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CHAPTER 1

INTRODUCTION

1.1 General

Cement is a very important building material used in the construction industry. Cement was invented by Joseph Aspdin in 1824 and in these 200 years it has established itself so well that now it is almost impossible to imagine the construction industry without cement. It is used for all types of construction, be it a small residential building or a multi-storeyed skyscraper, a dam, a highway, a bridge etc. Use of cement has been indispensable for development and its production has increased many fold in last few decades. The total volume of global production of cement was 1.39 billion tonnes in 1995 which has registered 200% growth in less than three decades and has reached 4.1 billion tonnes in 2022. This trend is likely to continue due to high demand of cement for infrastructural projects throughout the world [1].

In India, Manufacturing of cement started in early 19th century but by the end of the century cement production gained tremendous momentum. Today, with more than 7% of global capacity, India stands second among the cement producing countries in the world . India's overall cement production capacity for 2020-21 was placed at 537 million tonnes. According to the India Brand Equity Foundation (IBEF), there is an anticipated 5 to 7% increase in cement production in India, driven by the growing demands from sectors such as roads, urban infrastructure, and commercial real estate. Experts predict that cement demand in India will increase upto 800 million tonnes by 2030. It is also predicted that in case of high demand it may reach upto 1.4 billion tonnes till 2050. Thus, it is quite evident that for infrastructural development our dependence on cement is not going to diminish in near future [2]-[3].

1.2 Harmful effects of cement production

Cement manufacturing involves blending of various raw materials in required proportion and burning them at a high temperature so that required fusion of lime, silica and alumina are achieved in the final product which is called clinker. Limestone is used for calcium requirement, while clay, mudstone or shale as the source of silica and alumina. Clinker is finely ground with 2%-5% of gypsum to produce the cement. Starting from quarrying of raw materials then crushing, blending, burning, grinding of clinker and finally packing of cement, the entire cycle of cement production is highly energy intensive and requires 2.8 GJ of energy for producing one tonne of cement. Production of one tonne cement consumes about 1.5 tonne of calcium carbonate (i.e. limestone) which is around 80-90% of the raw material for the kiln feed, while remaining 10-15% is clayey raw material.[4]-[5]

On the other hand cement manufacture accounts for 7% of world energy sector emissions, including process emissions. 40 % of CO₂ emissions from a cement plant are generated by combustion while 60 percent emissions are due to calcification. The burning of fuels for maintaining high temperature required for calcination and fusion is responsible for combustion-generated CO₂ emissions. Decomposition of raw materials such as limestone and clay at about 1500°C liberates CO₂ during their calcification [6].

In recent decades, carbon dioxide emissions from cement manufacturing in India have seen a significant increase. In 2021, the recorded figures peaked at 149 million metric tons. It also releases huge amounts of air pollutants like PM (particulate matter), NO_x, CO, SO₂ and volatile organic compounds, O₃, H₂S etc. [7]-[8].

1.3 PPC as an alternative for OPC

In order to reduce the harmful effects of OPC production, PPC (Portland pozzolana cement) may be used as an alternative. The Indian Standards for

pozzolanic cements have prescribed two types of PPCs. Fly ash-based Portland Pozzolana Cement (PPC) is produced through either the intimate inter-grinding of Portland cement clinker and fly ash or by thoroughly and uniformly blending OPC with pulverized fly ash, along with the necessary addition of gypsum. This manufacturing process aims to create cement that meets standard specifications. The composition of fly ash in PPC should range from a minimum of 15% to a maximum of 35% by mass in relation to Portland Pozzolana Cement. Similarly calcined clay based PPC shall be manufactured with either calcined clay pozzolana conforming to IS 1344 [9] or a mixture of calcined clay pozzolana and fly ash [conforming to IS 3812 (Part 1)] [10]. The overall pozzolana content in Portland Pozzolana Cement (PPC) is carefully regulated, so that it remains between 10 percent and 25 percent by mass of the Portland Pozzolana Cement blend. The Indian Standard Codes [11]-[13] have prescribed compressive strengths of OPC and PPCs as given in Table 1. This difference in the strengths of OPC and PPC is definitely a hindrance in the use of pozzolanic cements as a replacement to OPC.

Table 1.1 Required strengths of cements at 7 days and 28 days as per Indian Standards

Name of the cement and its IS code	Compressive strength (MPa)	
	7 days	28 days
OPC 43 Grade (IS: 269-2015) [11]	33	43
Flyash based PPC [IS:1489 (Part 1) -2015][12]	22	33
Calcined clay based PPC [IS:1489 (Part 2) - 2015][13]	22	33

1.4 Types of Pozzolans

An effective solution to the above mentioned problem, lies in partial replacement of cement by pozzolans. “Pozzolans encompass a broad range of siliceous and aluminous materials that naturally lack substantial cementitious properties. Yet, finely divided and in the presence of water, these materials undergo a chemical reaction with calcium hydroxide $[Ca(OH)_2]$ at typical temperatures, yielding compounds that exhibit cementitious characteristics.”. Fortunately, a number of pozzolans are available in nature and also as industrial byproducts which may be categorized as under:

On the basis of origin:

1.4.1 Naturally Occurring Pozzolanic Materials: Natural SCMs are subdivided into two categories based on their origin i.e. volcanic and sedimentary.

1.4.1.1 Materials of volcanic origin: Pyroclastic rocks, originating from volcanic eruptions, are formed when explosive forces propel droplets of molten magma into the atmosphere. These particles undergo a rapid cooling process, either in air or water, leading to their characteristic glassy state. The pyroclastics can be altered by diagenetic processes to zeolite-rich tuffs.

1.4.1.2 Materials of sedimentary origin: Certain sedimentary rocks, such as specific clays and diatomaceous earths, have the ability to react²⁹ with lime. Clays arise from the alteration of igneous rocks, whereas diatomaceous earths form from the siliceous skeletons of microorganisms known as diatoms, which accumulate in freshwater or marine environments.. Diatomaceous earths exhibit high reactivity with lime due to their elevated content of amorphous silica and their large specific surface area. The sedimentary rocks comprise chemical and detrital (particles of

rock derived from pre-existing rock through weathering and erosion sediments). Naturally fired clays, like gliezh, exemplify the utilization of detrital sediments.

1.4.1.3 Materials of Mixed Origin (Hybrid Rocks): Apart from the above two categories there are stratified deposits of a crumbly rock made up of materials of different origin (volcanic, sedimentary and organic). In the upper layers, the silica content can reach up to 90%, along with and minor amounts of other oxides. The light coloration of these materials, often referred to as "white earths," is attributed to their low iron content. [14]-[15]

1.4.2 Artificial pozzolanic material: Artificial supplementary cementitious materials (SCMs) are commonly classified either based on the industrial processes used to produce them or on the original materials that undergo intentional thermal treatment for manufacturing.

1.4.2.1 Materials from industrial processes: these material are by-products or wastage from the industries:

- (a) Fly ash
- (b) Silica fume
- (c) Burnt oil shale
- (d) Granulated Blast furnace slag
- (e) Redmud

1.4.2.2 Materials manufactured by thermal treatment:

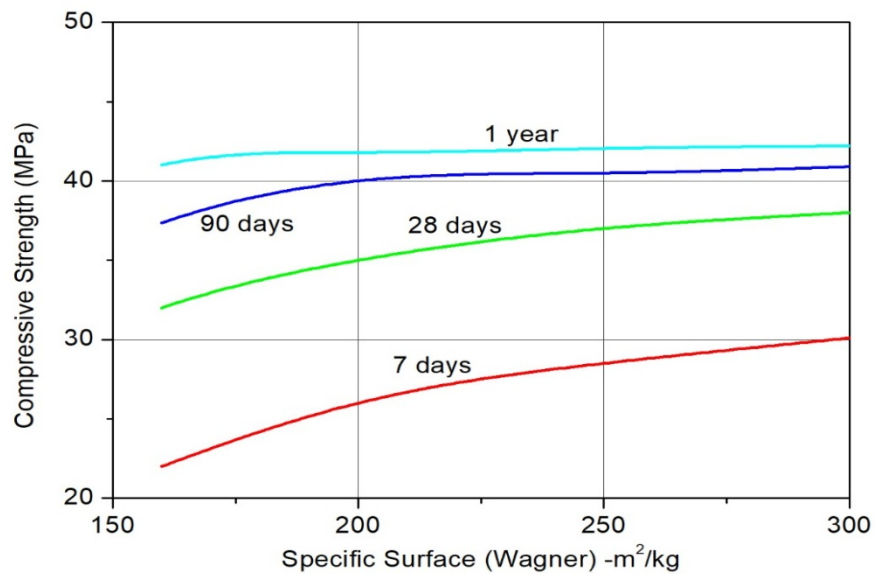
- (a) Burnt clay (Metakaolin)
- (b) Rice husk ash
- (c) Surkhi

Utilization of byproduct materials provides twofold benefit of material management as well as economy in addition to environmental concern of lesser cement consumption. The Indian standard has also published guidelines for two

types of Portland pozzolana cements i.e. fly ash based PPC and calcined clay based PPC .

1.5 Fineness of cement

The rate of a chemical reaction is directly correlated to the specific surface when a powder reacts with a liquid or gas at the surface of its particles. Hydration initiates at the surface of cement particles as soon as they come into contact with water and the material available for hydration is represented by the total surface area of cement. Finer cement results in rapid strength gain but long-term strength remains unaffected. As shown in Fig. 1.1 there is a nonlinear relationship between the specific surface of cement and the compressive strength of concrete. Consequently, increasing the fineness of cement particles can accelerate the rate of hydration.



60 Fig.1.1 Relation between strength of concrete at different ages and fineness of cement [16]

Additionally, the impact of fineness is more noticeable in the early stages, diminishing over time. This is attributed to the larger surface area of finer cement due to which it is more reactive with water during the initial stages. Apart from this grinding cement to achieve higher degree of fineness incurs substantial costs, and finer cement tends to deteriorate more rapidly when exposed to the atmosphere. Additionally, the increased fineness results in a greater surface area for the cement's alkalis, intensifying their reaction with alkali-reactive aggregates. It also exhibits a higher shrinkage and a greater proneness to cracking. [16]-[17]

1.6 Durability of concrete

Durability refers to the capacity to endure over an extended period without notable deterioration. A durable material contributes to environmental conservation by preserving resources, minimizing waste, and lessening the environmental consequences associated with repairs and replacements. In the context of concrete, durability is characterized by its resistance to weathering, chemical attacks, and abrasion, all while retaining its intended engineering properties. Recognizing the significance of ensuring the durability of concrete structures, the Indian Standard "IS:456-2000 [18] has included a complete clause covering different aspects of durability of concrete. As per this code a durable concrete is one that functions effectively in its operational environment, meeting the expected exposure conditions throughout its service life. The materials and their mixing ratios must be selected to maintain structural integrity and, where relevant, protect embedded metal components from corrosion. The code has widely covered the factors influencing durability e.g. shape and size of member, exposure conditions, general environment, exposure to sulphate attack, requirement of concrete cover, concrete mix proportions, mix constituents, concrete in aggressive soils and water, compaction, finishing and curing and concrete in sea-water.

Concrete is a composite material formed by combining fine and coarse aggregates, bonded with cement paste, which gain strength due to curing over time. It holds the distinction of being the second-most-utilized substance globally, following water, and stands as the most extensively employed building material. It is so widely used because of its strength, durability, reflectivity, sustainability and versatility. Concrete structures have to withstand normal to the most severe exposure conditions. Sometimes they are so located that their repair is very difficult. Hence, their durability is very important.

