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DEGRADATION OF CONCRETE-BASED STRUCTURES BY ATMOSPHERIC AND ENVIRONMENTAL FACTORS: A FAST AND VERSATILE ON-SITE MONITORING APPROACH

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ABSTRACT. We present a preliminary study on a fast and vesatile approach, based on the use of a portable Raman spectrometer, for the on-site monitoring of the degradation of concrete-based structures by atmospheric and environmental factors. The main results of our investigation evidence that most of the amorphous and crystal materials involved in Carbonation and Sulphate Sttack (the main deterioration processes of cement-based materials) can be detected and distinguished with the use of the Raman spectroscopy. The main wave numbers and changes in the relevant chemical phases (CO_3^{2-}, SiO_4^{2-}, SO_4^{2-} etc.) which generally occur under these durability attacks were discussed and summarized. The proposed approach may open new perspectives in the field of structural health monitoring and suggests a powerful instrument to investigate the relevant processes connected with the degradation processes (and the underlying chemical reactions) caused by atmospheric and environmental factors.

1. Introduction

Concrete-based structures (and infratructures) are the predominant type of constructions worldwide. Their performance during the time is therefore crucial to ensure the essential economic activities and services that they intend to support (Neville 1995). Although the rate of deterioration of constructions strongly depends on the construction processes and the employed material components, the deterioration process is also intimately connected with the atmospheric, environmental and climatic factors encountered during the construction service lifecycle (Yoon, Copuroglu, and Ki-Bong 2007). More specifically, carbon concentration, increase in temperature (due to the global warming) and the change of humidity are among the main factors that negatively influence the duration, serviceability and safety of concrete-based structures (Qu *et al.* 2021; Bastidas-Arteaga *et al.* 2022; Castorina *et al.* 2022). As it is well-known, the concentration of atmospheric CO_2 is strongly increasing at the global scale, due to the uncontrolled increase of anthropic activities. This increase

of CO_2 (together with other climate altering gases) cause also a correlated increase in air temperature (about 1°C compared to the preindustrial era) at the global scale. Finally, a third important environment factor is given by the atmospheric humidity, which evolutions is affected by local conditions (such as the orography, sea distance and urban environment) (Yoon, Copuroglu, and Ki-Bong 2007; Bastidas-Arteaga *et al.* 2022). In Table 1, we report the main changes of atmospheric, environment and climate factors that influence the durability of concrete (infra-)structures

TABLE 1. Principal modifications of atmospheric, environmental, and climatic factors influencing the durability of concrete (infra-)structures.

Atmospheric, environmental and climatic factors	**Consequences**
It increase of carbon concentration	It accelerates the carbonation process and increases carbonation depth in concrete structures (structural damage). It increases carbonation-induced reinforcement corrosion initiation in reinforced concrete structures.
Temperature increase (Global warming)	An increase in temperature accelerates the carbonation process, sulphate attack, chloride penetration, and the corrosion rate of reinforced structures.
Change of humidity	A decrease in relative humidity (RH) may reduce carbonation and sulphate attack, while an increase in humidity favours carbonation, chloride, and sulphate attack.

As evidenced in Table 1, carbonation, chloride and sulphate attacks represent the main outcome produced by the atmospheric and environmental factors. However, the severity of the deterioration effects in the construtions vary significantly from place to place and over the time. For this reason a precise determination of the impact of the carbonation-induced corrosion and sulphate/cloride attack on the concrete structures require a large scale investigation on numberous (infra-)structures by means of accurate laboratory tests. A *large scale (regional) mapping* of the those phenomena represents a first step for the comphension of the the main atmospheric and environmental factors influencing the degradation of Concrete-based structures (as a function of time) at various spatial scales, *e.g.*, city, region, country, etc... (Rouainia *et al.* 2020; Castorina *et al.* 2022)

Within this context, the main goal of this work is to propose a smart and rapid approach, based on the use of a portable Raman spectrometer, for the on-site monitoring of the carbonatation and sulphate attach processes on reinforced concrete structures. The identification of a smart and relatively economic tool for a fast (on-site) monitoring of the extent the degradation in a relevant number of reinforced concrete structures allow a fast monitoring and a better evaluation on concrete endurance and the prediction of the service life of the (infra-)structures at various spatial scales (*e.g.*, city, region, country, etc.) (Geiker, Hendriks, and Elsener 2023).

