Chapter 1
Introduction

1.1 Context

The Earth harbours finite resources within its boundaries. The continual exploitation of resources raises concerns about long-term viability and sustainability. The way we use and consume these resources contributes to environmental degradation, pollution, and greenhouse gas emissions, thereby impacting climate change. Maintaining the current standard of living and bringing the developing world to the same level requires a greater focus on preserving and protecting the natural environment [1]. Brundtland, in 1987, defined sustainable development as the development that meets the needs of the present without compromising the ability of future generations to meet their own needs [2].

One of the most widely used materials in the world is concrete, with an estimated 27.3 billion tonnes produced in 2015, averaging about 1.6 m^3 per person on Earth [3]. However, the production of Portland cement, a crucial binding material in concrete, is responsible for almost 80% of the total CO_2 emissions associated with concrete, contributing to 5-7% of the world's total CO_2 emissions [4-9]. The production of one tonne of Portland cement causes the release of one tonne of CO_2 into the atmosphere, a greenhouse gas that contributes to global warming [10]. The demand for Portland cement is predicted to rise by almost 200% by 2050 compared to 2010 levels, resulting in an annual production of 6,000 million tonnes [11].

Due to this significant size, the concrete industry substantially impacts the environment. However, it is worth noting that concrete is intrinsically eco-friendly, whereas Portland cement is not. To enhance the sustainability of the construction industry, it is imperative to utilise concrete with a focus on minimising reliance on Portland cement.

The primary sustainability challenges in the coming decades involve developing and producing concrete with reduced clinkers emitting less CO_2 than traditional methods while providing the same reliability but significantly better durability [12]. Eco-efficiency is impacted substantially by the durability of building material, with Peris Mora [13] suggesting that increasing concrete durability from 50 years to 500 years could reduce environmental impact by up to 10 times. By increasing the compressive strength of concrete, Pacheco et al. [11] reported that the use of reinforced steel could be reduced by as much as 50%. Thus, durable and high-strength concrete is a primary concern for future materials and eco-efficiency [2].

The mounting apprehensions about greenhouse gas emissions and the depletion of natural resources that arise from extensive cement production are the primary drivers for the constant advancement of concrete technology [14]. Therefore, there has been a growing global interest in the research to focus on finding appropriate supplementary cementitious materials (SCMs) that can partially or wholly replace Ordinary Portland Cement (OPC) without compromising concrete's strength, workability, and durability requirements. These materials can be either natural or artificial. Natural SCMs include pozzolanic materials (e.g., volcanic ash, diatomaceous earth, and rice husk ash), calcined clays (e.g., kaolin and metakaolin), and limestone. Artificial SCMs include fly ash, ground granulated blast furnace slag, and silica fume. These materials are by-products of industrial processes and are often used as replacements for Portland cement in concrete.

1.2 Need for natural pozzolans

Fly ash and slag are industrial by-products that are produced as a result of burning coal and steel production, respectively. In recent years, there has been a trend towards reducing the use of coal for energy production due to concerns about climate change and air pollution. Natural SCMs are generally preferred over artificial ones for several reasons. Natural SCMs have a lower embodied energy than artificial SCMs, as they do not require energy-intensive industrial processes to produce.

Numerous novel forms of concrete have been created throughout the years, ranging from mineral-admixed concrete to nanoparticle-admixed concrete, all to enhance its compressive strength and refine its functional features and efficiency. The mounting apprehensions about greenhouse gas emissions and the depletion of natural resources that arise from extensive cement production are the primary drivers for the constant advancement of concrete technology [14]. Compared to other SCMs, metakaolin (MK) provides extra advantages due to its lower processing temperature, reduced greenhouse gas emissions, and smaller embodied energy [15,16].