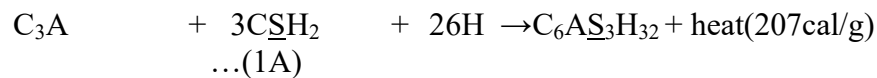
Additional concerns that have contributed to above mentioned pressures of environmental pollution and resource depletion due to cement industry are associated with a rise in the occurrences of concrete structures facing significant durability challenges. The durability of concrete structures is influenced by various factors, including:

- (i) Structural design: When a structure is conceived in the design phase, durability aspect is to be kept in mind during structural calculations, when details are prepared, for selection of materials and their proportions, and also for additional preventative measures to be selected.
- (ii) Concrete quality: Encompassing mix design, quality and consistency of raw materials, mixing, and delivery which are essential for integrity of concrete structure and protection of embedded metal from corrosion.
- (iii) Workmanship: In terms of mixing, placing, compaction, finishing, and curing which governs impermeability of concrete in addition to sufficient cement content and low water-cement ratio.
- (iv) Structure usage: Governs various stresses the structure may be exposed to during its service life and

(v) Environmental exposure: Controls physical and chemical effect of atmosphere [19].

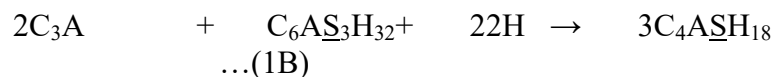
1.7 Need of the research

During the hydration of cement, tricalcium aluminate (C_3A) content of portland cement causes initial hydration and hence is beneficial to early strengths. Its rapidity is detrimental to concrete due to release of more heat. When alite i.e. ⁴⁷tricalcium silicate (C_3S) and belite i.e. dicalcium silicate (C_2S) react with water, they are transformed into calcium silicate hydrate ($C_3S_2H_3$) and hydrated lime [$Ca(OH)_2$]. Reactions of C_3A , alite and belite hydration are according to equations (1) to (3). The hydration of tetra calcium aluminoferrite does not contribute much to strength.

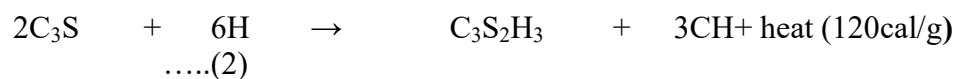


(tricalciumaluminate) (gypsum) (water) (ettringite)

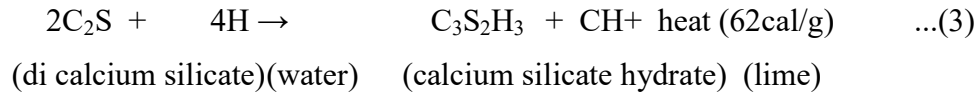
Upon the complete consumption of gypsum as per reaction (1A), the ettringite undergoes instability and proceeds to react with any remaining tricalcium aluminate, resulting in the formation of monosulfate aluminate hydrate crystals:



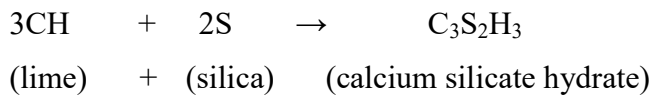
(tri calcium aluminate) (ettringite) (water) (mono sulfate aluminatehydrate)



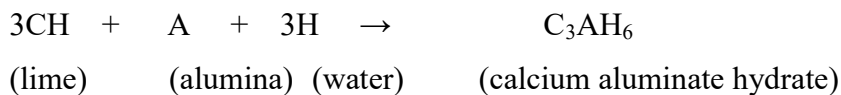
(tri calcium silicate)(water) (calcium silicate hydrate)(lime)



Alite yields 61% calcium silicate hydrate (C-S-H) gel and 39% calcium hydroxide [Ca(OH)₂] whereas belite produces much more C-S-H gel i.e. 82% and less than half Ca(OH)₂ than it i.e. only 18%. The hydration of C₃S starts quite early and contributes mainly up to 7 days strength. C₂S hydrates slowly and influences gain in later age strength. The released lime from equation (2) and (3) reacts with pozzolanic material, if used, mostly of silicious nature like fly ash, silica fume, ground granulated blast furnace slag etc., which makes additional calcium silicate hydrate at later stage and improves later age strength.



But, addition of pozzolanic material having high alumina content may give advantage of increased initial strength and enhance durability by consuming the free calcium hydroxide made available by the hydration of C₃S in the initial stage, as per following equation:



Incorporation of pozzolanic admixtures of silicious nature results in slow gain of strength, which can be improved by judicious blending of different pozzolans of aluminous nature [20]-[22]. The present research program involves the examination of effects of various blends of OPC and pozzolans on development of early age strengths of concrete and also study on its durability, so that suitable blend(s) of pozzolanic materials could be recommended to enhance the early age strengths of pozzolanic cementitious composites at par with OPC products of durable nature.

1.8 Objectives of the study :

The present research aims at suggesting suitable blend(s) of pozzolanic materials which could enhance the early age strengths of pozzolanic cementitious composites at par with OPC products.

The following objectives were proposed for this research program:

- Detailed study on strengths gained after 7 days and 28 days by various blends of pozzolans with regard to development of compressive strength, splitting tensile strength and flexural strength of pozzolanic cementitious products at par with pure OPC products.
- To study the durability aspect on these blends and OPC product under accelerated environmental effect.
- To suggest various blends of different pozzolans of optimum proportions, for high early age strength development of acceptable durability, at par with OPC products.

1.9 Outline of the thesis

The thesis comprises of six chapters as mentioned below :

- The chapter 1 elaborates the problem of large volumes of CO₂ emission, high energy requirement, huge consumption of natural resources (lime stone) and other associated problems. Fineness of cement and shortcomings associated with it are discussed. It proposes a possible solution of the problems related to OPC production by partial replacement of cement by pozzolans. It also focuses on the durability aspect of concrete which consumes most of the cement produced globally. Then it describes the importance of high early age strengths in construction, lack of which is a hindrance in the use of conventional pozzolans. Objectives of the present work to achieve high early age strengths and acceptable durability by using blends of selected pozzolan are described.

- Chapter 2 discusses the various studies, conducted by different researchers on use of different blends of pozzolan to enhance the early age strengths of concrete. It also discusses the durability studies conducted under various exposure conditions.
- Chapter 3 presents the materials used in the preparation of specimen to achieve the desired objectives of attaining high early age strengths i.e, compressive strength, splitting tensile strength and flexural tensile strength. This chapter covers the characterization of the materials, details of concrete mix and details of specimens to be tested.
- Chapter 4 describes methods adopted for preparation, curing and testing of specimens for the three key strengths at 7 days and 28 days period. Discussion on results of early age strengths tests obtained for various blends of pozzolan and their comparison with the strengths of control mix is also presented.
- Chapter 5 elaborates methodology for accelerated sulphate attack to assess the durability of different concrete mixes. Discussion on the loss of strengths and % weight loss of various concrete mixes under accelerated sulphate attack over 150, 300 and 500 cycles is also provided.
- Chapter 6 presents the conclusions and future scope of work.

Chapter 2

Literature Review

2.1 General

This chapter discusses the relevant literature and in perceiving the research gaps and to select materials, their combinations and experimental design for the present research study. As the present study concentrates on the high early age strengths of pozzolanic cementitious composites, firstly the research contributions related to the effect of different pozzolanic materials and their combinations in concrete, mortar and cement pastes have been discussed. Thereafter, literature related to accelerated sulphate attack on various cementitious composites has been discussed. A critical view on the basis of the literature surveyed has also been presented for achieving high early age strength and assessment of durability of concrete.

2.2 Effect of addition of pozzolanic materials on strength of OPC products

An extensive review of various studies done on the effect of addition of different pozzolanic materials such as metakaolin, flyash, redmud, high alumina cement, rice husk ash etc. on strength of OPC products was carried out.

2.2.1 Metakaolin (MK) blends

Wild S. et al. (1996) [24] investigated the impact of substituting OPC with MK in concrete mixes across a range of 0% to 30%, maintaining a water-to-binder ratio of 0.45. Compressive strength tests were conducted on cubes from each mix at 7, 14, 28, and 90-day intervals. Metakaolin's influence on concrete strength, when partially replacing cement, hinges on three key factors: the filler effect, enhancement of rate of cement hydration, and the pozzolanic reaction of MK with free lime. The filler effect manifests immediately, while OPC acceleration primarily occurs within the first 24 hours, and the peak effect of the pozzolanic

reaction is observed after a week ceases around 14 days. Optimal replacement of OPC by MK for maximal long-term strength enhancement is approximately 20%, whereas for silica fume it is 28%. Notably, the positive impact of metakaolin on strength enhancement ceases around 14 days, irrespective of replacement level.

Ribeiro D.V. et al. (2011) [25] utilized non-calcined red mud to streamline energy and time consumption, consequently reducing costs, thus aligning with the goal of waste reuse. Red mud, known for its high pH and hazardous nature, was incorporated into mortars. Those containing 30 wt. (%) of cement substituted by red mud exhibited enhanced strength in hardened products. The assessment of pozzolanic activity index relied on physical, mechanical, and chemical analyses. A comparison between the reference mixture (devoid of red mud) and the red mud-inclusive results underscored the potential of non-calcined red mud as a pozzolanic additive in cementitious materials. Although the setting time showed a tendency to increase, the workability remained largely unaffected.

Roziere (2009) [45] studied a leaching test on concrete, yielding indicators sensitive to potential durability variations and an accelerated test using high sulfate concentration on mortars. Results from both test series demonstrate a correlation between resistance to leaching and resistance to external sulfate attack.

Bassuoni M.T. and Nehdi M.L. (2009) [46] Studied to develop performance tests based on field conditions for assessment of the durability. A wide range of SCC mixture designs against sulfate attack is assessed, considering other concurrent damage mechanisms such as cyclic environmental conditions and flexural loading. Thermal, mineralogical, and microscopy analyses further elucidated the complex deterioration processes occurring in SCC under combined exposure, highlighting the fundamental difference between single damage mechanism scenarios (such as sulfate attack) and the coexistence of multiple damage mechanisms.

F. Liu et al. (2019) [47] investigated the combined effects of external sulfate attack, flexural fatigue loading, and drying-wetting cycles on concrete, focusing on various transportation infrastructures. The goal is to understand how these factors affect the integrity and mechanical performance of concrete over its service life. ¹Mass loss rate and relative dynamic elastic modulus are measured to assess the impact of these combined effects on concrete. Additionally, the sulfate content within concrete is determined to evaluate sulfate ion permeability under different conditions. The study also examines the influence of fly ash on sulfate attack. Fatigue loading induces cracking at interfaces and within the concrete, while drying-wetting cycles lead to water convection and diffusion within ²⁷the concrete. The results show that fatigue loading and drying-wetting cycles accelerate the transportation of sulfate ions within concrete and increase the degree of deterioration caused by sulfate attack. These findings provide insights into the complex interplay between fatigue loading, environmental exposure, and sulfate attack in concrete, aiding in the understanding of concrete durability in transportation infrastructure.

F. Liu et al. (2020) [48] investigated the deterioration and mechanisms of concrete subjected to dry-wet cycles and sulfate attack in seaside and saline areas. Measurement of variation of compressive strength of concrete and analysis of its pore structure by industrial computed tomography (ICT) and nuclear magnetic resonance (NMR) techniques was done under various erosion environments. The results indicate that the compressive strength initially increases and then decreases under different erosion environments, with dry-wet cycling accelerating sulfate erosion. During the early stage erosion products fill larger pores and transform into smaller pores but afterwards the proportion of larger pores increases, leading to internal cracking. Throughout the sulfate soaking and erosion process, smaller pores dominate in the concrete. As sulfate erosion progresses, the T2 spectrum distribution curve shifts to the right, indicating an increase in the signal intensity of larger pores. Overall, this study provides insights into the complex interaction

between dry-wet cycling, sulfate attack, and the pore structure of concrete in saline environments, contributing to a better understanding of concrete durability in such conditions.

Gao J. (2013) [49] investigated Environmental Scanning Electron Microscopy, Mercury Intrusion Porosimetry, and X-ray Diffraction to analyze changes in microstructure and corrosion products within the concrete subjected to sulfate attack under flexural loading and drying-wetting cycles. The results indicate that both of these attack regimes expedite the damage progression of concrete under sulfate attack when compared to singular sulfate attack. Furthermore, the impact of flexural loading on concrete deterioration relative to sulfate attack and drying-wetting cycles depends on the stress level. Moreover, the study reveals that the inclusion of admixtures enhances the sulfate resistance of concrete when subjected to mechanical loading and drying-wetting cycles.