2. In situ structure monitoring by means of portable Raman technology

The on-site measurements (and tests) of the chemical changes of concrete-based structures play an important role in the structure health monitoring as it provide crucial information about the cause (and evolution) of the degradation mechanisms of structures, thus furnishing valuable information for the diagnosis of the health condition and performance of concrete-based structures. For these reasons, there is an increasing interest in the design and development of smart sensor systems for the (on-site) monitoring the chemical environment of concrete, as well as to obtain non-destructive (and time dependent) information concerning the condition of concrete structure (Shevtsov *et al.* 2022). Some of the recent efforts are aimed at the identification of non-destructive monitoring methods and/or continuous monitoring systems based on electrochemical (Rodrigues *et al.* 2021), piezoelectric (Thakur 2022), fiber-optic (Fan and Bao 2021), control of chloride content (Robles, Yee, and Kee 2022) approaches. However, these approaches have not yet provided prototypes ready to be placed on the market.

Spectroscopic and scattering techniques have long provided a formidable tool for the analysis and characterization of materials in their complex aggregative states (Gierlinger and Schwanninger 2007; Gastaldi *et al.* 2010; M. T. Caccamo *et al.* 2020; Lombardo, Calandra, and Kiselev 2020; Simonpietro 2021), as well as a useful tool for investigating self-assembly processes in a wide range of space-time resolution of nanostructured systems in the field of materials science and engineering (Bonaccorsi *et al.* 2009, 2013a,b; Narayanan and Konovalov 2020; Wagatsuma 2021). These spectroscopic techniques are commonly employed not just for species identification but also for acquiring precise structural data, including bond lengths, bond angles, and flow analysis (Faraone *et al.* 1999; Magazù, Migliardo, and Benedetto 2011; Magazù *et al.* 2013; M. T. Caccamo *et al.* 2017; M. T. Caccamo and Magazù 2017b).

More specifically, Raman scattering provide a unique opportunity for developing a novel approach capable of monitoring the service-condition of concrete (Long 1977; Colomban and Slodczyk 2010; Martinez-Ramirez and Fernandez-Carrasco 2010). Raman spectroscopy is able to detect the rotational and vibrational modes (of the chemical bonds) of molecules inside a material system, by using specific laser wavelengths which are not absorbed by the material sample under investigation. More specifically, one of the most important characteristic of the Raman technique is its ability to perform in-situ (real-time) analysis (Martinez-Ramirez and Fernandez-Carrasco 2010; Ševčík and Mácová 2018; Yue *et al.* 2018). Moreover, Raman spectroscopy has attracted increasing interest for the investigation of various phases in concrete-based structures due to its unique capability to investigate various environmental attacks like carbonation (Martinez-Ramirez *et al.* 2003; Black *et al.* 2007; Ševčík and Mácová 2018; Yue *et al.* 2018; Tang, Ling, and Mo 2021) and sulfate attack (Sahu, Exline, and Nelson 2002; Irassar, Bonavetti, and González 2003; Yue *et al.* 2013).

In this study, the concrete deterioration of reinforced concrete samples subjected to multi-environmental factors are investigated by means of portable Raman spestroscopy set-up. More specifically, we provide an overview of the use of portable Raman spectroscopy in the characterization of carbonate, sulfate, and silicate phases to study carbonation, sulfate attacks on cement-based materials. Raman spectra were collected by using a Bruker BRAVO

equipment, in the 300-3200 cm^{-1} range. The instrument uses SSETM (Sequentially Shifted Excitation) a patented fluorescence mitigation method that permits to measure a much extensive range of materials with handheld Raman setup. Samples were excited by using two lasers centred at 785 and 853 nm working together, in order to mitigate the fluorescence phenomena and offering highest sensitivity across the entire spectral range.

