

**NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
POLITEHNICA BUCHAREST**



**Faculty of Chemical Engineering and Biotechnologies
Department of Science and Engineering of Oxide Materials and Nanomaterials**

PhD Thesis

**NANOPOWDERS USED IN BINDER MIXTURES
FOR SPECIAL APPLICATIONS
- Resume -**

PhD Supervisor

Prof. Dr. Eng. Georgeta VOICU

PhD Student

Eng. Andrei-Vlad ZANFIR

PhD committee

Committee president	Prof. Dr. Eng. Ștefan VOICU	From	National University of Science and Technology POLITEHNICA Bucharest
PhD Supervisor	Prof. Dr. Eng. Georgeta VOICU		
Member	Prof. Dr. Eng. Ștefania-Paula STOLERIU		
Member	Prof. Dr. Eng. Ionela POPOVICI	From	Ovidius University Constanța
Member	Prof. Dr. Eng. Constantin Dorinel VOINIȚCHI	From	Technical University of Construction Bucharest

BUCHAREST

2024

PART I – Literature Study

Chapter 1. Introductory Elements on Inorganic Binders

1.1 Inorganic Binders for Construction

1.2 Bio-inorganic Binders

Chapter 2. Additives Used in Inorganic Binder Systems

2.1 Hydraulically Active and Inert Additives

2.2 Nanopowders Used in Inorganic Binder Systems with Special Applications

2.2.1 Types of Nanopowders Used in Inorganic Binder Systems

2.2.2 Special Properties of (Nano)powders Used in Inorganic Binder Systems with Special Applications

PART II – Original Contributions

Chapter 3. Motivation and Objectives of the Study

Chapter 4. Special-purpose Construction Binder Mixtures with Added ultrafine silica (SUF) - TiO₂ Powders

Chapter 5. Bio-binders of Silicate Clinker - ammonium phosphate with and without Added Nanopowders

Chapter 6. Calcium Silicophosphate Bio-binders with Improved Properties through the Addition of Nanopowders

General Conclusions and Originality

Dissemination of Results

References

Keywords: Binding materials, nanoparticles, silicates, sol-gel, photocatalysis, tissue engineering, nano-biocellulose, nano-BaTiO₃, nano-TiO₂, self-cleaning, bioavailability, cell proliferation, oxidative stress.

LIST OF FIGURES

PARTEA I – Studiu literatură

Figure 1.1. Formation of mineralogical phases in the burning process of Portland cement clinker

Figure 1.2. Pseudostructure of tricalcium silicate [2]

Figure 1.3. Hydration rate of phases in Portland cement paste [3]

Figure 1.4. Compressive strength development over time by mineralogical phases in Portland cement [3]

Figure 1.5. Hydration stages of C3S based on heat evolution [3]

Figure 1.6. Classification of calcium phosphate cements, setting mechanism, and microstructural characteristics [19]

Figure 2.1. Hydration of pure cement (A) and cement with the addition of inert nanoparticles (B) or reactive nanoparticles (AHA type) forming C-S-H phases (C) at different times after mixing (1-3) [51]

Figure 2.2. Schematic of the photocatalytic process [130]

PART II – Original Contributions

Figure 4.1. Schematic for obtaining SUF-TiO₂ powder (M3)

Table 4.1. Compositions for TiO₂-based powders

Figure 4.2. Complex thermal analysis for dried M3 gel

Figure 4.3. Morphological and structural characterization of ultrafine silica powder (SUF): a- SEM images; b- EDX spectrum; c- X-ray diffraction pattern; d- TEM and HRTEM images

Figure 4.4. X-ray diffraction analysis for TiO₂ (a) and SUF-TiO₂ (M3) powders, both as dried gel and thermally treated at 450°C/2h. A- anatase (JCPDS 84-1286) and B- brookite (JCPDS 76-1934)

Figure 4.5. SEM (a) and TEM (b) images of TiO₂ powder thermally treated at 450°C/2h (an-anatase, br-brookite)

Figure 4.6. SEM (a) and TEM (b) images of M1 powder thermally treated at 450°C/2h (an-anatase)

Figure 4.7. SEM (a) and TEM (b) images of M2 powder thermally treated at 450°C/2h

Figure 4.8. SEM with EDX spectroscopy (a) and TEM (b) images of M3 powder thermally treated at 450°C/2h

Figure 4.9. FT-IR spectra for M1, M2, and M3 powders, thermally treated at 450°C/2h

Table 4.2. BET surface area and hydraulic activity of SUF and M1-M3 powders thermally treated at 450°C/2h