Sahmaran M. et al. (2007) [50] conducted experiments to compare the performance against sulphate attack of ordinary Portland cement (OPC), sulfate resistant Portland cement (SRPC), and blended cements incorporating natural pozzolan and Class F fly ash. Mortar specimens made from plain and blended cements were subjected to three distinct exposure conditions: (i) continuous curing in lime-saturated water, (ii) continuous exposure to a 5% Na_2SO_4 solution at room temperature, and (iii) cyclic exposure to the same Na_2SO_4 solution with alternating wetting-drying and heating-cooling cycles. The evaluation of sulfate resistance involved measuring the reduction in compressive strength and length change of mortar specimens over a period of one year. The study found that blended cements performed better than SRPC with a 3.6% C_3A content in terms of length change under sodium sulfate solution at room temperature. However, when considering structures exposed to sulfate attack with wetting-drying and heating-cooling cycles, SRPC exhibited superior performance in terms of compressive strength losses compared to blended cements.

Guneyisi E. et al. (2020) [51] investigated various experimental parameters to assess the efficacy of metakaolin (MK) in enhancing the durability of concrete against sulfate attack. The tests were conducted to record loss of compressive strength over a period of 365 days. After the initial curing phase, the concrete specimens were divided into groups: one group served as a control and was immersed in tap water, while the other groups were exposed to 10% Na_2SO_4 solution for 365 days under either continuous or cyclic exposures. The results revealed that the MK improved resistance of concrete against sulfate attack, with the extent of improvement depending mainly on the MK replacement level, water-to-cementitious materials ratio, and initial curing procedure adopted. This suggests that MK can effectively enhance the durability of concrete in sulfate-rich environments, offering potential benefits for infrastructure exposed to such conditions.

Guo J. et al. (2019) [52] investigated the impact of dry-wet time ratio on the sulfate erosion of concrete under drying-wetting cycle test conditions. ⁴Five different dry-wet time ratios (1:3, 1:1, 3:1, 5:1, and 10:1) were considered, with each cycle lasting 7 days. The study examines the basic properties of concrete, including compressive strength, splitting tensile strength, and dynamic elastic modulus. Additionally, ⁴scanning electron microscopy (SEM) is employed to analyze the microstructure of concrete before and after erosion. The results reveal that the mechanical properties of concrete undergo three distinct stages during sulfate drying-wetting cycle erosion: an ascending period, a fluctuating period, and a rapid descending period. Concrete experiences a cyclic damage process involving initial damage, filling compaction, cracking, further filling, and subsequent cracking. The dry-wet ratio significantly influences the extent of sulfate attack on concrete. Specifically, ⁴under the same drying-wetting cycle period, an increase in the dry-wet ratio initially exacerbates the deterioration of concrete due to sulfate attack, followed by a decrease in deterioration. Notably, the most severe deterioration occurs when the dry-wet ratio is 5:1. Overall, the findings

provide insights into the complex relationship between drying-wetting cycle conditions, dry-wet time ratio, and the sulfate erosion of concrete, contributing to a better understanding of concrete durability under sulfate exposure.

Wang K. et al. (2020) [53] conducted experimental study with four different drying -wetting cycles with : 1:1, 3:1, 5:1, and 7:1, under oven-drying conditions to assess ¹⁰ the deterioration of concrete under sulfate attack through compressive strength, splitting tensile strength, and relative dynamic elastic modulus (RDEM). Additionally, the ¹ microstructure and phase composition were analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively, while the evolution of pore characteristics was examined using mercury intrusion porosimetry (MIP). The results indicate that the concrete experiences the most deterioration when subjected to a dry-wet ratio of 3:1. The wetting time influences the chemical attack and the expansion of concrete, while ¹⁰ the drying process primarily deteriorates the concrete in the middle and late stages of erosion. The performance of concrete depends on generation and filling of micro-voids. In this process, the concrete undergoes fatigue damage characterized by a transition from a "steady state" to an "unsteady state," and ultimately to a "new steady state."

Bassuoni M.T. and Nehdi M.L. (2009) [55] conducted study on ¹³ the durability of a broad range of self-consolidating concrete (SCC) mixtures against sodium sulfate attack. It investigates various mixture design factors, including the type of binder (single, binary, ternary, and quaternary), air-entrainment, sand-to-aggregate ratio, and hybrid fiber reinforcement. Recognizing the limitations of current standard test methods like ASTM C 1012, which may not fully address the diverse sulfate attack scenarios encountered in real-world conditions, the study explores three different exposure regimes (full immersion, wetting-drying, and partial immersion). The results from wetting-drying and partial immersion exposure regimes revealed potential performance risks associated with certain SCC mixture designs that were not apparent in full immersion exposure. Physico-mechanical

property assessments highlighted these risks, indicating variations in performance across different exposure conditions. Thermal, mineralogical, and microscopy analyses shed light on the complex degradation mechanisms, showcasing variations in degradation patterns even within the same specimen. The study underscores the necessity for performance standard tests capable of simulating diverse real-world exposure regimes more accurately. This approach is crucial for achieving a thorough and reliable evaluation of concrete resistance to sulfate attack.

Alyami M.H. (2019) [56] evaluated several accelerated test methods for Potential Sulfate Attack (PSA). Concrete mixtures were subjected to ⁴⁸partial and full immersion in sodium sulfate solutions at varying concentrations, temperatures, and relative humidity cycling. Results indicated that a 5% sodium sulfate solution was too dilute for effective accelerated PSA testing, while increasing the concentration to 10% yielded better outcomes.

Sabir B.B. et al. (2001) [58] demonstrated that MK serves as a highly effective pozzolan, notably boosting early strength while slightly improving long-term strength. Additionally, MK alters the pore structure within cementitious composites, notably strengthening their resistance to water transportation and the diffusion of detrimental ions. Consequently, it helps alleviate the risk of matrix degradation.

Ramezani pour A. A. et al. (2012) [59] investigated the performance binary blends of OPC and metakaolin concrete mixtures pertaining to compressive strength, water penetration, sorptivity, salt ponding and chloride in penetration. Metakaolin replaced 0%, 10%, 12.5% and 15% of PC by mass. Results show that concrete incorporating metakaolin had higher compressive strength, enhanced durability and reduced chloride diffusion.

Folagbade S. O. (2013) [60] reported the laboratory investigation results on binary and ternary combination pastes of OPC, fly ash, silica fume, and metakaolin. Fly ash was found to contribute solely to later age strength development. The addition of silica fume and metakaolin led to heightened heat of hydration, reduced setting times, and enhanced strength both in early and later ages, whereas fly ash only enhanced later age strength. Silica fume outperformed metakaolin due to its finer particle size and shape, even at equal replacement levels. It was also noted that the metakaolin content should not exceed 10% for optimal performance.

Bai J. et al. (2004) [61] reported the strength development, especially in early ages, to assess the effectiveness of MK as an accelerating admixture. Pure PC mixes with five different addition levels of MK (ranging from 1% to 5%) and PC-PFA mixes (60% PC + 40% PFA) with various levels of MK admixture were employed, using four different water-to-cement ratios. Compressive strength test results reveal that MK significantly enhances early strength as an accelerating admixture. The interplay between the contrasting roles of PFA and MK in early age strength development, results in a more effective PC-PFA blend with MK admixture.

Murat M. (1983) [62] investigated that Metakaolin combined with calcium hydroxide and water, lead to hydration and the subsequent development of compressive strengths at 28 days, ranging approximately from 10-15 MPa (as assessed on mini cylinders). The predominant hydration products include C_2ASH_8 and CSH, along with minor amounts of C_4AH_13 . Extensive research has been conducted to examine the influence of various factors such as curing conditions, the ratio of metakaolinite to calcium hydroxide, water-to-cement ratios, and the addition of sand to the mixture.

Frias. M. and Cabrera J. (2000) [63] analyzed five cement pastes containing 0% to 25% MK with water-to-binder ratio of 0.55 for the evolution of total, capillary, gel porosity and pore size distribution, over one year curing time. The results revealed that the addition of 15% to 20% MK led to improvements in porosity and reduction in average pore diameter. Additionally, the paper proposes a method to estimate the degree of hydration in MK/OPC mixes based on the Ca(OH)_2 content available in the paste, using data from differential thermal analysis and thermogravimetry.

Frias M. et al. (2000) [64] studied the influence of the pozzolanic activity of metakaolin (MK) on hydration heat, comparing it to the behavior of other pozzolanic materials which are rich in silica content. High pozzolanic activity of MK results in slight increase in heat compared to a pure OPC mortar. The development of hydration heat in MK-blended mortar is similar to silica fume rather than to fly ash.

Shafiq N. et al. (2015) [65] confirmed the reactivity of locally produced metakaolin as a cement-replacing material by assessing compressive strength, splitting tensile strength, and flexural strength of concrete at four different ages. This metakaolin was found to enhance compressive strength by approximately 5% more than silica fume concrete at 28 days. The research indicates that calcination at 800°C for 3 hours is the optimal condition for converting kaolin into highly reactive metakaolin. Concrete mixes with 5–20% metakaolin substitution exhibited high early compressive strength, splitting tensile strength, and flexural strength. For optimal early compressive strength, a 15% metakaolin substitution is recommended.

Changling H. et al. (1995) [66] conducted extensive examination on six standard clays, both pre- and post-calcination. The process of calcination of clays was found to heighten their pozzolanic activity, subsequently enhancing the compressive strength of cement-clay mortars. Notably, the particle size

distribution of the dehydroxylated clays exhibit significant correlation with the compressive strength of mortars. Predominantly, the clay-calcium hydroxide interaction produce CSH (calcium silicate hydrate) and C_4AH_x , alongwith C_2ASH_8 and C_3AH_6 in clays abundant in aluminum content.

Sabir B. B. et al. (2001) [67] demonstrated that utilizing metakaolin (MK) alongside fly ash (FA) yields a primary advantage: an increase in early strength, which offsets, to some extent, the potential loss attributed to the use of fly ash. While it could be contended that the early strength decline could be mitigated by employing Portland cement (PC) alone, employing blends of PC/MK/FA is likely to offer advantages concerning durability and reductions in PC usage, thereby contributing to environmental benefits. Additionally, the data provided lay the groundwork for an economic analysis of incorporating MK and FA together as blends for Portland cement.

Zhang M.H. and Malhotra V. M. (1995) [68] investigated that concrete with 10% metakaolin (MK) addition exhibited higher strength than plain concrete at all ages up to 180 days. As compared to silica fume, MK concrete rapidly gains strength at early age but after 28 days rate of strength development becomes slower. It showed a little higher splitting-tensile and flexural strengths, Young's modulus of elasticity, and lower drying shrinkage than the plain and silica fume concretes. Moreover, MK concrete displayed significantly higher resistance to chloride-ion penetration and demonstrated excellent performance in freezing and thawing tests.

Mermerdas K. et al. (2012) [69] conducted an investigation on MK concrete mixes prepared by replacing four different percentages of cement from 5% to 20%. The compressive strength development was monitored at 3, 7, 28, and 90 days. The evaluation of concrete strength development utilized a statistical technique known as GLM-ANOVA. Gene expression programming based model was used to analyze and assess the factors influencing strength. The prediction

model proved to be a valuable tool for estimating the compressive strength of concrete incorporating MK. It was demonstrated that the strength enhancement of MK-modified concretes, even at early ages, was notably superior⁵⁶ to that of the control concrete.