2.1. Carbonation Degradation Process. Amongst various environmental and chemical deterioration mechanisms influencing the durability of concrete structures, carbonation is probably the most important action. This mechanism occurs from the chemical reactions between intruded CO_2 and calcium-bearing phases, and involves the reaction of carbon dioxide (CO_2) with alkaline ions from the pore solution. Most phases in hydrated cement paste can react with CO_2, to convert the calcium ions ($Ca_2{}^+$) from cement paste to calcium carbonate ($CaCO_3$). This process favourite the formation of calcium carbonate ($CaCO_3$) followed by the decrease of the alkalinity of concrete pore solution, thus causing the corrosion of the rebar in concrete (Masmoudi *et al.* 2017). Thus, detecting carbonation process, by determining the carbonation products formed against the depth into concrete structure, is of great importance to the diagnosis of the health condition of concrete-based structures and the prediction of their service life. Traditional methods used to evaluate carbonation process in cement-based materials, such as Phenolphthalein spray test, x-rays diffraction (XRD), thermogravimetric analysis (TGA), mercury intrusion porosimetry (MIP) often require a complex sample preparation, and the sample need to be taken (extracted) from the (infra-)structures (Balachandran, Muñoz, and Arnold 2017). These approaches are time-consuming and can severely damage the structural features of cementitious samples under investigation. Raman spectroscopy technique can be employed in-situ, without causing the damage the micro-structure of the reference material sample.

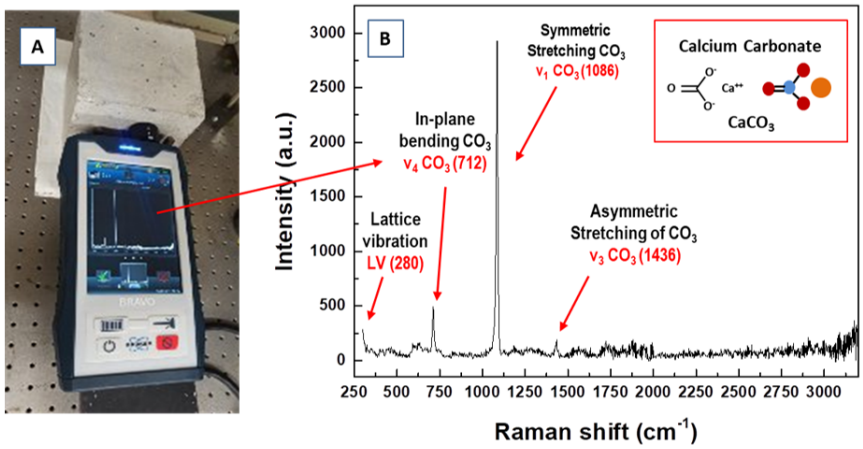

FIGURE 1. Portable Raman setup and Raman spectrum on a concrete cubic (150x150x150 mm) specimen showing typical characteristic peaks and associated $CaCO_3$ vibrational bands (modes), and the assignments corresponding to the Calcite phase (red).

In Figure 1, we report the main features of a test performed with the portable Raman setup (BRAVO-Bruker) on a cubic concrete specimen (150x150x150 mm). The recorded Raman spectrum evidence the precence of the typical characteristic peaks and associated vibrational bands (modes) of calcium carbonate ($CaCO_3$). This spectrum is dominated by a pronounced and intense peak (located in the range from 1076 to 1090 cm^{-1}), which is characteristic of the ν symmetric stretching band of the CO_3 groups, and by three minor bands which can be attributed to the Ca-O lattice vibration [LV] (< 350 cm^{-1}), the in-plane bending [ν_4] (700–750 cm^{-1}) and the asymmetric stretching vibration [ν_3] (ν_3=1436 cm^{-1}, for the Calcite)(Yue *et al.* 2018). The CO_3 phases precipitated within the concrete-based structures could exist in three different polymorphs, namely Calcite (a thermodynamically stable, well-crystallised phase) and Vaterite and Aragonite (less stable, poor-crystallised, phases) (Tang, Ling, and Mo 2021). The less thermodynamically stable Vaterite and Aragonite will undergo to a gradual transfomation in Calcite. The Raman spectroscopy technique is highly effective in distinguishing among those phases by the analysis of the spectral peaks position. In Figure 1, we reported the position of the characteristic peaks of the Calcite phase (namely ν_1=1086 cm^{-1}, LV=280cm^{-1}, ν_4=712 cm^{-1}, ν_3=1436 cm^{-1}) (Yue *et al.* 2018). Similarly, characteristic peaks assignments can be associated also to the phases of Vaterite (ν_1=1076/1090 cm^{-1}, LV=280 cm^{-1}, ν_4=712 cm^{-1}) and Aragonite (namely ν_1=1085 cm^{-1}, LV=206 cm^{-1}, ν_4=701/704 cm^{-1}) (Black *et al.* 2007; Tang, Ling, and Mo 2021). Generally, the content of CO_3 (degree of carbonation) decreases with increasing distance from the exposed surface of concrete, due to the reduced penetration of environment CO_2 into the interior part of concrete sample. This cause a decrease of the peak height with the increase of the carbonation depth of the most intense peak of the carbonates (*i.e.* the $\nu_1(CO_3)$ symmetric stretching band). This peak height can be used as an indicator to quantify the amount of carbonates formed in concrete samples, by comparing this parameter with a TG analysis used for a preliminary quantification of the calcium carbonate (used as calibration reference) (Yue *et al.* 2018). Finally, it is worth noticing that the Raman peak $\nu_1(CO_3)$ (at 1086 cm^{-1} for Calcite) is very close to that of the $\nu_1(SiO_4^{2-})$ of Q3 tetrahedra located at 1080 cm^{-1}, thus causing a sensitive overlap between these two different minerals.