Figure 4.10. Absorption spectra of methylene blue solution (MB-0h) and MB with TiO₂ nanopowder and SUF-TiO₂ powder after various UV exposure times

Table 4.3. Photocatalytic degradation rate constant for methylene blue solution

Figure 4.11. Photocatalytic activity of TiO₂ nanopowder and SUF-TiO₂ powders after various UV exposure times

Table 4.4. Oxide and phase composition of Portland cement

Table 4.5. Composition of mixed cements (%)

Figure 4.12. Standard consistency water for binder pastes with 0% and 5% photocatalytic powders

Figure 4.13. Setting time for binder pastes with 0% and 5% photocatalytic powders, at standard consistency

Figure 4.14. Compressive strength of plastic mortars based on binders with 0% and 5% SUF, cured for 1-90 days

Figure 4.15. Compressive strength of plastic mortars based on binders with 0% and 5% photocatalytic powders, cured for 1-90 days

Figure 4.16. Compressive strength of plastic mortars based on binders with 3% photocatalytic powders, cured for 1-90 days

Figure 4.17. Absorption spectra of rhodamine B solution (RB) in pastes with varying amounts (1%, 3%, 5%) of SUF-TiO₂ powder (M1, M2, M3) after different UV exposure times

Table 4.6. Mass loss from thermal analysis for E, M1, M2, M3, and SUF samples

Figure 4.18. Mass loss for E pastes and pastes with 1%, 3%, and 5% M1, M2, and M3, cured for 1, 7, and 28 days

Figure 4.19. X-ray diffraction images of pastes with 5% fine powders, cured for 1, 7, and 28 days: M1-5 -a; M2-5-b; M3-5-c; E-d

Figure 4.20. SEM images and energy-dispersive X-ray (EDX) spectrum for plastic mortars E cured for 7 (a) and 28 days (b)

Figure 4.21. SEM images and EDX spectrum for plastic mortars M1-5 cured for 7 (a) and 28 days (b)

Figure 4.22. SEM images and EDX spectrum for plastic mortars M2-5 cured for 7 (a) and 28 days (b)

Figure 4.23. SEM images and EDX spectrum for plastic mortars M3-5 cured for 7 (a) and 28 days (b)

Table 5.1. Oxide composition of the obtained silicate cements;

Table 5.2. BET specific surface area and density of the biocement components;

Table 5.3. Characteristics of the raw materials used in sol-gel synthesis;

Figure 5.1. Scheme of the composite biobinder synthesis of calcium-silico-phosphate cement type with/without biocellulose or barium titanate content;

Figure 5.2. X-ray diffraction patterns of the obtained calcium-silicate clinkers;

Figure 5.3. Scanning electron microscopy images of the synthesized clinkers;

Figure 5.4. Free CaO values for the synthesized clinkers;

Figure 5.5. X-ray diffraction for biocellulose treated by autoclaving at 100°C/24h in a basic medium - 8M KOH;

Figure 5.6. Complex thermal analysis for biocellulose treated by autoclaving at 100°C/24h in a basic medium - 8M KOH;

Figure 5.7. Scanning electron microscopy images for biocellulose powder treated by autoclaving at 100°C/24h in a basic medium - 8M KOH;

Figure 5.8. Scanning electron microscopy images and particle size distribution of barium titanate powder synthesized at 120°C, held for 24h, in a 4M KOH solution;

Figure 5.9. X-ray diffraction images (a), transmission electron microscopy (b1- TEM, b2- HRTEM, b3- SAED, b4- EDX) and Raman spectrum (c) for barium titanate powder obtained hydrothermally at 120°C, held for 24h, in a 4M KOH solution;

Table 5.4. Setting time characteristics of binder pastes obtained by mixing the solid component with an aqueous NH₄H₂PO₄ solution at 2.5M, for a p/l ratio of 1.5 (0.75g powder + 0.5 ml NH₄H₂PO₄ at 2.5M);

Figure 5.10. Setting time characteristics of binder pastes obtained by mixing the solid component with an aqueous NH₄H₂PO₄ solution at 2.5M in a p/l ratio of 1.5;

Table 5.5. Setting time and compressive strength of samples after different curing intervals;

Figure 5.11. Mechanical strength of hardened binder masses at 37°C, 100% relative humidity, stored in: water – a and air - a, b, c;

Figure 5.13. X-ray diffraction patterns of K1, K2, and K1' binder masses cured for 7, 14, and 28 days, at 37°C, 100% relative humidity, stored in water;

Figure 5.12. X-ray diffraction patterns of K1, K2, and K1' binder masses cured for 7, 14, and 28 days, at 37°C, 100% relative humidity, stored in air;

