composed of various types of aggregates held together with a binder to imitate the look of natural stone; in fact, it is also called imitation stone. Typical artificial stone sculptures are created by casting concrete or other materials, and are sometimes painted to provide a specific surface finish. Many artificial stone monuments have fallen into disrepair, and their conservation has become an integral part of preserving the heritage of many parishes, public monuments and parks.

The Centre de conservation du Québec (CCQ) initiated this study during the development of conservation treatments for artificial stone monuments in Quebec, when it became apparent that little was known about the composition of these types of monuments. Analysis by the Canadian Conservation Institute (CCI) was requested in order to provide more information on the materials and to help determine appropriate treatment protocols. In addition, obtaining information about the composition of a particular artificial stone might eventually help with identification of the manufacturer and the date of construction. The two institutions embarked on a study encompassing the analysis and identification of 16 samples from 12 monuments and statues from a variety of sites in Quebec (**Table I**).

Little historic or technical information exists on works of artificial stone in Quebec because these were produced in an artisanal setting where knowledge was exclusively passed on from master to apprentice. Most information uncovered was in the form of advertisements or workshop pamphlets.[1] Literature on the topic of artificial stone yielded information on important types developed in Europe and the United States.[2] Stuccos made of lime, gypsum and stone powder were used from the Roman era through to the Renaissance, when materials such as *bugnato* (a lime-based material compounded with marble powder) and clay-rich limes became popular.[3] Early hydraulic cements were developed and in use in England from the late 17th century onward[2] and became increasingly popular with the introduction of Portland cement in 1824.[4] Coade stone was developed in 1769,[5] and from this point on, the evolution of artificial stone materials continued with the creation of mixtures into the mid to late 19th century by Liardet, Dehl and Hamelin in England,[6] Ransome[7] and Frear[8] in the United States, and Coignet[9] and Sorel[10] in France, among others. Improvements to these recipes continued into the 20th century, when new development became focused on the use of novel polymeric binders.[2]

Table I. List of Monuments

Name of Monument	Location of Object	Sample No.	Visual Description of Sample
Admiral Nelson statue, Nelson's Column monument, by Coade and Sealy (Lambeth, England), *circa* 1809	Montreal (Centre d'histoire de la Ville de Montréal)	AS 1(surface)	Light grey-brown matrix with sparse white semi-translucent aggregates
		AS 2 (interior)	Marbled grey and light brown, fine matrix with sparse small to medium white semi-translucent aggregates
Restored tablet, Nelson's Column monument, by Barcerini and Filippi, *circa* 1871	Montreal (Chateau Ramezay)	AS 3	Ranges from (left to right) a light brown, fine matrix, followed by a grey matrix with fine black and red aggregates, followed by a dark grey matrix with medium to large black and red aggregates
François-Xavier, sculptures of the facade of the Saint-Jean-Baptiste church by M. Rigali, *circa* 1885	Quebec	AS 4	Light grey matrix with fine dark grey and red-brown aggregates
Saints Martyrs Canadians, by Barsetti brothers and G. Casini, *circa* 1940	Montreal (Roberval Park)	AS 5	Fine yellowed matrix with large white semi-translucent aggregates
Calvaire of Christ, *circa* 1900	Montreal (Roberval Cemetery)	AS 6	Light grey matrix with small to medium sized grey and dark red aggregates
Saint Joseph, *circa* 1900	Chicoutimi (Sacré-Cœur Presbytery Park)	AS 7	Light grey matrix with sparse small to large black and brown aggregates and slight yellowing of surface
Saint Joseph, *circa* 1900	Victoriaville (garden of the Monseigneur Côté School)	AS 8	White to light brown, fine matrix with medium to large white semi-translucent aggregates
Saint Joseph, *circa* 1950	St-George-de-Beauce (Beauce Health Centre)	AS 9	White, fine matrix with medium to large white semi-translucent aggregates
Virgin statue, Immaculate Conception, *circa* 1950	St. George-de-Beauce (Beauce Health Centre)	AS 10	White, fine matrix with medium to large white semi-translucent aggregates
Notre-Dame du Saint-Rosaire, *circa* 1900	Rimouski	AS 11 (statue)	White, soft, fine matrix with medium to large brown and black semi-translucent aggregates
		AS 12 (crown repair)	White, fine matrix with sparse small white semi-translucent aggregates
		AS 13 (dark base)	Red-brown bubbly/molten matrix with small to medium brown and black aggregates
Christ the King, by T. Carli-Petrucci and A. Laliberté, *circa* 1947	Roberval	AS 14	White, fine matrix with medium to large white and light brown semi-translucent aggregates
Sacré-Coeur, *circa* 1920	Sorel	AS 15	White, fine matrix with medium to large white semi-translucent aggregates
Marguerite D'Youville, by G. Casini, *circa* 1963	Beauport (Cardinal-Vachon Residence)	AS 16	White, fine matrix with medium to large white semi-translucent aggregates

Historical Background

The use of artificial stone for the creation of works of art and architectural ornaments first occurred in Quebec in the mid-19th century with the production of Italian statuary. Sculptors adopted artificial stone for economic reasons, and also because the material was well suited to their expertise in moulding and casting. These works are present around Quebec as individual sculptures with religious or political subjects (**Figure 1**) and as iconographic architectural details (**Figure 2**).[11]

Most of the sculptures were produced in the workshops of early Italian immigrants to Quebec, sculptors such as Michele Rigali, Angelo Barsetti, Luigi Bastiani, and the families of Guido, Casini and Daprato. Only a few of the sculptures in this study currently have attributions. One such sculpture, Christ the King (**Figure 1a**), was a collaboration between the workshop of T. Carli-Petrucci and sculptor Alfred Laliberté.[11]


A


B


D

C

Figure 1. Photographs of select monuments that were sampled in this study. Clockwise from top left:
a) Sculpture of Christ the King (AS 14), 2.45 m tall;
b) Sculpture of Admiral Nelson (AS 1), 2.5 m tall;
c) The tablet from Nelson's Column with questionable composition (AS 3), 1.14 m in diameter;
d) Sculpture of Saint Joseph (rear view) with obvious cracking and crumbling (AS 8), 1.65 m tall.
Photographs: © Centre de conservation du Québec.

One monument not manufactured by the workshops mentioned above is Nelson's Column, Montreal's oldest monument, dedicated to Admiral Horatio Nelson and manufactured in London, England. The composition of the sculpture of Admiral Nelson (**Figure 1b**) and the inscribed tablet from Nelson's Column (**Figure 1c**) were of special interest, since parts of the tablet appeared different in colour and grain compared to the statue. According to historic documents,[11] the statue of Nelson and the ornamental elements of the monument were made of Coade stone by the manufacturer Coade and Sealy in Lambeth, England, but only part of the tablet consisted of Coade stone's characteristic buff-coloured ceramic. In fact, an agreement between sculptors Baccerini and Filippi and the Corporation of the City of Montreal, dated 1871, mentioned restoring the tablet for Nelson's Monument with a patented Portland cement mixture (made with crushed red brick aggregates).[11,12] This monument made for an interesting study because of the availability of historic documents which included the cement patent; other monuments in this study did not have supporting documentation.

Literature Survey of Artificial Stone Materials

Although the composition of artificial stone used in Quebec sculpture is not that well documented, literature describing the types of materials used abroad and in related industries, such as the building industry, revealed some standard materials that may have been used for this purpose in Canada. These materials included components such as hydraulic calcareous cements (e.g., Portland cement, natural cement), non-hydraulic cements (e.g., non-hydraulic lime cement), gypsum-based materials (e.g., plasters, *scagolia*), magnesium-based cement (e.g., Sorel stone) and ceramic materials (e.g., Coade stone).

Artificial stone is a mixture of a binding agent, water and aggregates (inert granular material).[13] The binding agent hardens and forms the matrix of the stone that holds the aggregates together. The binding agent can be a cement, yielding a concrete, or it can be a clay, yielding a ceramic stone when fired. The terms "concrete" and "cement" are distinct: "concrete" is a mixture of cement with sand, other aggregates and water; "cement" is the binding medium that holds the sand and aggregates together to form the concrete.[14] Cements generally fall into two categories, hydraulic (requiring water to harden) and non-hydraulic (which usually set by reaction with carbon dioxide (CO_2) in the atmosphere). A mixture of coarse and fine aggregates can be included in the concrete, possibly including one or more of sand, crushed stone, crushed brick, coke-breeze, burnt clay, fly ash (a by-product of burning coal), *pozzolana* (a volcanic material), bituminous waste, or other material, including waste products sourced from the area of manufacture.[15]

The composition of artificial stone varies considerably and depends upon the manufacturer's formulations and processes. Environmental conditions are also considered when selecting the ideal composition for outdoor monuments. The aggregates, binding agent, colouring agents and methods of finishing are chosen to give a piece the illusion of being natural stone.[16]

The materials which might be expected to occur in monuments, sculptures and architectural decorations, and which were identified in the literature review, are described below. The identification of these components is key in determining the types of artificial stone used for the production of these outdoor monuments and sculptures.