1.3 Need for nanoparticles

Nanotechnology in concrete has also become an essential topic in sustainable development, as it offers several benefits, such as increased durability, strength, and reduced environmental impact. The concept of packing particles at the nanoscale has led researchers to focus on nanoparticles to improve the strength, durability, and processing characteristics of cementitious composites [17]. Nanoparticles are particles with at least one dimension less than 100 nanometers. RILEM Technical Committee 197-Nanotechnology in Construction Materials (TC 197-NCM) published a report exploring the utilisation of nanoparticles to enhance the mechanical and durable attributes of cementitious composites [18]. The application of nanoscience and nanotechnology in cementitious composites has been actively researched since the late 1980s, spanning nearly two decades [19]. Nanomaterials can deliver superior properties and functionalities, which can heighten the mechanical and durability properties of cementitious composites [20-24]. The nanometallic and non-metallic oxide cementitious composites were initially employed to modify or enhance the properties of cementitious materials [25]. However, NS, or nano-sized silicon dioxide, has gained significant attention in the construction industry due to its high pozzolanic activity and subsequent enhancement in the mechanical and durability properties [26]. Compared to conventional mineral admixtures, the superior filling effect and particle size distribution of NS-admixed concrete can result in improved performance; hence, NS has attracted the attention of researchers [30-34].

1.4 Need for ternary blended composition of concrete mix

Using ternary blends comprising cement and two SCMs enhances the sustainability of concrete mixtures. This approach creates superior-quality concrete with high mechanical and durability properties and reduced cement content, decreasing economic, environmental, and social impacts [27,28].

Therefore, combining MK and NS particles in concrete can result in a synergistic effect, where the combined use of these materials can provide better performance and properties than using them separately. This can lead to more sustainable and cost-effective concrete construction, a crucial factor in modern construction practices.

1.5 Objective of the study

Many previous studies [29–36] focused on the effect of MK and NS separately on the mechanical properties and durability of concrete. However, the effects of combining MK and NS in concrete have not been thoroughly examined. The strength of concrete partially replaced with MK is influenced by three mechanisms: the filler effect, the acceleration of OPC hydration, and the pozzolanic reaction [37]. The NS particles, however, with their high surface area, cause i). creation of additional sites for the CSH-gel nucleation, acceleration of the kinetics of C3S hydration and the formation of CSH-gel, which leads to a decrease in capillary pore volume [38-41], ii). pozzolanic reaction and formation of additional volume of CSH gel [38-40], iii). acceleration of the rate of polymerisation of silicon-oxygen tetrahedron (SiO_4) and degree of its polymerisation, which leads to an increase in the ordering of structure of the CSH-gel and subsequent increase in the volume packing density of CSH gel granules, reducing gel microporosity [25,38,42,43], iv). core-shell effect of NS nanoparticles [38,42,43] and v). improvement of the characteristics of interfacial transition zone ITZ [38,42,43].

The research addresses several key objectives in the study of MK and NS concrete. These objectives are structured to comprehensively understand the impact of these alternative cementitious materials on the performance and properties of concrete. The primary objectives are as follows:

Investigation of mechanical properties and durability performance:

- Examine the combined influence of MK and NS when partially replacing OPC in the concrete matrix.
- Assess the effects on mechanical properties, including early age and long-term compressive strength, split tensile strength, and flexural strength.
- Investigate durability performance by evaluating resistance against carbonation, water absorption, and acid attack.

Thermal stability analysis:

- Examine the thermal stability of MK and NS incorporated concrete by subjecting it to temperatures up to 800°C with 150°C intervals.
- Analyse the residual compressive strength after exposure to various temperatures.
- Study surface cracking and spalling of concrete under thermal stress.

Microstructural analysis:

- Conduct a comprehensive microstructural analysis using various techniques, including X-ray diffraction (XRD), thermogravimetric (TG) analysis, Brunauer-Emmett-Teller (BET) analysis for surface area, Barrett-Joyner-Halenda (BJH) Pore size and volume analyses, and scanning electron microscopy (SEM).
- Focus on investigating hydrated phases and morphology to gain insights into the concrete's internal structure.

Eco-efficiency assessment:

- Compare the eco-efficiency of binary and ternary MK and NS concrete compositions with normal concrete.

