# Nano-Engineered Cementitious Composites

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## Principles and Practices

Springer

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ISBN 978-981-13-7077-9 ISBN 978-981-13-7078-6 (eBook)
https://doi.org/10.1007/978-981-13-7078-6

Library of Congress Control Number: 2019933712

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*To the families!*
Baoguo Han, Siqi Ding, Jialiang Wang,
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# Preface

Cement has been used for millennia. However, no one knows for sure who first came up with the idea to use a cement substance to make civil engineering materials. In general terms, the word cement refers to any binder that sets, hardens, and tightly holds other materials together. Most used cement is inorganic and hydraulic including Portland cement and other cements (e.g., calcium aluminate cement, supersulfated cement, calcium sulfoaluminate cements, and geopolymer cement). Cement is seldom used solely but is used with sand to produce mortar, or with sand and gravel to produce concrete. Therefore, cementitious composites (also called cement-based composites) refer to all materials made of cement in a generalized concept. They include concrete (containing coarse and fine aggregates), mortar (containing fine aggregates), and binder only (containing no aggregate, whether coarse or fine). In this book, cementitious composites refer in particular to Portland cement-based composites unless otherwise stated, because of previous research and application of nano-engineered cementitious composites focused mainly on cementitious composites fabricated with Portland cement.

Thanks to their excellent mechanical strength, resistant to water, easily formed into various shapes and sizes, and cheap and readily available everywhere, cementitious composites are the most widely used civil engineering materials and serve as the primary materials in constructing the infrastructures necessary to provide society with basic safety and living requirements. It was reported that China had used more cementitious composites between 2011 and 2013 (3 years) that has been used by the USA in the entire twentieth century, indicating that Chinese economic growth is especially reliant on infrastructure development and more precisely on the usage of cementitious composites. This is not only evident in China as the pattern can be observed across the whole world with many countries demonstrating unprecedented growth in the cementitious composite industry. The usage of cementitious composites has been increasing with the result that cementitious composites have become the second-most used resources in the world after water. Twice as much cementitious composites are used in infrastructures around the world as the total of all other building materials, including wood, steel, plastic, and aluminum. Production and application of cementitious composites have a significant impact on resources, energy, and environment. Although the cement production needs intensive energy, cementitious composites have more excellent ecological profile than other construction materials such as metal, glass and polymers. Compared with other construction materials, the production of cementitious composites consumes the least amount of materials and energy, produces the least amount of harmful by-products, and causes the least amount of damage to environment. Cementitious composites are a responsible choice for sustainable development of society. As human populations continue to grow and urbanize, cementitious composites will continue to play an important role in infrastructure construction. However, the development of cementitious composites is encountering enormous problems and challenges. (1) Cement manufacturing has a direct and visible negative impact on the world's resources, energy consumption and environment. For example, making 1 ton of cement requires about 2 tons of raw material (limestone and shale), consumes about 4 GJ of energy in electricity, process heat, and transport (energy equivalent to 131 cubic meters of natural gas), produces approximately 1 ton of $CO_2$, about 3 kg of $NO_X$ (an air contaminant that contributes to ground-level smog), and about 0.4 kg of PM10 (an airborne particulate matter harmful to respiratory tract when inhaled). (2) The properties/performances (e.g., mechanical properties/performances, dimensional stability, durability, workability and functional/smart properties/performances) of cementitious composites should be further improved or modified to maintain sustainable development of cementitious composites and infrastructures. In general, cementitious composites have a relatively high compressive strength, but are significantly more brittle and exhibit a poor tensile strength. They carry flaws and micro-cracks both in the material and at the interfaces even before an external load is applied. These defects and micro-cracks emanate from excess water, bleeding, plastic settlement, thermal and shrinkage strains, and stress concentrations imposed by external restraints, etc. Under an applied load, distributed micro-cracks propagate, coalesce, and align themselves to produce macro-cracks. When loads are further increased, conditions of critical crack growth are attained at the tip of the macro-cracks, and unstable and catastrophic failure is precipitated. Under fatigue loads, cementitious composites crack easily, and cracks create easy access routes for deleterious agents. This will lead to early saturation, freeze-thaw damage and scaling, discoloration, and so on. Additionally, the durability of concrete has become increasingly important as there has been a push to extend the life expectancy of existing and planned infrastructures. Due to the degeneration of cementitious composites, complex interaction between cementitious composites and their service environment, absence of advanced design and condition assessment tools and timely maintenance, many infrastructures fabricated with cementitious composites are in a state of utter disrepair. For example, more than 50% of Europe's annual construction budget is devoted to repair and maintenance of existing infrastructures. For example, the cost of maintenance of bridges and buildings in Europe exceeds €1 and €20 billion per year, respectively; with a significant part of this being spent on repair of infrastructures made of cementitious composites. What's more, cementitious composites belong to primary and complex materials in nature. Their behaviors during the life cycle should be able to be controlled through mass, energy or information exchange with external environment. Multifunctional and smart cementitious composites are required since traditional cementitious composites just serving as structural materials cannot meet the upgrading requirement in terms of safety, longevity, and function of advanced engineering infrastructures. (3) Cementitious composites are multi-component, multi-phase, and multi-scale materials in nature. Its compositions mainly include cement, water, aggregates, chemical admixtures, and mineral admixtures. The proportion of these components can vary within a flexible and wide range. Hardened cementitious composites contain solid, liquid, and gas phases. Their structure covers over ten orders of magnitude in size, ranging from nanometers (e.g., hydration product) to micrometers (e.g., binder), and then from millimeters (e.g., mortar and concrete) to tens of meters (final structures). In addition, the cementitious composites feature time variant characteristic because cement hydration is a long-term evolutionary progress and hydration products are thermodynamic instability. The complex compositions and structures of cementitious composites have not been completely understood yet, which limits the utility and predictability of cementitious composites in critical applications but offers opportunities for the formulation of additional control.

