Chapter 3
Materials Methodology and Experimental Program- Mortar

3.1 Introduction

This chapter comprehensively describes the materials, methodology, and experimental programme undertaken in the present research context. A detailed analysis of the materials used to prepare the mortars and an in-depth explanation of the method followed to achieve the desired mortar compositions are provided. Furthermore, the chapter outlines the experimental programme conducted to evaluate the performance and characteristics of the mortars. By meticulously describing the materials, methodology, and experimental procedures, this chapter lays the foundation for subsequent analysis and interpretation of the obtained results.

3.2 Materials

The materials used to prepare mortars include ordinary Portland cement (OPC) 43 grade, metakaolin, colloidal nano-silica, Indian standard sand of I, II, and III grades, and water. The source and characteristics of these materials are detailed in subsequent sections of this chapter.

3.2.1 Ordinary Portland cement

Ordinary Portland cement (OPC) 43 grade, manufactured by Ultratech Cement Ltd. India, conforming to Indian Standard, IS 269: 2015, was used. Its physical and chemical properties are given in Table 3.1.

Table 3.1 Physical and chemical properties of cement

Physical properties		Chemical properties	
Specific gravity	3.18	$(CaO-0.7SO_3)$ / $(2.8SiO_2+1.2Al_2O_3+0.65Fe_2O_3)$	0.87 (0.66-1.02)
Surface area (m^2/kg)	284 (225 min.)	Al_2O_3/Fe_2O_3	1.22 (0.66 min.)
Consistency (%)	33	Insoluble residue, % by mass	1.76 (5 max.)
Initial setting time (minutes)	157 (30 min.)	Sulphuric anhydride (SO_3), % by mass	1.77 (3.5 max.)
Final setting time (minutes)	515 (600 max.)	Magnesia (MgO), % by mass	4.58 (6 max.)
Soundness (Le-Chatelier expansion)	1 (10 max.)	Total loss on ignition, % by mass	2.08 (5 max.)
Compressive strength (28-day) in MPa	45.40	Total chlorides, % by mass	0.017 (0.10 max.)
Minimum or maximum values, as per IS 269 -2015, are given in bracket.			

Note: The physical properties of the cement were determined through laboratory testing, while the chemical properties were supplied by the manufacturer.

3.2.2 Metakaolin powder

The MK powder produced by calcination and grinding clay minerals was used, characterised by the ratio $SiO_2/Al_2O_3 = 1.4$. The surface area, specific pore volume, and average pore diameter of the MK powder were determined using the low-temperature nitrogen adsorption BET and BJH method (Microtrac BEL Corp.) and determined to be 28.6 m^2/g, 0.08-0.1 cm^3/g, and 25 nm, respectively. The BET area of 28.6 m^2/g corresponded to an average diameter of MK primary particles of 84.5 nm. Images were obtained by BT-SEM scanning electron microscopy (JEOL Asia PTE Ltd.) at a magnification factor of 500-5000 times. The MK particles with off-white colour had sizes around 0.1µ (100 nm) and had a shape consisting of heterogeneous layered sheets (Figure 3.1). The chemical composition, provided by the manufacturer, of the MK is given in Table 3.2.

(a) (b)

Figure 3.1 (a) Metakaolin and (b) SEM image of metakaolin

Table 3.2 Chemical composition of metakaolin

Chemical composition of MK (% by mass)	
SiO_2	57.5
Al_2O_3	41.0
Fe_2O_3	0.4
CaO	0.3
MgO	0.2
Na_2O	0.4
K_2O	0.2

3.2.3 Nano-silica solution

A colloidal nano-silica solution known as *CemSynXFXLA,* manufactured by Bee Chems India, contains nano-silica particles with a mass content of 40 wt. %, density of 1300 g/l, SSA of 150 m^2/g and pH of 9.4 was used. The solution was added to cement mortars by mixing it with water, and the amount of water in the solution was subtracted from the

total mixing water volume. The nano-silica in the colloidal form in the SEM image of the clustered nano-silica particles is shown in Figure 3.2 a and b, respectively.

(a) (b)

Figure 3.2 (a) Colloidal nano-silica, (b) SEM image of nano-silica solid particles

3.2.4 Indian standard sand

In this study, the Ennore sand conforming to Indian Standard, IS 650:1991 [42] was used as fine aggregate. The standard sand must (100 per cent) pass through an IS sieve (conforming to IS 460 Part-I, 1985) with a size of 2 mm and must (100 per cent) be retained on an IS sieve with a size of 90 microns, with the particle size distribution given Table 3.3. The texture of the IS Ennore sand I, II and III grades of sands is seen in Figure 3.3.