Figure 2. Facade of the Saint-Jean-Baptiste church with detail of the figures (AS 4). The 13 figures stand approximately 1.2 m tall. Photographs: © Centre de conservation du Québec.

Hydraulic Cement-based Materials

Hydraulic cement is a category of calcium-containing cement that reacts with water to harden. It contains at least 20% silicon dioxides (or sand) and at least 7% iron oxides, or aluminum oxides, to facilitate the hydration reactions that harden the cement.[17] These components, which may be a combination of clay, slag, volcanic ash, etc., are crushed together with the main raw calcium-containing material and, when heated to high temperatures, form what is called "clinker."[18,19] Clinker is commonly a mixture of four compounds: tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$) and tetracalcium ferroaluminate ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$).[18] The cement chemist notation denotes these compounds as C_3S, C_2S, C_3A and C_4AF, respectively. When powdered clinker is mixed with water it hardens very quickly. Natural cement and Portland cement, described below, are just two of the most widely used types of hydraulic cement; other mixtures are possible. Hydraulic cements were sometimes named after specific natural deposits, such as Rosendale natural cement. Proprietary cement mixtures or formulas could include gums, preservatives or other compounds − an example of this is the stone mixture developed by McMurtie that contained alum and potash soap.[2]

Natural cement is a hydraulic cement produced by burning a mass of natural clay-based limestone containing 15–40% silicates, aluminates and/or iron oxides. When carbon dioxide is driven off, the lime (CaO) left behind reacts with the silicates, aluminates, or iron oxides to give clinker.[19] The final cement product is commonly yellow to brown in colour due to the high proportion of natural clay and the calcination temperature used during the process.[20]

Portland cement was patented by Joseph Aspdin in 1824 and named after the resemblance to the colour of stone from the Isle of Portland, England.[4] Portland cement is a hydraulic cement, made by heating a carefully crafted mixture of limestone, and clay, shale or ash in a kiln to a temperature of 1300–1500°C until partial vitrification is achieved. This recipe contains more limestone than the natural hydraulic cement and is more homogeneous.[20] The clinker formed is mostly a calcium silicate, $n\mathrm{CaO} \cdot \mathrm{SiO_2}$. Portland cement is usually composed of tricalcium silicate (C_3S) with moderate amounts of dicalcium silicate (C_2S) and tricalcium aluminate (C_3A), although tricalcium silicate reverts to a dicalcium state when cooled slowly.[21] The clinker is powdered and mixed with sand, fly ash or other aggregates, and with water to form concrete.[18] While Portland cement is similar to natural cements, it differs in three main respects. First, Portland cement has a precise initial composition while natural cement simply uses a mass of natural rock. Second, Portland cement is stronger than natural cement. Third, Portland cement has a distinct blue-grey colour, due to the different additives and proportions, in contrast to the brown colours of natural cement.[16] White concretes based on a Portland cement recipe do exist, in which materials such as China clay and limestone are used to make white and reflective aggregates instead of the typical dark aggregates, but this formulation is more costly.[18] The use of this white concrete dates to 1907.[22]

Hydraulic lime cement is produced from a limestone and clay mixture[18] from either naturally occurring clay-rich lime deposits, or from artificial mixtures.

Non-hydraulic Cement-based Materials

Non-hydraulic cements harden or cure by reactions with CO_2 in the atmosphere and include materials based on lime, gypsum, or magnesium oxychloride.

Lime-based cement is produced from limestone, which is powdered and heated into quicklime (CaO); water is then added to form slaked lime ($Ca(OH)_2$); on mixing this with sand, the material is ready for use. Products made with lime as the binding agent are usually referred to as "mortars," even though they technically fall under the definition of a cement or concrete. Reaction with carbon dioxide from the environment during the curing process yields a calcium carbonate matrix. One or more of the intermediate compounds CaO or $Ca(OH)_2$ is usually present when lime-based materials are analyzed. In certain cases where the limestone deposit contains veins of dolomite, a mineral with the chemical composition of $CaMg(CO_3)_2$, or where the limestone has been converted into dolomite through a natural sedimentary process called dolomitization, the intermediate quicklime compounds comprise a mixture of CaO and MgO.[21] This fact is important to consider when distinguishing between Sorel stone (described below) and other calcareous cement-based stones with magnesium in the matrix.

Gypsum-based stone, such as plaster of Paris and *scagliola*, an imitation marble, are sometimes used as artificial stone. Pure crude gypsum ($CaSO_4 \cdot 2H_2O$) is heated to drive off nearly all water, resulting in a partial anhydrous lime sulfate ($CaSO_4 \cdot 0.5H_2O$).[17] When mixed with water, a workable plaster results, that re-forms as gypsum upon drying. In the case of *scagliola*, the powdered plaster is mixed with glue and colourants to mimic the veins in marble. Pieces are often finished by heating and polishing.[23]

Magnesium-based stone includes Sorel stone, in which magnesium chloride is added to magnesium oxide ("burnt magnesia") and combined with sand, powdered marble, or other aggregates. This yields a concrete that hardens quickly but has poor water resistance.[24]

Ceramic Materials

Ceramics harden due to chemical reactions that occur at high temperatures during firing. One example of ceramic artificial stone is Coade stone, a fired ceramic that has clay as its matrix. Coade stone was produced from 1769 until approximately 1840 by Eleanor Coade's company, named "Coade's Artificial Stone Manufactory," "Coade and Sealy" and later "Coade." Its proprietary composition was difficult to reproduce until modern analytical methods were available. It contains a mixture of approximately 10% grog (crushed glass and fired clay), 5–10% crushed flint, 5–10% rounded quartz grains, 10% soda lime glass, and 60–70% clay (including kaolinite) which was fired in a kiln at 1100–1150°C for four days.[5] Firing at high temperature transforms the crystal structures of quartz (SiO_2) and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)

minerals into their polymorphs, cristobalite (SiO_2) and mullite ($2Al_2O_3{\cdot}SiO_2$); this transformation is indicative of a fired ceramic.[25]

Analytical Methodology

Most research conducted on artificial stones and mortar materials has focused on historic buildings in Europe. Groups such as those of Pecchioni, Moropoulou, Sanjuirjo-Sánchez and Rampazzi have investigated these materials using a combination of techniques in order to characterize the materials used in important cultural heritage properties.[26-29] Pecchioni's study of artificial stones used in historical palaces in Florence between the 19th and 20th centuries determined that all the samples were made of hydraulic cement and emphasized the use of petrographic examination.[26] Petrography is a technique which allows for visual identification of specific features based on optical or textural properties. Moropoulou's group presented an investigation of historic mortars of Rhodes, ranging from the Hellenistic period until the Ottoman period.[27] Their analysis relied primarily on X-ray diffraction and petrography, and calcite was identified as a main component. Again, petrography was stressed as a useful technique in determining the aggregate components. The materials identified in the study included non-hydraulic lime mortars, blended crushed brick and lime mortars, and hydraulic lime mortars. Sanjurjo-Sánchez's study on mortars from the Santa Eulalia de Bóveda temple in Spain was undertaken in order to determine the different periods of construction, thought to range from the Roman period to the 21st century. The study characterized a variety of mineral aggregates contained in lime binders by X-ray diffraction, neutron activation analysis and petrography.[28] Recent research led by Rampazzi focused on both mineralogical and chemical examination of mortars from Amalfi's Arsenale, a medieval shipyard in Italy, and identified historic lime mortars containing volcanic rock aggregates and a natural gum through the use of microscopy, X-ray diffraction, infrared spectroscopy, thermal analyses and gas chromatography-mass spectrometry.[29]

Many quantitative and qualitative analytical methods have been used to characterize artificial stone materials for various purposes in the academic, engineering and construction fields, including microscopy/petrography, instrumental identification of elements, compounds and minerals, and mechanical tests[30,31] of properties such as strength, porosity and density. The published research in conservation, as well as the ASTM standard test methods,[32,33] both suggest a basic strategy for analyzing artificial stone: first, that once the macroscopic properties have been studied, the microscopic structure of the material needs to be examined using petrographic methods (optical microscopy of thin and thick sections); and second, that analysis needs to be conducted separately on the matrix and on the aggregates to determine the elemental and mineralogical composition.

There are two methods to physically separate the aggregates from the matrix, chemical or mechanical. A study on the relative efficacy of each method for matrix and aggregate ratio calculations, compared to digital image analysis, concluded that most chemical methods were too aggressive and tended to dissolve calcareous aggregates, while mechanical separation yielded satisfactory results.[34] The digital image analysis gave accurate results with a few drawbacks, such as the need for large sample sizes and specialized software.[34] As written, the ASTM standards require relatively large samples for accurate results, anywhere from 10 g bulk samples to 100 mm diameter core samples.[32,33] The recommended representative surface area for thin sections for petrographic analysis is 100 cm^2.[35] These are much larger than the samples usually available for analysis of cultural heritage materials.