- Evaluate the eco-efficiency in terms of binder intensity and CO_2 intensity to understand the environmental impact of these alternative materials.

Economic evaluation:

- Assess the economy index of both binary and ternary MK and NS concrete compositions.
- Compare the economic aspects of MK and NS concrete with normal concrete, providing insights into the cost-effectiveness of these alternatives.

By addressing these objectives, the research aims to contribute valuable insights into utilising MK and NS as alternative cementitious materials, considering both performance and sustainability.

1.6 Experimental program

The research program was structured into two phases. In the first phase, the focus was on experiments with mortars incorporating MK and NS. Subsequently, the second phase centred on experiments involving concrete mixes incorporating MK and NS components.

In the first phase of the experimental program, sixteen OPC, MK and NS mortar compositions were prepared. Other than the reference mortar of OPC, mortars were categorised into three groups: two binary groups and a ternary group. The first two binary mixtures were produced by replacing OPC with 10, 15, and 20 wt.% of MK and 1.5, 3, and 4.5 wt.% of solid SiO_2 nanoparticles. The third set of compositions involved ternary blends, incorporating MK and NS in varying replacement levels of 10, 15, and 20 wt.%

for MK and 1.5, 3, and 4.5 wt.% for NS. Subsequently, the mortar cubes were tested for compressive strength after 3, 7, 28, and 56 days of curing.

To streamline the selection of compositions for the subsequent investigation on concrete in the second phase of the research, the dosage of MK and NS was determined based on the pozzolanic efficiency (k-factor) derived from the compressive strength of the mortars.

Compositions of MK and NS selected from the first phase were utilised for creating concrete mixes in the subsequent experimental phase. This involved a reference mix of OPC, four binary blends of MK (10%) and NS (1.5%, 3%, and 4.5%), and three ternary blends. This resulted in a total of eight distinct concrete compositions. These mixes underwent testing for various mechanical properties, including compressive strength, split tensile strength, and flexural strength. Additionally, evaluations were conducted for durability parameters such as carbonation resistance, water absorption, resistance to acid attack, and the impact of elevated temperatures.

The eco-efficiency and cost index was assessed to evaluate the effectiveness of the concrete mixes in sustainability and economy. The analysis was based on mechanical properties, particularly compressive strength and durability performance, specifically carbonation resistance.

1.7 Structure of the thesis

Chapter 2 comprehensively surveys pertinent scholarly works on utilising MK and NS as additives in mortar and concrete formulations.

Chapter 3 provides an elaborate exposition, encompassing materials employed, methodologies applied, and the experimental approach undertaken to evaluate mortar specimens. This includes detailed insights into the composition of raw materials, procedures for sample preparation, stipulated curing conditions, and methodologies employed for characterising samples.

The ensuing Chapter 4 is dedicated to the presentation and discourse of findings regarding compressive strength of mortars, their respective pozzolanic efficiency and their thermal stability. This chapter analyses the repercussions of elevated temperatures on various facets, encompassing residual compressive strength, heat resistance, surface cracking, spalling, and mass loss.

Chapter 5 furnishes an in-depth exposition of the materials employed, methodologies adopted, and the experimental framework undertaken to assess concrete specimens. This entails an intricate dissection of raw material composition, specimen preparation protocols, curing strategies, and techniques for microstructural analyses of concretes.

In continuation, Chapter 6 is dedicated to the presentation and comprehensive analysis of mechanical properties and durability parameters exhibited by concrete specimens incorporating MK and NS. This encompasses discussions on compressive strength, split tensile strength, flexural strength, carbonation, acid-induced deterioration and water absorption. This chapter also discusses the effect of elevated temperatures on various facets, encompassing compressive strength, heat resistance, surface cracking, spalling, mass loss, etc.

Chapter 7 explores the eco-efficiency and economic efficiency aspects of employing MK and NS blended concrete.

Chapter 8 presents the key findings obtained from the investigation on concrete and future scope of studies.

The schematic of the thesis structure is shown in Figure 1.1.