Table 3.3 Particle size distribution of IS sand in the mortar mix

Particle size	Percentage
Smaller than 2 mm and greater than 1 mm (Grade-I)	33.33
Smaller than 1 mm and greater than 500 microns (Grade II)	33.33
Below 500 microns but greater than 90 microns (Grade-III)	33.33

Figure 3.3 IS sand I, II and III grades

3.2.5 Water

Potable water from the IIT BHU campus with a temperature of 27±2ºC was used for preparing the mortar.

3.3 Mix proportions and mixing of mortars and cement pastes

Table 3.4 summarises the mortar composition and the respective quantities of the materials for each 70.6 mm cube following IS 4031 (Part 6)-1988 [224].

Table 3.4 Mix proportions of mortars

Mix	OPC (g)	MK (g)	CnS (g)	IS Sand G-I	IS Sand G-II	IS Sand G-III	Water
CM	200	0	0	200	200	200	92
MK10	180	20	0	200	200	200	92
MK15	170	30	0	200	200	200	92
MK20	160	40	0	200	200	200	92
NS1.5	197	0	7.5	200	200	200	87.5
NS3	194	0	15	200	200	200	83
NS4.5	191	0	22.5	200	200	200	78.5
MK10NS1.5	177	20	7.5	200	200	200	87.5
MK10NS3	174	20	15	200	200	200	83
MK10NS4.5	171	20	22.5	200	200	200	78.5
MK15NS1.5	167	30	7.5	200	200	200	87.5
MK15NS3	164	30	15	200	200	200	83
MK15NS4.5	161	30	22.5	200	200	200	78.5
MK20NS1.5	157	40	7.5	200	200	200	87.5
MK20NS3	154	40	15	200	200	200	83
MK20NS4.5	151	40	22.5	200	200	200	78.5
Amount of water = (P/4+3) percentage of cement plus sand according to IS : 4031 (Part 6)							

The nomenclature for mortar samples follows a system where MK and NS, followed by the numerals, represent their replacement levels for cement in weight percentage; for instance, MK10NS1.5 denotes 10% MK and 1.5% NS in the mix. The mortar of OPC, the reference mortar, is represented by CM.

The cement mortars included OPC, MK, NS (colloidal nano-silica), sand and water. All samples were prepared at a constant ratio of water-binder, W/B = 0.46, which was determined from the water required for the standard consistency of cement paste, and a binder-sand ratio B/S = 1:3. The amount of water equals (P/4+3)% of the total mass of cement and sand, where P is the percentage water needed, as per IS 4031 (Part 4)-1988 [225] for the standard consistency of cement paste. MK and NS were used in various weight ratios to replace OPC.

The study involved preparing sixteen different mixtures of mortar divided into three groups to make mortar cubes to examine the individual effects of MK and NS in their binary blended mortars and compare those effects to their combined use in their ternary blended mortars. The first two binary sets of mixtures were made by substituting OPC with 10, 15, and 20 wt.% of MK and with 1.5, 3, and 4.5 wt.% of solid SiO_2 nanoparticles. The third set comprises ternary compositions that blend MK and NS in varying replacement levels of 10, 15, and 20 wt.% of MK and 1.5, 3, and 4.5 wt.% of NS. The proportions of OPC, water, sand, MK and NS for each cube for the sixteen mixes are presented in Table 3.4. The flowchart for mixing the materials and casting mortar samples is shown in Figure 3.4.