Based on the literature surveyed, a combination of techniques, most of which were available at CCI, was selected as the methodology. These included microscopy and petrography of samples and thin sections, and non-quantitative analysis by energy dispersive X-ray spectrometry and X-ray diffraction of the matrices and aggregates. Where separation of the components was required, the aggregates and matrices were separated mechanically.

METHODS

Sampling

Samples of the artificial stone were taken from inconspicuous areas of the sculptures where the materials were readily accessible, i.e., along a crack in the back or under the base of the sculpture. When possible, the sampling areas were clean, without paint, and deeply recessed, in order to avoid areas where the cement might be altered and where the level of carbonatation (a reaction that occurs over time between the hydraulic cement surfaces and environmental CO_2) might be higher. The locations of the samples were recorded on a photograph of the work and kept filed with the sample documentation (file number, title of the work, client name, date, etc.).

Sample Preparation

Sixteen samples, listed in **Table I**, were gathered and sent to CCI. The samples ranged from approximately 6 cm^3 to 40 cm^3. Most had to be reduced in size by controlled breaking in sealed plastic pouches with a hammer and chisel before they could be mounted as cross-sections and analyzed. Sample AS 4 required crushing with a vise due to its hardness. Analysis was performed on both the matrix and the aggregates of each sample after mechanical separation.

Methods of Analysis

Optical Microscopy/Petrography

Photomicrographs were taken with a Leica M205C microscope and Leica DFC 500 camera to document the samples' appearance. Then small sections of each sample were prepared as cross-sections by embedding them in polyester resin, grinding and polishing using standard techniques, and examined with incident light and autofluorescence microscopy using a Leica DMRX microscope.

Geological petrography was performed to identify minerals and other compounds not easily identified by other analytical techniques. For the petrographic study, samples were prepared as thin sections ranging from 2 cm^2 to 6 cm^2 by Vancouver Petrographics using standard laboratory techniques and examined optically using a Nikon Labophot-Pol petrographic microscope. These thin sections were reviewed at CCI for confirmation of the presence of clinker in the matrix using a Leica DMRX microscope. Dyes and etching solutions were not applied.

Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometry

Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS) X-ray maps were acquired by analysing samples prepared as cross-sections, and served as visual aids for identifying general aggregate proportions and composition. The intensity of colour of the X-ray maps correlates with concentrations of select chemical elements. Additional SEM/EDS analysis of specific areas and select aggregates was performed to identify the elements present.

SEM/EDS was performed using a Hitachi S-3500N VP SEM integrated with an Oxford Inca X-act analytical silicon drift X-ray detector and an Inca Energy+ X-ray microanalysis system. The samples were prepared by coating them with carbon, and the SEM/EDS was operated in high vacuum mode at an accelerating voltage of 20 kV using a backscattered electron detector for imaging. Using this technique, elemental analysis of volumes down to a few cubic micrometers can be obtained for elements from boron (B) to uranium (U) in the periodic table at a level of approximately 0.1–1% or greater.

X-ray Diffraction

X-ray diffraction (XRD) was employed to identify the major and minor crystalline compounds contained in both the matrix and aggregate fractions of the samples. XRD was also essential in identifying minor to trace quantities of clinker in the matrix. Manual separation and powdering of both the matrix and aggregate fractions yielded purer samples with more crystalline facets resulting in better diffraction patterns. The crushed material was initially separated by hand for micro-XRD, for which only microscopic sample volumes are required.

Micro-XRD patterns of powdered portions of both the matrix and aggregates of the 16 samples were obtained using a Bruker D8 Discover with GADDS (General Area Detector Diffraction Solution) equipped with a rotating anode and cobalt target. The patterns were measured at 40 kV and 85 mA using a 0.5 mm collimator over the angular range 15 to 80° (2θ) in two frames using a Hi-Star area detector.

Only the major component, calcium carbonate, was detected in the matrix of many of the samples via micro-XRD. However, in some of these instances the SEM/EDS analysis detected major amounts of silicon in the matrix. As a result, samples were prepared in larger volumes and passed through sieves in order to isolate the powdered matrix for X-ray diffractometry, in an effort to uncover the possible presence of clinker. Seven samples which yielded inconclusive micro-XRD results (where the cement was not identified) were sent for X-ray diffractometry; these were samples AS 2, 4, 8, 9, 10, 13 and 16. These matrix samples were analyzed at CanmetENERGY using a Rigaku Ultima IV X-ray diffractometer equipped with a graphite diffracted beam monochromator and a copper target. The patterns were measured at 40 kV and 44 mA over the angular range 15 to 80° (2θ) in 0.01° steps and 0.5 deg/min using a high-speed semi-conductor element one-dimensional X-ray detector (D/teX Ultra). The Bragg-Brentano para-focusing geometry was used for the powder X-ray diffractometry analysis.

RESULTS AND DISCUSSION

Preliminary Microscopic Examination

Most of the 16 samples ranged from white to grey in colour, although some varied from light to dark brown (see **Table I** for descriptions). Aggregates also varied in colour, opacity, size and shape. In **Figure 3**, a selection of four samples demonstrates the variation in the observable characteristics of artificial stone. Sample AS 1 was made of a buff-coloured material with a homogeneous distribution of small aggregates. Sample AS 3 contained large red and black aggregates with a grey matrix, supporting the claim[11] that it was made of the patented mixture[12] of Portland cement with crushed red brick, charcoal and other additives. Sample AS 10 was composed of a white matrix containing many white aggregates. Sample AS 13 had a dark, bubbly matrix and few visible aggregates. The samples predating the 20th century tended to be more difficult to crush during sample preparation than the later samples, indicating their greater hardness.

Identification of Materials

The analytical results, listed in **Table II**, indicate that the majority of samples have a calcium-based matrix and quartz-based aggregates. Mineral names are provided for each compound identified by XRD, with the chemical composition included for the first instance a mineral is referenced. The cement chemist notation for clinker compounds is indicated in italics. The analyzed samples were grouped in different material categories using a decision tree, developed on the basis of the materials identified in the 16 samples and on probable components suggested by the literature survey; this is described further in the **Appendix**.

The proportion and the composition of the aggregates varied between samples, and further information was obtained from the X-ray maps. Important elements – other than carbon and oxygen – were assigned a colour and the results were combined to create the full map. Maps and EDS results from a selection of concrete samples are presented in **Figures 4** to **7**, and the samples are described in further detail in the following paragraphs. In order to show a variety of cement types with X-ray maps, sample AS 12 was included, even though it was sourced from a repair, as it was the sole example of a gypsum-based cement in the study.

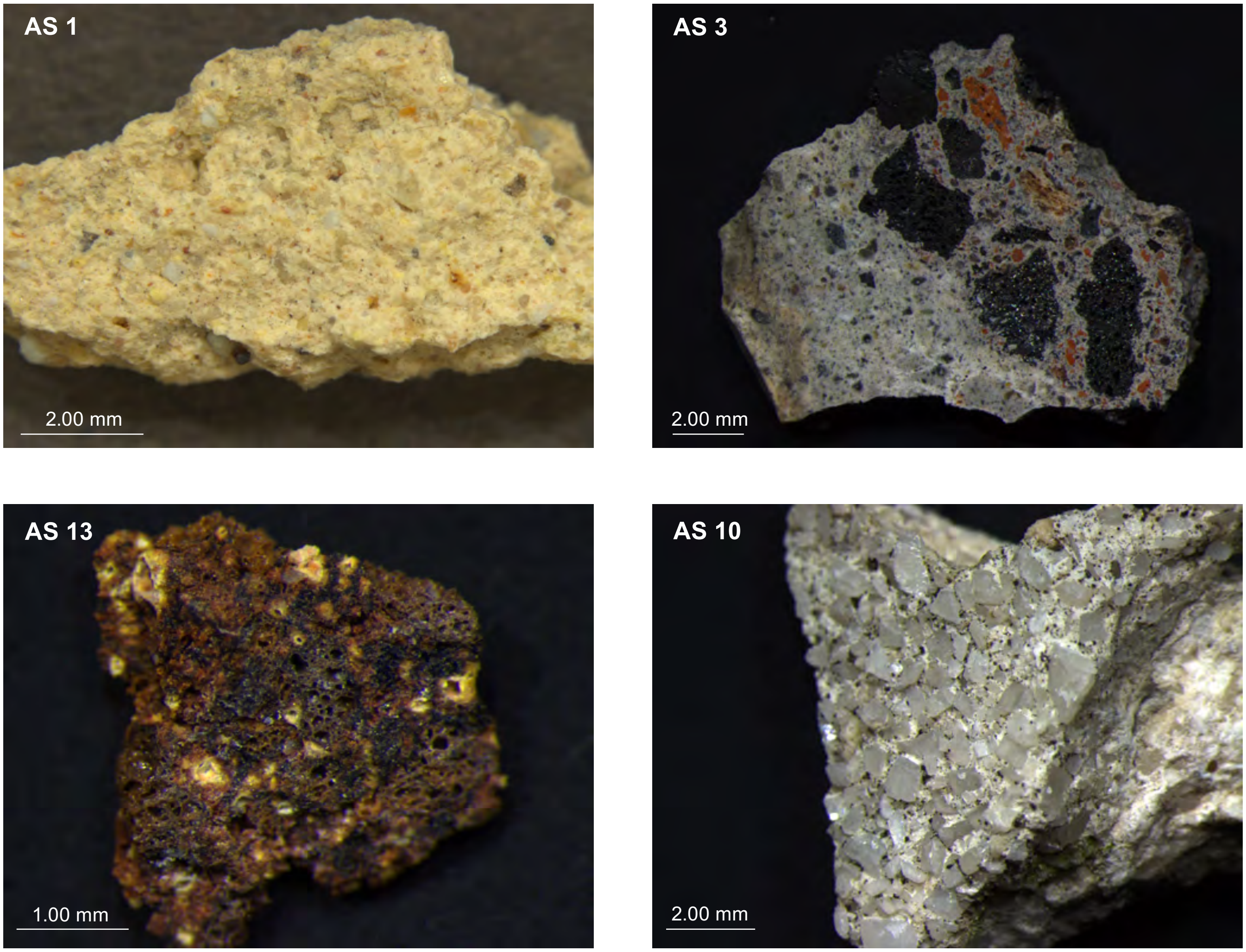

Figure 3. Photomicrographs of select samples, demonstrating the variation of colour and aggregate size in artificial stone.