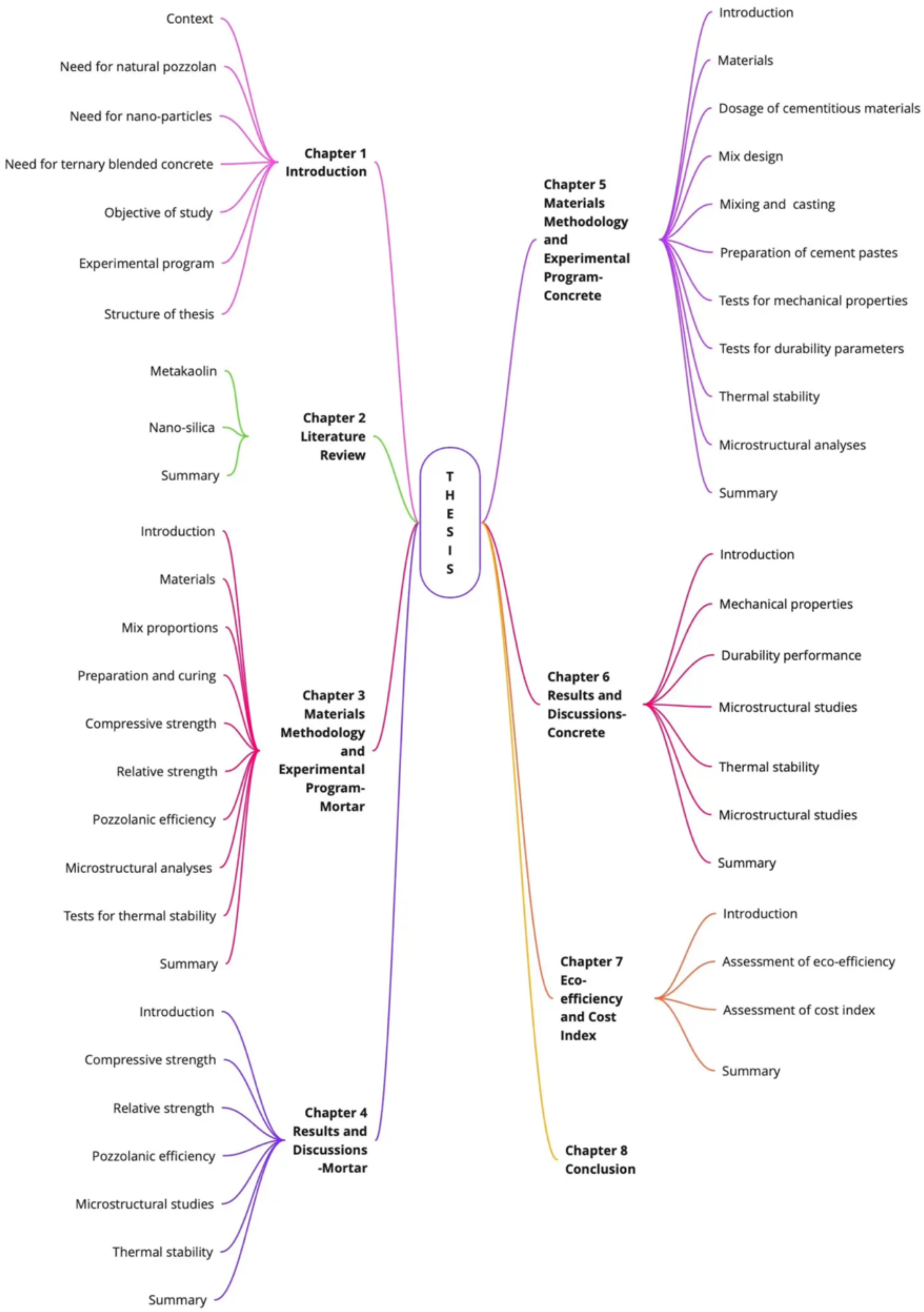

Figure 1.1 Schematic of thesis structure