

**EFFECT OF TEMPERATURE ON THE SUSTAINABILITY OF ECO-
ENGINEERED CEMENTITIOUS COMPOSITES: CURING, EXTREME
CONDITIONS AND SERVICE LIFE**

by

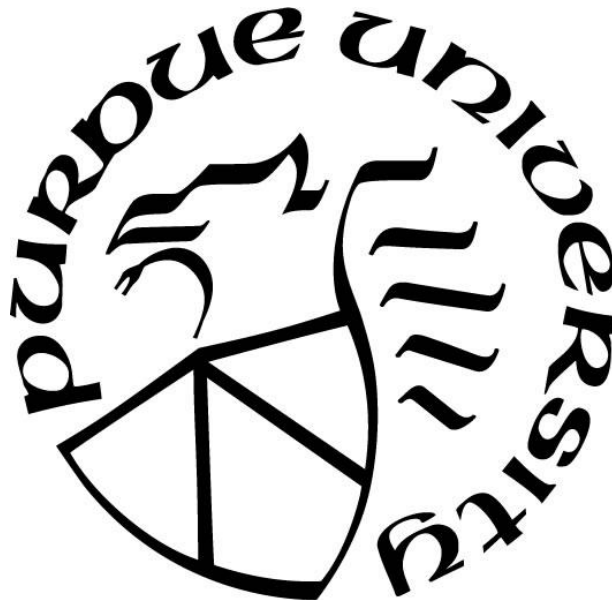
Vito Francioso

A Dissertation

Submitted to the Faculty of Purdue University

In Partial Fulfillment of the Requirements for the degree of

Doctor of Philosophy



Lyles School of Civil Engineering

West Lafayette, Indiana

May 2022

THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Dr. Maria Mirian Velay-Lizancos, Chair

Lyles School of Civil Engineering

Dr. Jan Olek

Lyles School of Civil Engineering

Dr. Nusrat Jung

Lyles School of Civil Engineering

Dr. Ramses V. Martínez

Industrial and Biomedical Engineering

Approved by:

Dr. Dulcy M. Abraham

*To my sister Mara,
and my parents Antonio and Isabella.*

*To my family,
for their endless love, support and encouragement.*

ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor and mentor *Prof. Mirian Velay-Lizancos*, for her support and consistent guidance over the past four years at Purdue University. The completion of this work could not have been possible without the expertise of Dr. Velay. Her unparalleled support, patience, and advice have encouraged me throughout the studies and the writing of this Ph.D. dissertation. Her vision and insights have strongly enriched my academic experience, and this research. Her unconditional trust in me, since the beginning of this insidious adventure, has been a pillar that has allowed me to achieve results that I would never have thought of. *Gracias, gracias, gracias*, Mirian, your dynamism, vision, sincerity, kindness and motivation have deeply inspired me.

I gratefully acknowledge my examination committee members, *Dr. Jan Olek*, *Dr. Nusrat Jung*, and *Dr. Ramses Martínez*, for their teachings throughout my Ph.D. studies at Purdue, and their insightful comments and suggestions. Their expertise and example have been of great inspiration. *Thank you*, professors.

Also, thanks to the *Lyles School of Civil Engineering* for giving me the opportunity to expand my vision and knowledge, and achieve the highest academic result. Thank you to the amazing professors and people at Purdue who made this journey incredible.

I would like to express my sincere gratitude to *Isabel*, who saw a spark in me and has opened my eyes to a completely unknown, but exciting research world. And to the other professors who believed in me.

Special thanks go to my colleagues and friends at Purdue University for their support throughout my Ph.D. studies and the uncountable hours spent together. Especially to those amazing people who shared my second home with me (HAMP G230/G223): *Hyungu* and *Raikhana*, for their valuable teachings and time; *Anan* and *Masoud*, for their free-food and financial advice; *Miguel*, “el general de la vieja y de la nueva escuela”; *Romika*, for her kindness and positive energy; *Fabian*, *Dan*, *Alberto*, and *Marina*, for their support, precious help and fun time together. I wish you the best in your present and future.

I must express my deepest gratitude to the big and unique Italo-Spanish family that has been formed and grown over the past years: *Adrian, Monica, Sara and Angel, Riccardo, Antonio, Fabrizio, Bea, Mario, Luzma* and countless others that have shared part of this journey and made me feel loved, but especially closer to Home. Thanks for all the fun and beautiful moments. A special thanks to my “little brother” *Carlos*, with whom I have shared a house and work space for 4 years, but especially laughed and cried, played and worked hard, debated and made peace. Know that I admire you.

Last, but not least, is the recognition of the support given by my *family* and many *friends* around the world. If I am the person I am today it is above all thanks to you. I am extremely grateful to my parents for their love, prayers, caring and sacrifices for educating and preparing me for my future. Thanks to my sister, for her selfless support and kind encouragement. Also, I would like to thank my best friend, *Marturo*, for being *with me* over the last 25+ years.

Finally, I would like to thank *myself* for never letting me down and believing in who I am through the good and the bad times.

Once again, thank you so much everyone for all of your support along the way,
Vito

TABLE OF CONTENTS

LIST OF TABLES	10
LIST OF FIGURES	12
LIST OF ABBREVIATIONS	15
ABSTRACT.....	18
1. INTRODUCTION	21
1.1 Motivation.....	21
1.2 Aim and Objectives.....	22
1.3 Structure of the dissertation	24
2. CURING TEMPERATURE: A KEY FACTOR THAT CHANGES THE EFFECT OF TiO ₂ NANOPARTICLES ON MECHANICAL PROPERTIES, CALCIUM HYDROXIDE FORMATION AND PORE STRUCTURE OF CEMENT MORTARS.....	26
2.1 Introduction.....	26
2.2 Materials	28
2.2.1 Materials	28
2.3 Methods.....	29
2.3.1 Flexural and Compressive strength	29
2.3.2 Response Surface Methodology (RSM)	30
2.3.3 Differential Scanning Calorimetry (DSC)	31
2.3.4 Thermogravimetric Analysis (TGA) at 7 days	32
2.3.5 3D X-ray Microscope characterization of pore structure	34
2.4 Results and Discussion	35
2.4.1 Compressive strength.....	35
2.4.2 Flexural strength	38
2.4.3 Response Surface Methodology (RSM)	41
2.4.4 Calcium hydroxide formation by DSC analysis	44
2.4.5 Pore structure analysis through 3D X-Ray Microscope (3D XRM).....	49
2.5 Conclusions.....	52
3. HIGH TEMPERATURE RESISTANCE OF ECO-MORTARS CONTAINING 100% RECYCLED CONCRETE AGGREGATES (RCA) AND NANO-TiO ₂	54

3.1	Introduction.....	54
3.2	Materials	57
3.2.1	Mix-design.....	57
3.3	Methods.....	59
3.3.1	Flexural and compressive strength test of mortar under standard conditions	59
3.3.2	Method to evaluate residual strength.....	59
3.3.3	Ductility	61
3.3.4	Correlation of mechanical properties with temperature and TiO ₂ percentage	61
3.3.5	Differential Scanning Calorimetry (DSC).....	62
3.3.6	X-Ray Diffraction (XRD).....	63
3.3.7	Scanner Electro-Microscope (SEM).....	63
3.4	Results and Discussion	63
3.4.1	Flexural and compressive strength	63
3.4.2	Visual analysis of samples.....	67
3.4.3	Correlation of mechanical properties with exposure temperature and TiO ₂ %	68
3.4.4	Ductility	68
3.5	DSC.....	70
3.6	Conclusions.....	76
4.	EFFECT OF ELEVATED TEMPERATURE ON FLEXURAL BEHAVIOR OF RECYCLED POLYPROPYLENE (PP) FIBER-REINFORCED ECO-MORTARS	77
4.1	Introduction.....	77
4.2	Materials	79
4.2.1	Characterization of the recycled polypropylene fibers.....	79
4.2.2	Mix-design.....	81
4.3	Methods.....	83
4.3.1	Sample preparation and curing	83
4.3.2	High temperature exposure.....	83
4.3.3	Flexural strength test of mortar before and after exposure.....	84
4.3.4	Digital Image Correlation	85
4.3.5	An indirect method to assess bonding strength changes	85
4.3.6	ITZ inspection by optical microscopy	86

4.3.7	Compressive strength test of mortar before and after exposure	87
4.4	Results and Discussion	87
4.4.1	Flexural strength under standard conditions.....	87
4.4.2	Effect of high-temperature exposure on flexural strength.....	88
4.4.3	Post-peak residual strength after high-temperature exposure.....	90
4.4.4	Digital Image Correlation.....	91
4.4.5	Fiber-matrix bonding, Secondary strength, and Secondary toughness.....	93
4.4.6	Fiber-matrix ITZ.....	94
4.4.7	Compressive strength test of mortar before and after exposure	95
4.5	Conclusions.....	96
5.	EFFECT OF RECYCLED CONCRETE AGGREGATE (RCA) ON MORTAR'S THERMAL CONDUCTIVITY SUSCEPTIBILITY TO VARIATION OF AMBIENT TEMPERATURE AND MOISTURE CONTENT.....	98
5.1	Introduction.....	98
5.2	Materials	102
5.2.1	Mix design, sample manufacturing, and curing conditions.....	103
5.3	Methods.....	104
5.3.1	Density and permeable porosity determination	104
5.3.2	Flexural and compressive strength test.....	104
5.3.3	Thermal conductivity.....	105
5.3.4	Response surface method	107
5.3.5	Generalized prediction equation and results validation.....	108
5.4	Results and Discussion	109
5.4.1	Density and permeable pore space (accessible porosity)	109
5.4.2	Flexural and compressive strength	110
5.4.3	Thermal conductivity.....	112
5.5	Conclusions.....	124
6.	IMPACT OF CURING TEMPERATURE ON THE SUSTAINABILITY OF SUGARCANE BAGASSE ASH AS A PARTIAL REPLACEMENT OF CEMENT IN MORTARS: AN LCA	126
6.1	Introduction.....	126

6.2	Materials	130
6.2.1	Mix design, sample manufacturing, and curing conditions	131
6.3	Methods.....	132
6.3.1	Compressive strength test.....	132
6.3.2	Life cycle assessment (LCA) of mortars	132
6.4	Results and discussion	138
6.4.1	Compressive strength and binder content variation based on designated FU	138
6.4.2	Life cycle assessment (LCA).....	140
6.5	Conclusions.....	148
7.	CONCLUSIONS AND FUTURE WORK.....	149
7.1	Conclusions.....	149
7.2	Future work.....	153
7.2.1	Other future research lines.....	154
	APPENDIX A. MATERIALS CERTIFICATIONS	155
	APPENDIX B. DSC AND TGA PLOTS	156
	APPENDIX C. LOAD-DISPLACEMENT CURVES	163
	REFERENCES	164
	PUBLICATIONS.....	191

LIST OF TABLES

Table 2.1 Proportions of mortar mixtures.....	29
Table 2.2 Experimental design.	30
Table 2.3 ANOVA analysis.	42
Table 2.4 Comparison between % CH based on TGA analysis before and after carbonation adjustment.	48
Table 2.5 Air voids percentage by total volume.	52
Table 3.1 Mix Proportions for Mortar Samples.....	57
Table 3.2 Particle size distribution of both aggregates.	58
Table 3.3 ANOVA analysis results.....	68
Table 3.4 Evaluation of ductility in each mixture after performing flexural strength test.	69
Table 3.5 CH calculation.	70
Table 4.1 Particle size distribution of fine natural aggregate.	82
Table 4.2 Mix proportions (per m ³ of mortar), flow and density.	82
Table 5.1 Mix proportions (per m ³ of mortar).	103
Table 5.2 Permeable pore space (adapted from ASTM C642).	110
Table 5.3 Thermal conductivity results.	113
Table 5.4 ANOVA results.....	117
Table 5.5 Constants C _n for each mortar.	118
Table 5.6 ANOVA results.....	120
Table 5.7 Constants (for each studied ambient temperature).	121
Table 5.8 Training and validation tests conditions.	123
Table 6.1 SCBA particle size.....	130
Table 6.2 Chemical composition of SCBA.....	131
Table 6.3 Mix proportions (per m ³ of mortar).	132
Table 6.4 Life inventory data used for this study.	135
Table 6.5 Designated impact categories from TRACI (last two added).....	137
Table 6.6 Estimation of cement content to obtain the FU.	140

Table 6.7 Environmental impacts for 1 m³ of mortars cured at 21 °C (* modified mortar that would have the same compressive strength as their reference). 144

Table 6.8 Environmental impacts for 1 m³ of mortars cured at 45 °C (* modified mortar that would have the same compressive strength as their reference). 146

LIST OF FIGURES

Figure 2.1 Modified method for CH calculation.	34
Figure 2.2 Trend surface of compressive strength at 7 days.....	35
Figure 2.3 Difference in compressive strength due to temperature changes compared to 20 °C. 36	
Figure 2.4 Relative compressive strength increase (%) respect to each curing temperature.....	37
Figure 2.5 Trend surface of flexural strength at 7 days.	39
Figure 2.6 Difference in flexural strength due to temperature changes compared to 20 °C.....	40
Figure 2.7 Relative flexural strength increase (%) respect to each curing temperature.	41
Figure 2.8 Contour plot of estimations at 7 days. (a) Compressive strength. (b) Flexural strength.	43
Figure 2.9 Strength estimations at 7 days according to RSM model. (a) Compressive strength. (b) Flexural strength.	43
Figure 2.10 Percentage of calcium hydroxide (DSC) by mortar mass vs age of mortar (a) MC-R. (b) MC-Ti0.5.....	46
Figure 2.11 TGA curves at 7 days for different curing temperatures. (a) 5 °C. (b) 20 °C. (c) 45 °C.	48
Figure 2.12 Pore structure of mortar samples cured at three temperatures.	49
Figure 2.13 Histogram of pore volume. (a) MC-R at 5 °C. (b) MC-R at 20 °C. (c) MC-R at 45 °C. (d) MC-Ti0.5 at 5 °C. (e) MC-Ti0.5 at 20 °C. (c) MC-Ti0.5 at 45 °C.....	50
Figure 2.14 Histogram of pore aspect ratio. (a) MC-R at 5 °C. (b) MC-R at 20 °C. (c) MC-R at 45 °C. (d) MC-Ti0.5 at 5 °C. (e) MC-Ti0.5 at 20 °C. (c) MC-Ti0.5 at 45 °C.	51
Figure 3.1 Evolution of the temperature exposure. (a) Target temperature 250 °C. (b) Target temperature 500 °C.	60
Figure 3.2 Ductility definition.	61
Figure 3.3 Strength before and after exposure to high temperature. (a) Flexural strength. (b) Compressive strength.....	64
Figure 3.4 Strength loss of recycled mortar. (a) Flexural strength. (b) Compressive strength.....	65
Figure 3.5 Photos of fracture face of flexural strength specimens.	67
Figure 3.6 Load-displacement curves of flexural strength test at a given temperature of mortars with different percentages of TiO ₂ . (a) 20 °C. (b) 250 °C. (c) 500 °C.....	69
Figure 3.7 Effect of TiO ₂ within the natural and recycled mixtures for each exposition temperature.	71

Figure 3.8 Effect of temperature on DSC curves for each mixture. (a) NM0 (b) RM0. (c) RM0.5. (d) RM1. (e) RM2.	72
Figure 3.9 XRD results. [CH-Calcium hydroxide; CaCO ₃ -Calcite; Q-Quartz; D-Dolomite; M-Muscovite]	75
Figure 3.10 SEM images.....	75
Figure 4.1 Recycled polypropylene fibers. (a) Sample of fibers. (b) Fibers under the microscope.	79
Figure 4.2 Extensional modulus test setup. (a) MCR 302 Anton Paar Rheometer. (b) Universal Extensional Fixture and temperature control oven. (c) Extensional strain and temperature ramp.	80
Figure 4.3 Extensional modulus behavior of recycled PP fibers as a function of the temperature.	81
Figure 4.4 Exposure and cooling process.	84
Figure 4.5 Fractured mortar matrix and fibers bridging after peak-load.	86
Figure 4.6 Flexural strength under standard conditions.....	87
Figure 4.7 Secondary strength under normal conditions.	88
Figure 4.8 Flexural strength variation after high-temperature exposure compared to standard conditions.....	90
Figure 4.9 Post-peak residual strength.....	91
Figure 4.10 (a) Load-displacement curves and, (b) DIC for PM-P0 under normal and slow cooling conditions.....	92
Figure 4.11 (a) Load-displacement curves and, (b) DIC for PM-P1.5 under normal and slow cooling conditions.....	93
Figure 4.12 Load-displacement curves (average) of PM-P1 and PM-P1.5 re-loaded specimens.	94
Figure 4.13 Microscopy images of fracture surface by EFI processing. (a) Unexposed sample. (b) Exposed sample.	95
Figure 4.14 Compressive strength of the composites (28 days).	96
Figure 5.1 Particle size distribution of natural, recycled aggregate and combined aggregate....	102
Figure 5.2 Flow chart of tests for each studied mixture.	107
Figure 5.3 Density of mortars at each saturation degree.	109
Figure 5.4 Flexural and compressive strength results.....	111
Figure 5.5 Reduction of strength due to increase of voids (by replacing NA with RA).	112
Figure 5.6 Effect of ambient (mean) temperature on thermal conductivity in dry-state.	114

Figure 5.7 Correlation between porosity and thermal conductivity's susceptibility to changes in ambient temperature in dry-state.	115
Figure 5.8 Thermal conductivity as function of saturation degree and RA replacement at 24 °C.	116
Figure 5.9 Maximum variation of thermal conductivity due to moisture content (%) vs. percentage of voids, at 24 °C.	117
Figure 5.10 Thermal conductivity as a function of ambient temperature (°C) and relative humidity (%): (a) NM, (b) RM50, and (c) RM100.	119
Figure 5.11 Thermal conductivity as a function of porosity (%) and relative humidity: (a) 4 °C, (b) 24 °C, and (c) 43 °C.	122
Figure 5.12 Correlation between experimental and predicted thermal conductivity.	124
Figure 6.1 LCA framework for this study.	133
Figure 6.2 LCA system boundary.	134
Figure 6.3 Compressive strength of mortars at 28 days. At (a) 21 °C and (b) 45 °C curing temperature.	138
Figure 6.4 28 days compressive strength as a function of cement content (no SCBA).	140
Figure 6.5 Environmental impact of the investigated mortars. (a) Global warming potential, (b) Ozone depletion potential, (c) Eutrophication potential, (d) Acidification potential, (e) Smog formation, (f) Respiratory effects, (g) Energy consumption, (h) Abiotic depletion potential. ...	143
Figure 6.6 LCA results of SCBA mortars normalized by the reference mortar (AP - Acidification potential, S - Smog formation, RE - respiratory effects, EC - energy consumption, WG - waste generation, ADP - abiotic depletion potential, GWP - global warming potential, ODP - ozone depletion potential, EP - eutrophication potential).	147
Figure 6.7 Normalized unified index as a function of the curing temperature.	148

LIST OF ABBREVIATIONS

ADP	Abiotic Depletion Potential
AP	Acidification Potential
BIM	Building Information Modeling
C ₃ S	Alite or tricalcium silicate
C ₂ S	Belite or dicalcium silicate
CaCO ₃	Calcium carbonate
CFC-11	Trichlorofluoromethane
CFC-114	1,2-Dichlorotetrafluoroethane
CFs	Characterization Factors
CH or Ca(OH) ₂	Calcium Hydroxide or Portlandite
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
C-S-H	Calcium Silica Hydrate
DIC	Digital Image Correlation
DSC	Differential Scanning Calorimeter
EC	Energy Consumption
EFI	Extended Focus Imaging
ELCD	European Platform on Life Cycle Assessment
EP	Eutrophication Potential
EPA	Environmental Protection Agency
eq	Equivalent
GHG	Greenhous Gasses
GWP	Global Warming Potential
ITZ	Interfacial Transition Zone
kg	Kilograms
LCA	Life Cycle Analysis or Life Cycle Assessment
LCI	Life Cycle Inventory

LCIA	Life Cycle Impact Assessment
N	Nitrogen
N ₂ O	Nitrous Oxide
NA	Natural Aggregate
Nano-TiO ₂	Titanium Dioxide nanoparticles
NFs	Normalization Factors
NO _x	Nitrogen oxides
ODP	Ozone Depletion Potential
OPD	Ordinary Portland Cement
PC	Portland Cement
PCA	Portland Cement Association
PO ₄ ⁻³	Phosphate
PP	Polypropylene
RA	Recycled Aggregate
RCA	Recycled Concrete Aggregate
RE	Respiratory Effects
re-	Recycled
S	Smog formation
SEM	Scanning Electron Microscope
SCBA	Sugarcane Bagasse Ash
SCMs	Supplementary Cementitious Materials
SO _x	Sulfur oxides
T	Temperature
TGA	Thermogravimetric analysis
TRACI	Tool for the reduction and assessment of chemical and other environmental impacts
UHSC	Ultra-high Strength Concrete
US	United States
UV	Ultraviolet
VOCs	Volatile organic compounds
w/c	Water-to-cement ratio
w/b	Water-to-binder ratio

WG	Waste Generation
XRD	X-ray Powder Diffraction
XRM	X-ray Microscope

ABSTRACT

With over 30 billion tons of global annual production, concrete is the most used construction material in the world. Its manufacturing is associated with a strong environmental impact due to the high natural resources' consumption, energy consumption, and a large generation of wastes and pollutants with significant global consequences. There are many different approaches to reduce the environmental impact of cementitious materials. Two examples are: (i) the use of recycled aggregate (RA) such as recycled concrete aggregate (RCA) and recycled plastics, or supplementary cementitious materials (SCMs) such as biomass ashes to reduce the use of natural aggregates and cement, respectively, and (ii) using nano-additives (for instance, nano-TiO₂) to enhance material's performance and to provide the material new properties that may have a positive proactive effect during its service life (i.e., photocatalytic properties that may reduce different pollutants concentrations from the environment). These approaches have been widely studied in standard conditions. However, boundary conditions such as temperature or moisture can be critical factors that directly or indirectly affect the effect of these approaches on the sustainability of cementitious composites in all stages of their life, from curing to service conditions.

It is known that curing temperature influences the effect of using recycled materials (such as RCA or SCMs) on the mechanical properties of cementitious materials. However, there were no studies concerning the influence of curing temperature on the nano-TiO₂ addition effect on mechanical properties of cementitious composites. A potential change will affect composites' sustainability; if curing temperature influences the effect of nano-TiO₂ on strength, the cement content needed to achieve a given performance will variate. This study concluded that curing temperature is a key factor that changes the effect of TiO₂ nanoparticles on mechanical properties and pore structure of Portland cement mortars; the lower the curing temperature, the higher the positive effect of TiO₂ on compressive strength.

Besides the use of nano-TiO₂, the substitution of NA with RCA might significantly benefit the sustainability of cementitious composites. However, the use of RCA may lead to a reduction in strength. On the other hand, the addition of nano-TiO₂ mixtures containing RCA might offset this reduction in strength. Nevertheless, studying their effects on the composites' performance

under extreme conditions is critical to assess the actual environmental impact since durability is one of the main pillars of cementitious materials sustainability. This study concluded that even though RCA may be beneficial to increase sustainability aspects in terms of net waste generation and natural abiotic depletion, its potential negative effects on high-temperature resistance should be considered to not lead to structural problems during its lifetime, especially if used in combination with nano-TiO₂. The addition of low percentages of nano-TiO₂ has a negative effect on the high-temperature resistance of mortar containing 100% RCA. Differences in thermal properties between old aggregate, old cement paste, and new cement paste with nano-TiO₂ may induce internal stresses at high temperatures that can produce a failure at lower strength due to the weaker interfacial transition zone (ITZ) between the stronger new cement paste (with nano-TiO₂) and the old cement paste. To the same extent, it is important to understand how extreme temperatures impact the effect of other recycled materials in cementitious composite performance. This study found that recycled polypropylene (re-PP) fibers may mitigate the strength loss caused by high-temperature exposure, enhance the residual flexural strength, and increase the energy absorption capability. The changes in the fiber-matrix ITZ after cooling observed through an optical microscope suggested that the mechanical improvements are related to an enhancement of the fiber-matrix ITZ after high-temperature exposure and cooling.

The next part of the dissertation focused on studying the thermal conductivity susceptibility to ambient conditions variation and how RCA substitution can affect this susceptibility. Understanding the effect of RCA on the thermal conductivity of cementitious composites would be crucial to assess their effects on the environmental impact during service life as part of a building component. Results showed that the higher percentage of porosity (due to RCA utilization) increases the susceptibility of thermal conductivity to moisture. Thus, actual moisture content and temperature should be considered when assessing the effect of RCA on thermal conductivity and its influence on sustainability in terms of energy savings when used as part of building envelopes.

Finally, the last part of this dissertation focused on assessing the impact of curing temperature on the sustainability of sugarcane bagasse ash (SCBA) as a partial replacement of cement in mortars. An experimental campaign was performed to evaluate the effect of partial replacement of cement with SCBA on compressive strength as a function of curing temperature. Hence, a life cycle assessment (LCA) was performed from the extraction of the raw materials to the material production part of the life cycle, using as a functional unit 1 m³ of mortar with the same

compressive strength as the reference mixture (plain Portland cement mortar without SCBA) cured at the same temperature. Results showed that a replacement of 97 kg of cement by SCBA (per m³ of mortar) may produce a reduction of the environmental impacts two times higher when the curing temperature was 45°C than when the temperature was 21°C. Results clearly indicate that the sustainability of SCBA utilization as a partial replacement for cement will be higher when mortar is poured in hot regions or during days with higher temperatures. Therefore, external curing temperature is an important factor that should be considered when assessing the sustainability of cementitious composites containing sugarcane biomass ashes.

1. INTRODUCTION

1.1 Motivation

The world is on the verge of a climatic and waste crisis. Our collective actions in the next decades have the potential to shape and determine the future of our planet. In this era of global warming, unsustainable processes regarding the construction industry will have to give way to greener alternatives. The last report of the World Green Building Council (WGBC) [1] estimated that the buildings and construction sector is currently responsible for 39% of global energy-related carbon emissions: 28% operational (energy needed for heating/cooling and power), and the remaining 11% from materials and construction. Still, as the world's population approaches 10 billion, by 2050 the global building stock is expected to double in size. At that point, the 'upfront carbon' emissions (carbon emissions released before the built asset is used) will be responsible for half of the entire carbon footprint from new constructions threatening to consume a large part of the remaining carbon budget [1]. Nevertheless, cementitious materials in human social and economic development are indispensable. Therefore, the built environment sector has a vital role to play in responding to the climate emergency, and addressing upfront carbon needs critical emphasis.

With over 30 billion tons of global yearly production, concrete is the most used artificial material in the world [2]. Thus, a relatively small improvement in its environmental impact would be translated into an enormous benefit for the planet. A significant contribution to the impact that the construction sector has on the environment is due to the cement industry, which is responsible for 8% of the total carbon dioxide (CO₂) emissions [3] each year. Besides cement, concrete and mortar require a significant amount of aggregate and water. Aggregates have a great impact on the sustainability of constructions since they represent around 60–70% of the total volume of concrete. Each year, approximately 8 billion m³ of aggregates are used in constructions [2]. The majority of them come from raw materials, consequently contributing to the depletion of natural resources.

There are different approaches to reduce the environmental impact of cementitious materials, for instance: (i) reducing the cement content required to achieve a given performance substituting it with supplementary cementitious materials (SCMs) [4,5]; (ii) replacing natural aggregate (NA) with recycled aggregate (RA) such as recycled concrete aggregate (RCA) and recycled plastics

among others which can contribute to reducing both natural depletion and waste generation [6,7]; (iii) enhancing durability, and (iv) providing the material new properties that may have a positive, proactive effect during its service life. For example, providing cementitious composites with photocatalytic properties through the addition of nano-TiO₂ may reduce different pollutants concentrations from the environment [8]. Besides, enhancing the thermal insulation capacity of cementitious composites used in building constructions might reduce concrete buildings' energy consumption during their service life [9]. However, if combined, the benefit for adopting one of the above-mentioned approaches may affect in an undesirable way another one. For instance, the reduction of the net waste generated by replacing NA with RA may come at the expense of strength which would increase the cement content needed to achieve a given performance, thus affecting the net CO₂ emissions associated with material production. Hence, for evaluating the real sustainability of these materials a holistic approach is needed, which must assess their synergistic effects.

The effects of RCA, plastic aggregates, nano-TiO₂ addition, and several SCMs on mechanical properties under standard conditions have been widely studied [6,7,10–17]. Notwithstanding, some boundary conditions such as temperature can be a key factor that directly or indirectly affects the influence of these changes on the sustainability of cementitious composites in all stages of their life, from curing to service conditions.

1.2 Aim and Objectives.

This research aims to study the impact of temperature on the effectiveness of several approaches to enhance the sustainability of cementitious composites from curing to service life.

The main objectives of this investigation are:

- I. To study the influence of curing temperature on the effect of nanoparticles (nano-TiO₂) addition on mechanical properties, hydration products formation, and pore structure of cement mortars.**

There are several studies about the effects of the addition of TiO₂ nanoparticles in mortar properties, but they were made at a given temperature [10,11]. However, are the effects of this addition independent of curing temperature? The hypothesis is that curing temperature changes the effect of nano-TiO₂ on mortar's microstructure and strength since the nanoparticles may have a different

effect when the temperature changes the rate of hydration. If curing temperature influences the effect of nano-TiO₂ on strength, the cement content needed to achieve a given performance will vary. Consequently, curing temperature would highly affect the environmental impact of nano-TiO₂ addition in cementitious composites, in particular, the CO₂ emissions associate with the materials' production.

II. To analyze the impact of using recycled concrete aggregate and nanomaterials (nano-TiO₂) addition on the high-temperature resistance of eco-mortars.

The use of recycled concrete aggregate (RCA) in mortar and concrete is a sustainable approach to reduce the depletion of natural resources and waste in landfills. Nevertheless, the use of RCA may lead to a reduction in strength [6]. On the other hand, previous research indicated that nano-TiO₂ could improve the mechanical properties of cement-based materials [18]. It is expected that, besides providing photocatalytic properties, the use of nano-TiO₂ addition on cementitious composites containing RCA may offset its negative effect on strength. Studying the effects of these additions on the composites' performance under extreme conditions is critical to assess the actual environmental impact since durability is one of the main pillars of cementitious materials sustainability. However, the effect of TiO₂ nanoparticles on the high-temperature resistance of recycled concrete and mortar has not yet been studied. The hypothesis is that the differences between mortars with NA vs. mortars with RCA (e.g., higher porosity, weaker ITZ) may change nanoparticles' effect under high-temperature exposure.

III. To analyze the impact of using recycled polypropylene fibers on the high-temperature resistance of eco-mortars.

There are several articles in the literature on the compressive strength performance of plastic fiber-reinforced concrete exposed to elevated temperature [19–21]. However, there is still no agreement in the literature regarding the positive role of recycled plastic waste in enhancing the mechanical performance of cement-based composites. In particular, the influence of elevated temperatures on the flexural performance of recycled PP fiber-reinforced mortars and its effect on interfacial transition zone (ITZ) bonding between the matrix and the recycled fibers has not been deeply investigated. Moreover, no studies have been found on the possible effects of the cooling process on the residual strength of these eco-mortars. The hypothesis is that the exposure to elevated

temperature will affect the ITZ bonding between the matrix and the recycled fibers, and this will impact the residual strength of the eco-mortar once cooled.

IV. To assess the effect of recycled concrete aggregate (RCA) on mortar's thermal conductivity susceptibility to ambient temperature and moisture content variations.

The thermal conductivity of cementitious composites affects the energy consumption of concrete buildings. It is known that mortar's thermal conductivity values are susceptible to changes in ambient temperature and moisture content. The use of recycled materials may affect this susceptibility producing a higher variation in thermal conductivity values. The effect of RCA on the thermal conductivity of mortar slabs as a function of ambient temperature and moisture content will be investigated. The synergistic effect of more approaches to reduce the environmental impact may lead to unforeseen results. The hypothesis is that a higher porosity due to the utilization of RCA may change the susceptibility of thermal conductivity measurements of recycled composites exposed to different ambient conditions.

VI. To study the influence of curing temperature on the sustainability of sugarcane bagasse ash as a partial replacement of cement in mortars.

Preliminary data showed that curing temperature influences biomass ashes' effect on the compressive strength of cementitious composites. Therefore, assessing and quantifying how this effect impacts the life cycle assessment of cementitious composites is critical to evaluating the real environmental savings of biomass ashes as a partial replacement for cement. However, no studies concerning the impact of curing temperature on the sustainability of biomass ashes (i.e., sugarcane bagasse ash, SCBA) as a partial replacement for cement were found. The hypothesis is that curing temperature is a critical factor that determines the environmental footprint of SCBA utilization as partial replacement of cement in cementitious composites production.

1.3 Structure of the dissertation

This dissertation comprises seven chapters. Chapters 2 to 6 contain the corresponding literature review in the introduction of each chapter.

Chapter 1 comprises the introduction identifying the motivation, aim and objectives, and structure of the dissertation.

Chapter 2 studies how the curing temperature affects the effect of nanoparticles (nano-TiO₂) on mechanical properties, hydration products formation, and pore structure of cement mortars.

Chapters 3 and 4 analyze the impact of using recycled materials (recycled concrete aggregate and recycled polypropylene fibers) and nanomaterials (nano-TiO₂) addition on the high-temperature resistance of eco-mortars.

Chapter 5 investigates the effect of recycled concrete aggregate (RCA) on mortar's thermal conductivity susceptibility to variation of ambient temperature and moisture content.

Chapter 6 assesses the effect of curing temperature on the environmental performance of sugarcane bagasse ash as a partial replacement for cement in mortars.

Chapter 7 includes the conclusions and consideration for future work.

2. CURING TEMPERATURE: A KEY FACTOR THAT CHANGES THE EFFECT OF TiO₂ NANOPARTICLES ON MECHANICAL PROPERTIES, CALCIUM HYDROXIDE FORMATION AND PORE STRUCTURE OF CEMENT MORTARS

A portion of this chapter has been published as:

Francioso V., Moro C., Martinez-Lage I., Velay-Lizancos M., “Curing temperature: A key factor that changes the effect of TiO₂ nanoparticles on mechanical properties, calcium hydroxide formation and pore structure of cement mortars”. *Cement and Concrete Composites*, Vol. 104, (2019), 103374. <https://doi.org/10.1016/j.cemconcomp.2019.103374>

2.1 Introduction

Nanoparticles applicability in various fields has sparked research on their efficacy to improve key mechanical properties of concretes and mortars [10,11]. Recent research suggests that the use of nanoparticles such as zinc oxide, titanium dioxide (TiO₂), and nanosilica, among others, improves the mechanical properties of concrete and mortar [10–12,22,23]. More substantially, the addition of TiO₂ to concretes or mortars also converts cement-based materials into photocatalytic and self-cleaning materials [24–28].

The high level of environmental pollutants emitted by the cement industry (above all carbon dioxide) has led to a need for strategies to reduce the environmental impact of cement production. Therefore, the environmental benefits of combining TiO₂ in cement-based building materials include its photocatalytic characteristics such as self-cleaning and disinfection [29], in addition to its high stability and relatively low cost compared with other photocatalysts [27,28]. Disinfection is primarily related to hydroxyl radicals and reactive oxygen species (ROS) formed during TiO₂ photoactivity and allows to eliminate microbial pollutants [29]. Besides, it is used successfully in the manufacture of self-cleaning concretes that contribute to the disposal of carbon compounds. Two well-known examples are those of the Jubilee Church and the Ara Pacis Archaeological Museum in Rome [11,30–36].

In conventional concrete, the addition of TiO₂ decreases setting time due to its increase in the rate of heat of hydration [24]. The higher specific surface area (to volume ratio) of the particles can promote cement hydration by adding more surface area to form hydration products

[18,22,24,37,38]. Nano-titanium dioxide refines the microstructure making it denser due to the small size effect and the filling effect. By adding TiO_2 , the growth of Ca(OH)_2 crystals is moderated, decreasing the size of CH. Previous research also showed that TiO_2 could control the growth of the hydration products and promote the hydration of cement [39,40]. Consequently, TiO_2 refines the pore structure and increases the chloride penetration resistance of concrete [41]. Nevertheless, no studies have been found which analyze the effect of the different crystallinity of TiO_2 (e.g., rutile, anatase, or brookite) on the hydration process. According to Tanaka et al. [42], anatase TiO_2 is a better catalyst for photocatalysis. However, it is not yet clear the impact of TiO_2 crystal structure on the hydration process since this approach has only been applied to rutile TiO_2 [43]. In contrast, numerous studies have reported that titanium dioxide reduces pore diameter and total specific pore volume [44–50].

These effects enable to increase compressive strength, flexural strength at early ages and fatigue strength [18,22,25,51,52]. Other studies have shown a slight decrease in compressive and flexural strength with the substitution of 1% of TiO_2 but some improvements with higher percentages [37,48]. In cements with fly ash, the addition of TiO_2 (starting at 0.5%) improves short and long-term compressive strength, with the best results obtained at 2% substitution [53]. Additionally, workability decreases, while resistance against ingress of chloride ions increases [53]. In self-compacting concrete, up to a 3% TiO_2 substitution, compressive, flexural and indirect tensile strength have been found to increase [26].

Nevertheless, these studies have been performed at a standard curing temperature (usually 20 °C or 21 °C). To our knowledge, the only study [54] analyzing the effect curing temperature has on compressive strength of TiO_2 -enriched materials compared merely 40 °C and 60 °C, but it was focused on cement paste. No studies were found regarding the influence of low curing temperature on mechanical properties of any type of cement-based material with TiO_2 substitutions. Additionally, there is a lack of research on the effects of curing temperature in mortars at early ages.

Previous studies showed that the addition of TiO_2 could also change the formation of hydration products [24,39]. The decomposition of calcium-silicate-hydrate (CSH) occurs in a wide range of temperatures (between 100 °C and 400 °C) and jointly with other components (i.e., calcium-silicate-hydrate, ettringite and calcium aluminate hydrate) [55–59]. This fact makes the

quantification of CSH based on thermal analysis not as accurate as in other compounds. Nonetheless, the main products of alite (C_3S) and belite (C_2S) hydration are CSH and calcium hydroxide (CH). These two compounds are formed together at a fixed proportion; therefore, in concrete without supplementary cementitious materials (in the absence of chemical attacks), the higher the CH, the higher the CSH. For that reason, calcium hydroxide is commonly used as an indicator of hydration in cementitious materials without pozzolans [60–62]. However, no research was found on CH formation of TiO_2 enriched cements as a function of curing temperature. No studies have been found on the influence of curing temperature on the effect of TiO_2 on mechanical properties of cement mortars. If curing temperature changes the effect of TiO_2 on hydration products formation and mechanical properties at early ages, it should be considered.

For all those reasons, the main objective of this study is to determine if curing temperature is a key factor that modifies the effect of the addition of TiO_2 on the strength and CH formation of cement mortars at early ages. Finally, the effect of these factors on pore structure will be studied. It could relate the influence of TiO_2 and temperature on the strength and formation of hydration products to better understand the mechanics that drive improvements in strength.

2.2 Materials

2.2.1 Materials

The main components of the mortars include:

- Portland cement Type I;
- Quartzite sand 0/2.5;
- Water;
- TiO_2 nanoparticles.

Cement was commercial grade Portland cement type I from Infinity™ meeting ASTM and EN standards [63,64]. Titanium (IV) oxide (TiO_2) nanoparticles were obtained from Sigma-Aldrich (St. Louis, MO) with a formula weight of 79.87 g/mol and >99.5% of trace metal basis. This titanium dioxide has a surface area of 35 – 65 m²/g and the primary particle size (d_{50}) is 21 nm (TEM - transmission electron microscopy). Its crystal structure consists of about 85 % anatase and 15 % rutile.

Table 2.1 reports the composition of all the mortars investigated, in accordance with EN-196 [65]. MC-R refers to the control mortar with no TiO₂. All the other mortars containing TiO₂ were labeled MC-TiNN, where “NN” is the percentage of cement replaced with TiO₂ nanoparticles.

Table 2.1 Proportions of mortar mixtures.

Component	MC-R	MC-Ti0.25	MC-Ti0.50	MC-Ti1
Cement (g)	450.00	448.88	447.75	445.50
Sand (g)	1350	1350	1350	1350
TiO ₂ (g)	---	1.13	2.25	4.50
w/(c+TiO ₂)	0.50	0.50	0.50	0.50

2.3 Methods

2.3.1 Flexural and Compressive strength

Nine specimens were cast per each mortar as described in Table 2.2. A total of 36 prismatic samples were fabricated with dimensions of 40 x 40 x 160 mm³, as indicated in EN-196 [65]. Specimens were divided into groups of three and each group cured at different temperatures (5 °C, 20 °C and 45 °C). During the first day, each group of specimens was cured in their molds inside a controlled temperature room at 5 °C, 20 °C or 45 °C. Molds were covered by a first layer of plastic, then a cloth moistened with water at the same temperature and finally in an airtight plastic bag to avoid evaporation. After one day, samples cured at 20 °C were demolded and immersed in water trays contained in a controlled temperature room. At the same age, samples cured at 45 °C were demolded and immersed in a temperature-controlled thermostatic bath. Due to the lower maturity of samples cured at 5 °C, these were demolded at two days, instead. Then, they were immersed in water trays contained in a controlled temperature room at 5 °C.

For each type of mortar, flexural strength tests were performed at 7 days including three specimens for each curing temperature. Compressive strength tests were carried out on the two halves of each broken prism from flexural strength. Both followed the standard procedure of EN-196 [65].

Table 2.2 summarizes the number of samples and data obtained for each mortar.

Table 2.2 Experimental design.

Mortar	Samples at each temperature			Test	
	5 °C	20 °C	45 °C	Flexural strength	Compressive strength
MC-R	3	3	3	9	18
MC-Ti0.25	3	3	3	9	18
MC-Ti0.50	3	3	3	9	18
MC-Ti1	3	3	3	9	18
TOTAL	12	12	12	36	72

2.3.2 Response Surface Methodology (RSM)

Many studies have applied central composite design in response surface methodology (RSM) as a common approach [66,67] to find the optimum solution by analyzing variables that influence results. This method was successfully applied in previous studies to obtain the optimum mix design varying the proportions of the mixture component [68–74].

RSM is applied in the present study to analyze how curing temperature and TiO₂ affect the strength jointly.

MINITAB (MINITAB Inc., Pennsylvania, USA) was used to perform RSM statistical experimental design. Besides, a second order model was applied in order to obtain a better approximation of results (Eq. (2.1)). In it, “y” is the variable that we wish to approximate. The “β” coefficients can be obtained by the least square method and “ε” is the total error. Significance threshold level (α) was chosen as 0.10.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_i \sum_j \beta_{ij} x_i x_j + \varepsilon \quad (2.1)$$

Two variables that can have an effect on the strength were analyzed, temperature (T) and percentage of TiO₂ (% TiO₂). Their ranges were 5-45 °C for T and 0-1 for % TiO₂. By inputting data into the software, an analysis of variance (ANOVA) was performed to know the accuracy of the model and to validate the results.

2.3.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (2010, TA Instruments) was employed to monitor *calcium hydroxide formation*. Previous studies showed that DSC is a useful method for CH determination in cementitious materials [60,75–77]. Tested samples include the reference mortar and mortar sample with the best percentage of TiO₂ (0.5%) for compressive and flexural strength (among the studied ones). Three samples of each mixture were cured at 5 °C, 20 °C and 45 °C, resulting in a total of 18 samples, 9 for each selected mortar. Samples were cast, then covered with a plastic film to prevent evaporation of surface water and analyzed at 1, 3, and 7 days. At each test age, samples were ground with a mortar and pestle, sieved (No. 200, 75-μm), then hydration was stopped with an acetone wash [77]. To confirm the accuracy of this method, DSC was performed after 1 and 28 days on the same powder. Comparison spectra showed negligible differences. All assays were performed in a nitrogen gas atmosphere at a heating rate of 10 °C/min starting at 20°C up to a final temperature of 600 °C. Both reference and sample pans were kept open. The sample pan contained 15 to 25 mg of ground materials, which passed a No. 200 (75-μm) sieve.

The quantitative determination of the Ca(OH)₂ content at 1, 3 and 7 days has been determined evaluating DSC curves. The calculation is based on the evaluation of the dehydration peak area of calcium hydroxide (CH). The decomposition of CH occurs around 450 °C [55,59,60,78], at which temperature range corresponds a sharp peak in the curve. To better outline the start and end points of the peak for CH, the second derivative curve has been used. The energy absorbed during the decomposition of the CH can be obtained through the area underlying the dehydration peak. This area should not contain the energy absorbed during the decomposition of other compounds that usually decompose continuously over a wide range of temperatures [60].

The content of CH was determined with Eq. (2.2), after obtaining the calibration curve of DSC analysis for the equipment. For this study, the calibration curve was obtained following the procedure described by Kim and Olek [60].

$$CH(\%) = 0.0917 \times (\text{peak area}) \quad (2.2)$$

Where CH (%) is the percentage of calcium hydroxide, based on the initial weight of the sample (by mass of mortar); 0.0917 is the slope of the calibration curve for the conversion of the absorbed

energy; the peak area is the energy absorbed during the dehydration of CH (in J/g). Note that the slope value of the new calibration curve (0.0917) is close to others calculated in previous studies: Kim et Olek [60] reported a slope of 0.08505, and Moukwa et al. [75] a slope value of 0.08943.

Partial carbonation of CH may occur during DSC sample preparation. Previous study revealed that it is not possible to prevent completely the carbonation of CH [60]. For that reason, the quantification of CH will be affected. Thermogravimetric Analysis (TGA) was found useful to quantify the carbonated CH [60]. The main objectives of the next section (TGA) are (i) evaluating if TiO_2 nanoparticles affect the rate of CH carbonated during the sample preparation and, in that case, (ii) obtaining a better quantification of percentage of CH.

2.3.4 Thermogravimetric Analysis (TGA) at 7 days

Thermogravimetric analysis was performed to quantify the actual calcium hydroxide formation at 7 days. Reference mortar (MC-R) and mortar with a 0.5% TiO_2 substitution (MC-Ti0.5) at the three different curing temperatures (5 °C, 20 °C and 45 °C) were tested. The same sample preparation of DSC was adopted. A Thermogravimetric Analyzer (2050, TA Instruments) was used in order to conduct the test. Specimen had an amount of 20-40 mg of grounded powder that was placed in a platinum pan. The test was run with the sample initially in isothermal condition for two minutes. The temperature was then raised at a rate of 10 °C/min until 900 °C. Percentage of total mass loss versus temperature was recorded during the experiment. The atmosphere in the machine was nitrogen gas at 20 psi and 60 mL/min purge flow.

For the calculation of CH the modified interpretation of TGA curve suggested by Kim et Olek [60] was assumed. While the traditional method considers mass loss to be equivalent to the vertical distance between two horizontal lines originating from the start and end decomposition points of the CH, the modified method uses the vertical distance (taken at the inflection point of the CH mass loss) between two tangential lines originated from the same points (Figure 2.1). Furthermore, the traditional method does not consider the amount of calcium carbonate that initially exists in the anhydrous cement and the carbonation effects due to sample preparation. In order to do that, Eq. (2.3) [60] was adopted:

$$\begin{aligned}
CH = & \frac{74.1}{18.0} \cdot \frac{1}{M_c} \cdot \left[\left(M_{start}^{CH} - S_{start}^{CH} (T_{inf}^{CH} - T_{start}^{CH}) \right) - \left(M_{end}^{CH} + S_{end}^{CH} (T_{end}^{CH} - T_{inf}^{CH}) \right) \right] + \\
& + \frac{74.1}{100.1} \left[\frac{100.1}{44.0} \cdot \frac{1}{M_c} \cdot \left[\left(M_{end}^{CH} - S_{end}^{CH} (T_{inf}^{CA} - T_{end}^{CA}) \right) - \left(M_{end}^{CA} + S_{end}^{CA} (T_{end}^{CA} - T_{inf}^{CA}) \right) \right] \right. \\
& \left. - CA_{ini} \right] \quad (2.3)
\end{aligned}$$

where:

- CH is the amount of calcium hydroxide in g/g of anhydrous cement;
- 74.1/18, 74.1/100.1 and 100.1/44.0 are, respectively, the molar weight ratios of Ca(OH)₂ to H₂O, Ca(OH)₂ to CaCO₃ and CaCO₃ to CO₂;
- M_c is the initial mass (g) in the TGA sample;
- M_{start}^{CH} , M_{end}^{CH} and M_{end}^{CA} are the masses (g) of the sample at the start and end point for Ca(OH)₂ decomposition and the end point for the CaCO₃ decomposition, respectively;
- T_{start}^{CH} , T_{inf}^{CH} , T_{end}^{CH} , T_{end}^{CA} and T_{inf}^{CA} are the temperatures (°C) of the start point, the mass inflection point, the end point for the Ca(OH)₂ decomposition, the end point and the inflection point for the CaCO₃ decomposition, respectively;
- S_{start}^{CH} , S_{end}^{CH} and S_{end}^{CA} are the slopes of the tangential lines of the start and end point for the Ca(OH)₂ decomposition and the end point for the CaCO₃ decomposition, respectively;
- CA_{ini} is the initial content of CaCO₃ in g/g of sample. In this case, the initial CaCO₃ comes from (i) anhydrous cement and (ii) aggregates.

All sample masses and temperatures are automatically recorded during TGA. The amount of calcium carbonate that initially exists in the sample (CA_{ini}), has to be deducted from the total amount of calcium carbonate (CaCO₃) determined from TGA analysis. Appendix B displays the TGA curves of aggregate and anhydrous cement and the corresponding data for the CA_{ini} calculation.

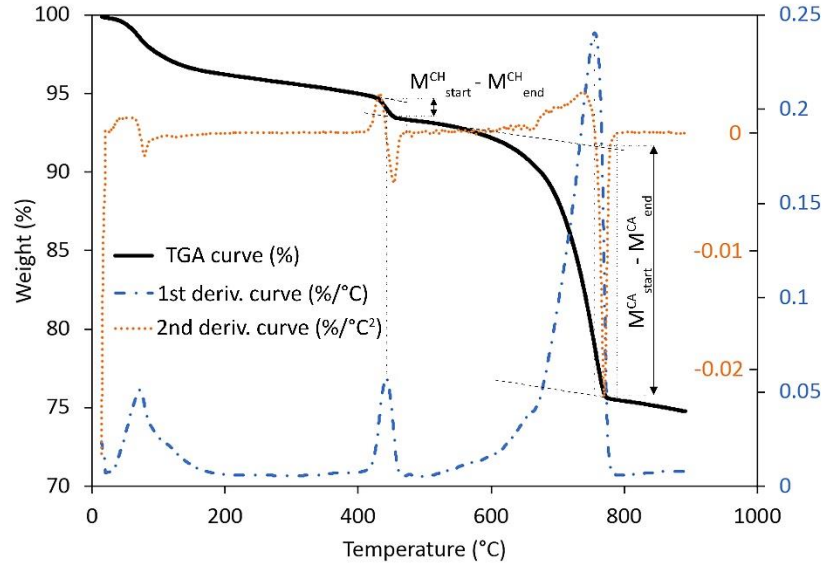


Figure 2.1 Modified method for CH calculation.

2.3.5 3D X-ray Microscope characterization of pore structure

Zeiss Xradia 510 Versa 3D X-Ray Microscope (3D XRM) at a 0.4X optical magnification was employed to study the effect of TiO_2 in the pore structure of mortars as a function of curing temperature. Tested samples include the reference (MC-R) and the mortar with the best percentage of TiO_2 for compressive and flexural strength (MC-Ti0.5). One sample of each mixture was cured at 5 °C, 20 °C and 45 °C, resulting in a total of 6 samples tested. The cylinder samples have a diameter of 3.2 cm and a height of 2.1 cm. The Zeiss Xradia 510 Versa system utilizes a two-stage magnification technique, employing both geometric and optical magnification to provide high-resolution imaging. All scans were performed at a voltage of 150 kV and power of 10 W, with an in-situ system temperature of ~28°C. In order to ensure that the test temperature does not affect the specimen, samples were tested at least at 28 days. Object Research Systems (ORS) Dragonfly Pro software was used to visualize (3D), analyze, and quantify porosity and pore network. A minimum of 2401 projections per samples were done.

2.4 Results and Discussion

2.4.1 Compressive strength

Figure 2.2 displays the trend surface of compressive strength at 7 days of mortars as a function of the percentage of TiO_2 and curing temperature according to the experimentally obtained data.

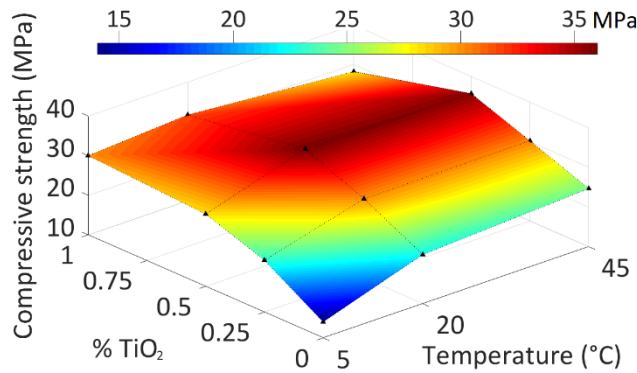


Figure 2.2 Trend surface of compressive strength at 7 days.