2.2. Sulphate attack. Sulfate attack is a complex physical-chemical process that causes the alterations to concrete. Absorption of sulfates (and moisture) from the external environment favourites multiple complex chemical reactions between sulfate ion-bearing water and cement hydration products, and give rise to the formation of Gypsum ($CaSO_4{\cdot}2H_2O$), Ettringite ($6CaO{\cdot}Al_2O_3{\cdot}3SO_3{\cdot}32H_2O$), Thaumasite ($CaCO_3{\cdot}CaSO_4{\cdot}CaSiO_3{\cdot}15H_2O$), and an alteration of the structure of the calcium silicate hydrate (C-S-H) gel (Irassar, Bonavetti, and González 2003; Yue *et al.* 2013). Formation of those products is considered to be the primary process for the sulfate attack damage, and is manifested in the form of expansion, surface softening and spalling, and overall loss of cohesiveness and mechanical properties of the concrete. It is worth pointing that, while for the monitoring on site of the carbonation and chloride attack the development of some electrical-resistance and fiber optic chemical sensors are under investigation, currently there is no detection system for the on site monitoring of the deterioration actions of sulfate attack.

In Figure 2 A-C, we report the main structural features of a reinforced concrete retaining wall, which has undergone a significant degradation effect due to atmospheric and environmental factors (including CO_2, water and humidity infiltrations, temperature variations). In Figure 2D we report the corresponding Raman spectrum obtained by using the portable Raman setup Bravo-Bruker. Generally, the Raman spectrum of a degraded cement-base structure present a given degree of complexity which is connected with the complex overlap of multiple degradation events (and their relevant phases). However, as the chemical group SO_4^{2-} is found to be Raman active (possessing 4 vibration modes $\nu_1 - \nu_4$ (SO_4^{2-})), it is possible to use the Raman spectroscopy to distinguish between the relevant phases for an (in-situ) monitoring the sulfate attack. For this reason it is very important to compare the spectra obtained from (on site) Raman measurements with the experimental results obtained on (reference) pure samples of Gypsum, Ettringite and Thaumasite.

In this respect, a previous investigation [33] evidenced that pure Gypsum has four major Raman peaks, ranging from the symmetric stretching ν_1 [SO_4^{2-}] (at 1006 cm $^{-1}$), the symmetric bending ν_2 [SO_4^{2-}] (at 415 cm $^{-1}$ and 435 cm $^{-1}$), the asymmetric stretching ν_3 [SO_4^{2-}], (at 1135 cm $^{-1}$), and the asymmetric bending ν_4 [SO_4^{2-}] (at 620 cm $^{-1}$ and 670 cm $^{-1}$).

