

Evaluating the durability of carbon-nanotube-reinforced cementitious composites: a systematic literature review of contemporary knowledge

Avaliação da durabilidade de compósitos cimentícios reforçados com nanotubos de carbono: uma revisão sistemática da literatura do conhecimento contemporâneo

Evaluación de la durabilidad de los materiales compuestos cementosos reforzados con nanotubos de carbono: una revisión sistemática de la literatura de los conocimientos contemporáneos

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Abstract

The reinforcement of cementitious matrices with multi-walled carbon nanotubes (MWCNTs) can enable crack control at the nanoscale, thus contributing to the durability and strength of these composites. The primary challenges associated with these composites are the difficulty of dispersing MWCNTs and the low interfacial interaction between the fiber and the matrix. In this study, a systematic literature review was conducted to identify the most common proportions of MWCNTs and the relevant dispersion techniques, and to correlate these with durability parameters under environmental conditions that degrade cementitious matrices, such as in environments rich in CO₂, chlorides, acids, and sulfates. A search string was used to identify papers in international databases from 2020 to 2024, which resulted in 18 articles. This review showed that MWCNTs improve the mechanical properties and microstructure of the composites, in addition to reducing the chloride ion migration coefficients and CO₂ diffusion. These effects were attributed to mechanisms such as nucleation points (formation of cement hydration products), stress transfer bridges in microcracks, and matrix densification. Although MWCNTs have shown potential for use in enhancing the durability of cementitious composites, the current diversity of methodologies and exposure conditions means that further studies are required to achieve greater consensus in the results.

Key-words: Composites; Concrete; Carbon nanotubes; Durability.

Resumo

O reforço de matrizes cimentícias com nanotubos de carbono de paredes múltiplas (NTCPM) pode permitir o controle de fissuração em escala nanométrica, contribuindo para a durabilidade e resistência desses compósitos. Um problema relacionado a esses compósitos está associado à dificuldade de dispersão dos NTCPM e baixa interação interfacial fibra-matriz. Assim, este estudo realizou uma Revisão Sistemática da Literatura (RSL) para identificar os principais teores de NTCPM e técnicas de dispersão, correlacionando-os com parâmetros de durabilidade em condições ambientais que degradam matrizes cimentícias, como ambientes com CO₂, cloretos, ácidos e sulfatos. Como método, foi aplicada uma *string* de busca nas bases de dados internacionais entre 2020 e 2024, resultando em 18 artigos. Os resultados mostraram que os NTCPM melhoram as propriedades mecânicas e a microestrutura dos compósitos, além de reduzir o valor dos coeficientes de migração dos íons cloreto e de difusão do CO₂. Isso foi atribuído pelos mecanismos de pontos de nucleação (formação de produtos de hidratação do cimento), pontes de transferência de tensões nas microfissuras e pela densificação da matriz. Embora os NTCPM tenham demonstrado potencial na durabilidade de compósitos cimentícios, a diversidade de metodologias e condições de exposição requer mais estudos para alcançar maior consenso nos resultados.

Palavras-chave: Compósito; Concreto; Nanotubos de carbono; Durabilidade.

Resumen

El refuerzo de matrices cementosas con nanotubos de carbono de paredes múltiples (NTCPM) puede permitir el control de fisuración a escala nanométrica, contribuyendo a la durabilidad y resistencia de estos compuestos. Un desafío relacionado con estos compuestos es la dificultad para dispersar los NTCPM y la baja interacción interfacial fibra-matriz. Este estudio realizó una Revisión Sistemática de la Literatura (RSL) para identificar los principales contenidos de NTCPM y técnicas de dispersión, correlacionándolos con parámetros de durabilidad en condiciones ambientales que degradan matrices cementosas, como ambientes con CO₂, cloruros, ácidos y sulfatos. Se aplicó una *string* de búsqueda en bases de datos internacionales entre 2020 y 2024, resultando en 18 artículos. Los resultados mostraron que los NTCPM mejoran las propiedades mecánicas y la microestructura de los compuestos, además de reducir los coeficientes de migración de iones cloruro y la difusión de CO₂. Esto se atribuyó a mecanismos como puntos de nucleación (formación de productos de hidratación del cemento), puentes de transferencia de tensiones en microfisuras y la densificación de la matriz. Aunque los NTCPM han demostrado potencial en la durabilidad de compuestos cementosos, la diversidad de metodologías y condiciones de exposición requiere más estudios para alcanzar mayor consenso en los resultados.

Palabras-clave: Compuestos; Concreto; Nanotubos de carbono; Durabilidad.

1 Introduction

Cementitious matrices are known for their low tensile strength and limited deformation capacity. According to Metaxa et al. (2021), cement-based materials have a very complex nanostructure that consists of hydration products, crystals, unhydrated cement particles, and nanopores, in which traditional reinforcement, inserted at the macro and micro scales, is not effective. According to Carriço et al. (2018), carbon nanotubes (CNTs) have proven to be ideal candidates for this nanoscale reinforcement in cementitious matrices.

Iijima (1991) discovered CNTs and defined them as metastable forms of carbon resulting from the rolling of a plane of carbon atoms into the shape of a cylinder, with a diameter on the order of 4 to 30 nm and a length on the order of 3 to 10 μm . CNTs have impressive mechanical properties: they have a strength that is more than 10 times greater than that of high-performance steels, with a tensile strength of around 11 to 63 GPa and a Young's modulus between 450 and 1500 GPa, according to Gleize and Pelisser (2017). They can be found in a single-walled form (SWCNTs) that is difficult to synthesize, which raises their cost and prevents their large-scale application in practice. In contrast, multi-walled carbon nanotubes (MWCNTs) can be produced on a large scale and are more widely used, especially when applied to cementitious composites.

Carriço et al. (2018) highlight that MWCNTs can act as nucleation points for the growth of calcium silicate hydrate (C-S-H), promoting faster and more uniform hydration of the hydration products of cement; they also function as a bridge for stress transfer in micro/nano cracks, contributing to create a denser matrix. The mechanical properties of these composites have been shown to be impacted in several ways, with reports ranging from subtle gains when adding MWCNTs to cementitious matrices, as shown by Bogas et al. (2021) and by Gao et al. (2020), to significant improvements in strength, as found by Sarvandani et al. (2021), Wang et al. (2022), Ming et al. (2020), and Karthiyaini et al. (2022). However, some studies, for example that by Mesquita et al. (2023), have also pointed to a decrease in strength, an effect that has been attributed to the insufficiency of the dispersion method and the reduction in the amount of water required for cement hydration when incorporating high proportions of MWCNTs.

Other studies, such as those by Liu et al. (2022) and Gao et al. (2021), have focused on combining MWCNTs with supplementary cementitious materials, and have compared these with materials that are more widely used in civil construction. By partially replacing the mass of cement with MWCNTs or silica fume, Chukka et al. (2022) verified that MWCNTs yielded results superior to those of silica fume, in terms of both mechanical properties and durability parameters; these authors attributed this finding to the smaller particle size of the MWCNTs.

The results found in the literature always condition the positive effects of the MWCNTs on their good dispersion within the composite. An ultrasound process, also known as sonication, has been widely identified as a method of dispersing the MWCNT nanoparticles before inserting them into the matrix. Although most studies report benefits such as densification of the matrix, formation of nucleation points and greater stress transfer, some authors do not associate these effects with the incorporation of MWCNTs. When comparing concretes prepared with deionized water, sonicated deionized water and sonicated deionized water with MWCNTs, Assi et al. (2020) reported that the positive effects observed in regard to compressive strength and the microstructure were not due to

the incorporation of MWCNTs, but to the sonication process of deionized water, since the sonication process could produce CaO_2 and the two compositions that underwent sonication had the same microstructure with more ettringite. In addition, Wang et al. (2022) state that MWCNTs cannot act as a diffusion point for the nucleation of hydration products of C_3S (for formation of C-S-H), and are only able to promote the local formation of calcium hydroxide (CH), which has weak bonding with the MWCNTs, and to reduce the formation of C-S-H.

Most researchers reported gains in compressive and flexural strength; however, when the content of MWCNTs was varied from 0.05% to 0.15% in relation to the mass of cement, Gao et al. (2021) obtained significant gains with a low proportion of MWCNTs (0.05%), and showed that a gradual increase in content made the concrete more conductive and porous.

The study of MWCNTs as reinforcement for cementitious material has yielded contradictory results. There are several companies that supply MWCNTs with distinct characteristics, and which are produced via different synthesis processes. The responses of cementitious composites reinforced with MWCNTs under exposure situations also vary, due to the diversity of variables considered in the literature. Within the group of MWCNTs, the literature has shown different types and contents, with modifications to their surface (functionalization with hydroxyl or carboxyl groups); all these variations can facilitate or hinder dispersion, implying the adoption of numerous physical-mechanical and chemical dispersion methodologies, aiming at the best result. For cementitious matrices, the type/content of cementitious material and the water/binder ratio are the main causes of variation. These factors contribute to the persistence of contradictory results in much of the extant research.