For each curing temperature, it was observed that higher percentage of TiO_2 was correlated with greater compressive strength at 7 days, excluding MC-Ti1 (1% TiO_2) cured at 20 °C and 45 °C. Even though compressive strength of MC-Ti1 samples is greater than that of the reference mortar, values were lower than the registered strength of the specimens with 0.5% TiO_2 substitution. It is also important to highlight that compressive strength of mortar with 0.5% and 1% TiO_2 were lower when cured at 45 °C than when cured at 20 °C. Additionally, samples substituted with 1% of TiO_2 , when cured at 45 °C presented lower compressive strength than when cured at 5 °C. It is commonly observed that higher curing temperatures, on plain concrete and mortar, is correlated with higher compressive strength at early ages [79,80]. Unexpectedly, the studied mortars with 0.5% and 1% of TiO_2 did not follow this trend. These observations suggest that addition of TiO_2 affects the strength of mortars, making the samples less susceptible to temperature changes at early ages.

Figure 2.3 presents how the difference in compressive strength between specimens with TiO_2 cured at 20 °C and those cured at 45 °C is negligible, with the exception of specimens with

1% TiO_2 , in which there is a slight negative influence due to the increase in temperature. This drop in strength for the temperature of 45 °C may be due to the fact that nanoparticles further accelerate the hardening process of mortar. For this reason, in mortars with TiO_2 at early age (7 days) it was possible to observe the *crossover effect* due to an accelerated hardening for high curing temperatures, reported in literature for long-term concrete compression strength [81]. Even when the presence of the nanomaterial is still beneficial at 45 °C for compressive strength in comparison to the results of reference mortar at the same temperature, the *crossover effect due to curing at high temperature is higher the higher is the percentage of TiO_2* .

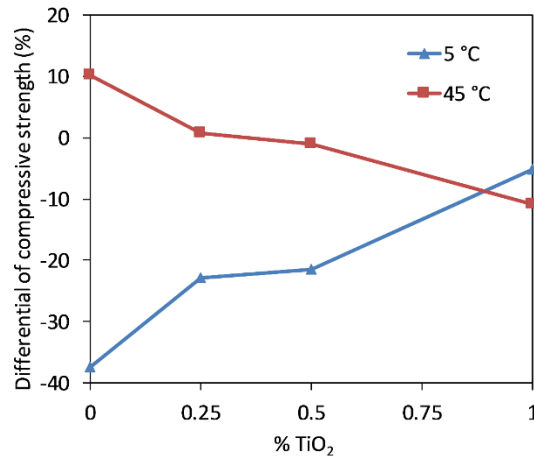


Figure 2.3 Difference in compressive strength due to temperature changes compared to 20 °C.

Furthermore, an important result to highlight is that the negative influence due to the decrease in temperature is lower in the case of mortars with TiO_2 . In the case of MC-R, in fact, specimens cured at 5 °C showed a 37% lower strength than specimens of the same mortar cured at 20 °C, while in the case of the MC-Ti0.5 mortar, specimens cured at 5 °C recorded a 21% lower strength than those cured at 20 °C. In the case of MC-Ti1 cured at 5 °C, there was a decrease in compressive strength of only 5%.

Figure 2.4 shows the increase in percentage of compressive strength due to the addition of TiO_2 with respect to the strength obtained by the reference mortar, for each of the curing temperatures. To calculate this increase in compressive strength, Eq. (2.4) was used.

Relative compressive strength increase (%) with respect to each of the curing temperature (T) =

(2.4)

$$\frac{S_{TiX}(T) - S_{MC0}(T)}{S_{MC0}(T)} \times 100$$

where:

$S_{TiX}(T)$ = Compressive strength of MC-TiX mortar, cured at temperature T (MPa)

$S_{MC0}(T)$ = Compressive strength of MC-R mortar, cured at temperature T (MPa)

T = Temperature (°C)

X = Percentage of additive used.

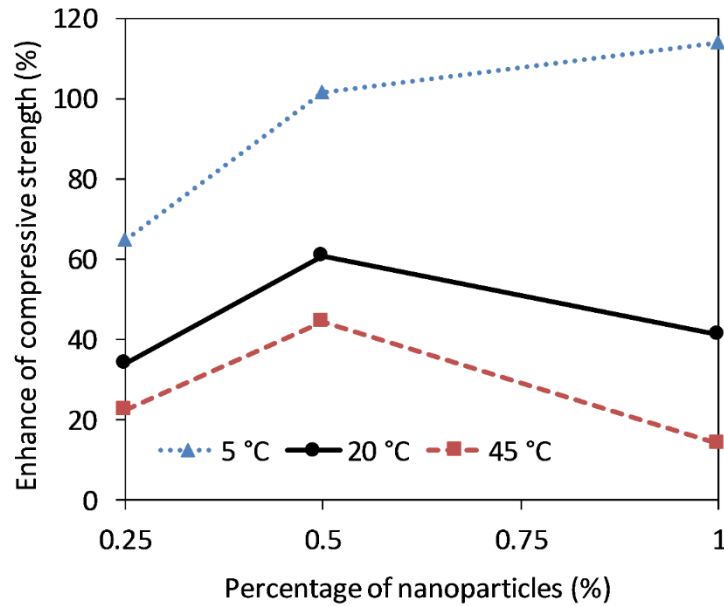


Figure 2.4 Relative compressive strength increase (%) respect to each curing temperature.

It is observed that the main benefits of using TiO_2 for compressive strength are obtained at a lower temperature than standard. For mortars cured at 5 °C, in fact, the increase in strength is greater the greater is the percentage of TiO_2 , until it reaches in the mortars with 0.5% and 1% of nanomaterial more than 100% more strength. By increasing curing temperature, this condition remains true for values up to 0.5% of substitution.

If we compare the results obtained at 5 °C (Figure 2.2), it can be seen that the 7-day average compressive strength of the MC-R samples is 14 MPa, while the strength of MC-Ti1 is 30 MPa,

so the latter has undergone an increase of 114% (Figure 2.2). If the same results are compared in samples cured at 20 °C, the gain in compressive strength is 41%, while in the MC-Ti0.5 mortar it is 61% higher.

Finally, it is important to highlight that in the studied cases, at higher temperatures than standard, the positive influence of the addition is zero or even lower than the standard (Figure 2.3). Thus, it must be a factor to consider as it could lead to an overestimation of the compressive strength, if one decides to use TiO₂, when the curing temperature is higher than the standard. At 20 °C, the addition of 1% of TiO₂ causes an increase in compressive strength of 41% more than the strength of the reference mortar MC-R at the same temperature, while at the temperature of 45 °C the same percentage of TiO₂ causes a 25% increase.

In summary, it can be concluded that the lower the curing temperature, the higher the positive influence of the addition of TiO₂ on compressive strength.

2.4.2 Flexural strength

Figure 2.5 presents the trend surface of flexural strength as a function of the percentage of TiO₂ and curing temperature according to the experimentally obtained data. Dots represent the average flexural strength obtained for each mortar from the specimens cured at a given temperature. It seems that high temperatures (in our case 45 °C) reduced effectiveness of the effect of these nanoparticles on flexural strength at 7 days since there are no significant differences between the results of MC-R cured at 45 °C and those of mortars with different percentages of TiO₂ at the same curing temperature. In fact, the only significant influence of TiO₂ that can be observed at 45 °C is a negative influence in the MC-Ti1 specimens. Furthermore, by comparing the flexural strength values of the MC-R and MC-Ti1 samples, both cured at a temperature of 45 °C, we observed that the addition of 1% of TiO₂ causes a decrease in flexural strength of about 12% (Figure 2.6 and Figure 2.7).

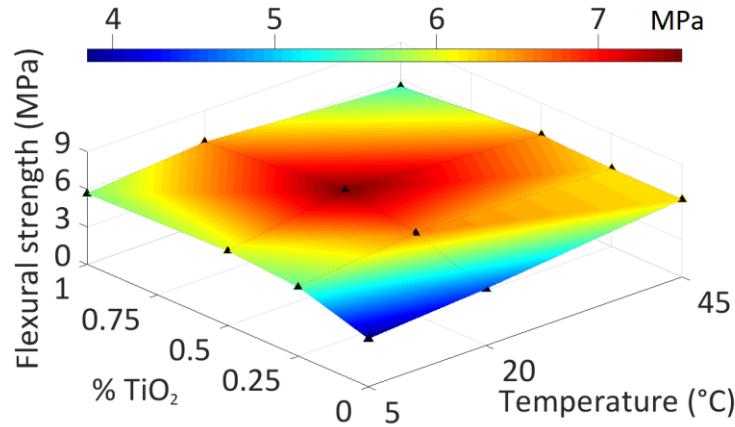


Figure 2.5 Trend surface of flexural strength at 7 days.

In contrast, with a curing temperature of 5 °C, the addition of nanoparticles improves flexural strength. The maximum gain is obtained with a substitution of 0.5% (Figure 2.5 and Figure 2.7). For larger substitutions, we observed a slight decrease (with respect to a 0.5% substitution) but always outperforming the reference mortar MC-R. At a curing temperature of 20 °C, the influence of TiO₂ seems to have a positive effect on flexural strength at 7 days; even here, the maximum gain is obtained for percentages of nanomaterials up to 0.5%. For MC-Ti1, it seems that this effect is smaller but still better than the absence of nanomaterial. This suggests that there may be an optimal percentage of TiO₂ between 0.5% and 1%, which maximizes flexural strength, even though more evidence is needed to confirm this observation.

Figure 2.6 shows that, by varying the percentage of nanomaterial, there is no appreciable difference in flexural strength between specimens cured at 20 °C and those cured at 5 °C. While for the specimens cured at 45 °C it was observed a decrease, increasing the percentage of TiO₂, with respect to the mortars cured at standard temperature (20 °C). Again, the addition of TiO₂ nanoparticles seems to neutralize the beneficial effect of high temperatures on strength at early ages.

For MC-R, the higher curing temperature, the higher flexural strength at 7 days, as it is expected according to maturity method [82–85]. In contrast, samples with TiO₂ showed a lower effect of curing temperature on flexural strength: with respect to the reference mortar, in samples with TiO₂ flexural strength variations due to changes of curing temperature are lower. This trend could be due to the fact that nanoparticles accelerate the hardening process of mortar, therefore,

already after a few days the *crossover effect* [81] due to an accelerated hardening at high curing temperatures can be observed.

Figure 2.7 displays the variation in term of percentage of flexural strength due to the addition of TiO_2 with respect to that obtained by the reference mortar, for each of the curing temperatures. To calculate this increase in flexural strength, Eq. (2.5) has been used.

Relative flexural strength increase (%) with respect to each of the curing temperature (T) =

(2.5)

$$\frac{FS_{TiX}(T) - FS_{MC0}(T)}{FS_{MC0}(T)} \times 100$$

where:

$FS_{TiX}(T)$ = Flexural strength of MC-TiX mortar, cured at temperature T (MPa)

$FS_{MC0}(T)$ = Flexural strength of MC-R mortar, cured at temperature T (MPa)

T = Temperature ($^{\circ}\text{C}$)

X = Percentage of additive used.

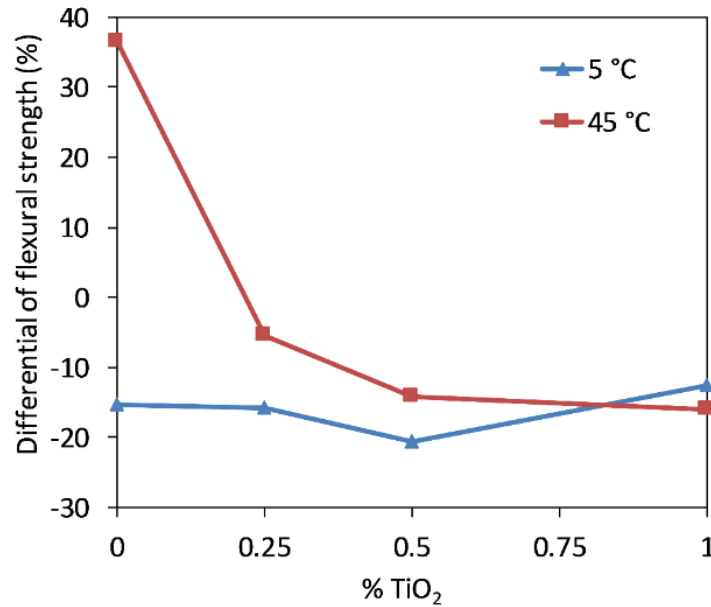


Figure 2.6 Difference in flexural strength due to temperature changes compared to 20 $^{\circ}\text{C}$.

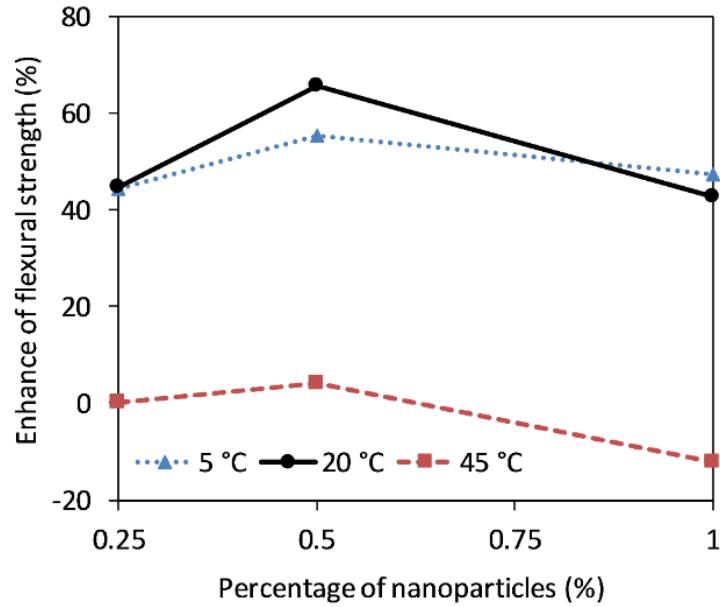


Figure 2.7 Relative flexural strength increase (%) respect to each curing temperature.

We noted that the increase in flexural strength due to the addition of TiO_2 is lower for samples cured at 45 °C than at standard temperature (20 °C). This should be considered in order not to overestimate flexural strength of mortar in real applications, outside the laboratory, where curing temperature can easily be higher than standard (20 °C).

With 1% of TiO_2 , the effect of the addition of nanoparticles depends on curing temperature with a constant tendency: at a lower curing temperature, it corresponds to a greater increase in percentage of flexural strength. With lower TiO_2 percentages (0.25% and 0.5%), the largest percentage gain is observed at 20 °C.

2.4.3 Response Surface Methodology (RSM)

After performing compression and flexural tests, RSM was applied to obtain an estimation model of the strength of mortars as a function of curing temperature and percentage of TiO_2 . Results shown in Figure 2.2 and Figure 2.5 were used as input for central composite design. Thereafter using ANOVA, we obtained the analysis displayed in Table 2.3. While compressive results have high accuracy (low p-values), flexural p-values have more dispersion, with values close to the significance threshold ($\alpha=0.10$).

Table 2.3 ANOVA analysis.

		Compressive strength			Flexural strength		
		DF ^b	F-value	P-value	DF	F-value	P-value
	Constant	5	0.000	0.000	5	0.012	0.012
Linear	X_1^a	1	0.001	0.001	1	0.093	0.093
	X_2	1	0.000	0.000	1	0.053	0.053
Square	$X_1 \cdot X_1$	1	0.001	0.001	1	0.048	0.048
	$X_2 \cdot X_2$	1	0.000	0.000	1	0.005	0.005
Interaction	$X_1 \cdot X_2$	1	0.002	0.002	1	0.033	0.033

^a X_1 : Temperature, X_2 : % TiO₂

^bDF: Degrees of freedom

As a result of the statistical analysis, two equations (Eq. (2.6) and (2.7)) were obtained. These equations estimate compressive (C.S.) and flexural strength (F.S.); in Eq. (2.6) and (2.7), respectively, by modifying both variables (temperature and percentage of TiO₂).

$$C.S. = 10.04 + 0.803 T + 47.69 \% TiO_2 - 0.01061 T \cdot T - 31.01 \% TiO_2 \cdot \% TiO_2 - 0.2908 T \cdot \% TiO_2 \quad (2.6)$$

$$F.S. = 3.094 + 0.1429 T + 7.61 \% TiO_2 - 0.001911 T \cdot T - 5.19 \% TiO_2 \cdot \% TiO_2 - 0.0612 T \cdot \% TiO_2 \quad (2.7)$$

where:

C.S. = Compressive strength (MPa)

F.S. = Flexural strength (MPa)

T = Temperature (°C)

% TiO₂ = Percentage of titanium dioxide nanoparticles.

Figure 2.8 displays the contour plot from MINITAB software representing strength estimations by using Eq. (2.6) (a) and (2.7) (b), respectively.

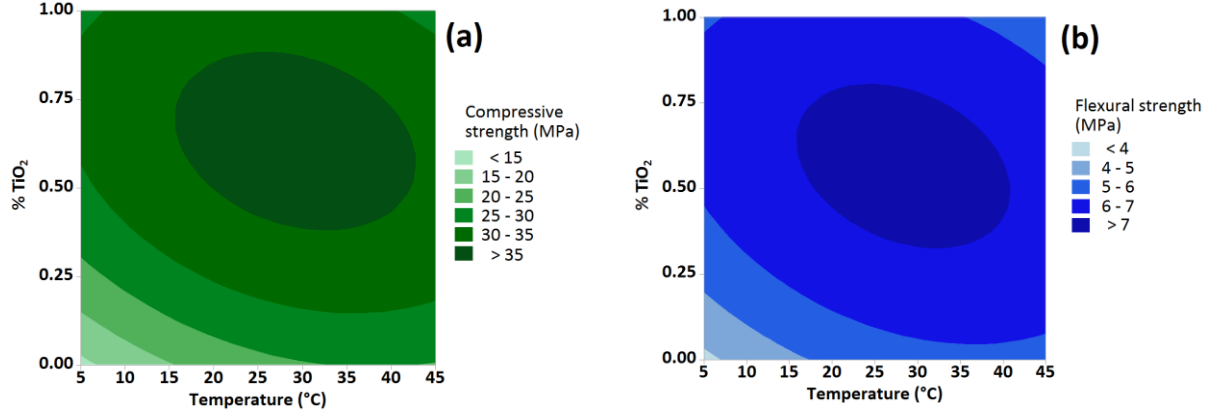


Figure 2.8 Contour plot of estimations at 7 days. (a) Compressive strength. (b) Flexural strength.

Figure 2.9 shows estimations calculated by using Eq. (2.6) (a) and (2.7) (b), respectively. While dash lines are related to estimations values, the points indicate experimental results. In the case of compressive strength, the error of estimations is lower than 5%. However, the estimation of flexural strength of the reference mortar at 20 °C has an error significantly higher (15%).

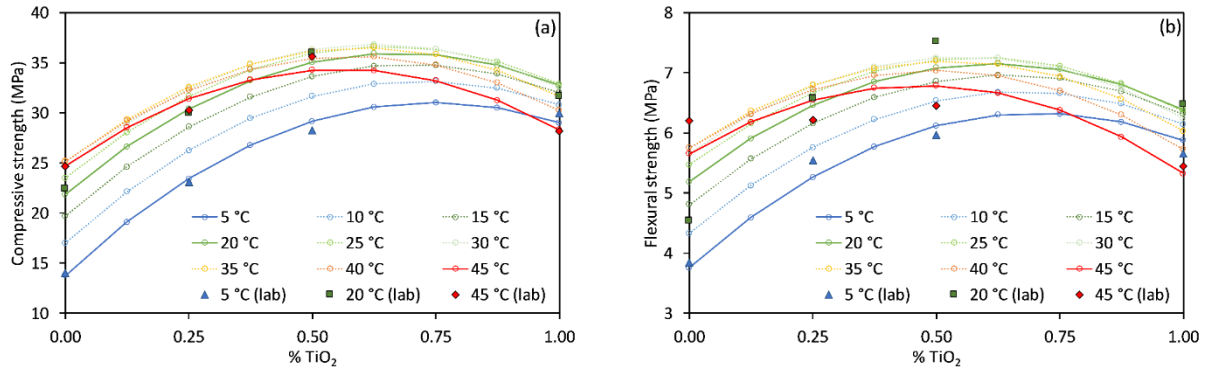


Figure 2.9 Strength estimations at 7 days according to RSM model. (a) Compressive strength. (b) Flexural strength.

As it is observed in Figure 2.9a, estimations of compressive strength show a trend: the optimum percentage of TiO₂ is between 0.5-0.75 percent. Moreover, the optimal temperature is between 25 and 30 °C.

Similar trend is shown in Figure 2.9b for flexural strength. Nevertheless, in the latter changes in peak values are more emphasized. The higher is the curing temperature, the lower is the optimum percentage of TiO₂. For example, for 5 °C the optimum percentage of TiO₂ (for

flexural strength) is 0.75%, but at 45 °C the optimum percentage of TiO₂ is 0.5%. It was observed that, for curing temperatures between 40 and 45 °C, adding 1% of TiO₂ has a negative effect on flexural strength taking as a reference the values of mortar without TiO₂ for the same temperatures.

2.4.4 Calcium hydroxide formation by DSC analysis

Differential scanning calorimetry (DSC)

Figure 2.10 shows the quantitative results and the development of CH formation over time. Plots from DSC tests are attached in APPENDIX B. As it was expected, the higher the curing temperature, the higher the amount of Portlandite (CH) generated. This occurs because elevated temperatures accelerate hydration, thus higher amount of hydration products are generated. Furthermore, the development of CH is in line with the evolution over time, at later ages more calcium hydroxide is generated. Finally, it is clear from results how hydration is promoted by high temperatures. In fact, the difference in the formation of CH over time decreases as curing temperature increases. After 1 day of curing at 45 °C, the amount of calcium hydroxide for the reference mortar is the 75% of the amount at 7 days. In contrast, the amount of CH for MC-Ti0.5 at 1 day with curing temperature 45 °C is almost 100% of the amount at 7 days. Therefore, the substitution of 0.5% of TiO₂ produced a great acceleration of CH formation during the first day at 45 °C, in comparison of the same value for reference mortar.

After 1 day of curing at 5 °C, the reference mortar developed only 22% of CH formed at 7 days. For MC-Ti0.5, the amount of calcium hydroxide at 1 day of the mortar cured at 5 °C is the 25% of the amount at 7 days for the same curing temperature. Therefore, addition of 0.5% of TiO₂ also accelerated CH formation during the first day at low temperature, but not in the same magnitude than at high temperature.

As it is presented in Figure 2.10a reference mortar samples cured at 45 °C presented 17%, 10% and 16% more CH than the same mortar cured at standard temperature (20 °C) at 1, 3 and 7 days, respectively. Instead, samples cured at 5 °C presented 69% and 19% less CH than the same cured at 20 °C for 1 and 3 days, but no significant difference at 7 days was observed.

The mortar with 0.5% of TiO_2 showed 42%, 18% and 3% more CH at 45 °C after 1, 3 and 7 days of curing than the same mortar at 20 °C (Figure 2.10b). On the contrary, at 5 °C was observed a decrease in the percentage of CH of 69%, 23% and 10% at 1, 3 and 7 days, respectively.

The addition of 0.5% of TiO_2 accelerated CH formation during the first day because the obtained percentage of CH comparing 1 and 7 days is bigger than in the reference mixture. Even though this acceleration, no positive effect of TiO_2 on the total percentage of CH at 7 days has been found. With respect to experimental results of compressive and flexural strength, it was expected that, with a substitution of 0.5% of TiO_2 by weight of cement, hydration would have been promoted.

According to literature [24,37,48,49,86,87], the intensity of Ca(OH)_2 (CH) can be promoted by TiO_2 , as more amount of hydration products is generated, due to the nucleation effect of nanoparticles. However, some opposite results that uphold our results have been reported [24,88]. Titanium dioxide nanoparticles have been found acting as inert in the cement hydration process and not participating in the pozzolanic reaction [24,88]. Furthermore, several authors [24,39,49,50,89] reported that due to the usage of nano-titanium dioxide the size of CH decrease because the presence of TiO_2 nanoparticles limit the growth space for Ca(OH)_2 crystals. Additionally, some other authors [39,90,91] indicated that the promotion of hydration is due to the acceleration of the formation of more C-S-H gel, thus limiting the growth of CH. This modification of CH size could promote the reaction between CH and CO_2 . Increasing the amount of carbonated CH during sample preparation. Consequently, DSC results would be only suitable to compare the development of CH in function of curing temperature of samples from the same mixture. This potential effect will be studied in the following section.

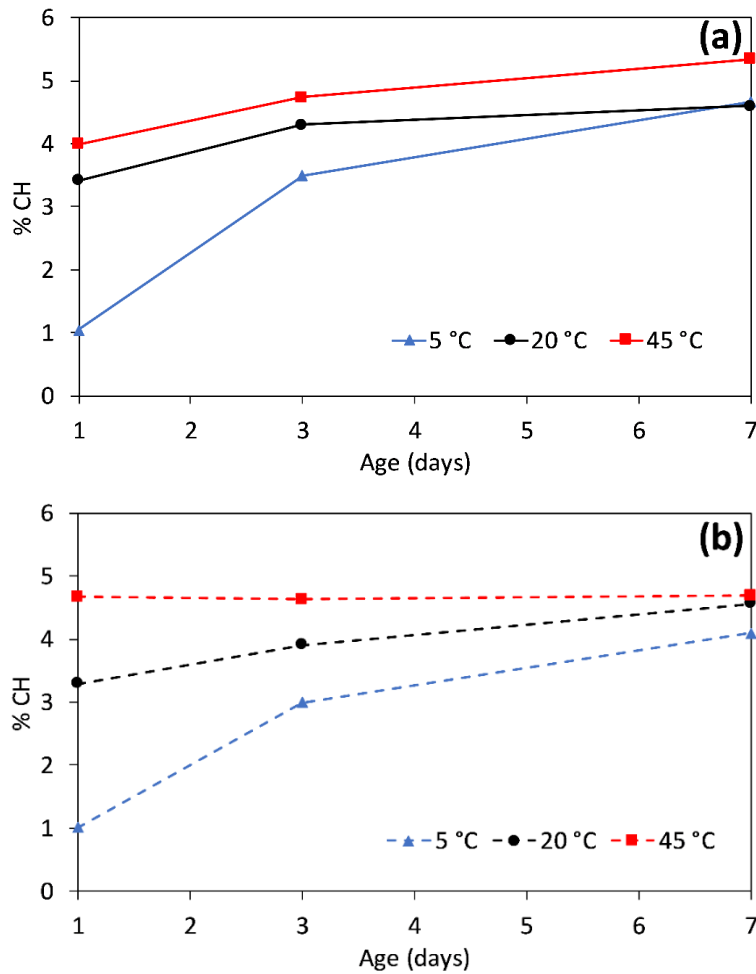


Figure 2.10 Percentage of calcium hydroxide (DSC) by mortar mass vs age of mortar (a) MC-R. (b) MC-Ti0.5.

TGA at 7 days

Using the software Universal Analysis 2000 (TA instruments), the percent mass loss was found for calcium hydroxide, and calcium carbonate. As aforementioned, the modified method proposed by Kim and Olek [60] was adopted. Plots for each of the mixtures were generated with the percent weight loss versus temperature, along with first and second derivative to better chose start, end and inflection points during the analysis. TGA curves are displayed in Figure 2.11.

Table 2.4 presents the CH percentage obtained based on TGA curves. The amount of CH increases with an increase of curing temperature for both standard and nano-modified samples as expected. During sample preparation, it was observed that while the ground cement paste was

completely passing, part of the aggregate was consistently retained in the 75- μm sieve. It was estimated that 40% of the aggregate was not completely ground during the process, and, therefore, was not part of the TGA sample. Thus, when CA_{ini} was calculated, the amount of aggregate/mortar in the sample was 0.40 instead of the full 0.67 in the original mortar. In the same way, the amount of cement/mortar in the TGA sample was estimated to be 0.40 instead of 0.22. The calculation for CA_{ini} is reported in Appendix B. At each age and temperature, samples with 0.5% nano- TiO_2 showed a higher CH content than samples without nanoparticles. This result agrees with outcomes from compressive and flexural strength, in fact, samples with 0.5% TiO_2 presented higher strength than reference samples. Additionally, results suggest that TiO_2 nanoparticles affect the amount of carbonated CH during sample preparation, making CH more susceptible to carbonation (Figure 2.11). As discussed in the previous section, the decrease of CH size due to the use of TiO_2 reported in previous studies [24,39,49,50,89–91] could explain this increase of carbonation ratio. For example, the value of CH for reference mortar cured at 5 °C is 6.55% before correction, and 7.93% after adjustment. It means the percentage of total CH that was carbonated due to the sample preparation process, in this case, was 17.4%. However, the percentage of CH carbonated during sample preparation in mortar with TiO_2 at the same curing temperature was 41.1%. For this reason, CH results of mortar with and without TiO_2 can be compared only after adjustment, considering the differences on CH carbonation during sample preparation.

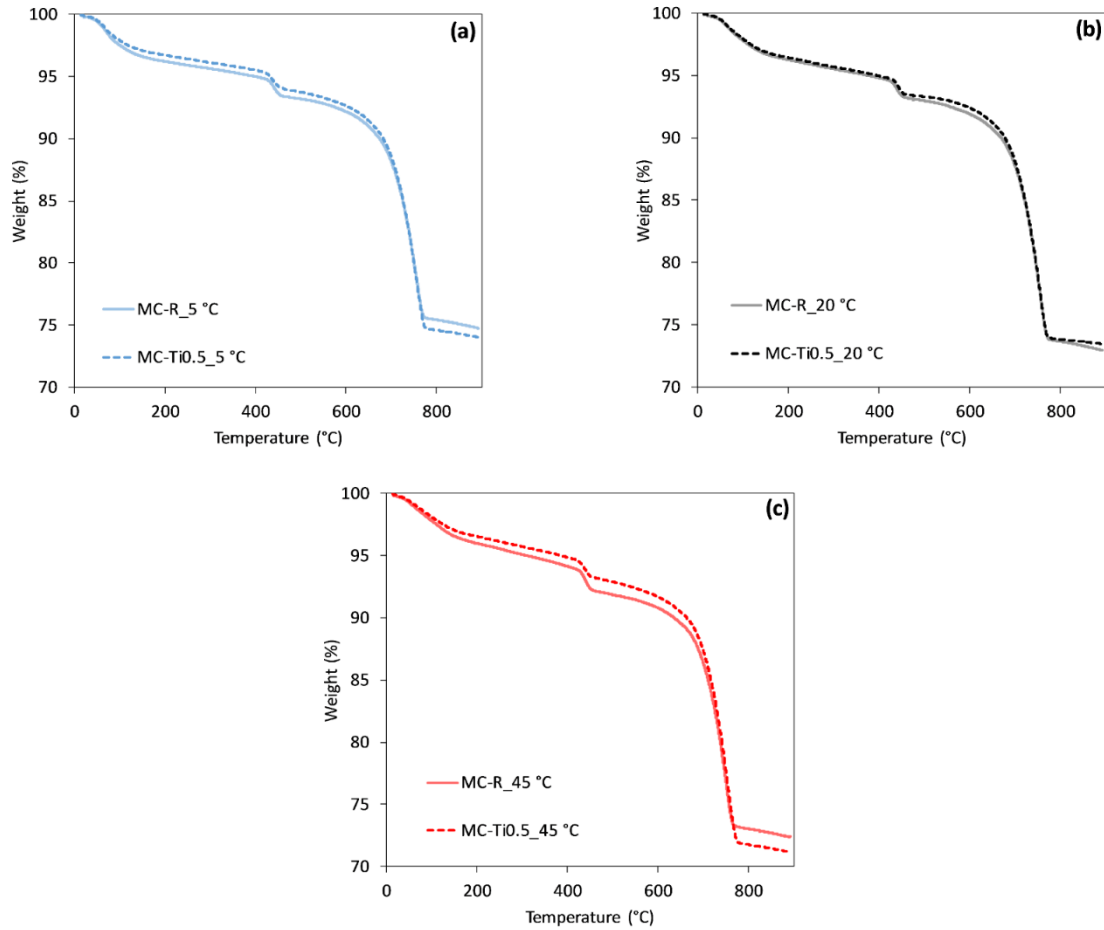


Figure 2.11 TGA curves at 7 days for different curing temperatures. (a) 5 °C. (b) 20 °C. (c) 45 °C.

Table 2.4 Comparison between % CH based on TGA analysis before and after carbonation adjustment.

% of CH in cement paste [7 days]			
		TGA without adjustment due to carbonation	TGA after adjustment due to carbonation
5 °C	MC-R	6.55	7.93
	MC-Ti0.5	6.13	10.40
20 °C	MC-R	6.46	9.54
	MC-Ti0.5	6.13	9.88
45 °C	MC-R	7.78	11.48
	MC-Ti0.5	6.79	12.14

2.4.5 Pore structure analysis through 3D X-Ray Microscope (3D XRM)

Figure 2.12 presents 3D pore structure of both reference mortar (MC-R) and mortar with 0.5% TiO_2 (MC-Ti0.5). Most researchers accept the standpoint that titanium dioxide decreases pore diameter and total specific pore volume [44–50]. This improves compactness of cementitious composites and enhances microstructure making it denser by filling pores. Nano-titanium dioxide possesses the *small size effect* and the *filling effect* that enable nanoparticles to serve as nuclei to influence pore structure of cementitious composites, which improves the performance of compressive and flexural strength and even durability [37,40,92].

However, all previous studies were focused on the effect of TiO_2 nanoparticles cured at standard temperature (20 or 21 °C). The present paper showed results in agreement to previous researches for standard curing temperature. Based on our data, total pore volume decreases due to the use of TiO_2 at 20 °C (Figure 2.13 and Figure 2.14). By using 0.5% of TiO_2 , at standard temperature, total porosity was reduced slightly more than half. Nevertheless, with low and high temperatures (5 and 45 °C) the effect of 0.5% of TiO_2 on total porosity is not significant. The mortar that presented the lowest porosity (MC-Ti0.5 cured at 20 °C) was the same mortar that showed the highest compressive strength at 7 days. However, a general correlation between total porosity and strength of mortars was not found.

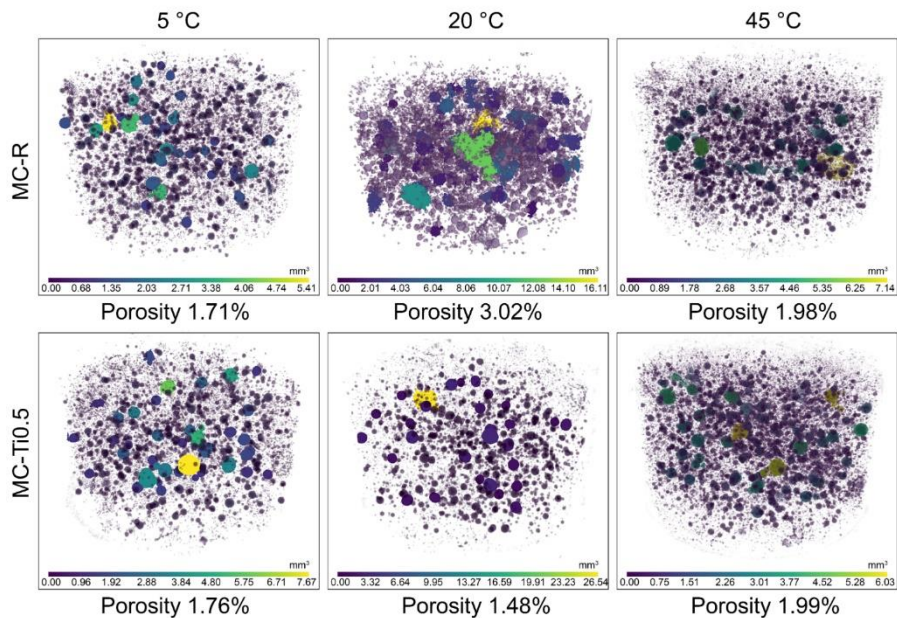


Figure 2.12 Pore structure of mortar samples cured at three temperatures.

Figure 2.13 displays pore volume histograms of each mortar cured at 5 °C, 20 °C and 45 °C. When curing temperature was 20 °C or 45 °C, samples with TiO₂ presented a more homogeneous pore structure and smaller pores than samples without nanoparticles. It could explain the higher strength at 7 days of samples with TiO₂ compared to samples without TiO₂. Whereas samples cured at 20 °C and 45 °C developed most of strength and structure at 7 days, samples cured at 5 °C have a lower equivalent age. It could explain that when curing temperature is 5 °C, porosity distribution and strength at 7 days are not showing a clear correlation, due to the different maturity of the samples. For high curing temperatures (45 °C), the effect of nanoparticles in the distribution of pore volume is less significant than at 20 °C. It also matches with the improvements observed in compressive strength due to the addition of TiO₂; while an addition of 0.5% TiO₂ showed an improvement in compressive strength of 60% in samples cured at 20 °C, samples cured at 45 °C presented an enhancement of only a 44% of compressive strength, by using the same percentage of TiO₂.

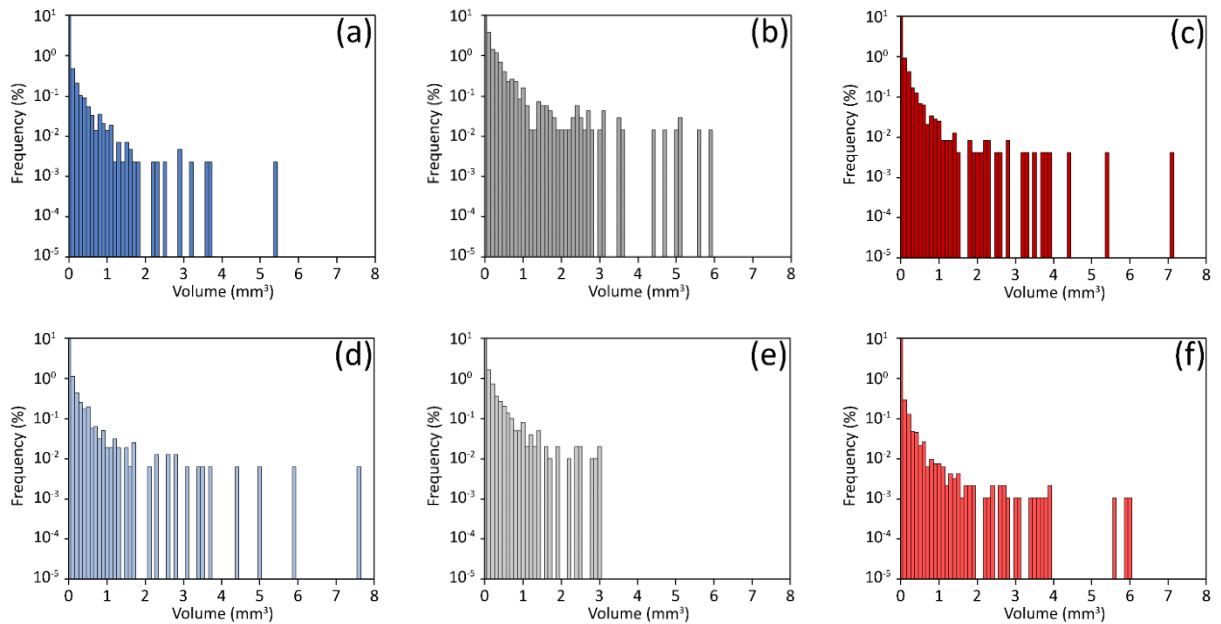


Figure 2.13 Histogram of pore volume. (a) MC-R at 5 °C. (b) MC-R at 20 °C. (c) MC-R at 45 °C. (d) MC-Ti0.5 at 5 °C. (e) MC-Ti0.5 at 20 °C. (f) MC-Ti0.5 at 45 °C.

Histograms of aspect ratio are shown in Figure 2.14. The aspect ratio describes the proportional relationship between the smallest eigenvalue and the largest one for the inertia eigenvectors of each pore, where aspect ratio equal to one means a perfect sphere. It is remarkable that, at standard temperature (Figure 2.14b and Figure 2.14e), aspect ratio seems to be increased by TiO_2 , making pores more spherical. A study of the effect of TiO_2 in air void system could be interesting, considering results of Figure 2.12, Figure 2.13, and Figure 2.14: at standard temperature, TiO_2 decreases porosity, reduces pore volume, and makes them more spherical.

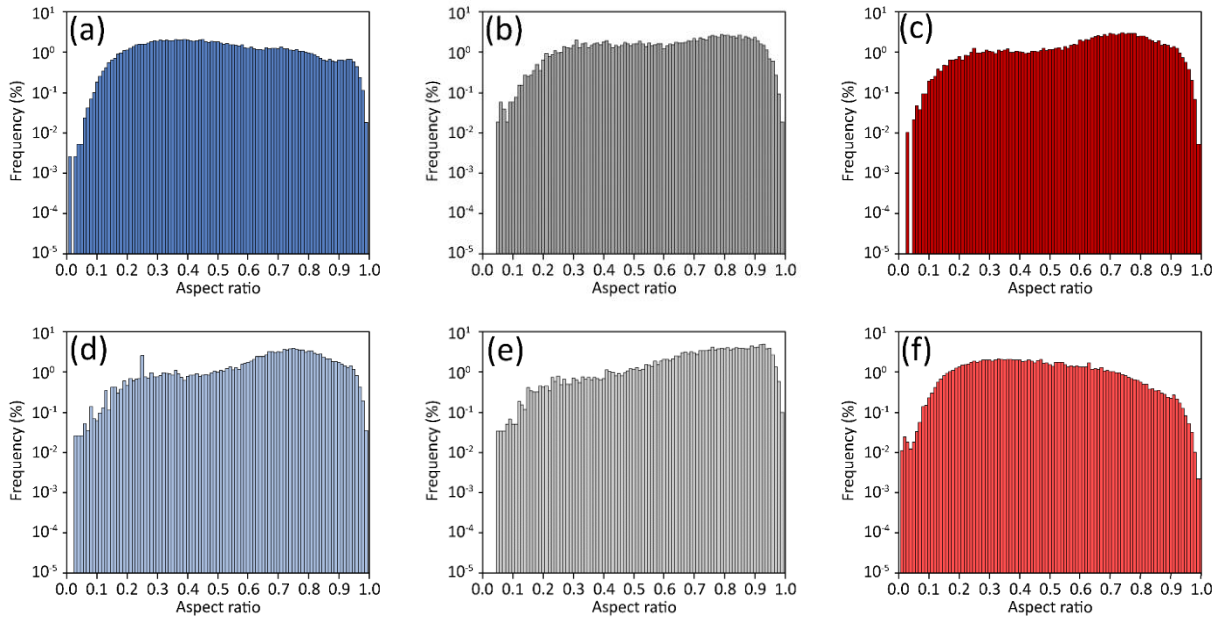


Figure 2.14 Histogram of pore aspect ratio. (a) MC-R at 5 °C. (b) MC-R at 20 °C. (c) MC-R at 45 °C. (d) MC-Ti0.5 at 5 °C. (e) MC-Ti0.5 at 20 °C. (f) MC-Ti0.5 at 45 °C.

Air voids in concrete and mortars are very small bubbles that improve freeze-thaw resistance of the material. The diameter of air voids is typically between ten microns and less than one millimeter [93]. These voids are usually spherical bubbles. In order to do a comparison between air voids of each system, pores with size equal or smaller than 1 mm and an aspect ratio bigger than 0.75 (0 means a line and 1 refers to a perfect sphere) were selected. This calculation does not pretend to be an exactly quantification of the percentage of air voids. However, it could help to give a preliminary idea of how TiO_2 could affect air voids. Results (Table 2.5) show two different effects of TiO_2 regarding curing temperature. At room temperature (20 °C) and 45 °C,

the percentage of air voids has been increased with the addition of TiO₂. In contrast, at 5 °C there is less percentage of air voids in mixtures modified with nanoparticles.

Focusing on the data at standard curing temperature, these results suggest that mixtures with TiO₂ have bigger percentage of air voids than non-modified ones. These results also suggest that with a very small amount of TiO₂ (0.5%), mortar durability could be improved significantly, since TiO₂ produced a reduction of total porosity and an enhancement of air voids in the system. Whereas the study of durability is out of the scope of this paper, observations suggest that it could be an interesting topic for the future and that addition of TiO₂ could help to improve durability of concretes and mortars beyond the improvement due to total porosity reduction.

Table 2.5 Air voids percentage by total volume.

Mortar	Air voids (%)		
	5 °C	20 °C	45 °C
MC-R	1.10	0.79	0.99
MC-Ti0.50	0.91	0.89	1.13

2.5 Conclusions

Based on what has been observed, the following conclusions can be drawn:

- The influence of TiO₂ on compressive strength is positive for all studied curing temperature, for the studied percentages of nano-TiO₂ addition. The greatest benefits have been observed at low temperatures (5 °C). A 1% replacement produces the largest increase in strength at 5 °C compared to the mortar with no TiO₂ (MC-R). However, it should be noted that, for higher temperatures (20 °C and 45 °C), the optimum level of TiO₂ substitution is not the highest one: the higher compressive strength for these curing temperatures was achieved with 0.5% of TiO₂. In addition, it is remarkable that, with 1% of TiO₂, compressive strength at 7 days of samples cured at 45 °C is lower than samples cured at 20 °C, and even at 5 °C, which is something a priori unexpected. Hydration process is still not completely finished at 7 days, consequently, the higher is the curing temperature, the higher should be the compressive strength due to the hydration acceleration as a function of temperature.

- In terms of flexural strength, nano-TiO₂ has no positive effects at high curing temperatures (45 °C) whatever the percentage of substitution. In contrast, at lower temperatures the addition of nanomaterial produces a noticeable improvement. In all cases the best results were observed with a percentage of substitution of 0.5% reaching a maximum at 20 °C (curing temperature) with an increase in flexural strength of 65% and exceeding the strength obtained from the reference mortar MC-R (without TiO₂) cured at 45 °C. For the same mortar (with 0.5% of TiO₂), cured at 5 °C, the increase in flexural strength was 50% respect to strength of the reference mortar cured at the same temperature (5 °C), with values very close to the flexural strength of the reference mortar cured at 45 °C. Finally, it is worth noting that when using TiO₂ as an additive in cement-based mortars particular care must be taken when curing temperature increases (45 °C). When curing temperature is high (45 °C), an overestimation of 7-day flexural strength can occur if the beneficial effects of nano-TiO₂ addition observed at standard temperature (20 °C) are assumed.
- For both flexural and compressive strength at 7 days, the optimum percentage of nano-TiO₂ depends on curing temperature. The lower the curing temperature, the higher the optimum percentage of nano-TiO₂.
- DSC results suggested that a 0.5% nano-TiO₂ addition accelerated CH formation during the first day at 45 °C. On the other hand, the total percentage of CH at 7 days was lower in mixtures with TiO₂ nanoparticles for all studied curing temperatures. However, TGA results obtained using the modified method for CH calculation showed that the use of 0.5% nano-TiO₂ increases the CH content.
- The use of nano-TiO₂ influences CH carbonation, increasing the percentage of CH carbonated during sample preparation. For that reason, to compare CH in mixtures with and without nanoparticles, TGA modified method should be used. Since samples were 7 days old, it is assumed carbonation occurred only due to sample preparation.
- 3D-XRM results suggest that the increase in strength due to the use of nanoparticles is more related to the homogenization of the pore structure than to the overall porosity reduction. In fact, the samples cured a low temperature showed a higher increase in strength due to the use of nano-TiO₂, however, nanoparticles addition did not produce a reduction in porosity in those samples. At standard temperature (20 °C), total porosity was strongly reduced by TiO₂ addition.

3. HIGH TEMPERATURE RESISTANCE OF ECO-MORTARS CONTAINING 100% RECYCLED CONCRETE AGGREGATES (RCA) AND NANO-TiO₂

A portion of this chapter has been published as:

Moro C., Francioso V., Velay-Lizancos M., “Nano-TiO₂ effects on high temperature resistance of recycled mortars”. *Journal of Cleaner Production*, Vol. 263, (2020), 121581. <https://doi.org/10.1016/j.jclepro.2020.121581>

3.1 Introduction

Concrete is among the most used materials in the world. Each year, over 30 billion tons of concrete are produced globally [2]. Consequently, a relatively slight improvement in its environmental impact would be translated into an enormous benefit for the planet. There are different approaches to reduce the environmental impact of concrete and similar construction materials. For example, using supplementary cementitious materials (SCM) as a cement replacement may be translated into a decrease of CO₂ emissions [4,5,94]. Another option could be using different types of recycled aggregates (RA) instead of natural aggregates. For instance, recycled concrete aggregates [6], mixed recycled aggregates [95], or recycled glass waste aggregates [96,97]. The use of recycled concrete aggregate may increase the sustainability of the construction industry by reducing the depletion of raw materials, the number of quarries and waste in landfills [6,7]. However, it also reduces strength [6,13,79] and increases porosity [98] of concrete. Moreover, during the last decades, some researchers have studied the photocatalytic concrete and its potential applications in terms of sustainability [99–101]. Incorporating TiO₂ could be beneficial for reducing contamination levels in air due to its photocatalytic property [101–103]. This effect is divided in two steps: depollution and self-cleaning. First, TiO₂ nanoparticles react with pollutants from air (NO_x, SO_x, CO_x, VOC_s) in the presence of light [8,104]. These chemical reactions turn the pollutants into non-hazardous compounds [8,104]. Secondly, self-cleaning refers to the ability to decompose those chemicals that are removed from the concrete [105]. Despite its photocatalytic potential, the effect of TiO₂ on mechanical properties is still debatable. Several publications have appeared documenting the influence of TiO₂ on compressive strength of mortars [18,24,34,48,106–112]. Previous research indicated that TiO₂ has a positive

impact on compressive strength of mortars with up to 5% nanoparticles [24,48,106–109], regardless the type of TiO_2 nanoparticles used [110]. A possible explanation for these results may be the acceleration of the hydration process and porosity reduction [48]. On the other hand, several studies have reported that compressive strength may be decreased with the rise of TiO_2 percentage under certain circumstances [18,34,111,112]. Besides, a recent publication [113] evaluates the influence of curing temperature on the effect of TiO_2 on mortars properties. This study [113] claims that the higher the curing temperature, the lower the positive effect of TiO_2 on the mechanical properties of mortars. In any case, incorporating TiO_2 in concrete and mortar would add value in terms of sustainability. Although extensive research has been carried out on the effect of nanoparticles in concrete and mortar with natural aggregate (NA), there is a lack of knowledge for RA.

Another approach, to make concrete more sustainable, rather than using different waste materials and air-purifying the environment, is improving its durability. Thus, reducing reconstructions and saving resources and energy. Durability in concrete and mortar with RA is generally lower than that of NA. Previous literature has shown that durability decreases with an increase in the percentage of RA [114]. Aggregates represent between 60-75% of the total volume of concrete [115]. Therefore, the type of aggregate is an important factor in durability. Recycled aggregates have higher water absorption and weaker bonding due to the presence of old mortar stuck to the surface. Consequently, porosity increases leading to a reduction in mechanical properties and resistance to chemical attack [114,116]. In the last few years, research on concrete and mortar made with recycled aggregates at high temperatures has been done [117–124]. However, the results are contradictory. Whereas some authors have observed that RA has higher residual strength than NA after exposure to elevated temperatures [117–121], others have remarked that NA samples experiment less drop than RA specimens after thermal exposure [122–124]. Consequently, there is no agreement on the effect of RA in thermal resistance of concretes and mortars. It is remarkable since fire resistance is one of the concrete properties that supports the use of this material for construction [125–127], in comparison with other materials as wood (combustible) or steel (non-combustible but non-fire resistant). Concrete protects from the spread of fire while keeping its structural capacity almost unchanged for some time [127–129], allowing evacuation completely before structural failure. Therefore, it may save lives. Even though concrete and mortar are fire-resistant, many properties (such as compressive strength or elasticity modulus)

after exposure to high temperatures are affected, as it was reported in several publications [130–133]. However, limiting these drops may be useful to obtain a more efficient material.

Under high temperatures exposure, concrete and mortar experience several changes in their composition due to complex physical and chemical phenomena. Primarily, an increase in temperature causes free moisture loss, followed by physically absorbed and chemically combined water loss of the hydrated products (around 100 °C) [55,56]. During this evaporation, mass and strength loss are higher due to the disappearing of free water and shrinkage in cement paste (or mortar), and the expansion of the aggregates causes micro cracking. Subsequently, there is a wide range, between 100 and 400 °C, where several components (i.e., bond water, calcium silica hydrate (C-S-H), ettringite, calcium aluminate hydrate, carboaluminate hydrates) decompose [55–59]. However, it is difficult to identify each single component undergoing its decomposition reaction along with the corresponding temperature peak. Afterward, portlandite or calcium hydroxide (CH) is broken down between 410 and 520 °C as several studies indicate [55,56,59,60,78,106]. This component is strongly related to mechanical strength in plain concretes (without supplementary cementitious materials) in the absence of chemical attacks (which implies no compounds reacting with CH); since the main products of Portland cement hydration are C-S-H and CH, and both compounds are formed together at fixed proportions, in this type of mortars, the higher is the CH, the higher will be the C-S-H. Finally, the decay of calcium carbonate happens among 630 and 830 °C, as several publications have argued in recent years [55,56,59,60].