Figure 5.14. X-ray diffraction patterns of K1, K2, and K1' binder masses with BT and BC additions cured for 28 days, at 37°C, 100% relative humidity, stored in air;

Figure 5.15. Variation in absorption, porosity, and density of binder masses: a- cured for 28 days at 37°C, 100% relative humidity, and b - immersed in SBF for 14 days at 37°C after curing for 14 days at 37°C, 100% relative humidity;

Figure 5.16. SEM images at different magnifications and EDAX for K1, K'1, and K2 cured for 28 days;

Figure 5.17. SEM images at different magnifications and EDAX for K1-BC, K'1-BC, and K2-BC cured for 28 days;

Figure 5.18. SEM images at different magnifications and EDAX for K1-BT, K'1-BT, and K2-BT cured for 28 days;

Figure 5.19. SEM images at different magnifications for K1, K'1, and K2 cured for 14 days and immersed in SBF for 14 days at 37°C;

Figure 5.20. SEM images at different magnifications for K1-BC, K'1-BC, and K2-BC cured for 14 days and immersed in SBF for 14 days at 37°C;

Figure 5.21. SEM images at different magnifications for K1-BT, K'1-BT, and K2-BT cured for 14 days and immersed in SBF for 14 days at 37°C;

Figure 5.22. Cell proliferation - a, and oxidative stress - b determined on different binder masses cured for 14 days in contact with AFSC;

Figure 5.23. Optical fluorescence microscopy (x20) for cements in contact with AFSC for 24 hours;

Figure 5.24. Optical microscopy (x20) for cements in contact with AFSC for 24 hours;

Table 6.1. Reagents used in the synthesis of calcium-silicate oxide masses;

Figure 6.1. Scheme for obtaining calcium-silicate powders based on wollastonite;

Figure 6.2. X-ray diffraction analysis - a, and complex thermal analysis - b for the dried calcium-silicate gel;

Figure 6.3. X-ray diffraction for the dried gel thermally treated at 1000°C/3h, cooled at equilibrium (W1) - a, and rapidly cooled (W2) - b;

Figure 6.4. Particle size distribution curves for calcium-silicate masses W1 - a and W2 - b.

Table 6.2. Composition characteristics of partially neutralized phosphoric acid aqueous solutions.

Table 6.3. Composition characteristics of partially neutralized phosphoric acid aqueous solutions.

Figure 6.5. Variation of setting time with the liquid-to-powder ratio (l/p) for the binding materials made with powder W1 and liquids C1, C2, F2, and F3.

Figure 6.6. Variation of setting time with the liquid-to-powder ratio (l/p) for the binding materials made with powder W2 and liquids C1, C2, F2, and F3.

Figure 6.8. Variation of compressive strength with the liquid-to-powder ratio (l/p) for the binding materials made with powder W2 and liquid F3, cured at 37°C, 100% relative humidity.

Figure 6.7. Variation of compressive strength with curing period and working temperature for the binding materials made with: liquid F1 and powders W1-a and W2-b, at $l/p=2$; liquid C2 and powder W2-c, at $l/p=1$.

Figure 6.9. X-ray diffraction images at different working temperatures and curing periods for binding materials made with powders W1 and W2 and liquid F1 ($l/p=2\text{ml/g}=0.91\text{ mol/mol}$).

Figure 6.10. X-ray diffraction images at different working temperatures and curing periods for binding materials made with powder W2 and liquid C2 ($l/p=1\text{ml/g}=1.42\text{ mol/mol}$).

Figure 6.11. X-ray diffraction images at different liquid-to-powder ratios and curing periods for binding materials made with powder W2 and liquid F3 ($l/p=0.7\text{ml/g}=2.07\text{ mol/mol}$; $l/p=0.8\text{ml/g}=1.81\text{ mol/mol}$), cured at 37°C, 100% relative humidity.

Figure 6.12. Complex thermal analyses at different working temperatures, 22°C- a1, a2 and 37°C- b1, b2, and curing periods of 7 and 14 days, for binding materials made with powder W1 (a1 and b1), W2 (a2 and b2) and liquid F1 ($l/p=2\text{ml/g}=0.91\text{ mol/mol}$).

Table 6.4. Setting time (min.) and compressive strength after 28 days at 37°C, 100% relative humidity, for binding pastes made with liquid F3 at different liquid-to-powder ratios (ml/g).