Reports in the literature indicate that small quantities of MWCNTs are able to give large improvements in the properties of composites, with changes in the microstructure that can offer advantages in terms of both mechanical properties and durability parameters. Although many analyses have focused on mechanical strength and microstructure, there are a significantly smaller number of studies that have investigated the reinforcement of cementitious matrices with MWCNTs under real environmental conditions. An understanding of the behavior of these composites in these circumstances will be essential in order to improve the impact of these nanoparticles and to create a solid basis for future research.

To explore the current state of the art in regard to the durability parameters of cementitious matrices incorporating MWCNTs, this work presents a systematic literature review of the behavior of composites reinforced with MWCNTs under situations of environmental exposure involving carbonation, chlorides, acidic media, and contact with sulfates. The details of the compositions, dispersion methods, optimal proportion of MWCNTs, and exposure conditions that interfere with the results were surveyed, and the main changes in the mechanical properties and microstructure were extracted.

2 Methodology

In view of the diversity of variables affecting this issue (such as the type and content of MWCNTs, dispersion methods, matrix composition and experimental procedures), which make a comparison between studies difficult, an SLR was conducted. This approach made

it possible to organize and critically synthesize the available evidence, evaluate the effects of MWCNTs on durability, mechanical properties and microstructure, and identify gaps for future investigations.

According to Dresch et al. (2015), a systematic literature review is a secondary study in which primary research on a topic is consolidated to produce a structured synthesis of existing knowledge. For this work, a methodology proposed by these authors was adopted, which comprised the following stages: (i) definition of the question and the conceptual structure; (ii) selection of the work team; (iii) search strategy; (iv) research, eligibility and coding; (v) quality assurance; (vi) synthesis of the results; and (vii) presentation of the studies.

2.1 Definition of the question and conceptual structure

The research question that guided this systematic literature review was as follows: What are the effects of the incorporation of MWCNTs into cementitious composites on the durability parameters, mechanical properties and microstructure, under different dispersion methods, dosages, and environmental exposure conditions, including carbonation, chlorides, acidic media and contact with sulfates?

The conceptual structure adopted for this review was applied to cementitious composites, including concretes, mortars and Portland cement pastes. The durability parameters that reflect the performance of composites in the face of different environmental exposure conditions were prioritized and evaluated in controlled laboratory tests that included variables such as the type of attack, concentration, time and other experimental conditions. Thus, both the transport coefficients (e.g., chloride diffusion and carbonation) and indirect indicators of degradation (e.g., mass loss, dimensional variation and ultrasonic pulse velocity) were considered valid in this review. The mechanical properties that were analyzed included the compressive strength and tensile/flexural strength, while the microstructural analyses, carried out by means of microscopy techniques and complementary tests (e.g., mercury intrusion porosimetry and X-ray tomography) were interpreted according to the different exposure environments and the dispersion methods used to incorporate the MWCNTs.

2.2 Selection of the work team and search strategy

The systematic literature review was conducted by a single researcher (the main author of this study) with supervision and technical support from the other co-authors. This collaboration involved discussions about the definition of the research question, conceptual structure and methodological approach, in order to ensure the consistency and scientific rigor of the review.

Four databases of international scope and recognized relevance to the topic were selected for the search strategy: Scopus, Science Direct, Web of Science and Engineering Village. The keywords were organized into three groups, relating to the nanomaterial of interest, the type of cementitious matrix, and the property under evaluation. The keywords were as follows: multi-walled carbon nanotubes and its abbreviation MWCNT (nanomaterial); concrete, mortar, cement paste, cementitious composite or Portland cement (cementitious matrix); and durability or performance (property evaluated), in addition to using Boolean operators to combine these three groups. The following strings were then used: “(‘carbon nanotube’ OR ‘CNT’) AND (‘concrete’ OR ‘mortar’ OR ‘cement paste’ OR

‘cementitious composites’ OR ‘Portland cement’) AND (‘durability’ OR ‘performance’)”. The specific term “multi-walled carbon nanotube” (MWCNT) was not included (as a string), since most of the articles typically do not use this term in their titles or abstracts. The inclusion of this term would have restricted the results excessively, although all the works selected for this SLR involved MWCNTs.

The string was applied to the “title, abstract and keywords” field of each of the selected databases. Filters were also applied to select the period (2020–2024), document type (articles) and areas of knowledge (materials science, engineering, chemistry, environmental science, physics and astronomy, chemical engineering, mathematics, energy and computer science).

The results of the searches were exported as files in *bibtex* format, and were organized using the *Parsifal* program, a tool that was developed to support systematic reviews. This process made it possible to consolidate the references in a standardized way, identify duplicate articles, and prepare the set of studies for the screening and subsequent analysis phases. The last search was carried out on July 1, 2024.

2.3 Research, eligibility and coding

To ensure consistency and reproducibility in the selection of the studies, inclusion and exclusion criteria were previously defined, as presented in Tables 1 and 2, respectively. These criteria were used to guide the screening process, in order to ensure that only studies relevant to this SLR were retained and that they included experimental results involving the incorporation of MWCNTs in cementitious composites, with a focus on durability parameters, mechanical properties and microstructure.

By exporting the results to *Parsifal*, duplicate documents could be identified and removed. Next, an initial screening was carried out which involved reading titles and keywords; when this was not sufficient to determine eligibility, the abstract was read. When this was insufficient, parts of the text or the full study were read. The previously defined inclusion and exclusion criteria were applied consistently.

Table 1: Inclusion criteria adopted.

Category	Application
Studies on durability, mechanical properties and microstructure	Studies that present durability parameters, mechanical properties and microstructural analyses, before and after exposure, allowing a comprehensive evaluation of the effect of the MWCNT.
Studies on durability and the microstructure	Studies that present durability parameters and microstructural analyses before and after exposure, allowing the interpretation of internal mechanisms associated with the performance of the composites with MWCNT.
Studies on durability and mechanical properties	Studies that present durability parameters and mechanical properties (compression and/or tensile/flexural) before and after exposure, allowing to relate the effects of the MWCNT to the structural behavior of the composites.
NOTE: In all cases, only studies that evaluated composites submitted to controlled environmental exposure conditions (carbonation, chlorides, sulfates or acidic media) and that allowed verifying the effect of the MWCNT in an isolated way, through comparison with reference matrices without addition of the nanomaterial, were included.	

At the coding stage, the relevant information from the selected articles was input to a standardized data spreadsheet, covering bibliographic data (title, authors, journal, and country); characteristics of the MWCNTs (supplier, dimensions, purity, surface functionalization, and content relative to the cement mass); dispersion method (magnetic

stirring, mechanical stirring and/or ultrasonication, with or without additives); composition of the cementitious matrix (type of cement, mineral additions, chemical admixtures, fine and coarse aggregates, water/binder ratio); durability parameters (steady-state and non-steady-state diffusion coefficients, carbonation coefficient, corrosion rate, electrical resistivity, mass loss, permeability, steel mass loss, water absorption by immersion and by capillarity, chloride diffusion depth); mechanical properties (compressive strength and/or tensile/flexural strength); and microstructural analyses (scanning electron microscopy, mercury intrusion porosimetry, and X-ray computed tomography).

Table 2: Exclusion criteria adopted.

Category	Application
Studies that do not involve cementitious composites	Use of MWCNT in sensors embedded in reinforced concrete structures; application of MWCNT in other construction systems (polymeric materials, wood, metallic composites); geopolymeric matrices.
Studies that do not add carbon nanotubes in the matrix	Use of carbon-derived materials, such as graphene oxide, carbon black, carbon fiber; use of another nanomaterial.
Studies that do not present experimental program	Review studies, meta-analyses, opinion articles, book chapters, conference articles, technical notes, short communications, extended abstracts. Theoretical, numerical or computational works.
Studies that do not address durability properties	Structural monitoring, self-sensing and piezoresistive concrete. Rheological, thermal, electrical properties, among others, without evaluating effects on durability parameters.
Studies that do not allow evaluating in an isolated way the effect of the MWCNT	The MWCNT were added as a fixed part of the composition, proceeding to vary another additive (ex.: silica fume, metakaolin, metallic fibers). Combination of MWCNT with other nanomaterials (such as graphene oxide), without presenting an isolated control group with MWCNT.

2.4 Quality assurance

Studies that included a detailed description of the experimental methods, adequate characterization of the MWCNT and consistent quantitative results were prioritized. Data extraction was carried out using a standardized spreadsheet, to reduce the risk of recording errors and to facilitate comparability between works. In cases where there was doubt as to compliance with the inclusion criteria, a new full reading was carried out before the final decision. This process involved critical review by the co-authors, thus ensuring greater reliability and scientific rigor in the selection and analysis of the studies.

2.5 Synthesis of results and presentation of the studies

The studies included in the review were organized along two main dimensions: bibliometric analysis, in which the aim was to characterize the range of publications, and technical analysis, which was conducted to explore the effects of the incorporation of MWCNTs into cementitious composites under different exposure conditions. The extracted data were consolidated in tables and analyzed using a descriptive method. Priority was given to the durability parameters, followed by the mechanical and microstructural properties.

The standardization process that was adopted, based on a comparison with a reference mixture (REF) and the classification of the results into gains, losses or absence of significant variation, made it possible to structure the analysis in a consistent way and guided the presentation of the results. This structure took into account the bibliometric

range and characterization of the studies, opening up the possibility of holding discussions about the behavior of the materials under different degradation environments.