The properties/performances of cementitious composites closely depend on their compositions, fabrication/processing, and structures. The compositions and structures of cementitious composites exist in multiple length scales (nano to micro to macro) where the properties/performances of each scale derive from those of the next smaller scale. Big changes in micro-macroscale behaviors of cementitious composites are predicted form the nanoscale impact. Even with small changes in the nanoscale where properties/performances differ significantly from those at a larger scale, need-driven innovative design and production of materials and infrastructures could lead to large accumulated benefits, such as lower use of raw materials, improved properties, and higher construction efficiency that make infrastructures stronger, more durable, multifunctional/smart, resource and energy-efficient, and environment-friendly throughout their life cycle. Therefore, nano science and technology opens up new visionary opportunities that may build up a fundamental for comprehensively understanding the genomic code of cementitious composites in nature, featuring the blueprint to describe, predict, and control properties of cementitious composites from the bottom-up (i.e., from nanoscale to micro–macro-scale) approach, and providing guide for design, fabrication, and applications of cementitious composites.

Since cementitious composites are nanostructure in nature and feature obvious nano-behaviour, nanoscience and nanotechnology has the great potential to engineer cementitious composites with superior mechanical performance, durability, and sustainability. For example, the size of the calcium silicate hydrate, the primary hydration products responsible for such properties as mechanical properties, dimensional stability, and durability in cementitious systems, lies in the few nanometers range. In addition, there inevitably exist nanoscale particles in cement or mineral admixtures (in the case of using mineral admixtures, especially submicron-scale silicon fume). However, these nanoscale phenomena or behaviors in cementitious composites do not receive enough attention. In the early 2000s, the nano science and technology in cementitious composites garnered increased scientific and commercial attention because the nano science and technology has created great excitement and expectations in other fields. The basic principle of nano-engineered cementitious composites is based on multiscale and multicomponent composition. The nano-engineered cementitious composites are achieved through material composition design, special processing, and modification of microstructure. The initial approach for developing nano-engineered cementitious composites is nano-modification by adding nanomaterials such as nano-$ZrO_2$, nano-$SiO_2$, and nano-$TiO_2$. Since then, some novel approaches (e.g., adding nano-seed, using nano-cement or mineral admixtures, and using cement, mineral admixtures, or aggregates with nanomaterial modification) are continuously developed. In the past nearly two decades, much work has been done on the development and deployment of nano-engineered cementitious composites. This book provides a summary report on current researches in the field of nano-engineered cementitious composites to help people working on this particular aspect to their job better.