Figure 6.13. Complex thermal analyses at different working temperatures, 22°C- a and 37°C- b, and curing periods of 7 and 14 days, for binding materials made with powder W2 and liquid C2 ($l/p=1\text{ml/g}=1.42\text{ mol/mol}$).

Figure 6.14. Complex thermal analyses at different curing periods of 7 and 14 days, for binding materials made with powder W2 and liquid F3 ($l/p=0.7\text{ml/g}=2.07\text{ mol/mol}$ -a, $l/p=0.8\text{ml/g}=1.81\text{ mol/mol}$ - b), cured at 37°C, 100% relative humidity.

Figure 6.15. Electron microscopy images of binding materials based on liquid F3 at an l/p ratio of 0.8 ml/g.

Figure 6.16. Cell proliferation determined on various binding materials cured for 14 days in contact with AFSC.

Figure 6.17. Oxidative stress determined on various binding materials cured for 14 days in contact with AFSC.

Figure 6.18. Molecular biology results on various binding materials cured for 14 days.

Figure 6.19. Variation in absorption, porosity, and density of cured binding materials: a- 28 days at 37°C, 100% relative humidity; b- cured for 14 days at 37°C, 100% relative humidity, and immersed in SBF for 14 days at 37°C.

PART I – Literature Study

Inorganic binders are materials or mixtures of materials in powder form that, through interaction with water or aqueous solutions, undergo hydration-hydrolysis processes, forming systems that harden into solid, durable materials [1–4].

Binders can be classified based on several criteria according to: the nature of the binder (single or mixed binders), the method of production (non-clinkered and clinkered binders), and the hardening conditions (aerial and hydraulic binders).

Hydraulic binders are those that require a moist environment to harden and, after hardening, resist well in the presence of water [1–4]. Among these, the most important are those based on Portland or aluminous cement, either single or mixed.

Inorganic bio-binders are phosphate-based, and depending on their compositional characteristics, they are used in dentistry and hard tissue engineering.

Dental cements are essential materials in dentistry, used for fixing prefabricated restorations (crowns, bridges), temporary fillings, temporary or permanent cementing, and other applications. Among the various types of dental cements, inorganic phosphate bio-cements, which include zinc-phosphate, silico-phosphate, and calcium-phosphate cements, are well-known for their specific properties and diverse uses [5–11].

These systems solidify and harden through acid-base reactions, which are exothermic processes that form very stable salts in their working environment. They consist of a solid component, generally basic, and a liquid component, usually acidic. With the exception of calcium-phosphate systems, the setting time for these systems ranges from 4 to 10 minutes, and the mechanical compressive strength after 24 hours of application represents over 95% of the maximum value reached.

Zinc-phosphate cements are classic materials widely used in dentistry for cementing crowns and bridges [6–8,13]. From a chemical engineering perspective, these represent a fascinating example of composite material obtained through an acid-base reaction, with properties well-controlled by compositional characteristics and operational conditions.

Compositionally, zinc-phosphate cements primarily consist of two components: the solid phase—sintered zinc oxide powder (ZnO , with sintering additives such as MgO , SnO_2 , CaF_2)—and the liquid phase—an aqueous solution of partially neutralized orthophosphoric

acid (H_3PO_4 , neutralizing agent: $\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$, ZnO). The aqueous solution of H_3PO_4 is typically in a concentration of 40-60%. Additionally, zinc oxide is known for its excellent biological properties.

Silico-phosphate cements represent a class of materials used in the medical field due to their unique properties, such as biocompatibility, durability, and mechanical performance [5,6,16].

Silico-phosphate dental cements consist of two components: the solid phase—an alumino-fluoro silicate glass powder—and the liquid phase—an aqueous solution of partially neutralized orthophosphoric acid (H_3PO_4 , neutralizing agent: $\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$, ZnO). The aqueous solution of H_3PO_4 is typically at a concentration of 48-55%.

These cements exhibit high translucency, which is why they were initially called "dental porcelain." However, due to their solubility in the oral cavity over time, they become matte due to microcracking.

Silico-phosphate cements possess remarkable physicochemical and biological properties, such as: compressive strength (170-235 MPa), chemical stability (resistance to acid attack and chemical degradation, providing increased durability), adequate setting time (3(4)-24 min, which can be adjusted according to clinical needs by factors such as system composition, powder/liquid ratio, working temperature), and biocompatibility (they do not cause adverse reactions when in contact with biological tissues).

Calcium-phosphate cements (CPC) are biomimetic materials widely used in medical applications due to their biocompatibility, bioactivity, resorption ability, and capability to form new bone. Additionally, they can carry active pharmaceutical compounds, functioning as local drug delivery systems [6,18–27]. From a chemical engineering perspective, CPCs are of major interest due to their properties and ability to harden in moist environments, mimicking the natural behavior of bones. CPCs allow applications, particularly in minimally invasive surgery for bone defect reconstruction.