Since the use of nanoparticles influences the growth of hydration products and the mortar microstructure [40,113], it also may change the behavior of concretes and mortars at elevated temperatures. Few studies have investigated the influence of TiO₂ nanoparticles on cementitious materials at high temperatures. Farzadnia et al. [134] found that adding TiO₂ on high strength mortars is beneficial for increasing their high temperature resistance up to 400 °C. They pointed out that it may have two reasons: higher hydration rate and nucleation effect produced by TiO₂. They observed that TiO₂ nanoparticles raise the brittleness in comparison with control samples up to 400 °C [134]. Besides, above that temperature, results may suggest that TiO₂ has no impact on the residual compressive strength compared to the reference mortar [134]. In addition, Biolzi et al. [135] have conducted an investigation using cement modified with TiO₂. They concluded that high temperatures stimulate the propagation of microcracks due to the incompatibility of constituents [135]. They also showed that ductility is increased after exposure to elevated temperatures. These

investigations were focused on mortars with NA. No previous study has been found evaluating the influence of TiO_2 in mortars made with RA at elevated temperatures. The differences between mortars with NA vs. mortars with RA (e.g., higher porosity or lower strength) may change the effect of the nanoparticles under high temperatures. Based on the aforementioned, this paper aims to study the potential effect of TiO_2 on high temperatures resistance of recycled mortars.

3.2 Materials

3.2.1 Mix-design

Five different mixtures were designed in accordance with EN196 [65]: a reference mortar (NM0) with neither recycled aggregates (RA) nor TiO_2 and four mortars (RM0, RM0.5, RM1, and RM2) with 100% RA and different percentage of TiO_2 from 0% to 2%. Specimens had dimensions of 40 mm x 40 mm x 160 mm, following ASTM standard [136,137]. Mixtures proportions are displayed in Table 3.1. the amount of water was adjusted based on the absorption test.

Table 3.1 Mix Proportions for Mortar Samples.

Batch	NM0	RM0	RM0.5	RM1	RM2
Cement (g)	400	400	398	396	392
Natural Sand (g)	1200	0	0	0	0
Recycled Sand (g)	0	1200	1200	1200	1200
Effective w/c	0.55	0.55	0.55	0.55	0.55
Effective Water (g)	219.6	219.6	218.5	217.4	215.2
Absorption (%)	2.20	7.73	7.73	7.73	7.73
Abs. Water (g)	26.4	92.8	92.8	92.8	92.8
Total Water (g)	246.0	312.4	311.3	310.2	308.0
TiO_2 (g)	0	0	2	4	8

Mortars were made with Portland cement Type 1 (Infinity, commercial grade). NM0 is the only mortar made with quarzitic natural fine aggregate. The remaining mortars (RM0, RM0.5, RM1, RM2) were made with recycled fine aggregate, which comes from construction and demolition waste, obtained from a Lafayette aggregate distributor (Purdy Materials, Lafayette IN). It is mainly made from old concrete, but it also presents small drops of asphalt and brick. Particle size distribution and absorption were performed, according to ASTM [138,139], in order to characterize both aggregates. Data from the sieve analysis can be found in Table 3.2.

Titanium (IV) oxide (TiO₂) nanoparticles (85% anatase and 15% rutile, >99.5% of trace metal basis) were purchased by Sigma-Aldrich (St. Louis, MO). Its primary particle size (d₅₀) is 21 nm (TEM - transmission electron microscopy). It exhibits a surface area of 35-65 m²/g and a formula weight of 79.87 g/mol.

Table 3.2 Particle size distribution of both aggregates.

Sieve No.	Natural Aggregate Cumulative Percent Passing (%)	Recycled Aggregate Cumulative Percent Passing (%)
4	99.96	99.72
8	90.8	83.2
16	63.2	60.6
30	35.5	36.7
50	10.7	16.5
100	1.3	8.2
Pan	0.0	0.0

Mortars were mixed as follows: First, cement and TiO₂ (if applicable) were mixed at low speed for two minutes. Later, container walls are scraped to mix in any cement that is stuck to the sides. Fine aggregate is then included in the pan and mixed for two minutes. Water is incorporated and batch mixed for two minutes. Mixer is stopped, and any mortar that may have been collected on the side of the bowl is quickly scraped down into the batch. Finally, mortar is mixed for 1 minute and 20 seconds more.

When the mixture process is finished, the mortar is cast into the molds and leveled with a trowel. The molds are then vibrated for 45 seconds. Afterward, they are wrapped in plastic film and left for 24 hours at 23 ± 1 °C and 90% humidity. After one day of curing, samples are demolded and submerged in water trays at the same controlled temperature until testing.

3.3 Methods

3.3.1 Flexural and compressive strength test of mortar under standard conditions

Flexural and compressive tests were conducted according to ASTM standards [136,137]. Samples were tested at 90 + 1 days after exposure to high temperatures (except for those cured at 20 °C). Flexural strength test was performed using an MTS machine with a load capacity of 10 kN, a velocity of 0.05 mm per second, and displacement control. Compressive strength test was carried out on the two halves of each broken prism from the previous test. Beforehand, four-centimeter cubes from the ends of the broken prisms were cut. Compressive test was performed by an MTS machine with a load capacity of 300 kN and at a velocity of 0.05 mm per second.

3.3.2 Method to evaluate residual strength

In order to evaluate the effect of high temperature exposure on mechanical properties of studied mortars, a muffle oven (Figure 3.1a) was used to treat samples before the tests. At least four samples of each mortar were tested. Two samples of each mortar were exposed to 250 °C for two hours. Test started from room temperature (23 °C) and reached the target temperature with a heating ramp of 5 °C /min. After two-hour exposure at maximum temperature, the oven is turned off, and samples are left inside for 30 minutes to let the temperature decrease avoiding a thermal shock when the door is open. After this time, the oven is opened (marking a temperature of 220 ± 5 °C), and samples are removed, letting them cool down at room temperature during one day before testing. The other two samples, for each mortar, were exposed to 500 °C using the same procedure aforementioned. The only differences are starting point (50 °C), duration of the test (ramp period), 3.5 and 4.5 hours respectively, and temperature inside the oven when samples exposed to 500 °C are removed (440 ± 5 °C). Temperature history is showed in Figure 3.1b.

After the exposure, flexural and compressive strength test were performed as it was previously described for standard conditions.

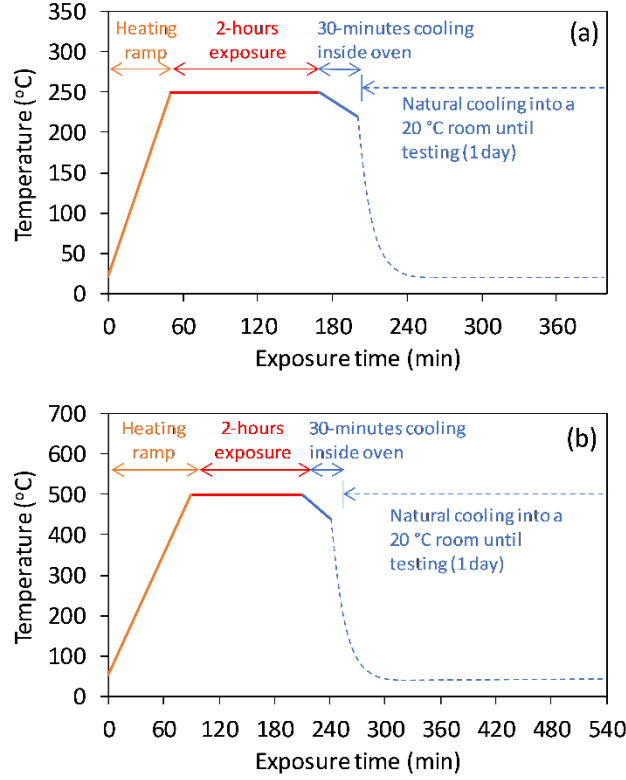


Figure 3.1 Evolution of the temperature exposure. (a) Target temperature 250 °C. (b) Target temperature 500 °C.

Finally, percentages of residual flexural and compressive strength are calculated according to Eq. (3.1) and Eq. (3.2), respectively, for each studied mortar.

$$\% \text{ of residual flexural strength after exposure at } T = \frac{FS_T}{FS_{20}} \times 100 \quad (3.1)$$

$$\% \text{ of residual compressive strength after exposure at } T = \frac{CS_T}{CS_{20}} \times 100 \quad (3.2)$$

where:

T = Target exposure temperature (°C).

FS_T = Flexural strength of mortar exposed to high temperature with target temperature T (MPa).

FS_{20} = Flexural strength of mortar under standard conditions (20 °C) (MPa).

CS_T = Compressive strength of mortar exposed to high temperature with target temperature T (MPa).

CS_{20} = Compressive strength of mortar under standard conditions (20 °C) (MPa).

3.3.3 Ductility

Ductility can be defined as the ability to undergo plastic deformations before fracture. There are some ways to evaluate. In this case, it is calculated from flexural strength test curves. After performing the test, the area under the curve after peak load (energy dissipation) is obtained, and the result is called G_f (N*mm), as it is shown in Figure 3.2.

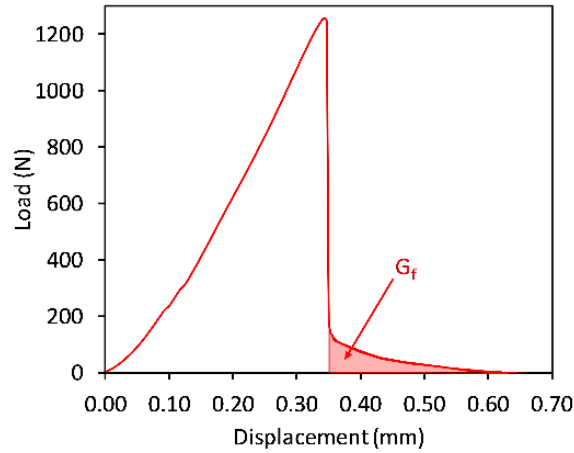


Figure 3.2 Ductility definition.

3.3.4 Correlation of mechanical properties with temperature and TiO_2 percentage

Several publications have appeared in recent years documenting the use of central composite design in response surface methodology (RSM) as a useful tool [66,67] to get the optimum solution. The focus of recent research has been on obtaining the optimum mix design by changing mix proportions [69–73].

In order to perform RSM statistical experimental design, the chosen software was JMP (SAS Institute, North Carolina, USA). A second-order model was performed in order to get a better approximation of results (Eq. (3.3)). In it, the response variable is "y" the " β " coefficients are calculated using the least square method, and " ϵ " is the total error. The significance threshold level (α) was chosen as 0.05.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_i \sum_j \beta_{ij} x_i x_j + \epsilon \quad (3.3)$$

RSM analysis was performed in order to study the influence of temperature and TiO₂ in mechanical properties. Their ranges are 20-500 °C for temperature exposure and 0-2% for TiO₂ percentage. After a simulation process, the analysis of variance (ANOVA) was evaluated to obtain the significance of these properties.

3.3.5 Differential Scanning Calorimetry (DSC)

DSC (2010 differential scanning calorimeter, TA Instruments (New Castle, DE, USA)) was performed at 90 days to monitor Calcium Hydroxide (CH) formation. Tests were executed in a nitrogen gas atmosphere at a heating rate of 10 °C /min from 23 °C up to 600 °C. Both reference pan (empty) and sample pan (containing 15 mg to 25 mg of ground material) were kept open. After compression, samples of each mixture were ground with mortar and pestle and sieved through a 75-µm sieve. For the specimens heated at 500 °C, as they showed two distinct shades inside, powder from both center and external part was obtained cutting and sorting the specimen before the grinding process. Cores have maintained the original color in contrast to the most external part that underwent most of the effect of high temperature.

The determination of CH content at 90 days of the investigated mortars has been determined by evaluating the curves obtained from DSC analysis. Around 450 °C CH is decomposed [56,60,106]; at that temperature, a sharp peak in the curve can be identified. The dehydration peak area corresponding to the decomposition of CH is used to calculate its percentage. During the analysis, to better determine the start and endpoints of the CH peak, the second derivative curve has been displayed. The content of CH has been determined with Eq. (3.4).

$$CH (\%) = 0.0917 \times (peak\ area) \quad (3.4)$$

with:

CH (%): Percentage of calcium hydroxide;

0.0917: Slope of the calibration curve;

peak area: Energy absorbed during the dehydration of CH (J/g).

3.3.6 X-Ray Diffraction (XRD)

The preparation of the powder samples for XRD follows the same steps as DSC sample preparation. The XRD analysis was conducted using a Siemens D500 diffractometer (30 mA, 50 kV) at 0.02°/sec scanning rate (in 10-65° 2 θ range). Profex software [140] was used to analyze the XRD patterns.

3.3.7 Scanner Electro-Microscope (SEM)

SEM analysis was used to investigate changes in the microstructure due to the high-temperatures exposure. First, a sample of each mixture was dry-cut with a saw. Then, SEM specimens were completely vacuum impregnated with epoxy. After the vacuum is finished, samples are oven-dried for 8 h at 70 °C. Samples were then lapped using Hillquist (Denver, Colorado, USA) mesh flat diamond laps (45, 30, and 15 μ m). Subsequently, Buehler (Lake Bluff, Illinois, USA) microclothes lubricated with diamond pastes were used to polish the specimens with different grit sizes (9 μ m, 6 μ m, 3 μ m, 1 μ m, and 1/4 μ m). To prevent the accumulation of electrostatic charge, a palladium sputter-coated was applied on the top surface of the specimens. Finally, SEM analysis was conducted with 15 keV of accelerated voltage and using the ASPEX Personal SEM equipped with the energy dispersive x-ray (EDX) analyzer.

3.4 Results and Discussion

3.4.1 Flexural and compressive strength

Figure 2.1 displays flexural and compressive strength (Figure 3.3a and Figure 3.3b, respectively), before and after exposure to high temperature, for each type of mortar. After exposure to 250 °C, NM0 specimens presented higher either flexural or compressive strength than those non-exposed. These results are consistent with other studies that have shown that compressive strength of concretes and mortars may enhance when exposed up to 300 °C [126,141]. In contrast, this effect is not the same in specimens made with recycled aggregate (except for flexural strength of RM0).

Moreover, as it is expected, natural mortar (NM0) showed higher either flexural or compressive strength than recycled mortar (RM0) before exposure. Even NM0 samples exposed

to 500 °C exhibited higher strength than non-exposed RM0 specimens. In addition, RM0 specimens exposed to 500 °C suffered a drop in compressive and flexural strength of 45% and 38%, respectively, compared to the corresponding samples under normal conditions. In contrast, natural mortar exposed to 500 °C decreased by 18% and 33%, respectively. It could suggest that even though recycled aggregate may be beneficial to increase sustainable aspects, its potential negative effects on fire resistance should be considered in order not to lead to structural problems during its lifetime.

In terms of the TiO_2 effect, recycled mortar without nanoparticles showed a lower flexural strength than recycled mortars with TiO_2 before exposure (20 °C). In contrast, after exposure to high temperatures, the higher the percentage of TiO_2 , the lower the flexural strength. These results suggest that, while TiO_2 increases flexural strength under standard conditions, it may have a negative effect on the same property after exposure to high temperature. Besides, 0.5% and 1% of TiO_2 improve compressive strength under standard conditions. After two-hour exposure to 250 °C, the positive effect of TiO_2 on compressive strength decreased, and only RM0.5 presented higher compressive strength than the reference recycled mortar under the same conditions. After two-hour exposure to 500 °C, the compressive strength of mortars with TiO_2 was lower than the compressive strength of the mortar without nanoparticles. These results indicate that the use of TiO_2 in cement mortars with recycled aggregates has a negative effect on high temperature resistance in terms of compressive strength.

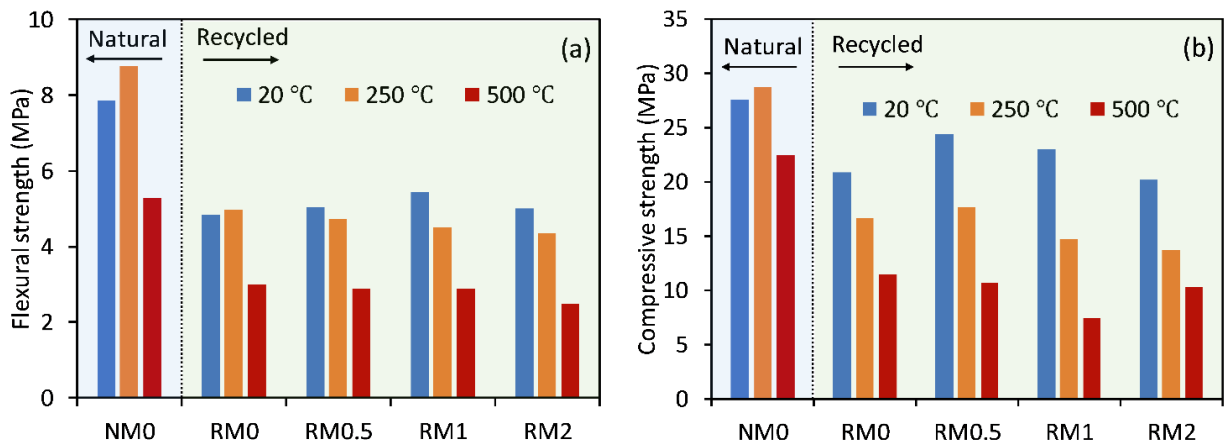


Figure 3.3 Strength before and after exposure to high temperature. (a) Flexural strength. (b) Compressive strength.

This effect is also observed in Figure 3.4. The percentage of flexural strength loss increases with the percentage of TiO_2 after two-hour exposure at 500 °C. The same trend is observed at 250 °C, except for RM2. In all cases, the percentage of flexural strength loss on mortars with TiO_2 is higher than the percentage loss of the reference mortar (RM0) without TiO_2 (Figure 3.4a). In fact, RM0 showed a higher flexural strength after exposure at 250 °C than in normal conditions (3% more). In contrast, under the same conditions, RM1 exhibited a decrease in flexural strength of 17% compared to the same mortar before exposure. After 500 °C exposure, while flexural strength loss is 38% for RM0, the drop for RM2 is over 50%. Figure 3.4b displays compressive strength loss, after exposure, for each recycled mortar. In all studied cases, the higher the TiO_2 , the higher the loss of compressive strength after exposure to high temperature, especially in RM0.5 and RM1, which are the mortars that showed an improvement of compressive strength at standard conditions in comparison to the same property of mortar without TiO_2 (RM0).

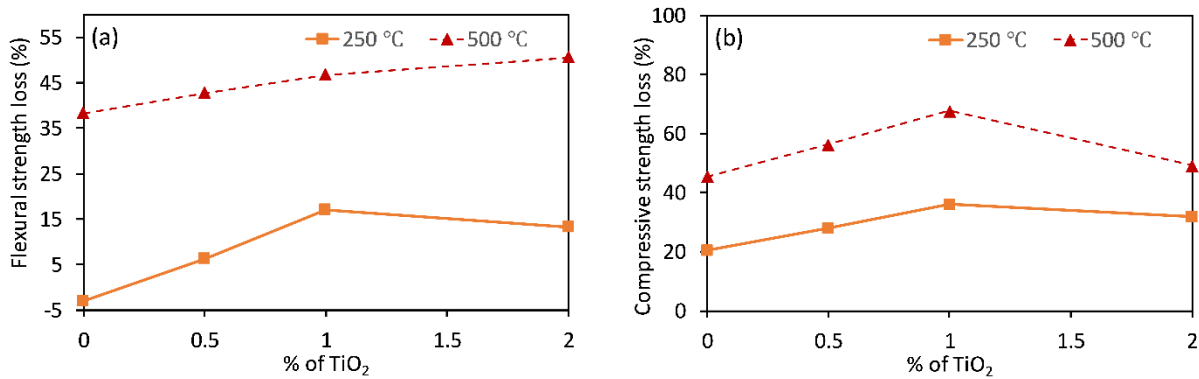


Figure 3.4 Strength loss of recycled mortar. (a) Flexural strength. (b) Compressive strength.

The higher loss of modified- TiO_2 mortars may be due to the increase of microcracks attributable to different thermal properties of constituents [135]. Several studies show that the coefficient of thermal expansion (CTE) varies with porosity and with the composition of the cement paste [142,143]. Since the old cement paste attached to the recycled aggregates and the new cement paste are from different mixture designs, it is expected that they will not have the same CTE. This difference is expected to be greater when nano- TiO_2 is used in the new cement paste, since these nanoparticles will reduce its porosity. In any composite, different coefficients of thermal expansion of the different compounds may cause internal stresses when the temperature changes. Previous research showed that the use of different percentages of recycled aggregate on

concrete reduces the overall coefficient of thermal expansion of concrete [144]. It suggests that the RA has lower CTE than natural aggregate, since concrete is a composite, and the thermal properties of the composite are the result of a combination of the properties of each compound.

It is known that the CTE of typical ordinary Portland cement paste (18×10^{-6} to 20×10^{-6} $1/^{\circ}\text{C}$) is generally higher than the CTE of natural aggregates (4×10^{-6} to 13×10^{-6} $1/^{\circ}\text{C}$) [145]. Previous research suggested that RAs have lower CTE than natural aggregates [144]. Therefore, the difference between the CTE of cement paste and RA is higher than the difference between the CTE of natural aggregates and cement paste. The higher the difference between the CTE of the different compounds, the higher the internal stresses when the temperature rises. It means mortars with RA may exhibit higher internal stresses than the same mortar with natural aggregates with temperature changes. Besides, it is well known that RA has a negative effect on the interfacial transition zone (ITZ). Thus, the different thermal properties of cement paste with nano- TiO_2 may induce additional thermal stresses that cause damage in the weak ITZ of mortars with RAs.

The results at 250°C on recycled mortars with TiO_2 exhibited different effects of the nanoparticles in comparison to a previous investigation on natural mortars [134]. Whereas TiO_2 showed a positive effect on the behavior of natural mortars at elevated temperatures [134], the results of the present study showed the opposite effect in case of using recycled mortars.

However, this difference may be explained by three main reasons: (i) the type of TiO_2 crystals used since, in the study with natural mortars, TiO_2 crystals were anatase, rutile and amorphous with proportions of 78%, 14% and 8%, respectively [134], while in the present study TiO_2 crystals were 85% anatase and 15% rutile without amorphous phases. TiO_2 crystals could also modify the behavior of the mortars because they may change the effect on several properties [42,146]. (ii) The exposure time is lower (1 hour); therefore, it cannot be enough for all the thermal processes in order to be developed. (iii) Different thermal properties of TiO_2 and the rest of mortar constituents may cause thermal stresses that affect in greater extend the weaker ITZ of mortars with RA, causing failure at low strength in the ITZ. On mortars with NA, the ITZ is stronger, and failure usually is produced on cement paste. For that reason, natural mortar may benefit its high temperature resistance because the addition of TiO_2 improves the microstructure of cement paste, while the potential thermal stresses could not be high enough to damage the stronger ITZ of natural mortars.

3.4.2 Visual analysis of samples

Figure 3.5 displays the inner section of the samples after thermal exposure and flexural test. The analysis exhibits a different coloration between the samples exposed to 250 °C and 500 °C with the samples left at room temperature. The higher the temperature, the lighter the sample. It was also observed the presence of more pores within the paste of the heated mortars. Manifestation of various black dots in the heated mortars are due to the presence of asphalt in the RA. It is more evident in the heated samples because the asphalt melting point occurs between 54-173 °C [147]. Additionally, samples heated at 500 °C showed two different shade. While the outer part exhibited a lighter shade, the core preserved the original color. After two hours of exposure at 500 °C; in fact, specimens are not homogeneously affected by the heating process. To ensure this, a supplementary test was made, exposing the same mortars at 500 °C for 4 hours, resulting in the same shade throughout the sample. Finally, no change in color was observed in the sample heated at 500 °C of the mortar mixed with NA, but a fading with increasing exposure temperature (Figure 3.5).

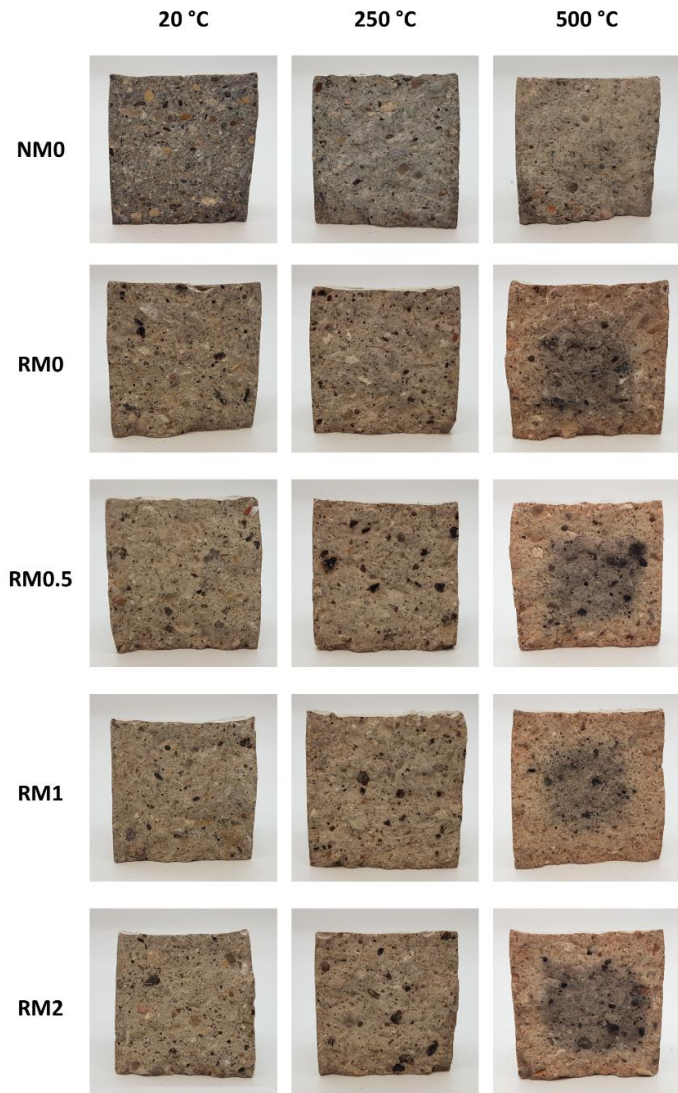


Figure 3.5 Photos of fracture face of flexural strength specimens.

3.4.3 Correlation of mechanical properties with exposure temperature and TiO₂ %

Table 3.3 reflects the ANOVA analysis results. The adequacy of the model is confirmed by checking residual plots and lack-of-fit. They showed residual values are independent, normally distributed, and their variance is the same.

In both simulations, the temperature exposure factor is significant at 5%, and the TiO₂ percentage is not. Therefore, TiO₂ percentage is unrelated to mechanical properties. In order to contrast this fact, it may be useful to repeat this study in a higher range of TiO₂ percentage.

The only difference between both strengths is related to the square temperature factor. While in the case of flexural strength it is significant, in terms of compressive strength is not. However, it is a quadratic factor, so the relevance is lower.

Table 3.3 ANOVA analysis results.

Responses	Compressive strength		Flexural strength	
Variable	F Ratio	P-value	F Ratio	P-value
X ₁ ^a	1.1969	0.3354	2.4556	0.1922
X ₂ ^b	63.7202	0.0013*	130.2924	0.0003*
X ₁ ²	0.1531	0.7155	0.5617	0.4953
X ₂ ²	0.1959	0.6810	14.9478	0.0181*
X ₁ *X ₂	0.0125	0.9163	1.9431	0.2358

*significant at 5% (p-value)

^aX₁: TiO₂ percentage

^bX₂: Temperature exposure

3.4.4 Ductility

Figure 3.6 displays a comparison between load-displacement curves of flexural strength tests for each studied mixture. As shown, samples at room temperature (20 °C) and 250 °C have experimented with a brittle fracture during bending. In contrast, after two-hour exposure to 500 °C, samples have increased their ductility. Samples exposed at 500 °C are the only specimens that have had no brittle fracture. The trend in samples with recycled aggregate is the same. Apparently, there is no change in failure mode depending on the percentage of TiO₂. Besides, TiO₂ may be

positive for ductility because, in almost all cases, mixtures with TiO_2 have more displacement before failure than the recycled reference mortar (RM0). Furthermore, results suggest that natural aggregate is less influential in ductility performance at 500 °C.

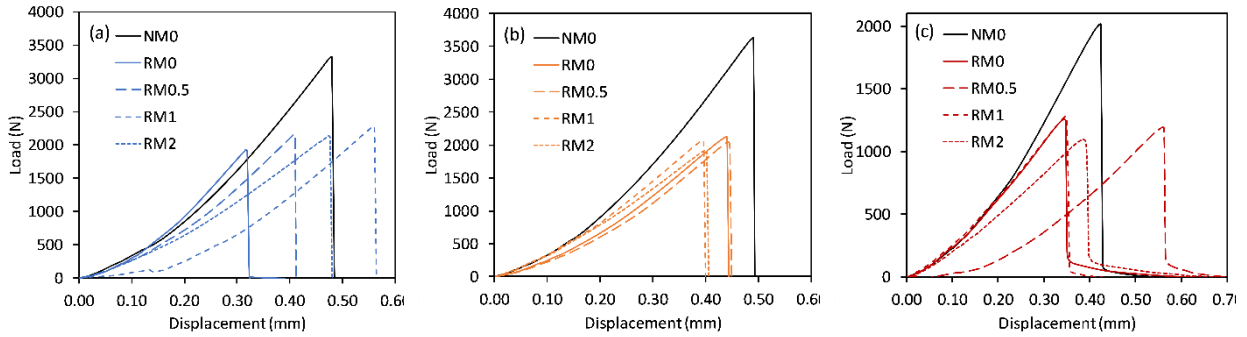


Figure 3.6 Load-displacement curves of flexural strength test at a given temperature of mortars with different percentages of TiO_2 . (a) 20 °C. (b) 250 °C. (c) 500 °C.

Table 3.4 summarizes ductility values for each mixture and each temperature. RM2 mortar (with 2% of TiO_2) showed the maximum value after exposure to 500 °C (20% more than reference recycled mortar). However, even though TiO_2 could seem positive for ductility, reference recycled mortar value (RM0) is higher than RM0.5 (51% less) and RM1 (90% less). In other words, there is no evident connection between ductility and the percentage of TiO_2 . Besides, in terms of ductility at 500 °C, the effect of NA is lower than RA. This fact may be related to the decrease of thermal conductivity observed in literature for the RA.

Nevertheless, results showed that exposure to 500 °C increases the ductility in fracture. These results concur with other studies [148,149], made with NA concrete, which have shown that, after exposure to 400 °C, strains attained were extremely bigger. The data obtained also suggests that the effect of NA is lower than RA.

Table 3.4 Evaluation of ductility in each mixture after performing flexural strength test.

Mixture	NM0	RM0	RM0.5	RM1	RM2
G_f (N*mm)	1.89	10.83	5.28	1.13	12.98

3.5 DSC

Previous studies [24,37,48] have found a correlation between TiO_2 substitution and CH formation as the intensity of the latter can be promoted by the former. Unexpectedly, for the recycled mortars studied, no trend has been found with the addition of TiO_2 (Table 3.5). Furthermore, samples left at room temperature showed a higher amount of CH. Even if the values of CH obtained for the samples heated at 250 °C are slightly higher, it is evident that at this temperature, hydration products such as C-S-H, ettringite, calcium aluminate hydrate have already decomposed [55–59], therefore, in proportion to the initial weight of the sample, the percentage is lower. As expected, in mortars heated at 500 °C, CH has been in part consumed [56,60,106]. Consequently, less amount of CH resulted from the DSC analysis. It is important to highlight the difference in the samples heated at 500 °C between the inner part and the external part. For these samples, DSC tests were performed for both the core and the external part, as explained in the methods section. Even though the mortar was kept at a set temperature of 500 °C for two hours, the core was not as much affected as the external part. A higher percentage of CH was consumed in the second.

Table 3.5 CH calculation.

Sample	Peak area [J/g]	CH [%]	Temp peak [°C]
NM0 20 °C	50.18	4.60	433.78
NM0 250 °C	76.81	7.04	438.80
NM0 500 °C	44.19	4.05	436.86
RM0 20 °C	49.07	4.50	440.68
RM0 250 °C	54.78	5.02	441.11
RM0 500 °C int	21.60	1.98	443.68
RM0 500 °C ext	4.03	0.37	431.65
RM0.5 20 °C	46.99	4.31	436.18
RM0.5 250 °C	50.74	4.65	446.49
RM0.5 500 °C int	14.06	1.29	455.30
RM0.5 500 °C ext	0.75	0.07	446.37
RM1 20 °C	58.47	5.36	440.56
RM1 250 °C	66.88	6.13	441.06
RM1 500 °C int	25.68	2.35	448.02
RM1 500 °C ext	5.68	0.52	442.86
RM2 20 °C	57.85	5.30	441.55
RM2 250 °C	57.50	5.27	443.17
RM2 500 °C int	45.94	4.21	445.75
RM2 500 °C ext	15.27	1.40	448.39

However, the percentage of CH variation, in samples exposed at high temperatures in comparison to specimens non-exposed, is entirely different between NM0 samples and specimens made with RA (Figure 3.7). Results display that in almost all samples exposed at 250 °C, CH percentage has been increased. Nevertheless, whereas NM0 experimented with a rise of 50%, the recycled mortars gain is below 15%. In addition, the overall trend is maintained at 500 °C. Even though the CH drop in NM0 samples is slightly higher than 10%, in specimens with RA, CH has been decreased up to a maximum of 98% (in comparison to the value under normal conditions) in RM0.5 mixture. Besides, as it is expected, in every sample, the inner part maintains a higher CH amount than the outer part due to being less exposed.

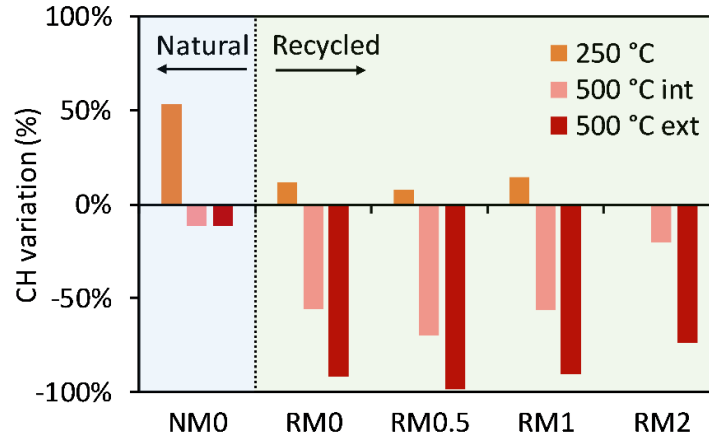


Figure 3.7 Effect of TiO₂ within the natural and recycled mixtures for each exposition temperature.

The DSC curves obtained from each mixture at 20 °C and after exposure to 250 °C and 500 °C are showed in Figure 3.8. This figure also presents the section of the samples exposed to 500 °C as they showed two different shades inside (except for the natural mortar). Samples under normal conditions exhibited a pronounced mass loss between 50 °C and 150 °C due to the decomposition of free moisture. On the contrary, specimens exposed to 250 °C and 500 °C did not show this loss because free moisture has been evaporated during the heating process. However, there are differences between DSC curves (250 °C and 500 °C) due to the decomposition of other compounds, such as C-S-H, ettringite, calcium aluminate hydrate or carboaluminate hydrates, in a wide range between 100 and 400 °C [55–59]. Besides, whereas NM0 mortar exposed to 250 °C

presented a huge increase in the CH percentage (Figure 8.a), recycled mortar curves only exhibited a slight rise.

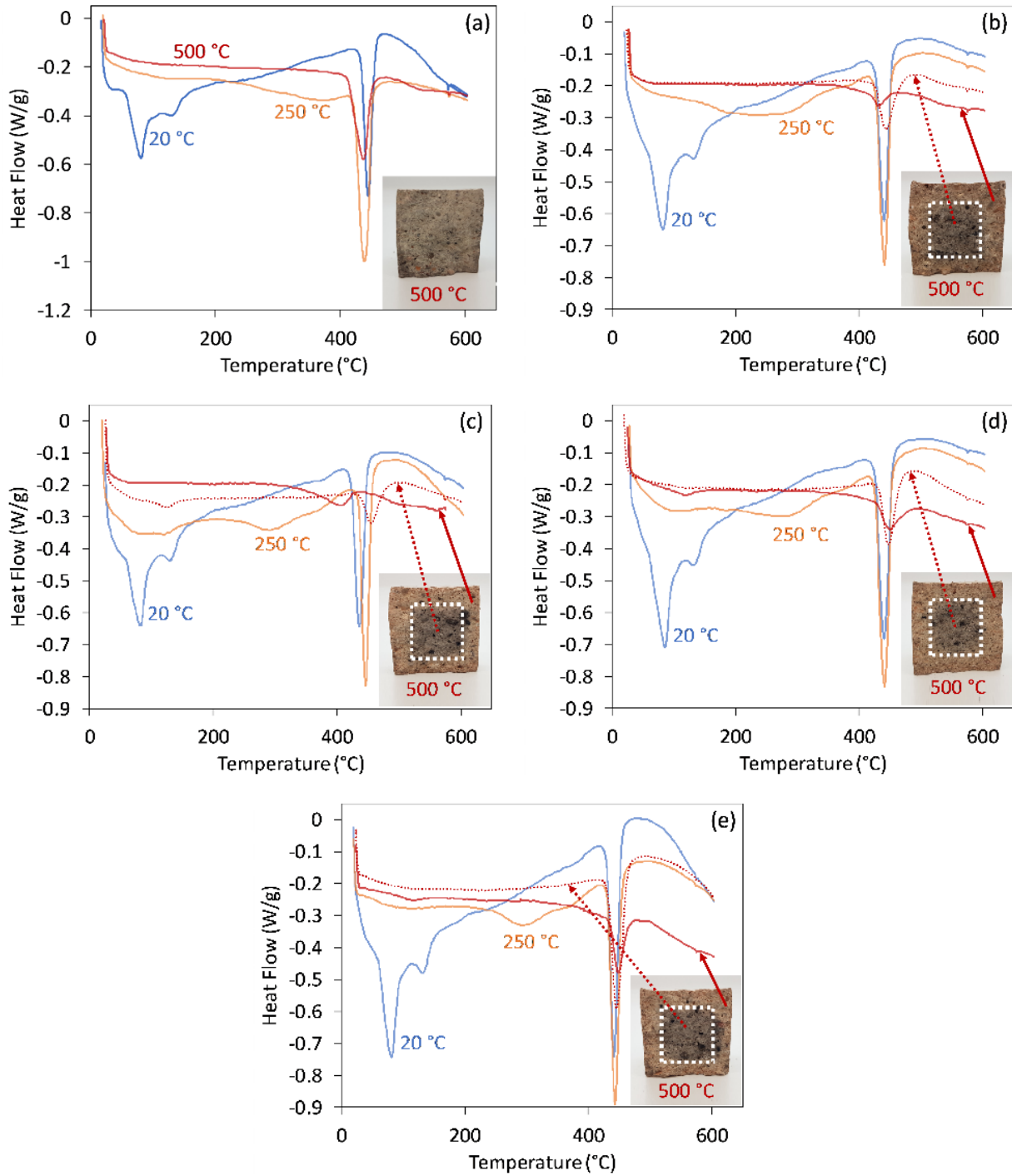


Figure 3.8 Effect of temperature on DSC curves for each mixture. (a) NM0 (b) RM0. (c) RM0.5. (d) RM1. (e) RM2.

The significant increase of CH in NM0 samples exposed to 250 °C is in agreement with the rise of flexural and compressive strength observed in the same specimens after the 250 °C exposure. The increase of compressive strength of NM0 after 250 °C exposure also may imply that there was not an important consumption of C-S-H. On the other hand, according to DSC results, mortars with recycled aggregate and nano-TiO₂ did not show a clear correlation between CH loss and strength loss after 250 °C. XRD results (Figure 3.9) also did not show remarkable differences between the CH content in recycled mortars before and after 250 °C exposure. These results from DSC and XRD suggest that the loss of strength on recycled mortars exposed at 250 °C is not related to the decomposition of the hydration products of the cement paste. Therefore, there must be another reason why recycled mortars lose compressive strength after 250 °C exposure.

Results from SEM (Figure 3.10) show the difference between the ITZ in NM0 (Figure 3.10a) and RM0 (Figure 3.10b) in normal conditions (20 °C). Due to the potentially different coefficient of thermal expansion (CTE) of aggregates and paste, the increase in temperature may cause internal stresses. These stresses would cause damage on both matrix (cement paste) and aggregates, as well as damages in what usually is the weakest part of these composites: the ITZ. Figure 3.10d shows the undamaged ITZ of the NM0 after 250 °C exposure, while ITZ of RM0 presented damage under the same conditions (Figure 3.10e). This image of RM0 after 250 °C exposure showed a crack that goes through the ITZ in the bottom part of the image and grows into the recycled aggregate.

Figure 3.10b exhibits the double ITZ zone of RM0 (aggregate-old paste-new paste). These two weak planes (two ITZ) of RM0 may fail easier, in comparison to NM0, due to the internal stresses. This may explain the drop in strength after 250 °C exposure observed in recycled mortars that it was not found in NM0. The addition of 1% nano-TiO₂ produced a reduction of porosity under normal conditions (Figure 3.10c vs. Figure 3.10b) and a densification of the ITZ. It is in agreement with the fact that RM1 showed higher strength than RM0 at 20 °C. However, after exposure to high temperatures, the strength in RM1 samples decreased more than in RM0 specimens. This higher drop of the strength in RM1 than in RM0 could be related to a potential change of the thermal expansion due to the use of nano-TiO₂. Since RM1 has two ITZ (aggregate-old cement paste and old cement paste-new cement paste), using nano-TiO₂ may cause variations in the coefficient of thermal expansion of the new cement paste in comparison to the old cement

paste. These changes may lead to the generation of the additional internal stresses that would reduce the strength of the samples after high-temperature exposure.

According to XRD patterns (Figure 3.9), the main difference between the chemical composition of the natural mortars (NM0) and the recycled mortars (RM0 and RM1) is the higher content of dolomite and quartz in the mortars made with natural aggregate. This is in accordance with the fact that recycled aggregate contains mineral aggregates plus old cement paste, while natural aggregate that was used in this study contains pure dolomite and quartz.

Note that it is assumed that after 500 °C exposure, the C-S-H of both mortars (RM0 and RM1) is already consumed [55,57,58]. Therefore, C-S-H content cannot be the source of the difference between the compressive strength of RM0 and RM1 after 500 °C exposure. Since the temperature decomposition of CH is around 450 °C, CH content could be related to the residual compressive strength after 500 °C exposure. Whereas the exposure to 500 °C almost reduces to zero the intensity of the CH peak in RM0, the addition of 1% of nano-TiO₂ seems to reduce the consumption of CH due to the exposure to 500 °C. This result contrasts with the lower compressive strength after 500 °C exposure presented by RM1 in comparison to RM0. However, it may suggest that the higher loss of compressive strength of RM1 after 500 °C exposure, rather than being related to changes due to the decomposition of hydration products, it could be more related to potential changes of thermal expansion of the newer cement paste with nano-TiO₂ in comparison to the CTE of the old cement paste. These possible differences between the CTE of old and new cement paste could produce higher internal stresses during high-temperature exposure, as 250 °C results also suggested it. In fact, Figure 3.10i shows a crack between the old cement paste and the new cement paste in RM1 after 500 °C, which is in accordance with this explanation. Another potential source of this variation can be the porosity reduction when TiO₂ nanoparticles are used [113]. A reduction of porosity may lead to an increase in the thermal conductivity [150], and therefore, a faster propagation of the damage through the sample due to high-temperature exposure.

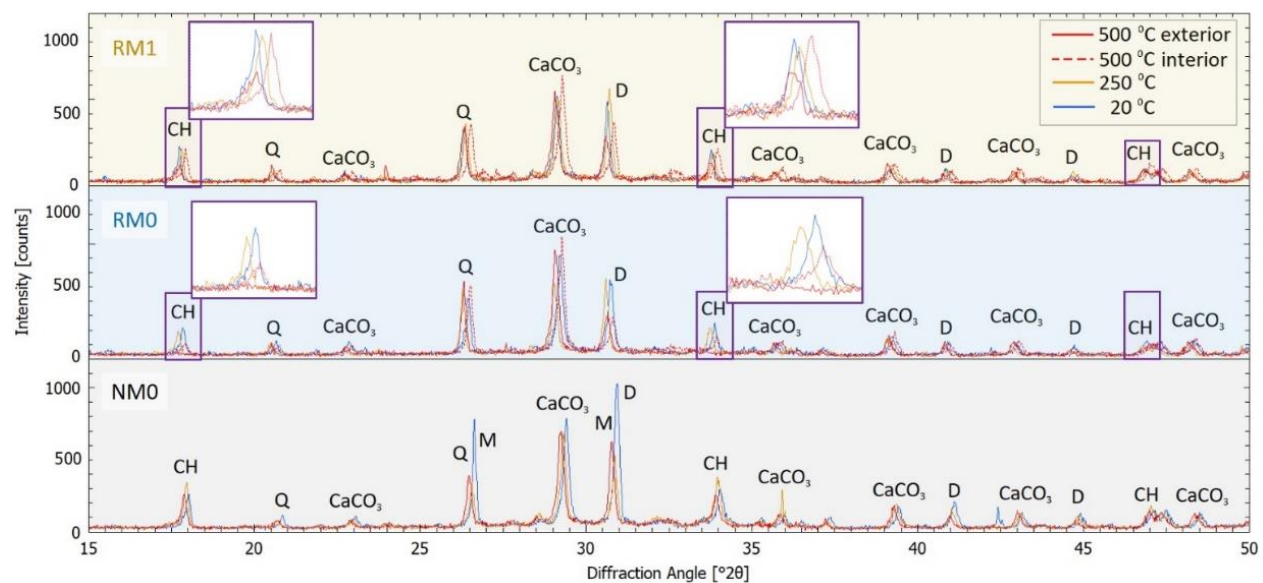


Figure 3.9 XRD results. [CH-Calcium hydroxide; CaCO₃-Calcite; Q-Quartz; D-Dolomite; M-Muscovite]

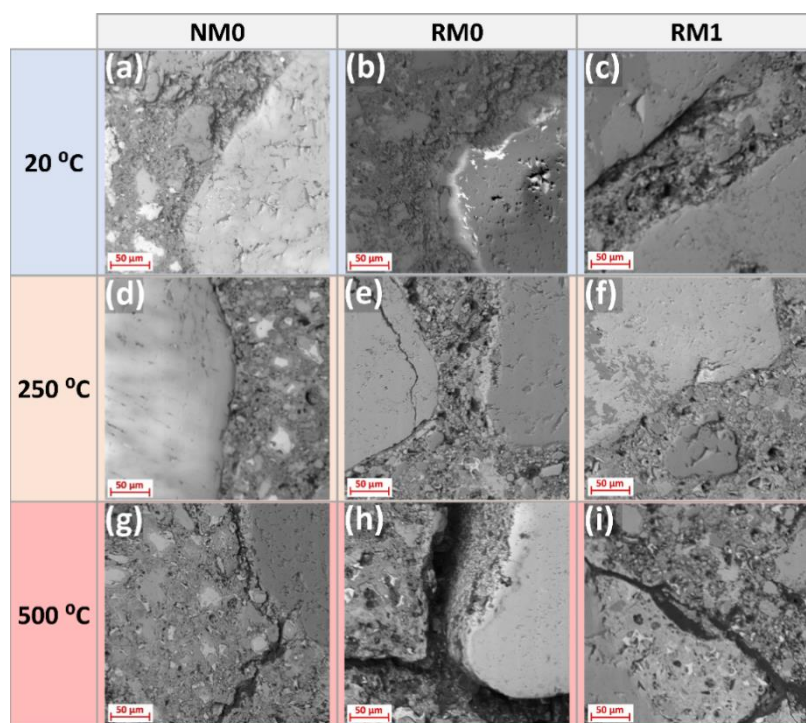


Figure 3.10 SEM images

3.6 Conclusions

This study has discussed the influence of TiO₂ nanoparticles on the high-temperature resistance of recycled mortars. After analyzing the results, the following conclusions may be drawn:

- The use of 100% recycled aggregate instead of natural aggregate produced a negative effect on high-temperature resistance in terms of compressive and flexural strength. Consequently, this aspect should be considered when fire resistance is evaluated.
- Even though the addition of low percentages of TiO₂ nanoparticles increases compressive and flexural strength of recycled mortars under normal conditions, this addition produced a negative effect on high-temperature resistance. A possible explanation may be the different thermal properties of all materials (e.g., old cement paste, new cement paste with nano-TiO₂, or RA) may produce internal stresses when the temperature rises. These internal stresses can produce a failure at lower strength due to the weaker ITZ between the new cement paste (with nano-TiO₂) and the old cement paste, as SEM images showed in the recycled mortar with 1% of nano-TiO₂ after 500 °C exposure. Nevertheless, further testing on the CTE difference is required.
- XRD and DSC results showed that the negative effect of the addition of 1% TiO₂ in terms of strength loss after 500 °C exposure is not related to a higher CH decomposition. In fact, nano-TiO₂ may increase the high-temperature resistance of CH.
- After thermal exposure, whereas recycled mortars exhibit two different shades, NM0 samples only show a uniform coloration. Therefore, specimens with recycled aggregate are not homogeneously affected by temperature, possibly due to their lower thermal conductivity.
- Results suggest that ductility before failure is increased after exposure at 500 °C on recycled aggregate mortars. Mortar with natural aggregate showed lower ductility under the same conditions.

4. EFFECT OF ELEVATED TEMPERATURE ON FLEXURAL BEHAVIOR OF RECYCLED POLYPROPYLENE (PP) FIBER-REINFORCED ECO-MORTARS

A portion of this chapter has been published as:

Francioso V., Moro C., Castillo A., Velay-Lizancos M., “Effect of elevated temperature on flexural behavior and fibers-matrix bonding of recycled PP fiber-reinforced cementitious composite”. *Construction and Building Materials*, Vol. 269, (2021), 121243. <https://doi.org/10.1016/j.conbuildmat.2020.121243>

4.1 Introduction

According to the US Environmental Protection Agency (EPA), in 2017, 35.4 million tons of plastics were produced in the United States, which generated 13.2 percent of Municipal Solid Waste (MSW) [151,152]. Of all plastic waste generated, 19.2% ended up in landfills, while 16.4% was combusted for energy recovery and only 8.4% was recycled [151]. In fact, as per the principle of waste hierarchy [153], landfilling is the main form of disposal for post-consumer plastics, the second main treatment is incineration, and in the third-place recycling. However, the first two methods can no longer be considered environmentally sustainable. Despite the high calorific value of polymers and the likelihood of eliminating the waste, a significant number of pollutants and chemicals are released in the atmosphere, and toxic fly and bottom ashes are produced through incineration. Furthermore, considering the long-term pollution related problems and both cost of solid waste disposal increasing and space decreasing, landfilling is no more considered a viable option. Therefore, recycling would be the best choice to reduce environmental impact and possibly transform waste into useful products.

Among others, the reuse of recycled plastic material in the construction industry has been considered ideal for valorizing plastic waste. Besides ecological benefits, while minimizing its environmental impact, the use of recycled plastic materials can enhance the performance of cement mortar and concrete [15,16]. Furthermore, most types of plastics are not biodegradable and have high chemical stability [154], therefore, they are suitable even in a highly alkaline environment such as pore solution of concrete [155,156]. Recycled plastic within cementitious materials is used mainly in two forms (i) as a replacement of natural aggregates and (ii) as a fiber-reinforcement

(substituting other types of fibers, i.e., steel fibers). Among the most commonly used plastic (e.g., LDPE/HDPE, PP, PET), polypropylene (PP) has the highest rate of discard (landfilling and other disposals) [157]. Hence recycling such type of plastic in construction materials can be a solution to reduce its amount. Research results showed that the performance of cementitious composites reinforced with PP plastic fibers can be enhanced, including its mechanical properties and durability [16]. Plastic fibers can act as reinforcement and produce a bridging force across cracks and prevent their propagation [158]. Because of the fibers bridging cracks in the matrix, fiber-reinforced mortar may exhibit a significantly higher flexural toughness than plain mortar (up to a volume fraction of 1.5%) [159]. Compared to other options (e.g., steel fibers), plastic fibers have a lower carbon footprint, are cost-effective and corrosion-resistant [16]. Furthermore, plastic fibers exhibit better strength to weight ratio and elongation [158]. However, there is no agreement in the literature regarding the positive role of recycled plastic waste, in enhancing the mechanical performance of cement-based composites. PP fibers are often utilized to control the fresh and hardened properties of cement-based materials [16]. One of the main applications is to reduce plastic shrinkage, but they also affect the compressive and flexural strength. In fact, the effect on strength has been reported to be contradictory [19]. It has been observed that the interfacial transition zone (ITZ) between the matrix and plastic fibers is affected by the smooth surface and hydrophobic nature of plastic resulting in poor anchoring [160]. Though the utilization of fibers with high surface roughness and treated fibers showed to favor the interaction and anchoring of the fibers to the cement matrix [16]. Furthermore, fibers embedded in concrete increase the porosity at room temperature by increasing the pore connectivity in the ITZ [161,162].