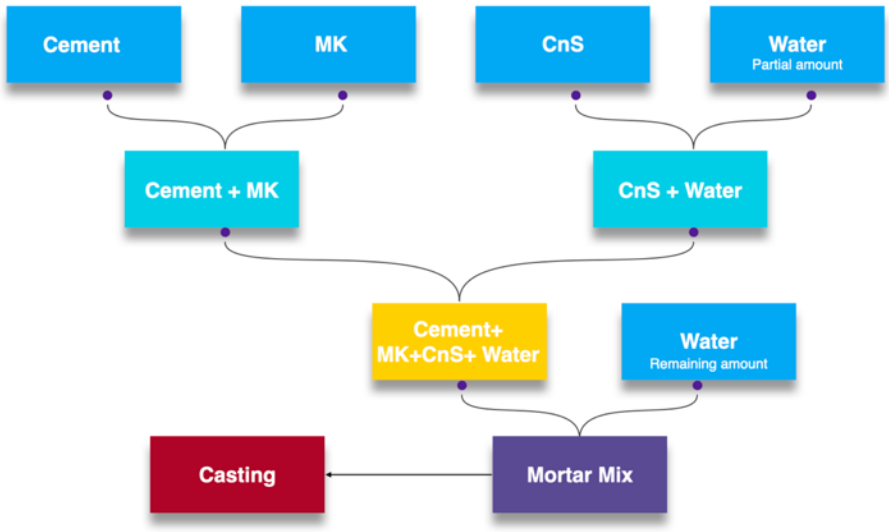
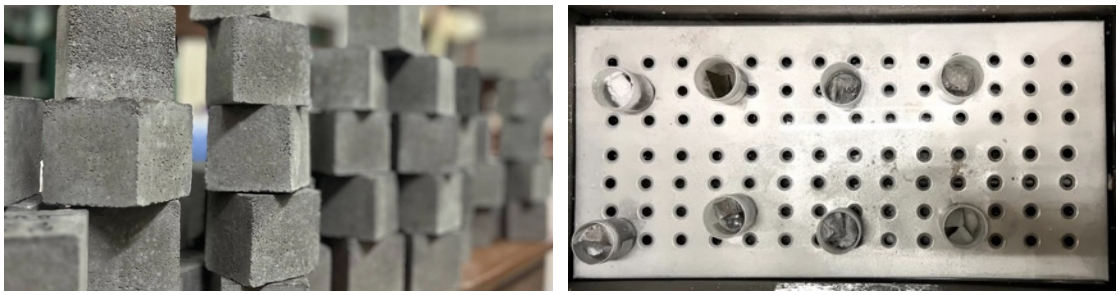


Figure 3.4 Flowchart- mixing and casting of mortar samples

(a) (b)

Figure 3.5 (a) Mortar preparation (b) mortar curing setup

Figure 3.5a shows the preparation of mortar, and Figure 3.5b shows the curing setup. Figure 3.6a shows the mortar cubes after removing moulds after 24 hours. To perform morphological analysis, separate cement pastes of the compositions were prepared with 0.46 W/B and cured for 28 days in a water bath with the temperature set at 27±2°C (Figure 3.6b).



(a) (b)

Figure 3.6 (a) Mortars after removing mould and (b) curing of cement pastes

3.4 Preparation and curing of mortar samples

IS 4031 (Part 6)-1988 [224] was followed during the preparation of the mixes. A dry mixture of cement, sand and MK powder was prepared, mixing water was combined with NS solution, mixed and vibrated for 60 seconds; moulds were filled and left to harden for 24 hours. After hardening, solid mortar samples of a cubic shape with dimensions of 70.6x70.6x70.6 mm^3 were removed (Figure 3.5b) from the moulds and immersed under water (Figure 3.6a) at 27±2 ºC for further hardening. Compressive strength tests were carried out at the age of 3, 7, 28 and 56 days on the compression testing machine by breaking mortar cubes.

3.5 Compressive strength

Three cubes of each mixture were tested for compressive strength on the 2000 KN capacity compression strength testing machine of AIMIL Ltd., India (Figure 3.7), following IS 4031 (Part 6), at 3, 7,28 and 56 days using a compression testing machine by applying load steadily and uniformly.