Acid-base hardening CPCs result from mixing with water or a diluted orthophosphoric acid solution (0.2%) of a powder formed from two phosphates—one more basic than hydroxyapatite and the other more acidic but with greater solubility than hydroxyapatite. At pH values corresponding to the physiological environment, after solidification and hardening,

hydroxyapatite (apatite cement, AC) or dicalcium phosphate dihydrate (brushite cement, BC) forms.

Silico-calcium-phosphate cements are materials developed from calcium-phosphate cements and are used in hard tissue substitution and regeneration. These materials exhibit excellent bioactivity and osteogenicity.

They are produced by mixing calcium phosphates doped with Si^{4+} (e.g., TCP, DCPD) or their mixtures with calcium silicates (e.g., wollastonite, calcium orthosilicate, tricalcium silicate), either undoped or doped (e.g., Sr^{3+} , Mg^{2+} , Fe^{3+}), with water or an aqueous orthophosphoric acid solution to primarily improve their physicochemical and biological properties [26,32–38].

Various powders can be added to inorganic binder systems to improve their hardening behavior, with positive consequences for their physicochemical properties and durability.

Recently, the development of nanotechnologies has enabled both in-depth characterization of these systems and the creation of micro- or nanocomposite binders with superior properties for special applications (e.g., in construction materials—self-cleaning binders, antibacterial materials, systems for monitoring crack propagation in mortar/concrete, and in biomedicine, particularly for enhancing biological behavior, such as antibacterial properties) [39–43].

Nanopowders are ultrafine particles ranging from 1 to 100 nanometers (nm) in at least one dimension. These particles, which fall under the category of nanomaterials, are distinguished by their extremely high specific surface area relative to their volume, giving them unique physical, chemical, and biological properties compared to bulk (macroscopic) materials of the same composition [44].

Thus, the main characteristics of nanopowders are [44]:

- Large specific surface area—This property increases chemical reactivity and interaction with the reaction environment, making nanopowders ideal for applications such as catalysis, sensors, or drug delivery.
- Unique optical, electrical, and magnetic properties—Due to quantum effects at the nanoscale, these materials can exhibit exceptional behaviors such as superconductivity, magnetism, or fluorescence.

- Potential to cross biological barriers—Their small size allows nanoparticles to cross cellular membranes, making them effective in targeted therapies and medical imaging.

PART II – Original Contributions

Motivation and Objectives of the Study

The aim of the undertaken study was to explore and highlight the advantages of using nanopowders within binder systems, with potential applications either in the field of construction materials with special uses or in the medical field, particularly in tissue engineering. Nanotechnologies have a significant impact on improving material properties, both in construction and biomedical applications.

The main objectives of the thesis were:

1. Development of special binder systems based on Portland cement with photocatalytic properties, containing ultrafine silica (UFS; a by-product from the ferroalloy industry, characterized by a large specific surface area and pozzolanic activity) on which TiO₂ nanopowder (with photocatalytic properties) was deposited.

It was considered in the study that fixing the photocatalyst on the surface of a hydraulically active material would allow for better dispersion of the photocatalytic agent and improved stability. The sol-gel method was used for synthesis.

Both the individual components and the final composite materials were subjected to complex characterization using modern investigative techniques such as: thermal analysis, X-ray diffraction, electron microscopy (scanning and transmission), FT-IR and UV-Vis spectroscopy, specific surface measurements (Blaine and BET), and binder properties (standard consistency water, setting time, and mechanical strength).

2. Development of new bio-binder composites for medical applications, specifically for dental use in endodontics, for root canal filling or perforation filling, and dentin mineralization, using nanobio-cellulose (BC) and barium titanate (BT).

The main stages in obtaining these biomaterials were as follows:

- i. Decomposition of the 3D porous structure of bacterial cellulose (BC), consisting of fibers and fibrils, through autoclaving treatment at 100°C for 24 hours in a basic medium (8M KOH), followed by grinding for 1.5 hours (150 rpm) in a planetary ball mill in an ethanol medium.
- ii. Synthesis of barium titanate (BT) via the sol-gel hydrothermal method, where the gel was obtained from titanium butoxide and barium acetate, with a molar ratio of BaO = 1:1. Gelation occurred within 24 hours at room temperature, and drying was performed at 80°C for 24 hours. Hydrothermal treatment was carried out at 120°C for 24 hours in 4M KOH.
- iii. Synthesis of silicate cement by thermal treatment at 1400°C for 2 hours and 1450°C for 4 hours of a precursor mixture obtained by the sol-gel method, followed by grinding for 30 minutes (150 rpm) in a dry medium in a planetary ball mill to obtain a fine white powder.
- iv. Homogenization by sifting the silicate cement with BC or BT powder in a 9:1 ratio.