Sample AS 6 (**Figure 4**) was determined most likely to be hydraulic cement, with large and small aggregates of varied composition. Some aggregates are primarily silicon-based (shown in cyan), corresponding to the identification of quartz by XRD, while others contain significant levels of aluminum (green) and potassium (red), corresponding to the identification of albite by XRD. The matrix contained major amounts of both calcium (yellow) and silicon (cyan). The matrix contained calcite, as identified by XRD, and the presence of C_2S clinker was determined by petrography (see **Figure 10**).

Sample AS 8 (**Figure 5**) was identified as a hydraulic cement and contained large and small aggregates of similar composition. The matrix contained major amounts of both calcium (yellow) and silicon (cyan). Calcite, vaterite and grossular were identified as major components in the matrix by XRD; grossular is a clinker product with a C_3A cement chemist notation. The aggregates were silicon-based (cyan) and were identified by XRD as quartz.

Sample AS 9 (**Figure 6**) was determined to be a lime- and dolomite-based, non-hydraulic cement. Magnesium (magenta) was dispersed through certain aggregates and the matrix. The matrix contained major amounts of calcium (yellow) and silicon (not pictured), as well as magnesium; calcite, dolomite, aragonite and quartz were identified in the matrix by XRD. This sample contained aggregates that ranged in both size and composition. Several of these were magnesium-based (magenta), calcium-based (yellow) or barium-based (blue); however, only calcite and dolomite aggregates were identified by XRD. Since the barium and sulfur (white) areas corresponded to each other, it was reasonable to conclude the material also contained a baryte aggregate.

Sample AS 12 (**Figure 7**) was identified as a gypsum-based, non-hydraulic cement repair. It contained a small quantity of fine aggregates composed of magnesium (magenta) and silicon (cyan), with a few aggregates containing calcium (yellow). Only quartz aggregates were identified by XRD. The matrix, containing major amounts of both sulfur (not pictured) and calcium (yellow), was identified by XRD as gypsum. The matrix also contained minor amounts of titanium (white) dispersed throughout and this was identified by XRD as rutile titanium white.

Table II. Combined Analytical Results

No.	SEM/EDS*	Identified Components**	Material Category
AS 1	Matrix: **Si, Al, O,** C, K, Na, Ca, Ti Aggregate type 1: **Si, Ca, O,** C, Al, Mg, K (Cl) Aggregate type 2: **Si, O,** Al, C	Matrix: mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), aragonite ($CaCO_3$) Aggregate: wollastonite ($CaSiO_3$)	Ceramic
AS 2[§]	Matrix: **Al, O, Ca, Si,** Fe, C, Mg, S, Cl (K) Aggregate: **Si, O,** Al (Ca, C, Cl, Fe)	Matrix: calcite ($CaCO_3$), vaterite ($CaCO_3$), aragonite, quartz, hatrurite (Ca_3SiO_5, C_3S), larnite (Ca_2SiO_4, C_2S), nordstrandite ($Al(OH)_3$), periclase (MgO) Aggregate: aluminum silicates	Hydraulic Cement
AS 3	Matrix: **Ca, Si, O,** Al, S, P, C (Mg, Cl, Fe) Aggregate type 1: **Ca, Si, O,** Al, Mg, Fe Aggregate type 2: **Ca, Si, O, Al,** Fe	Matrix: calcite, vaterite, aragonite, larnite (C_2S) Aggregate: periclase, hematite (Fe_2O_3), quartz, charcoal	Hydraulic Cement
AS 4[§]	Matrix: **Ca, Si, O,** C, Al, Mg, S, Cl (Fe, Na) Aggregate: **Si, Al, O,** Ca, Na, C	Matrix: calcite, vaterite, larnite (C_2S), gypsum, ferrite/brownmillerite ($Ca_2(Al,Fe)_2O_5$, C_4AF), berlinite ($AlPO_4$), quartz Aggregate: quartz	Hydraulic Cement
AS 5	Matrix: **Ca, Si, O,** Al, Mg, C, S, Cl Aggregate type 1: **Ca, Mg, O,** C, Si Aggregate type 2: **Ca, O,** C, Mg (Si) Aggregate type 3: **Mg, O, Si,** Ca, C	Matrix: calcite, larnite (C_2S) Aggregate: dolomite, calcite, quartz	Hydraulic Cement
AS 6	Matrix: **Ca, Si, O,** Al, C Aggregate type 1: **Si, O, Al,** Na, Ca, K, C (Fe, Ti) Aggregate type 2: **Si, O** (C, Ca)	Matrix: calcite, clinker[‡] (C_2S) Aggregate: quartz, albite ($NaAlSi_3O_8$), ulvospinel (Fe_2TiO_4)	Probable Hydraulic Cement
AS 7	Matrix: **Ca, Si, O,** Al, Mg, Fe, C (Na, S, Cl, K, Ti) Aggregate type 1: **Si, O, Al,** Ca, Na (C, K) Aggregate type 2: **Si, O,** Ca (C)	Matrix: calcite, larnite (C_2S) Aggregate: quartz, microcline ($KAlSi_3O_8$)	Hydraulic Cement
AS 8[§]	Matrix: **Si, O, Ca,** Al, Mg, C, Cl Aggregate: **Si, O** (C, Ca)	Matrix: calcite, vaterite, quartz, grossular ($3\,CaO\cdot Al_2O_3$, C_3A) Aggregate: quartz	Hydraulic Cement
AS 9[§]	Matrix: **Ca, C, O, Si, Mg,** Cl, Ca Aggregate type 1: **Ca, Mg, O, C,** Si, Cl Aggregate type 2: **Ca,** C, O, Mg, Si (Cl) Aggregate type 3: **S, Ba, O, C,** Ca, Cl	Matrix: calcite, dolomite $(CaMgCO_3)_2$, aragonite, quartz, enstatite ($MgSiO_3$) Aggregate: calcite, dolomite	Non-hydraulic cement (Lime containing dolomite)
AS 10[§]	Matrix: **Ca, Si, C, O,** Al, Mg, Cl, K, (Na, S, Fe) Aggregate: **Ca, Mg, O**, C, Si	Matrix: calcite, dolomite, clinker[‡] (C_2S) Aggregate: calcite, quartz	Probable Hydraulic Cement
AS 11	Matrix: **Ca, Si, O, C,** Al, Mg, S, K (Fe) Aggregate type 1: **Si, O, Al,** K, C, Ca (Na) Aggregate type 2: **Si, O,** C (Al, Ca) Aggregate type 3: **Si, O,** Al, Mg, Ca, Fe, C (Na, Ti)	Matrix: vaterite, aragonite, calcio-olivine (Ca_2SiO_4, C_2S) Aggregate: possible calcium and aluminum silicates	Hydraulic Cement
AS 12	Matrix : **S, Ca, O, C,** Ti, Si, (Mg, Al) Aggregate: **Si, O, Mg Ca,** C, S	Matrix: gypsum ($CaSO_4\cdot 2H_2O$), rutile titanium white (TiO_2) Aggregate: quartz	Gypsum-based Cement
AS 13[§]	Matrix: **Si, O, Al,** C, Ca, K, Mg, Fe (Na, Ti) Aggregate: **Si, C, Mg, O,** Ca, Al, Fe	Matrix: labradorite ($(Ca, Na)(Al, Si)_4O_8$), hercynite ($FeAl_2O_4$), goethite, calcite, quartz, berlinite, hedenbergite ($FeCaSi_2O_6$), perovskite ($CaTiO_3$), diopside ($MgCaSi_2O_6$) Aggregate: quartz, possible calcium, aluminum, and magnesium silicates	Non-hydraulic Cement or Other
AS 14	Matrix: **Ca, Si, O, C,** Al, S, Mg, Fe Aggregate: **Ca,** O, C, Si (Mg, Fe)	Matrix: calcite, vaterite, calcio-olivine (C_2S) Aggregate: quartz, calcite	Hydraulic Cement
AS 15	Matrix: **Ca,** O, C (Si, S, Al) Aggregate: **Ca, O,** C, S, (Si, Al)	Matrix: calcite Aggregate: quartz, microcline	Non-hydraulic Cement (Lime-based)
AS 16[§]	Matrix: **Ca, O, Si**, Mg, Al, C, (K, Na, P, S, Ti, Fe) Aggregate: **Ca, Mg, O**, (Si, Al, C)	Matrix: calcite, dolomite, aragonite, titanite ($CaTiSiO_5$), trace gibbsite ($Al(OH)_3$) Aggregate: quartz, dolomite	Non-hydraulic Cement (Lime containing dolomite)

* Elements are listed qualitatively in **major**, minor, and (trace) quantities.