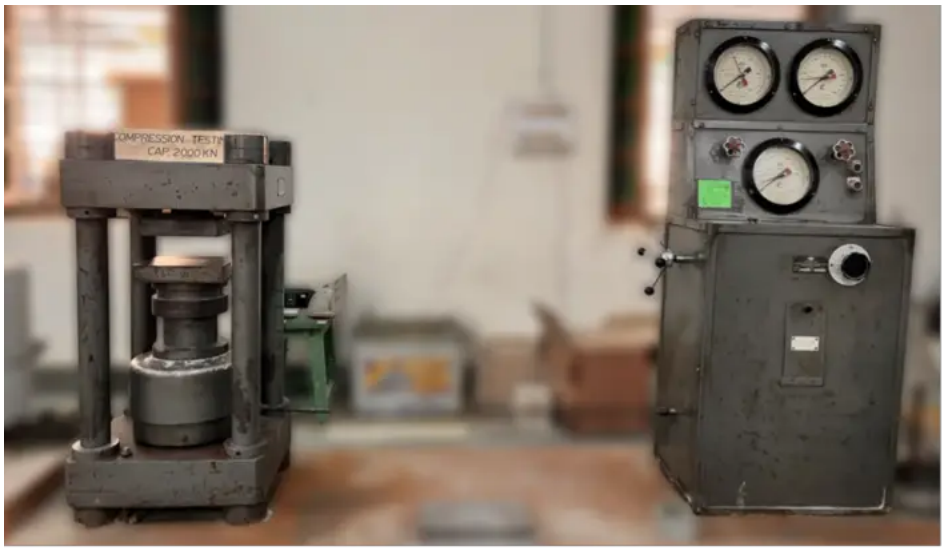


Figure 3.7 Compression testing machine

3.6 Relative strength

The relative strength is the ratio of the strength of a particular blended cement mortar to that of the reference mortar at a specific age of curing [30]. The development of strength in OPC depends on the hydration rate over time. However, strength gain in the blended cement mixture depends on the filler effect, hydration process and pozzolanic activity. The relative strength gives the effectiveness of additives in terms of strength.

3.7 Pozzolanic efficiency factor

To compare the relative performance of blended cement mortars with the reference mortar in compressive strength, the pozzolanic efficiency factor, also known as the coefficient of pozzolanic activity, or k-factor, was considered. Smith [226] was the first to introduce the idea of the fly ash cementing efficiency factor (k), which allows for the strength to W/C relation for regular concretes to also apply in fly ash concretes, with the modification that the content of effective cementitious materials replaces the cement content, as given by [W/(C+k.P)], where W is the weight of water in kg/m^3, C is the weight of cement in

kg/m^3, and P is the weight of blended pozzolanic material. The concept of efficiency, initially intended for fly ash, can also be utilised in other SCMs such as silica fume, slag, and natural pozzolans [227]. A method was also proposed by Papadaki et al. [228,229] to assess the effectiveness of various natural and artificial pozzolans using the pozzolanic activity index. Wong and Razak later proposed another method that utilises a relative strength to determine the pozzolan efficiency of cementitious materials [227].

Numerous empirical expressions are commonly used to characterise or predict the compressive strength of standard hardened cement paste. Bolomey's equation, a well-established expression, is widely utilised to predict the compressive strength of concrete through its correlation with the W/C. The k-factor derived from Bolomey's strength equation was employed to express the effect of cementitious materials on the compressive strength enhancement without differentiating between the effect of filler effect and chemical reactions in blended cement mortar. The strength of blended mortars was determined by the overall cementing efficiency factor, a combination of factors related to the age (k_a) and percentage of cementitious materials (k_p) present. Therefore, the relationship between these factors can be represented as $k = k_a + k_p$ [230]. The current study investigated the pozzolanic efficiency of MK and NS in their binary and ternary combinations in mortar in terms of their compressive strength at 3, 7, 28 and 56 days by modifying Bolomey's expression.

The Bolomey equation [231] relates W/C and compressive strength,

$$f_c = A\left(\frac{C}{W} + B\right) \qquad \text{Equation 3.1}$$

and is modified [50,51] to

$$f_c = A\left(\frac{C}{W} - 0.5\right) \quad \text{Equation 3.2}$$

The k-factor of the cement blended mortar can be determined from the following modified Bolomey equation [232].

$$f_c = A\left(\frac{C+k.P}{W} - 0.5\right) \quad \text{Equation 3.3}$$

Therefore,

$$k = \frac{1}{P}\left\{W\left(\frac{f_c}{A} + 0.5\right) - C\right\} \quad \text{Equation 3.4}$$

Where f_c is the compressive strength in MPa, C is the mass of OPC, P is the mass of cementitious material replaced, W is the water content, A is the Bolomey constant, and k is the efficiency factor.

From the above expression, it is clear that the strength of a mortar depends not solely on 'k' but also on the w/c and, more significantly, the quantity of cement and other cementitious materials present in the mixture.

3.8 Microstructural analyses

3.8.1 X-ray diffraction (XRD) analysis

The results of X-ray diffraction (XRD) analysis are useful for developing the correlation between the amorphous reaction products and the compressive strength [233]. The XRD analysis of the mortar samples was carried out using the MiniFlex 600 benchtop diffractometer (Figure 3.9) from Rigaku Co. Japan, with copper K**α** radiation (λ=1.5418 Å) and a scanning 2ø range between 5º and 80º. The mortar was extracted with care and then crushed and ground into powder using a pestle and mortar, removing as much fine aggregate as possible. The powder was sieved through an 80 µm mesh and dried at 40°C for 12 hours in an oven to eliminate moisture. Figure 3.8 shows the representative regions of mortar cubes from which the samples for XRD analysis were collected in powdered form.