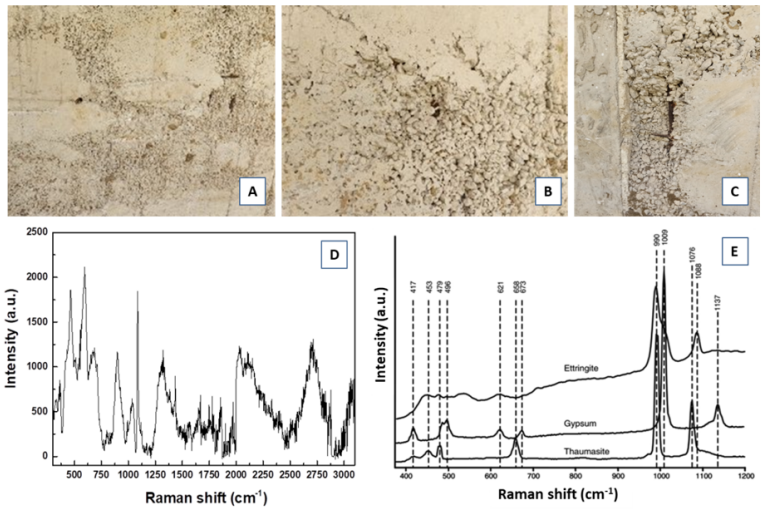

FIGURE 2. Example of the main structural features of a reinforced concrete retaining wall, exhibiting a significant degradation effect due to environmental factors (A-C), and corresponding Raman spectrum obtained by using the portable Raman spectrometer (D). Summary of the main characteristic bands of Raman spectra of Gypsum, Ettringite and Thaumasite (From Sahu, Exline, and Nelson 2002.

In Table 2 are reported the main Raman bands and assignments of pure gypsum and ettringite under bench-mounted Raman spectroscopy (Yue *et al.* 2013). Apart from the Gypsum and Ettringite, the sulfate attack from the Thaumasite phase has been recognized

TABLE 2. Raman bands and assignments of pure Gypsum and Ettringite under bench-mounted Raman spectroscopy (Yue *et al.* 2013).

Raman Shift (cm^{-1})		**Vibrational Bands**
Gypsum	**Ettiringite**	
1008	988	ν_1 symmetric stretching of (SO_4)
414, 493	448	ν_2 symmetric bending of (SO_4)
1136	1119	ν_3 asymmetric stretching of (SO_4)
618, 670	612	ν_4 asymmetric stretching of (SO_4)

to be particularly deleterious and more severe than the other forms, because its reaction products transform the surface of the concrete into a soft pulpy mass. Raman spectra of Thaumasite evidences three strong peaks at $\nu_1[SiO_6]$ (658 cm^{-1}), $\nu_1[SO_4^{2-}]$ (990 cm^{-1} and 1076 cm^{-1}), and four weak bands at symmetric bending of ν_2 (SO_4^{2-}) (at 417, 453, 479 cm^{-1}) and at 3300 cm^{-1} (Sahu, Exline, and Nelson 2002; Irassar, Bonavetti, and González 2003; Black *et al.* 2007; Yue *et al.* 2013). A summary of the main characteristic of Raman spectra of Gypsum, Ettringite and Thaumasite is reported in Figure 2E (Sahu, Exline, and Nelson 2002).

In Figure 3 we report the analysis (assignments) of main characteristic bands of Gypsum (green) and Ettiringite (red) of a reinforced concrete retaining wall, obtained (on site) by using the portable Raman system (Bravo-Bruker). It is worth noticing that despite the complexity of the recorded Raman spectrum (which is connected with the complexity of multiple overlapping degradation events) the Raman spectroscopy allow to clearly identify the relevant phases of the sulfate attack.

Raman spectroscopy can provide also important information concerning the water molecules changes within the cement (and concrete) matrix (Masmoudi *et al.* 2017). More specifically, the water inside cement-based materials can be divided into bound water (involved in the cement hydration reaction) and free water (that does not participate in hydration), and is identified by broad Raman peak between 3200 and 3600 cm^{-1}). Finally, since Raman technique is sensitive to less-crystalline structures, it has been experimented in the investigation of the time evolution gels products of ASR, a chemical reaction occurring between poorly crystalline (or amorphous) silica in aggregates and alkaline pore solution of concrete (Balachandran, Muñoz, and Arnold 2017; Shi *et al.* 2019).