** The chemical formula is listed after the first recorded instance of the compound in the table. Cement chemist notation is listed between parentheses in italics for clinker compounds.

[§] These samples yielded inconclusive micro-XRD results (where the cement was not identified) and were additionally analysed by X-ray diffractometry.

[‡] In these instances, the clinker was determined solely by the identification of one or more C_2S clusters present in the thin-section petrography. The presence of major amounts of silicon identified by SEM/EDS supported this possibility.

Certain pivotal compounds required identification by XRD. These included ceramic polymorph compounds (cristobalite and/or mullite) as well as clinker. These compounds are somewhat challenging for several reasons: they are usually present in trace quantities; they are polymorphs which lead to severe peak overlap; they have preferred orientation problems; they have variable peak positions due to element substitution and solid solution effects; and they can be poorly crystalline.[36-39] Samples that contained major amounts of silicon in the matrix by EDS, but did not yield any calcium silicates in the micro-XRD pattern, were prepared and sent to CanmetENERGY for X-ray diffractometry (samples AS 2, 4, 8, 9, 10, 13 and 16). A diffractogram of sample AS 4 in **Figure 8** illustrates minor quantities of clinker. Here, peaks

Figures 4-7. SEM/EDS X-ray maps of select samples demonstrating variations in matrix and aggregate composition. *Upper*: composite images obtained with a backscattered electron detector, overlaid with coloured shading corresponding to various elements. *Lower*: X-ray maps of individual elements of interest.

X-ray map colours: calcium (Ca) - yellow; aluminum (Al) - green; potassium (K) - red; silicon (Si) - cyan; magnesium (Mg) - magenta; titanium (Ti) - white; barium (Ba) - blue; sulfur (S) - white.

EDS element lists are provided below for the matrix and most common aggregates; for each figure, elements are listed as **major**, minor or (trace).

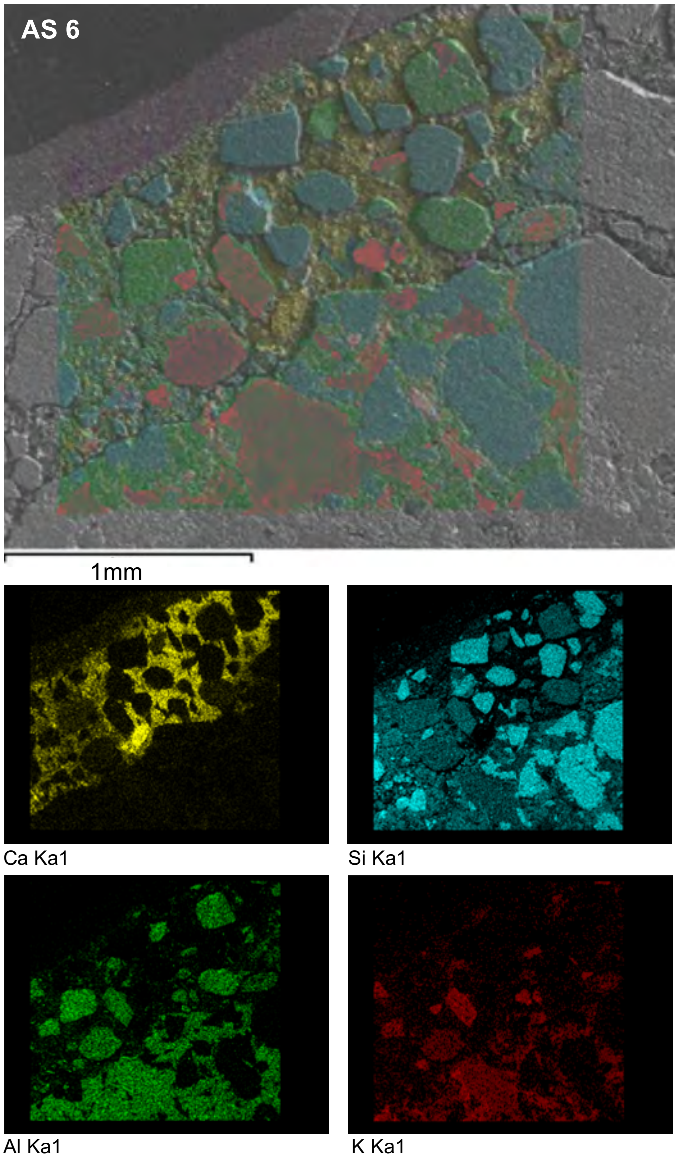

Figure 4. Elements determined by SEM/EDS in sample AS 6, collected from the Calvaire of Christ sculpture (*circa* 1900) from Montreal's Roberval Cemetery.

Matrix: **Ca, Si, O,** Al, C

Aggregate type 1: **Si, O, Al,** Na, Ca, K, C (Fe, Ti); Aggregate type 2: **Si, O** (C, Ca)

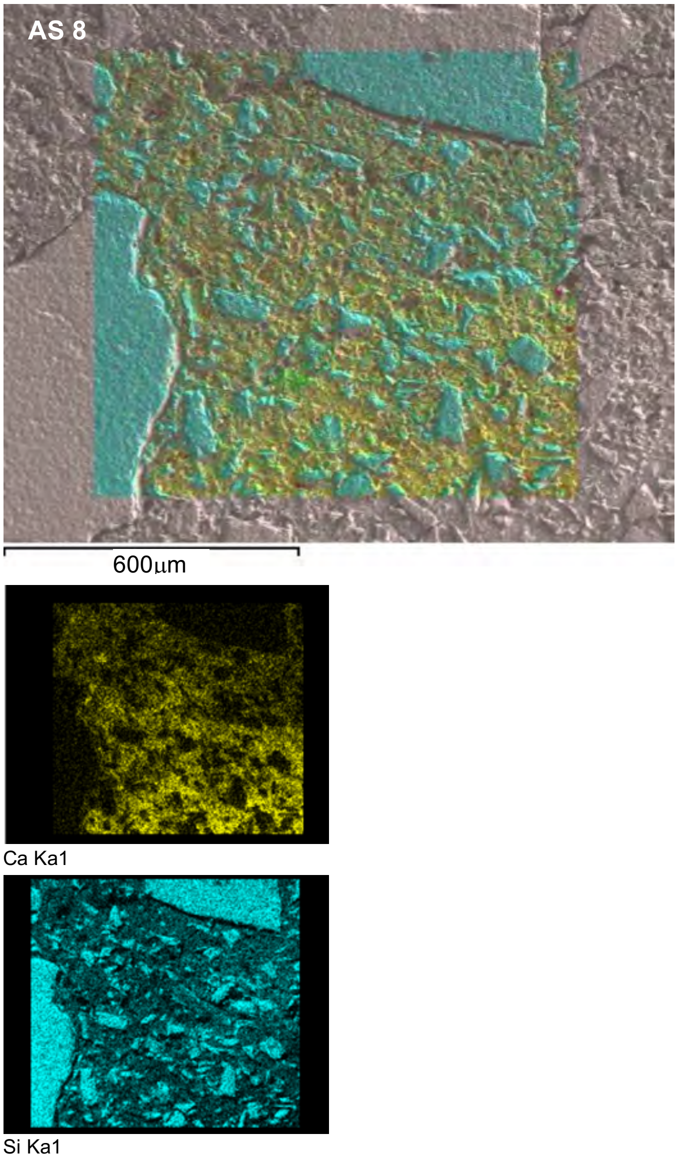

Figure 5. Elements determined by SEM/EDS in Sample AS 8, collected from the Saint Joseph sculpture (*circa* 1900) in Victoriaville.

Matrix: **Si, O, Ca,** Al, Mg, C, Cl

Aggregates: **Si, O** (C, Ca)

assigned to the Ca_2SiO_4 (C_2S) type clinker with the mineral name larnite are apparent in the 30 to 45°, 2θ region. In a few instances (AS 6 and AS 10), both XRD techniques were unsuccessful in the identification of clinker components, even though major amounts of silicon were detected in these matrices; however, clinker was identified through thin-section petrography, which allows for visual identification of features that can be mineral (e.g., calcite), man-made (e.g., clinker) or plant-based (e.g., charcoal). As sample size was limited in this study, only small petrographic thin sections were studied for clinker features, and this did not always yield an accurate representation of the cement.