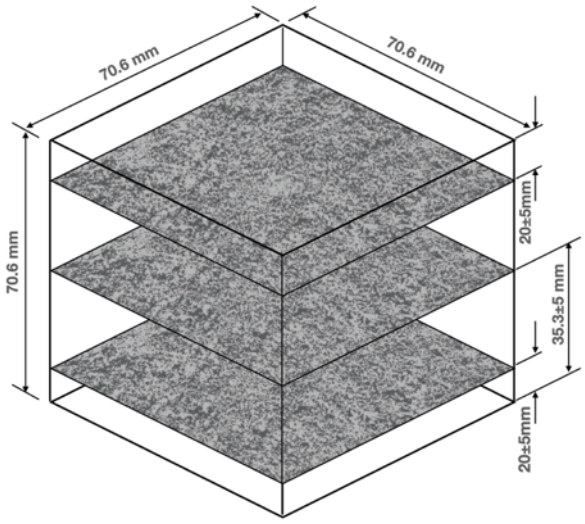


Figure 3.8 Representative zones of mortar cube used for XRD and TG analyses

Figure 3.9 Rigaku MiniFlex 600, Benchtop XRD (Dept. of Metallurgical Engineering, IIT BHU)

3.8.2 Thermogravimetric analysis

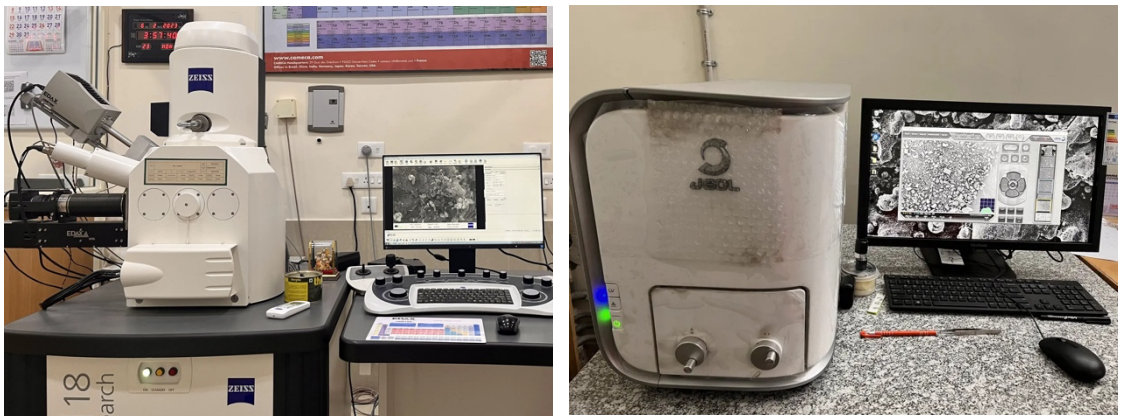
TGA was carried out using the Shimadzu TGA50 instrument (Figure 3.10) on the extracted samples from the mortar (28-day cured CM, MK10, NS4.5 and MK10NS4.5) regions, as shown in Figure 3.8. The extracted mortar samples were ground into powder using a pestle and mortar, removing as much fine aggregate as possible. The powder was sieved through an 80 µm mesh and dried at 40°C for 12 hours in an oven to eliminate moisture. The finely ground samples, weighing around 7 to 11 mg and having a particle size below 80 µm, were heated under a nitrogen environment from 25 °C to 1100 °C at a rate of 10 °C/min during the TGA analysis.

TGA results were compared with 28-day compressive strength, where mass loss during thermal decomposition directly indicates hydration product quantity. The mass loss between 110°C and 650°C is attributed to hydration product dehydration, with higher mass loss indicating increased hydration product content.

Figure 3.10 TGA instrument (Central instrumentation facility, IIT BHU)

3.8.3 Morphology

The morphology of the hardened paste of cement, binary blends of MK10 and NS4.5, and the ternary blend of MK10NS4.5 was analysed using ZEISS EVO-18 high-magnification scanning electron microscopy (SEM) equipment Figure 3.11a. The heat-exposed mortar samples for the thermal stability study were morphologically analysed using BT-SEM (Figure 3.11 b). Before imaging, a sputter coating of gold was applied to the surface of the test sample to ensure the conductivity of the electron beam onto the sample.