Dinakar P. et al. (2013) [70] studied the impact of incorporating metakaolin on the mechanical properties and durability of high-strength concrete. MK mixtures were designed with cement replacements of 5%, 10%, and 15% and water/binder ratio of 0.3. Results revealed that a 10% cement replacement was optimal for compressive strength, Splitting tensile strength and elastic modulus. In durability tests, MK concretes were found to be better than the control, with resistance increasing as the cement replacement increased. The study suggests that high-strength and high-performance concretes can be produced with local MK.

Badogiannis E. et al. (2002) [71] studied five mixture proportions to create high-performance concrete, with metakaolin replacing 10% and 20% of the cement. The study evaluated the properties of fresh concrete, strength development, and various durability aspects such as chloride permeability, air permeability, sorptivity, and porosity. The findings suggest that both the produced metakaolin and commercial variants exhibit similar behavior regarding strength development and durability. This similarity indicates the potential for producing concrete of excellent performance using metakaolin.

Bai J. et al. (2001) [72] determined compressive strength at 7, 28, and 90 days for cement concrete containing pulverized fuel ash (PFA) and metakaolin (MK), with MK ranging from 2.5% to 15% in PC-MK mixtures, and PFA ranging from 2.5% to 40% in ternary mixes. The water-to-binder ratio (w/b) was set at 0.4, 0.5, and 0.6. Metakaolin was found to be capable of replacing up to 15% of the cement in a structure, resulting in significant strength gains in the short and medium term. Only mixes with low PC replacement levels and high MK/PFA ratios achieved strengths greater than the control mix at short curing durations.

Poon C. S. et al. (2006) [73] studied to correlate the mechanical properties and durability of high performance metakaolin (MK) and silica fume (SF) concretes to their microstructure characteristics. The tests were conducted on control and blended concretes for assessment of compressive strength and chloride penetrability while pore size distribution and porosity were also measured. MK concrete exhibited superior strength development than SF concrete, while demonstrating similar resistance to chloride penetration. Pozzolanic concretes displayed enhancement in interfacial microstructure .

Poon C. S. et al. (2001) [74] examined the progression of hydration in high-performance cement pastes blended with metakaolin (MK) over time, focusing on measurements of compressive strength, porosity, pore size distribution, degree of pozzolanic reaction, and the content of Ca(OH)_2 in the MK-blended cement pastes at a water-to-binder ratio (w/b) of 0.3.. The heightened pozzolanic activity of MK resulted in a faster rate of strength development and refinement of pore structure in the cement pastes during the initial stages.

Soriano L. et al. (2013) [75] investigated the hydration processes in cement pastes and mortars blended with metakaolin (MK) or another pozzolan (FCC) and cured at low temperatures. The quantities of hydrates and calcium hydroxide were determined after four curing periods of 3 to 28 days at temperatures ranging from 5 to 20°C. MK and FCC were found to be effective materials even for low curing temperatures as compared to an inert limestone filler, when used to partially replace aggregates.

Khan S.U. et al. (2014) [76] reviewed the properties of fresh concrete, including workability, heat of hydration, setting time, bleeding, and reactivity, through the utilization of mineral admixtures such as fly ash (FA), silica fume (SF), ground

granulated blast furnace slag (GGBFS), metakaolin (MK), and rice husk ash (RHA). The review categorizes mineral admixtures based on their predominant activity i.e. either chemical or physical. Increased heat of hydration and reactivity with decreased workability and setting time of concrete results due to chemically active mineral admixtures while microfiller mineral admixtures act conversely. In general, mineral admixtures with small particle size and higher specific surface area enhance density and impermeability of concrete. Reduced workability and increased water requirement, can be corrected by incorporating suitable superplasticizers.

Shekarchi M. et al. (2010) [77] studied the qualities of metakaolin-blend concrete concerning transport properties. Different percentages of MK (0%, 5%, 10%, and 15%) were investigated for achieving a target compressive strength of 50 MPa at various ages (1, 3, 7, 14, and 28 days), alongside assessments of transport properties for concrete with a water-to-binder ratio (w/b) of 0.38. The transport properties examined included ionic diffusion, water penetration, gas permeability, water absorption, and electrical resistivity. Results indicated that the incorporation of MK led to a 20% reduction in the initial setting time, while the final setting time remained unaffected. Concrete with 15% MK enhanced the compressive strength by 20%. Transport characteristics demonstrated notable improvement, with up to a 50% enhancement observed. Additionally, the 28-day alkali-silica reaction (ASR) expansion was reduced by up to 82% with the inclusion of MK.

Justice J. M. et al. (2007) [78] Two metakaolins, possessing similar mineralogical compositions but differing in surface area, were examined for their suitability as SCMs. Various properties such as workability, setting time, strength, elastic modulus, heat evolution, calcium hydroxide (CH) content, and surface area were evaluated. Concrete's compressive and flexural strength were notably higher and

displayed a faster rate of increase when the finer metakaolin was utilized, as anticipated. Incorporating metakaolin led to a substantial enhancement in early-age flexural strength, reaching up to a 60% increase. The influence of metakaolin surface area on compressive strength was notably evident at lower water-to-binder ratios and generally beyond one week. However, the elastic modulus at 28 days, despite being higher in metakaolin-cement concretes compared to ordinary ones, especially at lower water-to-cementitious materials ratios (e.g., 0.40), was unaffected by metakaolin surface area. The higher surface area metakaolin exhibited greater and faster heat evolution, suggesting heightened reactivity and accelerated formation of hydration products. Compared to control, both metakaolin concretes show more CH consumption, which extends beyond 14 days, and a more refined pore structure by 28 days.

Badogiannis E.G. et al. (2015) [79] studied role of Metakaolin in Self-Compacting Concrete's durability. MK was used to substitute cement or limestone powder at various levels. They looked at porosity, sorptivity, water and gas permeability, and chloride penetrability. The addition of MK enhanced durability, particularly resistance to chloride penetration.

Jiang G. et al. (2015) [80] studied at a 0.17 w/b ratio, the effects of metakaolin on the mechanical characteristics, pore structure, and hydration heat of mortars. MK has a 0%, 6%, 10%, and 14% share of the market. SF FA 35 percent ten percent Steel fibres (0-2 percent) by weight at a constant w/b ratio of 0.17. Mortars' mechanical characteristics, pore structure, and hydration heat The addition of MK improves the flexural strength, compressive strength, and flexural toughness of steel fiber reinforced mortars. MK should be replaced at a rate of 10% of the time.

Wei J. et al. (2007) [81] studied a ternary blend of metakaolin, sodium bentonite and OPC to overcome the constraint of decreasing strength in Mk-OPC blends, especially at higher MK substitution. Characterization of hydration kinetics and products related to microstructural and physico-chemical variables were done to

assess the combined effect of these two pozzolans on cement hydration. The simultaneous use of these materials results in improved cement hydration. Due to addition of bentonite, metakaolin dissolution is increased which results in better Al/Si ratio. This leads to increase in ¹the conversion of ettringite to monosulfate, the formation of strätlingite, and the length of aluminosilicate chains. The results of the study are also supported by thermodynamic simulation.

2.2.2 Blends of Redmud

Xiaoming Liu. et al. (2011) [82] studied cementitious activity of bauxite residue were Red mud was the subject of a structural investigation. To increase the pozzolanic activity of red mud, it was calcined in the range of 400–900 °C and then analyzed in depth using XRD, FTIR, and ²⁹Si MAS-NMR methods. Due to the development of poorly-crystallized Ca₂SiO₄, red mud calcined at 600 °C had the best cementitious activity.

Sawant A.B., et al. (2012) [83] conducted experimental study on partially replaced cement in concrete with neutralized red mud. At 7, 28, and 56 days, neutralized red mud (5-25%) was employed in M30, M40, and M50 concrete. The average gain in strength is approximately 15%, while the economy attained with red mud is approximately 8%. The optimal level of replacement is 15%.

Ribeiro D.V. et al. (2010) [84] conducted research to explore the potential of integrating red mud into Portland cement mortars. Due to its significant production volume, finding efficient applications for red mud as an incorporation matrix is crucial. This study evaluated ³the properties of Portland cement mortars containing substantial proportions of red mud, including pH variations, fresh characteristics (such as setting time, workability, normal consistency, and water retention), and hardened state attributes (mechanical strength, capillary water absorption, density, and apparent porosity). The findings suggest promising results for incorporating red mud up to 20 wt%.

Rathan R. R. et al. (2013) [85] presented a simplified method for designing HSC mixes, integrating guidelines from the Bureau of Indian Standards (BIS) and the American Concrete Institute (ACI), along with insights from existing literature on HSC. Using this approach, a specific M60 mix of ternary blended high-strength concrete was formulated, incorporating different percentages of metakaolin and redmud to replace cement. These HSC mixes underwent experimental testing for compressive strength, splitting tensile strength flexural strength, and workability. The results demonstrate excellent performance of the designed mixes, as detailed in this paper.

Pontikes V. and Angelopoulos G. N. (2011) [86] reviewed the works of the utilization of red mud as a pozzolanic material, showing promising outcomes at the laboratory level. This study aims to offer a comprehensive review of such cases, critically examining ongoing research spanning the past four decades. To facilitate the transition from laboratory experiments to industrial application, this review also analyzes and presents the barriers and driving factors involved in incorporating redmud into the raw meal of cement clinker. It is demonstrated that tangible progress can indeed be made using current technology, with economic viability emerging as a major obstacle. To expedite the shift towards a more sustainable management of redmud, several concrete actions are proposed.

Wang P. (2012) [87] analyzed the compositions, mechanical properties, and microstructure of Bayer red mud and Sintering red mud through XRD, TG, and SEM analysis in order to investigate their performance. Additionally, assessments were made on their shear strength, particle size, density, and hydraulic characteristics. The study proposes Sintering red mud as a potential primary filling material for supporting structures in red mud stocking yards. Bayer red mud, on the other hand, holds significant reuse value and can be utilized as a mixing material for masonry mortar.

Ortega J. M. et al. (2011) [88] investigated mortars containing up to 20% red mud as a clinker replacement to study the short-term effects of this replacement on pore structure, mechanical performance, and durability. For comparison, mortars made with ordinary Portland cement and fly ash Portland cement were also examined. The findings of microstructure study, pore network evolution, pozzolanic activity, chloride migration and mechanical properties indicate that incorporating red mud led to a finer microstructure in the mortar, did not compromise resistance against chloride ingress, but resulted in reduced compressive strength.

2.2.3 Blends of Fly Ash

Hussein A.A.E. et al. (2013) [89] examined the influence of fly ash on various properties of concrete prepared by replacing OPC with fly ash ranging from 5% to 50%. Test results reveal that a ⁴¹10% fly ash substitution yielded the highest compressive strength across all ages. While the use of 15% to 30% fly ash significantly enhanced only later age compressive strength. Moreover, fly ash contributed to an improvement in the bond strength of concrete across all replacement levels. Conclusively, 10% and 15% replacements of cement by fly ash were found ideal for achieving desirable properties across all investigated aspects.

Elshekh A.E.A. et al. (2013) [90] aimed at reducing the production costs and time requirements while enhancing HSC properties by establishing control mixes and incorporating fly ash as a partial replacement for cement. HSC utilizing 10%, 20%, and 30% replacement of cement with fly ash was investigated to determine the optimum replacement content. All fly ash mixes exhibited homogeneity in the

fresh concrete state, showed no signs of segregation, and maintained slump values between 80-110mm. Strengths were enhanced with the inclusion of fly ash. However, it was noted that higher strength concrete exhibited reduced ductility, with ultimate strain values less than 0.35%. In general, a fly ash content of 20% was found to be the optimum replacement level.

Kosior-Kazberuk M. and Lelusz M. (2010) [91] developed mathematical models on the basis of experimental results for predicting the compressive strength development of concrete with fly ash replacement levels of up to 30%. The study analyzed the strength of concrete with various types of cement after curing periods of 2, 28, 90, and 180 days to assess the influence of fly ash content, curing duration, and cement type on compressive strength changes. Statistical methods were employed to verify the adequacy of the obtained equations. After a curing period of 180 days, concrete mixtures incorporating 20% fly ash by mass of cement exhibited a roughly 25% enhancement in compressive strength compared to concrete without the inclusion of fly ash.