3 Results and Discussion

The results of the systematic literature review are presented here in a structured way, in order to handle the great heterogeneity observed among the included studies. This diversity, which involved the type of cementitious matrix, the content and characteristics of the MWCNTs, dispersion methods, exposure conditions, and test parameters, made it impossible to carry out a formal statistical meta-analysis. A strategy based on synthesis without meta-analysis was therefore adopted, a practice recommended in systematic reviews when studies do not allow for direct quantitative comparisons.

In this approach, the results were standardized in relation to the reference cementitious matrix (REF), and were classified according to the observed behavior in terms of gains, losses, or absence of significant variation in the evaluated properties. Wherever possible, the discussion is contextualized by key variables such as the type of matrix, MWCNT content, and exposure time, to allow for the identification of general trends, divergences, and gaps. For presentation purposes, the results were organized into four sub-items:

- I. Bibliometric data characterizing the general range of publications;
- II. Characterization of the included articles, based on bibliographic, experimental, and methodological information;
- III. Technical tests in sulfate and acidic environments, with summaries of the gains and losses of mechanical properties, durability parameters, and microstructural aspects under conditions of aggressive chemical attack; and
- IV. Technical tests of chlorides, carbonation, and reinforcement corrosion, with a discussion of the effects of incorporating MWCNTs on the mechanical properties, transport parameters, and degradation indicators associated with ion penetration and carbonation of the cementitious matrix.

3.1 Bibliometric data

A systematic search resulted in 1,408 documents from the four selected databases (Table 3). After identifying and removing 685 duplicate records, 723 unique documents remained, which were subjected to the initial screening process based on titles and keywords.

Table 3: Results of applying the search string to the databases.

Category	Number of documents
<i>Scopus</i>	485
<i>Web of Science</i>	418
<i>Science Direct</i>	267
<i>Engineering Village</i>	238
Total works	1408
Total duplicate works	685
Total works evaluated	723

Of the total number of articles evaluated at this stage, 705 were excluded based on the criteria presented in Section 2.3. A detailed breakdown by stage is shown in Table 4. A total of 18 articles remained that fully met the inclusion criteria, and these made up the set analyzed in this systematic literature review .

Table 4: Results after applying exclusion criteria.

Category	Number of documents	Exclusion by title/keywords	Exclusion by abstract	Exclusion by partial/full reading
Studies that do not involve cementitious composites	284	204	80	0
Studies that do not add carbon nanotubes in the matrix	92	0	81	9
Studies that do not present experimental program	54	47	7	0
Studies that do not address durability properties	112	0	49	63
Studies that do not allow evaluating in an isolated way the effect of the MWCNT	163	0	68	95
Total number of excluded studies	705			

About 40% of the exclusions occurred because the studies did not involve cementitious composites, and instead focused on geopolymers, asphalt binders, and other materials. Although this result shows the breadth of the search string, it also reinforces the need for careful screening to ensure that only relevant studies are selected.

Although there is growing interest in the use of MWCNTs, few studies have directly evaluated durability or isolated its effect. Almost 25% of the exclusions involved combinations with other additives, reflecting the maturity of the field but making it difficult to identify mechanisms specific to nanotubes.

Table 5 presents the distribution of the included articles according to the evaluation scope. It can be seen that investigations with a simultaneous focus on durability, mechanical properties, and microstructure predominate, reflecting the recurring interest in the literature in elucidating the internal mechanisms responsible for the performance of cementitious composites with MWCNTs.

Table 5: Results after applying inclusion criteria.

Category	Number of documents
Studies on durability, mechanical properties and microstructure	10
Studies on durability and the microstructure	5
Studies on durability and mechanical properties	4
Total number of included studies	18

For bibliometric purposes, each article was counted only once. A study that addresses more than one exposure environment (for example, chlorides and sulfates) is discussed in the corresponding sections (Sections 3.3 and 3.4), but without duplicating the count. This final set, although small in number, contains the most relevant and methodologically consistent publications, allowing for a more comparable and well-founded critical analysis.

3.2 Characterization of the included articles

The 18 selected articles (Figure 1) were characterized in terms of bibliographic, methodological, and experimental information, in order to support the critical analysis presented in Sections 3.3 and 3.4.

Figure 1: Bibliographic data on the articles.

Reference	Article title	Journal	Countries of authors' institutions
Alafogianni et al. (2020)	<i>Effect of Environmental Exposure on the Pore Structure and Transport Properties of Carbon Nanotube-Modified Mortars</i>	<i>Materials</i>	Greece
Bhatrola, Kothiyal e Sameer (2023)	<i>Durability & mechanical properties of functionalized multiwalled carbon nanotube incorporated pozzolana portland cement composite</i>	<i>Materials Today: Proceedings</i>	India
Bogas, Ahmed e Diniz (2021)	<i>Influence of Cracking on the Durability of Reinforced Concrete with Carbon Nanotubes</i>	<i>Applied Sciences</i>	Portugal
Chukka et al. (2022)	<i>Experimental Testing on Mechanical, Durability, and Adsorption Dispersion Properties of Concrete with Multiwalled Carbon Nanotubes and Silica Fumes</i>	<i>Adsorption Science & Technology</i>	India
Gamal et al. (2021)	<i>Enhancement of the concrete durability with hybrid nano materials</i>	<i>Sustainability</i>	Egypt
Gao et al. (2021)	<i>Effect of the dosage of MWCNT's on deterioration resistant of concrete subjected to combined freeze–thaw cycles and sulfate attack</i>	<i>Structural Concrete</i>	China
Han et al. (2023)	<i>Chloride ion penetration resistance of matrix and interfacial transition zone of multi-walled carbon nanotube-reinforced concrete</i>	<i>Journal of Building Engineering</i>	China
Karthiyaini et al. (2022)	<i>Implications of Multi-Walled Carbon Nanotubes in the Performance of Concrete Subjected to Chloride and Acid Environment</i>	<i>Polish Journal of Environmental Studies</i>	India
Li et al. (2020)	<i>Chloride-induced corrosion behavior of reinforced cement mortar with MWCNTs</i>	<i>Science and Engineering of Composite Materials</i>	China
Liu et al. (2022)	<i>Effect of multi-walled carbon nanotube on reactive powder concrete (RPC) performance in sulfate dry-wet cycling environment</i>	<i>Construction and Building Materials</i>	China
MacLeod, Gates e Collins (2020)	<i>Durability characterisation of portland cement-carbon nanotube nanocomposites</i>	<i>Materials</i>	Australia
Ming et al. (2020)	<i>Portland Cement Partially Replaced by Blast Furnace Slag and Multi-Walled Carbon Nanotubes: Effect on Corrosion Resistance of Carbon Steel Reinforcement in 3% NaCl</i>	<i>International Journal of Electrochemical Science</i>	China
Sarvandani et al. (2021)	<i>Effect of functionalized multi-walled carbon nanotubes on mechanical properties and durability of cement mortars</i>	<i>Journal of Building Engineering</i>	Iran
Sumathi et al. (2023)	<i>Mechanical, Durability, and Microstructure Investigations on High-Strength Concrete Incorporating Nanosilica, Multi-Walled Carbon Nanotubes, and Steel Fibres</i>	<i>Advances in Materials Science and Engineering</i>	India
Varisha, Zaheer e Hasan (2021)	<i>Mechanical and durability performance of carbon nanotubes (CNTs) and nanosilica (NS) admixed cement mortar</i>	<i>Materials Today: Proceedings</i>	India
Wang et al. (2022)	<i>Effect of CNT-COOH Addition on the Compressive Strength, Chloride Resistance, and Microstructure of Cement Mortar</i>	<i>Advances in Materials Science and Engineering</i>	China
Yu et al. (2024)	<i>Chloride penetration resistance of ultra-high performance concrete with various multi-walled carbon nanotubes</i>	<i>Construction and Building Materials</i>	China
Zhang et al. (2023)	<i>Research on Performance Deterioration of Multi-Walled Carbon Nanotube–Lithium Slag Concrete under the Coupling Effect of Sulfate Attack and Dry–Wet Cycles</i>	<i>Materials</i>	China

Figure 2 highlights the wide heterogeneity of the nanotubes considered in the selected studies. The external diameters ranged from < 8 to 100 nm, with a greater concentration in the range of 10 to 30 nm, while the lengths varied between 0.5 and 100 µm. The specific surface area had values of 60 to > 400 m²/g, while the purity ranged from 85% to > 99%. Although the use of pure surfaces predominated, some studies considered nanotubes functionalized with –COOH or –OH.

Figure 2: Characteristics of MWCNTs incorporated into cementitious matrices.