Several studies [16,19,20,161,163,164] demonstrated that PP fibers can be used effectively to prevent spalling failure of concrete under compressive loads. The cause of explosive spalling, when concrete is subjected to elevated temperature, has been attributed to two main contributions: (i) thermal stresses, generated by a thermal gradient between the surface and the interfacial zone and between aggregates and cement matrix; (ii) and the pore pressure generated in concrete when the internal water evaporates [21,165]. Nonetheless, previous research showed that at temperatures up to 300 °C, the compressive and flexural strength of plain concrete and plain mortars (no fibers) will not be highly affected and even it could increase [165–168]. At higher temperatures (above 300 °C), the hydration products will be decomposed, and therefore, the strength of the composite will decrease [169].

There are several articles in the literature on the compressive strength performance of fiber-reinforced concrete exposed to elevated temperature ([19–21,164,170]). However, the influence of elevated temperatures on the flexural performance of recycled PP fiber-reinforced mortars and its effect on ITZ bonding between the matrix and the recycled fibers has not been deeply investigated. Moreover, no studies have been found on the possible effects of the cooling process on the residual strength of these eco-mortars. Based on that, the main objective of this investigation is to assess the effect of recycled PP fibers content and the impact of the cooling process after exposure to elevated temperature on the flexural performance of recycled PP fiber-reinforced cementitious composites. Besides, flexural strength tests before and after exposure, an ITZ analysis through microscopy, Digital Image Correlation and an indirect method to assess bonding strength changes were employed to better understand these effects.

4.2 Materials

4.2.1 Characterization of the recycled polypropylene fibers

The fibers used (Re-Bind™) for this study come from the recycling of twine for the hay export industry. They are made from 100% recycled Polypropylene compliant with all ASTM standards for construction (as specified by the manufacturer). Their melt index is 6-8, they have a tensile strength of 5228 psi, it is a UV treated product, chemical resistant, and is made from isotactic PP homopolymer. Length ranges from 2 to 40 mm and they have an aspect ratio ranging from 0.75 to 106.9. Specific gravity was calculated following the ASTM D792 [171] and was found to be 0.9 g/cm³. Figure 4.1 shows a representative sample of the fibers.

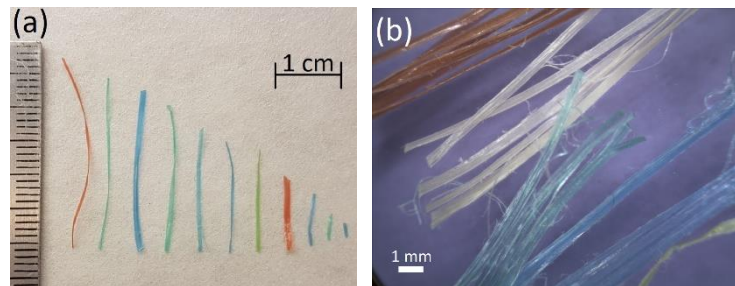


Figure 4.1 Recycled polypropylene fibers. (a) Sample of fibers. (b) Fibers under the microscope.

The extensional storage modulus and extensional loss modulus as a function of the temperature of the recycled PP fibers were analyzed using a Universal Extensional Fixture (UXF) in an MCR 302 Anton Paar Rheometer with temperature control oven (Figure 4.2a and Figure 4.2b). The width of the fiber was measured with a caliper, and the value was 0.11 mm. The temperature ramp started at 25 °C and finished when the fibers started to melt, with a rate of 2 °C/min (Figure 4.2c). The strain set to increase linearly from 0.1% to 1% over the temperature ramp.

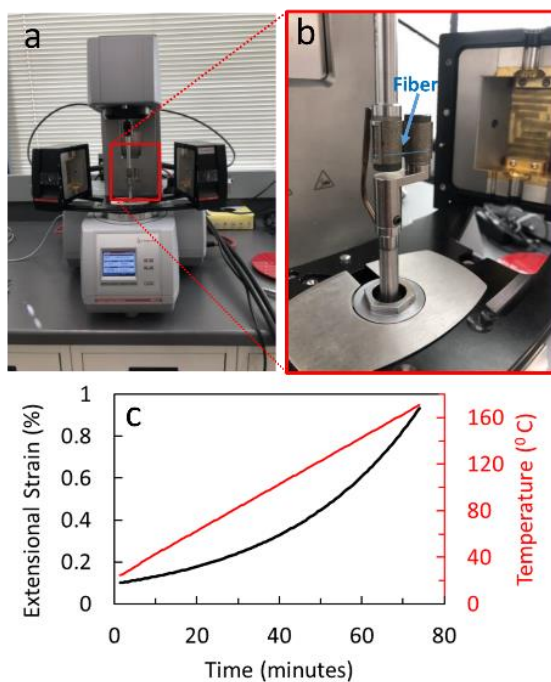


Figure 4.2 Extensional modulus test setup. (a) MCR 302 Anton Paar Rheometer. (b) Universal Extensional Fixture and temperature control oven. (c) Extensional strain and temperature ramp.

Figure 4.3 shows the effect of temperature on the extensional storage modulus (E') and extensional Loss Modulus (E''). A transition can be observed in the state as temperature increases (E' and E'' gradually decrease) at the beginning of the test. The glass-transition temperature (T_g) was observed at 92.7 °C (by mean of the maximum of the loss factor $\tan\delta$). The sharp increase in $\tan\delta$ begins around 170 °C, indicating that the fiber melting starts at this temperature.

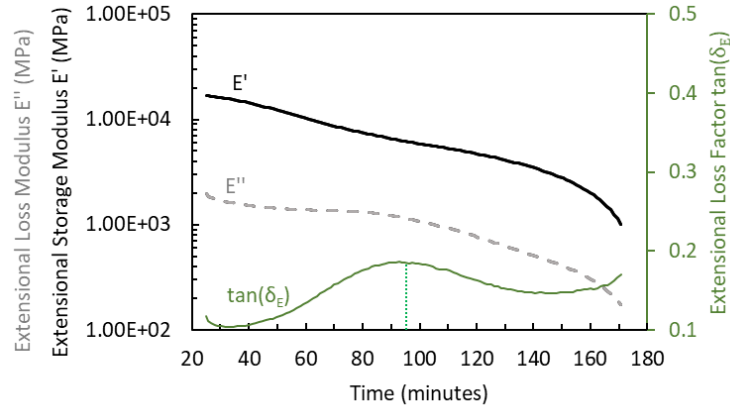


Figure 4.3 Extensional modulus behavior of recycled PP fibers as a function of the temperature.

4.2.2 Mix-design

Mortars were made with Portland cement Type 1 (Infinity, commercial grade) and quarzitic natural fine aggregate (compliant with ASTM C33/C33M-18 [172]). Table 4.1 presents the particle size distribution of the fine aggregate. For the fiber-reinforced mixtures, 100% recycled PP fibers were used in this study. The mix proportions are provided in Table 4.2. For comparative analysis, a reference mortar was produced in the same proportions shown in Table 4.2, without fibers. The amount of fibers used was 0.5%, 1% and 1.5% by volume of sand (to keep constant the volume of cement paste per volume of composite), as most of the previous studies demonstrated that the optimal percentage ranged from 0% to 3% [16]. The mixtures are named PM-PX, where PM means “plain mortar” and PX indicates the percentage of fibers (e.g., 0%, 0.5%, 1% and 1.5%). Finally, Table 4.2 presents the results of the flow test (ASTM C1437-15 [173]) and the fresh and hardened densities of mixes after casting and at the age of 28 days, respectively.

Table 4.1 Particle size distribution of fine natural aggregate.

Sieve #	Sieve opening (mm)	Cumulative Percent Passing (%)
4	4.75	99.96
8	2.36	90.8
16	1.18	63.2
30	0.6	35.5
50	0.3	10.7
100	0.15	1.3
Pan	0	0

Table 4.2 Mix proportions (per m³ of mortar), flow and density.

Component	PM-P0	PM-P0.5	PM-P1	PM-P1.5
Cement (kg)	498.1	498.1	498.1	498.1
Dry fine sand (kg)	1494.4	1486.9	1479.4	1471.9
w/c	0.55	0.55	0.55	0.55
Effective water (l)	274.0	274.0	274.0	274.0
Absorption (%)	2	2	2	2
Abs. water (kg)	29.9	29.7	29.6	29.4
Total water (kg)	303.9	303.7	303.6	303.4
Recycled-PP fibers (kg)	0	2.6	5.1	7.7
Flow (%)	154	144	138	130
Fresh density (kg/m ³)	2239	2199	2162	2156
Hardened density (kg/m ³)	2229	2195	2165	2154

4.3 Methods

4.3.1 Sample preparation and curing

All mortar mixtures were prepared using a mechanical mixer with a nominal capacity of 50 l. The process of mixing the mortar was done in the following order: first, cement was placed into the mixer and fibers were carefully separated and sprinkled by hand in small amounts on the surface, followed by a short period of hand mixing. This step was taken to avoid fibers balling and to achieve the highest uniformity in fiber distribution. Cement and fibers were mixed at low speed for 30 s. Next, water was gradually added and mixed for 30 s. Then, sand was gradually added over a period of 30 s and finally mixed for 2 minutes. Between each step, any material attached to the walls was scraped down for 15 s.

All mixtures were prepared under controlled room temperature 20 ± 1 °C and relative humidity conditions $50 \pm 5\%$ RH. For the test specimens, mixtures were cast into steel molds with $16 \times 4 \times 4$ cm dimensions. Molds were then covered with plastic sheets and demolded after 1 day. Specimens were moisture-cured in a $95 \pm 5\%$ RH and 25 ± 1 °C room for 27 days, and air-cured at $65 \pm 5\%$ RH and 23 ± 1 °C for 1 day until the age of 28 days. A total of 36 samples were cast; for each mixture, three samples were tested in standard conditions and six samples were exposed to elevated temperature, following two different cooling procedures that will be explained in detail in the next paragraphs. Samples were air-cured at $65 \pm 5\%$ RH and 23 ± 1 °C for at least 6 h before high-temperature exposure.

4.3.2 High temperature exposure

According to the recommendations of RILEM [174], service conditions normally involve long-term temperature exposure in the range 20 °C to 200 °C. In this study, temperature exposure was set at a boundary of 200 °C. Exposure to a temperature of 200 °C will not significantly affect the mechanical properties of the matrix of our fiber-reinforced composite (cement paste plus aggregates) since exposure to this temperature will not decompose the main part of hydration products [175]. Therefore, studying the effect of exposure to 200 °C allows us to isolate the changes on the fiber's performance due to the high-temperature exposure without significantly affecting the matrix. At higher temperatures exposure, the damage of the matrix will be

predominant, making it unfeasible to study the changes in fiber-matrix bonding after exposure and the effect of the cooling process. The effect of high-temperature exposure on the mortar matrix was assessed comparing the data of reference samples of mortar (without fibers) tested before and after exposure. With these data, the effect of high-temperature exposure on the recycled PP fibers can be isolated, assessed and quantified. Assuming that the impact of high-temperature exposure on the mortar matrix of samples with fibers will be the same as the effect on the reference mortar (no fibers, 100% mortar matrix) on hydration products and mechanical properties of the matrix of the composites.

At the age of 28 days, 6 specimens of each mixture were heated in an electric furnace with a heating rate of 50 °C/min up to 200 °C. When the target temperature was achieved, the specimens were maintained at this temperature in the furnace for 2 hours to ensure a steady-state thermal condition (Figure 4.4). Besides, three control specimens of each mixture were stored at 20 °C and were not subjected to heating (unexposed samples). After the exposure, two different cooling regimes were followed: (i) three samples were taken from the oven at the end of the cycle (inducing a thermal shock, since room temperature is at ~20 °C) and tested right after; (ii) three samples were left inside the oven until cooled down (± 12 h) to room temperature, then tested.

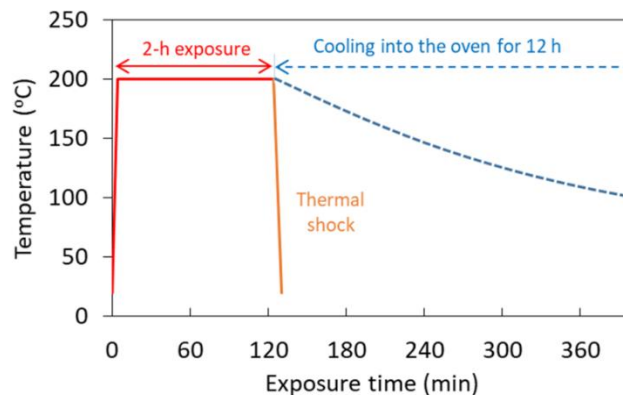


Figure 4.4 Exposure and cooling process.

4.3.3 Flexural strength test of mortar before and after exposure

Flexural tests were performed at 28 days according to ASTM C348-18 standard [136] on exposed and unexposed samples. To assess the effect of elevated temperature on the flexural

strength of the investigated mortar mixtures, specimens were tested before and after exposure, following the two cooling procedures. A total of 36 samples were tested. Each test was performed using an MTS machine with a load capacity of 10 kN under a displacement control of 0.2 mm/min.

4.3.4 Digital Image Correlation

Digital Image Correlation (DIC) technique was adopted to study the evolution of crack propagation and strain distribution in specimens during the three-point bending test. This technique identifies the crack growth paths in the different specimens and measures the strain in the samples under flexural stress. The surface of the specimen was prepared with a speckle pattern, consisting of randomly distributed black dots over a white background, both realized by means of spray-painting. Specimens stored at 20 °C and specimens slowly cooled after 200 °C exposure were prepared for Digital Image Correlation before the flexural strength test. That was not possible for the specimens subjected to shock as they were tested hot right after the high-temperature exposure. After recording the test with two high-definition cameras, the analysis of different timed captured pictures allows the software (Vic 3D) to create a representation of different space-related variables, like position, surface changes, and strain measurement.

4.3.5 An indirect method to assess bonding strength changes

In order to evaluate the changes due to the high-temperature exposure on the bonding strength between the recycled plastic fibers and the mortar matrix, an indirect method was employed. This indirect method is based on the assumption (and observation) that after reaching the peak-load, the mortar matrix is completely fractured and the fibers still hold the two pieces of the broken sample after the matrix failure, as it can be observed in Figure 4.5. After the total fracture of the matrix, the remaining post-peak strength is provided by the fibers. Part of these fibers may have a low or negligible contribution to this post-peak strength due to bonding failure. The stronger the fiber-matrix bonding, the higher the secondary post-peak flexural strength. Based on that, three new properties were defined and evaluated to assess potential changes on bonding due to high-temperature exposure:

- (i) **Post-peak residual strength** was defined as the strength showed by the fiber-reinforced composite after the maximum peak was reached. From the load-displacement curves, a plateau was clearly identified before the flexural strength test is stopped.
- (ii) **Secondary strength** was defined as the maximum strength recorded in a second test performed on broken samples. After the three-point bending was stopped, samples with a high percentage of recycled fibers (1% and 1.5%) were unloaded and loaded again (new three-point bending test).
- (iii) **Secondary toughness** was defined as the fracture toughness calculated based on the results of the new three-point bending test on the broken samples (with 1% and 1.5% of fibers). In general, toughness is a quantitative measure of the energy absorption capability of a material, and it is quantified in terms of the area under a load-displacement curve. For the estimation of the secondary toughness, the area under the new load-displacement curves was calculated.

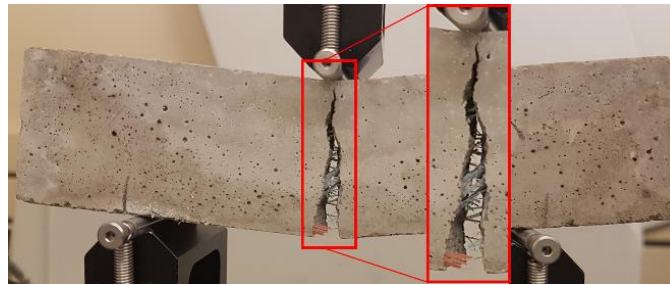


Figure 4.5 Fractured mortar matrix and fibers bridging after peak-load.

4.3.6 ITZ inspection by optical microscopy

The ITZ inspection between the recycled plastic fibers and the mortar matrix was performed using an Olympus BX53M microscope in fractured samples before and after exposure to elevated temperature. The Extended Focus Imaging (EFI) was used to capture focused images, even though the fractured surfaces were not flat. Several microscopy images are acquired at different heights and stacked together so that the final compiling image is focused by EFI processing. The software automatically identifies and selects the part of each constituent image that is focused, and it allows to visually analyze the ITZ between the fibers and matrix without any disruption or modification that could occur if sample preparation such as polishing or lapping is required such as in other microscopy techniques (e.g., Scanning Electron Microscopy).

4.3.7 Compressive strength test of mortar before and after exposure

In order to assess the effect of elevated temperature on the compressive strength of the mortar mixes investigated, specimens were tested before and after exposure to 200 °C. Compressive tests were performed at 28 days according to ASTM standards [176] on the two halves of each broken prism from flexural strength test, using a MTS machine with a load capacity of 300 kN and a displacement control of 0.05 mm/s.

4.4 Results and Discussion

4.4.1 Flexural strength under standard conditions

The use of recycled PP fibers did not significantly impact flexural strength under standard conditions (unexposed samples). The variation with respect to the flexural strength of the reference mortar is within 15% (Figure 4.6). In fact, PM-P0.5 and PM-P1 showed a slight decrease in the flexural strength compared to the reference mortar. In general, fibers are expected to increase flexural strength. However, the low bond strength between the recycled fibers and the mortar matrix may cause adhesion problems and negatively impact the potential positive effect of fibers on the ultimate flexural strength.

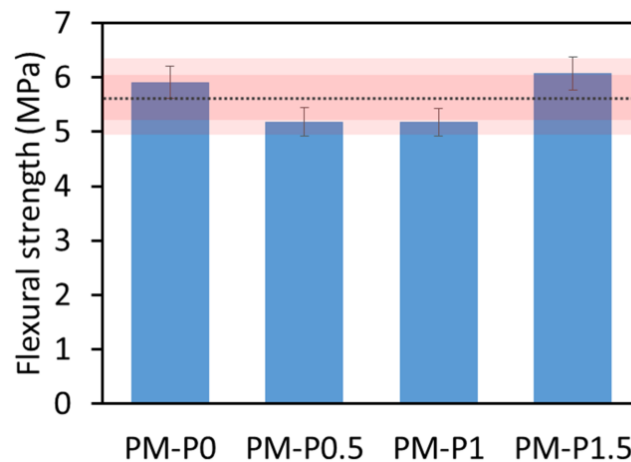


Figure 4.6 Flexural strength under standard conditions.

Even though the recycled fibers are not remarkably affecting the flexural strength, they have been found to increase the maximum strain before ultimate failure and provided the composite material a secondary flexural strength (or post-peak residual strength). As expected, after reaching the peak load, samples without fibers broke in two halves and, therefore, they were not able to carry any further load. Conversely, samples with fibers presented a post-peak residual strength identified by a constant plateau load (Figure 4.7). This post-peak residual strength is delivered by nothing but the fibers adhering to the mortar. The higher the amount of fibers, the higher the secondary strength observed. PM-P1.5 preserved one-third of its original flexural strength after reaching the peak load, while samples with 0.5% of fibers preserved just one-fifth of their original strength.

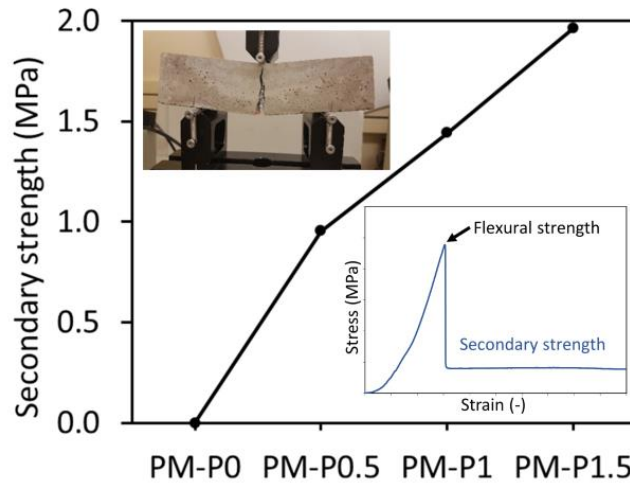


Figure 4.7 Secondary strength under normal conditions.

4.4.2 Effect of high-temperature exposure on flexural strength

Results presented in Figure 4.8 show that high-temperature exposure and cooling process strongly affected the flexural behavior of the studied fiber-reinforced eco-composites. The thermal shock caused by removing the samples from the oven right at the end of the exposure produced an important reduction of the flexural strength due to thermally induced dimensional changes (stresses) [165], and release of moisture and gases resulting from the migration of free water [21]. However, the addition of recycled PP fibers reduced flexural strength loss. For all fiber-reinforced mortars, the loss of flexural strength after the exposure and thermal shock (removing samples from

the furnace right after the 2 hours exposure) was lower compared to the strength loss of plain mortar at the same conditions. Remarkably, the high-temperature exposure with slow cooling had a positive effect on flexural strength. All fiber-reinforced mortars exhibited an enhancement of flexural strength when samples were left to cool down in the furnace for 12 hours compared to the corresponding unexposed samples. Though, no trend was observed with respect to the fibers' content.

Mortar without fibers exhibited 20% higher flexural strength than its reference (no exposure) after high-temperature exposure and slow cooling. It suggests that the mortar matrix experienced an enhancement of the flexural strength over the high-temperature exposure and slow cooling. This was also observed in previous studies of plain mortars and concretes [166–168]. However, the enhancement due to the high-temperature exposure and slow cooling was higher for samples with fibers; the presence of 1% recycled PP fibers enhanced the flexural strength over 40% after 200 °C exposure for 2 hours and slow cooling, compared to the unexposed samples. Therefore, this enhancement of the fiber-reinforced mortar cannot be explained as just an enhancement of the flexural strength of the mortar matrix. An enhancement of the strength of the fibers itself due to exposure to 200 °C and slow cooling is not expected. Thus, the higher enhancement of flexural strength in the fiber-reinforced samples (compared to plain mortars) due to the exposure and slow cooling suggests that ITZ between fibers and matrix could be enhanced after the exposure and cooling process.

Plain mortar (no fibers) specimens tested right after high-temperature exposure showed the highest negative impact on the flexural strength. The thermal shock caused by removing samples from the oven at 200 °C directly to the room temperature (20 °C) caused micro-cracking that is detrimental to the mortar matrix of all studied mixtures. However, fibers were able to reduce the loss of flexural strength, even though samples were tested hot (at a temperature close to the melting point of the fibers) and therefore, their strength could be negatively affected. It suggests that high-temperature exposure may have an important positive effect on the ITZ bonding between the recycled PP fibers and the mortar matrix.

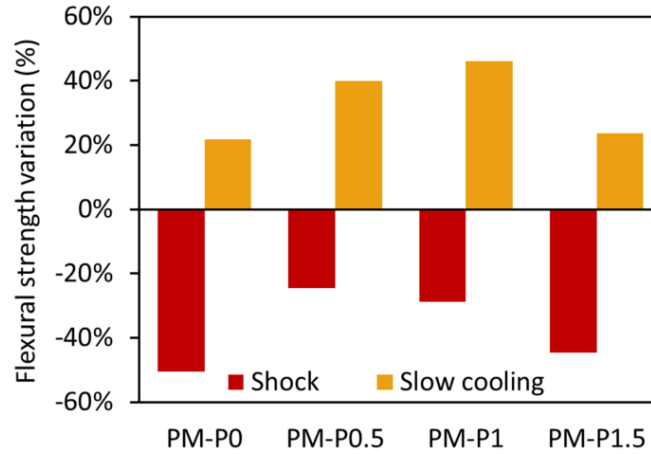


Figure 4.8 Flexural strength variation after high-temperature exposure compared to standard conditions.

4.4.3 Post-peak residual strength after high-temperature exposure

As per the fiber-reinforced mixtures tested under normal conditions, fiber-reinforced mixtures exposed to high temperature exhibited a post-peak residual strength after the maximum load was reached. In the fiber-reinforced composites, after reaching the peak load, the load did not drop to zero. Indeed, a constant plateau could be clearly identified (as shown in Figure 4.7). The post-peak residual flexural strengths of composites after exposure to high-temperature exposure (and under normal conditions, as reference) are shown in Figure 4.9. The higher the percentage of fibers (up to 1.5%), the higher the post-peak residual strength. This trend was followed at normal, shock and slow cooling test conditions. The slow cooling process has been found to improve the post-peak residual strength. However, in the case of 1% fibers substitution, the residual strength of the slowly cooled composite was similar to the one of the composite tested at normal conditions. This may be due to an unsuitable dispersion of the fibers in the region of the crack. A high percentage of fibers may present fiber dispersion issues, having a negative impact on the overall composite behavior. The thermal shock reduced the post-peak residual strength with respect to the normal conditions, regardless of the fiber fraction. It cannot be explained as an effect of the thermal shock on the mortar matrix since the post-peak residual strength is governed by the fibers and the mortar matrix-fiber bonding. These samples were tested in hot conditions a few minutes after extracting the samples from the oven, and therefore fibers were at a temperature close to the melting point, thus not fully contributing to the post-peak residual strength. However, in samples

tested after slow cooling, fibers could recover all their strength and properly contribute again to the strength of the composite.

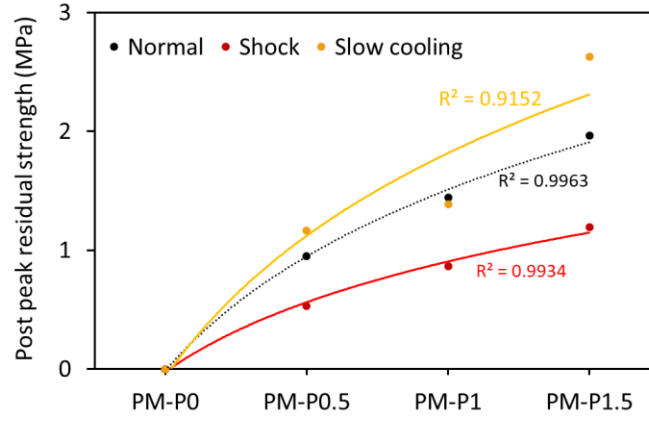


Figure 4.9 Post-peak residual strength.

4.4.4 Digital Image Correlation

Figure 4.10 shows DIC results for the reference mortar with the corresponding load-displacement curves for both standard and slow cooling after 200°C exposure conditions. Figure 4.11 shows the DIC results of mortar with 1.5% fibers content under the same conditions. The highlighted points on the curves of Figure 4.10a and Figure 4.11a, correspond to the peak-load instant (2-4) and a few seconds before (1-3), showed in Figure 4.10b and Figure 4.11b, respectively. Both unexposed and exposed reference mortars presented a brittle failure, as it can be observed in both load-displacement curves (Figure 4.10a) and DIC images (Figure 4.10b). However, it is remarkable that the mortar exposed to 200 °C, after a slow cooling, presented higher peak-load and higher maximum strain before failure than the unexposed mortar. The extremely brittle behavior of the reference mortars makes it very difficult to capture the evolution of the fracture and strain with DIC. Samples with fibers presented a more ductile behavior reflected in the quality of the DIC images (Figure 4.11). Samples with fibers showed no damage before the peak-load is achieved (images 1 and 3 of Figure 4.11b) in both unexposed and exposed conditions. When the peak-load is achieved, samples with fibers clearly showed a more extensive area affected by strains (Figure 4.11b, images 2 and 4) compared to samples without fibers that presented a single and very localized crack (Figure 4.10b, images 2 and 4). The DIC results are in agreement with the

load-displacement curves that showed that the fibers enhanced the maximum strain before peak-load and the toughness of mortars. Additionally, samples with fibers exposed to high temperature showed a larger area affected by strains (Figure 4.11b, image 4) than samples with fibers unexposed (Figure 4.11b, image 2). In agreement with the previous sections, results also suggest that exposure to 200 °C with slow cooling may enhance the toughness of recycled fiber-reinforced PP samples as well as the effectiveness of the fibers. These results can indicate that exposure to elevated temperatures and slow cooling may improve the ITZ between the recycled PP fibers and the mortar matrix, enhancing the anchoring and, therefore, making more fibers work as reinforcement effectively.

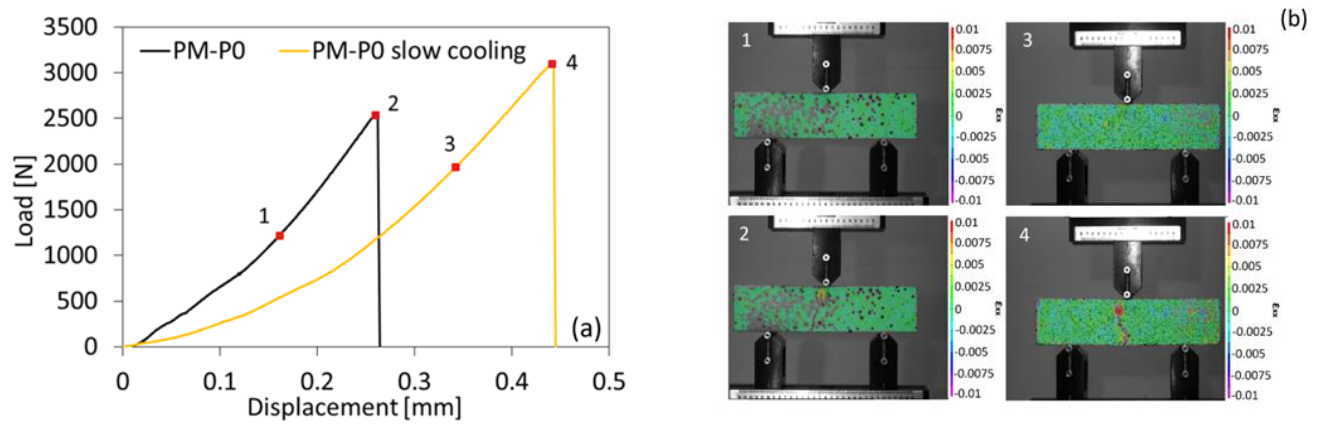


Figure 4.10 (a) Load-displacement curves and, (b) DIC for PM-P0 under normal and slow cooling conditions.

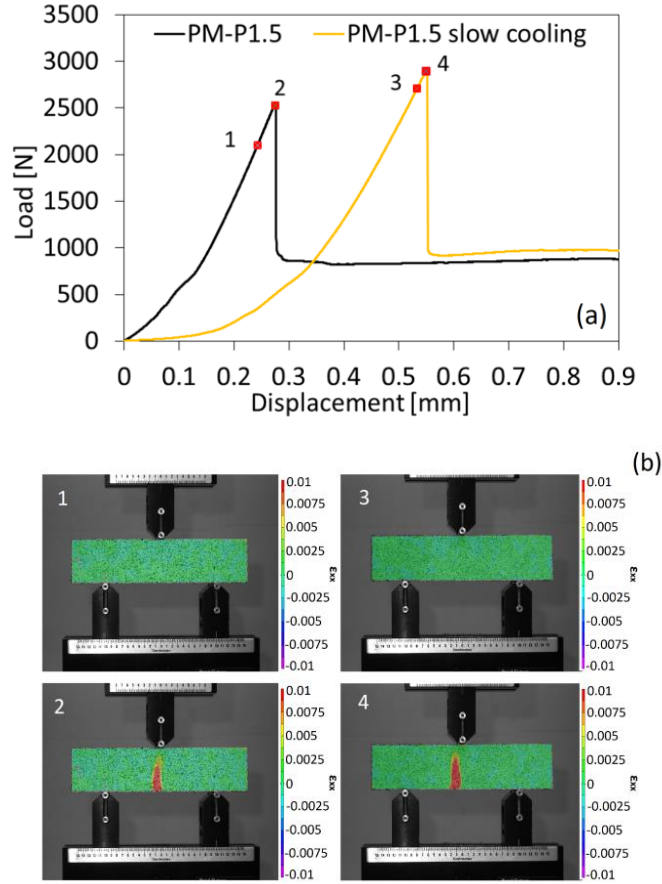


Figure 4.11 (a) Load-displacement curves and, (b) DIC for PM-P1.5 under normal and slow cooling conditions.

4.4.5 Fiber-matrix bonding, Secondary strength, and Secondary toughness

As previously observed, after reaching the peak-load, the fiber-reinforced composites did not fail completely. The bearing capacity dropped until the post-peak residual strength is reached and a plateau load can be observed in the load-displacement curves. After this post-peak residual strength is identified and the displacement reached 1 mm, the flexural strength test was stopped. Then, samples with a high volume of fibers (1% and 1.5% addition of fibers) were unloaded and tested again. Figure 4.12 displays the average load-displacement curves of PM-P1 and PM-P1.5 specimens that have been re-loaded. The area under the load-displacement curves for this second test was calculated, and its value corresponds to secondary toughness (N·mm), as defined in the method section.

During the re-load, the mortar matrix cannot carry any further load since it is completely fractured from the beginning of this second test, meaning that fibers are the only working component. The flexural strength observed over this second cycle of testing will mainly depend on two factors: (i) the tensile strength of the fibers and (ii) the bonding between matrix and fibers.

Results showed that not only were the composites able to sustain further load, but also the energy absorption capability increased with the amount of fibers substitution and after elevated temperature exposure. Besides, the higher load and toughness observed after exposure (compared to unexposed samples with the same fiber content) suggest an improvement in the anchoring of the fibers to the matrix, which is in agreement with what observed in the previous sections. Both PM-P1 and PM-P1.5 samples showed higher toughness after exposure to 200 °C and slow cooling, than the same mixtures at standard conditions (unexposed samples). The secondary strength increased with a higher percentage of fibers and samples exposed to 200 °C that were cooled slowly exhibited higher strength than the same mixture tested at standard temperature. These results suggest an enhancement of the fiber-matrix ITZ.

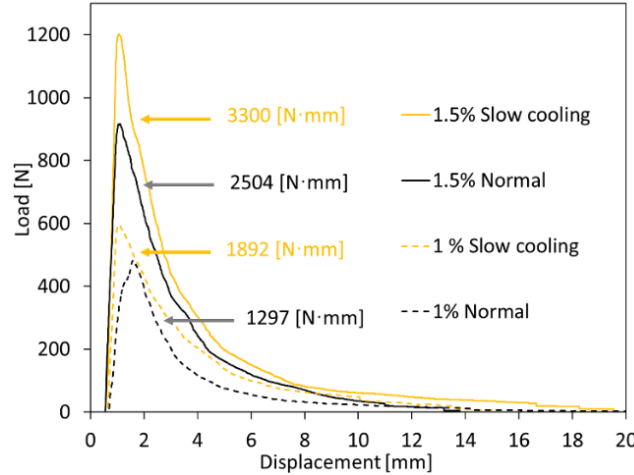


Figure 4.12 Load-displacement curves (average) of PM-P1 and PM-P1.5 re-loaded specimens.

4.4.6 Fiber-matrix ITZ

Figure 4.13 shows how high-temperature exposure affected the ITZ between the mortar and the recycled PP fibers. The images revealed a sharp, clear and well-defined interface between the mortar matrix and the fibers in the unexposed sample, whereas, in the case of 200 °C exposure,

the fibers penetrated the pores of the mortar matrix. This suggests an enhancement of the adhesion between the fibers and the mortar matrix, and consequently, the increase in flexural strength, post-peak residual strength, secondary strength and the secondary toughness as it was observed in previous sections. Assuming that the high-temperature exposure is not responsible for improving the mechanical properties of the plastic fibers, along with the results of the post-peak residual strength and secondary flexural strength, the microscope observations suggest that the enhancement in the flexural behavior after high-temperature exposure and slow cooling is due to the improved ITZ between fibers and matrix.

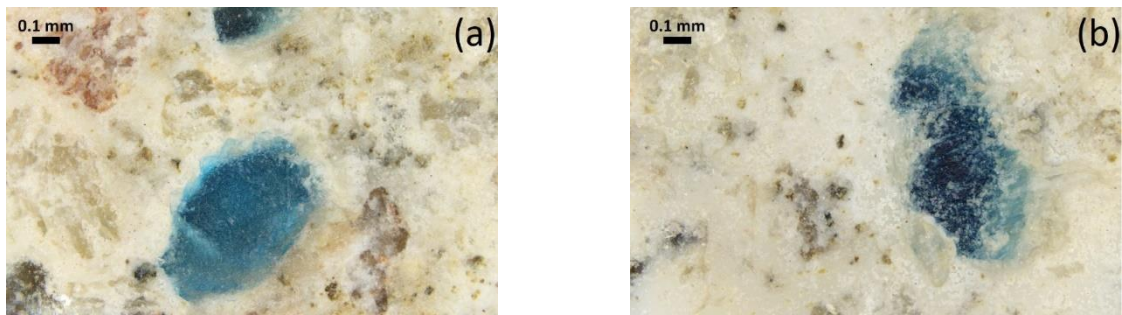


Figure 4.13 Microscopy images of fracture surface by EFI processing. (a) Unexposed sample. (b) Exposed sample.

4.4.7 Compressive strength test of mortar before and after exposure

Figure 4.14 shows the results of the compressive strength tests before and after exposure to elevated temperature (and two cooling processes). The recycled PP fibers used in this study had almost no influence on the compressive strength under normal conditions (no exposure). The mortar without fibers showed the highest compressive strength. The lowest compressive strength reached by 0.5% substitution was about 9% lower than the mortar without fibers. Compressive strength of all mortars presented a decrease (between 2% to 20%) after 2-hour exposure to elevated temperature (200 °C) regardless of the amount of fibers, and no trend has been observed with respect to the cooling process.

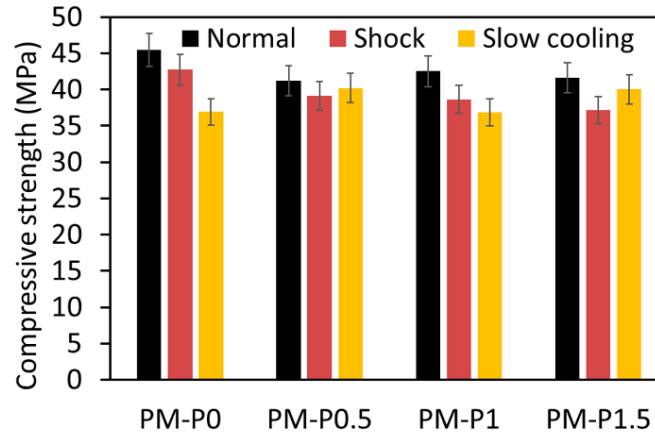


Figure 4.14 Compressive strength of the composites (28 days).

4.5 Conclusions

Based on the findings of the present work, which focused on the effect of high-temperature exposure on the flexural performance and bonding of recycled fiber-reinforced composite, with different percentages of recycled PP fibers, the following conclusions can be drawn:

- Recycled PP fibers have a negligible effect on the mortar flexural strength under standard conditions (no exposure to high-temperature). However, they have been found to increase the maximum strain before failure and provided the composite material a post-peak residual flexural strength. Upon reaching the maximum load, samples with fibers presented a ductile-like behavior showing a plateau in the load as the displacement increased. This load is carried only by the fibers adhering to the mortar matrix. In fact, as the fiber fraction increases, the post-peak residual strength increases.
- The addition of recycled PP fibers mitigated the flexural strength loss caused by high-temperature exposure and thermal shock. A high volume of fibers increases the risk of connectivity between fibers and the possibility that weak planes are formed, which may negatively impact the overall composite behavior. For all fiber-reinforced samples, the thermal shock reduced the post-peak residual strength, with respect to the normal conditions. It was expected since samples with thermal shock were tested in hot conditions, reducing the strength of the fibers.

- Even though all mixtures, including the one without fibers, showed an enhancement of flexural strength after high-temperature exposure and slow cooling, fiber-reinforced mortars exhibited a higher enhancement of flexural strength than samples without fibers under the same conditions. Besides, in fiber-reinforced samples tested after slow cooling, the post-peak residual strength was higher than in unexposed samples. Results also showed that the secondary strength and the energy absorption capability increased with the amount of fibers. After elevated temperature exposure, this enhancement is higher than in unexposed samples. These results suggest an enhancement of the fiber-matrix ITZ after high-temperature exposure and slow cooling.

The optical microscopy analysis of the unexposed samples revealed a distinct interface between the fibers and the mortar matrix. In the case of 200 °C exposure, microscopy images showed that fibers penetrated the pores network of the mortar matrix after high-temperature exposure. Consequently, the observed increase in flexural strength, post-peak residual strength, secondary strength and secondary toughness, after high-temperature exposure and cooling, may be directly related to enhancing the adhesion between the fibers and the mortar matrix.

5. EFFECT OF RECYCLED CONCRETE AGGREGATE (RCA) ON MORTAR'S THERMAL CONDUCTIVITY SUSCEPTIBILITY TO VARIATION OF AMBIENT TEMPERATURE AND MOISTURE CONTENT

A portion of this chapter has been published as:

Francioso V., Moro C., Velay-Lizancos M., “Effect of recycled concrete aggregate (RCA) on mortar’s thermal conductivity susceptibility to variations of moisture content and ambient temperature”. Journal of Building Engineering, Vol. 43, (2021), 103208. <https://doi.org/10.1016/j.jobbe.2021.103208>.

5.1 Introduction

Concrete is the most widely used artificial material in the world [2]. It is widely used in buildings to make (either cast-in-place or precast) slabs, walls, columns, floors, blocks, and any structural or non-structural element. Concrete is a composite porous material made of cement, water, fine and coarse aggregates, and air (pores). The variable nature of its constituents, volume fraction, and morphology strongly influence its thermal properties [9]. Understanding the thermal properties of building materials such as concrete and mortar is essential to design more energy-efficient buildings, improve thermal comfort and reduce energy consumption. The energy efficiency of buildings depends on the hygrothermal behavior of the building envelope, and thermal conductivity plays an important role when considering the amount of heat transfer through conduction. Cementitious materials with low thermal conductivity reduce the heat transfer and energy consumption in buildings [9,177,178].

The thermal conductivity (TC) of concrete depends on several factors, such as type of cementitious material, type of aggregate, density/porosity, humidity, temperature, and the presence of phase-changing materials [9,179]. Water/cement ratio, degree of hydration and moisture content are responsible for the thermal properties of the cement paste (and pore structure). On the other hand, the composition of sand and coarse aggregate influences the thermal properties of the whole composite [180,181].

The thermal conductivity of cementitious materials is strongly affected by the presence of moisture [182,183].—Previous studies indicated that the thermal conductivity of cement-based

materials changes whether the dry or saturated condition is present [182,183]. For instance, Zhang et al. [184] observed that plain cement mortar specimens exhibited a thermal conductivity over 65% higher in saturated conditions than in dry conditions. In general, the thermal conductivity of cement-based materials in saturated conditions has been found 1.4 to 3 times higher than in dry conditions [9]. The primary reason is that the thermal conductivity of water (0.598 W/m·K, at 20 °C and atmospheric pressure) is over 20 times higher than that of the air (0.0259 W/m·K, at 20 °C and atmospheric pressure) [185]. Several authors [183,186] indicate a linear dependence between thermal conductivity and moisture content of building materials such as cement-based mortars. However, there is no agreement if the thermal conductivity (λ -value) of building materials containing a known percent of moisture (by volume or by weight) can be represented by a linear expression or by a correction factor to be applied to the λ -value in the dry state [186–189]. To this extent, assessing the actual moisture content under in-service conditions becomes essential for designers and professionals to guarantee the accuracy of the thermal performance evaluation.

Furthermore, previous literature has shown a dependency of thermal conductivity on temperature [169,190–193]. In general, at high temperatures (> 100 °C), the thermal conductivity of concrete decreases with increasing temperature [169,192,193]. However, some authors [190,191] have found that depending on material type and density, the TC values of insulation materials are affected at different degrees by operating temperature. The effective thermal conductivity of insulation materials increases with increasing operating temperature (in the range of 20 - 100 °C). Hence, thermal losses may become higher than the design values.

In practical application, building standards and regulations use fixed conductivity values for normalized conditions [194,195], which do not necessarily represent the real in-service conditions. For example, the EN ISO 10456 standard [194] considers the variation of thermal conductivity for thermally homogeneous building materials and products as a function of conversion coefficients for the temperature, moisture content, and aging. This standard and most studies related to mortars' thermal conductivity focus only on dry and fully saturated conditions [9]. However, under the operating conditions of a building (in-service life), the temperature and moisture content of the materials may vary with time and depend on both the climatic conditions of each specific location and the environmental conditions within the building. Clarke and Yaneske [186] reported that the presence of moisture increases the effect of temperature on the

thermal conductivity of inorganic materials. Thus, considering that (i) ambient temperature affects the thermal conductivity of each of the compounds of the cementitious composites as well as the thermal conductivity of the water that the composite may absorb, and (ii) the saturation level and porosity determine the amount of moisture inside the composite, it is expected an interrelation between the effects of saturation level, ambient temperature, and porosity on thermal conductivity. This might be especially relevant for cementitious composites with high porosity, such as RCA mortars.

Research has shown that replacing natural aggregate with recycled aggregate reduces the thermal conductivity of cementitious materials [196–202], therefore improving their thermal and energy-saving performance in building applications where insulation is important [196,197,203,204]. The improvement is quite significant in mixes where 100% of the natural aggregate is replaced by recycled aggregate [196]. For instance, Bravo et al. [196] observed a reduction of TC up to 42% when replacing 100% of NA with fine recycled concrete aggregate (RCA), while Sargam et al. [205] observed a drop in the TC of 40% with the same percentage of replacement. The reduction in thermal conductivity is attributed to the higher porosity of the recycled aggregate, which increases the porosity of the new composite [196,202].

Besides, using recycled materials as aggregate substitutes in concrete is no more a growing interest but a need. Due to the energy required for their generation, aggregates' production accounts for about 15% of the total CO₂ emissions resulting from concrete production [196]. Significant research is being done on using various types of recycled waste materials (e.g., industrial waste, plastic waste, and especially construction and demolition waste) in the production of various types of mortars and concretes [206]. The use of recycled aggregates for concrete production can help relieve the problems related to landfills, depletion of natural resources, lack of aggregate in construction sites, waste disposal. The use of recycled aggregate can also reduce the cost of concrete production [207,208]. Aggregates account for 70-80 % of the total volume of concrete and significantly control its properties; thus, type and amount of aggregate are two critical factors. Due to its derivation, recycled aggregate reduces the density [206], and it is known that thermal conductivity is correlated with material density [186,209]. For example, Real et al. [210] observed that, on average, each 1% increment in aggregate porosity reduces the thermal conductivity of lightweight concrete by about 0.6%. However, individual values might deviate by

up to 30% for a given density because the internal structure of the composite affects the thermal conductivity [186,187,211].

Whereas some studies assess the effect of saturation degree on concrete and mortar's thermal conductivity [182–184,189,191], no studies were found on the effect of saturation level on the thermal conductivity of cement mortars containing RCA. It is also important to note that no studies on the effect of operating temperatures on RCA mortar's thermal conductivity have been found. Moreover, no research was found on the combined effect of saturation degree, porosity, and ambient temperature on cement mortar's thermal conductivity. Different methods, mixture designs, and hygrothermal conditions can lead to different thermal conductivity results. Therefore, it would not be possible to study the interrelation of the effects of moisture content and ambient temperature on thermal conductivity based on data from different studies that are mainly focused on the effect of one single factor.

In order to comprehend the extent to which the combination of boundary conditions influences thermal conductivity, this research focused on studying the thermal conductivity susceptibility to moisture and temperature variations and how recycled concrete aggregate substitution can affect this susceptibility. Understanding the effect of RCA on the thermal conductivity of cementitious composites and how it changes within transitional levels of saturation and temperature would be key to assess their effects on the environmental impact during service life as part of a building component.

For this study, a total of 135 thermal conductivity tests were performed using mortar slabs with different RCA levels and under several temperatures and saturation conditions, as well as tests to assess mechanical properties and porosity. Finally, a combination of response surface method (RSM) [66] and analytical analysis was used to evaluate the combined effect of ambient temperature, moisture content, and porosity on the thermal conductivity of cement mortars with natural and recycled aggregate. This work unveils the possibility of formulating a prediction equation that accurately estimates the thermal conductivity of cement mortars containing RCA as a function of accessible porosity, saturation degree, and ambient temperature. It will help researchers, designers, and other professionals to evaluate the hygrothermal performance of mortars containing RCA in actual exposure conditions.

5.2 Materials

Mortars were made with Portland cement Type I (Infinity, commercial-grade), quarzitic natural fine aggregate (NA) compliant with ASTM C33 [212], and recycled concrete fine aggregate (RCA).

Mortar with natural aggregate was used as a reference for this study. The NA used has a fineness modulus of 2.99, absorption of 1.97%, and a relative density (specific gravity in saturated surface dry (SSD) condition) of 2.45.

Recycled concrete aggregate used in this study comes from construction and demolition waste. It was obtained from a Lafayette (IN) paving company and aggregate distributor (American Paving & Asphalt, IN USA), and it is mainly obtained from old concrete. The aggregate was first sieved with a No.4 sieve to meet the size specifications for fine aggregate according to ASTM C33 [212]. Particle size distribution and absorption were performed according to ASTM C136 and ASTM C128 [213,214] specifications to characterize the aggregate. The RCA used in this study has a fineness modulus of 3.41, absorption of 8.37%, and a relative density of 2.34. The absorption was used to adjust the water amount during mix proportioning.

The particle size distribution of both NA and RA and the combined aggregate particle size distribution for the studied mixtures can be found in Figure 5.1.

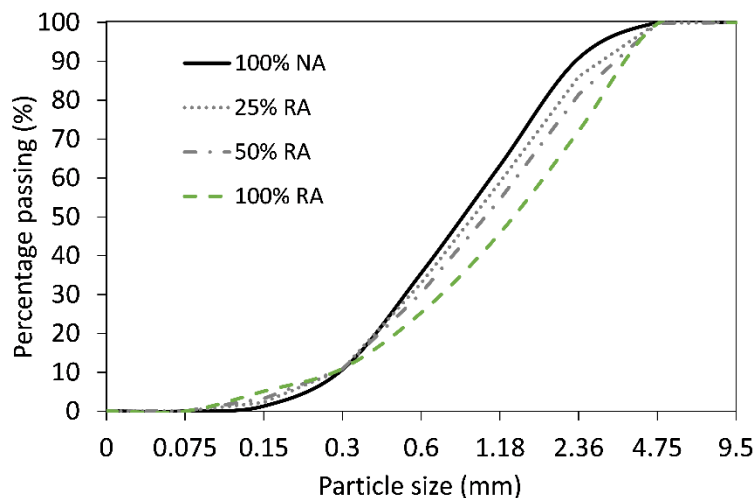


Figure 5.1 Particle size distribution of natural, recycled aggregate and combined aggregate.

5.2.1 Mix design, sample manufacturing, and curing conditions

In this study, four different mixtures were investigated: a reference mortar (NM) with fine natural aggregate and three mortars with different percentages of recycled concrete fine aggregate (RM25, RM50, RM100, indicating 25%, 50%, and 100% replacement of NA with RCA by volume in SSD condition). Mix proportions of the studied composites are presented in Table 5.1.

Table 5.1 Mix proportions (per m³ of mortar).

Component	NM	RM25	RM50	RM100
Cement (kg)	478.0	478.0	478.0	478.0
NA in SSD (kg)	1434.1	1075.6	717.0	358.5
RCA in SSD (kg)	0	342.9	685.7	1028.6
w/c	0.55	0.55	0.55	0.55

The composites are made by first mixing in a separate bowl the dry sand (NA and/or RA) with its absorption water for 30 s and wait for 10 min allowing it to be absorbed and ensure SSD condition. Then, cement is added to the mixer, and water (22.5 ± 1 °C) is added to the cement while mixing at low speed for 30 s. Consecutively, the fine aggregate (NA and/or RCA) is added over a 30 s period while mixing at low speed and mixed for other 30 s at medium speed. Mortar is left to rest for 90 s and finally mixed for 60 s at medium speed. At each interval, any mortar adhering to the side of the bowl is quickly scraped down into the batch. All mixtures were prepared under controlled room temperature (21 ± 1 °C) and relative humidity conditions ($50 \pm 5\%$ RH).

A total of 12 prismatic specimens (3 per mixture) of 16 x 4 x 4 cm were cast into steel molds for flexural and compressive strength determination. Twelve slab specimens with 20 x 20 x 4.5 cm dimensions were cast into special wooden (impermeable) mold to assess and compare density, accessible porosity, and thermal conductivity. At the end of the casting stage, molds were covered with plastic sheets to preserve moisture and demolded after 1 day. Specimens were moisture-cured in a $95 \pm 5\%$ RH and 25 ± 1 °C room for another 27 days. After 28 days, prismatic specimens were tested for strength evaluation, and slabs samples were kept in laboratory conditions (21 ± 1 °C and $50\% \pm 5\%$ RH) until the day of the first thermal conductivity test.

Thermal conductivity tests were performed after 72 days since the test requires temperature changes, which can influence cement hydration if the test is performed at early age, affecting the results.

5.3 Methods

5.3.1 Density and permeable porosity determination

The test for permeable porosity was adapted from ASTM C642 [215], assuming that all permeable porosity will be saturated after the 28 days of wet-curing. First, the apparent mass in water at 100% saturation degree (M_{sw} , in g), the saturated surface dried mass (M_s , in g) and the oven-dry mass (M_d , in g) of the slab specimens were obtained. Then, the bulk density in dry condition (d_1 , in Mg/m^3) and the apparent density (d_2 , in Mg/m^3) were calculated through Eq. (5.1) and Eq. (5.2), respectively:

$$d_1 = \frac{M_d}{(M_s - M_{sw})} \cdot \rho_w \quad (5.1)$$

$$d_2 = \frac{M_d}{(M_d - M_{sw})} \cdot \rho_w \quad (5.2)$$

where ρ_w is the density of water (Mg/m^3).