Rao T. D. G. and Andal M. (2013) [92] aimed to investigate the impact of fly ash on both the workability and strength characteristics of concrete. Given that a significant number of thermal power plants in India produce low calcium fly ash, this specific type of fly ash was utilized in the research. The study focused on the partial replacement of cement with fly ash in concrete. The replacement percentage ranged from 0% to 40%, with intervals of 10%. Additionally, the ratio of fine aggregate to coarse aggregate was also varied. Replacement of 30% cement by fly ash in concrete mixes resulted in a reduction in water demand, while beyond 30% replacement, additional water content was required to maintain consistent workability. Moreover, replacing cement with fly ash up to 10% led to an increase in the compressive strength and could be recommended without compromising the compressive strength up to 20% .

Oner A. et al. (2007) [93] investigated on the progressive strength enhancement of concrete incorporating fly ash and explores the optimal utilization of it in concrete mixtures. Fly ash was introduced via partial replacement in various mixtures. A total of 28 mixtures with diverse designs were prepared, including four control mixtures with cement contents of 250, 300, 350, and 400 kg/m³, utilized to calculate Bolomey and Feret coefficients (KB, KF). These mixtures were divided into four groups, each comprising six mix designs based on the cement content of one of the control mixtures. Within each experimental group, 20% of the cement content from the control mixture was taken out, resulting in initial mixtures with cement contents of 200, 240, 280, and 320 kg/m³. Subsequently, fly ash was added in quantities approximately equal to 15%, 25%, 33%, 42%, 50%, and 58% of the remaining cement content as partial cement replacement. The maximum compressive strength was determined using Bolomey and Feret strength equations. The study unveiled a pattern of increasing strength with the elevation of fly ash content up to an optimal value of 40%, beyond which the strength began to diminish. Additionally, the ratio of fly ash to cement emerged as a pivotal factor influencing the efficacy of fly ash utilization.

Singh M. and Garg M. (1999) [94] explored the formulation of cementitious binders through a thoughtful combination of fly ash with Portland cement and the incorporation of fly ash with calcined phosphogypsum, fluorogypsum, lime sludge, and chemical activators of varying fineness. The study also investigates the impact of adding calcined clay to these binder types. The data revealed that these cementitious binders exhibit high compressive strength and water retentivity. Additionally, the inclusion of chemical activators enhances the strength of masonry mortars. The strength development of these binders is attributed to the formation of ettringite, C-S-H, and C₄AH₁₃. Furthermore, the binders demonstrate suitability for partial replacement (up to 25%) of cement in concrete without compromising strength. The results indicate that fly ash can be effectively utilized

in formulating these binders in the range of 45% to 70%, alongside other industrial wastes, thus contributing to environmental pollution mitigation efforts.

Papadakis V. G. et al. (1999) [95] incorporated a typical low-calcium fly ash into mortar, replacing a portion of either Portland cement or aggregate volume. The research focused on assessing the development of strength, heat generation, porosity, bound water content, and calcium hydroxide content. Aggregate replacement and cement replacement by fly ash give higher strengths after 14 days and after 91 days respectively. The Active silica content in the concrete volume plays main role in final strength gain. Findings regarding bound water content and porosity revealed that fly ash interacts with calcium hydroxide, consequently binding modest quantities of water. A simplified scheme outlining the chemical reactions of low-calcium fly ash during the hydration process of cement was proposed based on the experimental results. Additionally, quantitative expressions for estimating the chemical and volumetric composition of fly ash concrete were derived using reaction stoichiometry. These model expressions offer practical utility in mix design and predicting concrete performance.

Babu K.G. and Rao G. S.N. (1993) [96] conducted an evaluation of fly ash efficiency in concrete across a wide range of replacement percentages (15-75%). The findings clearly indicated that the overall efficiency of fly ash cannot be accurately predicted using a single efficiency factor across all replacement percentages. Therefore, the authors introduced the concept of an overall efficiency factor (k) evaluated at all replacement percentages, taking into account both a general efficiency factor (k_e) and a percentage efficiency factor (k_p). This research conducted a quantitative evaluation of fly ash performance at various levels of replacement in concrete, with specific emphasis on the 28-day compressive strength. By considering both general and percentage efficiency factors, a more

comprehensive understanding of the influence of fly ash on concrete properties was achieved.

Murumi K. and Gupta S. (2014) [97] highlighted the usefulness of designing the concrete mix by efficiency factor (k-value) concept in predicting the strength of fly ash concrete. This efficiency factor is relevant across a broad spectrum of strengths and percentages of fly ash incorporation. The strength of concrete at early ages has become increasingly significant in modern construction due to specific requirements like early form striking or prestress transfer. The suggested efficiency factor applies to a wide range of strengths and percentages of fly ash utilization.

2.2.4 Blends of High Alumina Cement

Thidar A. et al. (2014) [98] experimented with mortar specimens made of Portland cement and high alumina cement subjected to 7 cycles of drying at 40°C, cooling at 20°C, and immersion in Na₂SO₄ and MgSO₄ solutions at 20°C. The resistance of the mortars was evaluated by visually inspecting them and measuring alterations in surface hardness and specimen weight. Both mortars exhibited a decrease in surface hardness when treated with Na₂SO₄ solution, while an increase in surface hardness was observed when treated with MgSO₄ solution. The combined chemical and physical attack by Na₂SO₄ resulted in complete failure of the Portland cement mortar, whereas only marginal damage was observed in the high alumina cement mortar, believed to be due to physical salt crystallization. None of the two mortars was damaged when treated with MgSO₄ solution.

Zhang X. et al. (2009) [99] investigated the early hydration of the Ordinary Portland Cement (OPC)-High Alumina Cement (HAC) system using microwave and calorimetry methods. It was observed that the hydration process of this blend

varies depending on the fraction of HAC. The correlation between the results obtained from the two methods was discussed.

Ping G. et al. (1994) [100] studied impedance measurement technique to explore the hydration process and setting behavior of paste systems containing ordinary Portland cement-high alumina cement. The findings suggest that impedance and capacitive response serve as sensitive indicators for detecting changes in ionic concentration within the liquid phase and for monitoring the microstructural evolution of hydrating pastes. The initial surge in impedance, at around 30 minutes, corresponded to the nucleation of ettringite, contributing to rapid setting behavior, while the subsequent increase at 450 minutes was associated with HAC hydration processes. Moreover, a decline in matrix impedance was observed beyond 450 minutes of hydration, possibly due to the dissolution of calcium hydroxide (CH) resulting from the hydration of C_3S and C_2S .

Ping G. et al. (1997) [101] investigated ²⁴ the early strength development of pastes comprising ordinary Portland cement (OPC) and calcium aluminate cement (CAC) in different ratios (92.5/7.5, 80/20, and 20/80). Heat evolution and microstructural changes were monitored using conduction calorimetry, X-ray diffraction, and scanning electron microscopy methods. In the 80/20 paste, it was observed that ettringite formation significantly contributed to the early "set strength." The rapid formation of numerous needle-like ettringite crystals in this mixture likely explains its quick setting and early compressive strength development. The early strength development of OPC/CAC pastes was found to be dependent on the OPC/CAC ratio. The delay in the hydration of C_3S was identified as a factor contributing to the slow strength development in the binary cement system.

Nithya R. et al. (2010) [102]. studied pastes containing High Alumina Cement (HAC) and Ordinary Portland Cement (OPC) were prepared with varying proportions of Ground Water (GW) and 5%, 10%, 15%, and 20% Silica Fume

(SF). Additionally, the hydrated HAC blends underwent DTA/TG and DSC analysis, and the recorded spectra were compared with observed mechanical measurements. The results indicated that 10% SF addition was optimal for this blend, and the hydration kinetics were well explained through these findings.

2.2.5 Blends of other SCMs

V. Kannan et al. (2012) [103] investigated the effects of rice husk ash and metakaolin additions on magnesium sulfate and corrosion resistance properties of self-compacting concrete are reported. Cement is replaced on binary basis by 5–30% and 10–40%, respectively, of rice husk ash and metakaolin whereas in four ternary mix cement was replaced by 5%,10%,15% and 20% of each material. The observational results after magnesium sulfate immersion in 5% magnesium sulfate solution for one year and with an accelerated corrosion test showed the lowest weight loss for some blends of metakaolin and rice husk ash.

Zhang M. H. and Malhotra V. M (1996) [104] examined the characteristics of freshly prepared Rice Husk Ash (RHA) concrete, including aspects like workability, bleeding, setting time, and autogenous temperature rise. Additionally, the properties of hardened concrete were assessed, such as compressive strength, splitting tensile strength, flexural strength, modulus of elasticity, drying shrinkage, resistance to chloride ion penetration, resistance to freezing and thawing damage, and salt-scaling resistance. The study also compared these properties with those of conventional Portland cement concrete and silica fume concrete. The findings demonstrate that RHA exhibits high pozzolanic activity, making it a viable supplementary cementitious material for producing high-performance concrete. The investigation analyzed the influence of RHA percentage and water-cementitious materials ratio on these properties, providing insights into the potential applications and benefits of RHA concrete.

Zareei et al. (2017) [105] explored the benefits derived from incorporating various ratios of rice husk ash (RHA) into concrete, utilizing five mixture designs

with proportions of 5% - 25% RHA by weight of cement, alongwith 10% microsilica. Test results revealed that a 15% replacement of RHA led to a notable 20% increase in compressive strength. Generally, the optimal level of strength and durability properties was observed with additions of up to 20% RHA. Notably, substituting 25% of the cement with rice husk ash resulted in a significant 26% reduction in water permeability and a remarkable 78% reduction in chloride permeation.

Johari M.A.M. et al. (2011) [106] studied, the impact of SCMs on the engineering properties of high strength concrete (HSC). The findings indicate that the incorporation of SCMs has a significant effect on both the workability and compressive strength of HSC. Silica fume and metakaolin were found to notably enhance the strength of HSC, while fly ash and ground granulated blast-furnace slag led to a reduction in early age strength but contributed to enhanced long-term strength of the concrete. Additionally, the addition of the various SCMs resulted in a reduction in porosity and pore size of the HSC.

Phul A. A. et al. (2012) [107] determined the optimal levels of GGBS and Fly Ash within a percentage range of 0 to 30% across various curing periods. The findings demonstrate⁴⁴ that the addition of GGBS and Fly Ash enhances both the workability and compressive strength of the concrete, resulting in overall improved performance.

Medjigbodo G. et al. (2007) [108] conducted study on mortars using binary and ternary binders composed of Portland cement, metakaolin, and limestone filler. The objective was to explore the activating effect of a reduced water cement ratio. Various parameters such as heat of hydration, portlandite content, shrinkage, porosity, and carbonation were monitored on mixtures designed with w/c ratios of 0.42 and 0.5. The study found that the strength development of mortars with ternary binders was influenced by the properties of metakaolin, including its manufacturing process and particle size distribution. Moreover, reducing the w/c

ratio accelerated the pozzolanic reaction, leading to improvements in early-age strength and durability parameters.

Ismeik M. (2011) [109] studied concrete specimens with different proportions of silica fume and fly ash at varying water-to-cementitious material ratios. The findings revealed that both compressive and flexural strengths increased with the incorporation of mineral admixtures. However, the optimal replacement percentage varied depending on the w/cm ratio of the mix. Silica fume (SF) contributed to the short and long-term properties of concrete, whereas fly ash (FA) demonstrated its beneficial effects over a relatively extended period. Although the addition of both SF and FA did not lead to an immediate increase in compressive strength, improvements were observed in the long-term. Furthermore, the flexural strength of SF concretes exhibited greater enhancements compared to compressive strength. Statistical methods were utilized to establish relationships between the 28-day flexural and compressive strengths. In conclusion, the study suggests that local concrete materials, in conjunction with mineral admixtures, can effectively produce High Strength Concrete in Jordan, which can be suitably utilized in structural applications.