Reference	Supplier	Outer diameter (nm)	Length (μm)	Apparent density (g/cm^3)	Specific surface area (m^2/g)	Purity (%)	Surface type
Alafogianni <i>et al.</i> (2020)	Glontech AS	20 - 45	> 10	NI	> 150	> 94	Pure surface
Bhatrola, Kothiyal e Sameer (2023)	NI	NI	NI	NI	NI	NI	Functionalized (did not specify type)
Bogas, Ahmed e Diniz (2021)	TimesNano	20 – 80	10 – 20	2,1	> 60	> 98	Pure surface
Chukka <i>et al.</i> (2022)	NI	NI	NI	NI	NI	NI	NI
Gamal <i>et al.</i> (2021)	NI	50	10 – 100	NI	NI	NI	Pure surface
Gao <i>et al.</i> (2021)	NI	10 – 20	5 – 15	NI	100 - 160	> 97	Pure surface
Han <i>et al.</i> (2023)	Chengdu Organic Chemistry Co.	30 – 80	5 – 10	0,18	> 60	> 95	Pure surface
Karthiyaini <i>et al.</i> (2022)	NI	25	10	NI	220	> 98	Pure surface
Li <i>et al.</i> (2020)	Chengdu Institute of Organic Chemistry Research Institute	10 – 20	10 – 30	NI	> 150	> 95	Pure surface
Liu <i>et al.</i> (2022)	Shandong Dazhan Nano materials Co.	10 – 20	5 – 50	0,06 – 0,1	160 – 210	> 85	Pure surface
MacLeod, Gates e Collins (2020)	Eden Innovations	25	NI	0,107	NI	> 95	Pure surface
Ming <i>et al.</i> (2020)	NI	NI	NI	NI	NI	NI	NI
Sarvandani <i>et al.</i> (2021)	Research Institute of Iran Petroleum Industry	out/20	10	NI	250	95 - 99	–COOH (functionalization was performed by the authors using pure NTCMP purchased)
Sumathi <i>et al.</i> (2023)	Go Green Technologies	10 – 30	> 10	0,14	110 – 350	99	Pure surface
Varisha, Zaheer e Hasan (2021)	Adano Technology	10 – 20 30 – 50	1 – 5 10 – 20	NI	370 400	> 99	Pure surface and functionalized –COOH
Wang <i>et al.</i> (2022)	Shenzhen Nanoport Co.	5 – 15	10 – 30	0,221	200 – 240	> 95	Functionalized –COOH
Yu <i>et al.</i> (2024)	NI	< 8	10 – 30	NI	> 350	NI	Pure surface
		< 8	0,5 – 2		> 350		Pure surface
		20 – 30	10 – 30		> 110		Pure surface
		20 – 30	0,5 – 2		> 120		Pure surface
		< 8	10 – 30		> 400		functionalized –COOH
		< 8	0,5 – 2		> 380		functionalized –OH
		< 8	10 – 30		> 400		Pure surface
		< 8	0,5 – 2		> 270		Pure surface
20 – 30	10 – 30	> 90	Pure surface				
100 – 200	1 – 10	> 30	Pure surface				
30 – 60	1 – 10	> 200	Pure surface				
Zhang <i>et al.</i> (2023)	Chengdu Jiakai Technology	40 - 60	< 10	NI	60 - 100	> 98	Pure surface

Caption:
NI – Not informed by the authors
OH – Insertion of hydroxyl groups for surface functionalization
COOH – Insertion of carboxyl groups for surface functionalization

The suppliers were equally diverse, as they included international companies (Glonatech, Eden Innovations) and Asian laboratories (Chengdu, Shandong, Shenzhen), in addition to nanotubes synthesized by the researchers themselves. This diversity of parameters directly impacted the length/diameter ratio (aspect ratio) and made direct comparisons between studies difficult.

Figure 3 summarizes the variables associated with the reference compositions. Mortars and concretes predominated, with water/cement ratios ranging between 0.18 and 0.55. The proportions of MWCNTs added generally ranged from 0.01% to 0.4% of the cement mass, although in two studies, much higher levels of replacement (2.0% and 12.5%) of the cement mass by MWCNTs were tested. The nanomaterials were supplied in powder form, dispersed in solution or synthesized in the laboratory. The most frequently used method of dispersion was based on a combination of ultrasonication (2 to 120 min), mechanical stirring, and admixtures such as superplasticizers or polyvinylpyrrolidone. The heterogeneity extended to the mixing procedures: some studies described in detail the order in which the constituents were mixed, while others were limited to brief descriptions or did not provide complete information.

Figure 4 shows the experimental parameters of the studies. The most common preparation method was wet curing for 28 days before exposure. The aggressive environments included chloride solutions (3–10% NaCl), sulfates (Na_2SO_4 and MgSO_4), accelerated carbonation, and acidic media (pH 4–6). Exposure times ranged from 28 to 960 days, reflecting different acceleration strategies for the attacks. The evaluated properties included compressive and flexural strength, transport coefficients (chloride diffusion and migration, carbonation depth), absorption and porosity, mass loss, corrosion rate, and analyses of microstructural porosity.

There was a high level of methodological variability in terms of the characteristics of MWCNTs, matrix compositions, dispersion strategies, and testing conditions. This diversity made direct comparisons difficult but provided a comprehensive overview of recent experimental practices, and guided a critical analysis of the effects of MWCNTs in different exposure environments, as discussed in the following sections.

Another important aspect was the lack of consistency in the use of technical standards for exposure tests. Several studies did not mention the standard that was followed, while in others, it was used only as an initial reference and modifications to the fundamental parameters were introduced. For example, Liu et al. (2022) evaluated attack by magnesium sulfate using a 10% solution, rather than the 5% concentration required by the Chinese standard (GB/T 50082). The authors justified this change based on the conditions within certain regions of China, where concrete structures are exposed to significantly higher concentrations of magnesium sulfate. This type of adaptation reflects the concern with reproducing local conditions of high severity, and highlights the difficulty in establishing direct comparisons among different studies.

Figure 3: Characteristics of dispersion processes and cementitious matrices.

Reference	Matrix	w/c	MWCNT content in relation to cement mass	Form of MWCNT supply	Dispersion method	Cement class and standard	Mixing procedure for obtaining cementitious composites
Alafogjanni et al. (2020)	M	0.5	0.2; 0.4; 0.6; 0.8%	NI	(water + P-SP + MWCNT) were US (T: NI) → the solution was placed in a vacuum to remove bubbles for 45 min.	OPC I 42.5R (ASTM C150 – EUA)	The cement and sand were dry mixed; the MWCNT solution was added.
Bhatrola, Kothiyal e Sameer (2023)	M	0.42	0.0015; 0.003; 0.006; 0.012%	Synthesized by chemical vapor deposition	US (T: 20 min.)	PPC (IS 1489 – India)	NI
Bogas, Ahmed e Diniz (2021)	C	0.55	0.1%	NI	(40% da water + MWCNT) were MS (T: 60 min.) and US (T: 45 min.)	OPC 42.5R (EN 197-1 – Europe)	Mix all aggregates in descending order of size for 3 min with 60% water; add the MWCNT solution with the cement and mix for 4 min.
Chukka et al. (2022)	C	0.31	1.0; 1.5; 2.0; 3.0% *	NI	NI	OPC 53-grade (IS 12269 – India)	NI
Gamal et al. (2021)	C	NI	0.01; 0.02; 0.04%	NI	(33% of water + nanoclay) mixed and US (T: 10 min.) → (33% of water + MWCNT) mixed and US (T: 10 min.) → (33% of water + P-SP) mixed for 2 min.	OPC 42.5N (EN 197-1 – Europe)	The cement, sand, and gravel were mixed for 2 min. (dry mix) in the concrete mixer → the nano-clay dispersion was added and mixed for another 2 min.; the MWCNT solution was added and mixed for another 2 min.; the P-SP dispersion was added and mixed for another 2 min.
Gao et al. (2021)	C	0.45	0.05; 0.1; 0.15%	NI	(40% of water + MWCNT + PVP) were MS (T: 10 min.) and US (T: 60 min.)	OPC 42.5 (GB 175 – China)	The aggregates were mixed with 60% water for 3 min.; the cement and MWCNT solution were added and mixed.
Han et al. (2023)	C	0.53	0.05; 0.1; 0.15%	Samples already dispersed in solution	(40% of water + MWCNT) were MS (T: 60 min.) and US (T: 45 min.)	PC P.II 42.5 (GB 175 – China)	O cement, areia e brita foram misturados por 2 min. (mistura seca) na betoneira; a solução de MWCNT foi colocada e misturada por mais 2 min.
Karthiyaini et al. (2022)	C	0.35	0.05; 0.1; 0.15; 0.2; 0.25%	Powder samples	(50 ml of water + SR-S + MWCNT) were US (T: 30 min.)	OPC 53-grade (IS 1489 – India)	The MWCNT solution is added directly to the concrete.
Li et al. (2020)	M	0.4 e 0.5	0.02; 0.1; 0.2%	NI	(water + MWCNT + PVP) were MS (T: 15 min.) and US (T: 20 min.)	OPC I 42.5 (GB 175 – China)	The MWCNT solution is mixed with water and placed in a mortar mixer; cement and sand are added and mixed for 1 min.
Liu et al. (2022)	C	0.18	0.1%	Powder samples	(water + MWCNT + PVP) were MS (T: 15 min.) and US (T: 40 min.)	PC P.O.52.5 (GB 175 – China)	The sand, cement, fly ash, silica fume, and slag powder were mixed for 1 min.; water was added and mixed; the MWCNT solution was added and mixed for 3 min.
MacLeod, Gates e Collins (2020)	P	0.4	0.025; 0.05; 0.1%	Powder samples	(water + P-SP) were MS (T: 2 min.) → added MWCNT and US (T: 10 min.)	GP PC (AS 3972 – Australia)	3 types of composition: In the first, the cement was mixed with the water, P-SP, and MWCNT solution; in the second, MWCNT and cement were added to the water and P-SP solution; in the third, cement was added to the water and MWCNT solution.
Ming et al. (2020)	C	0.37	12.5%*	NI	NI	PC (GB 175 – China) [type not specified]	NI
Sarvandani et al. (2021)	M	0.485	0.05; 0.1; 0.2; 0.3; 0.4%	NI	(water + P-SP + MWCNT) passed for 2 cycles of US (T: 5 min.)	OPC II (ASTM C150 – EUA)	The MWCNT solution was mixed (electric mixer at 140 rpm/min.); the cement was added and mixed for another minute; the sand was added and mixed for 30 sec.; the mixture was mixed for another 30 sec. at 285 rpm/min; a 90-sec. pause was taken to remove the mortar stuck to the bottom; mixing was completed for another minute at 285 rpm/min.
Sumathi et al. (2023)	C	0.38	0.025; 0.05; 0.1; 0.15; 0.2%	Powder samples	(50% of water + P-SP + MWCNT) were MecS (T: 30 min.) → The rest of the water was added and mixed slowly for 60 sec.	OPC 53-grade (IS 12269 – India)	The MWNTC solution was placed in the concrete.
Varisha, Zaheer e Hasan (2021)	M	0.55	0.3%	Powder samples	(water + P-SP + nanosilica + MWCNT) were US (T: 20 min.)	OPC 43-grade (IS 8112 – India)	The cement and sand were dry mixed; the MWCNT solution was added.
Wang et al. (2022)	M	0.45	0.01; 0.05; 0.1%	NI	(distilled water + MWCNT) were US (T: 120 min.)	PC P.O.42.5 (GB 175 – China)	The cement and sand were dry mixed for 30 seconds; the MWCNT solution was added and mixed for another 3 minutes.
Yu et al. (2024)	C	0.38	0.25; 0.5%	NI	(30 ml of water + SR-S + MWCNT) were US (T: 5 min.)	OPC III 42.5R (EN 197-1 – Europe)	The MWCNT solution was mixed with silica fume for 60 sec. (at 1000 ± 100 rpm); cement and fly ash were added and mixed for 60 sec. (at 1000 ± 100 rpm) and another 120 sec. (at 2000 ± 10 r/min); sand was added to the mixture and stirred for 60 sec. (at 1000 ± 100 r/min) and for another 240 sec. (at 2000 ± 10 r/min).
Zhang et al. (2023)	C	0.35 0.4 0.45	0.05; 0.1; 0.15%	NI	NI	OPC P.O.42.5 (GB 175 – China)	NI