This book covers theory, techniques, and applications of nano-engineered cementitious composites containing their design, fabrication/processing, test/characterization and simulation, properties/performances and their control methods, mechanisms and models, applications, and future development. This book is organized as shown below. The first part provides a general introduction to the basic principles of nano-engineered cementitious composites (Chap. 1) and current progress of nano-engineered cementitious composites (Chap. 2). The second part presents the authors' research results in this area involving carbon nanotubes-engineered cementitious composites (Chap. 3), graphene-engineered cementitious composites (Chap. 4), nano-$SiO_2$-engineered cementitious composites (Chap. 5), nano-$TiO_2$-engineered cementitious composites (Chap. 6), nano-$ZrO_2$-engineered cementitious composites (Chap. 7), nano-BN-engineered cementitious composites (Chap. 8), and electrostatic self-assembled carbon nanotube/nano-carbon black composite fillers-engineered cementitious composites (Chap. 9). Finally, the third part discusses the future developments and challenges of nano-engineered cementitious composites (Chap. 10).

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| Dalian, China | Jinping Ou |

# Acknowledgements

Many professional colleagues and friends have contributed directly or indirectly to this book: Xun Yu, Wei Zhang, Danna Wang, Liqing Zhang, Yanfeng Ruan, Zhen Li, Xia Cui, Shan Jiang, Qiaofeng Zheng, Shengwei Sun, Yunyang Wang, Chenyu Zhang, Zhu Wang, Linyang Han, Shuzhu Zeng, Sufen Dong, and Xinyue Wang. The authors thank all of them most sincerely. This book is funded by the National Science Foundation of China (grant nos. 51578110, 51428801, 51178148, and 50808055), Program for New Century Excellent Talents in University of China (grant no. NCET-11-0798), the Ministry of Science and Technology of China (grant no. 2011BAK02B01), and the Fundamental Research Funds for the Central Universities in China (grant no. DUT18GJ203). We also thank Springer for his enthusiastic and hard work to make the publication of possible.

# Contents

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# Abbreviations

| | |
|---|---|
| AC | Alternating current |
| AFM | Atomic force microscope |
| AFm | Monosulfate |
| AFt | Ettringite |
| ANT | Aluminosilicate nanotube |
| B | Binder |
| C | Cement |
| CF | Carbon fiber |
| CH | Calcium hydroxide |
| CL | Crushed limestone |
| CNC | Cellulose nanocrystals |
| CNF | Carbon nanofiber |
| CNF* | Cellulose nanofibrils |
| CNM | Calcined nano-montmorillonite |
| CNT | Carbon nanotube |
| C-S-H | Calcium silicate hydrate |
| DC | Direct current |
| DSC | Differential scanning calorimetry |
| DTG | Derivative TG |
| EDS | Energy-dispersive spectrometer |
| EIS | Electrochemical impedance spectroscopy |
| FA | Fly ash |
| G | Gravel |
| GGBFS | Ground granulated blast furnace slag |
| GO | Graphite oxide |
| HD | Hydration degree |
| ITZ | Interfacial transition zone |
| MCL | Mean chain length |
| MIP | Mercury intrusion porosimetry |
| MLG | Multi-layer graphene |

| | |
|---|---|
| MWCNT | Multi-walled CNT |
| NaDDBS | Sodium dodecylbenzene sulfonate |
| NCB | Nano-carbon black |
| NCBF | Nano-carbonized bagasse fiber |
| NFC | Nanofibrillated cellulose |
| NK | Nano-kaolinite |
| NM | Nano-montmorillonite |
| NMK | Nano-metakaolin |
| NMR | Nuclear magnetic resonance |
| PD | Polymerization degree |
| PVA | Polyvinyl alcohol |
| RH | Relative humidity |
| RHA | Rice husk ash |
| S | Sand |
| SDS | Sodium dodecyl sulfate |
| SEM | Scanning electron microscope |
| SF | Silica fume |
| SHM | Structural health monitoring |
| SP | Superplasticizer |
| SWCNT | Single-walled CNT |
| TEM | Transmission electron microscope |
| TG | Thermogravimetry |
| W | Water |
| W/B | Water-to-binder ratio |
| W/C | Water-to-cement ratio |
| XRD | X-ray diffraction |