Eight samples contained clinker compounds identified by XRD and thus were labelled as hydraulic cements − samples AS 2, 3, 4, 5, 7, 8, 11 and 14. Clinker is a mixture of components primarily having formulas of $n\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (including minerals such as larnite, calcio-olivine and grossular). Examples of typical $n\text{CaO}\cdot\text{SiO}_2$ (C_2S) clinker petrography features are presented in **Figure 9**. Gypsum was identified in the matrix of sample AS 4 by XRD. Two additional samples, AS 6 and AS 10, both contained calcite, identified by XRD, and major amounts of silicon, identified by SEM/EDS, and at least one $n\text{CaO}\cdot\text{SiO}_2$ (C_2S) type clinker feature was found on petrographic examination (**Figure 10**). These were classified as probable hydraulic cements as clinker was not detected by XRD.

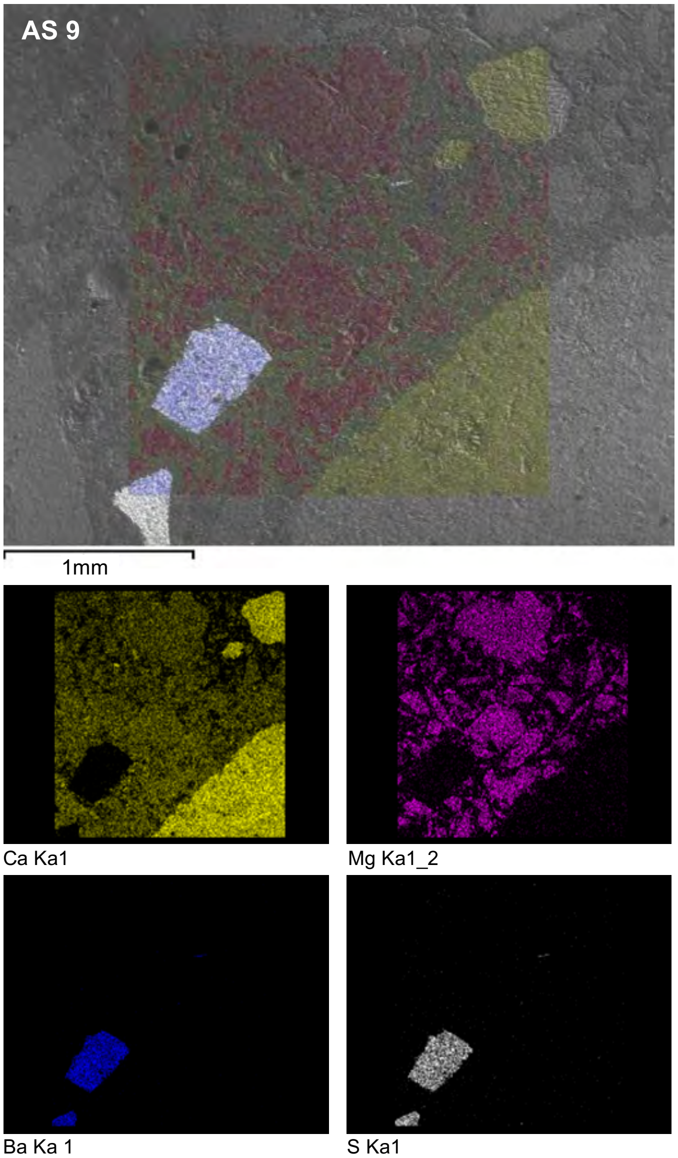

Figure 6. Elements determined by SEM/EDS in Sample AS 9, collected from the Saint Joseph sculpture (*circa* 1950) in St. George-de-Beauce.
Matrix: **Ca, C, O, Si, Mg,** Cl, Ca
Aggregate type 1: **Ca, Mg, O, C,** Si, Cl; Aggregate type 2: **Ca,** C, O, Mg, Si (Cl); Aggregate type 3: **S, Ba, O, C,** Ca, Cl

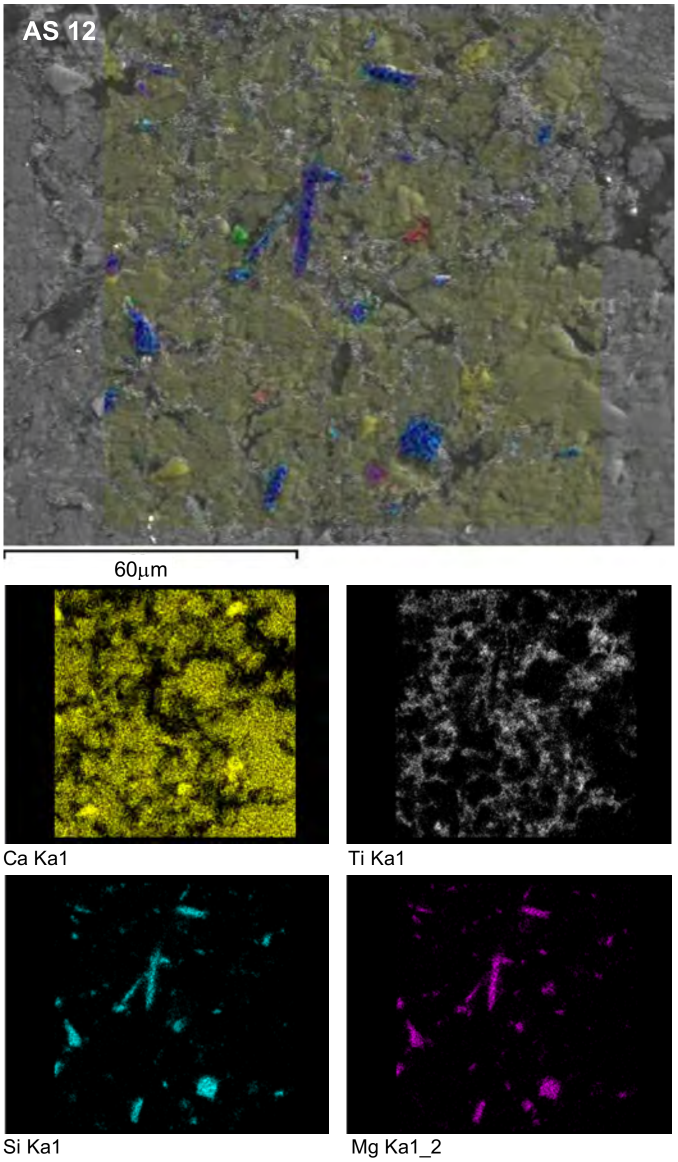

Figure 7. Elements determined by SEM/EDS in sample AS 12, collected from the Notre-Dame du Saint-Rosaire sculpture (*circa* 1900) in Rimouski.
Matrix: **S, Ca, O, C,** Ti, Si, (Mg, Al)
Aggregate: **Si, O, Mg Ca,** C, S