Caption: P = paste; M = Mortar; C = concrete; * cement content replaced by MWCNT; T = time; US = ultrasonication; MS = magnetic stirring; MecS = mechanical stirring; P-SP = polycarboxylate-based superplasticizer; SR-S = set-retarding superplasticizer; PVP = polyvinylpyrrolidone additive; PC = Portland Cement; OPC = Ordinary Portland Cement; PPC = Pozzolana Portland Cement; GP PC = General Purpose Portland Cement.

Figure 4: Conditions and tests performed.

Reference	Curing process	Description of environmental exposure conditions studied and test standards	Mechanical tests	Microstructural analyses	Direct and indirect durability tests
Alafogjanni et al. (2020)	Demolded after 24 hours, cured in water for 27 days	Immersion in sodium sulfate solution (5% Na ₂ SO ₄), in accordance with ASTM C 1012, for 112 days.	-	Porosity by mercury intrusion porosimetry (WAE e AAE)	Water absorption by capillarity (WAE and AAE); Mass loss (WAE and AAE)
Bhatrola, Kothiyal e Sameer (2023)	Demolded after 24 hours, cured immersed in water	Immersion in sulfuric acid solution (1% H ₂ SO ₄) for 90 days.	Compressive strength (WAE and AAE); Flexural strength (WAE)	-	Electrical resistivity (WAE)
Bogas, Ahmed e Diniz (2021)	Demolded after 24 hours, wet curing (20 ± 2 °C and RH of 95%)	Carbonation: After 14 days of curing, the samples remained in a dry chamber until testing (in accordance with LNEC E391). The TS were placed in the carbonation chamber (23 ± 3°C, RH of 60 ± 5%, and 5 ± 0.1% CO ₂) for 28, 56, and 90 days. Chloride: The TS were kept in a humid chamber until the date of the rapid chloride migration test (in accordance with LNEC E463 and Ntbuild 492).	Compressive strength (WAE)	-	Water absorption by capillarity (WAE); Carbonation coefficient K _c (AAE); Chloride ion migration diffusion coefficient D _{cl} (AAE)
Chukka et al. (2022)	Demolded after 24 hours, cured immersed in water	Chloride: rapid chloride migration test	Compressive strength (WAE); Flexural strength (WAE)	-	Water absorption (WAE); Porosity (WAE); Mass loss (AAE); Passing electrical charge (AAE)
Gamal et al. (2021)	Demolded after 24 hours, wet curing (20 ± 2 °C and RH of 95%)	Chloride: chloride penetration resistance test (according to ASTM C1202)	Compressive strength (WAE); Flexural strength (WAE)	-	Water absorption by capillarity (WAE); Adhesion of bars (WAE); Passing electrical charge (AAE); Corrosion rate (WAE) by ASTM C876 (corrosion test)
Gao et al. (2021)	Demolded after 24 hours, wet curing for 24 days	Immersion in sodium sulfate solution (5% Na ₂ SO ₄) for 4 days and 200 freeze-thaw cycles.	Compressive strength (WAE and AAE)	-	Mass loss (WAE e AAE)
Han et al. (2023)	Demolded after 24 hours, wet curing (20 ± 2 °C and RH of 95%)	Chloride: kept for 28 days in a humid chamber until rapid migration testing (in accordance with GB/T 50082-2009).	-	Porosity by mercury intrusion porosimetry (WAE)	Depth of chloride ion diffusion (rapid and aggregate migration) (AAE); Diffusion coefficient in non-stationary state D _{ns} (AAE)
		Chloride: kept for 28 days in a humid chamber until testing. Immersion in sodium chloride solution (3% NaCl) for 120 days.		-	Free chloride ions (AAE)
		After the coarse aggregate was processed, it was placed in a mold and filled with mortar. It was demolded after 24 hours and cured for 28 days until the rapid migration test (empirical test).		-	Depth of chloride ion diffusion in the matrix and transition zone (AAE)
Karthiyaini et al. (2022)	Demolded after 24 hours, cured immersed in water for 28 days	Immersion in sulfuric acid solution (5% H ₂ SO ₄) for 56 days. Chloride: immersion in chloride solution (5 kg of sodium chloride salts NaCl + 100 kg of water) for 56 days.	Compressive strength (WAE and AAE)	-	Density (WAE and AAE) of the two situations
Li et al. (2020)	NI	Chloride: after 28 days of curing, immersion in sodium chloride solution (3% NaCl) for rapid migration testing (NORDTEST).	Compressive strength (WAE)	-	Diffusion coefficient in non-stationary state D _{ns} (AAE); Diffusion coefficient in stationary state D _s (AAE); Electrical resistivity (DE); Corrosion rate (AAE); Loss of steel mass (AAE);
		Chloride: after 28 days of curing, immersion in sodium chloride solution (3% NaCl) for 65 days for natural migration testing (NT Build 443).			
		Chloride: Immersion of reinforced concrete in sodium chloride solution (3.5% NaCl) for 3 days for electrochemical corrosion.			
Liu et al. (2022)	Demolded after 24 hours, cured in water for 28 days	Cycles of immersion in sodium sulfate solution (10% Na ₂ SO ₄) for 12 hours and drying in an oven (60°C) for 11 hours, ending with cooling for 1 hour, for 150 days. Cycles of immersion in magnesium sulfate solution (10% MgSO ₄) for 12 hours, drying in an oven (60°C) for 11 hours, ending with cooling for 1 hour, for 150 days.	Compressive strength (AAE)	Porosidade pela tomografia computadorizada de Raio-X (AAE)	Mass loss (AAE)
MacLeod, Gates e Collins (2020)	Demolded after 24 hours, immersed in lime water curing (23 ± 2°C)	Chloride: After 28 days, immersion in two solutions. One with sodium hydroxide and sodium chloride (0.6 M NaOH + 0.6 M NaCl) on one side and another with only sodium chloride (0.6 M NaCl) on the other side, for 270 days.	-	-	Water absorption (WAE); Water permeability (WAE); Diffusion coefficient in stationary state D _s (AAE)
Ming et al. (2020)	Demolded after 24 hours, wet curing (20 ± 2 °C and RH of 95%)	Chloride: Immersion of reinforced concrete in sodium chloride solution (3.5% NaCl) for 30 days for electrochemical impedance spectroscopy (EIS).	Compressive strength (WAE)	-	Corrosion rate (AAE)
Sarvandani et al. (2021)	Demolded after 24 hours, cured immersed in water with lime (to evaluate samples without exposure)	After demolding after 24 hours, immersion in a sodium sulfate and magnesium sulfate solution (5% Na ₂ SO ₄ + 5% MgSO ₄) eat pH 4 was carried out for 960 days.	Compressive strength (WAE and AAE); Flexural strength (WAE and AAE)	-	Water absorption by capillarity (WAE)
Sumathi et al. (2023)	Demolded after 24 hours, cured immersed in water	Immersion in sulfuric acid solution (1% H ₂ SO ₄) for 60 days. Immersion in hydrochloric acid solution (1% HCl) for 60 days.	Compressive strength (WAE)	-	Water absorption by capillarity (WAE); Mass loss (AAE)
Varisha, Zaheer e Hasan (2021)	Demolded after 24 hours, cured in water for 28 days	Immersion in magnesium sulfate solution (10% MgSO ₄) at pH 6.5 for 120 days.	Compressive strength (AAE); Flexural strength (AAE)	-	Length expansion (AAE); Ultrasonic pulse velocity (AAE)
Wang et al. (2022)	Demolded after 24 hours, wet curing (20 ± 2 °C and RH of 90%)	Chloride: rapid migration test (according to GB/T 50082-2009)	-	Porosity by mercury intrusion porosimetry (WAE)	Depth of chloride ion diffusion (AAE); Diffusion coefficient in non-stationary state D _{ns} (AAE)
Yu et al. (2024)	Demolded after 24 hours, cured immersed in water for 180 days	Chloride: Drying for 24 hours (50°C) and immersion in a 10% NaCl solution (according to GB/T 50082-2009)	-	-	Diffusion coefficient in non-stationary state D _{ns} (AAE)
Zhang et al. (2023)	Demolded after 24 hours, wet curing for 26 days	The samples were dried (80°C) for 2 days, followed by cycles of immersion in sodium sulfate solution (5% Na ₂ SO ₄) at pH 6-8 for 15 hours, natural drying for 1 hour, and drying in an oven (80°C) for 6 hours, ending with cooling for 2 hours. This cycle was repeated for 120 days.	Compressive strength (AAE)	-	Mass loss (AAE)