(a) (b)

Figure 3.11 (a). ZEISS EVO-18 high magnification SEM (Dept. of Geology, BHU), (b). JEOL JCM-7000 (Central instrumentation facility, IIT BHU)

3.9 Test for thermal stability

A thermal stability test was conducted on 70.6 mm mortar cubes after 56 days of curing. The mortar specimen in each composition was heated to four target temperatures of 200, 350, 500 and 650°C. The heating process was performed in a muffle furnace (Figure 3.12), employing a heating rate of 10°C per minute and maintaining the desired temperature (target temperature) for two hours.

Figure 3.12 Muffle furnace (Dept. of Civil Engineering, IIT BHU)

The muffle furnace was equipped with a thermostat, which allowed precise control over the temperature and heating rate throughout the process. After the two-hour fixed-temperature exposure, the specimens were left at ambient temperature to cool down naturally, as illustrated in the schematic diagram (Figure 3.13). Following a 24-hour cooling period, load testing was conducted on the specimens, as shown in the diagram (Figure 3.14), in which t_1 is the heating time, t_2 is the holding time, and t_3 is the cooling time. To assess the mortars' response to high temperatures, the percentage mass loss of the cubes after heating was recorded by comparing it to their initial mass.

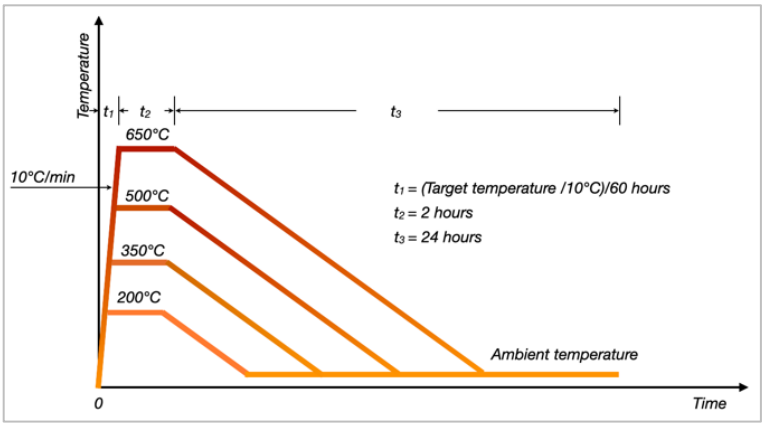


Figure 3.13 Schematic of the heating and cooling process of mortar cubes, Abhilash et al. [234]

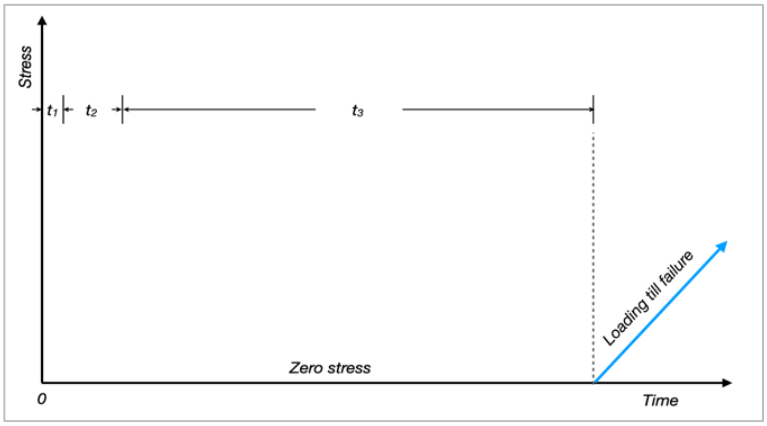


Figure 3.14 Schematic of the loading process of mortar cubes after being exposed to elevated temperature

The development of surface cracks and spalling of the specimens was also observed. These visual observations provided valuable information about the structural changes and potential weaknesses induced by the heating process. The SEM technique further investigated the microstructural defects, such as microcracks and voids.

3.10 Summary

This chapter discussed the materials used in formulating mortars, detailing their mix proportions and the procedures for mixing, casting, and curing the mortar compositions incorporating MK and NS. Additionally, it covered the experimental process to determine mortar compressive strength and analytical processes for evaluating relative strength and pozzolanic efficiency across each mortar composition. Procedures for examining thermal stability within the mortar were also explored, and various microstructural analyses conducted in this investigation were succinctly outlined.