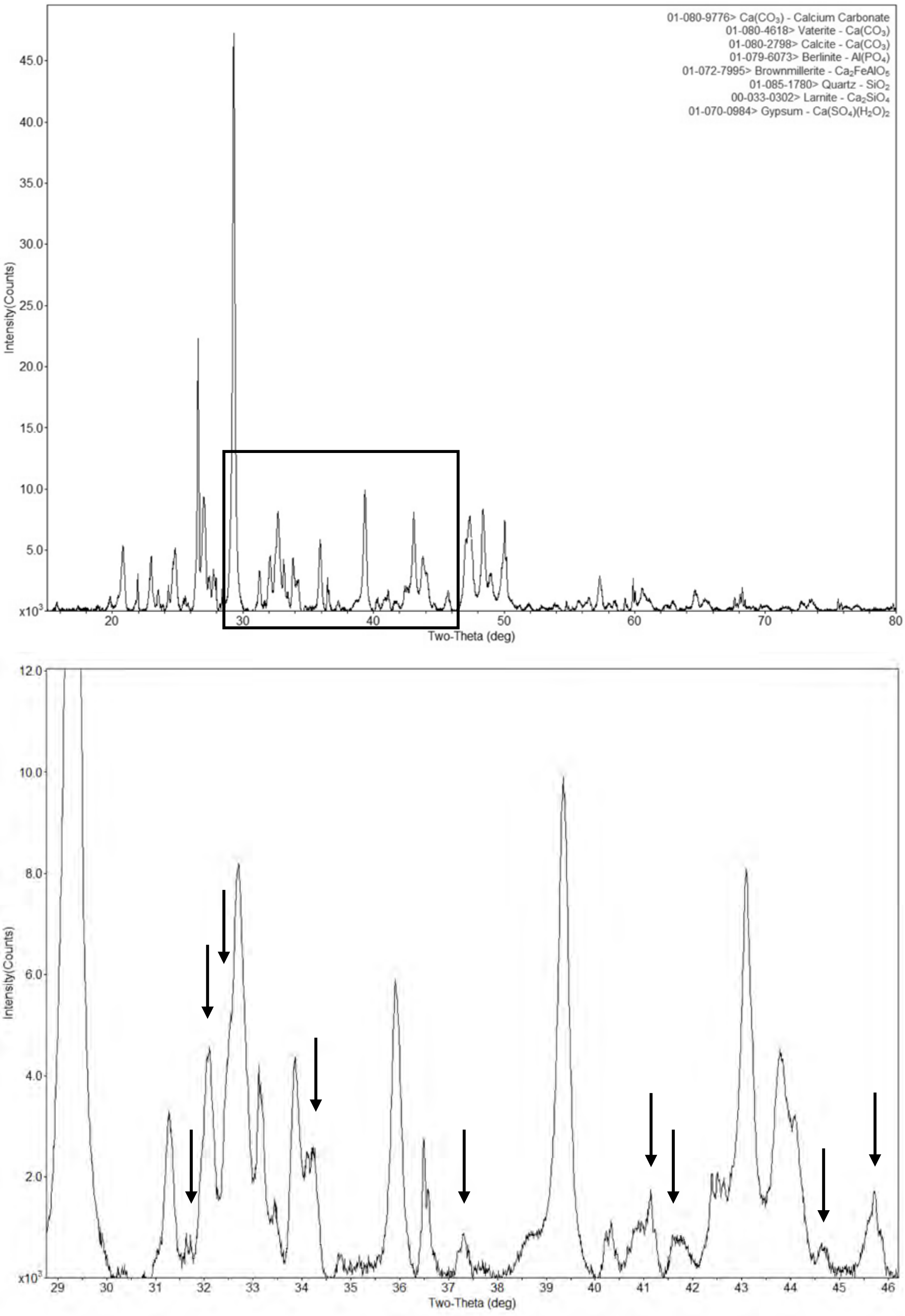

Figure 8. XRD pattern of the matrix of sample AS 4 (upper), with an enlargement between 30 and 45°, 2θ (lower) to highlight minor Ca_2SiO_4 clinker peaks (indicated with arrows) characteristic of hydraulic cement. The XRD pattern of AS 4 contained the most intense clinker peaks of all samples studied.

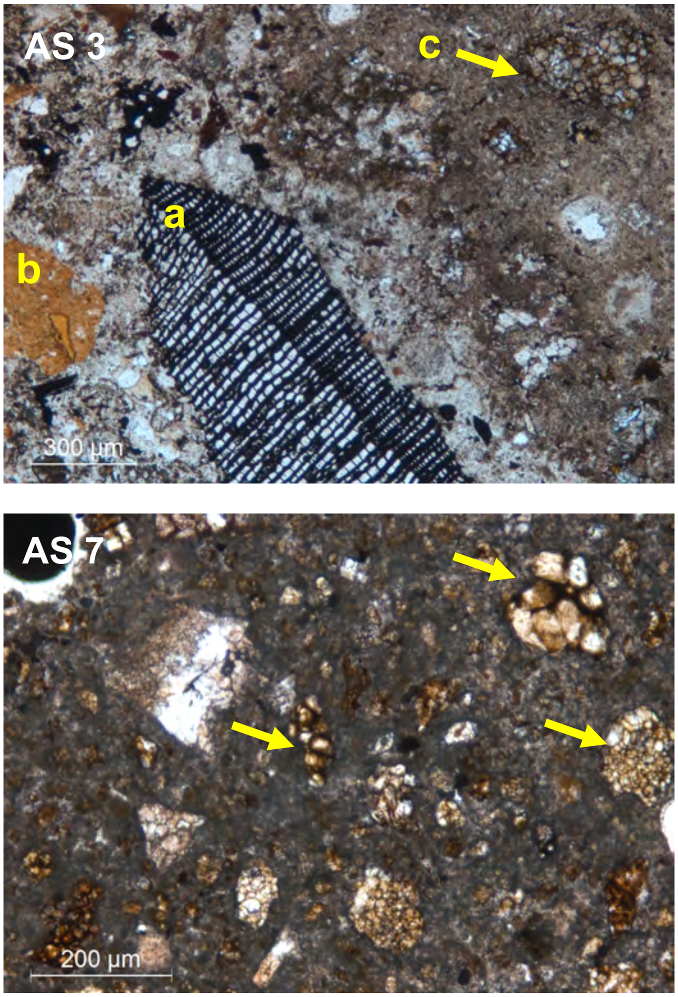

Figure 9. Photomicrographs of petrographic thin sections. *Upper*: AS 3, with features a) charcoal, b) brick and c) C_2S clinker. *Lower*: AS 7, with many C_2S clinker features visible. In transmitted light.

Eight of the samples did not contain clinker and varied in composition. Sample AS 1 was confirmed as Coade stone, a ceramic, due to the identification of the ceramic component mullite, the presence of aggregates, and the archival evidence that accompanied the sample. The identification of Coade stone can present a challenge since the presence of fired ceramic material (mullite and/or cristobalite) is also observed in concretes that include ceramic waste aggregates. Consequently, the matrix in suspected Coade stone needs to be separated particularly well from the aggregates for examination.

Three samples, AS 9, 15 and 16, were identified as non-hydraulic lime-based or dolomite-based cements. An example of such material is seen in **Figure 11**, which featured large and rough calcite aggregates throughout the sample. Sample AS 12 was identified as a gypsum-based cement. Sample AS 13, sourced from inside the base of a monument, contained major quantities of silicon, oxygen and aluminum in the matrix, and also contained iron-rich mineral compounds. Since clinker was not identified in this sample, it was labelled as “other.” It is probable that sample AS 13 was a cement of a non-standard composition containing waste material.

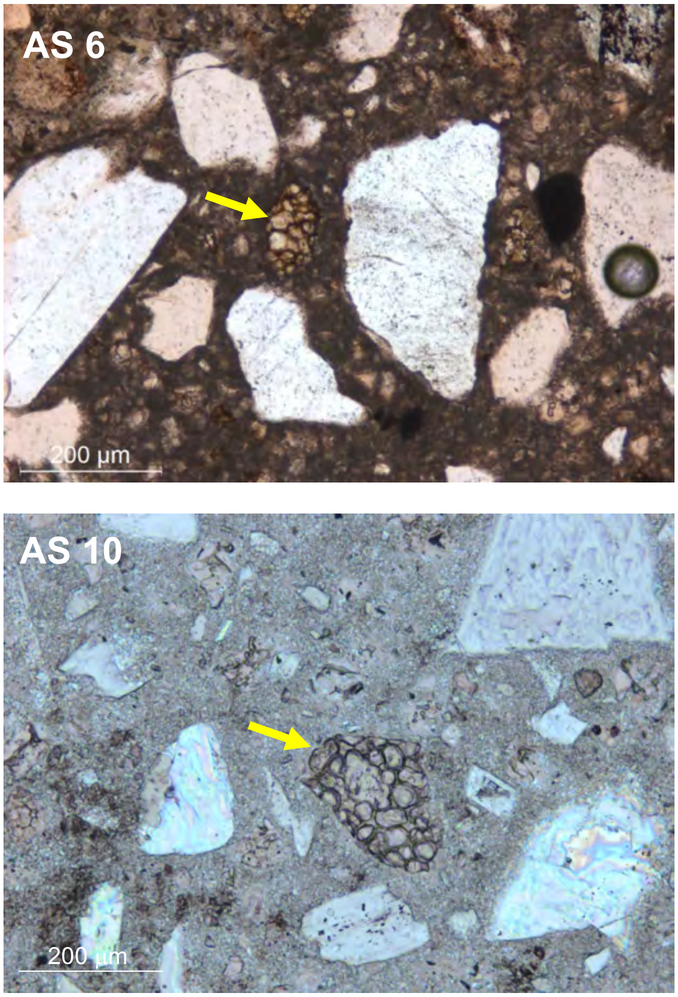

Figure 10. Photomicrographs of petrographic thin sections. *Upper*: AS 6, with C_2S clinker visible in the centre. *Lower*: AS 10, with C_2S clinker visible in the centre. In transmitted light.

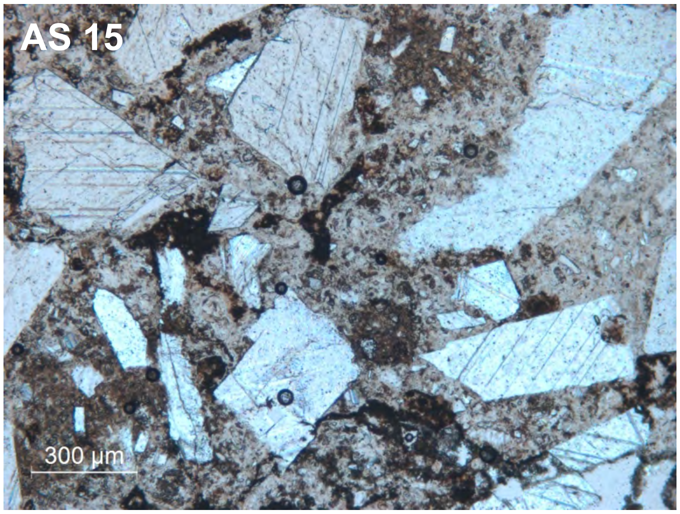

Figure 11. Photomicrograph of a petrographic thin section from sample AS 15, showing large calcite crystals. In transmitted light.