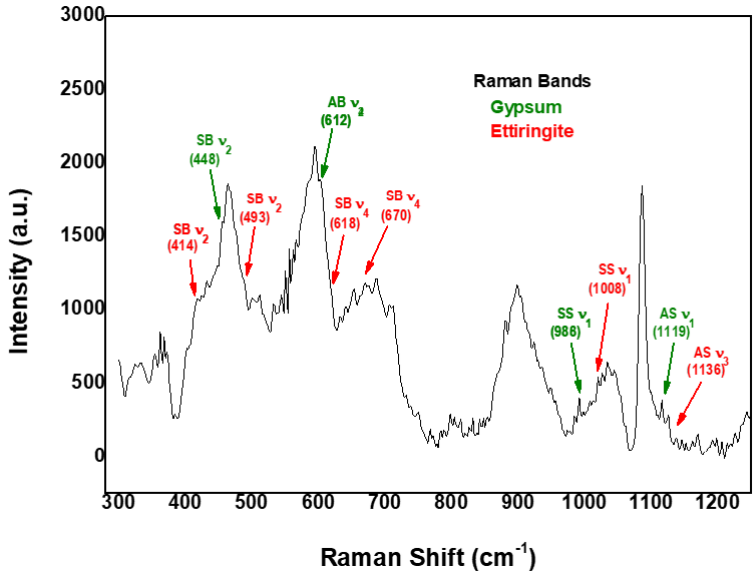

FIGURE 3. On site Raman spectrum (using the portable Raman spectrometer) of a reinforced concrete retaining wall, with the indication of the main characteristic bands of Gypsum (green) and Ettiringite (red).

2.3. Use of Complementary Techniques (Fourier Transform Infrared Spectroscopy - FTIR). Because of the complexity of the processes involved in the degradation of the concrete-based materials, very often it is necessary to employ complementary techniques for an exaustive characterization of the degree of deterioration of materials and to understand its effects on the properties and integrity of the structures. In this context, Fourier Transform Infrared (FTIR) spectroscopy represent a powerful technique that allow a versatile (non-destructive) complementary investigation, capable of evaluating (in a qualitative or semi-quantitative way) both amorphous and crystalline materials, and to evaluate hydration or carbonation products of cement-based materials (Valliant *et al.* 2016; Jose *et al.* 2020). In Figure 4, we report the FTIR spectra of the reinforced concrete retaining wall, with the indication of the detected main characteristic bands.

From the FTIR spectral profile it is possible to describe the following characteristics:

(A) the presence of a weak peak at 3640 cm^{-1} related to the OH stretching of portlandite (CH),
(B) a broad band at the 3000-3700 cm^{-1} range, attributed to the OH stretching of the water (within the cement matrix),
(C) a small peak at 1640 cm^{-1}, attributed to bending vibration of water in sulfates,
(D) the carbonate (CO_3^{2-}) peaks at 1410 cm^{-1} (asymmetric C-O stretching), 873 cm^{-1} (out-of-plane vibration), and 713 cm^{-1} (in-plane vibration), associated with calcite ($CaCO_3$ polymorph),

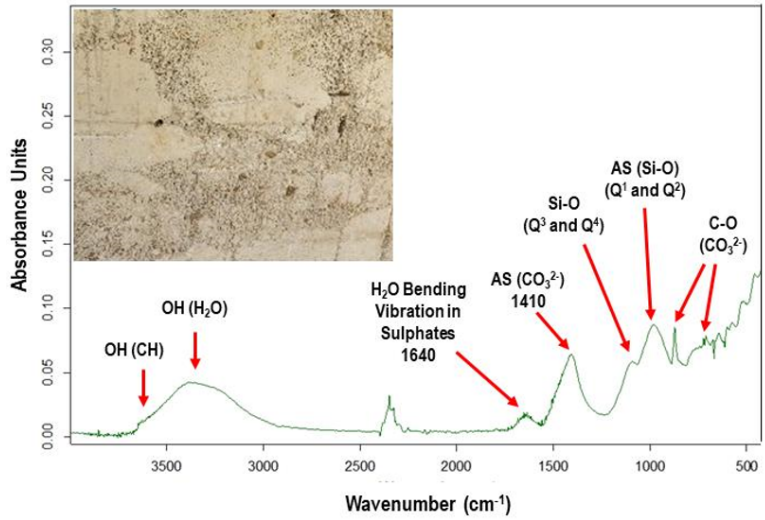

FIGURE 4. FTIR spectra of a degraded (reinforced concrete) retaining wall, with the indication of the main characteristic vibrational bands detected.