CAUTION: TS = test specimens; WAE = property evaluated without aggressive exposure (reference condition); AAE = property evaluated after aggressive exposure; NI = not informed.

3.3 Technical aspects: sulfates and acids

Figure 5 shows a compilation of the main results from those studies that investigated cementitious composites exposed to sulfate solutions and/or acidic media, a total of nine papers. It is worth noting that the study by Karthiyaini et al. (2022) analyzed more than one exposure group, and is discussed both here and in Section 3.4.

To standardize the interpretation, a convention was adopted where positive values represent performance gains and negative values indicate losses, always in relation to the reference mixture (REF). This scheme is also applied in Section 3.4. Thus, for properties in which higher values are desirable (e.g., mechanical strength), the variation was calculated as (MWCNT – REF)/REF; whereas for those in which lower values are favorable (e.g., mass loss, transport coefficients, porosity), the expression (REF – MWCNT)/REF was used. In the scheme used here, gains are shown in green and losses in orange; absolute variations $\leq 5\%$ are considered negligible, and are not colored.

Figure 5: Main results of work involving sulfate and acid attack.

Reference	Matrix	MWCNT content	Exposure	Mechanical strength				Durability and microstructure parameters		
				Gain/Loss in compressive strength		Gain/Loss in flexural strength		Evaluated property	Gain/Loss	
				WAE	AAE	WAE	AAE		WAE	AAE
Alafogianni et al. (2020)	M	0.5%	Sodium sulfate (5% Na ₂ SO ₄)	-	-	-	-	Porosity	+ 21% (112 days)	+ 16% (112 days)
								Water absorption	+ 51% (112 days)	+ 52% (112 days)
								Mass loss	+ 52% (112 days)	+ 7% (112 days)
Bhatrola, Kothiyal e Sameer (2023)	M	0.42%	Sulfuric acid (1% H ₂ SO ₄)	- 2.7% (28 days) + 1.3% (90 days)	+ 42.8% (28 days) + 67% (90 days)	- 1.9% (28 days) - 3.5% (90 days)	-	Electrical resistivity	+ 34.6% (28 days) + 9.8% (90 days)	-
Gao et al. (2021)	C	0.05%	Sodium sulfate (5% Na ₂ SO ₄)	+ 6.5% (28 days)	+ 13% (200 days)	-	-	Mass loss	-	+ 26% (200 days)
Karthiyaini et al. (2022)	C	0.15%	Sulfuric acid (5% H ₂ SO ₄)	+ 27% (28 days)	+ 52% (56 days)			Density	+ 2% (28 days)	+ 52% (56 days)
Liu et al. (2022)	C	0.1%	Sodium sulfate (10% Na ₂ SO ₄)	-	+ 36% (150 days)	-	-	Porosity	-	- 25% (150 days)
			Mass loss		-			- 14% (150 days)		
			Magnesium sulfate (10% MgSO ₄)		+ 59% (150 days)			Porosity	-	+ 13% (150 days)
			Mass loss		-			+ 11% (150 days)		
Sarvandani et al. (2021)	M	0.2%	Sodium sulfate and magnesium sulfate solution (5% Na ₂ SO ₄ + 5% MgSO ₄)	+ 19% (960 d)	+ 41% (960 days)	+ 30% (960 days)	+ 42% (960 days)	Water absorption	+ 39% (90 days)	-
Sumathi et al. (2023)	C	0.2%	Sulfuric acid (1% H ₂ SO ₄)	+ 20% (28 days)	-	-	-	Mass loss	-	+ 28% (60 days)
			Water absorption					+ 70% (28 days)	-	
			Hydrochloric acid (1% HCl)					Mass loss	-	+ 64% (60 days)
Varisha, Zaheer e Hasan (2021)	M	0.3%	Magnesium sulfate (10% MgSO ₄)	-	+ 31.4% (120 days)	-	+ 15.3% (120 days)	Length expansion	-	+ 13% (120 days)
					Ultrasonic pulse velocity		-	+ 25% (120 days)		
Zhang et al. (2023)	C	0.15%	Sodium sulfate (5% Na ₂ SO ₄)	-	+ 21% (120 days)	-	-	Mass loss	-	+ 20% (120 days)

Caption: P = paste; M = Mortar; C = concrete; * cement content replaced by MWCNT; WAE = property evaluated without aggressive exposure (reference condition); AAE = property evaluated after aggressive exposure; NI = not informed.

Highlighting composites with NTCMP that have improved properties. Highlighting composites with NTCMP that worsened the properties.

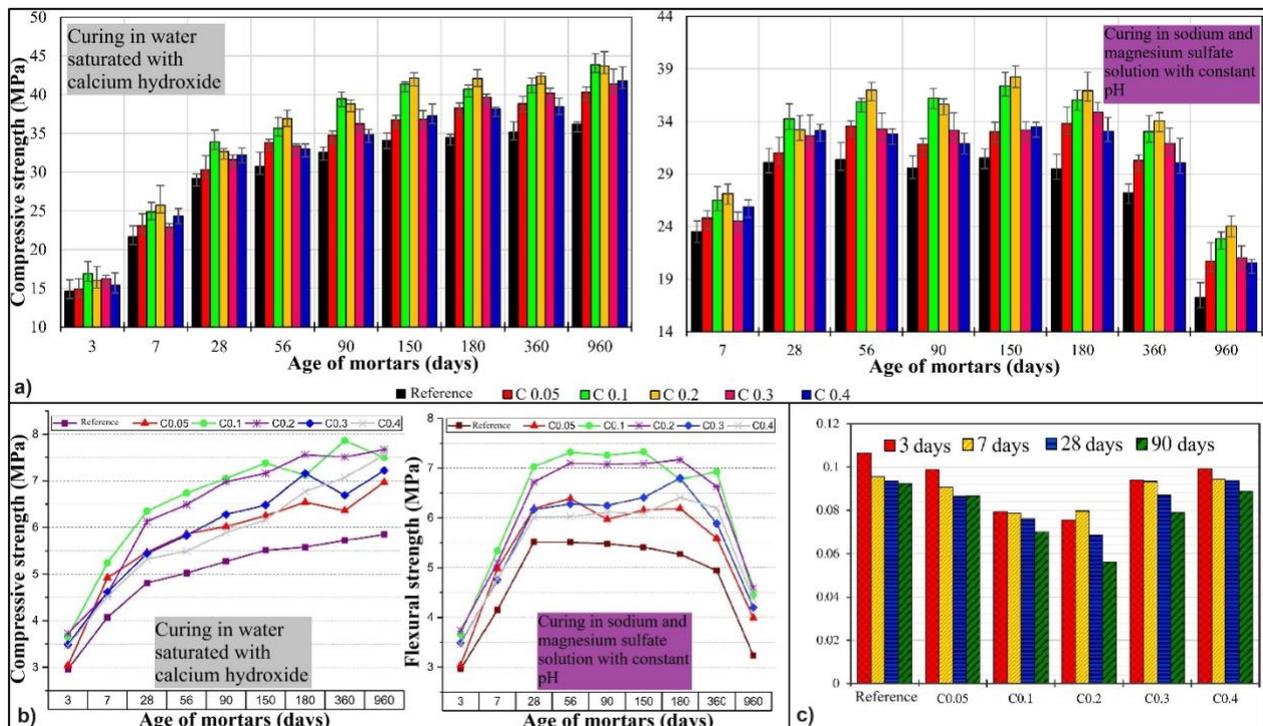
The terms WAE (without aggressive exposure) and AAE (after aggressive exposure) are used to indicate measurements before and after contact with the aggressive medium, respectively. The results are expressed as a percentage variation in relation to REF, and the age of the test appears in parentheses. When a study reported the value of a property at 28 days and this value differed significantly from later ages, the 28-day value was also kept in Figure 5, following the scheme of Bhatrola et al. (2023). When additional evidence was not supplied, only the most representative ages were shown, as in Sarvandani et al. (2021). When the same study involved the testing of multiple MWCNT contents, only the mixture

with the most prominent performance (largest gain or greatest loss) is presented in Figure 5, for ease of reading.