Finally, the volume of permeable pore space (permeable porosity, in %) was calculated with Eq. (5.3):

$$v_{\%} = \frac{d_2 - d_1}{d_1} \cdot 100 \quad (5.3)$$

5.3.2 Flexural and compressive strength test

Flexural and compressive strength tests were performed according to ASTM standards C348 and C349 [176,216]. Samples were tested at 28 days. Flexural strength test was conducted using an MTS machine with a load capacity of 10 kN, under a displacement control of 0.2 mm/m. Compressive strength test was conducted by an MTS machine with a load capacity of 300 kN,

under a displacement control of 0.05 mm/s. Tests were carried out on the two halves of each broken prism from the flexural test.

5.3.3 Thermal conductivity

In this study, thermal conductivity of mortars was measured using a 446 Lambda series Heat Flow Meter (HFM) by NETZSCH (Selb, Germany). The test specimen is placed between two heated plates controlled to a user-defined mean temperature and temperature difference (ΔT), and the heat flow through the specimen is measured. The sample thickness (L) corresponds to the actual sample dimension and is recorded by the instrument. The area (A) of the plane element is inputted by the operator. The heat flow (q_x) through the sample is measured by two calibrated heat flux transducers covering a large area on both sides of the specimen. More details about the HFM used in this study are presented in the supplementary material. After reaching thermal equilibrium, the test is completed. The thermal conductivity (λ) is then determined through the heat flow and the difference in mean temperature between the specimen surfaces, in accordance with Fourier's Law for conduction and considering one-dimensional steady heat flow [217] (Eq.(5.4)):

$$q_x = \lambda \frac{\Delta T}{L} \cdot A \quad (5.4)$$

The three mixtures containing 0%, 50%, and 100% RCA were selected to assess the effects of RCA, ambient temperature, and saturation degree on mortars' thermal conductivity. A total of 135 thermal conductivity tests were performed. Three slabs for each of the selected mixtures were cast, and thermal conductivity tests were performed after 72 days. Each sample was tested in five saturation conditions (dry condition, 25%, 50%, 75%, and 100% water saturation) and three different mean temperatures. The mean temperatures of 4 °C, 24 °C, and 43 °C were selected according to the recommendation of ASTM C1058 [218], and the ΔT was set to 10 °C. The saturation levels ranged from 0% to 100% to study all possible scenarios. Intermediate equally distributed saturation levels were selected to consider potential nonlinear variations of the thermal conductivity within levels. For the dry state, specimens were oven-dried at 110 ± 5 °C and weighed at 24h intervals until the loss in weight did not exceed 1% in a 24h period (~72h in total). To obtain

different saturation degrees, specimens were immersed in water until the target moisture content (target weight) was reached. Before testing, the surface of the slabs was dried, and specimens weighed. Then, slabs were kept at room temperature for 20 ± 5 min. After that, specimens were weighed again to check if the moisture content was stable. If the moisture content was within a $\pm 1\%$ range of accuracy (in total weight), the test was started; otherwise, the process was repeated until the target conditions were met.

Results were used to obtain an estimation model of the thermal conductivity of the mortars. Furthermore, samples containing 25% RCA were similarly tested to validate the proposed model, along with the training samples tested under conditions that differ from the original experimental campaign.

To determine the weight of samples at each saturation degree (S_x , where x is the saturation degree in percentage), the weight after the 28 days of wet curing was recorded and assumed as 100% saturation. The weight after oven drying the specimens was also recorded. Thus, the maximum water that can be absorbed by the sample (W_s , or absorbed water) was obtained as the difference between the mass of the saturated sample and the sample's mass in dry conditions. Finally, Eq. (5.5) was used to obtain the desired target saturation:

$$S_x = M_d + \frac{x \cdot W_s}{100} \quad (5.5)$$

where M_d (g) is the mass of oven-dried specimen in air, x (%) is the target percentage of saturation, W_s (g) is the absorbed water, and S_x (g) is the mass of the specimen at the target saturation degree x (in %).

Figure 5.2 displays a flow chart describing the overall experimental work done in this study, for each of the investigated mixtures.

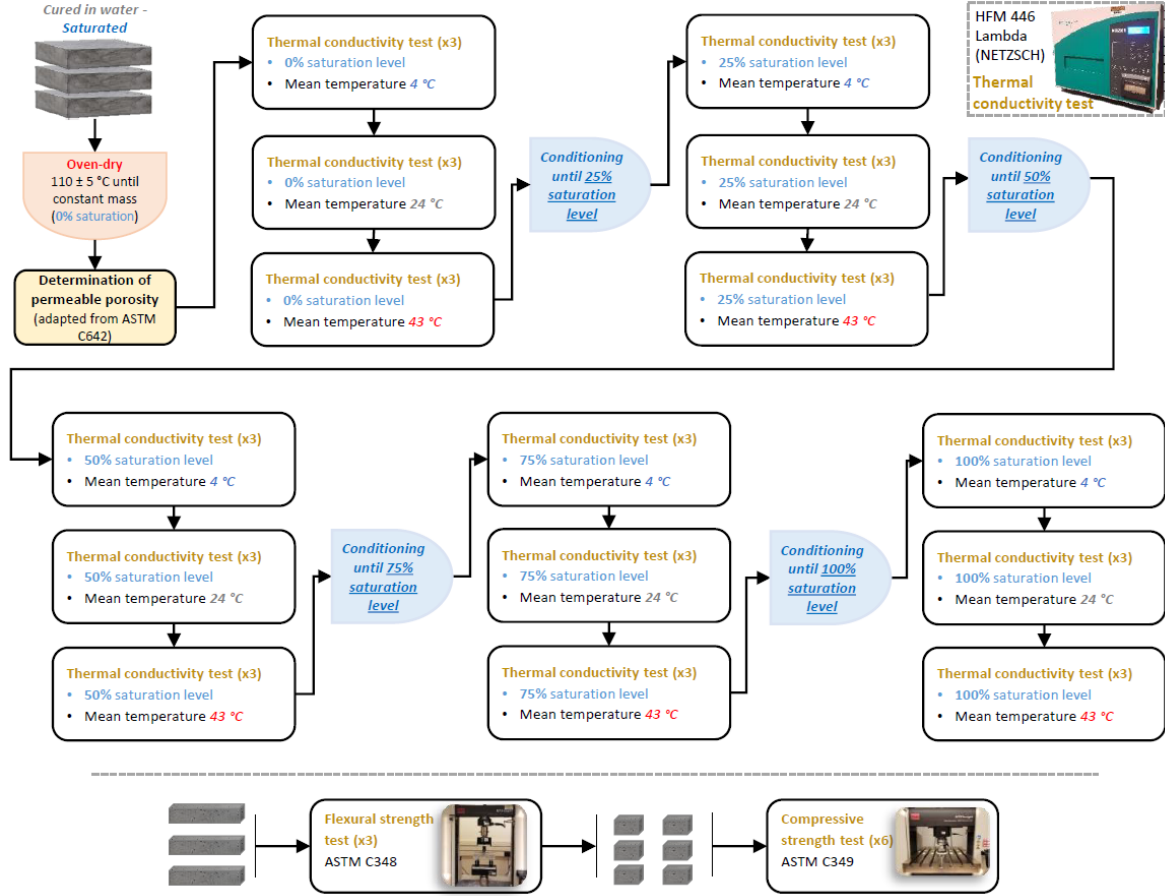


Figure 5.2 Flow chart of tests for each studied mixture.

5.3.4 Response surface method

The use of central composite design in response surface methodology (RSM) is a useful tool to find the optimum solution by analyzing variables that influence results [66,67]. This method has been successfully employed in previous studies to obtain the optimum mix design by varying the proportions of the mixture components [68,113,219]. The software JMP (SAS Institute, North Carolina, USA) was used to perform the RSM statistical experimental design. A second-order model was applied to obtain a better approximation of results (Eq. (5.6)):

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_i \sum_j \beta_{ij} x_i x_j + \varepsilon \quad (5.6)$$

where "y" is the response variable that we want to approximate (thermal conductivity), " β " the coefficients are calculated using the least square method, and " ε " is the total error. The significance threshold level (α) for each constant that was chosen was 0.05.

The RSM is applied in the present study to analyze how accessible porosity and saturation degree affect thermal conductivity jointly and at different ambient temperatures. Furthermore, the combined effect of ambient temperature and moisture content on thermal conductivity was evaluated for each of the recycled mixtures and compared to the natural mortar. Finally, the analysis of variance (ANOVA) was evaluated to check the accuracy of the model and to validate the results.

5.3.5 Generalized prediction equation and results validation

A general estimating equation for the thermal conductivity was developed based on the RSM analysis model, where the effects of porosity, saturation degree and ambient temperature on thermal conductivity were evaluated. Different coefficients were obtained for different ambient temperatures when analyzing the combined effect of porosity and saturation degree on thermal conductivity. Thus, the variations of each of these coefficients as a function of ambient temperature were analyzed. If the difference between the same coefficient at different temperatures was less than 1%, the average was taken as the final value of the coefficient for the generalized equation. Instead, if the difference was higher than 1%, equations that correlate each coefficient as a function of temperature were obtained and used as the final value of the coefficient in the generalized estimating equation.

Finally, to validate the model, a set of additional thermal conductivity tests were performed. Mixtures and conditions for validation were selected based upon the following criteria: (i) one or more than one variable (ambient temperature, saturation degree and/or porosity) different from the set of training data, and (ii) variable values within the set of training data (temperature between 4 °C and 43 °C, saturation between 0% and 100%, and porosity between minimum and maximum measured values for natural and recycled aggregate mortar, respectively).

5.4 Results and Discussion

5.4.1 Density and permeable pore space (accessible porosity)

The unit weight of each sample was measured before thermal conductivity tests at each water saturation degree. Figure 5.3 displays how the density of mortars decreased with an increase in RCA replacement and increased with a higher water saturation degree due to the water absorbed into the pores, as expected according to previous literature [9,196,208]. The magnitude of this decrease depends on the volume, density, and type of aggregate used [179]. The difference between the dry and the fully saturated state was higher with higher recycled aggregate replacement. While mortars with natural aggregate (NM0) showed an increase in density of 10.3% (when saturated, assuming as reference the dry-density of the same samples), mortars with 100% RCA (RM100) exhibited an increase in density of 15.9%, from 1777.8 kg/m³ in dry condition to 2060.7 kg/m³ in fully saturated conditions.

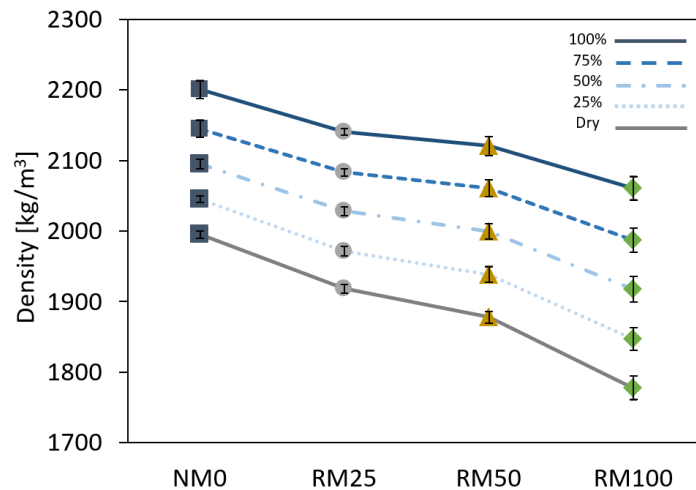


Figure 5.3 Density of mortars at each saturation degree.

The decrease in density is strictly correlated with the increase in macro porosity. Table 5.2 presents the percentage of permeable pore space (accessible porosity) for each mixture, and their standard deviation. Each value results from the average of the accessible porosity of three slab specimens used for the thermal conductivity test. The higher the RCA replacement, the higher the porosity, as expected. Changes in porosity will affect thermal conductivity. Compared to the reference mortar, the replacement of 25%, 50%, and 100% of NA with RA resulted in a 12%, 22%, and 38% higher accessible porosity, respectively.

Table 5.2 Permeable pore space (adapted from ASTM C642).

Mixture	Porosity	<i>Standard deviation</i>
NM	20.62 %	<i>0.12 %</i>
RM25	23.17 %	<i>0.35 %</i>
RM50	25.14 %	<i>0.20 %</i>
RM100	28.49 %	<i>0.23 %</i>

5.4.2 Flexural and compressive strength

Figure 5.4 displays and correlates compressive and flexural strength results to the recycled aggregate replacement for all studied mixtures. The higher the percentage of RCA, the lower the compressive strength for all studied mortars. Generally, previous research reported that the compressive and flexural strength of cement mortars and concrete decreased as the RCA content increased [206,208,220,221]. In this study, compressive strength was reduced by 9%, 12%, and 21% when 25%, 50%, and 100% of NA were replaced with RCA, respectively. The decrease in compressive strength can be attributed to (i) the lower strength of the RCA, (ii) the increase in porosity, and (iii) the weak adhesion between old and new cement paste in the ITZ. Flexural strength also decreased with higher RCA content. Results showed a reduction in flexural strength of 10%, 19% and 27% for RM25, RM50 and RM100, respectively, compared to NM. The reduction of flexural strength due to the use of RCA is slightly higher compared to the reduction of compressive strength within the same mixture (Figure 5.4). This result contrasts with previous studies, which reported that the addition of RCA does not reduce flexural strength as substantially as compressive strength [206]. However, this reduction is dependent on the variations of different factors such as replacement amount, origin and quality of the RCA, mixture design [206]. Finally, a good linear correlation was found between flexural and compressive strength results, as evidenced by the high value of $R^2 = 0.97$.

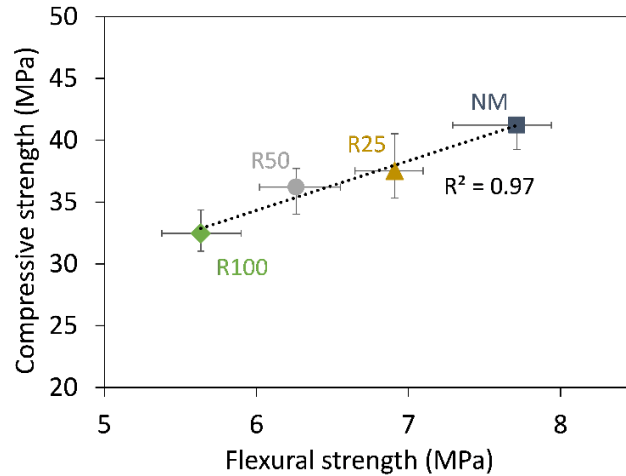


Figure 5.4 Flexural and compressive strength results.

Figure 5.5 displays the linear correlation between the reduction of strength and the porosity after NA is replaced with RCA. The correlation between increase of porosity (due to the incorporation of RCA) and reduction of strength showed a trend similar to that reported in the literature [206,208,220,221]. For the mortar with natural aggregate, a 25% replacement of NA with RCA produced an increase in the accessible porosity of 13%, reducing the compressive and flexural strength by 9% and 10%, respectively. When 50% NA was replaced by RCA, the increase in porosity was 22%, producing a decay of 12% in compressive and 19% in flexural strength, respectively. Finally, with 100% RCA, the observed increase in porosity compared to the mortar with NA was 33%, and the reduction of compressive and flexural strength was 21% and 27%, respectively.

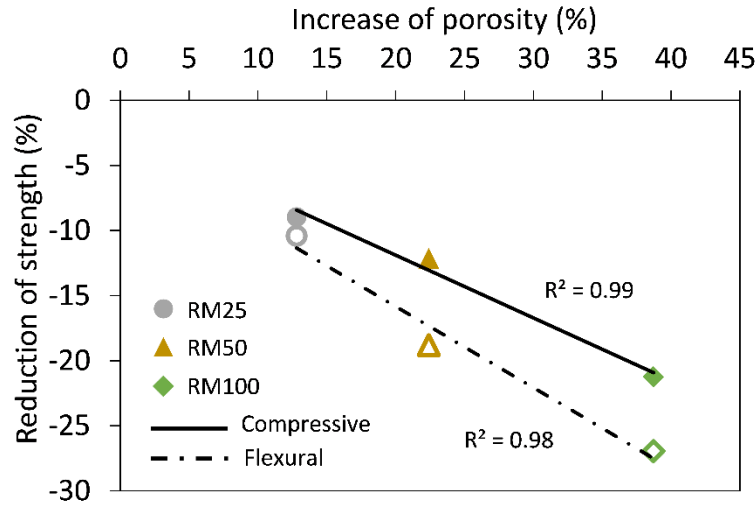


Figure 5.5 Reduction of strength due to increase of voids (by replacing NA with RA).

5.4.3 Thermal conductivity

The thermal conductivity of each specimen for every selected mixture was tested at five different water saturation conditions (dry, 25%, 50%, 75% and saturated) and three different mean temperatures (4 °C, 24 °C and 43 °C, with a ΔT of 10 °C). The average value for three specimens of the same mixture and same conditions was taken as the final thermal conductivity measurement for each condition. The results of thermal conductivity for the studied cementitious composites are shown in Table 5.3. Δ represents the variation (in %) of the thermal conductivity with respect to that of the reference mortar (NM0) calculated at the same ambient temperature and saturation degree. It can be observed that the replacement of NA with RCA reduced the thermal conductivity of the composites. Therefore, it could improve their thermal and energetic performance for building applications where insulation is important. This improvement is quite significant in mixes in which 100% of the NA is replaced, reaching a decrease in thermal conductivity (TC or λ -value) as high as 32.76% in dry conditions. The decrease in TC was expected because of the more porous nature of the recycled composite and its reduced density. However, the extent of this variation strongly depends on the moisture content and the ambient temperature at which thermal conductivity is calculated. The lowest TC value (0.696 W/m·K) was obtained from the RM100 mixture in dry conditions at 4 °C, while the highest value (1.757 W/m·K) from the NM0 mixture at 43 °C in fully saturated conditions.

Table 5.3 Thermal conductivity results.

		Saturation									
		Dry		25%		50%		75%		100%	
Mix.	T	λ	Δ	λ	Δ	λ	Δ	λ	Δ	λ	Δ
	°C	W/(mK)	%	[W/(mK)]	%	W/(mK)	%	W/(mK)	%	W/(mK)	%
NM	4	1.03	-	1.16	-	1.22	-	1.32	-	1.57	-
	24	1.09	-	1.21	-	1.31	-	1.44	-	1.64	-
	43	1.14	-	1.26	-	1.39	-	1.54	-	1.76	-
RM 50	4	0.80	-22.26	0.91	-21.25	1.04	-15.24	1.18	-10.24	1.35	-14.15
	24	0.85	-21.91	0.98	-18.84	1.12	-14.74	1.28	-11.03	1.41	-13.75
	43	0.89	-21.52	1.04	-17.52	1.21	-13.24	1.39	-9.79	1.55	-11.58
RM 100	4	0.70	-32.76	0.81	-30.31	0.88	-27.78	1.04	-20.94	1.22	-22.29
	24	0.74	-32.41	0.87	-28.41	0.98	-25.25	1.15	-20.11	1.29	-21.47
	43	0.77	-32.33	0.91	-27.89	1.06	-23.53	1.25	-18.81	1.40	-20.19

Effect of ambient temperature and RCA in dry conditions

Figure 5.6 shows the variation of thermal conductivity in dry conditions as a function of the ambient temperature (the mean temperature at which the test was performed) for each of the selected mixtures. For each mixture, the higher the ambient temperature, the higher the thermal conductivity. Besides, for each ambient temperature, the higher the RCA%, the lower the thermal conductivity. The thermal conductivity of RM100 at 43 °C is close to the thermal conductivity of RM50 at 4 °C, while comparing the two recycled mixtures at the same temperature, it is clear that RM100 possesses a lower thermal conductivity than RM50. This example highlights the importance of the ambient temperature on the determination of thermal conductivity values of cement mortars, and it should be considered when the energy efficiency of this components is evaluated. Previous research has also shown that depending on the material type and density, the TC values of insulation materials are affected at different degrees by operating temperature [190,191]. Higher operating temperatures lead to higher λ -values.

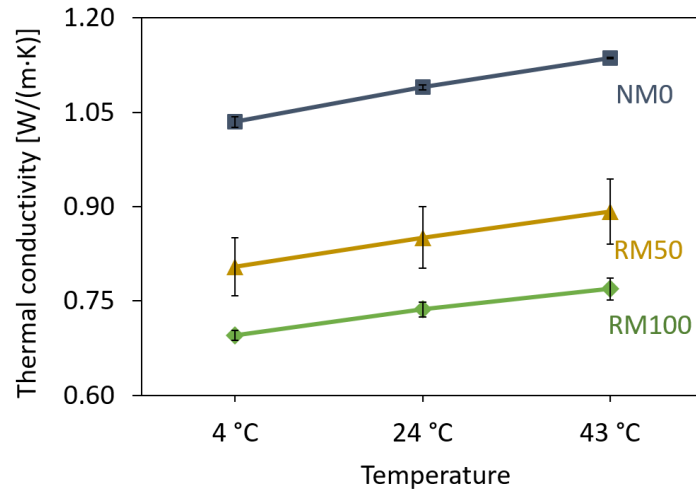


Figure 5.6 Effect of ambient (mean) temperature on thermal conductivity in dry-state.

As shown in Figure 5.7, thermal conductivity's susceptibility to ambient temperature correlates with the amount of permeable porosity. For all assessed porosities, it was observed that thermal conductivity is more susceptible to changes of ambient temperature at a low-temperature range (4-24 °C) than at a higher temperature range (24-43 °C).

Furthermore, the greater the porosity, the lower the thermal conductivity susceptibility to changes in ambient temperature. Mortars with recycled aggregate (i.e., mortars with higher porosity) presented less thermal conductivity variation due to changes in ambient temperature. Thus, if the ambient temperature changes, no special attention would be required when evaluating RCA mortars' thermal conductivity.

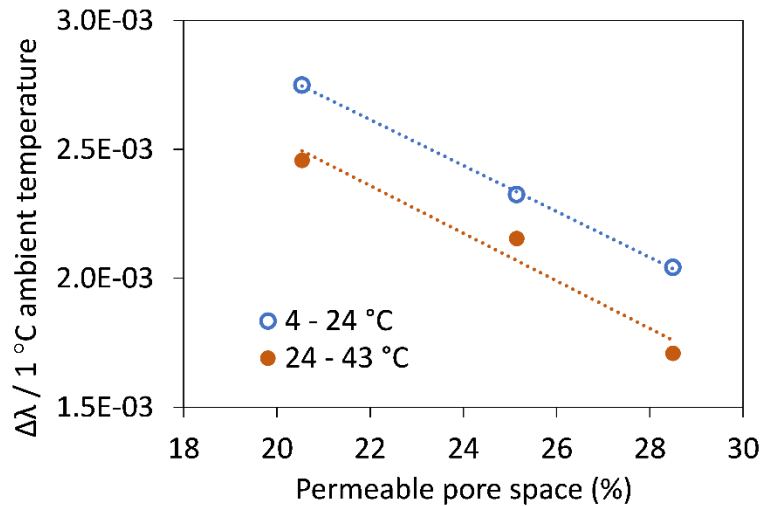


Figure 5.7 Correlation between porosity and thermal conductivity's susceptibility to changes in ambient temperature in dry-state.

Effect of moisture content and RCA content at 24 °C

Figure 5.8 illustrates the effect of RCA replacement on the thermal conductivity as a function of saturation degree, with a constant ambient temperature of 24 °C. Thermal conductivity increased notably with moisture content. It was observed that the thermal conductivity measured at 100% saturation is 1.5 to 1.8 times higher than that measured in the dry state. Previous research observed that the TC of cement mortar and concrete in saturated conditions is about 70% and 50% higher than in dry conditions, respectively [9,184]. The increase of thermal conductivity with saturation degree is mainly due to the higher conductivity of water (0.605 W/m·K, at 24 °C and atmospheric pressure) compared to that of the air (0.02617 W/m·K, at 24 °C and atmospheric pressure).

While the sample with natural aggregate showed an increase of thermal conductivity of 50% due to complete saturation (taking as reference dry condition), the increase exhibited in samples with 100% RCA was 75%. These differences may be related to the differences in accessible porosity of the studied mixtures since the higher the RCA level, the higher the accessible porosity (Table 5.2).

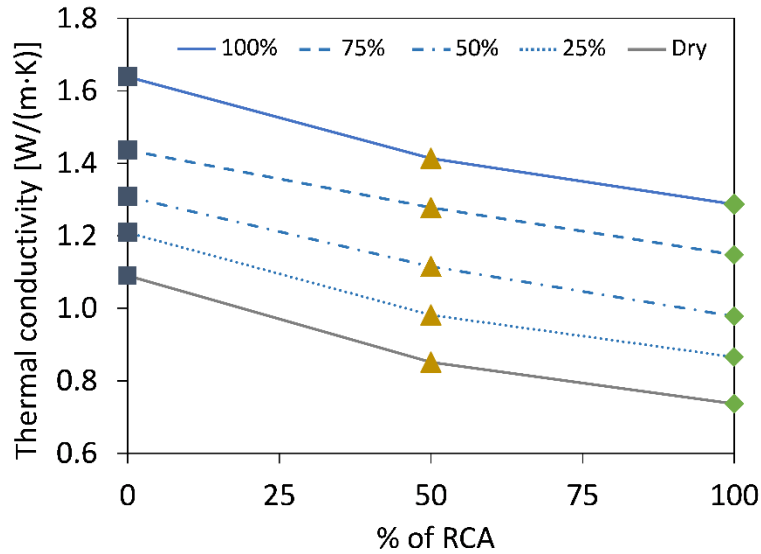


Figure 5.8 Thermal conductivity as function of saturation degree and RA replacement at 24 °C.

Figure 5.9 displays the maximum variation of thermal conductivity due to moisture content versus the corresponding porosity for the studied mixtures. The higher the permeable porosity, the greater the maximum variation of thermal conductivity. Thus, the higher the porosity, the more susceptible the composite is to changes in thermal conductivity due to a variation in moisture content. Since the mortars with RCA present a higher porosity, they will be more susceptible to changes in thermal conductivity due to changes in moisture content. In other words, when evaluating the thermal conductivity of cementitious composites with RCA, considering that saturation degree is more important than in mortars with NA, and special consideration must be taken when assessing RCA mortar's thermal insulation properties.

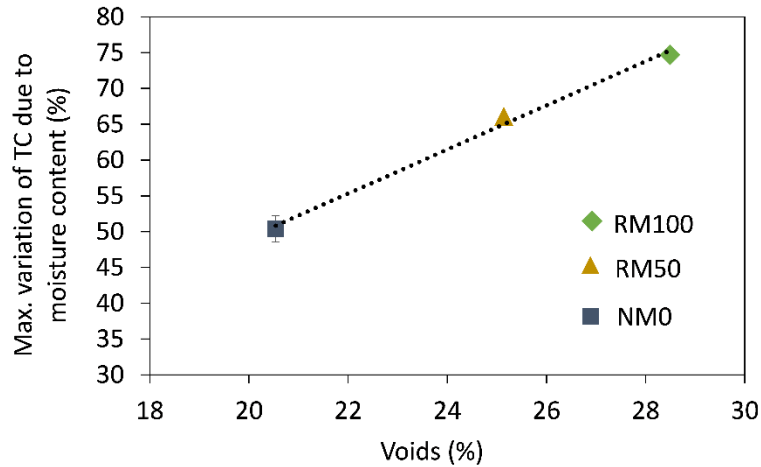


Figure 5.9 Maximum variation of thermal conductivity due to moisture content (%) vs. percentage of voids, at 24 °C.

TC as a function of ambient temperature and saturation degree with RSM

RSM was used to study the combined effect of saturation degree (in %) and ambient temperature (in °C) on mortars' thermal conductivity. Results exposed in Table 5.3 were used as input for central composite design to obtain an estimation model of the thermal conductivity for each of the studied mortars (NM0, RM50, and RM100). Then, ANOVA was performed. Results of P-values are presented in Table 5.4. While linear and square ($X_1 \cdot X_1$) combinations have high accuracy (low P-values), square ($X_2 \cdot X_2$) and interaction P-values are over the significance threshold ($\alpha = 0.05$).

Table 5.4 ANOVA results.

		Thermal conductivity		
		<i>P-value (α)</i>		
	^a	NM0	RM50	RM100
Linear	X_1	0.000	0.000	0.000
	X_2	0.000	0.000	0.000
Square	$X_1 \cdot X_1$	0.004	0.017	0.012
	$X_2 \cdot X_2$	0.762	0.121	0.729
Interaction	$X_1 \cdot X_2$	0.043	0.000	0.002

^a X_1 : Saturation degree; X_2 : Ambient temperature.

Hence, RSM analysis was performed again without non-significant terms. From the new statistical analysis, Eq. (5.7) was obtained. This equation estimates the thermal conductivity (TC) by modifying both temperature (°C) and saturation degree (%).

$$\lambda = c_1 + c_2 \cdot t + c_3 \cdot s + c_4 \cdot t \cdot s + c_5 \cdot s \cdot s \quad (5.7)$$

where:

λ is the estimated thermal conductivity;

$c_1, 2, 3, 4, 5$ are constant (for each mixture; see Table 5);

$t = (\text{ambient temperature (in } ^\circ\text{C)} - 23.5)/19.5$;

$s = (\text{saturation degree (in \%)} - 50)/50$.

Table 5.5 Constants C_n for each mortar.

	NM0	RM50	RM100
c₁	1.304844695	1.1223796249	0.9865485272
c₂	0.0782368131	0.0797615594	0.0746902471
c₃	0.2708350498	0.2959731279	0.2841325834
c₄	0.0286240782	0.0310834019	0.0320833373
c₅	0.0650604286	0.0209788581	0.0331335238

Figure 5.10 shows the thermal conductivity as a function of temperature (°C) and saturation degree (%) for each of the studied mixtures (NM0, RM50, and RM100). While the surfaces were obtained from Eq. (5.7), the black dots indicate the actual thermal conductivity obtained from the tests. Figure 5.10 demonstrates a good fit between the predicted values and the experimental data. It can be noted that thermal conductivity is susceptible to changes in moisture content and ambient temperature, as well as the type of mortar (comparing Figure 5.10 (a) NM, (b) RM50, and (c) RM100).

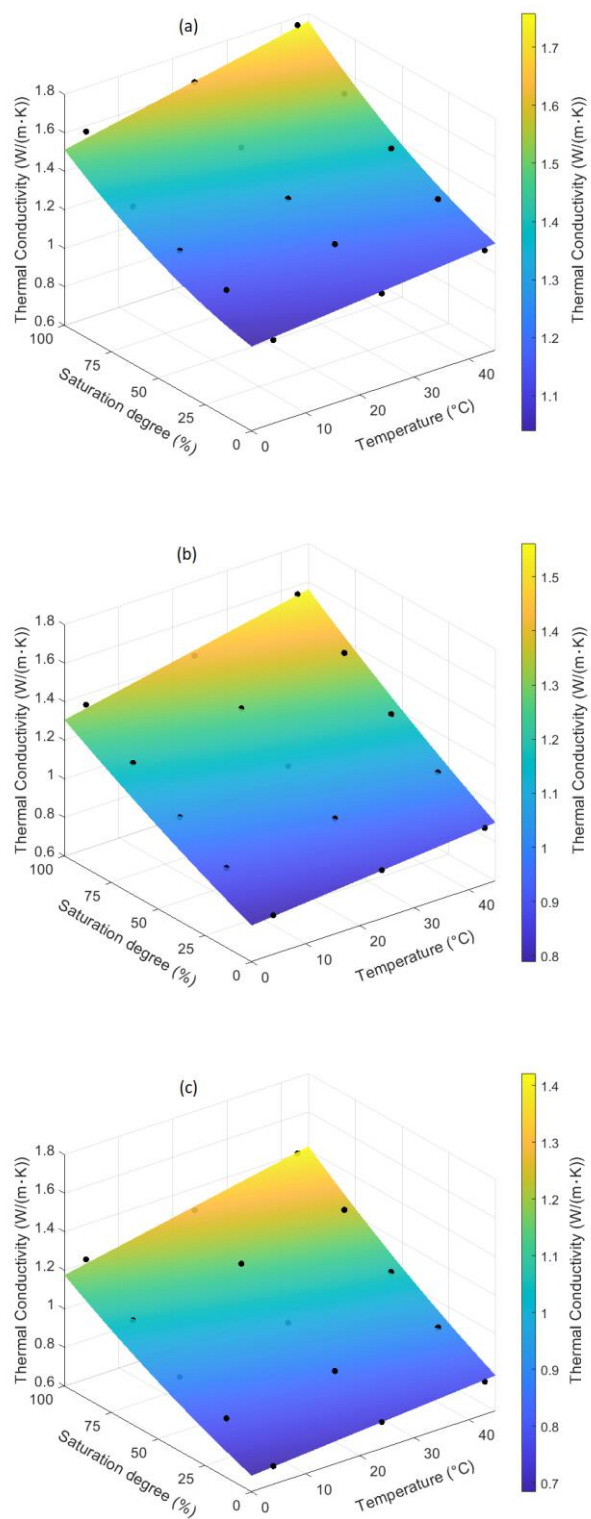


Figure 5.10 Thermal conductivity as a function of ambient temperature ($^{\circ}C$) and relative humidity (%):
(a) NM, (b) RM50, and (c) RM100.

TC as a function of porosity and saturation degree with RSM

RSM analysis was performed to assess the combined effect of RCA (in terms of % permeable pore space) and saturation degree (%) on the thermal conductivity of mortars. After collecting all thermal conductivity test results (presented in Table 5.3), central composite design was applied to obtain a second-order estimation model for each ambient temperature investigated (4 °C, 24 °C, and 43 °C). The range for both RCA content and saturation degree was 0-100%.

Thereafter using ANOVA, the results displayed in Table 5.6 were obtained. While linear and square ($X_1 \cdot X_1$) combinations have high accuracy (low P-values), square ($X_2 \cdot X_2$) and interaction P-values are over the significance threshold ($\alpha = 0.05$).

Table 5.6 ANOVA results.

		Thermal conductivity		
		<i>P-value (α)</i>		
	<i>a</i>	4 °C	24 °C	43 °C
Linear	X_1	0.000	0.000	0.000
	X_2	0.000	0.000	0.000
Square	$X_1 \cdot X_1$	0.007	0.020	0.022
	$X_2 \cdot X_2$	0.384	0.105	0.234
Interaction	$X_1 \cdot X_2$	0.617	0.431	0.509

^a X_1 : Saturation degree; X_2 : Porosity.

Therefore, RSM was applied again, removing non-significant terms. As a result of the new statistical analysis, a prediction equation (Eq. (5.8)) was obtained. This equation estimates the thermal conductivity (TC) at each of the three ambient temperatures evaluated by inputting both accessible porosity (%) and saturation degree (%).

$$\lambda = a_1 + a_2 \cdot p + a_3 \cdot s + a_4 \cdot s \cdot s \quad (5.8)$$

where:

λ is the estimated thermal conductivity;

$a_1, 2, 3, 4$ are constant (for each ambient temperature; see Table 7);

$p = (\text{accessible porosity (in \%)} - 24.555)/3.935$;

$s = (\text{saturation degree (in \%)} - 50)/50$.

Table 5.7 Constants (for each studied ambient temperature).

	4 °C	24 °C	43 °C
a₁	1.0607958251	1.1490054639	1.231216691
a₂	- 0.166209024	- 0.167553767	- 0.169409658
a₃	0.2575232213	0.2752495433	0.3189525333
a₄	0.0596384762	0.0299491286	0.0295852057

Figure 5.11 displays the thermal conductivity as a function of porosity (%) and saturation degree (%) at each of the investigated ambient temperatures (4 °C, 24 °C, and 43 °C). Whereas the graphed surfaces were obtained from Eq. (5.8), the black dots represent the actual thermal conductivity obtained from the tests. As shown in Figure 5.11, the predicted values fit well the experimental data. Besides, it can be observed that the higher the ambient temperature, the higher the thermal conductivity. However, the variations of TC as a function of porosity and saturation degree are similar for each of the studied ambient temperatures, with surfaces being almost parallel but translated on the vertical axis.

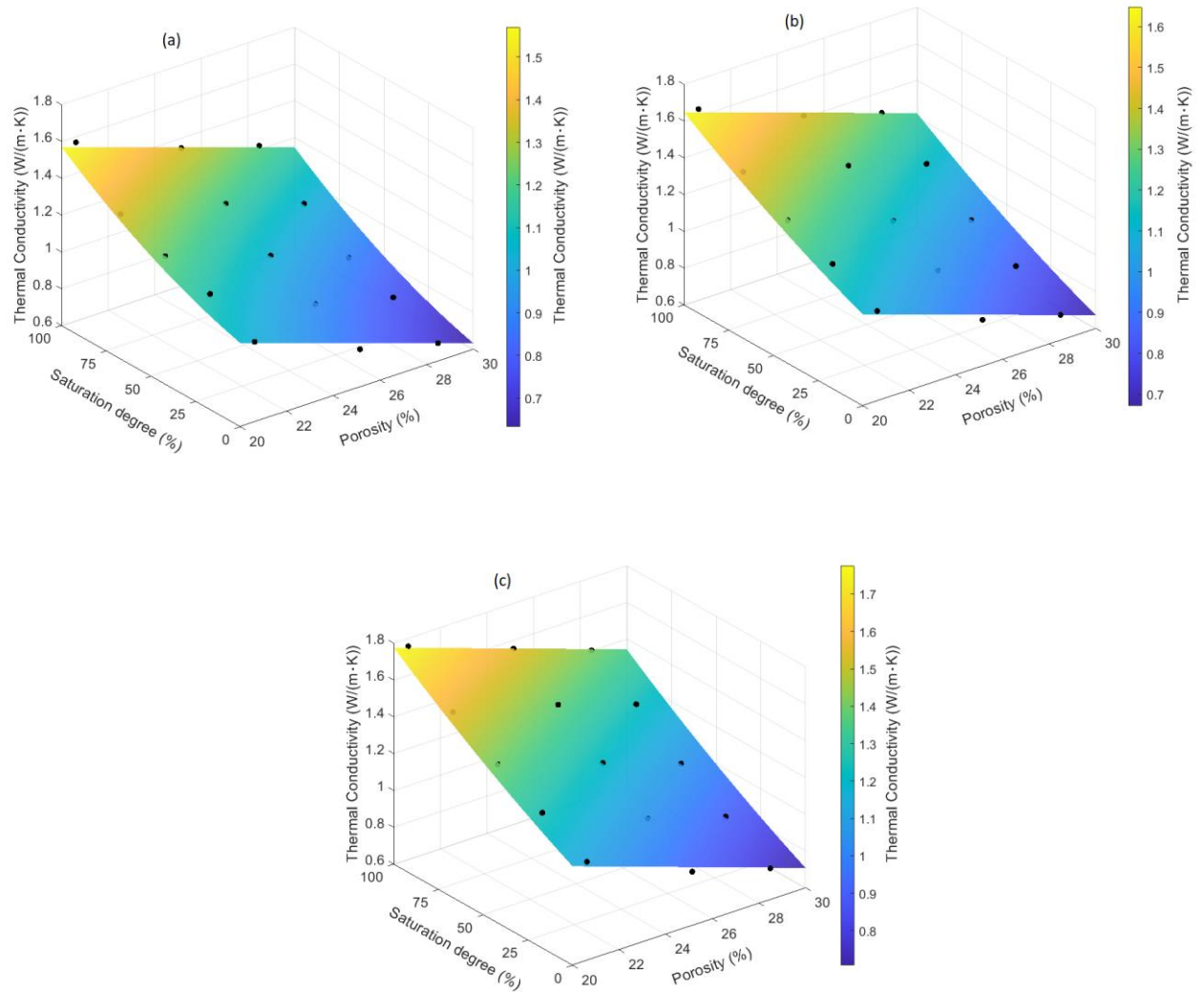


Figure 5.11 Thermal conductivity as a function of porosity (%) and relative humidity: (a) 4 °C, (b) 24 °C, and (c) 43 °C.

General prediction equation

Based on the RSM analysis where TC was evaluated as a function of porosity and saturation degree, for each ambient temperature (Eq. (5.8), Table 5.7), correlations between temperature and the coefficients a_1 , a_2 , a_3 , and a_4 were identified. Then, an equation (Eq. (5.9)) that estimates the thermal conductivity of cement mortars as a function of permeable porosity, saturation degree and ambient temperature is proposed:

$$\lambda' = v_1 + v_2 \cdot p + v_3 \cdot s + v_4 \cdot s \cdot s \quad (5.9)$$

where:

λ' is the predicted thermal conductivity;

$v_1 = 0.00437 \cdot T + 1.04358$ (with T = ambient temperature, in °C);

$v_2 = -0.16772$ (constant, does not significantly change with ambient temperature);

$v_3 = 0.00157 \cdot T + 0.24677$ (with T = ambient temperature, in °C);

$v_4 = -0.0007769 \cdot T + 0.0581098$ (with T = ambient temperature, in °C);

p = (accessible porosity (in %) – 24.555)/3.935;

s = (saturation degree (in %) – 50)/50.

Table 5.8 reports the thermal conductivity tests and conditions used to train and validate the model, according to the validation criteria exposed in the Method's section.

Table 5.8 Training and validation tests conditions.

	Ambient temperature [°C]	Saturation degree [%]	RCA content (Porosity) [%]	Tests conditions
Training tests (135 tests)	4, 24, 43	0, 25, 50, 75, 100	0, 50, 100 (20.62, 25.14, 28.49)	Experimental campaign
Validation test 1	24	37	0 (20.62)	≠ saturation degree than training tests
Validation test 2	24	21	100 (28.49)	≠ saturation degree than training tests
Validation test 3	24	0	25 (23.17)	≠ porosity than training tests
Validation test 4	24	100	25 (23.17)	≠ porosity than training tests
Validation test 5	35	25	50 (25.14)	≠ ambient temperature than training tests
Validation test 6	20	42	25 (23.17)	≠ porosity, saturation degree, and ambient temp. than training tests

The accuracy of the model was assessed for both training data and validation data. As shown in Figure 5.12, a very good agreement was found between the predicted (numerical) and experimental results. The two dotted lines represent an error of $\pm 5\%$. Therefore, the proposed

model (Eq. (5.9)) is accurate and able to predict the thermal conductivity of cement mortars knowing the amount of permeable porosity, saturation degree, and ambient temperature (in the range of 4 to 43 °C).

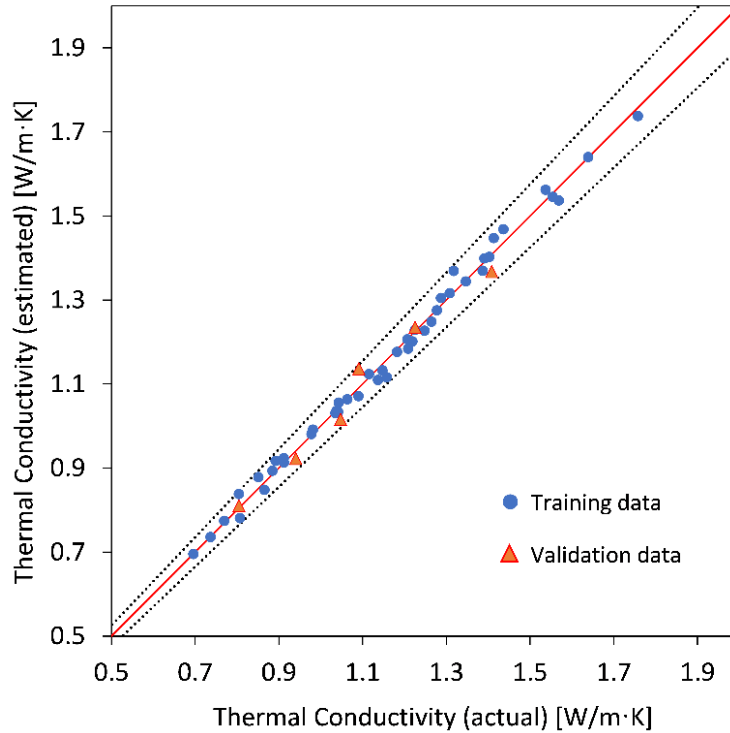


Figure 5.12 Correlation between experimental and predicted thermal conductivity.

5.5 Conclusions

This paper aimed to study the effect of RCA on thermal conductivity's susceptibility to moisture content and ambient temperature variations of cement mortars.

Based on the results of this investigation, the following conclusions can be drawn:

- The replacement of NA by RCA reduced the composite's thermal conductivity and consequently increased its thermal insulation capacity. The decrease in TC was expected because of the more porous nature of the recycled composite and its reduced density. However, the extent of this variation strongly depends on the moisture content and the ambient temperature at which thermal conductivity is calculated.

- Mortars with recycled aggregate (i.e., mortars with higher porosity) presented less thermal conductivity variation due to changes in ambient temperature. Thus, if the ambient temperature changes, no special consideration would be required when evaluating RCA mortar's thermal conductivity of RCA mortars instead of plain mortars with NA.
- Thermal conductivity variations as a function of moisture content were higher in the case of mortar containing RCA. The use of RCA increased the mortar accessible porosity, which heightened the importance of saturation degree on thermal conductivity determination. Results showed that the higher the porosity, the more susceptible the mortar's thermal conductivity to changes in moisture content. Thus, special attention to the variability of thermal conductivity due to saturation degree should be taken when evaluating the thermal performance of mortars with high porosity.
- The increase in the heat insulation capacity when using RCA is achieved at the expense of strength. Both compressive and flexural strength decreased with the incorporation of RCA. The higher the RCA content, the higher the reduction in strength. However, if the strength sufficient for a given use is known, these composites may find an important application in building components as a sustainable mortar for energy efficiency in buildings.
- Finally, an equation that estimates thermal conductivity of cement mortars as a function of permeable porosity, saturation degree and ambient temperature has been proposed. A robust agreement (with an error of less than 5%) was found between the experimental and predicted results.

To summarizing, mortars with RCA provided higher thermal insulation ability than plain mortars. However, it was found that the variation of thermal conductivity due to changes in saturation degree is more significant in mortars containing RCA. Thus, these variations should be considered when thermal insulation is used as a factor for environmental impact assessment. Understanding the effect of recycled concrete aggregate on the thermal conductivity of cementitious composites is key to assess their effects on the environmental impact during service life as part of a building component. This study proposed a general prediction equation that accurately estimates mortars' thermal conductivity as a function of accessible porosity, saturation degree, and ambient temperature.

6. IMPACT OF CURING TEMPERATURE ON THE SUSTAINABILITY OF SUGARCANE BAGASSE ASH AS A PARTIAL REPLACEMENT OF CEMENT IN MORTARS: AN LCA

This chapter will be submitted for publication in April 2022 as:

Francioso V., Lopez-Arias M., Moro C., Velay-Lizancos M., “*Impact of curing temperature on the sustainability of sugarcane bagasse ash as a partial replacement of cement in mortars: an LCA*”. [To be submitted in April 2022]

6.1 Introduction

The demand for construction materials has surged due to the enormous development in the construction industry and the increase in the world's population. This has been translated into a worldwide increase of 175% in cement production over the last 20 years [222]. Regrettably, cement manufacturing consumes a great deal of energy and negatively impacts the environment by consuming raw materials and releasing a massive amount of CO₂ [223]. Furthermore, besides the consumption of natural resources for building materials production, continuous waste generation has become one of our society's most prominent environmental issues. Hence, much endeavor is being made to design viable solutions to solve these problems, including developing more sustainable cementitious composites with the inclusion of industrial waste, by-products, or alternative aggregates [224,225]. The partial or total replacement of ordinary Portland cement with supplementary cementitious materials (SCMs) and natural aggregate by recycled aggregates are potential pivotal approaches to reduce the environmental concerns and carbon footprint deriving from the construction industry [225].

Nowadays, there is a large availability of artificial pozzolanic materials that are by-products and, most often, waste from industrial or agricultural applications and processes. These include coal fly ash, ground granulated blast furnace slag, silica fume, rice husk ash, and sugar cane bagasse ash (or others biomass combustion ash). In particular, the use of coal fly ash as a supplementary cementitious material for concretes and mortars production has been extensively studied, implemented in standards, and is widely accepted by the concrete industry. However, the current trend of closing coal-based power plants in developed countries will reduce the availability of this valuable substitute for cement. As a result, recent attention has been shifted to the utilization

of alternative ashes from agricultural waste in cementitious composites, which may reduce the environmental impact of constituent materials such as cement. Besides, the valorization of these agricultural wastes avoids negative impacts which may arise from their disposal.

In this context, sugarcane bagasse ash (SCBA) has shown to be a viable alternative option as a partial cement replacement due to its chemical composition and physical properties. SCBA is a biomass waste resulting from sugarcane bagasse burning (calcination) for electricity production [226,227]. Sugarcane bagasse is a by-product of the sugarcane industry in sugar and ethanol production [226]. The sugarcane industry plays an important role and holds a significant share in the economy of many countries [228]. More than 50% of the countries are involved with sugarcane crops [227,228], totaling an annual global production of about 2 billion metric tons. Brazil is the world's undisputed leader, with 757 million tons of sugarcane production in 2020, followed by India (370 million tons) and China (108 million tons) [229–231]. As its production increases [232], the amount of ash (waste) generated will also increase, contributing to the ongoing issue of biomass waste management [233,234]. These ashes are often disposed of in landfills without any environmental control or, in some cases, used as fertilizer [235–237]. However, several investigations [237–240] have already determined the feasibility of using ashes resulting from agro-industrial by-products (such as SCBA) as supplementary cementitious material (SCM). Thus, there is an opportunity to reduce both the environmental impact of cementitious materials and the generation of waste. Numerous recent research efforts have been undertaken to incorporate SCBA to produce sustainable mortar and concrete [227,235,236,238,241–244].

Literature has shown that the mechanical performance of cementitious composites containing SCBA may range from 80% to 160% compared to the same without SCBA, depending on the ash mineral and morphological characteristics [227]. Nevertheless, more systematic investigations will be essential to understand further the pozzolanic behavior of SCBA. Moreover, a crucial task will be finding the most ecological post-processing for the SCBA, with the lowest energy demand and CO₂ emissions, that yields the higher reactivity. It will help instill more confidence in the concrete and construction industry stakeholders for adopting SCBA as an alternative pathway for sustainable concrete production.

Besides, to effectively evaluate the environmental impact of cementitious composites by using SCBA and define their best application, an environmental assessment that accounts for the

effects of their substitution in cement is crucial. Many methodologies exist today to evaluate the environmental impact of processes and products. The most widely acknowledged and standardized is the so-called Life Cycle Assessment (LCA). According to the U.S. Environmental Protection Agency (EPA), an LCA is a tool for evaluating the environmental burdens associated with a product, material, process, or activity. The ISO standard 14040, the standard that describes the principles and framework for LCA, defines it as “the compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle” [245]. In other words, LCAs identify and quantify energy and material used and pollutants released into the environment to model the complex processes included in the life cycle of a product. It can cover a specific fragment, or the entire product’s life-cycle, from materials acquisition, manufacturing, use, and final disposition (disposal or reuse). However, it must be reminded that an LCA is a relative tool intended for comparison and not absolute evaluation, thereby serving to help decision-makers to compare all major environmental impacts when choosing between alternative courses of action [246].

Remarkably, the use of LCA to evaluate the environmental impact of SCBA in cementitious composites has been found as lacking in the literature. Very few studies have been found evaluating the environmental impact of SCBA as a binder replacement in cementitious composites. Two studies [247,248] only evaluated the potential reduction of greenhouse gasses (mainly CO₂) emissions as a single factor in utilizing SCBAs as partial cement replacement. Whereas a third study [249] performed an LCA of SCBA as partial cement replacement in concrete, using as a functional unit a school building constructed as a 3-D digital model employing building information modeling (BIM) and considering 17 impact categories. All of the previous studies concluded that the utilization of SCBA can indeed contribute to the net reduction of greenhouse gasses (GHG) emissions and almost all other impact categories.

Nevertheless, to make a realistic estimation of the environmental footprint of cementitious composites, the functional unit used in the assessment should include a reference performance. For instance, some authors suggest that the appropriate functional unit to assess the effect of admixtures and recycled materials in cementitious composites should have the same quantity of material (e.g., 1 m³) with a given fixed value of compressive strength [95,250]. In this way, it is possible to compare the sustainability of using recycled materials, accounting for their effects on one of the main target properties of a cementitious composite, its strength. Thus, accounting for

the effect of SCBA substitution on the strength and the changes in the cement content to achieve the same performance as the reference material (without SCBA) will be key to assessing the real benefits of using this biomass waste as a partial replacement of cement.

Besides, external factors may also affect SCBA replacement's impact on the mechanical properties of cementitious composites. A previous study has pointed out that the effect of another type of biomass ashes (from the paper industry) on the concrete strength highly depends on the curing temperature [79]. Curing conditions strongly impact the hydration of cementitious composites, significantly influencing their strength, porosity, and durability [251], consequently, the environmental impact during their life-cycle. The effect of curing temperature has been extensively investigated in plain Portland cement mortar and concretes. In particular, research has shown that curing temperature is a key factor influencing the evolution of the compressive strength of cementitious composites [79,113,252–255], indicating that the higher the curing temperature, the faster the development of strength at early ages. However, after 28 days, the strength may be lower in samples cured at higher temperatures (crossover effect) [255,256]. The same may be true in cementitious composite containing SCMs. Indeed, research suggested that different curing temperatures and processes may increase the compressive strength and reduce the permeability of concrete and mortars where cement is replaced by SCMs [79,257,258].