Nelson's Column and Notre-Dame du Saint-Rosaire

The surface portion of the Admiral Nelson statue from Nelson's Column (AS 1) was identified as Coade stone, and the sample from the sculpture interior next to the armatures (AS 2) was identified as hydraulic cement. The sample from a tablet at the base of the column (AS 3), which was suspected to be a restoration, given that it had documentation linking it to a patented Portland cement recipe[11,12] and that it had a different hue than the statue, was indeed identified as a hydraulic cement upon analysis. The patented recipe used for the restoration – three parts Portland cement, two parts crushed red bricks, two parts coal and four parts water – was confirmed in sample AS 3 with the identification of charcoal, brick aggregates (containing Fe_2O_3) and clinker (C_2S) (**Figure 9**).

Other interesting results include those of the statue Notre-Dame du Saint-Rosaire from Rimouski (AS 11, 12 and 13). Three different areas of this statue were analyzed, including: the body of the statue, identified as hydraulic cement (AS 11); the crown, believed to have significant repairs, identified as gypsum-based cement (AS 12); and the dark base, where the cement type could not be precisely identified and was categorized as "other" (AS 13). The crown of the statue, now confirmed as a gypsum-based repair, and one of its hands were very white in appearance, in contrast to the body which appeared to be typical grey hydraulic cement. In addition, rutile titanium white (first produced industrially in the late 1930s[40]) was identified in the matrix of sample AS 12 (**Figure 7**), indicative of a pigmented repair postdating the creation of the monument.

CONCLUSIONS

Sixteen artificial stone samples from monuments in Quebec were analyzed with a variety of complementary techniques. The methodology used in this case study to identify the artificial stone materials in a qualitative way proved to be suitable for a conservation application. A comprehensive analysis is recommended for identification of artificial stone, involving a complement of techniques, including optical microscopy, SEM/EDS, XRD and petrography on smaller thin sections (which may prove to be non-representative due to the size limitations imposed on sampling heritage objects).

In this limited study, half of the samples from these monuments were hydraulic cement-based. Of the ten samples from seven monuments dating from 1900 or earlier, the majority were grey-brown and comprised a hydraulic cement, quite possibly Portland cement. The material in a sample from the surface of Nelson's Column (*circa* 1809) was identified as ceramic Coade stone.

The six samples dating from later in the 20th century tended to be white in colour and were either composed of hydraulic cement or lime-based non-hydraulic cement. One repair was identified as a gypsum-based non-hydraulic cement material.

With the results from this study, we can begin to make ties between certain monuments and the materials used in various Quebec workshops. We hope that this information will prove to be useful in the continuation of preservation efforts in the province's heritage areas.

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APPENDIX

Decision Tree

A decision tree (**Figure 12**) to aid in the classification of the more common artificial stone types was developed on the basis of the materials identified in the analysis of the 16 samples and on formulations documented in the literature.

A literature review revealed that the main difference between ceramic- and cement-based stones was that ceramic-based stones such as Coade stone contain the minerals mullite and/or cristobalite in the matrix – two products formed in high-temperature conditions such as those of kiln-firing.[25] These minerals may also be present as aggregates in concrete, so diligent preparation of matrix samples is essential.

Next, the elemental composition of the matrices was considered. It was determined that a matrix can be calcium-based, or a mixture of calcium and magnesium when dolomitic or high magnesium limestone is used as raw material, or entirely magnesium-based. While magnesium-based stones can usually be classified as a non-hydraulic cement, such as Sorel stone,[24] a calcium-containing material may be gypsum-based cement, or another non-hydraulic or hydraulic cement; further classification requires the identification of individual compounds such as calcium sulfates, lime cycle intermediates, or clinker components.[18]

The identification of aggregates in the mixture at this next step enables us to classify the material as a concrete.

Hydraulic cement requires a mixture of water and a cement binder, generally with admixed aggregates, to harden into artificial stone. The presence of clinker (various calcium silicates and/or aluminates, including compounds with the same crystal structure as the minerals larnite or calcio-olivine) identified by XRD and/or petrography indicates that the matrix is a type of hydraulic cement, either natural, Portland, or another regional mixture.[17] The absence of clinker indicates that the material, containing both calcium and aggregates, could be a non-hydraulic cement, possibly lime-based, or another non-standard variety of cement.

By following the decision tree, a sample of artificial stone can be sorted into one of six categories:

1. "Pure" ceramic
2. Ceramic with aggregates
3. Magnesium-based cement
4. Gypsum-based cement
5. Hydraulic cement
6. Non-hydraulic cement or other

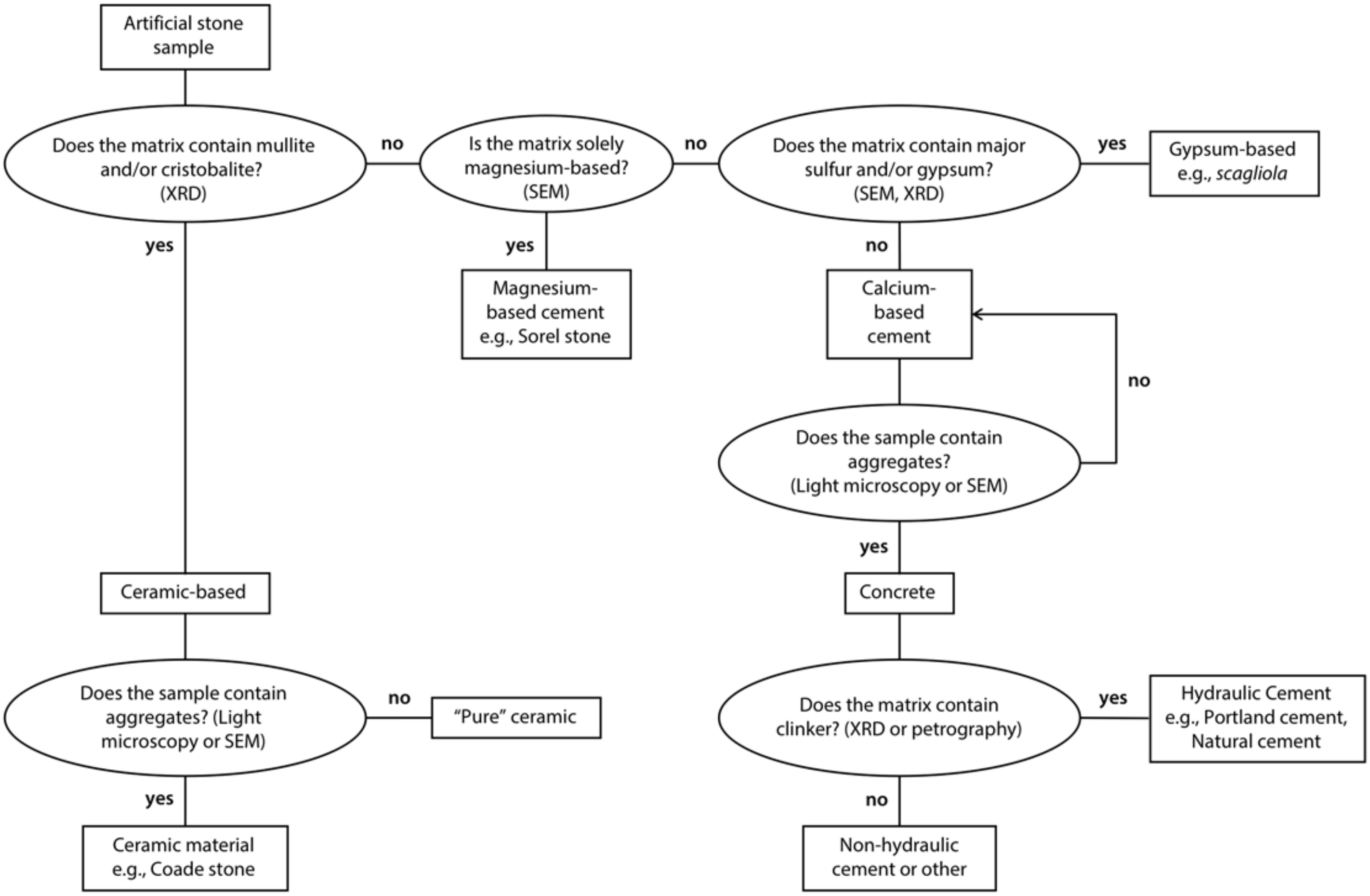

Figure 12. Artificial Stone Decision Tree

This tree can also be applied to other heritage building materials such as mortars and building facade material, but the user should be aware that some masons and contractors have used unusual formulations (such as mixtures of Portland cement and lime) which are difficult both to identify and to classify. Generally, the identification of a lime-cycle intermediate (quicklime, slaked lime) in combination with a calcium silicate and/or aluminate clinker is necessary to confirm that the cement is composed of a hydraulic lime.

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