Most studies evaluated sodium and/or magnesium sulfates, while a smaller number investigated sulfuric acid and only one involved hydrochloric acid. In all cases, the exposure was external, and the gains/losses in each case are compared to the REF under the same condition.

In general, the addition of MWCNTs provided gains in mechanical strength compared to the reference mixtures, even after exposure to sulfates and acids. However, all composites showed a progressive loss of performance compared to their own initial conditions, indicating that the nanotubes act only as retarders of deterioration. This effect became clearer in long-term tests, such as that by Sarvandani et al. (2021), reinforcing the view that the results obtained over short periods may overestimate the benefit of MWCNTs.

Figure 6: (a) Results for the compressive strength of mortars cured with lime-saturated water (left side) and sulfate-saturated water (right side) for 960 days; (b) results for flexural strength of mortars cured with lime-saturated water (left side) and sulfate-saturated water (right side) for 960 days; (c) water absorption by capillarity over 90 days.



Source: adapted from Sarvandani et al. (2021)

Figure 6 illustrates the results reported by Sarvandani et al. (2021) in one of the most extensive studies, conducted over 960 days. It can be observed that in terms of both compressive and flexural strength, the composites with MWCNTs showed superior performance to the reference mortar, especially at proportions of 0.1% and 0.2%. Their results showed that although all mortars lost strength over the exposure period, those containing MWCNTs performed better than the REF, with gains of up to 41% in compression and 42% in flexure with 0.2% MWCNTs over 960 days. The authors attributed this effect to the formation of a nanotube network, greater densification of the microstructure, and the bridging effect between hydration products. However, degradation

was found to be inevitable over prolonged periods, confirming that MWCNTs merely delay deterioration mechanisms.

Over the short term, the diffusion of sulfate ions may fill capillary pores and form gypsum and secondary ettringite, producing an apparent gain in strength and lower permeability. With continued exposure, the growth of these products causes volumetric expansion, internal stresses, and detachment, resulting in a sharp loss of strength. This behavior, as noted by Sarvandani et al. (2021), shows that evaluations restricted to short periods overestimate the benefit of MWCNTs, and that long-term tests are essential in order to capture the degradation regime.

In the mortars tested by Sarvandani et al. (2021), which were exposed simultaneously to sodium and magnesium sulfates, the inflection point of strength occurred around 150 days, whereas in the high-performance concretes evaluated by Liu et al. (2022), which were subjected to isolated exposures to each sulfate, the inflection appeared as early as 60 days. This discrepancy is mainly related to the difference in the water/cement ratio (0.485 in mortars and 0.18 in concretes), but also to the exposure regime adopted, which involved continuous immersion in the former study and wet-dry cycles in the latter.

When comparing the two aggressive agents separately, Liu et al. (2022) concluded that sodium sulfate was more harmful than magnesium sulfate, and that it promoted greater increases in porosity. However, according to Escadeillas and Hornain (2014), magnesium sulfate is also recognized as highly aggressive, as it reacts with portlandite and progressively degrades C-S-H, forming brucite and secondary ettringite. In this scenario, MWCNTs contributed to delaying ion diffusion and strengthening the matrix through nucleation and bridging across cracks, although they did not prevent degradation.

Microstructural analyses indicated that the influence of MWCNTs is associated with matrix densification and changes in pore distribution. In some cases, a reduction in total porosity was observed, however showing a redistribution toward pores of greater interconnectivity, which compromises long-term durability. The primary techniques that were applied in these studies were mercury intrusion porosimetry, nitrogen adsorption, capillary absorption, water and gas permeability, as well as complementary tests such as ultrasonic pulse velocity and mass loss as an indicator of deterioration.

In a shorter-term study, Alafogianni et al. (2020) reported that mortars with up to 0.4% MWCNTs showed a porosity reduction of up to 16% after 112 days of exposure to sodium sulfate. Before exposure, the addition of nanotubes increased the proportion of gel and medium capillary pores, reducing the amount of large pores; however, after exposure, this effect was partially reversed, with an increase in medium capillary pores and a reduction in gel pores, indicating that the initial gain was not sustained over the long term.

Studies involving acidic media were fewer, but the results indicated that the incorporation of MWCNTs also helped to mitigate degradation effects, especially in sulfuric acid. The only study that involved hydrochloric acid showed a similar trend, but the authors provided little information about the experimental conditions, which prevented a more accurate comparison.

In summary, MWCNTs provided consistent gains in mechanical strength and durability parameters compared to the reference mixtures, especially in the early periods of exposure to sulfates and acids. However, in all cases, the composites suffered progressive

degradation over time, indicating that the nanotubes act as retarders of deterioration rather than as a definitive barrier. The consensus among the authors is that this improvement is associated with matrix densification, the formation of nucleation sites, and the bridging effect between microcracks, but that long-term durability remains dependent on the severity and duration of exposure.

3.4 Technical aspects: chloride-induced corrosion and carbonation

Figure 7 shows the results for carbonation, chloride action, and reinforcement corrosion, drawn from a total of 10 studies. Only one article addressed the issue of carbonation of the matrix; these authors presented a positive result and adopted an empirical approach to analyze cracking.

Bogas et al. (2021) compared artificial and natural cracks (Figure 8). These authors observed that the carbonation coefficient was always higher in cracked regions, but that the presence of MWCNTs reduced the width of these cracks and resulted in an improvement of up to 18% in carbonation resistance. Despite variability among the cracking conditions, the study suggested that nanotubes may mitigate the propagation of the carbonation front in critical zones. Although their method was interesting, there were large variations in the results, especially between artificial and natural cracks, since the depths of the natural cracks had random values. According to these researchers, the carbonation rate was significantly higher in the cracked area than in the uncracked region. In addition, K_c was increased in concretes with wider cracks.

These results are consistent with those of Carriço et al. (2018), who reported that the carbonation resistance of reinforced concrete with MWCNTs could be improved by up to 16% compared to non-reinforced concrete, and that this effect was scarcely affected by the type of MWCNT. According to Carriço et al. (2018), as their samples were progressively dried, microcracks developed and small micropores became available for gas diffusion. Hence, the addition of MWCNTs could improve this property.

The MWCNT bridges crossing cracks can help to reduce pore connectivity and consequently the diffusion of CO_2 in concrete, as this restrains crack propagation and reduces the width of microcracks. It is possible that the nucleation effect improved carbonation resistance by densifying the concrete microstructure and increasing the amount of carbonated compounds in the cementitious matrix (BOGAS et al., 2021).

Figure 7: Main results of studies involving chlorides and carbonation.