Velay-Lizancos et al. [79] indicated that curing temperature influences the effect that biomass ashes from the paper industry have on concrete compressive strength, with higher curing temperature showing better results in terms of biomass ashes' impact on compressive strength. More importantly, their results suggest that replacing cement with biomass ash might mitigate the crossover effect due to higher curing temperature on the compressive strength evolution of eco-concrete. However, the effect of curing temperature has been little investigated in mixtures containing SCBA as a partial cement replacement. Murugesan et al. [259] analyzed the effect of eight different curing methods on concrete specimens, including accelerated hot water curing at 100 °C for one day, obtaining the lowest compressive strength among the studied methods. Rajasekar et al. [260] studied the effect of three different curing regimes on the compressive strength of ultra-high-strength concrete (UHSC) with SCBA replacements: (i) normal water curing at 27 °C ± 2 °C, (ii) steam curing for 24h at 90 °C, and (iii) heat curing for 24h at 160 °C. They concluded that heat curing seems more efficient in improving concrete performance than normal

and steam curing. Thus, based on previous research, higher curing temperature may improve the mechanical properties of mixes containing SCBA as cement replacement.

If curing temperature changes the effect of SCBA on the composites' compressive strength, it can be an important factor that affects the actual change in sustainability produced by the use of biomass ash in cementitious composite production and must be included in the environmental assessments. Therefore, this research aims to understand and quantify the impact of curing temperature on the environmental performance of mortars with different replacements of cement by SCBA.

6.2 Materials

Mortars were produced with Portland cement Type I with a specific gravity of 3.02. The fine aggregate used was natural siliceous sand compliant with ASTM C33/C33M [212] and had a fineness modulus of 2.99, an absorption of 1.97%, and a relative density (specific gravity in saturated surface dry - SSD - condition) of 2.45. The sugar cane bagasse ash (SCBA) was supplied by a sugar plant located in Valle del Cauca, Colombia, and is a waste generated after the combustion of sugarcane bagasse for energy production. The received ash was ground with a RETSCH ZM-1 Lab Benchtop Ultra Centrifuge Mill Grinder (passing an 80 μm mesh) for 2 minutes to reduce the particle size and improve homogenization and reactivity. The original and final particle size was obtained with a PSA 1090 (Anton Paar, Austria) and is reported in Table 6.1.

Table 6.1 SCBA particle size.

Type	D10 (μm)	D50 (μm)	D90 (μm)	Mean size (μm)
As received	8.0	31.9	71.6	37.6
Ground	3.7	18.7	47.5	23.6

The chemical configuration of the ash was obtained by a Lab X500 XRF analyzer (Hitachi, Japan) and is reported in Table 6.2. The SCBA used in this study satisfied the minimum requirement of 70% in the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ pozzolanic oxides conform to the ASTM 618 [261]. However, the loss of ignition (LOI) was about 7% higher than the minimum 10% requirement [261].

Table 6.2 Chemical composition of SCBA.

Compound	Percentage (%)	Standard deviation - σ
Na ₂ O	0.509	0.0052
MgO	2.074	0.0123
Al ₂ O ₃	13.85	0.019
SiO ₂	54.97	0.026
P ₂ O ₅	0.213	0.006
SO ₃	0.926	0.0015
K ₂ O	1.385	0.0017
CaO	9.98	0.013
TiO ₂	1.595	0.0064
Cr ₂ O ₃	0.089	0.0006
Mn ₂ O ₃	1.245	0.0067
Fe ₂ O ₃	8.568	0.0054
ZnO	0.087	0.0003
SrO	0.158	0.0005

6.2.1 Mix design, sample manufacturing, and curing conditions

The mortar formulation used as reference was prepared with a 1:3:0.5 (cement:sand:water) weight ratio. Two percentages of cement replacement with SCBA were selected for this study based on previous literature. The amount of cement replaced was 10% and 20% (by mass of cement). Water to binder (cement + SCBA) and binder to aggregate ratios were constant for all mixes at 0.50 and 3, respectively. Mix proportions of the composites are presented in Table 6.3.

Table 6.3 Mix proportions (per m³ of mortar).

Component	Reference	10% SCBA	20% SCBA
Cement (kg)	486.39	437.75	389.12
SCBA (kg)	0.00	48.64	97.28
Sand (SSD) (kg)	1459.18	1459.18	1459.18
w/b	0.50	0.50	0.50

Six cubes with dimensions of 50.8x50.8x50.8 mm³ were cast per each mortar mixture. All the samples were cured in their molds at room temperature and covered with a plastic sheet during the first day. After demolding, three samples per mixture were cured at 21 °C, while another three were cured at 45 °C, until the testing day.

6.3 Methods

6.3.1 Compressive strength test

Compressive strength tests were carried out according to ASTM standards C349 [176]. An MTS (Eden Prairie, MN) machine with a load capacity of 300 kN, under a displacement control of 0.05 mm/s, was used. The mortar compressive strength was examined at 28 days.

6.3.2 Life cycle assessment (LCA) of mortars

The framework of the LCA performed in this study is presented in Figure 6.1. The LCA methodology of this study follows the ISO standards 14040 and 14044 [245,262]. According to these standards, four steps are identified:

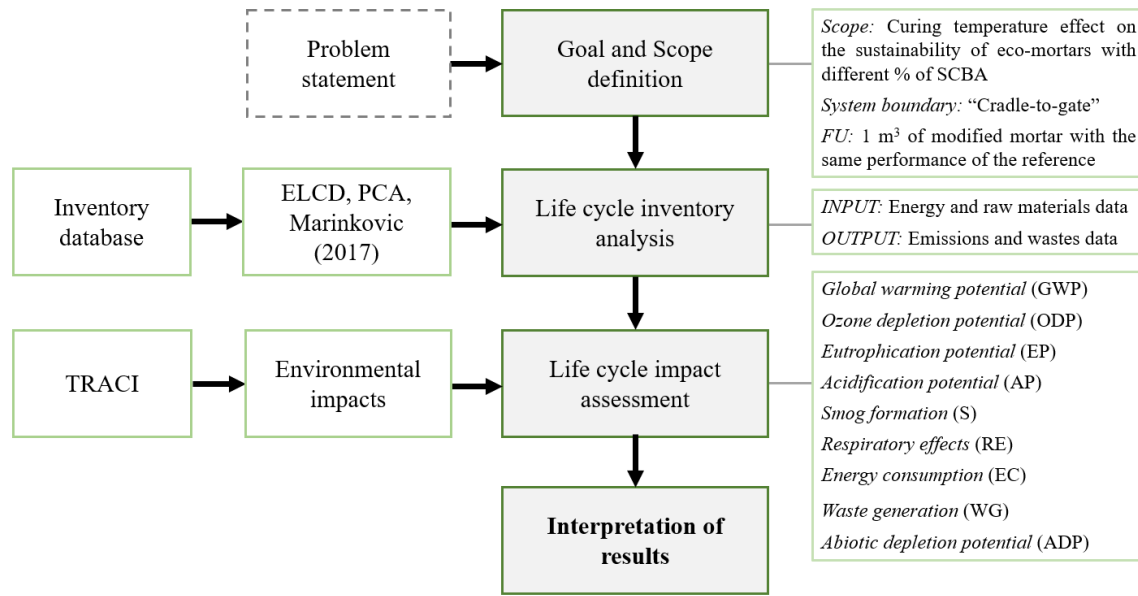


Figure 6.1 LCA framework for this study.

(i) Goal and scope

This research aims to understand and quantify how curing temperature affects the environmental performance of eco-mortars with different percentages of sugarcane bagasse ash (SCBA). Three mixes with 0%, 10%, and 20% replacement of SCBA by mass of cement and two different curing temperatures (21 °C and 45 °C) were studied. A "cradle-to-gate" analysis was considered as the system boundary, which allows for the quantification of the embodied environmental impacts of the material from the extraction of raw materials (cradle) to the mortar production (gate) stages. The boundary of the LCA is illustrated in Figure 6.2. The functional unit (FU) selected for this study was 1 m³ of mortar with the same compressive strength as the reference mixture (plain Portland cement mortar without SCBA cured at the same curing temperature). To compare the environmental impact of the investigated mortars, an experimental campaign was performed beforehand to obtain a curve exhibiting the development of compressive strength as a function of cement content for the reference mortar. This curve estimates the variations in the cement content needed for achieving the same compressive strength as the reference mortar when SCBA is used to replace part of the cement.

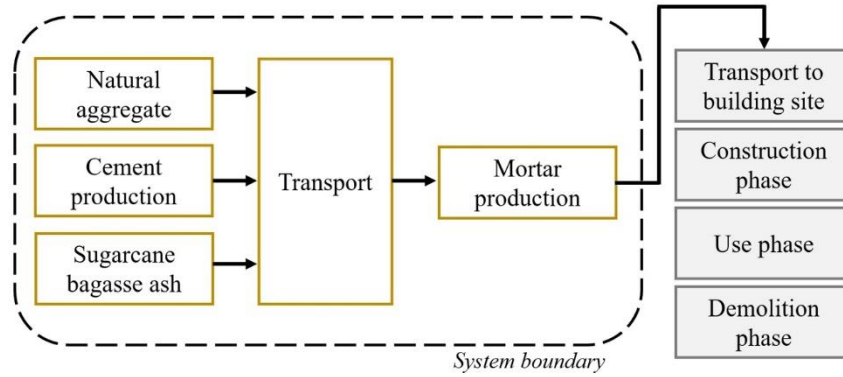


Figure 6.2 LCA system boundary.

(ii) Life cycle inventory (LCI)

In this stage, energy and raw materials data (input) and emissions and wastes data (output) must be identified and allocated for each material production. In order to facilitate the LCI phase, numerous databases have been developed. These databases provide essential inventory data such as raw materials, electricity generation, transport, and waste generation data that are essential in every LCA and are based on average data representing average production and supply conditions for products and services. Since no global database exists, different sources were used in this study depending on their availability and reliability. Cement and natural fine aggregate production and total transportation impact data were obtained from the European Platform on Life Cycle Assessment (ELCD database) [263]. Mortar production input data was assumed to be equivalent to concrete production based on their essentially identical composition (aggregate, cement, and water) and because of the more abundant and reliable data on concrete production. The main difference between the two products is the aggregate size (with mortar using only the fraction passing through a 4.75 mm sieve). This data was obtained from a previous study [264]. Waste generation was estimated considering the density of the studied mortars, where the average density of all hardened samples was 2220 kg/m³ (with a standard deviation lower than 2.1%). Finally, transport distances were collected from the Life Cycle Inventory of Portland Cement Concrete by the Portland Cement Association (PCA) [265].

Table 6.4 presents the LCI data considered in this study.

Table 6.4 Life inventory data used for this study.

	Cement (kg)	Sand (kg)	SCBA (kg)	Mortar (m ³)	Transport (t·km)
<i>INPUTS Fossil fuels (kg)</i>					
Diesel	3.56E-02	3.29E-04	0.00	2.00E-02	2.06E-02
Gas	8.53E-03	1.24E-04	0.00	5.30E-02	1.13E-03
Soft coal	2.67E-02	3.13E-04	0.00	5.25E+00	7.31E-05
Hard coal	4.83E-02	2.18E-04	0.00	4.01E-02	9.01E-05
<i>OUTPUTS Emissions in the air (kg)</i>					
CO ₂	8.85E-01	2.34E-03	0.00	4.59E+00	6.40E-02
CO	2.14E-03	4.19E-06	0.00	8.81E-04	1.10E-04
CH ₄	5.80E-04	3.72E-06	0.00	2.19E-03	6.25E-05
C ₂ H ₄	3.95E-10	9.24E-12	0.00	7.36E-08	3.70E-10
CFC-11	5.22E-09	1.75E-10	0.00	2.09E-15	6.08E-11
CFC-114	5.35E-09	1.79E-10	0.00	3.67E-09	6.23E-11
SO _x	1.05E-03	9.49E-06	0.00	5.34E-02	3.41E-05
NO _x	1.79E-03	1.52E-05	0.00	8.01E-02	5.39E-04
N ₂ O	2.22E-06	3.81E-08	0.00	2.20E-05	7.32E-07
NH ₃	3.91E-02	7.24E-09	0.00	3.27E-07	4.00E-07
NMVOC	2.26E-01	1.37E-06	0.00	9.20E-05	3.20E-05
HCl	1.99E-02	1.80E-07	0.00	4.00E-04	8.20E-08
N (water)	1.16E-04	4.23E-09	0.00	4.81E-06	2.35E-07
PO ₄ ⁻³ (groundwater)	5.14E-07	1.23E-08	0.00	3.85E-03	5.88E-07

As shown in Table 6.4, no allocation (waste status) was applied to the SCBA. This scenario is based on the following assumptions: (i) SCBA results from a by-product (sugarcane bagasse) of a multifunctional process (sugarcane processing) and thus is a waste; (ii) even if considered as a by-product, the resulting impact is likely to be very small, therefore, the environmental impact of its production will not be relevant; (iii) it is believed that the CO₂ emissions from biomass burning

do not contribute to the greenhouse effect, since the carbon released from crops already existed in the atmosphere and was absorbed during the plant growth, thus the net CO₂ associated to the whole process should be considered neutral. Besides, the authors deliberately avoided estimating the cost for the industrial implementation of SCBA because it was out of the scope of the present paper which was to study the effect of curing temperature on the embodied environmental impacts of the material. An economic analysis should consider market variables such as availability, local cost (which in the very first moment would be zero – waste value), and demand (like other residual pozzolans, the cost of the material will increase with the increasing demand), as well as the cost of further processing, but also potential revenues from carbon credits.

(iii) Life cycle impact assessment (LCIA)

The LCIA phase is crucial to evaluate the importance and relevance of the environmental impact of a product based on the LCI results. In this study, the TRACI methodology (mid-point approach) was employed to assess the total environmental impact of the investigated mortars. The life cycle impacts were assessed by analyzing nine environmental impact categories. The categories (from TRACI) used to analyze and compare the environmental impact of the studied mixes, and their units are displayed in Table 6.5. Among these, ecotoxicity was excluded from the analysis since no evidence of this impact has been found in the main components of mortars [266,267]. Moreover, the characterization factors, which estimate the relative contribution of each substance (inputs and outputs in the LCI) to each impact category in its corresponding unit, were considered. The characterization factors were obtained from the study of Ryberg et al. [268].

Besides, two other categories (not measured in TRACI) were considered to account for the potential reduction of raw materials due to the replacement of cement by SCBA: (i) waste generation (WG) and (ii) abiotic depletion potential (ADP). Waste generation quantifies the net kilograms of material produced that can become waste at the product's end of life. Abiotic depletion potential is defined as the consumption of non-renewable mineral (raw materials) resources. Therefore, if ADP and WG are not considered in the environmental assessment of mixes with SCBA, the real environmental benefits of using this waste in mortars will not be fully reflected.

Table 6.5 Designated impact categories from TRACI (last two added).

Category	Units
(i) Global warming potential (GWP)	kg CO ₂ eq
(ii) Ozone depletion potential (ODP)	kg CFC-11 eq
(iii) Eutrophication potential (EP)	kg N eq
(iv) Acidification potential (AP)	kg SO ₂ eq
(v) Smog formation (S)	kg O ₃ eq
(vi) Respiratory effects (RE)	kg PM _{2.5} eq
(vii) Energy consumption (EC)	MJ surplus
(viii) Waste generation (WG)	kg
(ix) Abiotic depletion potential (ADP)	kg Sb eq

(iv) Interpretation of the results

The last phase of the LCA is the interpretation of the results obtained from the impact assessment. This phase is not strictly defined as the previous ones, allowing practitioners to apply findings from the LCA to various situations, knowing the uncertainty and the assumptions used to generate the results. In this study, the analysis was conducted following two different approaches:

- (i) Single categories analysis: Single impact categories were analyzed, and the results were discussed to appreciate the potential implications of replacing cement with SCBA as a function of curing temperature.
- (ii) Normalized unified index: Environmental impacts of single categories were normalized using the normalization factors (NFs) recommended by Ryberg et al. [52] to relate the environmental impact results of each category to a common reference. The goal of this normalization is to put each environmental impact in relation to the impact of society's production and consumption activities. As a result, normalized values will better reflect the product system's contribution to each category's environmental impact compared to those of the reference system. The reference system used was the environmental impacts of each category per year in the US [52]. The normalized values

were calculated by dividing the environmental impact of each category by its corresponding normalization factor. Note that this section did not consider WG and ADP since there are no NFs available for these two categories.

6.4 Results and discussion

6.4.1 Compressive strength and binder content variation based on designated FU

Figure 6.3 displays the compressive strength results of the studied mortars after 28 days of curing at 21 °C and 45 °C. Results showed that the replacement of cement with SCBA at standard curing temperature (21 °C) had a slightly negative effect on the compressive strength. The higher the replacement level, the higher the reduction of compressive strength. Nevertheless, the recorded loss was lower than 8% (6.3% and 7.3% for 10 and 20% replacement, respectively) compared to the reference mortar cured at the same temperature. However, when the curing temperature was higher (45 °C), the replacement of SCBA positively influenced the compressive strength when the results were compared to the reference mortar cured at 45 °C. Mortars with 10 and 20% SCBA replacement exhibited an increase in compressive strength of 24.5% and 22.2% compared to the plain mortar cured at the same temperature, respectively. Besides, the use of SCBA mitigated the high-temperature crossover effect observed in the reference mortar. It means that replacing Portland cement with SCBA may be beneficial when the external curing temperature is high or when a lower heat of hydration is required.

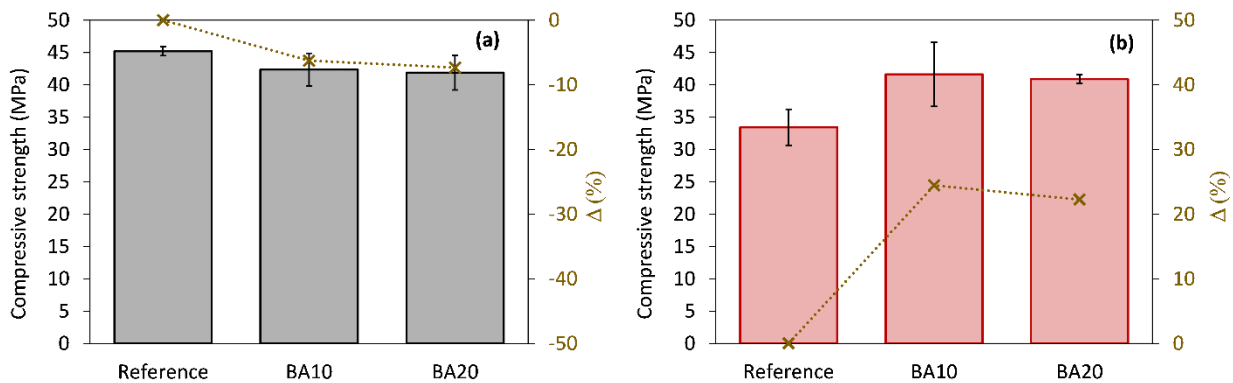


Figure 6.3 Compressive strength of mortars at 28 days. At (a) 21 °C and (b) 45 °C curing temperature.

Thus, results show that curing temperature modifies the effect of SCBA on the mortar's compressive strength. Therefore, a secondary experimental campaign was performed to assess the influence of partial replacement of cement by SCBA on the compressive strength of the mortar with different water to cement ratios. The objective of this secondary experimental campaign was to estimate the variation of cement content required to obtain a compressive strength equal to the compressive strength of the reference mortar (no SCBA) for each SCBA replacement level. Thus, the savings or additions of cement content needed for each case can be estimated. The results of this additional experimental campaign contribute as input data to the LCA.

Two extra reference mixtures (besides the one listed in Table 6.3) were made, varying the cement content (w/c ratio). Figure 6.4 displays the compressive strength of the reference plain mortar (no SCBA) as a function of the cement content for two different curing temperatures. This graph was used to estimate the cement content required in the modified mixes to obtain the same compressive strength as the reference mortar (at the same curing temperature). First, the compressive strength obtained from the modified mixtures was introduced in the graph to estimate the corresponding cement content of a mixture with the same strength if SCBA was not used. Next, the difference between this estimate and the cement content needed to achieve the reference strength was calculated. Then, this variation was added to the initial cement content used for the specific mortar. The result is the estimated cement content required to achieve the same compressive strength as the reference mortar (without SCBA). The binder content of each modified mixture is the estimated cement content plus the SCBA content (applicable). The results are presented in Table 6.6, which displays the initial and required binder content to achieve the same compressive strength as the reference mortar at 28 days when SCBA is used, as a function of the curing temperature. The aggregate content was kept constant, and therefore, the changes in the binder content to achieve the desired strength only affected the water-to-binder ratio.

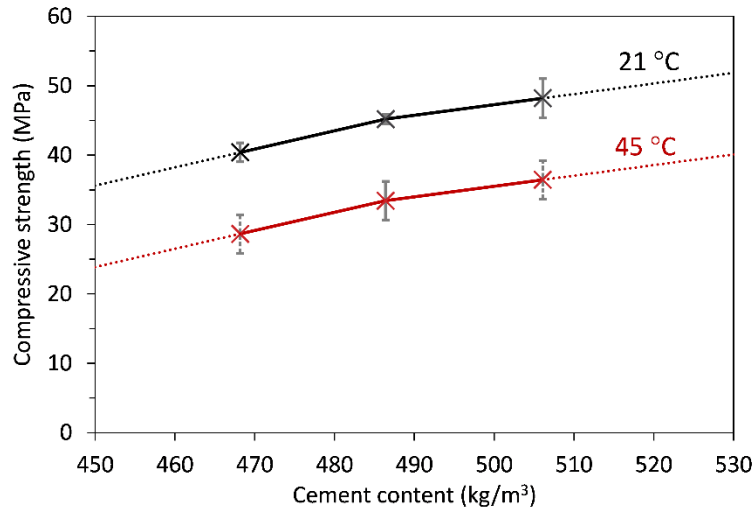


Figure 6.4 28 days compressive strength as a function of cement content (no SCBA).

Table 6.6 Estimation of cement content to obtain the FU.

Mixture	Curing Temperature (°C)	Compressive strength f_{ck} (MPa)	Initial cement content (kg/m³)	Estimated binder [<i>cement</i> , <i>SCBA</i>] content to achieve reference f_{ck} (kg/m³)
Reference		45.20	486.4	486.4 [486.4, 0]
BA10	21 °C	42.37	437.8	497.1 [448.5, 48.64]
BA20		41.88	389.1	499.0 [401.7, 97.28]
Reference		33.44	486.4	486.4 [486.4, 0]
BA10	45 °C	41.62	437.8	414.1 [365.5, 48.64]
BA20		40.88	389.1	420.6 [323.4, 97.28]

6.4.2 Life cycle assessment (LCA)

Environmental impact of single categories

Figure 6.5 displays the environmental impacts of each LCA category considered for the studied mortars as a function of curing temperature differentiating the contribution of each component. In the graphs, for each material (including mortar production), the transport impact

data was included in the results. The amount of component materials (cement, natural aggregate, and SCBA) used in the mix design is according to tests performed for determining the mix proportions of the modified mortars that would have the same compressive strength as their reference (without SCBA).

Table 6.7 reports the contribution of each material and process to the total environmental impact of the mortars cured at 21 °C. In Table 6.7, the transportation contribution to the environmental impact was separated from the impact of the materials.

Results show that cement is the most significant contributor to all impact categories. The main reason is the great deal of CO₂ emissions due to the calcination of limestone and fossil fuel and energy use required for clinker production. Thus, as expected, the reduction of the cement content produced by the utilization of SCBA reduced the environmental impact of mortars, not only on the global warming potential (which is expressed in kg CO₂ eq) but also on all other categories, as can be seen in Table 6.7. The impacts from cement production are, for each category, at least one order of magnitude higher than the other two largest contributors (natural aggregate and mortar production). The contribution of aggregate and mortar production does not change, regardless of the amount of cement replaced by SCBA, because the amount does not change in the mortar formulation considered for the LCA in this study.

Besides cement production, transportation of component materials is the major contributor to the environmental burden of cementitious materials. Transport impacts directly depend on the transportation type and distance. While transportation impact data was obtained from the European Platform on Life Cycle Assessment (ELCD database) [263], transport distances were obtained from the Life Cycle Inventory of Portland Cement Concrete by the PCA [265] and multiplied by two (round-trip). In Figure 6.5, transportation was added up to the impact of each material. Therefore, the impacts coming from SCBA are none other than the impact of their transportation to the mixing location. That leaves the transport phase as a possible source of varying the environmental impact of these eco-friendly mortars. In this analysis, the transportation distance for SCBA was assumed to be the same as the transportation distance for Portland cement, fly ash, and other SCMs indicated in the Life Cycle Inventory of Portland Cement Concrete [265].

The use of SCBA produced important changes in the environmental impact of several impact categories, especially on the ADP and the GWP. The GWP quantifies the greenhouse gases

released into the atmosphere (carbon dioxide (CO_2), methane (CH_4), and nitrous oxides (N_2O)) as a function of the amount of CO_2 that would have the same impact over a 100-year period [157]. When the curing temperature was 21 °C, BA20* presented a decrease of over 16% in GWP compared to the reference mortar while keeping the same estimated strength. Moreover, the ODP impact was reduced by 7% and 16% for BA10* and BA20*, respectively, for the same curing temperature. The ODP refers to a decrease in the ozone density through the thinning of the stratospheric ozone layer due to anthropogenic pollutants (e.g., halocarbons). That implies an increased exposure of human skin to UV light, which may lead to a higher risk of melanoma [269]. Besides, for the same curing temperature, the total energy demand was reduced by 6% and 13% in BA10* and BA20*, respectively, compared to the energy demand for the reference mortar.

The S, AP, RE, and EP impact categories were also reduced by 13%, 14%, 15%, and 11%, respectively, when SCBA was used (BA20*) and when the curing temperature was 21 °C. It is important because of the consequences that those impact categories have on the environment. The S impact category ponders the air pollution caused by the reaction between sunlight and emissions from fossil fuel combustion during the production of raw materials. As a result, the formation of other chemicals is promoted (e.g., ozone and peroxide), which leads to an increase in ground-level ozone concentration [270]. The AP impact category is also associated with the combustion of fossil fuels (e.g., nitrous and sulfide oxides), which may leach in the presence of oxygen and water and endanger the surrounding ecosystems [271]. The EP impact category relates to the natural or artificial discharge of nutritional elements to a body of water. These compounds decrease the oxygen available in aquatic systems, consequently reducing the water quality. The water contaminated by these organisms can be a threat to public health and biodiversity, thus, it must be monitored [272].

Finally, regarding abiotic depletion and waste generation, the replacement of cement by SCBA also reduced the impact of these two categories. The ADP impact category reflects the exhaustion of non-renewable resources and consequent environmental impacts, thus, a reduction of cement used for mortar production will have a positive effect. ADP and WG were reduced by 18% and 4% for BA20*, respectively, compared with the corresponding values for the reference mortar, both with 21 °C curing temperature.

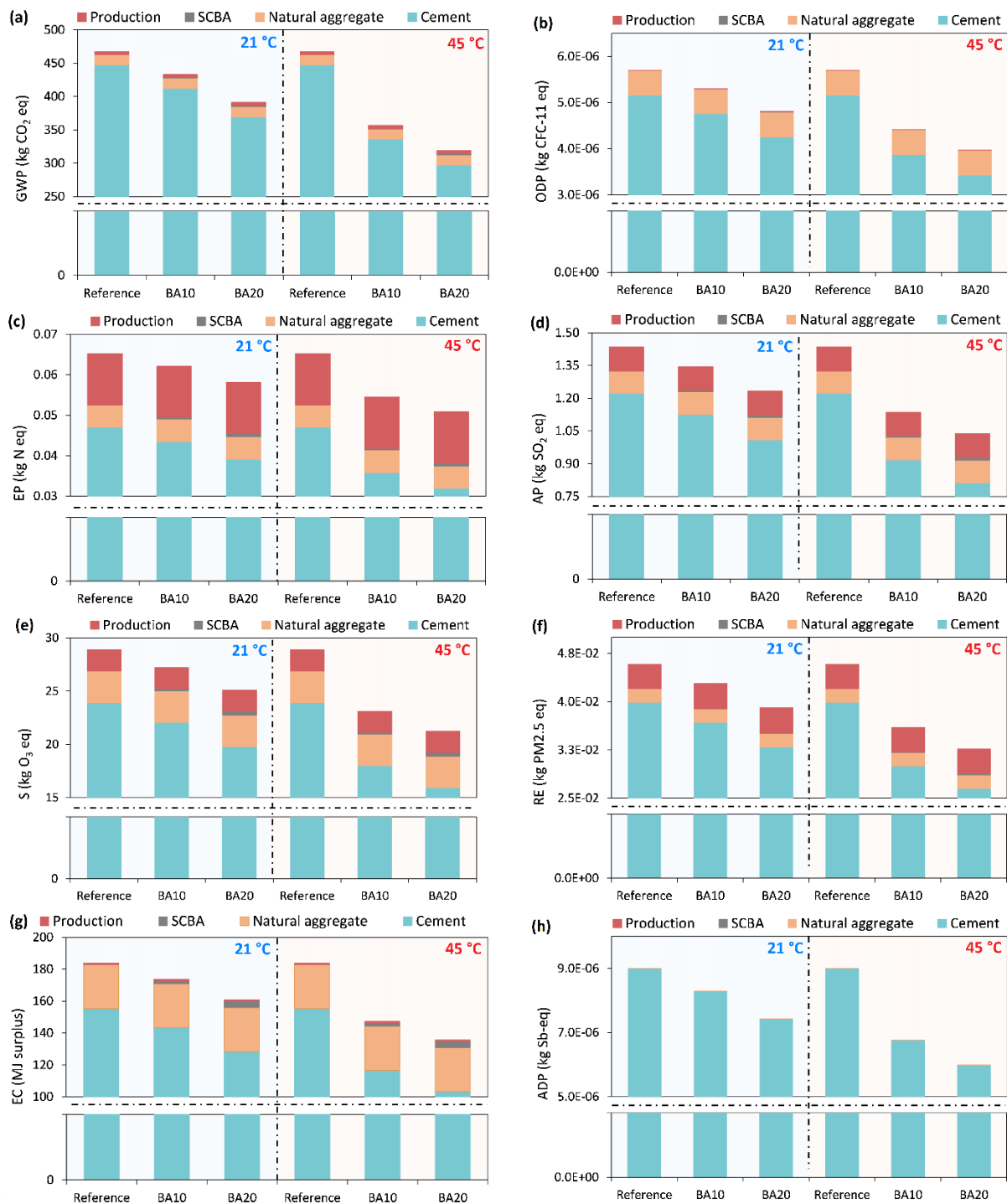


Figure 6.5 Environmental impact of the investigated mortars. (a) Global warming potential, (b) Ozone depletion potential, (c) Eutrophication potential, (d) Acidification potential, (e) Smog formation, (f) Respiratory effects, (g) Energy consumption, (h) Abiotic depletion potential.

Table 6.7 Environmental impacts for 1 m³ of mortars cured at 21 °C (* modified mortar that would have the same compressive strength as their reference).

Mortar	Cement	Natural aggregate	SCBA	Production	Transportation	Total
GWP - Global warming potential (kg CO₂ eq)						
<i>Reference</i>	437.84	3.57	0.00	4.65	21.04	467.10
<i>BA10*</i>	403.73	3.57	0.00	4.65	21.24	433.19
<i>BA20*</i>	361.62	3.57	0.00	4.65	21.28	391.12
ODP – Ozone depletion potential (kg CFC-11 eq)						
<i>Reference</i>	5.14E-06	5.17E-07	0.00	3.67E-09	3.94E-08	5.70E-06
<i>BA10</i>	4.74E-06	5.17E-07	0.00	3.67E-09	3.98E-08	5.30E-06
<i>BA20</i>	4.24E-06	5.17E-07	0.00	3.67E-09	3.98E-08	4.81E-06
EP – Eutrophication potential (kg N eq)						
<i>Reference</i>	4.13E-02	1.03E-03	0.00	1.27E-02	8.16E-03	6.32E-02
<i>BA10</i>	3.81E-02	1.03E-03	0.00	1.27E-02	8.24E-03	6.01E-02
<i>BA20</i>	3.41E-02	1.03E-03	0.00	1.27E-02	8.25E-03	5.61E-02
AP – Acidification potential (kg SO₂ eq)						
<i>Reference</i>	1.16	2.96E-02	0.00	1.10E-01	1.32E-01	1.43
<i>BA10</i>	1.07	2.96E-02	0.00	1.10E-01	1.33E-01	1.35
<i>BA20</i>	0.96	2.96E-02	0.00	1.10E-01	1.34E-01	1.23
S – Smog formation (kg O₃ eq)						
<i>Reference</i>	22.02	0.56	0.00	1.99	4.31	28.88
<i>BA10</i>	20.31	0.56	0.00	1.99	4.36	27.21
<i>BA20</i>	18.19	0.56	0.00	1.99	4.36	25.09
RE – Respiratory effects (kg PM_{2.5} eq)						
<i>Reference</i>	3.91E-02	1.01E-03	0.00	3.84E-03	1.93E-03	4.58E-02
<i>BA10</i>	3.60E-02	1.01E-03	0.00	3.84E-03	1.95E-03	4.28E-02
<i>BA20</i>	3.23E-02	1.01E-03	0.00	3.84E-03	1.95E-03	3.91E-02
EC – Energy consumption (MJ surplus)						
<i>Reference</i>	136.48	4.09	0.00	0.96	42.44	183.98
<i>BA10</i>	125.84	4.09	0.00	0.96	42.86	173.76
<i>BA20</i>	112.72	4.09	0.00	0.96	42.93	160.71
ADP – Abiotic depletion potential (kg Sb eq)						
<i>Reference</i>	9.00E-06	1.69E-09	0.00	0.00	0.00	9.00E-06
<i>BA10</i>	8.30E-06	1.69E-09	0.00	0.00	0.00	8.30E-06
<i>BA20</i>	7.43E-06	1.69E-09	0.00	0.00	0.00	7.43E-06

Table 6.8 presents the environmental impacts of the production of 1 m³ of the studied modified mortars cured at 45 °C, with the same target compressive strength as the reference. The environmental results of the mortars cured at 45 °C followed the same trend of mortars cured at 21 °C, with the environmental impact decreasing as the replacement of cement increased. However, at 45 °C, the use of SCBA reduced the environmental impact of mortars to a greater extent than at 21 °C, as is clearly shown in Figure 6.6.

Considering the results for each analyzed impact category, Figure 6.6 displays the reduction of the environmental impacts of modified mortars in comparison to the reference (no SCBA) for both 21 °C and 45 °C. The results of each impact category for mortars containing SCBA were normalized to the corresponding results for the reference mortar (no SCBA). The result is a dimensionless value equal to 1 for the reference – the lower the value, the lower the environmental impact. Figure 6.6 shows that replacing cement with SCBA can help reduce the environmental impact of cementitious composites and that the higher the replacement, the lower the environmental footprint of mortars in the studied range of SCBA replacement. While WG impact did not change, all other categories showed important differences produced by curing temperature. Whereas at 21 °C, BA20* presented a reduction of single impact categories ranging between 11.23% and 17.40% (in comparison to reference mortar), at 45°C, the reduction of the environmental impacts due to the use of SCBA doubled, ranging from 22.61% to 33.51%.

These results can be explained by looking at the compressive strength results and the functional unit chosen for the LCA. The reference mortar cured at 45 °C presented a compressive strength 26% lower than the same mixture cured at 21 °C. This tendency of high curing temperatures to induce lower strength after 28 days is well documented in the literature as a consequence of the poorer quality of the hydration products [81], and it is known as the crossover effect. However, the data of the present study showed that SCBA was effective in mitigating the crossover effect.

Table 6.8 Environmental impacts for 1 m³ of mortars cured at 45 °C (* modified mortar that would have the same compressive strength as their reference).

Mortar	Cement	Natural aggregate	SCBA	Production	Transportation	Total
GWP - Global warming potential (kg CO₂ eq)						
<i>Reference</i>	437.84	3.57	0.00	4.65	21.04	467.10
<i>BA10*</i>	328.98	3.57	0.00	4.65	19.65	356.85
<i>BA20*</i>	291.08	3.57	0.00	4.65	19.77	319.08
ODP – Ozone depletion potential (kg CFC-11 eq)						
<i>Reference</i>	5.14E-06	5.17E-07	0.00	3.67E-09	3.94E-08	5.70E-06
<i>BA10</i>	3.86E-06	5.17E-07	0.00	3.67E-09	3.68E-08	4.42E-06
<i>BA20</i>	3.42E-06	5.17E-07	0.00	3.67E-09	3.70E-08	3.97E-06
EP – Eutrophication potential (kg N eq)						
<i>Reference</i>	4.13E-02	1.03E-03	0.00	1.27E-02	8.16E-03	6.32E-02
<i>BA10</i>	3.11E-02	1.03E-03	0.00	1.27E-02	7.62E-03	5.24E-02
<i>BA20</i>	2.75E-02	1.03E-03	0.00	1.27E-02	7.67E-03	4.89E-02
AP – Acidification potential (kg SO₂ eq)						
<i>Reference</i>	1.16	2.96E-02	0.00	1.10E-01	1.32E-01	1.43
<i>BA10</i>	0.87	2.96E-02	0.00	1.10E-01	1.23E-01	1.14
<i>BA20</i>	0.77	2.96E-02	0.00	1.10E-01	1.24E-01	1.04
S – Smog formation (kg O₃ eq)						
<i>Reference</i>	22.02	0.56	0.00	1.99	4.31	28.88
<i>BA10</i>	16.55	0.56	0.00	1.99	4.03	23.12
<i>BA20</i>	14.64	0.56	0.00	1.99	4.05	21.24
RE – Respiratory effects (kg PM_{2.5} eq)						
<i>Reference</i>	3.91E-02	1.01E-03	0.00	3.84E-03	1.93E-03	4.58E-02
<i>BA10</i>	2.93E-02	1.01E-03	0.00	3.84E-03	1.81E-03	3.60E-02
<i>BA20</i>	2.60E-02	1.01E-03	0.00	3.84E-03	1.82E-03	3.26E-02
EC – Energy consumption (MJ surplus)						
<i>Reference</i>	136.48	4.09	0.00	0.96	42.44	183.98
<i>BA10</i>	102.55	4.09	0.00	0.96	39.64	147.25
<i>BA20</i>	90.73	4.09	0.00	0.96	39.90	135.69
ADP – Abiotic depletion potential (kg Sb eq)						
<i>Reference</i>	9.00E-06	1.69E-09	0.00	0.00	0.00	9.00E-06
<i>BA10</i>	6.76E-06	1.69E-09	0.00	0.00	0.00	6.76E-06
<i>BA20</i>	5.98E-06	1.69E-09	0.00	0.00	0.00	5.98E-06

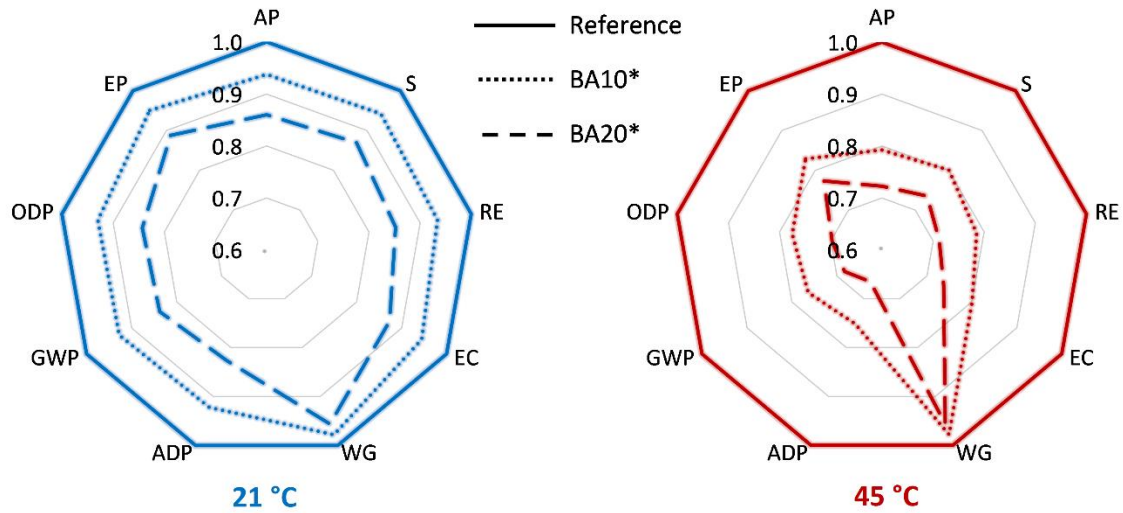


Figure 6.6 LCA results of SCBA mortars normalized by the reference mortar (AP - Acidification potential, S - Smog formation, RE - respiratory effects, EC - energy consumption, WG - waste generation, ADP - abiotic depletion potential, GWP - global warming potential, ODP - ozone depletion potential, EP - eutrophication potential).

Environmental impact assessed with a normalized unified index

Normalization factors (NFs) may be used as an optional aid for the interpretation of the results of the LCA. LCIA results for each impact category were first normalized by the NFs. A unified index was calculated by adding the normalized impacts of each category. Next, the normalized unified index was calculated as the unified index of each mixture divided by the unified index of their reference mortar. While previous results considered ADP and WG, as mentioned in the methods section, these two impact categories were not considered in the analysis to obtain the normalized unified index due to the lack of NFs.

The normalized unified index represents with a single score the relative environmental impact of each mixture compared to the reference one. Figure 6.7 displays the results of this approach. For a curing temperature of 21 °C, BA10* and BA20* reduced their environmental impact by 6% and 14%, respectively, compared to the reference mortar cured at the same temperature. Nevertheless, the best results in terms of environmental performance were obtained when the curing temperature was higher (45 °C). At 45 °C curing temperature, the reduction in the environmental impact was more pronounced on BA10* and BA20*, with values of 23% and 31%, respectively, compared to their reference mortar cured at 45 °C.

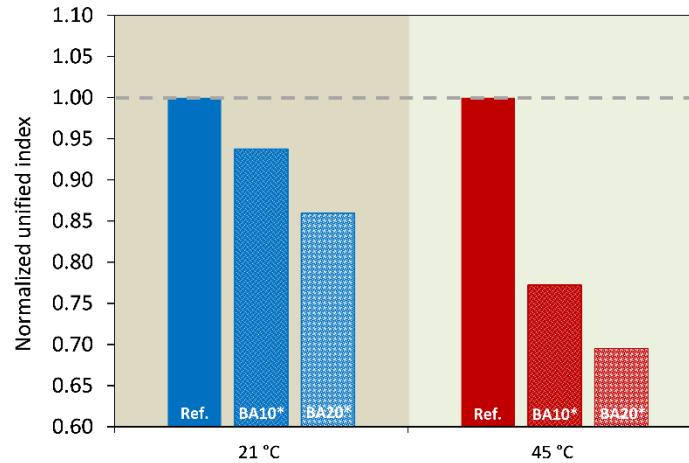


Figure 6.7 Normalized unified index as a function of the curing temperature.

6.5 Conclusions

The impact of curing temperature on the sustainability of sugarcane bagasse ash as a partial replacement of cement in mortars was assessed. Global warming potential (GWP), ozone depletion potential (ODP), eutrophication potential (EP), acidification potential (AP), smog formation (S), respiratory effects (RE), energy consumption (EC), abiotic depletion potential (ADP), and waste generation (WG) categories were analyzed for each mixture and curing temperature. Waste generation is the only impact category that was not affected by curing temperature. For the rest of the analyzed categories, when mortars were cured at 45°C, the use of SCBA reduced the environmental impact of mortars two times with respect to the reduction at 21°C.

Thus, the reduction of environmental impact when using SCBA as a partial replacement for cement highly depends on the curing temperature. At 45°C, a replacement of 97 kg of cement with SCBA (per m³ of mortar) produced a reduction of the environmental impact (presented with the normalized unified index) of 31%, while the reduction produced by the same amount of SCBA with a curing temperature of 21°C was 14%. These results clearly indicate that the sustainability of SCBA utilization as a partial replacement of cement will be better when mortar is poured in hot regions or during days with higher ambient temperatures. In the same way, the advantages of using SCBA in terms of sustainability will decrease if the external temperature is low. Therefore, external curing temperature is an important factor that should be considered when the sustainability of cementitious composites containing SCBA is assessed.

7. CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

This dissertation has investigated the role of temperature on the effectiveness of several approaches to enhance the sustainability of cementitious composites considering aspects of the material's life that array from curing to service conditions.

In the first study, it has been concluded that the effect of TiO_2 nanoparticles on mechanical properties, CH formation, and pore structure of cement-based mortars strongly depends on curing temperature. Results have shown that the lower the curing temperature (down to 5 °C), the greater the beneficial influence of nano- TiO_2 on strength. Besides, for both flexural and compressive strength at early ages (7 days), the optimum percentage of nano- TiO_2 depends on curing temperature. The lower the curing temperature, the higher the optimum percentage of nano- TiO_2 needed to enhance the strength at early ages. Thus, it is critical to consider curing temperature when designing cementitious composites with nano- TiO_2 . When curing temperature is high (45 °C), the 7-days flexural strength can be overestimated if the beneficial effects of nano- TiO_2 addition observed at standard temperature (20 °C) are assumed. DSC results suggested that a 0.5% nano- TiO_2 addition accelerates CH formation during the first day at 45 °C. On the other hand, DSC results suggest that the total percentage of CH at 7 days is lower in mixtures with TiO_2 nanoparticles for all studied curing temperatures. However, TGA results obtained using the modified method for CH calculation showed that the use of 0.5% nano- TiO_2 increases the CH content. Besides, TGA results showed that samples with nano- TiO_2 presented a higher carbonation than reference samples. Since samples were 7 days old, it is assumed carbonation occurred mainly due to sample preparation. Thus, nano- TiO_2 addition increases the percentage of CH carbonated during sample preparation. For that reason, to compare CH content in mixtures with and without nanoparticles, the modified method for TGA that accounts for the carbonated CH must be used instead of DSC results. Furthermore, 3D-XRM results displayed that the increase in strength due to the addition of nano- TiO_2 cannot be explained solely based on an overall reduction of porosity. In fact, the samples cured a low temperature were the ones that showed a higher increase in strength due to the use of nano- TiO_2 , however, nanoparticles addition did not produce a reduction in porosity of samples cured at low temperature. A general correlation between total porosity and

strength of mortars containing nano-TiO₂ was not found. Nonetheless, 3D-XRM scans were performed at 28 days. Thus, results suggest that the greater enhancement due to the use of nanoparticles in the 7 days strength on samples cured at low temperature (compared to the enhancement at higher temperatures) is related to an acceleration of hydration rather than an overall greater development in long term strength. Results may also suggest that the increase in strength due to the use of nanoparticles is more related to the homogenization of the pore structure than to the overall porosity reduction. Further investigation on the role of curing temperature on the effect of nano-TiO₂ addition at later age will be required to evaluate which one of these two potential mechanisms is more significant.

Regarding the impact of using recycled materials (RCA and re-PP fibers) and nanomaterials (nano-TiO₂) addition on the high-temperature resistance of eco-mortars, this research concluded that:

- (i) The use of 100% RCA instead of NA produces a negative effect on high-temperature resistance in terms of compressive and flexural strength. Consequently, this aspect should be considered when fire resistance is evaluated. Even though low percentages of TiO₂ nanoparticles increase the compressive and flexural strength of recycled mortars under normal conditions, this addition produces a negative effect on high-temperature resistance. This may be due to the different thermal properties of all materials (e.g., old cement paste, new cement paste with nano-TiO₂, or RCA) that may produce internal stresses when the temperature rises. These internal stresses in RCA mortars can produce a failure at lower stress due to the weaker ITZ between the new cement paste (with nano-TiO₂) and the old cement paste, as SEM images showed in the recycled mortar with 1% of nano-TiO₂ after 500 °C exposure. Results based on XRD and DSC showed that the negative effect of the addition of 1% TiO₂ in terms of strength loss after 500 °C exposure is not related to a higher CH decomposition. In fact, nano-TiO₂ may increase the high-temperature resistance of CH. Moreover, results suggest that the ductility before failure of RCA mortars is increased after exposure at 500 °C, while mortar with NA showed lower ductility under the same conditions. Finally, whereas the cross-section of fractured RCA mortars samples after high-temperature exposure showed two different shades, natural mortar samples only showed a uniform coloration. This observation suggests that specimens with recycled aggregate are not homogeneously affected by temperature, possibly due to their lower thermal conductivity.

(ii) Recycled PP fibers have a negligible effect on the mortar flexural strength under standard conditions (no exposure to high-temperature). However, they have been found to increase the maximum strain before failure and provided the composite material a post-peak residual flexural strength. Upon reaching the maximum load, samples with fibers presented a ductile-like behavior showing a plateau in the load as the displacement increased. Besides, as the fiber fraction increases, the post-peak residual strength increases. Furthermore, the addition of recycled PP fibers mitigated the flexural strength loss caused by high-temperature exposure and thermal shock. A high volume of fibers increases the risk of connectivity between fibers and the possibility that weak planes are formed, which may negatively impact the overall composite behavior. Even though all mixtures, including the one without fibers, showed an enhancement of flexural strength after high-temperature exposure (200 °C) and a slow cooling, fiber-reinforced mortars exhibited a higher enhancement of flexural strength than samples without fibers under the same conditions. Besides, in fiber-reinforced samples tested after a slow cooling, the post-peak residual strength was higher than in unexposed samples. Results also showed that the secondary strength and the energy absorption capability increased with the amount of fibers. After elevated temperature exposure, this enhancement is higher than in unexposed samples. These results suggest an enhancement of the fiber-matrix ITZ after high-temperature exposure and slow cooling. Finally, the optical microscopy analysis of the unexposed samples revealed a distinct interface between the fibers and the mortar matrix. In the case of 200 °C exposure, microscopy images showed that fibers penetrated the pores network of the mortar matrix after high-temperature exposure. Consequently, the observed increase in flexural strength, post-peak residual strength, secondary strength and secondary toughness, after high-temperature exposure and cooling, may be directly related to enhancing the adhesion between the fibers and the mortar matrix.

This research also studied the effect of RCA on thermal conductivity's susceptibility to moisture content and ambient temperature variations of cement mortars. Understanding the effect of recycled concrete aggregate on the thermal conductivity of cementitious composites is crucial to assess their effects on the environmental impact during service life as part of a building component. The replacement of NA by RCA reduces the composite's thermal conductivity and consequently increases its thermal insulation capacity. The decrease in TC is due to the more porous nature of the recycled composite and its reduced density. However, the extent of this

variation strongly depends on the moisture content and the ambient temperature at which thermal conductivity is calculated. Besides, mortars with recycled aggregate (i.e., mortars with higher porosity) presented less thermal conductivity variation due to changes in ambient temperature. Thus, if the ambient temperature changes, no special consideration would be required when evaluating RCA mortar's thermal conductivity instead of plain mortars with NA. Furthermore, thermal conductivity variations as a function of moisture content are higher in mortars containing RCA. The use of RCA increases the mortar accessible porosity, which heightens the importance of saturation degree on TC determination. Results showed that the higher the porosity, the more susceptible the mortar's thermal conductivity to changes in moisture content. Thus, special attention to the variability of TC due to saturation degree should be taken when evaluating the thermal performance of mortars with high porosity. Lastly, the increase in the heat insulation capacity when using RCA is achieved at the expense of strength. Both compressive and flexural strength decreases with the incorporation of RCA. The higher the RCA content, the higher the reduction in strength. However, if the strength sufficient for a given use is known, these composites may find an important application in building components as a sustainable mortar for energy efficiency in buildings. Finally, an equation that estimates (with an error of less than 5% between the experimental and predicted results) the thermal conductivity of cement mortars as a function of permeable porosity, saturation degree, and ambient temperature was proposed.

Finally, the impact of curing temperature on the sustainability of sugarcane bagasse ash (SCBA) as a partial replacement for cement in mortars was assessed. The life cycle assessment considered nine different environmental impact categories, including waste generation, global warming potential, ozone depletion potential, eutrophication potential, acidification potential, smog formation, respiratory effects, energy consumption, and abiotic depletion potential. Among these, waste generation was the only one not affected by the curing temperature. For all other analyzed impact categories, curing temperature significantly changed the environmental impact of mortars containing SCBA. Results showed that a replacement of 97 kg of cement by SCBA (per m³ of mortar) produced over two times higher reduction of the environmental impacts when external curing temperature was 45°C than when temperature was 21°C. These results clearly indicate that the sustainability of SCBA utilization as a partial replacement for cement will be higher when mortar is poured in hot regions or during days with higher temperatures. Therefore,

external curing temperature is an important factor that should be considered when sustainability of cementitious composites containing SCBA is assessed.

7.2 Future work

Effect of using recycled materials (RCA and recycled-PP fibers) and/or alternative SCMs on the environmental performance of cementitious composites building envelopes: from material production to service life

It has been estimated that over 11% of the global carbon emissions are related to energy use to produce building and construction materials [1]. Besides, 28% of the global energy-related carbon emissions are related to the operational usage of energy in buildings (energy needed for heating/cooling and power) [1]. Therefore, if we want to reduce cementitious composites' environmental impact, we need to focus on both material performance and its effects on energy consumption during service life.