The addition of BC or BT to the cement aimed to improve its properties, from binder characteristics (setting time, mechanical strength) to biological performance.

Both the individual components and the final composite materials were subjected to complex characterization using modern investigative techniques, such as thermal analysis, X-ray diffraction, electron microscopy, specific surface measurements, and mechanical strength tests. Additionally, to demonstrate the applicability potential of the silicate cement-bio-cellulose or silicate cement-barium titanate materials, as well as their biocompatibility and bioactivity properties, *in vitro* tests were performed by immersion in simulated biological fluid (SBF) and behavioral evaluations in the presence of cell cultures (cell proliferation test – MTT and fluorescence optical microscopy, oxidative stress test - GSH).

3. Development of calcium silico-phosphate binder systems with the addition of nanobio-cellulose (BC) and/or barium titanate (BT), which can be successfully used in the substitution and regeneration of hard tissue, such as in endodontics for canal fracture filling.

These binders were obtained using a two-component system, consisting of:

- Solid component - calcium-silicate powders based on wollastonite with or without the addition of nanopowders (bio-cellulose and barium titanate), aimed at improving the binder's characteristic properties, particularly its biological behavior.

- Liquid component - aqueous phosphate solutions.

Both the individual components and the final composite materials were subjected to complex characterization using modern investigative techniques such as: complex thermal analysis, X-ray diffraction, electron microscopy (scanning and transmission), FT-IR and RAMAN spectroscopy, particle size distribution measurements, setting time, and mechanical strength tests.

General Conclusions and Originality

During the doctoral study, all proposed objectives were achieved, and all the materials obtained and examined for their properties demonstrated significant potential for application in fields such as construction materials or dentistry.

The doctoral study was divided into two main parts:

- Part I provided an overview of the importance of binder systems, the types of nanopowders used in construction materials with self-cleaning properties, or in tissue engineering, as well as the main synthesis methods for these materials.
- Part II presented an extensive account of the original contributions and the results obtained and disseminated in the specialized literature.

This structure allowed for a comprehensive exploration of both theoretical and practical aspects, showcasing the innovative potential of the research conducted.

Chapter 4 - Special-Purpose Construction Binder Systems with ultrafine silica (SUF) - TiO₂ Powders

In Chapter 4, special binder systems based on Portland cement, incorporating ultrafine silica (SUF) and TiO₂, were developed. The originality of this work lies in the fact that SUF was used as the surface on which TiO₂ nanopowder was deposited. The chapter explored and developed the idea that fixing TiO₂ on the surface of a hydraulically active material would enable better dispersion of the photocatalytic agent and improve its stability.

To demonstrate the initial hypothesis, both the individual components and the final composite materials were subjected to complex characterization using modern investigation techniques, including: Complex thermal analysis, X-ray diffraction Scanning and transmission

electron microscopy, FT-IR and UV-Vis spectroscopy, Surface area measurements (Blaine and BET), Binder properties: standard consistency water, setting time, and mechanical strength.

The studied samples exhibited promising mechanical and photocatalytic properties through the addition of nanopowders, suggesting that these materials could be desirable solutions for self-cleaning construction materials.

The results obtained and presented in this chapter were reported in the paper "Synthesis and characterization of titania-silica fume composites and their influence on the strength of self-cleaning mortar" published in *Composites Part B: Engineering* in 2018 [155].

Chapter 5 - Biobinders of the Silicate-Clinker Type with ammonium phosphate, with and without Nanopowder Additives

Chapter 5 demonstrated the novel development of bio-binder composites with medical applications by using nano-powders such as bacterial cellulose (BC) and barium titanate (BT). The addition of nano-BC or nano-BT to the cement matrix aimed to enhance both the binder properties (setting time, mechanical strength) and the biological properties of the material. The potential applicability of silicate-bacterial cellulose or silicate-barium titanate cements, with a focus on biocompatibility and bioactivity, was highlighted through in-vitro tests, including immersion in simulated biological fluid (SBF) and behavioral evaluations in the presence of cell cultures (cell proliferation assay - MTT, optical fluorescence microscopy and oxidative stress - GSH).