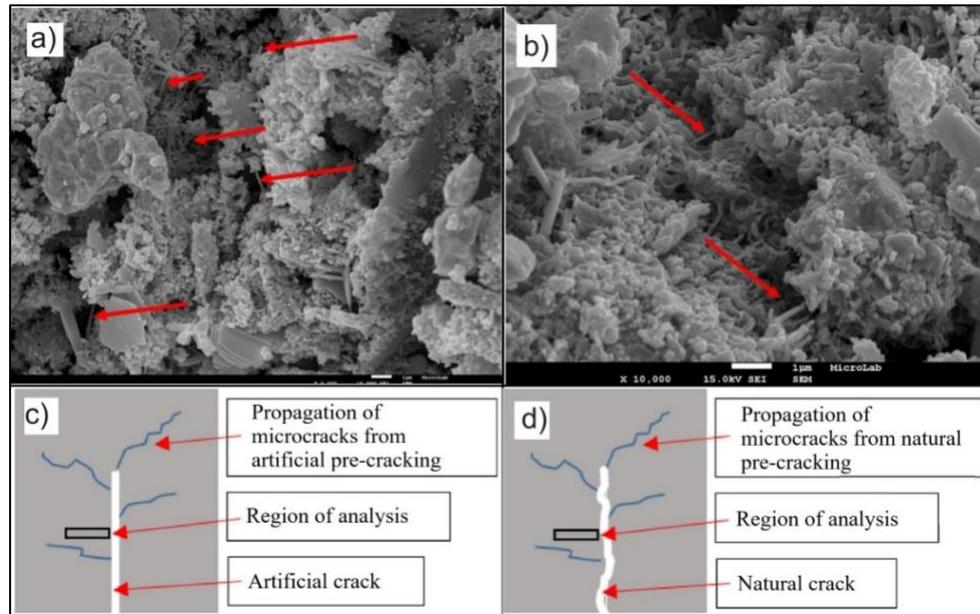
Reference	Matrix	MWCNT content	Exposure	Mechanical strength				Durability and microstructure parameters		
				Gain/Loss in compressive strength		Gain/Loss in flexural strength		Evaluated property	Gain/Loss	
				WAE	AAE	WAE	AAE		WAE	AAE
Bogas, Ahmed e Diniz (2021)	C	0.1%	Carbonation	+ 9.7% (28 days)	-	-	-	K _c	-	+ 18% (90 days)
			Chloride (rapid migration)					Water absorption	+ 12% (28 days)	-
			D _{ns}					-	+ 6.7%	
Chukka et al. (2022)	C	2.0% *	Chloride	+ 17% (90 days)	-	+ 40% (90days)	-	Water absorption	+ 8% (90 days)	-
								Porosity	+ 9% (90 days)	-
								Mass loss	-	+ 23% (28 days)
								Passing electrical charge	-	+ 68% (28 days)
Gamal et al. (2021)	C	0.01%	Chloride	+ 13% (28 days)	-	+ 15% (28 days)	-	Water absorption	- 150% (28 days)	-
								Passing electrical charge	-	- 78% (28 days)
								Corrosion rate	-	+ 62% (30 days)
								Adhesion of bars	- 18%	- 31%
Han et al. (2023)	C	0.15%	Chloride (rapid migration)	-	-	-	-	Depth of chloride ion diffusion	-	+ 26% (28 days)
			Chloride (natural migration)					D _{ns}	-	+ 19% (28 days)
			Chloride: transition zone analysis					Free chloride ions	-	+ 17% (120 days)
			Chloride					Depth of chloride ion diffusion in matriz	-	+ 17% (28 days)
			Chloride					Depth of chloride ion diffusion in transition zone	-	+ 17% (28 days)
Karthiyaini et al. (2022)	C	0.15%	Chloride	+ 27% (28 days)	+ 30% (56 days)	-	-	Density	+ 1.2% (28 days)	+ 0.9% (56 days)
Li et al. (2020)	M	0.2%	Chloride (rapid migration)	+ 12% (28 days)	-	-	-	D _{ns}	-	- 427%
			Chloride (natural migration)					D _s	-	- 18% (65 days)
			Electrochemical corrosion by sodium chloride					Electrical resistivity	- 16% (28 days)	-
								Corrosion rate	-	- 330% (3 days)
								Loss of steel mass	-	- 385 % (3 days)
MacLeod, Gates e Collins (2020)	P	0.05%	Chloride	-	-	-	-	Water absorption	+ 1.2 (28 days)	-
								Water permeability	- 280 (28 days)	-
								D _s	-	+ 63% (270 days)
Ming et al. (2020)	C	12.5%*	EIE in sodium chloride	+ 41% (30 days)	-	-	-	Corrosion rate	-	+ 44% (30 days)
Wang et al. (2022)	M	0.1%	Chloride (rapid migration)	+ 25% (28 days)	-	-	-	Porosity	+ 34% (28 days)	-
								D _{ns}	-	+ 26% (28 days)
								Depth diffusion	-	+ 13% (28 days)
Yu et al. (2024)	C	0.25%	Chloride (rapid migration)	-	-	-	-	D _s	-	+ 74%

Caption: P = paste; M = Mortar; C = concrete; * cement content replaced by MWCNT; WAE = property evaluated without aggressive exposure (reference condition); AAE = property evaluated after aggressive exposure; NI = not informed.

Highlighting composites with NTCPM that have improved properties.	Highlighting composites with NTCPM that worsened the properties.
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The authors also evaluated the rapid migration of chlorides through the cementitious matrix, and observed a large difference in the diffusion coefficient for the naturally cracked zone compared to the standard method. When the effect of MWCNTs was isolated, a significant reduction was found when comparing the two concretes within the region, with reduction in the diffusion coefficient of up to 35%. This demonstrates the importance of applying methods that can approximate real exposure conditions and can simulate what happens after cracking.

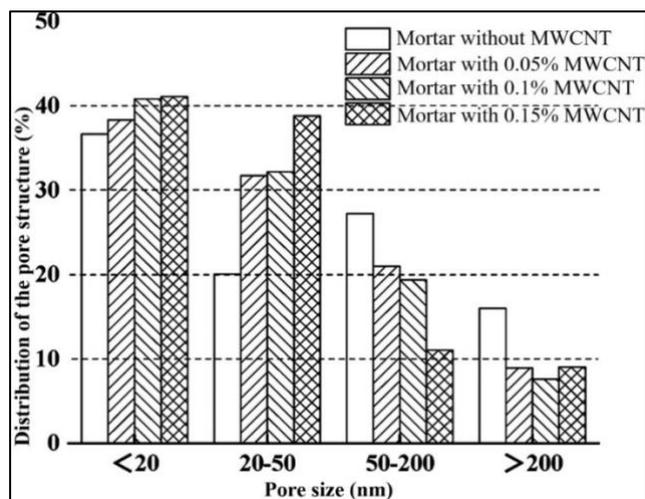
Figure 8: SEM images of concrete with MWCNT (a) artificially cracked and (b) naturally cracked, where the arrows indicate MWCNT tips or bridges; (c) and (d) diagram the concrete region analyzed in the SEM analysis.



Source: adapted from Bogas et al. (2021).

Yu et al. (2024) evaluated mortars with different types of MWCNT (varying in diameter, length, functionalization, and morphology), and observed reductions of up to 77% in chloride penetration for MWCNT proportions of 0.25% and 0.5%. These gains were attributed to microstructural refinement, with the formation of denser C-S-H gels, smaller CH crystals, and reduced capillary pores. Similarly, Han et al. (2023) observed reductions in porosity proportional to the MWCNT content in concretes, and highlighted the pore-filling and crack-bridging effects as the main mechanisms. This effect can be seen in Figure 9, which shows that the pore structure distribution gradually improves with increasing MWCNT content.

Figure 9: Pore size distribution.



Source: Han et al. (2023).

Han et al. (2023) conducted an empirical test to evaluate the depth of chloride ion diffusion in the transition zone between limestone and mortar. Despite porosity reductions in both

the matrix and the transition zone (-17%, Figure 7), a comparison of these two regions indicated that the chloride ion diffusion depth increased in the interfacial transition zone, regardless of the presence of MWCNTs. This highlights the importance of using more sophisticated methods to assess chloride diffusivity. Han et al. (2023) stated that under natural immersion conditions, the MWCNTs filled concrete pores and improved the structure, thus reducing the connectivity of the pores as well as increasing the compactness and resistance to chloride ions.

With the exception of the study by MacLeod et al. (2020), which evaluated pastes, most works on cementitious composites under the action of chlorides and carbonation reported improvements in mechanical properties and durability parameters with the addition of MWCNTs. These gains were attributed to matrix densification, the role of nanotubes as nucleation sites, and the bridging effect in stress transfer across microcracks. However, some studies emphasized that simply reducing the total porosity does not necessarily imply lower interconnectivity or smaller pore size, which reinforces the importance of conducting thorough and well-designed long-term studies capable of accurately and reliably assessing the long-term performance.

The results for reinforcement corrosion were less consistent. Ming et al. (2020) observed significant benefits by partially replacing cement with blast-furnace slag and adding 12.5% MWCNTs. They found that such concretes exposed to a 3.5% NaCl solution had higher compressive strength, lower water absorption, and a significant reduction in corrosion current density, which they attributed to lower chloride permeability and decreased interstitial solution conductivity.

In contrast, Li et al. (2020) and Gamal et al. (2021) reported negative results. These studies, in addition to being fewer in number, lacked detailed information on methodology and testing conditions, which makes direct comparisons difficult. Hence, there is still no conclusive evidence that the addition of MWCNTs consistently contributes to reducing reinforcement corrosion, although several studies report gains in performance regarding chloride action and carbonation, as well as in terms of matrix densification (which projects potentially positive results in relation to reinforcement corrosion).

4 Final Considerations

This systematic literature review has shown that the incorporation of MWCNTs into cementitious composites, even at low proportions, tends to improve mechanical strength and refine the microstructure, resulting in temporary gains against attacks by sulfates, chlorides, carbonation, and acidic media. The most frequent mechanisms that could be identified were the formation of nucleation sites, a bridging function between microcracks, and matrix densification.

However, it was found that these benefits do not eliminate long-term degradation studies, with careful analysis of the effective long-term gain and the discarding of actions that only delay deterioration. Furthermore, the great heterogeneity of the available nanotubes (in terms of their dimensions, purity, and functionalization), combined with the different dispersion methodologies, matrix compositions, and testing conditions, explains the lack of consensus in part of the results.

Thus, although the addition of MWCNTs appears to be promising in regard to increasing the durability of cementitious composites, realizing this potential will depend on greater

experimental standardization, evaluation under exposure conditions that are closer to reality, and comparative analyses among different dispersion routes. Future research should prioritize the optimization of nanotube content and dispersion, in order to maximize the benefits with lower costs and greater practical applicability.

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