In this dissertation the effect of recycled aggregates on the thermal conductivity of mortars as well as how moisture changes the effect of recycled aggregates on the thermal conductivity of mortars was investigated. Based on these data, that focused on the material scale, the future work should focus on a building scale, computing the effect of these sustainable composites (mortars containing recycled materials and/or alternative SCMs) on the energy consumption of a real building as a function of the variation of boundary conditions such as moisture and temperature during its service life. This will be done implementing the building information modeling (BIM) methodology and creating a digital twin for several building functional units. A comparative analysis of energy consumption of an actual building unit will be developed. Then, the effects of using recycled materials on the environmental performance of cementitious composites, considering all obtained results, from material production to service life, will be assessed through a life cycle analysis (LCA). The process will be repeated using different functional building units (with different volume-surface envelop ratios) and different climate conditions. Based on that, a retrofitted methodology will be used to optimize the mixture design's sustainability with a multicriteria LCA approach as a function of the building unit and location.

Assessment of post processing treatments for the valorization of sugar cane bagasse ash (SCBA): the effect of particle size and loss of ignition on the mortar microstructure modification.

The effect of curing temperature on the sustainability of sugarcane bagasse ash (SCBA) as a partial replacement of cement in mortars was assessed in this dissertation. Nevertheless, there are potential post processing treatments that may enable a greater valorization of this biomass waste. To evaluate the actual environmental performance of each post processing approach and the sustainability of the final product, every aspect of each treatment as well as their effects on the mechanical performance and durability of the final composites should be considered. Furthermore, understanding how different composition of SCBA affect the microstructure of the cement paste will be important to be able to predict other effects on the performance and durability of cementitious composites contain these alternative supplementary cementitious materials.

7.2.1 Other future research lines

Other prospective lines of investigations based on the findings of these dissertation are:

- (i) Effect of curing temperature on the sustainability of other alternative binders and its correlation to the chemical composition and particle size;
- (ii) Impact of curing temperature on microstructure of cementitious composites and its effect on fire resistance and thermal behavior of materials;
- (iii) Modification of concrete durability produced by SCBA and RCAs.

APPENDIX A. MATERIALS CERTIFICATIONS



MILL CERTIFICATION REPORT PORTLAND CEMENT - TYPE I

Certification date: 10/15/2019
Cement Type: Type I
Laboratory: Greencastle, IN Plant

We hereby certify that this cement complies with current ASTM C150, AASHTO M85 and CSA-3001_ GU Specifications. The following data represents the average for the Buzzi Unicem USA cement that was produced in the month of September-19

ASTM STANDARD REQUIREMENTS		MILL CERTIFICATION VALUES	
CHEMICAL DATA C150			
SiO ₂ - %	*	SiO ₂ - %	19.54
Al ₂ O ₃ - %	*	Al ₂ O ₃ - %	5.26
Fe ₂ O ₃ - %	*	Fe ₂ O ₃ - %	2.71
CaO - %	*	CaO - %	63.49
MgO - %	max 6.0	MgO - %	2.18
SO ₃ - %	max 3.0***	SO ₃ - %	3.12
Loss on Ignition - %	max 3.0 (when limestone is not an ingredient)	Loss on Ignition - %	2.85
Loss on Ignition - %	max 3.5 (when limestone is an ingredient)		
Insoluble Residue - %	max 1.50	Insoluble Residue - %	0.39
CO ₂ in Cement - %	^A	CO ₂ in Cement - %	1.67
Limestone - %	max 5.0	Limestone - %	3.94
CaCO ₃ in Limestone - %	min 70.0	CaCO ₃ in Limestone - %	96.7
Potential Phase Compounds:**		Potential Phase Compounds:**	
C ₃ S - %	*	C ₃ S - %	59.5
C ₂ S - %	*	C ₂ S - %	9.0
C ₃ A - %	*	C ₃ A - %	9.0
C ₄ AF - %	*	C ₄ AF - %	7.9
C ₄ AF +2(C ₃ A) - %	*	C ₄ AF +2(C ₃ A) - %	25.9
C ₃ S + 4.75C ₃ A - %	*	C ₃ S + 4.75C ₃ A - %	102.2
Na ₂ O Equivalent - %	*	Na ₂ O Equivalent - %	0.62
Free CaO - %	*	Free CaO - %	1.05
PHYSICAL DATA C150			
Fineness- Blaine - m ² /kg	min 260	Blaine - m ² /kg	417
Fineness- #325 Sieve Passing (%)	*	#325 Sieve Passing (%)	93.2
Autoclave Expansion % (C151)	max 0.80	Autoclave Expansion % (C151)	0.04
Time of Set		Time of Set	
Vicat (minutes)	min 45	Vicat (minutes)	Initial 101
	max 375		Final 209
Air Content %	max 12	Air Content %	10.9
Compressive Strength:		Compressive Strength:	
1 day - psi (MPa)	*	1 day - psi (MPa)	2480 (17.1)
3 day - psi (MPa)	1740 (12.0)	3 day - psi (MPa)	3850 (26.5)
7 day - psi (MPa)	2760 (19.0)	7 day - psi (MPa)	4730 (32.6)
28 day - psi (MPa)	*	28 day - psi (MPa)	5910 (40.7) Previous Month Avg.

Additional Data			
Type	Limestone	I.P.A. Addition Data	Base Cement Phase Composition
Amount (%)			
SiO ₂ - %	3.93	.	C ₃ S - % 62
Al ₂ O ₃ - %	0.82	.	C ₂ S - % 9
Fe ₂ O ₃ - %	0.45	.	C ₃ A - % 9
CaO - %	49.91	.	C ₄ AF - % 8
MgO - %	2.01	.	
SO ₃ - %	0.29	.	

* Not applicable.

** Adjusted per ASTM C150 Annex A15

*** It is permissible to exceed the values for SO₃ content, provided that the Mortar Bar Expansion C1038 does not exceed 0.020 % at 14 days.

ATTN:

Silo	Bill of Lading	Tons	Date
------	----------------	------	------

BUZZI UNICEM USA, Greencastle Plant

3301 S CR 150W, Greencastle, IN 46135, Phone 765.653.9766

STATE OF INDIANA

COUNTY OF PUTNAM

Before me the undersigned, a Notary Public for Putnam County, State of Indiana personally appeared Marcia L. Dyrud and acknowledged the execution of the foregoing instrument this day 2019.

Stephanie A. Richardson, Notary Public

My commission expires March 10, 2024.

By *Marcia L. Dyrud Case*

Marcia L. Dyrud Case
Quality Control Manager

APPENDIX B. DSC AND TGA PLOTS

DSC curves obtained from each mixture at 1, 3 and 7 days, for the three curing temperatures used in this study, are showed in Figure B.1 (MC-R) and Figure B.2 (MC-Ti0.5).

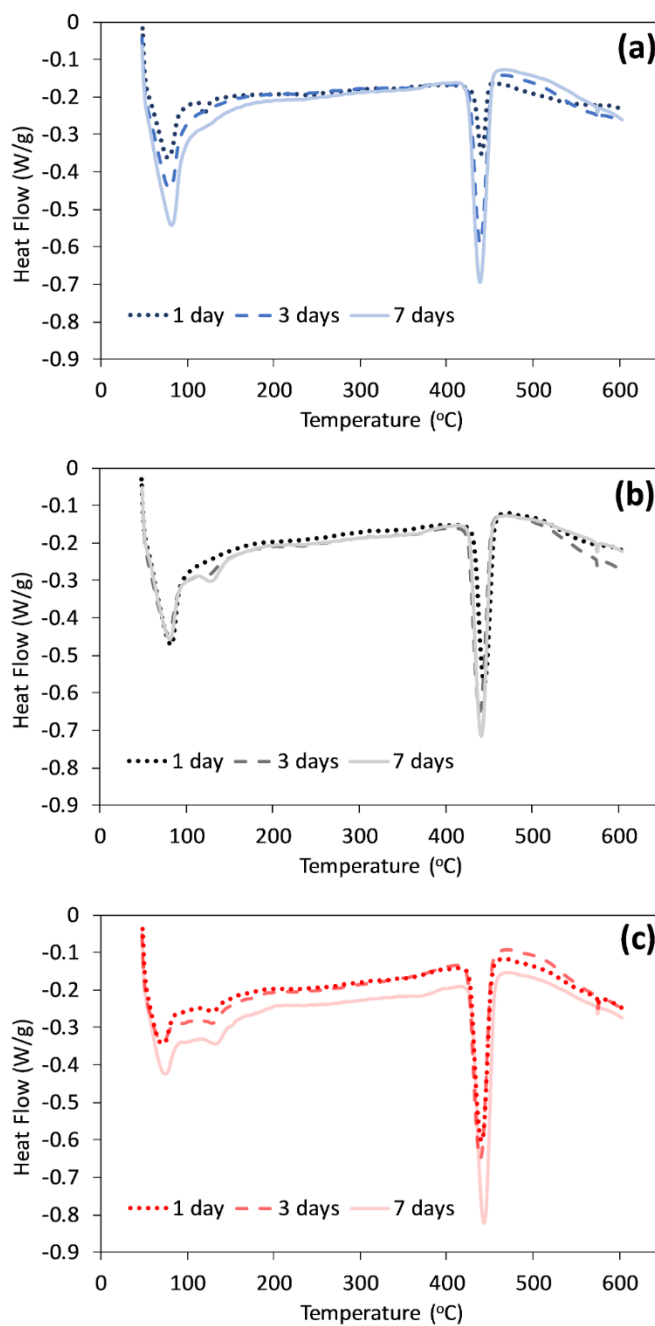


Figure B.1 Comparison between the MC-R DSC curves at 1, 3 and 7 days. (a) At 5 °C. (b) At 20 °C. (c) At 45 °C.

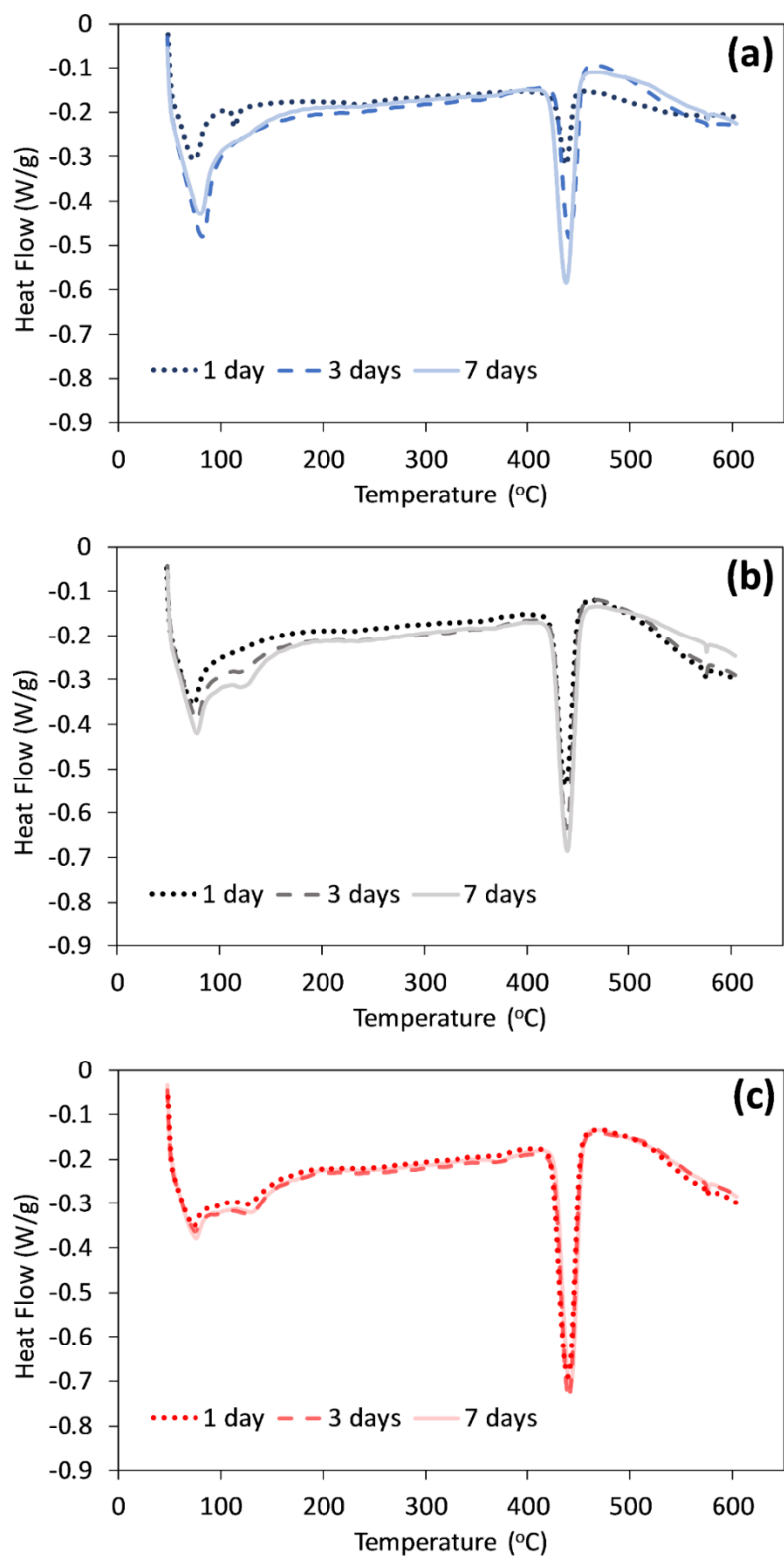


Figure B.2 Comparison between the MC-Ti_{0.5} DSC curves at 1, 3 and 7 days. (a) At 5 °C. (b) At 20 °C. (c) At 45 °C.

From TGA curves of the three curing regimes, the amount of hydrates formed below 200 °C appears to be lower in mixtures modified with TiO₂ than their respective reference. However, this difference between the curves may be due to a higher weight loss at temperatures equal or below 100 °C (mainly due to the evaporation of water). The percentage of weight loss between 100 and 200 °C is not significantly different (1.32% vs. 1.19% at 5°C, for instance). Since less water was available to evaporate in samples with TiO₂, it may suggest that TiO₂ has promoted the hydration. In addition, Table B.1 shows the percentage of weight loss before 100 °C and between 100 and 200 °C in each mixture.

Table B1. Weight loss (%) below 200 °C (TGA).

Curing temperature	0 - 200 °C			0 - 100 °C			100 - 200 °C		
	MC-R	MC-Ti0.5	Δ	MC-R	MC-Ti0.5	Δ	MC-R	MC-Ti0.5	Δ
5 °C	3.79%	3.28%	0.51%	2.47%	2.09%	0.38%	1.32%	1.19%	0.13%
20 °C	3.61%	3.61%	0.00%	2.04%	2.04%	0.00%	1.57%	1.57%	0.00%
45 °C	4.00%	3.46%	0.54%	2.18%	1.87%	0.31%	1.82%	1.59%	0.23%

Moreover, the amount of calcite in the cement before hydrating is 0.15 g/g obtained by TGA of anhydrous cement, as it was mentioned in *Section 2.3.4*. In order to clarify this value, Figure B.3 displays the corresponding percentage of weight loss (6.7%) of the anhydrous cement. Besides, Figure B.4 shows the TGA curve obtained from the fine aggregate used in this study.

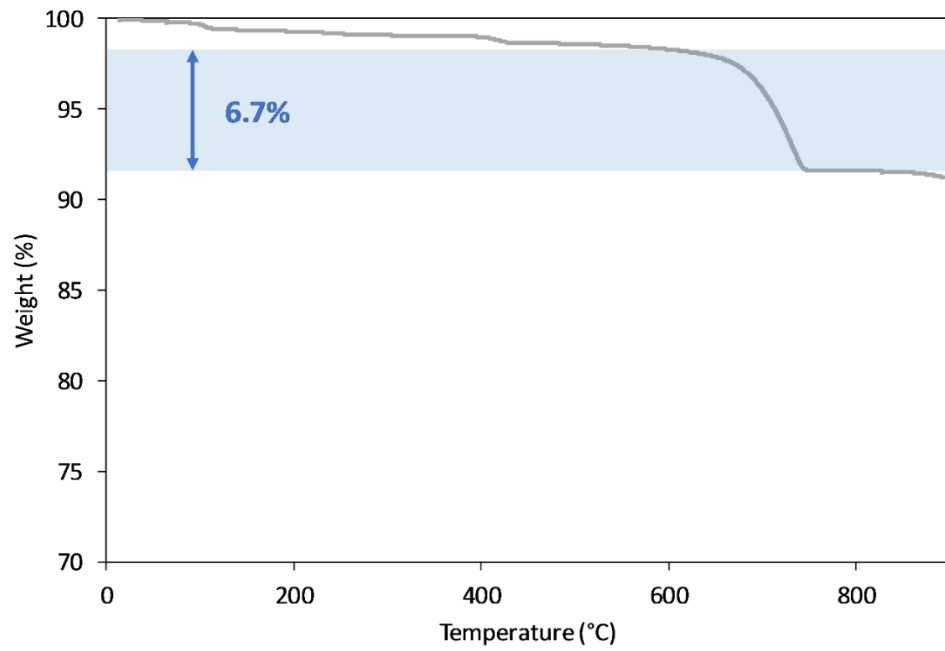


Figure B.3. TGA curves of anhydrous cement.

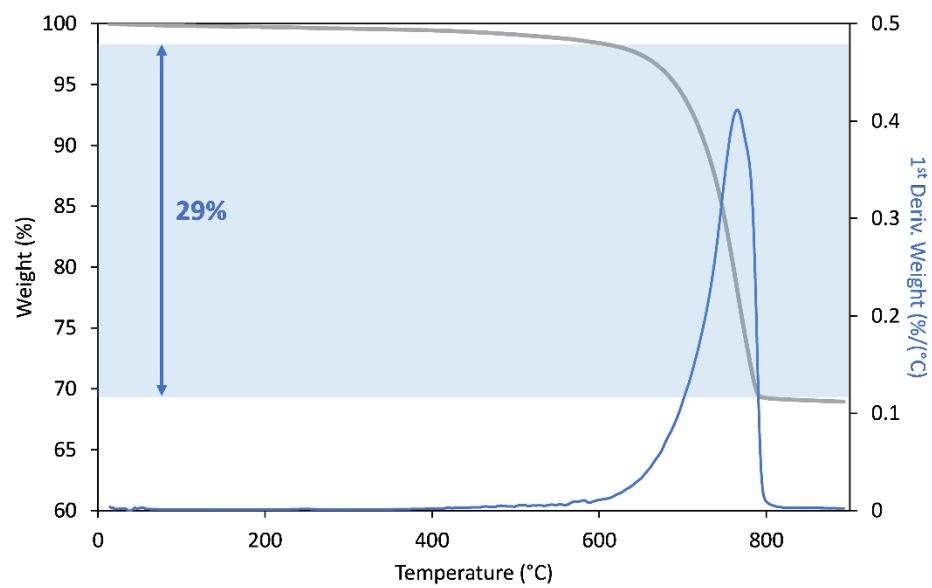


Figure B.4. TGA curves of fine aggregate.

Table B.2 shows the calculated amount of CaCO_3 due to the fine aggregate and the anhydrous cement that was estimated in the sample for TGA analysis.

Table B2. Adjusted amount of CaCO_3 in the sample (TGA).

Compound	Amount of CaCO_3 (g/g_{compound})	g_{compound}/g_{sample}	Amount of CaCO_3 (g/g_{sample})
Cement	0.1522	0.40*	0.0609
Sand	0.6598	0.40*	0.2639
CA_{ini}			32.48 %

*During sample preparation, it was observed that while the ground cement paste was completely passing, part of the aggregate was consistently retained in the 75- μm sieve. It was estimated that 40% of the aggregate was not completely ground during the process, and, therefore, was not part of the TGA sample. Thus, when CA_{ini} was calculated, the amount of aggregate/mortar in the sample was 0.40 instead of the full 0.67 in the original mortar. In the same way, the amount of cement/mortar in the TGA sample was estimated to be 0.40 instead of 0.22.

Furthermore, Figures B.5 and B.6 present the TGA curves of each test with first and second derivative in order to provide the complete data used to do the analysis.

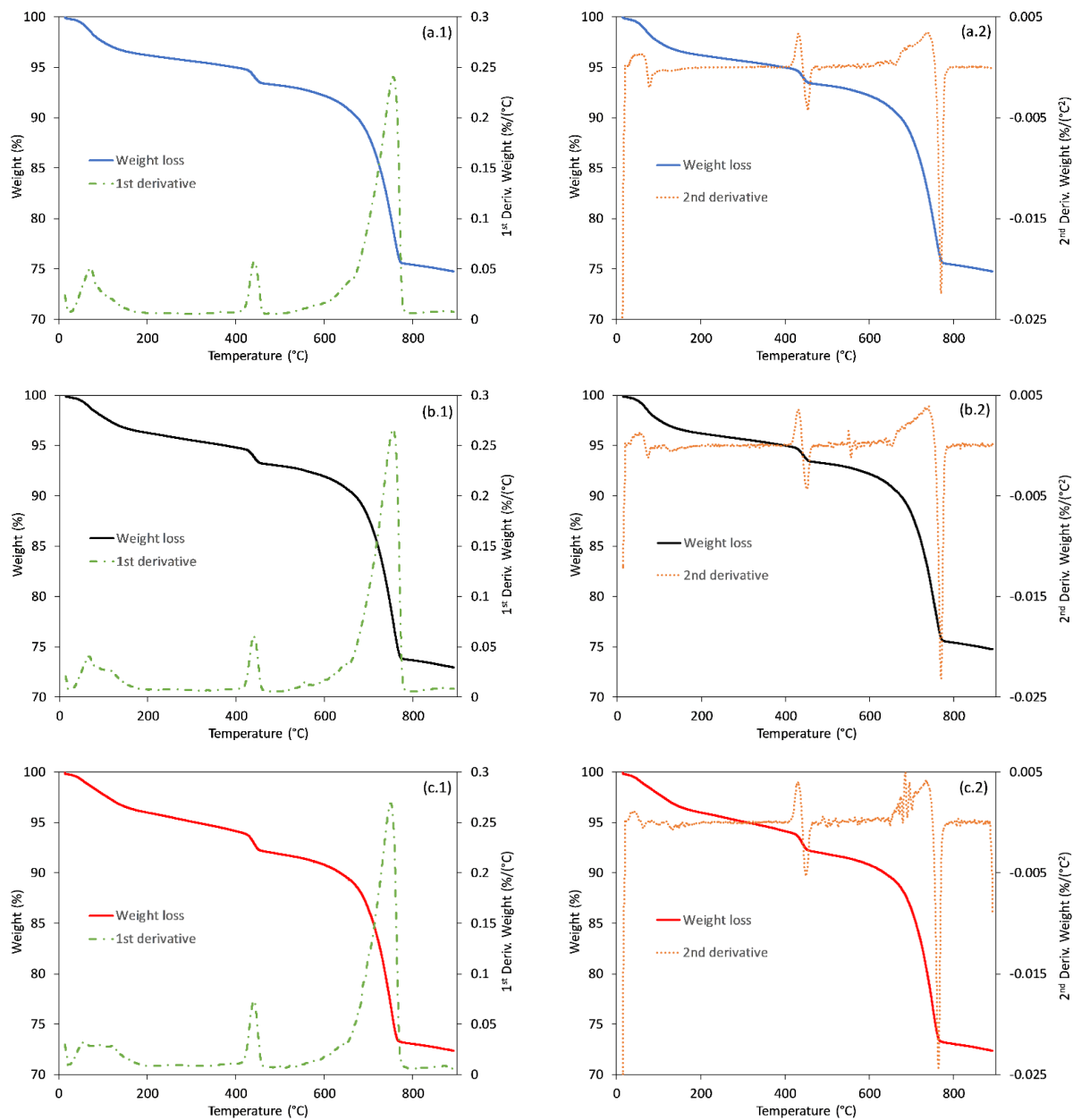


Figure B.5. TGA curves of MC-R at 7 days for different curing temperatures. (a.1 and a.2) 5 °C. (b.1 and b.2) 20 °C. (c.1 and c.2) 45 °C.

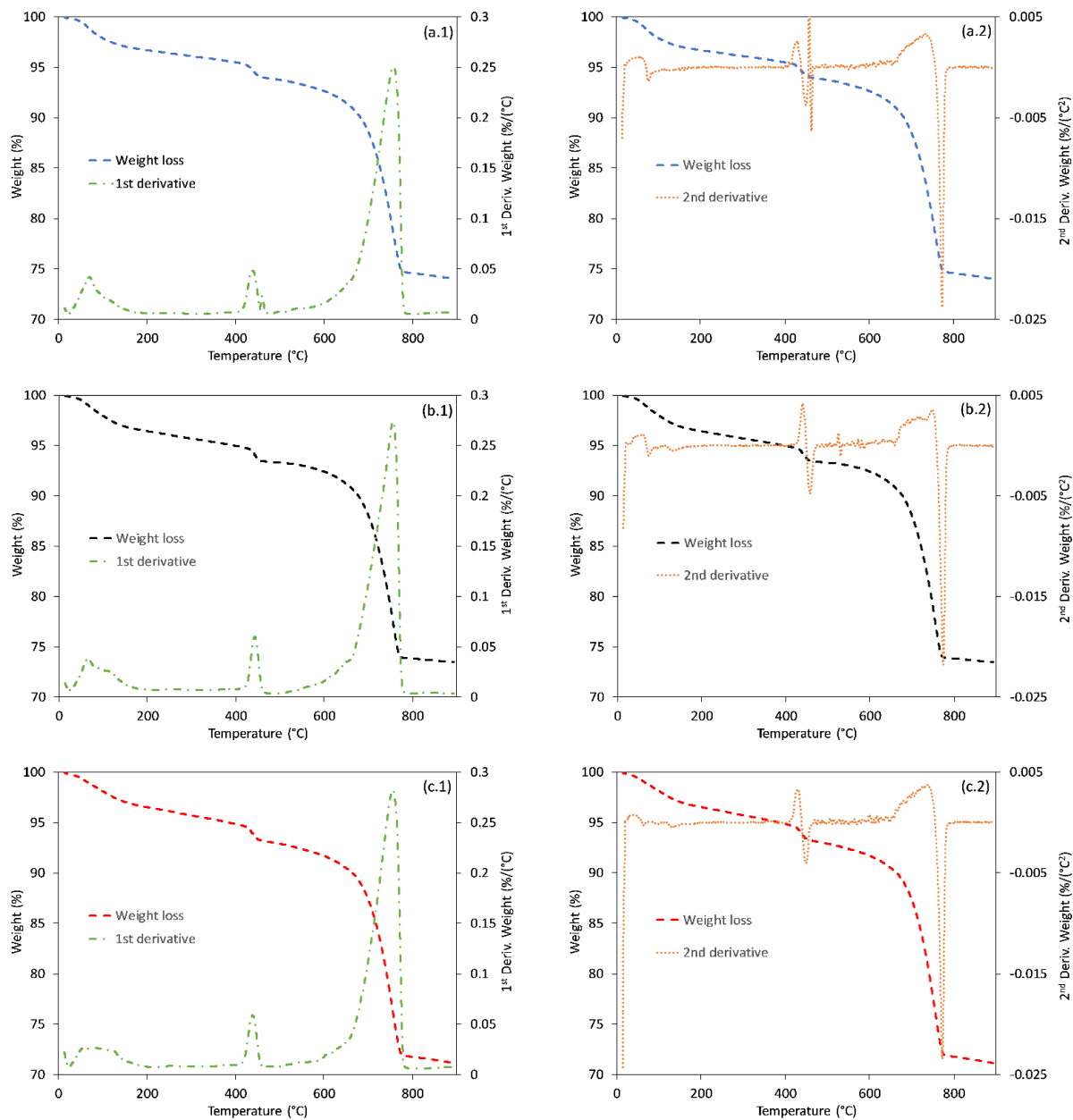


Figure B.6. TGA curves of MC-Ti_{0.5} at 7 days for different curing temperatures. (a.1 and a.2) 5 °C. (b.1 and b.2) 20 °C. (c.1 and c.2) 45 °C.

APPENDIX C. LOAD-DISPLACEMENT CURVES

Load-displacement curves obtained from the flexural strength tests of mortars with re-PP fibers are showed in Figure C.1.

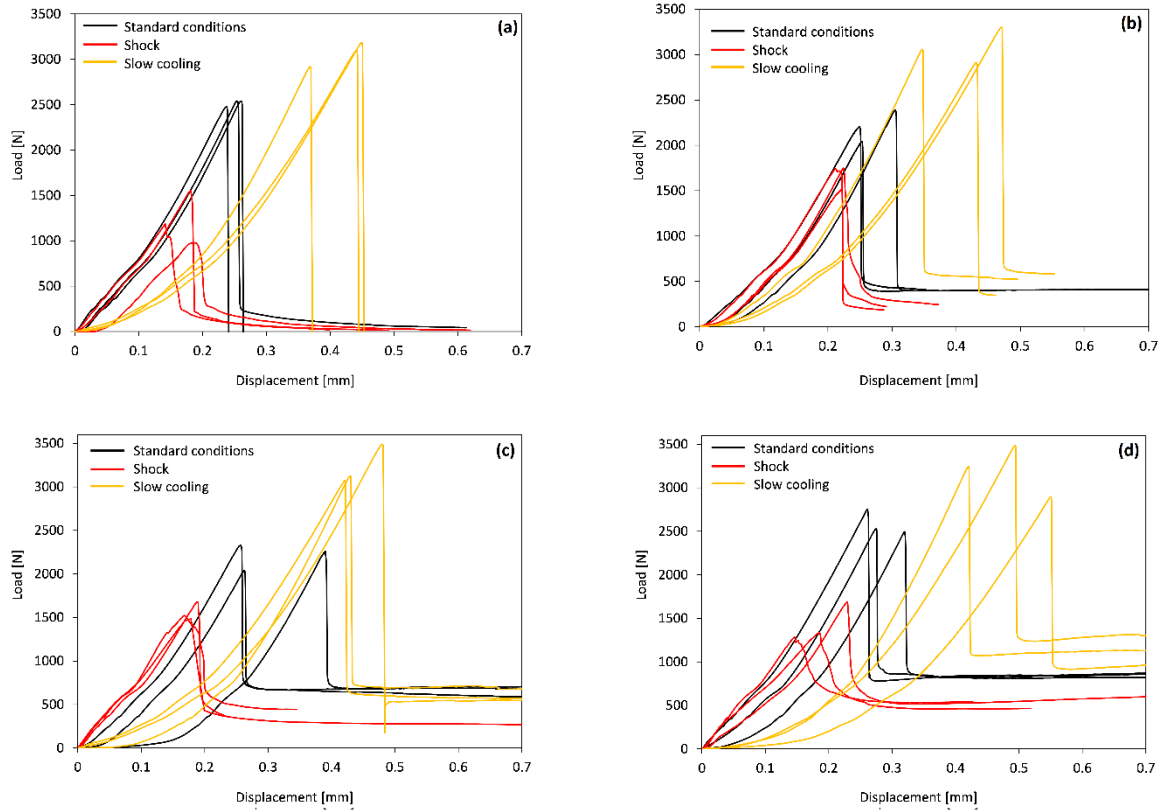


Figure C.1. Load-displacement curves of flexural tests for mortars with re-PP fibers. (a) PM0, (b) PM0.5, (c) PM1, and (d) PM1.5.

REFERENCES

- [1] Bringing Embodied Carbon Upfront | World Green Building Council, (2019). <https://www.worldgbc.org/news-media/bringing-embodied-carbon-upfront>.
- [2] P.J.M. Monteiro, S.A. Miller, A. Horvath, P.J.M. Monteiro, S.A. Miller, A. Horvath, Towards sustainable concrete, *Nat. Mater.* 16 (2017) 698–699. <https://doi.org/10.1038/NMAT4930>.
- [3] R.M. Andrew, Global CO₂ emissions from cement production, *Earth Syst. Sci. Data.* 10 (2018) 195–217. <https://doi.org/10.5194/essd-10-195-2018>.
- [4] S.A. Miller, Supplementary cementitious materials to mitigate greenhouse gas emissions from concrete: can there be too much of a good thing?, *J. Clean. Prod.* 178 (2018) 587–598. <https://doi.org/10.1016/j.jclepro.2018.01.008>.
- [5] K.M. Rahla, R. Mateus, L. Bragança, Comparative sustainability assessment of binary blended concretes using Supplementary Cementitious Materials (SCMs) and Ordinary Portland Cement (OPC), *J. Clean. Prod.* 220 (2019) 445–459. <https://doi.org/10.1016/j.jclepro.2019.02.010>.
- [6] L. Evangelista, J. de Brito, Mechanical behaviour of concrete made with fine recycled concrete aggregates, *Cem. Concr. Compos.* 29 (2007) 397–401. <https://doi.org/10.1016/j.cemconcomp.2006.12.004>.
- [7] M. Velay-Lizancos, I. Martinez-Lage, M. Azenha, J. Granja, P. Vazquez-Burgo, Concrete with fine and coarse recycled aggregates: E-modulus evolution, compressive strength and non-destructive testing at early ages, *Constr. Build. Mater.* In press (2018). <https://doi.org/https://doi.org/10.1016/j.conbuildmat.2018.10.209>.
- [8] Z. Shayegan, C.S.S. Lee, F. Haghighat, TiO₂ photocatalyst for removal of volatile organic compounds in gas phase – A review, 2018. <https://doi.org/10.1016/j.cej.2017.09.153>.
- [9] I. Asadi, P. Shafigh, Z.F. Bin Abu Hassan, N.B. Mahyuddin, Thermal conductivity of concrete – A review, *J. Build. Eng.* 20 (2018) 81–93. <https://doi.org/10.1016/j.job.2018.07.002>.
- [10] W. Zhu, P.J.M. Bartos, A. Porro, Application of nanotechnology in construction Summary of a state-of-the-art report, *Mater. Struct. Constr.* 37 (2004) 649–658. <https://doi.org/10.1617/14234>.

- [11] J. Silvestre, N. Silvestre, J. De Brito, Review on concrete nanotechnology, *Eur. J. Environ. Civ. Eng.* 20 (2016) 455–485. <https://doi.org/10.1080/19648189.2015.1042070>.
- [12] F. Sanchez, K. Sobolev, Nanotechnology in concrete - A review, *Constr. Build. Mater.* 24 (2010) 2060–2071. <https://doi.org/10.1016/j.conbuildmat.2010.03.014>.
- [13] V. Corinaldesi, Mechanical and elastic behaviour of concretes made of recycled-concrete coarse aggregates, *Constr. Build. Mater.* 24 (2010) 1616–1620. <https://doi.org/10.1016/j.conbuildmat.2010.02.031>.
- [14] J. de Brito, N. Saikia, *Recycled aggregate in concrete : use of industrial, construction and demolition waste*, Springer, 2013.
- [15] R. Siddique, J. Khatib, I. Kaur, Use of recycled plastic in concrete: A review, *Waste Manag.* 28 (2008) 1835–1852. <https://doi.org/10.1016/j.wasman.2007.09.011>.
- [16] L. Gu, T. Ozbakkaloglu, Use of recycled plastics in concrete: A critical review, *Waste Manag.* 51 (2016) 19–42. <https://doi.org/10.1016/j.wasman.2016.03.005>.
- [17] I. Almeshal, B.A. Tayeh, R. Alyousef, H. Alabduljabbar, A. Mustafa Mohamed, A. Alaskar, Use of recycled plastic as fine aggregate in cementitious composites: A review, *Constr. Build. Mater.* 253 (2020) 119146. <https://doi.org/10.1016/j.conbuildmat.2020.119146>.
- [18] T. Meng, Y. Yu, X. Qian, S. Zhan, K. Qian, Effect of nano-TiO₂ on the mechanical properties of cement mortar, *Constr. Build. Mater.* 29 (2012) 241–245. <https://doi.org/10.1016/j.conbuildmat.2011.10.047>.
- [19] F. Aslani, B. Samali, High Strength Polypropylene Fibre Reinforcement Concrete at High Temperature, *Fire Technol.* 50 (2014) 1229–1247. <https://doi.org/10.1007/s10694-013-0332-y>.
- [20] P. Kalifa, G. Chén  , C. Gall  , High-temperature behaviour of HPC with polypropylene fibres - From spalling to microstructure, *Cem. Concr. Res.* 31 (2001) 1487–1499. [https://doi.org/10.1016/S0008-8846\(01\)00596-8](https://doi.org/10.1016/S0008-8846(01)00596-8).
- [21] G.A. Khoury, B. Willoughby, Polypropylene fibres in heated concrete. Part 1: Molecular structure and materials behaviour, *Mag. Concr. Res.* 60 (2008) 125–136. <https://doi.org/10.1680/mac.2008.60.2.125>.
- [22] M. Safiuddin, M. Gonzalez, J. Cao, S.L. Tighe, State-of-the-art report on use of nano-materials in concrete, *Int. J. Pavement Eng.* 15 (2014) 940–949. <https://doi.org/10.1080/10298436.2014.893327>.

- [23] F. Aslani, Nanoparticles in self-compacting concrete – a review, *Mag. Concr. Res.* 67 (2015) 1084–1100. <https://doi.org/10.1680/mac.14.00381>.
- [24] J. Chen, S.C. Kou, C.S. Poon, Hydration and properties of nano-TiO₂ blended cement composites, *Cem. Concr. Compos.* 34 (2012) 642–649.
- [25] H. Li, H. gang Xiao, J. ping Ou, A study on mechanical and pressure-sensitive properties of cement mortar with nanophase materials, *Cem. Concr. Res.* 34 (2004) 435–438. <https://doi.org/10.1016/j.cemconres.2003.08.025>.
- [26] A. Nazari, S. Riahi, The effects of TiO₂ nanoparticles on physical, thermal and mechanical properties of concrete using ground granulated blast furnace slag as binder, *Mater. Sci. Eng. A.* 528 (2011) 2085–2092. <https://doi.org/10.1016/j.msea.2010.11.070>.
- [27] C. Cárdenas, J.I. Tobón, C. García, J. Vila, Functionalized building materials: Photocatalytic abatement of NO_x by cement pastes blended with TiO₂ nanoparticles, *Constr. Build. Mater.* 36 (2012) 820–825. <https://doi.org/10.1016/j.conbuildmat.2012.06.017>.
- [28] K. Hashimoto, H. Irie, A. Fujishima, TiO₂ Photocatalysis: A Historical Overview and Future Prospects, *Jpn. J. Appl. Phys.* 44 (2005) 8269–8285. <https://doi.org/10.1143/JJAP.44.8269>.
- [29] P.V. Laxma Reddy, B. Kavitha, P.A. Kumar Reddy, K.H. Kim, TiO₂-based photocatalytic disinfection of microbes in aqueous media: A review, *Environ. Res.* 154 (2017) 296–303. <https://doi.org/10.1016/j.envres.2017.01.018>.
- [30] T. Mendes, D. Hotza, W. Repette, Nanoparticles in Cement Based Materials: a Review, *Rev. Adv. Mater. Sci.* 40 (2015) 89–96. http://www.ipme.ru/e-journals/RAMS/no_14015/06_14015_mendes.pdf.
- [31] E. Cerro-Prada, M. Manso, V. Torres, J. Soriano, Microstructural and photocatalytic characterization of cement-paste sol-gel synthesized titanium dioxide, *Front. Struct. Civ. Eng.* 10 (2016) 189–197. <https://doi.org/10.1007/s11709-015-0326-6>.
- [32] N. Ganji, A. Allahverdi, F. Naeimpoor, M. Mahinroosta, Photocatalytic effect of nano-TiO₂ loaded cement on dye decolorization and *Escherichia coli* inactivation under UV irradiation, *Res. Chem. Intermed.* 42 (2016) 5395–5412. <https://doi.org/10.1007/s11164-015-2374-x>.
- [33] J. Cohen, G. Sierra-Gallego, J. Tobón, Evaluation of Photocatalytic Properties of Portland Cement Blended with Titanium Oxynitride (TiO₂-xNy) Nanoparticles, *Coatings.* 5 (2015) 465–476. <https://doi.org/10.3390/coatings5030465>.

- [34] A. Zhao, J. Yang, E.H. Yang, Self-cleaning engineered cementitious composites, *Cem. Concr. Compos.* 64 (2015) 74–83. <https://doi.org/10.1016/j.cemconcomp.2015.09.007>.
- [35] A.M. Waked, Nano materials applications for conservation of cultural heritage, *WIT Trans. Built Environ.* 118 (2011) 577–588. <https://doi.org/10.2495/STR110481>.
- [36] G. Bastos, F. Patiño-Barbeito, F. Patiño-Cambeiro, J. Armesto, Nano-inclusions applied in cement-matrix composites: A review, *Materials (Basel)*. 9 (2016). <https://doi.org/10.3390/ma9121015>.
- [37] J. Liu, Q. Li, S. Xu, Influence of nanoparticles on fluidity and mechanical properties of cement mortar, *Constr. Build. Mater.* 101 (2015) 892–901. <https://doi.org/10.1016/j.conbuildmat.2015.10.149>.
- [38] B.Y. Lee, Effect of titanium dioxide nanoparticles on early age and long term properties of cementitious materials, (Doctoral Dissertation). Georgia Institute of Technology, 2012. <https://smartech.gatech.edu/handle/1853/44834>.
- [39] B. Han, L. Zhang, S. Zeng, S. Dong, X. Yu, R. Yang, J. Ou, Nano-core effect in nano-engineered cementitious composites, *Compos. Part A Appl. Sci. Manuf.* 95 (2017) 100–109. <https://doi.org/10.1016/J.COMPOSITESA.2017.01.008>.
- [40] Z. Li, S. Ding, X. Yu, B. Han, J. Ou, Multifunctional cementitious composites modified with nano titanium dioxide: A review, *Compos. Part A Appl. Sci. Manuf.* 111 (2018) 115–137. <https://doi.org/10.1016/J.COMPOSITESA.2018.05.019>.
- [41] M.H. Zhang, H. Li, Pore structure and chloride permeability of concrete containing nanoparticles for pavement, *Constr. Build. Mater.* 25 (2011) 608–616. <https://doi.org/10.1016/j.conbuildmat.2010.07.032>.
- [42] K. Tanaka, M.F.V. Capule, T. Hisanaga, Effect of crystallinity of TiO₂ on its photocatalytic action, *Chem. Phys. Lett.* 187 (1991) 73–76. [https://doi.org/10.1016/0009-2614\(91\)90486-S](https://doi.org/10.1016/0009-2614(91)90486-S).
- [43] W.A. Gutteridge, J.A. Dalziel, Filler cement: The effect of the secondary component on the hydration of Portland cement, *Cem. Concr. Res.* 20 (1990) 778–782.
- [44] L.Y. Yang, Z.J. Jia, Y.M. Zhang, J.G. Dai, Effects of nano-TiO₂ on strength, shrinkage and microstructure of alkali activated slag pastes, *Cem. Concr. Compos.* 57 (2015) 1–7. <https://doi.org/10.1016/J.CEMCONCOMP.2014.11.009>.

- [45] F. Soleymani, Assessments of the effects of limewater on water permeability of TiO₂ nanoparticles binary blended palm oil clinker aggregate-based concrete, 2012. <http://www.americanscience.org.76> (accessed December 11, 2018).
- [46] B. Ma, H. Li, J. Mei, X. Li, F. Chen, Effects of nano-TiO₂ on the toughness and durability of cement-based material, *Adv. Mater. Sci. Eng.* 2015 (2015) 1–10. <https://doi.org/10.1155/2015/583106>.
- [47] Y.A. Fawzy, Effect of nano-titanium on properties of concrete made with various cement types, *J Am Sci.* Volume 12 (2013) Pages 116-126. <https://www.scopus.com/record/display.uri?eid=2-s2.0-85047614244&origin=inward> (accessed December 11, 2018).
- [48] R. Zhang, X. Cheng, P. Hou, Z. Ye, Influences of nano-TiO₂ on the properties of cement-based materials: Hydration and drying shrinkage, *Constr. Build. Mater.* 81 (2015) 35–41. <https://doi.org/10.1016/j.conbuildmat.2015.02.003>.
- [49] Z. Li, B. Han, X. Yu, S. Dong, L. Zhang, X. Dong, J. Ou, Effect of nano-titanium dioxide on mechanical and electrical properties and microstructure of reactive powder concrete, *Mater. Res. Express.* 4 (2017) 095008. <https://doi.org/10.1088/2053-1591/aa87db>.
- [50] M.M. Salman, K.M. Eweed, A.M. Hameed, *Al-Nahrain journal for engineering sciences : (NJES).*, 2016. <https://nahje.com/index.php/main/article/view/20> (accessed December 11, 2018).
- [51] H. Li, M. hua Zhang, J. ping Ou, Flexural fatigue performance of concrete containing nanoparticles for pavement, *Int. J. Fatigue.* 29 (2007) 1292–1301. <https://doi.org/10.1016/j.ijfatigue.2006.10.004>.
- [52] Z. Metaxa, M. Konsta-Gdoutos, S. Shah, Carbon Nanofiber-Reinforced Cement-Based Materials, *Transp. Res. Rec. J. Transp. Res. Board.* 2142 (2010) 114–118. <https://doi.org/10.3141/2142-17>.
- [53] K. Kumari, R. Preetha, D. Ramachandran, V. Vishwakarma, R.P. George, C. Sundaramurthy, U. Kamachi Mudali, C. Sivathanu Pillai, Nanoparticles for enhancing mechanical properties of fly ash concrete, in: *Mater. Today Proc.*, 2016: pp. 2387–2393. <https://doi.org/10.1016/j.matpr.2016.04.152>.

- [54] K. Pimenta Teixeira, I. Perdigão Rocha, L. De Sá Carneiro, J. Flores, E. Dauer, A. Ghahremaninezhad, The Effect of Curing Temperature on the Properties of Cement Pastes Modified with TiO₂ Nanoparticles, *Materials (Basel)*. 9 (2016) 952. <https://doi.org/10.3390/ma9110952>.
- [55] L.P. Singh, A. Goel, S.K. Bhattacharyya, S. Ahalawat, U. Sharma, G. Mishra, Effect of Morphology and Dispersibility of Silica Nanoparticles on the Mechanical Behaviour of Cement Mortar, *Int. J. Concr. Struct. Mater.* 9 (2015) 207–217. <https://doi.org/10.1007/s40069-015-0099-2>.
- [56] N. Ukrainczyk, M. Ukrainczyk, J. Sipusic, T. Matusinovic, XRD and TGA Investigation of Hardened Cement Paste, 11. Conf. Mater. Process. Frict. Wear MATRIB'06, Vela Luka. (2006) 22–24. <http://tubiblio.ulb.tu-darmstadt.de/73982/> (accessed July 25, 2018).
- [57] V.S. (Vangipuram S. Ramachandran, Handbook of thermal analysis of construction materials, Noyes Publications, 2002.
- [58] R. Gabrovšek, T. Vuk, V. Kaučič, Evaluation of the hydration of Portland cement containing various carbonates by means of thermal analysis, *Acta Chim. Slov.* 53 (2006) 159–165.
- [59] B. El-Jazairi, J.M.M. Illston, A simultaneous semi-isothermal method of thermogravimetry and derivative thermogravimetry, and its application to cement pastes, *Cem. Concr. Res.* 7 (1977) 247–257. [https://doi.org/10.1016/0008-8846\(77\)90086-2](https://doi.org/10.1016/0008-8846(77)90086-2).
- [60] T. Kim, J. Olek, Effects of Sample Preparation and Interpretation of Thermogravimetric Curves on Calcium Hydroxide in Hydrated Pastes and Mortars, *Transp. Res. Rec. J. Transp. Res. Board.* 2290 (2012) 10–18. <https://doi.org/10.3141/2290-02>.
- [61] W. Sha, E.A. O'Neill, Z. Guo, Differential scanning calorimetry study of ordinary Portland cement, *Cem. Concr. Res.* 29 (1999) 1487–1489. [https://doi.org/10.1016/S0008-8846\(99\)00128-3](https://doi.org/10.1016/S0008-8846(99)00128-3).
- [62] L.P. Esteves, On the hydration of water-entrained cement-silica systems: Combined SEM, XRD and thermal analysis in cement pastes, *Thermochim. Acta.* 518 (2011) 27–35. <https://doi.org/10.1016/j.tca.2011.02.003>.
- [63] ASTM, ASTM C150/C150M - Standard Specification for Portland Cement, ASTM Int. (2020). https://compass.astm.org/EDIT/html_annot.cgi?C150+20.

- [64] CEN Standard, EN 197-1:2011 Cement - Part 1: Composition, specifications and conformity criteria for common cements., (2011). <http://store.uni.com/catalogo/index.php/en-197-1-2011.html>.
- [65] EN196-1, Methods of testing cement - Part 1: Determination of strength, Eur. Stand. (2005) 1–33. <https://doi.org/10.1111/j.1748-720X.1990.tb01123.x>.
- [66] R.H. Myers, D.C. Montgomery, C.M. Anderson-Cook, Response Surface Methodology, Wiley, 2009. https://doi.org/10.1007/978-3-642-04898-2_492.
- [67] A.I. Khuri, Response Surface Methodology, Springer Berlin Heidelb. (2011) 1229–1231. https://doi.org/10.1007/978-3-642-04898-2_492.
- [68] M.J. Simon, T.P. Teng, Concrete Mixture Optimization Using Statistical Methods: Final Report, (2003).
- [69] N.H. Mtarfi, Z. Rais, M. Taleb, K.M. Kada, Effect of fly ash and grading agent on the properties of mortar using response surface methodology, Elsevier Ltd, 2017. <https://doi.org/10.1016/j.jobte.2016.12.004>.
- [70] B.S. Mohammed, V.C. Khed, M.F. Nuruddin, Rubbercrete mixture optimization using response surface methodology, J. Clean. Prod. 171 (2018) 1605–1621. <https://doi.org/10.1016/j.jclepro.2017.10.102>.
- [71] K.E. Alyamac, E. Ghafari, R. Ince, Development of eco-efficient self-compacting concrete with waste marble powder using the response surface method, J. Clean. Prod. 144 (2017) 192–202. <https://doi.org/10.1016/j.jclepro.2016.12.156>.
- [72] J. García-Cuadrado, I. Santamaría-Vicario, A. Rodríguez, V. Calderón, S. Gutiérrez-González, Lime-cement mortars designed with steelmaking slags as aggregates and validation study of their properties using mathematical models, Constr. Build. Mater. 188 (2018) 210–220. <https://doi.org/10.1016/j.conbuildmat.2018.08.093>.
- [73] B. Şimşek, T. Uygunoğlu, H. Korucu, M.M. Kocakerim, Analysis of the effects of dioctyl terephthalate obtained from polyethylene terephthalate wastes on concrete mortar: A response surface methodology based desirability function approach application, J. Clean. Prod. 170 (2018) 437–445. <https://doi.org/10.1016/j.jclepro.2017.09.176>.

- [74] Y. Rostamiyan, A. Fereidoon, M. Rezaeiashtiyani, A.H. Mashhadzadeh, A. Salmankhani, Experimental and optimizing flexural strength of epoxy-based nanocomposite: Effect of using nano silica and nano clay by using response surface design methodology, *Mater. Des.* 69 (2015) 96–104. <https://doi.org/10.1016/j.matdes.2014.11.062>.
- [75] M. Moukwa, S. Farrington, D. Youn, Determination of Ca(OH)_2 in hydrated cement paste by differential scanning calorimetry, *Thermochim. Acta.* 195 (1992) 231–237. [https://doi.org/10.1016/0040-6031\(92\)80066-6](https://doi.org/10.1016/0040-6031(92)80066-6).
- [76] W. Sha, G.B. Pereira, Differential scanning calorimetry study of hydrated ground granulated blast-furnace slag, *Cem. Concr. Res.* 31 (2001) 327–329. [https://doi.org/10.1016/S0008-8846\(00\)00472-5](https://doi.org/10.1016/S0008-8846(00)00472-5).
- [77] J. Zelić, D. Rušić, D. Veža, R. Krstulović, The role of silica fume in the kinetics and mechanisms during the early stage of cement hydration, *Cem. Concr. Res.* 30 (2000) 1655–1662. [https://doi.org/10.1016/S0008-8846\(00\)00374-4](https://doi.org/10.1016/S0008-8846(00)00374-4).
- [78] J. Jain, N. Neithalath, Analysis of calcium leaching behavior of plain and modified cement pastes in pure water, *Cem. Concr. Compos.* 31 (2009) 176–185. <https://doi.org/10.1016/j.cemconcomp.2009.01.003>.
- [79] M. Velay-Lizancos, I. Martinez-Lage, M. Azenha, P. Vázquez-Burgo, Influence of temperature in the evolution of compressive strength and in its correlations with UPV in eco-concretes with recycled materials, *Constr. Build. Mater.* 124 (2016) 276–286. <https://doi.org/10.1016/j.conbuildmat.2016.07.104>.
- [80] ASTM Committee C09.64, ASTM C1074-11 Standard Practice for Estimating Concrete Strength by the Maturity Method, in: *Annu. B. ASTM Stand.* Vol. 04.02, 2015: p. 10. <https://doi.org/10.1520/C1074-11>.
- [81] K.M. Alexander, J.H. Taplin, Concrete strength, paste strength, cement hydration, and the maturity rule, *Aust. J. Appl. Sci.* 13 (1962) 277–284.
- [82] N.J. Carino, R.C. Tank, Maturity functions for concretes made with various cements and admixtures, *ACI Mater. J.* 89 (1992).
- [83] V.M. Malhotra, N.J. Carino, *Handbook on Nondestructive Testing of Concrete*, 2004.