2.3 Durability study under accelerated sulphate attack on concrete and other cementitious composites

Tian W. and Han N. (2014) [110] investigated the mechanism behind concrete degradation in sodium sulfate solution. The overall performance of concrete was assessed based on its observable properties, such as mass loss and compressive strength. Analysis of ion changes in the solution throughout various sulfate attack periods was conducted using inductively coupled plasma (ICP). The progression of damage, along with the examination of concrete's meso- and microstructure, was unveiled through scanning electron microscope (SEM) and computed

tomography (CT) scanning techniques. Findings suggest that concrete characteristics varied across different sulfate attack periods, with drying-wetting cycles generally expediting the degradation process.

Jiang L. and Niu D. (2020) [111] investigated the evolution of damage in concrete exposed to drying-wetting cycles in different concentrations of sodium sulfate solution, by assessing weight loss, loss of compressive strength, and the thickness of the damaged layer of concrete. Furthermore, degradation in mechanical properties within the affected layer was scrutinized. SEM and X-ray diffraction were utilized to scrutinize corrosion products of corrosion, while contemporary microanalysis techniques were deployed to delve into the mechanism of damage of concrete. The test results revealed that the deterioration of physical properties of concrete specimens increased with higher concentrations of sodium sulfate solution. Although weight loss caused by sulfate attack was not prominently evident compared to other evaluation indices, the thickness of the damage layer of concrete and the corresponding decrease in ultrasonic speed indicated increased deterioration. Moreover, the compressive strength loss in the damage layer was significant, with a clear correlation observed between compressive loss and the thickness of the affected layer. Furthermore, the quantity of primary products of corrosion, ettringite and gypsum, was found to be directly proportional to the concentration of the solution.

Gao R.D. et al. (2013) [112] investigated to explore the mechanisms of concrete deterioration under alternating exposure to repeated ³⁰ sub-high temperature/cooling by water and sodium sulfate solution attack (TW-SA), in comparison to single sodium sulfate solution attack (SA), employing analysis of corrosion products through thermal analysis methods and determining sulfate-ion content from the top layer to the interior using modified barium sulfate gravimetric method. Compressive strength and splitting tensile strength were measured to observe mechanical behaviour. Experimental results revealed that in both scenarios, the

primary attack product was ettringite, with some gypsum observed solely in the initial layer of the SA case. In the SA case, sulfate ions primarily concentrated in the surface layer, resulting in relatively mild attack. However, in the TW-SA case, the repeated exposure to sub-high temperature/cooling by water facilitated the diffusion of sulfate ions inward, leading to noticeable strength degradation.

³⁷ **Al-Akhras N.M. (2006)** [113] examined the impact of metakaolin (MK) replacement of cement on concrete durability to sulfate attack. Sulfate attack severity was assessed by measuring concrete prism expansion, loss of compressive strength, and visual assessment for cracks. Results indicated that concrete sulfate resistance was proportional to quantity of MK replacement. Additionally, sulfate resistance was higher in MK concrete at a water-to-binder ratio of 0.5 compared to 0.6. Autoclaved MK concrete exhibited superior sulfate resistance, air-entrained MK concrete demonstrated greater improvement in sulfate resistance. However, air-entrained plain concrete exhibited lower sulfate resistance improvement than non-air-entrained concrete..

Khatib J.M. (2005) [114] investigated the impact of partially substituting cement with metakaolin (MK) on the ³⁸resistance of MK mortar to sodium sulfate solution, along with strength, porosity, pore size distribution, and calcium hydroxide (CH) content. Sulphate expansion results indicate that sulphate resistance increases with higher levels ¹of cement replacement with MK, up to at least 25% replacement. There's observed refinement in pore structure and reduction in CH content with increasing MK content in moist-cured mortar. These changes are considered the primary factors contributing to improved sulphate resistance. Mortars with high levels of MK (15, 20, and 25%) consistently experience strength gain over time, whereas Portland cement (PC) mortars and mortars with low levels of MK (5 and 10%) perform poorly on prolonged exposure to Na_2SO_4 solution.

Zhou Y. et al. (2015) [115] studied accelerated sulfate attack in a dry-wet cycle focussing on the trend of concrete strength deterioration and the development

pattern of sulfate-induced corrosion depth. The concrete section affected by corrosion was divided into two layers: uncorroded and corroded, delineated by the sulfate corrosion depth. Experimental results from accelerated corrosion tests revealed a significant correlation between concrete strength degradation and corrosion depth induced by sulfate attack. As a result, the aim of this paper was to elucidate this relationship and develop models to predict strength degradation. Extensive experimental data was collected and analyzed to validate the proposed models, demonstrating their effectiveness and applicability. These models provide a theoretical framework for predicting strength degradation and assessing the residual life of in-service concrete structures exposed to sulfate attacks.

Chen D. et al. (2012) [116] investigated the behavior of mortar specimens exposed to three different concentrations of Na_2SO_4 solution (0.5%, 5%, and 10%) and subjected to various drying-wetting cycles (20, 30, 40, and 75). The analysis focuses on the influence of cycle number and solution concentration on mechanical properties, mass variation, and appearance of the mortar specimens. The results reveal that specimens exposed to 5% and 10% solution exhibit evident surface desizing, sandiness, and some cracking after 75 drying-wetting cycles. Regarding mass variation, specimens generally show an initial increase followed by a subsequent decrease, with more pronounced fluctuations observed in higher concentration solutions. In terms of mechanical behavior, both peak stress and modulus of elasticity demonstrate an initial increase followed by a decrease in the early erosion stage, with a more pronounced change observed in specimens exposed to higher concentration solutions. Conversely, peak strain exhibits an initial decline followed by an increase in the later erosion stage. Overall, the study highlights the varying effects of solution concentration and drying-wetting cycles on the mechanical properties, mass, and appearance of mortar specimens, providing valuable insights into their durability under sulfate exposure.

Chen H. et al. (2017) [117] investigated the deterioration process of mortars subjected to sulfate attack under both restricted and unconstrained conditions. A 5 wt. % sodium sulfate solution and a dry-wet circulation method are employed to accelerate the deterioration process. Various parameters such as ⁹ deformation, damage rate, and porosity are measured using linear variable differential transducers (LVDTs), ultrasonic velocity measuring technology, and X-ray computed tomography (XCT), respectively. Additionally, mass loss, as well as the loss rates of flexural and compressive strengths, are evaluated to assess the deterioration outcomes. The degradation mechanisms are analyzed using ³ scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD). The experimental findings reveal that mortars with higher water-to-cement (w/c) ratios exhibit more severe deterioration. XCT images and porosity analysis indicate that, among the mortars subjected to ⁹ 60 drying-wetting cycles of sulfate exposure, the M30-SR sample under restricted conditions experiences the most significant deterioration. SEM/EDS and XRD analysis further reveal notable changes in the microstructure of hydration products, with the presence of sodium sulfate and gypsum observed after exposure to sodium sulfate. Overall, the study provides valuable insights into the deterioration mechanisms of mortars under sulfate attack, highlighting the importance of water-to-cement ratio and exposure conditions in determining the extent of deterioration.

Yang Y. et al. (2018) [118] investigated ⁵⁵ the deterioration behavior of concrete with varying degrees of initial damage under the combined effects of sulfate attack and drying-wetting cycles. The study evaluates the mass change and relative dynamic elastic modulus (E_{rd}) of the concrete specimens, along with the pore structure and corrosion products formed during exposure to sodium sulfate solution under drying-wetting cycles, using ⁵⁴ mercury intrusion porosimetry (MIP) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS), respectively. The findings indicate that concrete with pre-existing

damage exhibits greater mass change and reduction in E_{rd} compared to undamaged concrete. Furthermore, it is observed that a higher slag content in concrete enhances its resistance to sulfate attack, while a lower slag content diminishes sulfate resistance. Over time, the porosity and number of large pores in damaged concrete increase, indicating progressive deterioration. The internal corrosion products in concrete with a high water-to-cement ratio primarily consist of gypsum, whereas those in concrete with a low water-to-cement ratio predominantly comprise ettringite. Overall, the study sheds light on the complex interaction between sulfate attack, drying-wetting cycles, and pre-existing damage in concrete, highlighting the importance of material composition and exposure conditions in determining the durability performance of concrete structures subjected to sulfate exposure.

J. Yuan et al. (2015) [119] employed X-ray CT to analyze the failure process of concrete subjected to the combined effects of sulfate attack and drying-wetting cycles. This study investigated both the macroscopic performance of concrete and the microscopic changes in concrete pores under these environmental conditions. The correlation between macroscopic and microscopic observations was analyzed using grey incidence theory. The results revealed that this combined attack badly affect the internal structure of concrete pores. Higher concentrations of sulphate led to rather severe damage to the pore structure. Additionally, the drying-wetting cycles caused coarsening of the concrete pores, making it easier for sulfate to penetrate the interior of the concrete. Consequently, this accelerated the failure of the concrete material. Overall, this study highlights the detrimental effects of sulfate attack and drying-wetting cycles on the pore structure of concrete, providing valuable insights into the mechanisms of concrete deterioration under these environmental conditions.

Plowman C. and Cabrera J.G. (1984) [120] Studied flyash cement concrete in aggressive conditions. They found that the presence of fly ash considerably

reduces the rate of diffusion and stabilizes calcium aluminate hydrates, thereby increasing resistance to sulfate attack. These findings have been consistent for cements with C_3A contents ranging from 9% to 12%. However, further research is needed to explore the effects of fly ash in conjunction with lower C_3A content cements. The test method employed, derived from the work of Mehta, is deemed to be the most promising approach for developing an accelerated test that aligns with long-term performance data.

Ming F. et al. (2016) [121] studied the durability of concrete under sulfate corrosion attacks was investigated to assess its behavior in environments prone to such damage, such as cold regions and saline zones. Two sets of concrete specimens were submerged in sulfate solutions with concentrations of 10% and 20%, respectively. The strength development of these specimens was monitored over various immersion times. The study also presented a steady diffusion equation for sulfate ions in concrete based on Fick's law, allowing for the determination of the depth of penetration of sulfate ions into the concrete. By defining damage based on the depth of penetration, a damage model for concrete material was developed. Additionally, a new equation describing the relationship between strength and time during chemical corrosion of concrete was proposed. The study results illustrate that the proposed analytical methods can accurately quantify the damage process of concrete under sulfate attack. Furthermore, the power-law damage development formula proposed in the study offers a useful tool for describing the damage progression of concrete structures subjected to chemical corrosion. Overall, this research provides valuable insights into the behavior of concrete in sulfate-rich environments and offers practical tools for assessing and predicting its durability under such conditions.

Marchand J. et al. (2002) [122] conducted theoretical analysis of the detrimental effects of weak sodium sulfate solutions (Na_2SO_4) on concrete durability.. Various simulations were conducted on a numerical model to explore the influence of

parameters including water/cement (w/c) ratio, type of cement, sulfate concentration, and gradient in relative humidity across the material. It revealed that exposure to weak sulfate solutions can lead to significant changes in the microstructure of concrete. Sulfate ion cause precipitation of ettringite and possibly gypsum as well as dissolution of calcium hydroxide and decalcification of calcium silicate hydrate phases. Additionally, the study highlights that the w/c ratio remains a critical parameter governing concrete durability against sulfate attack. Overall, this theoretical analysis provides valuable insights into the mechanisms underlying sulfate attack on concrete and underscores the importance of controlling the w/c ratio to enhance concrete durability in sulfate-rich environments.

Menendez et al. (2003) [123] Increased utilization of industrial wastes and by-products in concrete production and blended cements is a significant step towards achieving carbon neutrality in the construction industry. Two key observations support this trend: (i) the application of additions leads to greater mitigation of alkali-silica reaction (ASR), and (ii) silica fume and fly ash are identified as the most effective additives for inhibiting ASR. The reduction in ASR expansion is attributed to a decrease in the calcium-to-silica (Ca/Si) ratio. This reduction limits the dissolution of silica, as there is less available calcium to facilitate silica dissolution and a higher concentration of aluminum to impede this process. As a result, the overall ASR expansion is minimized, contributing to improved concrete durability and performance.