(E) a broad band (800-1100 cm^{-1}), centered at 960 cm^{-1}, assigned to the Si-O asymmetric stretching (ν_3) of Q1 and Q2 species of calcium silicate hydrate (C-S-H) (Zhan *et al.* 2018; Skocek, Zajac, and Ben Haha 2020; Higl *et al.* 2021),

(F) a band (1000-1250 cm^{-1}), weakly centered at 1140 cm^{-1} and 1050 cm^{-1}, that can be assigned to the Si-O asymmetric stretching (ν_3) of the decalcified C-S-H (Q3 at 1050 cm^{-1}) and polymerized silica (Q4 at 1140 cm^{-1}) phases (Hidalgo *et al.* 2008; Skocek, Zajac, and Ben Haha 2020; Saillio *et al.* 2021).

The analysis of the FTIR spectra confirms the main features of the Raman spectroscopy results and indicates the total consumption of CH by the weakening of the typical OH stretching band at 3640 cm^{-1}, with the formation of Calcite, evidenced by the visible carbonate (CO_3^{2-}) peaks at 1410 cm^{-1} (asymmetric C-O stretching), 873 cm^{-1} (out-of-plane vibration) and 713 cm^{-1} (in-plane vibration). Moreover, the contemporary presence of the Si-O asymmetric stretching (ν_3) centered at 960 cm^{-1}, (typical of non-carbonated cement) and the band centered at 1140 cm^{-1} and 1050 cm^{-1} (typical of carbonated samples) (Hidalgo *et al.* 2008), indicate the partial consumption of Q1 and Q2 species of calcium silicate hydrate (C-S-H) of non-carbonated cement by the carbonation process, resulting in a decalcification-polymerization process of C-S-H (Q1 and Q2) and leading to the production of decalcified C-S-H (Q3) and polymerized silica (Q4) phases (Saillio *et al.* 2021). In summary, the spectroscopic and scattering techniques represent powerful methods that investigate the structural ordering and phase transitions brought about by the relevant parameters of materials systems such as chemical reactivity and polydispersity, surface charge density, nanoparticle volume fraction, and can be considered as pivotal techniques to investigate in a wide range of material systems (Magazù *et al.* 1989; Lombardo 2009; Gordon *et al.* 2013; M. T. Caccamo and Magazù 2017a; C. Chen *et al.* 2017; Lombardo *et al.*

2019). Furthermore, those techniques allow to obtain important information concerning the collective modes and interactions in material systems, thus allowing the modeling of the main sinergistic interactions that regulate the (colloidal) stability and phase transition in complex supramolecular aggregates (Micali *et al.* 1998; S. Chen *et al.* 2002; Zemb and Lindner 2002; Lee 2008; Narayanan and Konovalov 2020; Anker *et al.* 2023).

3. Conclusions and Future Perspectives

As severity of constructions deterioration by atmospheric and environmental factors vary significantly from place to place and over the time (Jouzel *et al.* 1987; M. T. Caccamo and Magazù 2019; Castorina, M. T. Caccamo, and Magazù 2019; Lacasse, Gaur, and Moore 2020; Castorina *et al.* 2021; Magazù and M. Caccamo 2022; M. T. Caccamo and Magazù 2023), a precise determination of its impact on structures requires a large scale investigation (and mapping) on numberous (infra-)structures by means of a smart and rapid on-site monitoring approach. Our study shows a potential for the use of portable Raman spectroscopy system for the on-site monitoring of the degradation processes (namely carbonatation and sulphate attack) on reinforced concrete-based structures. With the use of Raman spectroscopy, we evidenced that most of the crystal and amorphous materials involved in the deterioration reactions of cement-based materials can be detected and distinguished by their specific molecular structure. The main wave numbers and changes in chemical phases (CO_3^{2-}, SiO_4^{2-}, SO_4^{2-} etc.) which generally occur under these durability attacks were discussed and summarized. The use of the portable Raman system represents then a smart method for a (on-site) fast monitoring of the degradation of reinforced concrete structures for a better evaluation of the service life of a numberous (infra-)structures. It also represents a powerful tool to study the relevant mechanisms and processes connected with the degradation processes caused by atmospheric and environmental factors.

Acknowledgments

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