- [84] M. Velay-Lizancos, I. Martinez-Lage, M. Azenha, P. Vázquez-Burgo, Influence of temperature in the evolution of compressive strength and in its correlations with UPV in eco-concretes with recycled materials, *Constr. Build. Mater.* 124 (2016). <https://doi.org/10.1016/j.conbuildmat.2016.07.104>.
- [85] M. Velay-Lizancos, I. Martinez-Lage, P. Vazquez-Burgo, The effect of recycled aggregates on the accuracy of the maturity method on vibrated and self-compacting concretes, *Arch. Civ. Mech. Eng.* 19 (2019) 311–321. <https://doi.org/10.1016/J.ACME.2018.11.004>.
- [86] A.R. Jayapalan, B.Y. Lee, K.E. Kurtis, Effect of Nano-sized Titanium Dioxide on Early Age Hydration of Portland Cement, in: *Nanotechnol. Constr.* 3, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009: pp. 267–273. https://doi.org/10.1007/978-3-642-00980-8_35.
- [87] B. Han, Z. Li, L. Zhang, S. Zeng, X. Yu, B. Han, J. Ou, Reactive powder concrete reinforced with nano SiO₂-coated TiO₂, *Constr. Build. Mater.* 148 (2017) 104–112. <https://doi.org/10.1016/J.CONBUILDMAT.2017.05.065>.
- [88] A. Folli, I. Pochard, A. Nonat, U.H. Jakobsen, A.M. Shepherd, D.E. Macphee, Engineering Photocatalytic Cements: Understanding TiO₂ Surface Chemistry to Control and Modulate Photocatalytic Performances, *J. Am. Ceram. Soc.* 93 (2010) 3360–3369. <https://doi.org/10.1111/j.1551-2916.2010.03838.x>.
- [89] R. Kurihara, I. Maruyama, Influences of nano-TiO₂ particles on alteration of microstructure of hardened cement, 38 (2016) 219–224. <https://www.researchgate.net/publication/304755102>.
- [90] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars: Effect of inert materials on short-term hydration, *Cem. Concr. Res.* 33 (2003) 1939–1947. [https://doi.org/10.1016/S0008-8846\(03\)00183-2](https://doi.org/10.1016/S0008-8846(03)00183-2).
- [91] A. Nazari, S. Riahi, TiO₂ nanoparticles' effects on properties of concrete using ground granulated blast furnace slag as binder, *Sci. China Technol. Sci.* 54 (2011) 3109–3118. <https://doi.org/10.1007/s11431-011-4421-1>.
- [92] T. Nochaiya, A. Chaipanich, Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials, *Appl. Surf. Sci.* 257 (2011) 1941–1945. <https://doi.org/10.1016/J.APSUSC.2010.09.030>.

- [93] H.S. Wong, A.M. Pappas, R.W. Zimmerman, N.R. Buenfeld, Effect of entrained air voids on the microstructure and mass transport properties of concrete, *Cem. Concr. Res.* 41 (2011) 1067–1077. <https://doi.org/10.1016/J.CEMCONRES.2011.06.013>.
- [94] K.H. Yang, Y.B. Jung, M.S. Cho, S.H. Tae, Effect of Supplementary Cementitious Materials on Reduction of CO₂ Emissions From Concrete, *Handb. Low Carbon Concr.* 103 (2014) 89–110. <https://doi.org/10.1016/B978-0-12-804524-4.00005-1>.
- [95] I. Martínez-Lage, P. Vázquez-Burgo, M. Velay-Lizancos, Sustainability evaluation of concretes with mixed recycled aggregate based on holistic approach: Technical, economic and environmental analysis, *Waste Manag.* 104 (2020) 9–19. <https://doi.org/10.1016/j.wasman.2019.12.044>.
- [96] R. Xiao, Y. Ma, X. Jiang, M. Zhang, Y. Zhang, Y. Wang, B. Huang, Q. He, Strength, microstructure, efflorescence behavior and environmental impacts of waste glass geopolymers cured at ambient temperature, *J. Clean. Prod.* 252 (2020) 119610. <https://doi.org/10.1016/j.jclepro.2019.119610>.
- [97] R. Xiao, P. Polaczyk, M. Zhang, X. Jiang, Y. Zhang, B. Huang, W. Hu, Evaluation of Glass Powder-Based Geopolymer Stabilized Road Bases Containing Recycled Waste Glass Aggregate, *Transp. Res. Rec. J. Transp. Res. Board.* 2674 (2020) 036119811989869. <https://doi.org/10.1177/0361198119898695>.
- [98] J.M.V. Gómez-Soberón, Porosity of recycled concrete with substitution of recycled concrete aggregate: An experimental study, *Cem. Concr. Res.* 32 (2002) 1301–1311. [https://doi.org/10.1016/S0008-8846\(02\)00795-0](https://doi.org/10.1016/S0008-8846(02)00795-0).
- [99] K. Nakata, A. Fujishima, TiO₂ photocatalysis: Design and applications, *J. Photochem. Photobiol. C Photochem. Rev.* 13 (2012) 169–189. <https://doi.org/10.1016/j.jphotochemrev.2012.06.001>.
- [100] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C Photochem. Rev.* 1 (2000) 1–21. [https://doi.org/10.1016/S1389-5567\(00\)00002-2](https://doi.org/10.1016/S1389-5567(00)00002-2).
- [101] A. Fujishima, X. Zhang, Titanium dioxide photocatalysis: present situation and future approaches, *Comptes Rendus Chim.* 9 (2006) 750–760. <https://doi.org/10.1016/j.crci.2005.02.055>.

- [102] L. Cassar, A. Beeldens, N. Pimpinelli, G.L. Guerrini, S.D. Milanese, Photocatalysis of cementitious materials, *Int. RILEM Symp. Photocatal. Environ. Constr. Mater.* 8 (2007) 131–145. <https://doi.org/10.1617/2912143640.043>.
- [103] L. Cassar, Photocatalysis of cementitious materials: Clean buildings and clean air, *MRS Bull.* 29 (2004) 328–331. <https://doi.org/10.1557/mrs2004.99>.
- [104] J.S.S. Dalton, P.A.A. Janes, N.G.G. Jones, J.A.A. Nicholson, K.R.R. Hallam, G.C.C. Allen, Photocatalytic oxidation of NO_x gases using TiO₂: A surface spectroscopic approach, *Environ. Pollut.* 120 (2002) 415–422. [https://doi.org/10.1016/S0269-7491\(02\)00107-0](https://doi.org/10.1016/S0269-7491(02)00107-0).
- [105] P. Ragesh, V. Anand Ganesh, S. V. Nair, A.S. Nair, A review on “self-cleaning and multifunctional materials,” *J. Mater. Chem. A.* 2 (2014) 14773–14797. <https://doi.org/10.1039/c4ta02542c>.
- [106] H. Noorvand, A.A. Abang Ali, R. Demirboga, N. Farzadnia, H. Noorvand, Incorporation of nano TiO₂ in black rice husk ash mortars, *Constr. Build. Mater.* 47 (2013) 1350–1361. <https://doi.org/10.1016/j.conbuildmat.2013.06.066>.
- [107] E. Mohseni, F. Naseri, R. Amjadi, M.M. Khotbehsara, M.M. Ranjbar, Microstructure and durability properties of cement mortars containing nano-TiO₂ and rice husk ash, *Constr. Build. Mater.* 114 (2016) 656–664. <https://doi.org/10.1016/j.conbuildmat.2016.03.136>.
- [108] B. Ma, H. Li, X. Li, J. Mei, Y. Lv, Influence of nano-TiO₂ on physical and hydration characteristics of fly ash–cement systems, *Constr. Build. Mater.* 122 (2016) 242–253. <https://doi.org/10.1016/J.CONBUILDMAT.2016.02.087>.
- [109] P. Duan, C. Yan, W. Luo, W. Zhou, Effects of adding nano-TiO₂ on compressive strength, drying shrinkage, carbonation and microstructure of fluidized bed fly ash based geopolymer paste, *Constr. Build. Mater.* 106 (2016) 115–125. <https://doi.org/10.1016/j.conbuildmat.2015.12.095>.
- [110] M. Lackhoff, X. Prieto, N. Nestle, F. Dehn, R. Niessner, Photocatalytic activity of semiconductor-modified cement - Influence of semiconductor type and cement ageing, *Appl. Catal. B Environ.* 43 (2003) 205–216. [https://doi.org/10.1016/S0926-3373\(02\)00303-X](https://doi.org/10.1016/S0926-3373(02)00303-X).
- [111] S. Rao, P. Silva, J. De Brito, Experimental study of the mechanical properties and durability of self-compacting mortars with nano materials (SiO₂ and TiO₂), *Constr. Build. Mater.* 96 (2015) 508–517. <https://doi.org/10.1016/j.conbuildmat.2015.08.049>.

- [112] R. Khataee, V. Heydari, L. Moradkhannejhad, M. Safarpour, S.W. Joo, Self-cleaning and mechanical properties of modified white cement with nanostructured TiO₂, *J. Nanosci. Nanotechnol.* 13 (2013) 5109–5114. <https://doi.org/10.1166/jnn.2013.7586>.
- [113] V. Francioso, C. Moro, I. Martinez-Lage, M. Velay-Lizancos, Curing temperature: A key factor that changes the effect of TiO₂ nanoparticles on mechanical properties, calcium hydroxide formation and pore structure of cement mortars, *Cem. Concr. Compos.* 104 (2019) 103374. <https://doi.org/10.1016/j.cemconcomp.2019.103374>.
- [114] J. Thomas, N.N. Thaickavil, P.M. Wilson, Strength and durability of concrete containing recycled concrete aggregates, *J. Build. Eng.* 19 (2018) 349–365. <https://doi.org/10.1016/J.JOBE.2018.05.007>.
- [115] S.H. Kosmatka, M.L. Wilson, *Design and Control Design and Control of Concrete Mixtures*, 2016.
- [116] J. Ying, B. Zhou, J. Xiao, Pore structure and chloride diffusivity of recycled aggregate concrete with nano-SiO₂ and nano-TiO₂, *Constr. Build. Mater.* 150 (2017) 49–55. <https://doi.org/10.1016/j.conbuildmat.2017.05.168>.
- [117] J. Xiao, Y. Fan, M.M. Tawana, Residual compressive and flexural strength of a recycled aggregate concrete following elevated temperatures, *Struct. Concr.* 14 (2013) 168–175. <https://doi.org/10.1002/suco.201200037>.
- [118] S.R. Sarhat, E.G. Sherwood, Residual mechanical response of recycled aggregate concrete after exposure to elevated temperatures, *J. Mater. Civ. Eng.* 25 (2013) 1721–1730. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000719](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000719).
- [119] Y. Guo, J. Zhang, G. Chen, Z. Xie, Compressive behaviour of concrete structures incorporating recycled concrete aggregates, rubber crumb and reinforced with steel fibre, subjected to elevated temperatures, 72 (2014) 193–203. <https://doi.org/10.1016/j.jclepro.2014.02.036>.
- [120] H. Salahuddin, A. Nawaz, A. Maqsoom, T. Mehmood, A. Zeeshan, Effects of elevated temperature on performance of recycled coarse aggregate concrete, *Constr. Build. Mater.* 202 (2019) 415–425. <https://doi.org/10.1016/j.conbuildmat.2019.01.011>.
- [121] C.J. Zega, A.A. Di Maio, Recycled concrete exposed to high temperatures, *Mag. Concr. Res.* 58 (2006) 675–682. <https://doi.org/10.1680/mac.2006.58.10.675>.

- [122] C. Laneyrie, A.-L. Beaucour, M.F. Green, R.L. Hebert, B. Ledesert, A. Noumowe, Influence of recycled coarse aggregates on normal and high performance concrete subjected to elevated temperatures, *Constr. Build. Mater.* 111 (2016) 368–378. <https://doi.org/10.1016/j.conbuildmat.2016.02.056>.
- [123] J. Liang, Z. Yang, P. Yi, J. Wang, Compressive Behavior of Recycled Mortar After Exposure to High, (2016) 807–812. <https://doi.org/10.2174/1874149501610010807>.
- [124] G.M. Chen, Y.H. He, H. Yang, J.F. Chen, Y.C. Guo, Compressive behavior of steel fiber reinforced recycled aggregate concrete after exposure to elevated temperatures, *Constr. Build. Mater.* 71 (2014) 1–15. <https://doi.org/10.1016/j.conbuildmat.2014.08.012>.
- [125] U. Schneider, Concrete at high temperatures - A general review, *Fire Saf. J.* 13 (1988) 55–68. [https://doi.org/10.1016/0379-7112\(88\)90033-1](https://doi.org/10.1016/0379-7112(88)90033-1).
- [126] Q. Ma, R. Guo, Z. Zhao, Z. Lin, K. He, Mechanical properties of concrete at high temperature - A review, *Constr. Build. Mater.* 93 (2015) 371–383. <https://doi.org/10.1016/j.conbuildmat.2015.05.131>.
- [127] V. Kodur, Properties of concrete at elevated temperatures, *ISRN Civ. Eng.* 2014 (2014). <https://doi.org/10.1155/2014/468510>.
- [128] K.D. Hertz, Concrete strength for fire safety design, *Mag. Concr. Res.* 57 (2005) 445–453. <https://doi.org/10.1680/mac.2005.57.8.445>.
- [129] G.T.G. Mohamedbhai, Effect of exposure time and rates of heating and cooling on residual strength of heated concrete, *Mag. Concr. Res.* 38 (1986) 151–158. <https://doi.org/10.1680/mac.1986.38.136.151>.
- [130] O. Arioz, Effects of elevated temperatures on properties of concrete, *Fire Saf. J.* 42 (2007) 516–522. <https://doi.org/10.1016/j.firesaf.2007.01.003>.
- [131] H.Y. Zhang, V. Kodur, B. Wu, L. Cao, S.L. Qi, Comparative Thermal and Mechanical Performance of Geopolymers derived from Metakaolin and Fly Ash, *J. Mater. Civ. Eng.* 28 (2016) 04015092. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0001359](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001359).
- [132] H.L. Malhotra, The effect of temperature on the compressive strength of concrete, *Mag. Concr. Res.* 8 (1956) 85–94. <https://doi.org/10.1680/mac.1956.8.23.85>.
- [133] L. Xiaoyong, B. Fanjie, Residual Strength for Concrete after Exposure to High, *Innov. Comput. Inf.* (2011) 382–390.

- [134] N. Farzadnia, A.A. Abang Ali, R. Demirboga, M.P. Anwar, Characterization of high strength mortars with nano Titania at elevated temperatures, *Constr. Build. Mater.* 43 (2013) 469–479. <https://doi.org/10.1016/j.conbuildmat.2013.02.044>.
- [135] L. Biolzi, G. Di Luzio, J.F. Labuz, Mechanical properties of photocatalytic white concrete subjected to high temperatures, *Cem. Concr. Compos.* 39 (2013) 73–81. <https://doi.org/10.1016/j.cemconcomp.2013.03.016>.
- [136] ASTM C348, Standard Test Method for Flexural Strength of Concrete, 98 (n.d.) 98–100. <https://doi.org/10.1520/C0348-08.2>.
- [137] ASTM C349, C349-97. Standard Test Method for Compressive Strength of Hydraulic-Cement Mortars (Using Portions of Prisms Broken in Flexure), *Annu. B. ASTM Stand.* (2019) 1–4. <https://doi.org/10.1520/C0349-97>.
- [138] ASTM, ASTM C136/C136M - Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates, ASTM Int. (2014). <https://doi.org/10.1520/C0136>.
- [139] ASTM, ASTM C128 - Standard Test Method for Relative Density (Specific Gravity) and Absorption of Fine Aggregate, ASTM Int. (2015). <https://doi.org/10.1520/C0128-15.2>.
- [140] N. Doebelin, R. Kleeberg, Profex: A graphical user interface for the Rietveld refinement program BGMN, *J. Appl. Crystallogr.* 48 (2015) 1573–1580. <https://doi.org/10.1107/S1600576715014685>.
- [141] N. Yuzer, F. Aköz, L.D. Oztürk, Compressive strength – color change relation in mortars at high temperature, *Cem. Concr. Res.* 34 (2004) 1803–1807. <https://doi.org/10.1016/j.cemconres.2004.01.015>.
- [142] Z.H. Shui, R. Zhang, W. Chen, D.X. Xuan, Effects of mineral admixtures on the thermal expansion properties of hardened cement paste, *Constr. Build. Mater.* 24 (2010) 1761–1767. <https://doi.org/10.1016/j.conbuildmat.2010.02.012>.
- [143] Q. Zeng, K. Li, T. Fen-Chong, P. Dangla, Effect of porosity on thermal expansion coefficient of cement pastes and mortars, *Constr. Build. Mater.* 28 (2012) 468–475. <https://doi.org/10.1016/j.conbuildmat.2011.09.010>.
- [144] J.T. Smith, S.L. Tighe, Recycled concrete aggregate coefficient of thermal expansion: Characterization, variability, and impacts on pavement performance, *Transp. Res. Rec.* (2009) 53–61. <https://doi.org/10.3141/2113-07>.

- [145] Federal Highway Administration Research and Technology, Thermal Coefficient Of Portland Cement Concrete, 2016.
- [146] J.V. Staub de Melo, G. Trichês, Study of the influence of nano-TiO₂ on the properties of Portland cement concrete for application on road surfaces, *Road Mater. Pavement Des.* 19 (2018) 1011–1026. <https://doi.org/10.1080/14680629.2017.1285811>.
- [147] J. (Joann) Wess, L.D. Olsen, M.H. Sweeney, United Nations Environment Programme., International Labour Organisation., Inter-Organization Programme for the Sound Management of Chemicals., World Health Organization., International Program on Chemical Safety., Asphalt (bitumen), World Health Organization, 2004. <https://books.google.co.id/books?id=g0ePYMgok18C> (accessed February 18, 2019).
- [148] F.-P. Cheng, V.K.R. Kodur, T.-C. Wang, Stress-Strain Curves for High Strength Concrete at Elevated Temperatures, *J. Mater. Civ. Eng.* 16 (2004) 84–90. [https://doi.org/10.1061/\(ASCE\)0899-1561\(2004\)16:1\(84\)](https://doi.org/10.1061/(ASCE)0899-1561(2004)16:1(84)).
- [149] Y.F. Fu, Y.L. Wong, C.S. Poon, C.A. Tang, Stress–strain behaviour of high-strength concrete at elevated temperatures, *Mag. Concr. Res.* 57 (2005) 535–544. <https://doi.org/10.1680/mac.2005.57.9.535>.
- [150] J.C. Mendes, R.R. Barreto, A.C.B. de Paula, F.P. da F. Elói, G.J. Brigolini, R.A.F. Peixoto, On the relationship between morphology and thermal conductivity of cement-based composites, *Cem. Concr. Compos.* 104 (2019) 103365. <https://doi.org/10.1016/j.cemconcomp.2019.103365>.
- [151] Plastics: Material-Specific Data | Facts and Figures about Materials, Waste and Recycling | US EPA, (n.d.). <https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data>.
- [152] American Chemistry Council, (n.d.). <https://www.americanchemistry.com/>.
- [153] J. Gertsakis, H. Lewis, Sustainability and the Waste Management Hierarchy – A Discussion Paper, (2003). [http://www.sustainability.vic.gov.au/~media/resources/documents/Publications and Research/Publications/Q - T/Publications Towards Zero Waste Sustainability and the Waste Hierarchy 2003.pdf](http://www.sustainability.vic.gov.au/~media/resources/documents/Publications%20and%20Research/Publications/Q-T/Publications%20Towards%20Zero%20Waste%20Sustainability%20and%20the%20Waste%20Hierarchy%202003.pdf).

- [154] H. Webb, J. Arnott, R. Crawford, E. Ivanova, Plastic Degradation and Its Environmental Implications with Special Reference to Poly(ethylene terephthalate), *Polymers (Basel)*. 5 (2012) 1–18. <https://doi.org/10.3390/polym5010001>.
- [155] F. Puertas, T. Amat, A. Fernández-Jiménez, T. Vázquez, Mechanical and durable behaviour of alkaline cement mortars reinforced with polypropylene fibres, *Cem. Concr. Res.* 33 (2003) 2031–2036. [https://doi.org/10.1016/S0008-8846\(03\)00222-9](https://doi.org/10.1016/S0008-8846(03)00222-9).
- [156] D.A. Silva, A.M. Betioli, P.J.P. Gleize, H.R. Roman, L.A. Gómez, J.L.D. Ribeiro, Degradation of recycled PET fibers in Portland cement-based materials, *Cem. Concr. Res.* 35 (2005) 1741–1746. <https://doi.org/10.1016/j.cemconres.2004.10.040>.
- [157] US EPA, Overview of Greenhouse Gases Nitrous Oxide Emissions, (2016) 2–3. <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>.
- [158] W. Yao, J. Li, K. Wu, Mechanical properties of hybrid fiber-reinforced concrete at low fiber volume fraction, *Cem. Concr. Res.* 33 (2003) 27–30. [https://doi.org/10.1016/S0008-8846\(02\)00913-4](https://doi.org/10.1016/S0008-8846(02)00913-4).
- [159] B.S. Al-Tulaian, M.J. Al-Shannag, A.R. Al-Hozaimy, Recycled plastic waste fibers for reinforcing Portland cement mortar, *Constr. Build. Mater.* 127 (2016) 102–110. <https://doi.org/10.1016/J.CONBUILDMAT.2016.09.131>.
- [160] A.M. López-Buendía, M.D. Romero-Sánchez, V. Climent, C. Guillem, Surface treated polypropylene (PP) fibres for reinforced concrete, *Cem. Concr. Res.* 54 (2013) 29–35. <https://doi.org/10.1016/j.cemconres.2013.08.004>.
- [161] G.A. Khoury, Polypropylene fibres in heated concrete. Part 2: Pressure relief mechanisms and modelling criteria, *Mag. Concr. Res.* 60 (2008) 189–204. <https://doi.org/10.1680/mac.2007.00042>.
- [162] D.P. Bentz, Fibers, Percolation, and Spalling of High-Performance Concrete, 97 (n.d.) 351–359.
- [163] C.G. Han, Y.S. Hwang, S.H. Yang, N. Gowripalan, Performance of spalling resistance of high performance concrete with polypropylene fiber contents and lateral confinement, *Cem. Concr. Res.* 35 (2005) 1747–1753. <https://doi.org/10.1016/j.cemconres.2004.11.013>.
- [164] B. Chen, J. Liu, Residual strength of hybrid-fiber-reinforced high-strength concrete after exposure to high temperatures, *Cem. Concr. Res.* 34 (2004) 1065–1069. <https://doi.org/10.1016/j.cemconres.2003.11.010>.

- [165] C. Thomas, J. Rico, P. Tamayo, F. Ballester, J. Setién, J.A. Polanco, Effect of elevated temperature on the mechanical properties and microstructure of heavy-weight magnetite concrete with steel fibers, *Cem. Concr. Compos.* 103 (2019) 80–88. <https://doi.org/10.1016/j.cemconcomp.2019.04.029>.
- [166] C. Moro, V. Francioso, M. Velay-Lizancos, Nano-TiO₂ effects on high temperature resistance of recycled mortars, *J. Clean. Prod.* 263 (2020). <https://doi.org/10.1016/j.jclepro.2020.121581>.
- [167] Q. Ma, R. Guo, Z. Zhao, Z. Lin, K. He, Mechanical properties of concrete at high temperature-A review, *Constr. Build. Mater.* 93 (2015) 371–383. <https://doi.org/10.1016/j.conbuildmat.2015.05.131>.
- [168] N. Yüzer, F. Aköz, L.D. Öztürk, Compressive strength-color change relation in mortars at high temperature, *Cem. Concr. Res.* 34 (2004) 1803–1807. <https://doi.org/10.1016/j.cemconres.2004.01.015>.
- [169] D.J. Naus, The Effect of Elevated Temperature on Concrete Materials and Structures - a Literature Review., Oak Ridge, TN (United States), 2006. <https://doi.org/10.2172/974590>.
- [170] W. Khaliq, V. Kodur, Thermal and mechanical properties of fiber reinforced high performance self-consolidating concrete at elevated temperatures, *Cem. Concr. Res.* 41 (2011) 1112–1122. <https://doi.org/10.1016/j.cemconres.2011.06.012>.
- [171] ASTM D792-08 Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, (2013). <https://doi.org/10.1520/D0792-13>.
- [172] ASTM C33/C33M, Standard Specification for Concrete Aggregates, Annu. B. ASTM Stand. (2013) 11. <https://doi.org/10.1520/C0033>.
- [173] ASTM, C1437 - Standard test method for flow of hydraulic cement mortar, 2013. <https://doi.org/10.1520/C1437-15>.
- [174] U. Schneider, R. Felicetti, G. Debicki, U. Diederichs, J.M. Franssen, U.M. Jumppanen, G.A. Khoury, S. Leonovich, A. Millard, W.A. Morris, L.T. Phan, P. Pimienta, J.P.C. Rodrigues, E. Schlangen, P. Schwesinger, Y. Zaytsev, Recommendation of RILEM TC 200-HTC: Mechanical concrete properties at high temperatures-modelling and applications : PGeneral presentation, *Mater. Struct. Constr.* 40 (2007) 841–853. <https://doi.org/10.1617/s11527-007-9285-2>.

- [175] R. Vedalakshmi, A.S. Raj, S. Srinivasan, K.G. Babu, Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique, *Thermochim. Acta.* 407 (2003) 49–60. [https://doi.org/10.1016/S0040-6031\(03\)00286-7](https://doi.org/10.1016/S0040-6031(03)00286-7).
- [176] ASTM International, C349-18 Standard Test Method for Compressive Strength of Hydraulic-Cement Mortars (Using Portions of Prisms Broken in Flexure), (2018). <https://doi.org/https://doi.org/10.1520/C0349-18>.
- [177] J. Karlsson, Possibilities of using thermal mass in buildings to save energy, cut power consumption peaks and increase the thermal comfort, Division of Building Materials, LTH, Lund University, 2012.
- [178] R. Lindberg, A. Binamu, M. Teikari, Five-year data of measured weather, energy consumption, and time-dependent temperature variations within different exterior wall structures, *Energy Build.* 36 (2004) 495–501. <https://doi.org/10.1016/j.enbuild.2003.12.009>.
- [179] K.H. Kim, S.E. Jeon, J.K. Kim, S. Yang, An experimental study on thermal conductivity of concrete, *Cem. Concr. Res.* 33 (2003) 363–371. [https://doi.org/10.1016/S0008-8846\(02\)00965-1](https://doi.org/10.1016/S0008-8846(02)00965-1).
- [180] C. Clauser, H. E., Rock Physics and Phase Relations. A Handbook of Physical Constants, in: T. Ahrens (Ed.), American Geophysical Union, Washington, 1995: pp. 105–126. https://www.researchgate.net/publication/256372062_Rock_Physics_and_Phase_Relations_A_Handbook_of_Physical_Constants.
- [181] K. ito Horai, G. Simmons, Thermal conductivity of rock-forming minerals, *Earth Planet. Sci. Lett.* 6 (1969) 359–368. [https://doi.org/10.1016/0012-821X\(69\)90186-1](https://doi.org/10.1016/0012-821X(69)90186-1).
- [182] M.G. Gomes, I. Flores-Colen, L.M. Manga, A. Soares, J. de Brito, The influence of moisture content on the thermal conductivity of external thermal mortars, *Constr. Build. Mater.* 135 (2017) 279–286. <https://doi.org/10.1016/j.conbuildmat.2016.12.166>.
- [183] E. Mňahončáková, M. Jiříčková, Z. Pavlík, L. Fiala, P. Rovnaníková, P. Bayer, R. Černý, Effect of moisture on the thermal conductivity of a cementitious composite, *Int. J. Thermophys.* 27 (2006) 1228–1240. <https://doi.org/10.1007/s10765-006-0073-y>.
- [184] W. Zhang, H. Min, X. Gu, Y. Xi, Y. Xing, Mesoscale model for thermal conductivity of concrete, *Constr. Build. Mater.* 98 (2015) 8–16. <https://doi.org/10.1016/j.conbuildmat.2015.08.106>.

- [185] CRC, Handbook of Chemistry and Physics 101st Edition, (2020).
<http://hbcponline.com/faces/contents/ContentsSearch.xhtml;jsessionid=D5515C4F93EAF69A9CEE1C32168E65B2>.
- [186] J.A. Clarke, P.P. Yaneske, A rational approach to the harmonisation of the thermal properties of building materials, *Build. Environ.* 44 (2009) 2046–2055.
<https://doi.org/10.1016/j.buildenv.2009.02.008>.
- [187] M. Jakob, *Heat transfer - Volume 1*, Wiley, New York, 1949.
- [188] H.B. Jespersen, Thermal conductivity of moist materials: its measurement, *J. Inst. Heat. Vent. Eng.* 21 (1953) 157–174.
- [189] A. Siwińska, H. Garbalińska, Thermal conductivity coefficient of cement-based mortars as air relative humidity function, *Heat Mass Transf. Und Stoffuebertragung.* 47 (2011) 1077–1087. <https://doi.org/10.1007/s00231-011-0772-1>.
- [190] A.A. Abdou, I.M. Budaiwi, Comparison of Thermal Conductivity Measurements of Building Insulation Materials under Various Operating Temperatures, *J. Build. Phys.* 29 (2005). <https://doi.org/10.1177/1744259105056291>.
- [191] F. Ochs, W. Heidemann, H. Müller-Steinhagen, Effective thermal conductivity of moistened insulation materials as a function of temperature, *Int. J. Heat Mass Transf.* 51 (2008) 539–552. <https://doi.org/10.1016/j.ijheatmasstransfer.2007.05.005>.
- [192] H. Zhao, F. Liu, H. Yang, Thermal properties of coarse RCA concrete at elevated temperatures, *Appl. Therm. Eng.* 140 (2018) 180–189.
<https://doi.org/10.1016/J.APPLTHERMALENG.2018.05.032>.
- [193] C. Laneyrie, A.L. Beaucour, M.F. Green, R.L. Hebert, B. Ledesert, A. Noumowe, Influence of recycled coarse aggregates on normal and high performance concrete subjected to elevated temperatures, *Constr. Build. Mater.* 111 (2016) 368–378.
<https://doi.org/10.1016/J.CONBUILDMAT.2016.02.056>.
- [194] ISO, ISO 10456:2007 - Building materials and products — Hygrothermal properties — Tabulated design values and procedures for determining declared and design thermal values, (2007). <https://www.iso.org/standard/40966.html>.
- [195] BS EN 1745:2020 - Masonry and masonry products - Methods for determining thermal properties, (2020). <https://standards.iteh.ai/catalog/standards/cen/32cd5334-5e9c-4ab2-a08b-dda449ae7458/en-1745-2020>.

- [196] M. Bravo, J. Brito, L. Evangelista, Thermal Performance of Concrete with Recycled Aggregates from CDW Plants, *Appl. Sci.* 7 (2017) 740. <https://doi.org/10.3390/app7070740>.
- [197] L. Zhu, J. Dai, G. Bai, F. Zhang, Study on thermal properties of recycled aggregate concrete and recycled concrete blocks, *Constr. Build. Mater.* 94 (2015) 620–628. <https://doi.org/10.1016/j.conbuildmat.2015.07.058>.
- [198] B. Cantero, M. Bravo, J. de Brito, I.F.S. del Bosque, C. Medina, Thermal performance of concrete with recycled concrete powder as partial cement replacement and recycled CDW aggregate, *Appl. Sci.* 10 (2020). <https://doi.org/10.3390/app10134540>.
- [199] I.J.A. Callejas, L.C. Durante, A.S. de Oliveira, Thermal resistance and conductivity of recycled construction and demolition waste (RCDW) concrete blocks, *Rev. Esc. Minas.* 70 (2017) 167–173. <https://doi.org/10.1590/0370-44672015700048>.
- [200] M. Fenollera, J. Míguez, I. Goicoechea, J. Lorenzo, Experimental Study on Thermal Conductivity of Self-Compacting Concrete with Recycled Aggregate, *Materials (Basel)*. 8 (2015) 4457–4478. <https://doi.org/10.3390/ma8074457>.
- [201] I. Marie, Thermal conductivity of hybrid recycled aggregate – Rubberized concrete, *Constr. Build. Mater.* 133 (2017) 516–524. <https://doi.org/10.1016/j.conbuildmat.2016.12.113>.
- [202] A. Adesina, Overview of the influence of waste materials on the thermal conductivity of cementitious composites, *Clean. Eng. Technol.* 2 (2021) 100046. <https://doi.org/10.1016/j.clet.2021.100046>.
- [203] J.Z. Xiao, Z.W. Song, F. Zhang, An experimental study on thermal conductivity of concrete, *Jianzhu Cailiao Xuebao/Journal Build. Mater.* 13 (2010) 17–21. <https://doi.org/10.3969/j.issn.1007-9629.2010.01.004>.
- [204] F.M. Díez Ramírez, F.B. Muñoz, E.L. López, A.V. Polanco, Thermal evaluation of structural concretes for construction of biodigesters, *Energy Build.* 58 (2013) 310–318. <https://doi.org/10.1016/j.enbuild.2012.11.036>.
- [205] Y. Sargam, K. Wang, J.E. Alleman, Effects of Modern Concrete Materials on Thermal Conductivity, (2020). [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0003026](https://doi.org/10.1061/(ASCE)MT.1943-5533.0003026).
- [206] J. de Brito, N. Saikia, Recycled Aggregate in Concrete: Use of Industrial, Construction and Demolition Waste, *Green Energy Technol.* 54 (2013). <https://doi.org/10.1007/978-1-4471-4540-0>.

- [207] Recycling Concrete Pavements ENGINEERING BULLETIN EB043P EB043P, 2009. www.pavement.com.
- [208] K.P. Verian, N. Whiting, J. Olek, J. Jain, M. Snyder, Using Recycled Concrete as Aggregate in Concrete Pavements to Reduce Materials Cost, 2013. <https://doi.org/10.5703/1288284315220>.
- [209] R.C. Valore, Calculations of U-Values of Hollow Concrete Masonry, *Concr. Int.* 2 (1980) 40–63.
- [210] S. Real, J.A. Bogas, M. da G. Gomes, B. Ferrer, Thermal conductivity of structural lightweight aggregate concrete, *Mag. Concr. Res.* 68 (2016) 798–808. <https://doi.org/10.1680/jmacr.15.00424>.
- [211] N.S. Billington, *Thermal Properties of Buildings*, Cleaver-Hume Press, London, 1952.
- [212] ASTM International, C33/C33M-18 Standard Specification for Concrete Aggregates, (2018). https://doi.org/https://doi.org/10.1520/C0033_C0033M-18.
- [213] ASTM International, C136/C136M-19 Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates, (2016). https://doi.org/https://doi.org/10.1520/C0136_C0136M-19.
- [214] ASTM International, C128-15 Standard Test Method for Relative Density (Specific Gravity) and Absorption of Fine Aggregate, (2015). <https://doi.org/https://doi.org/10.1520/C0128-15>.
- [215] ASTM International, C642-13 Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, (2013). <https://doi.org/https://doi.org/10.1520/C0642-13>.
- [216] ASTM International, C348-20 Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars, (2020). <https://doi.org/https://doi.org/10.1520/C0348-20>.
- [217] F.P. Incropera, D.P. DeWitt, *Introduction to heat transfer*, Wiley, 1985.
- [218] ASTM International, ASTM C1058-15 Standard Practice for Selecting Temperatures for Evaluating and Reporting Thermal Properties of Thermal Insulation 1, (2015). https://doi.org/https://doi.org/10.1520/C1058_C1058M-10R15.
- [219] Z. Li, D. Lu, X. Gao, Optimization of mixture proportions by statistical experimental design using response surface method - A review, *J. Build. Eng.* 36 (2021). <https://doi.org/10.1016/j.job.2020.102101>.

- [220] L. Li, B.J. Zhan, J. Lu, C.S. Poon, Systematic evaluation of the effect of replacing river sand by different particle size ranges of fine recycled concrete aggregates (FRCA) in cement mortars, *Constr. Build. Mater.* 209 (2019) 147–155. <https://doi.org/10.1016/J.CONBUILDMAT.2019.03.044>.
- [221] Z. Zhao, S. Remond, D. Damidot, W. Xu, Influence of fine recycled concrete aggregates on the properties of mortars, *Constr. Build. Mater.* 81 (2015) 179–186. <https://doi.org/10.1016/J.CONBUILDMAT.2015.02.037>.
- [222] Cement production global 2021 | Statista, (2021). <https://www.statista.com/statistics/1087115/global-cement-production-volume/>.
- [223] R.M. Andrew, G.P. Peters, The Global Carbon Project's fossil CO₂ emissions dataset, (2021). <https://doi.org/10.5281/ZENODO.5569235>.
- [224] M.S. Imbabi, C. Carrigan, S. McKenna, Trends and developments in green cement and concrete technology, *Int. J. Sustain. Built Environ.* 1 (2012) 194–216. <https://doi.org/10.1016/J.IJSBE.2013.05.001>.
- [225] A. Adesina, Recent advances in the concrete industry to reduce its carbon dioxide emissions, *Environ. Challenges*. 1 (2020) 100004. <https://doi.org/10.1016/J.ENVC.2020.100004>.
- [226] Asocaña, Más que azúcar, una fuente de energía renovable para el país, *Sect. Agroindustrial La Caña*. (2017) 10.
- [227] J.T. Kolawole, A.J. Babafemi, E. Fanijo, S. Chandra Paul, R. Combrinck, State-of-the-art review on the use of sugarcane bagasse ash in cementitious materials, *Cem. Concr. Compos.* 118 (2021) 103975. <https://doi.org/10.1016/j.cemconcomp.2021.103975>.
- [228] S. Pratap, M. Jawaid, M. Chandrasekar, K. Senthilkumar, B. Yadav, N. Saba, S. Siengchin, Sugarcane wastes into commercial products: Processing methods, production optimization and challenges, *J. Clean. Prod.* 328 (2021) 129453. <https://doi.org/10.1016/j.jclepro.2021.129453>.
- [229] M.R. Cherubin, M.R.A. Franchi, R.P. de Lima, M.T. de Moraes, F.B. da Luz, Sugarcane straw effects on soil compaction susceptibility, *Soil Tillage Res.* 212 (2021) 105066. <https://doi.org/10.1016/j.still.2021.105066>.
- [230] F. and A.O. of the U.N. (FAO), FAOSTAT - Production quantities of Sugar cane by country, (2020). <https://www.fao.org/faostat/en/#data/QCL/visualize>.

- [231] Global sugar cane production 2020 | Statista, (2020). <https://www.statista.com/statistics/249604/sugar-cane-production-worldwide/>.
- [232] G.M. de Almeida, G.T. Pereira, A.S.R. de S. Bahia, K. Fernandes, J. Marques Júnior, Machine learning in the prediction of sugarcane production environments, *Comput. Electron. Agric.* 190 (2021) 106452. <https://doi.org/10.1016/j.compag.2021.106452>.
- [233] S. Staples, M., Malina, R. & Barrett, The limits of bioenergy for mitigating global life-cycle greenhouse gas emissions from fossil fuels., *Nat Energy.* 2 (2017) 1–8. <https://doi.org/10.1038/nenergy.2016.202>.
- [234] N.R.D. de Souza, D.G. Duft, K.M.B. Bruno, D. de S. Henzler, T.L. Junqueira, O. Cavalett, T.A.D. Hernandez, Unraveling the potential of sugarcane electricity for climate change mitigation in Brazil, *Resour. Conserv. Recycl.* 175 (2021). <https://doi.org/10.1016/j.resconrec.2021.105878>.
- [235] V. Jittin, S.N. Minnu, A. Bahurudeen, Potential of sugarcane bagasse ash as supplementary cementitious material and comparison with currently used rice husk ash, *Constr. Build. Mater.* 273 (2021) 121679. <https://doi.org/10.1016/j.conbuildmat.2020.121679>.
- [236] K. Montakarnthiwong, N. Chusilp, W. Tangchirapat, C. Jaturapitakkul, Strength and heat evolution of concretes containing bagasse ash from thermal power plants in sugar industry, *Mater. Des.* 49 (2013) 414–420. <https://doi.org/10.1016/j.matdes.2013.01.031>.
- [237] J.M. Medina, I.F. Sáez del Bosque, M. Frías, M.I. Sánchez de Rojas, C. Medina, Design and properties of eco-friendly binary mortars containing ash from biomass-fuelled power plants, *Cem. Concr. Compos.* 104 (2019) 103372. <https://doi.org/10.1016/j.cemconcomp.2019.103372>.
- [238] B. Yogitha, M. Karthikeyan, M.G. Muni Reddy, Progress of sugarcane bagasse ash applications in production of Eco-Friendly concrete - Review, *Mater. Today Proc.* 33 (2020) 695–699. <https://doi.org/10.1016/j.matpr.2020.05.814>.
- [239] V.D. Katare, M. V. Madurwar, Process standardization of sugarcane bagasse ash to develop durable high-volume ash concrete, *J. Build. Eng.* 39 (2021) 102151. <https://doi.org/10.1016/j.jobe.2021.102151>.
- [240] R.N. González-Kunz, P. Pineda, A. Bras, L. Morillas, Plant biomass ashes in cement-based building materials. Feasibility as eco-efficient structural mortars and grouts, *Sustain. Cities Soc.* 31 (2017) 151–172. <https://doi.org/10.1016/j.scs.2017.03.001>.

- [241] G. Athira, A. Bahurudeen, P.K. Sahu, M. Santhanam, P. Nanthagopalan, S. Lalu, Effective utilization of sugar industry waste in Indian construction sector: A geospatial approach, *J. Mater. Cycles Waste Manag.* 22 (2020) 724–736. <https://doi.org/10.1007/s10163-019-00963-w>.
- [242] P.G. Quedou, E. Wirquin, C. Bokhoree, Sustainable concrete: Potency of sugarcane bagasse ash as a cementitious material in the construction industry, *Case Stud. Constr. Mater.* 14 (2021) e00545. <https://doi.org/10.1016/j.cscm.2021.e00545>.
- [243] P. Jha, A.K. Sachan, R.P. Singh, Agro-waste sugarcane bagasse ash (ScBA) as partial replacement of binder material in concrete, *Mater. Today Proc.* 44 (2021) 419–427. <https://doi.org/10.1016/j.matpr.2020.09.751>.
- [244] F.L. Barbosa, G.C. Cordeiro, Partial cement replacement by different sugar cane bagasse ashes: Hydration-related properties, compressive strength and autogenous shrinkage, *Constr. Build. Mater.* 272 (2021) 8–11. <https://doi.org/10.1016/j.conbuildmat.2020.121625>.
- [245] International Organization for Standardization (ISO), ISO 14040:2006 - Environmental management - Life cycle assessment - Principles and framework, (2006). <https://www.iso.org/standard/37456.html>.
- [246] LIFE-CYCLE ASSESSMENT | Science Inventory | US EPA, (2008). https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&count=10000&dirEntryId=156704&searchall=&showcriteria=2&simplesearch=0&timstype=.
- [247] E.M.R. Fairbairn, T.P. De Paula, G.C. Cordeiro, B.B. Americano, R.D. Toledo Filho, Evaluation of partial clinker replacement by sugar cane bagasse ash: CO₂ emission reductions and potential for carbon credits, *Rev. IBRACON Estruturas e Mater.* 5 (2012) 229–251. <https://doi.org/10.1590/S1983-41952012000200007>.
- [248] J.B. Jamora, S.E.L. Gudia, A.W. Go, M.B. Giduquio, J.W.A. Orilla, M.E. Loretero, Potential reduction of greenhouse gas emission through the use of sugarcane ash in cement-based industries: A case in the Philippines, *J. Clean. Prod.* 239 (2019). <https://doi.org/10.1016/J.JCLEPRO.2019.118072>.
- [249] S.S. Sinoh, Z. Ibrahim, F. Othman, L.M. Kuang, A. Zaki, Life Cycle Assessment of Sugarcane Bagasse Ash as Partial Cement Replacement in Concrete, *Proc. 4th Int. Conf. Sustain. Innov. 2020–Technology, Eng. Agric. (ICoSITEA 2020)*. 199 (2021) 144–150. <https://doi.org/10.2991/AER.K.210204.028>.

- [250] C. Moro, V. Francioso, M. Schager, M. Velay-Lizancos, M. Schrager, M. Velay-Lizancos, TiO₂ nanoparticles influence on the environmental performance of natural and recycled mortars: A life cycle assessment, *Environ. Impact Assess. Rev.* 84 (2020) 106430.
- [251] A. Chajec, A. Chowaniec, A. Królicka, Ł. Sadowski, A. Żak, M. Piechowka-Mielnik, B. Šavija, Engineering of green cementitious composites modified with siliceous fly ash: Understanding the importance of curing conditions, *Constr. Build. Mater.* 313 (2021) 125209. <https://doi.org/10.1016/j.conbuildmat.2021.125209>.
- [252] J. Yang, J. Fan, B. Kong, C.S. Cai, K. Chen, Theory and application of new automated concrete curing system, *J. Build. Eng.* 17 (2018) 125–134. <https://doi.org/10.1016/j.job.2018.02.009>.
- [253] Z. Zhang, Q. Wang, H. Chen, Properties of high-volume limestone powder concrete under standard curing and steam-curing conditions, *Powder Technol.* 301 (2016) 16–25. <https://doi.org/10.1016/j.powtec.2016.05.054>.
- [254] S. Hamzah, E. Aprianti, The Effect of Supplementary Cementitious Material Using Thermal Method, 2017. https://doi.org/10.1007/978-981-10-5433-4_10.
- [255] T. Kim, K.L. Rens, Concrete Maturity Method Using Variable Temperature Curing for Normal and High-Strength Concrete. I: Experimental Study, *J. Mater. Civ. Eng.* 20 (2008) 727–734. [https://doi.org/10.1061/\(ASCE\)0899-1561\(2008\)20:12\(727\)](https://doi.org/10.1061/(ASCE)0899-1561(2008)20:12(727)).
- [256] S. Yousuf, P. Shafigh, Z. Ibrahim, H. Hashim, M. Panjehpour, Crossover effect in cement-based materials: A review, *Appl. Sci.* 9 (2019). <https://doi.org/10.3390/AP9142776>.
- [257] P. Jiang, L. Jiang, J. Zha, Z. Song, Influence of temperature history on chloride diffusion in high volume fly ash concrete, *Constr. Build. Mater.* 144 (2017) 677–685. <https://doi.org/10.1016/j.conbuildmat.2017.03.225>.
- [258] M. Wang, Y. Xie, G. Long, C. Ma, X. Zeng, Microhardness characteristics of high-strength cement paste and interfacial transition zone at different curing regimes, *Constr. Build. Mater.* 221 (2019) 151–162. <https://doi.org/10.1016/j.conbuildmat.2019.06.084>.
- [259] T. Murugesan, R. Vidjeapriya, A. Bahurudeen, Reuse of Silica Rich Sugarcane Bagasse Ash in Concrete and Influence of Different Curing on the Performance of Concrete, *Silicon.* (2021). <https://doi.org/10.1007/s12633-021-01089-1>.

- [260] A. Rajasekar, K. Arunachalam, M. Kottaisamy, V. Saraswathy, Durability characteristics of Ultra High Strength Concrete with treated sugarcane bagasse ash, *Constr. Build. Mater.* 171 (2018) 350–356. <https://doi.org/10.1016/j.conbuildmat.2018.03.140>.
- [261] ASTM, ASTM C618—17a Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, (n.d.) 2017. https://compass.astm.org/EDIT/html_annot.cgi?C618+17a.
- [262] International Organization for Standardization (ISO), ISO 14044:2006 Environmental management - Life Cycle Assessment - Requirements and Guidelines, (2006). <https://www.iso.org/standard/38498.html>.
- [263] European Platform on Life Cycle Assessment, (2018). <https://eplca.jrc.ec.europa.eu/>.
- [264] S. Marinković, J. Dragaš, I. Ignjatović, N. Tošić, Environmental assessment of green concretes for structural use, *J. Clean. Prod.* 154 (2017) 633–649. <https://doi.org/10.1016/J.JCLEPRO.2017.04.015>.
- [265] M.L. Marceau, M.A. Nisbet, M.G. Vangeem, Lyfe Cycle Inventory of Portland Cement Concrete, (2007).
- [266] R. Kurda, J.D. Silvestre, J. de Brito, Life cycle assessment of concrete made with high volume of recycled concrete aggregates and fly ash, *Resour. Conserv. Recycl.* 139 (2018) 407–417. <https://doi.org/10.1016/J.RESCONREC.2018.07.004>.
- [267] P. Rodrigues, J.D. Silvestre, I. Flores-Colen, C.A. Viegas, J. de Brito, R. Kurad, M. Demertzi, Methodology for the Assessment of the Ecotoxicological Potential of Construction Materials, *Mater.* 2017, Vol. 10, Page 649. 10 (2017) 649. <https://doi.org/10.3390/MA10060649>.
- [268] M. Ryberg, M.D.M. Vieira, M. Zgola, J. Bare, R.K. Rosenbaum, Updated US and Canadian normalization factors for TRACI 2.1, *Clean Technol. Environ. Policy.* 16 (2014) 329–339. <https://doi.org/10.1007/S10098-013-0629-Z>.
- [269] T. Kim, S. Tae, C.U. Chae, V.W.Y. Tam, K.N. Le, L. Shen, Analysis of Environmental Impact for Concrete Using LCA by Varying the Recycling Components, the Compressive Strength and the Admixture Material Mixing, *Sustain.* 2016, Vol. 8, Page 389. 8 (2016) 389. <https://doi.org/10.3390/SU8040389>.

- [270] A.J. Haagen-Smit, C.E. Bradley, M.M. Fox, Ozone Formation in Photochemical Oxidation of Organic Substances, *Ind. Eng. Chem.* 45 (2002) 2086–2089.
<https://doi.org/10.1021/IE50525A044>.
- [271] I. Dincer, A. Abu-Rayash, Sustainability modeling, *Energy Sustain.* (2020) 119–164.
<https://doi.org/10.1016/B978-0-12-819556-7.00006-1>.
- [272] R. Wetzel, *Limnology - Lake and River Ecosystems*, Academic Press, 2001.

PUBLICATIONS

Publications related with the Dissertation

Francioso V., Moro C., Martinez-Lage I., Velay-Lizancos M., “*Curing temperature: A key factor that changes the effect of TiO₂ nanoparticles on mechanical properties, calcium hydroxide formation and pore structure of cement mortars*”. Cement and Concrete Composites, Vol. 104, (2019), 103374. <https://doi.org/10.1016/j.cemconcomp.2019.103374>

Francioso V., Moro C., Castillo A., Velay-Lizancos M., “*Effect of elevated temperature on flexural behavior and fibers-matrix bonding of recycled PP fiber-reinforced cementitious composite*”. Construction and Building Materials, Vol. 269, (2021), 121243. <https://doi.org/10.1016/j.conbuildmat.2020.121243>

Moro C., Francioso V., Velay-Lizancos M., “*Nano-TiO₂ effects on high temperature resistance of recycled mortars*”. Journal of Cleaner Production, Vol. 263, (2020), 121581. <https://doi.org/10.1016/j.jclepro.2020.121581>

Francioso V., Moro C., Velay-Lizancos M., “*Effect of recycled concrete aggregate (RCA) on mortar’s thermal conductivity susceptibility to variation of moisture content and ambient temperature*”. Journal of Building Engineering, Vol. 43, (2021), 103208. <https://doi.org/10.1016/j.jobbe.2021.103208>

Francioso V., Lopez-Arias M., Moro C., Velay-Lizancos M., “*Impact of curing temperature on the sustainability of sugarcane bagasse ash as a partial replacement of cement in mortars: an LCA*”. [To be submitted in April 2022]

Other Publications

Moro C., Francioso V., Schrager M., Velay-Lizancos M., “*TiO₂ nanoparticles influence on the environmental performance of natural and recycled mortars: A life cycle assessment*”. Environ. Impact Assess. Rev., Vol. 84, (2020), 106430. <https://doi.org/10.1016/j.eiar.2020.106430>

Moro C., El Fil H., Francioso V., Velay-Lizancos M., “*Influence of water-to-binder ratio on the optimum percentage of nano-TiO₂ addition in terms of compressive strength of mortars: A laboratory and virtual experimental study based on ANN model*”. Construction and Building Materials, Vol. 267, (2021), 120960. <https://doi.org/10.1016/j.conbuildmat.2020.120960>

Moro C., Francioso V., Velay-Lizancos M., “*Modification of CO₂ capture and pore structure of hardened cement paste made with nano-TiO₂ addition: influence of water-to-cement ratio and CO₂ exposure age*”. Construction and Building Materials, Vol. 275, (2021), 122131. <https://doi.org/10.1016/j.conbuildmat.2020.122131>

Moro C., Francioso V., Velay-Lizancos M., “*Impact of nano-TiO₂ addition on the reduction of net CO₂ emissions of cement pastes after CO₂ curing*”. Cement and Concrete Composites, Vol. 123, (2021), 104160. <https://doi.org/10.1016/j.cemconcomp.2021.104160>

Moro C., Francioso V., Lopez-Arias M., Velay-Lizancos M., “*Modification of self-cleaning activity on cement pastes containing nano-TiO₂ due to CO₂ curing*”. Construction and Building Materials, Vol. 330, (2022), 127185. <https://doi.org/10.1016/j.conbuildmat.2022.127185>