2.4 Critical conclusions:

2.4.1 High early age strength of pozzolanic cementitious composites: An extensive survey of the previous research works was carried out which covered the effect of addition of different quantities of various pozzolans on the strength development of cementitious composites. Apart from the variation in quantities and combinations of pozzolans these experimental programs have involved various combinations of parameters such as type of cementitious composite (cement paste, mortar, concrete), specimen shape and size, water to cementitious material ratio, curing procedure (media, method, duration), testing procedure (type of strength, time of testing, microstructural examination) etc. The literature clearly reveals that inclusion of small quantities of pozzolans to cementitious composites positively influence the development of early age as well as later age strengths. The pozzolans of silicious nature help strength gain at a slow rate while aluminous pozzolans can improve gain of early age strength. Thus a prudent blending of silicious and aluminous pozzolans may be selected to enhance early age strength of pozzolanic cementitious products at par with pure OPC products.

2.4.2 Durability of pozzolanic cementitious composites: The literature survey covers a variety of durability tests conducted on various pozzolanic cementitious composites. The experimental programmes have used different parameters such as type of chemical (sulphate, chloride), solution percentage concentration, type of immersion (full, partial, under stress, continuous, cyclic), duration of immersion, duration of wetting, drying etc. Durability of cementitious composites is a vital issue with regard to their service life, difficulty in repair and maintenance, waste generation etc.. An accelerated chemical attack environment consisting of cyclic wetting and drying may be designed to assess the durability performance of various blends of pozzolans.

Chapter 3

Material Properties and Mix Designations

3.1 GENERAL

This chapter presents the properties and specification of the materials used alongwith scheme of experimental investigation performed to achieve the desired objectives of attaining high early age strengths in cement replaced concretes i.e. compressive strength, splitting tensile strength and flexural strength. Mix designation alongwith their constituent details are also given in this chapter.

3.2 MATERIALS

Previous research work has revealed that the pozzolanic materials can contribute in improving the strength of the cementitious composites in following ways:

- (i) Pozzolanic effect which is a chemical effect caused by the pozzolanic reaction between silicious or aluminous content of pozzolan and calcium hydroxide of cement. It is reported that materials rich in alumina content promote early age strength and those rich in silica support later age strength [21]-[23].
- (ii) Filler effect which is a physical effect owing to the fineness of the particles [24]-[25]

Thus in order to select suitable blends of pozzolanic materials for high early age strength, characterization of materials is necessary.

3.2.1 Basic Ingredients of Concrete:

The following materials/ingredients of concrete were procured for experimental work :

- (i) **Coarse Aggregate:** Crushed granite of size 20 mm and down was used. The specific gravity and water absorption of coarse aggregates were found to be 2.91,

0.57%. As per the sieve analyses test results shown in table 3.2 the coarse aggregate is specified as 20 mm nominal size

(ii) **Fine Aggregate:** Stone dust having particles of maximum size 4.75 mm and below was used.

6 The specific gravity and water absorption of fine aggregates were found to be 2.73 and 0.80% respectively. As per the sieve analyses test results shown in table 3.2 the fine aggregate falls in the Grading zone I .

6 The properties of the aggregates were determined in accordance with IS 2386 [26]-[27] and the sieve analysis results of these aggregates carried out according to IS 383 [28] .

Table 3.1 Details of ⁴⁵sieve analysis of coarse aggregate

IS sieve designation	Weight retained (g)	Weight retained (%)	Cumulative weight retained (%)	Weight passing (%)	Range for 20 mm nominal size (%) (as per IS:383)[28]
40 mm	0	0	0	100	100
20 mm	92	1.84	1.84	98.16	95-100
16 mm	838	16.76	18.60	81.40	--
12.5 mm	1599	31.98	50.58	49.42	--
10 mm	1158	23.16	73.74	26.26	25-55
4.75 mm	1307	26.14	99.88	0.12	0-10

21 Table 3.2 Details of sieve analysis of fine aggregate

IS sieve designation	Weight retained (g)	Weight retained (%)	Cumulative weight retained (%)	Weight passing (%)	Zone I fine aggregate range (%) (as per IS:383)[28]
10 mm	0	0	0	100	100
4.75 mm	32.5	1.65	1.65	98.35	90-100
2.36 mm	485	24.71	26.36	73.64	60-95
1.18 mm	547	27.86	54.22	45.78	30-70
600 μm	415.4	21.16	75.38	24.62	15-34
300 μm	290	14.77	90.15	9.85	5 -20
150 μm	193.6	9.85	100.0	0.15	0-10

(i) **Cement** ⁶ The cement used in all mixtures was normal OPC (43 grade) conforming to IS: 269:2015 [11]. The details of chemical composition and physical properties of the OPC determined in accordance with IS 4032 [29] and IS 4031 [30] are given in Table 3.3 and physical properties are presented ³⁶ in Table 3.4.

Table 3.3 Chemical composition of OPC

S.No.	Oxide	Test value (% mass)
1	SiO ₂	21.3
2	Al ₂ O ₃	5.0
3	Fe ₂ O ₃	4.1

4	CaO	60.2
5	SO ₃	2.73
6	MgO	0.89
7	Na ₂ O	0.13
8	K ₂ O	0.43
9	Chloride	0.024
10	Insoluble residue	2.67
11	L.S.F.	0.884
12	A/F	156
13	LOI	2.04

Table 3.4 Physical properties of OPC

S.No.	Name of test (Unit)	Test results
1	Fineness (m ² /kg)	290.5
2	Normal Consistency (%)	28.50
3	Soundness: Le-Chatelier (mm) Autoclave Expansion (%)	1.00 0.032
4	42 Setting Time: (minutes) Initial Setting Time Final Setting Time	115 160
5	Compressive Strength (MPa) 3 Days (72 ± 1Hrs.) 7 Days (168 ± 2Hrs.) 28 Days (672 ± 4Hrs.)	34.0 43.5 55.5

(ii) **Water:** Normal potable tap water available in the laboratory was used for preparing all the mixes and their curing.

3.2.2 Pozzolanic materials: The following pozzolanic materials were used :

(a) Predominantly Aluminous Materials:

(i) Metakaolin (MK) : Commercially available metakaolin was used .Metakaolin is obtained by calcination of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) at 600°C - 800°C . .Due to its highly disordered structure it offers good properties as mineral additive. Oxide contents of MK alongwith its physical properties are shown in Table 3.5. The particle size analysis carried out on laser diffraction analyser and its XRD graph are shown in Figs. 3.1 and 3.2.

Table 3.5 Oxide content and other properties of metakaolin

S.No.	Oxide/property	Mass (%)
1	SiO_2	50-52
2	Al_2O_3	40-45
3	Fe_2O_3	0.70
4	CaO	0.90
5	MgO	0.30
6	TiO_2	0.70
7	Na_2O	0.10
8	K_2O	0.30
9	SO_3	--
10	Loss on ignition (LOI)	0.20-0.50
11	Specific gravity	2.65
12	Fineness (m^2/kg)	1342(LD)**

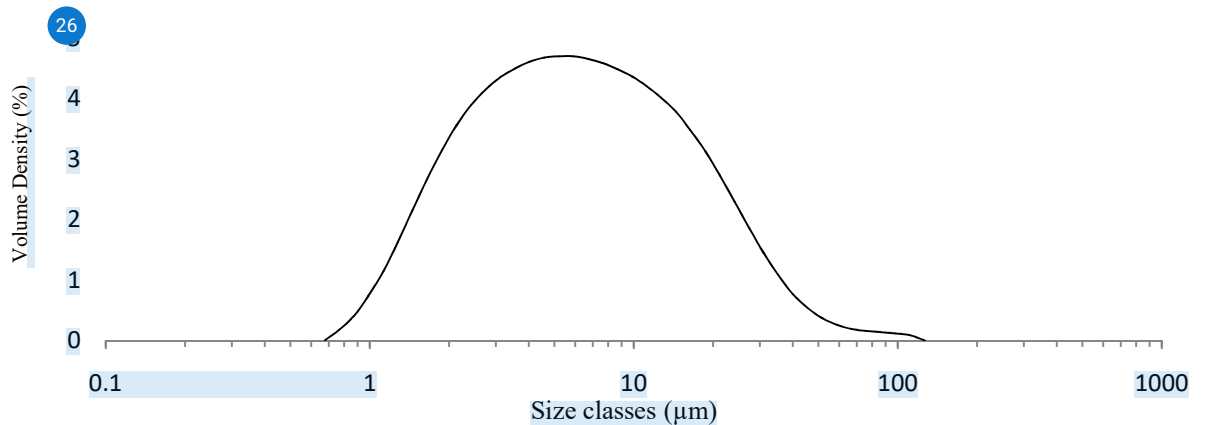


Figure 3.1 Particle size distribution of metakaolin

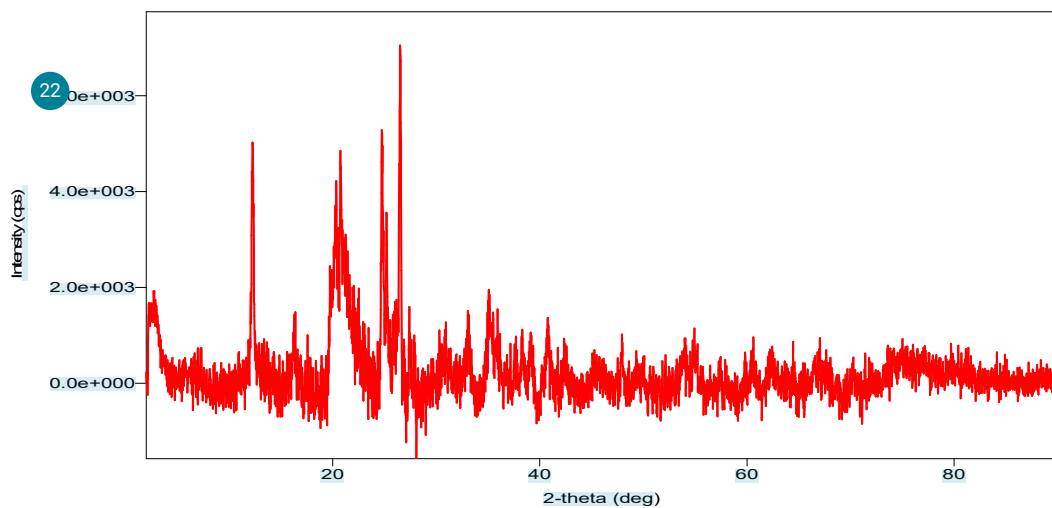


Figure 3.2 XRD graph of metakaolin

(ii) **High Alumina Cement (HAC):** Commercially available HAC was used. This cement is manufactured from aluminous and calcareous materials either by fusion or by sintering, and grinding the resulting clinker. The minimum alumina (Al_2O_3) content as prescribed by IS 6452 (B) [31] should be 32%. Chemical composition of HAC along with physical properties of it are shown in Table 3.6. The particle size analyses of HAC carried out on laser diffraction analyzer and XRD graphs are presented in figure 3.3 and 3.4.

Table 3.6 Chemical composition and other properties of HAC

S.No.	Name of oxide/property	Specification
1	Al ₂ O ₃	(Min.)70%
2	CaO	26-29%
3	SiO ₂	(Max.)1.0%
4	Fe ₂ O ₃	(Max.)0.30%
5	Specific gravity	2.90-3.10g/cm ³
6	Specific surface area	3600-4000 cm ² /g
9	Fineness	+170to+200Mesh:5% Max. +35 Mesh :20%Max.
10	Setting time	Initial set: 30-45 minutes Final set: 200-300minutes
11	Cold Crushing strength(Kg/cm ²)	24 hrs curing :400 Min. 24 hrs curing +24 hrs drying at 110° :550Min.