Specific in-vitro tests (mineralization by immersion in SBF, MTT, GSH, and fluorescence microscopy) showed that all the studied materials have high applicability potential, with no adverse effects, making them suitable for integration into the human body for hard tissue substitution. Additionally, samples with BC or BT nanopowder additives demonstrated enhanced bio-efficiency.

Chapter 6 - Calcium Silico-Phosphate Biobinders with Improved Properties Through Nanopowder Addition

Chapter 6 focused on the novel development and analysis of calcium silico-phosphate binder systems with added nano-biocellulose (BC) and/or nano barium titanate (BT), with applications in grafting or repairing hard tissue, particularly for canal fracture treatment in endodontics. In-vitro tests and molecular biology studies showed that cells proliferate during

contact with the obtained materials, and the studied genetic sequences indicated that materials with BC and BT generally promote the formation of mature osteoblasts.

The results obtained and presented in this chapter were reported in the paper "Modified calcium silicophosphate cements with improved properties" published in Materials Chemistry and Physics in 2019 [164].

Dissemination of Results

a) Publications in ISI-Cited Journals

1) **Zanfir, A.-V.**; Voicu, G.; Bădănoiu, A.-I.; Gogan, D.; Oprea, O.; Vasile, E. Synthesis and Characterization of Titania-Silica Fume Composites and Their Influence on the Strength of Self-Cleaning Mortar. *Compos B Eng* 2018, 140, 157–163, doi:10.1016/j.compositesb.2017.12.032 (Q1, FI2018=6,864).

2) **Zanfir, A.-V.**; Nenu, N.; Voicu, G.; Badanoiu, A.-I.; Ghitulica, C.-D.; Iordache, F. Modified Calcium Silicophosphate Cements with Improved Properties. *Mater Chem Phys* 2019, 238, 121965, doi:10.1016/j.matchemphys.2019.121965 (Q2, FI2019=3,408)

3) Pârvan, M-G.; **Zanfir, A.-V.**; Nicoară, A-I.; Voicu G. Influence of different synthesis routes on barium titanate powder characteristics, *U.P.B. Sci. Bull., Series B*, 83 (2), 95-104, 2021, ISSN 1454-2331, WOS: 000661663200010.

Journal	Impact factor
Composites B	6.864
Materials Chemistry & Physics	3.408
Factor de impact cumulativ	10.262

b) Presentations at National/International Conferences

- **Zanfir, A.-V.**; Voicu, G; Bădănoiu, A.-I.; Gogan, D.; Oprea, O.; Truşcă, R. The coating of silica fume with titanium oxide nanoparticles and the effect on photocatalytic and pozzolanic activities, S6-124, 20th Romanian International Conference on Chemistry and Chemical Engineering (RICCCE 20), 6-7 September, 2017, Brasov, România.

Selective bibliography

1. Peter C. Hewlett, M.L. Lea's Chemistry of Cement and Concrete; Fifth.; 2019;

2. Annemarie Puri, A.B.G.V. *Tehnologia Silicaților*; 2001;
3. Anjan Kumar Chatterjee *Cement Production Technology Principles and Practice*; 2018;
4. Wieslaw Kurdowski *Cement and Concrete Chemistry*; 2014;
5. Alan D. Wilson, J.W.N. *Acid-Base Cements Their Biomedical and Industrial Applications*; CAMBRIDGE UNIVERSITY PRESS, 2005;
6. Georgeta Voicu, M.G. *Lianți Anorganici Și Organo-Minerali Cu Utilizare În Stomatologie*; POLITEHNICA Press, 2009;
7. Wingo, K. A Review of Dental Cements. *J Vet Dent* 2018, 35, 18–27, doi:10.1177/0898756418755339.
8. Sheoran, L.; Sehrawat, M.; Fatima, D.; Nandal, N.; Budhiraja, D. A Literature Review on Selection of Dental Cement in Dentistry. *International Journal of Oral Health Dentistry* 2021, 7, 94–96, doi:10.18231/j.ijohd.2021.021.
13. Flanagan, D. Zinc Phosphate as a Definitive Cement for Implant-Supported Crowns and Fixed Dentures. *Clin Cosmet Investig Dent* 2017, Volume 9, 93–97, doi:10.2147/CCIDE.S146544.
16. Arun S. Wagh *Chemically Bonded Phosphate Ceramics*; Second.; Elsevier, 2016; ISBN 9780081003800.
18. *Advances in Calcium Phosphate Biomaterials*; Ben-Nissan, B., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2014; Vol. 2; ISBN 978-3-642-53979-4.
24. Lodoso-Torrecilla, I.; van den Beucken, J.J.J.P.; Jansen, J.A. Calcium Phosphate Cements: Optimization toward Biodegradability. *Acta Biomater* 2021, 119, 1–12, doi:10.1016/j.actbio.2020.10.013.
25. Richter, R.F.; Vater, C.; Korn, M.; Ahlfeld, T.; Rauner, M.; Pradel, W.; Stadlinger, B.; Gelinsky, M.; Lode, A.; Korn, P. Treatment of Critical Bone Defects Using Calcium Phosphate Cement and Mesoporous Bioactive Glass Providing Spatiotemporal Drug Delivery. *Bioact Mater* 2023, 28, 402–419, doi:10.1016/j.bioactmat.2023.06.001.
26. Lucas-Aparicio, J.; Manchón, Á.; Rueda, C.; Pintado, C.; Torres, J.; Alkhraisat, M.H.; López-Cabarcos, E. Silicon-Calcium Phosphate Ceramics and Silicon-Calcium Phosphate Cements: Substrates to Customize the Release of Antibiotics According to the

Idiosyncrasies of the Patient. *Materials Science and Engineering: C* 2020, 106, 110173, doi:10.1016/j.msec.2019.110173.

27. Ghosh, S.; Wu, V.; Pernal, S.; Uskoković, V. Self-Setting Calcium Phosphate Cements with Tunable Antibiotic Release Rates for Advanced Antimicrobial Applications. *ACS Appl Mater Interfaces* 2016, 8, 7691–7708, doi:10.1021/acsami.6b01160.

32. Lucas-Aparicio, J.; Rueda, C.; Alkhraisat, M.H.; López-Cabarcos, E. Effect of Silicon in Calcium Phosphate Cements to Obtain Nanopore Scaffolds for Medical Applications. *Emergent Mater* 2024, 7, 1219–1226, doi:10.1007/s42247-023-00617-6.

38. Huan, Z.; Chang, J. Calcium–Phosphate–Silicate Composite Bone Cement: Self-Setting Properties and in Vitro Bioactivity. *J Mater Sci Mater Med* 2009, 20, 833–841, doi:10.1007/s10856-008-3641-9.

39. Antonella D’Alessandro; Annibale Luigi Materazzi; Filippo Ubertini *Nanotechnology in Cement-Based Construction*; Antonella D’Alessandro, Annibale Luigi Materazzi, Filippo Ubertini, Eds.; Jenny Stanford Publishing Pte. Ltd., 2020;

40. Du, S.; Wu, J.; AlShareedah, O.; Shi, X. Nanotechnology in Cement-Based Materials: A Review of Durability, Modeling, and Advanced Characterization. *Nanomaterials* 2019, 9, 1213, doi:10.3390/nano9091213.

41. Goel, G.; Sachdeva, P.; Chaudhary, A.K.; Singh, Y. The Use of Nanomaterials in Concrete: A Review. *Mater Today Proc* 2022, 69, 365–371, doi:10.1016/j.matpr.2022.09.051.

42. Senff, L.; Tobaldi, D.M.; Lemes-Rachadel, P.; Labrincha, J.A.; Hotza, D. The Influence of TiO₂ and ZnO Powder Mixtures on Photocatalytic Activity and Rheological Behavior of Cement Pastes. *Constr Build Mater* 2014, 65, 191–200, doi:10.1016/j.conbuildmat.2014.04.121.

43. Mohseni, E.; Miyandehi, B.M.; Yang, J.; Yazdi, M.A. Single and Combined Effects of Nano-SiO₂, Nano-Al₂O₃ and Nano-TiO₂ on the Mechanical, Rheological and Durability Properties of Self-Compacting Mortar Containing Fly Ash. *Constr Build Mater* 2015, 84, 331–340, doi:10.1016/j.conbuildmat.2015.03.006.

44. Ozin, G.A.; Arsenault, A.; Cademartiri, L. *Nanochemistry: A Chemical Approach to Nanomaterials*; The Royal Society of Chemistry, 2008; ISBN 978-1-84755-895-4.

51. Land, G.; Stephan, D. Controlling Cement Hydration with Nanoparticles. *Cem Concr Compos* 2015, *57*, 64–67, doi:10.1016/j.cemconcomp.2014.12.003.

130. Herrmann, J.-M. Heterogeneous Photocatalysis: State of the Art and Present Applications In Honor of Pr. R.L. Burwell Jr. (1912–2003), Former Head of Ipatieff Laboratories, Northwestern University, Evanston (Ill). *Top Catal* 2005, *34*, 49–65, doi:10.1007/s11244-005-3788-2.