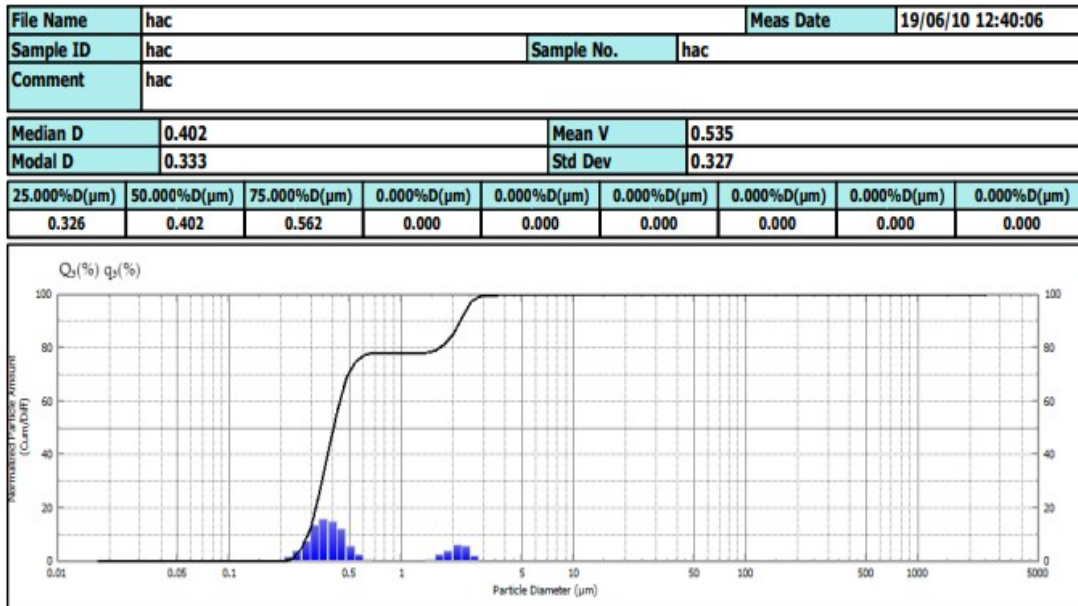


Figure 3.3 Particle size distribution of HAC

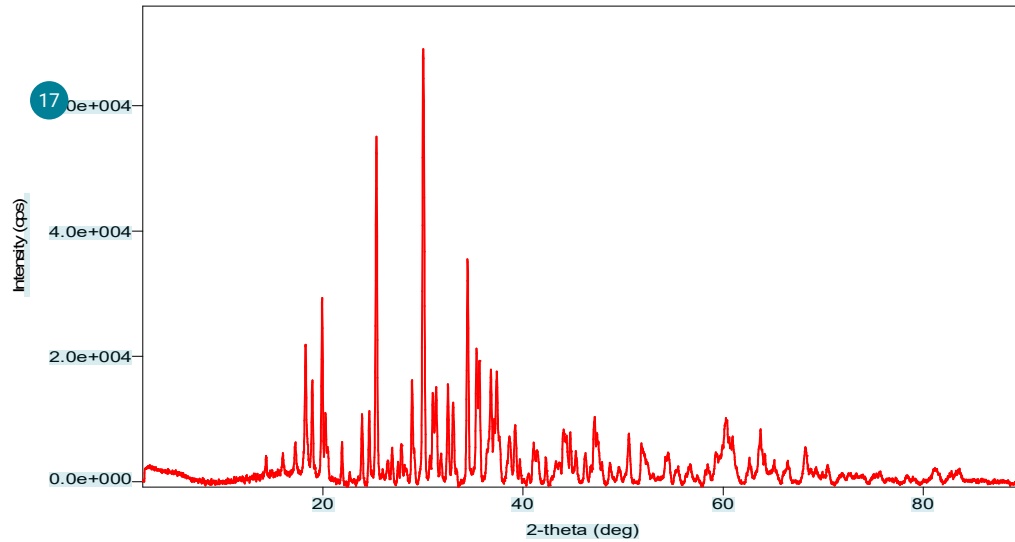


Figure 3.4 XRD graph of HAC

(b) Predominantly siliceous materials:

(i) Fly ash (FA): Fly ash was obtained from Rajghat Thermal Power Station, Delhi. It falls in the category of “Siliceous Pulverized Fuel Ash — Pulverized fuel ash with reactive calcium oxide less than 10 %” as per IS 3812 (Part 1) [32]. Fly ash is a residual product generated during the coal combustion process in thermal power stations. It takes the form of a finely textured, gray powder containing spherical glassy particles, which ascend with the flue gases and are collected by electrostatic precipitators.

Chemical composition and other physical properties of it are shown in table 3.7. Particle size distribution and X-ray diffraction graph are shown in Fig. 3.5 and 3.6 respectively

Table 3.7 Oxide content and other properties of fly ash [33]

S.No.	Oxide/Property	Fly ash (%)
1	SiO ₂	61.21
2	Al ₂ O ₃	30.07
3	Fe ₂ O ₃	4.17
4	CaO	0.10
5	MgO	0.40
6	TiO ₂	2.60
7	Na ₂ O	0.01
8	K ₂ O	0.02
9	SO ₃	0.01
10	LOI	1.40
11	Specific gravity	2.19
12	Fineness (m ² /kg)	1343(LD)**

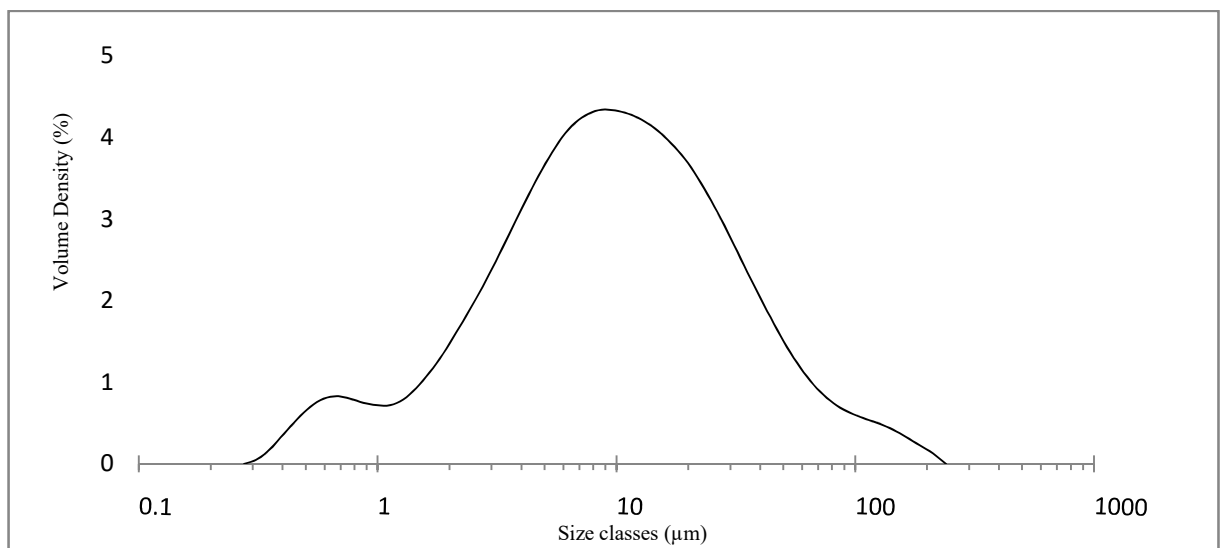


Figure 3.5: Particle size distribution of fly ash

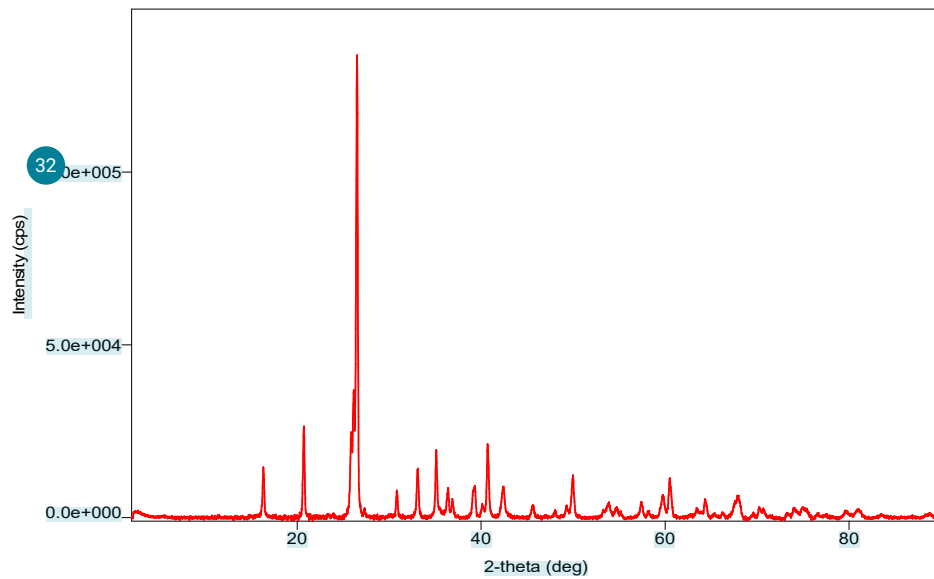


Figure 3.6 XRD graph of fly ash

(C) Other pozzolanic materials

(i) **Red mud (RM):** Red mud was collected from Hindalco industries limited, Renukoot (U.P). Red Mud refers to the waste produced in the Bayer process of extracting alumina from bauxite during alumina production. It is alternatively named as bauxite residue. Its Chemical composition, particle size analysis and X-ray diffraction graph are given in Table 3.8 and Fig 3.7 and 3.8 respectively.

Table 3.8: Chemical analysis⁵⁰ of red mud

S. No.	Constituents	Mass %
1	LOI	8 - 10
2	Al ₂ O ₃	17 - 19
3	Fe ₂ O ₃	34 - 40
4	SiO ₂	7 - 8
5	TiO ₂	15 - 16
6	Na ₂ O	5 - 6
7	CaO	1.8 - 5.0
8	P ₂ O ₅	0.31 - 0.47
9	V ₂ O ₅	0.035

File Name	RM2	Meas Date	19/06/15 10:49:17												
Sample ID	RM2	Sample No.	RM2												
Comment															
Median D	0.043	Mean V	0.043												
Modal D	0.039	Std Dev	0.079												
25.000%D(μm)	0.038	50.000%D(μm)	0.043	75.000%D(μm)	0.050	0.000%D(μm)	0.000	0.000%D(μm)	0.000	0.000%D(μm)	0.000	0.000%D(μm)	0.000	0.000%D(μm)	0.000

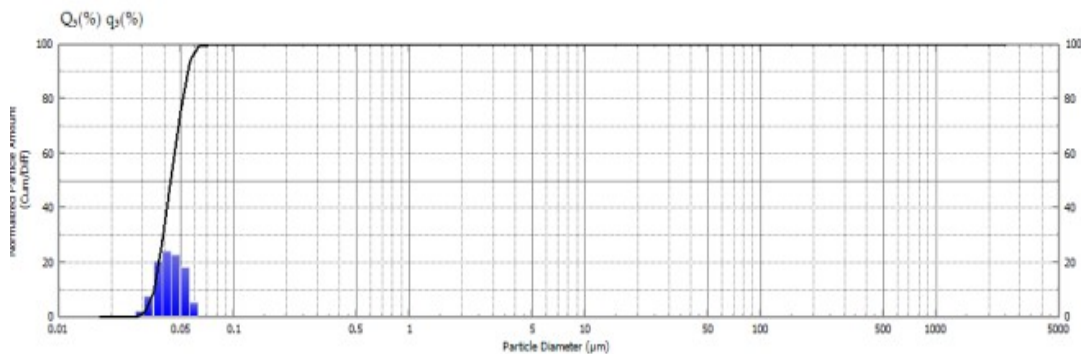


Figure 3.7 Particle size distribution of red mud

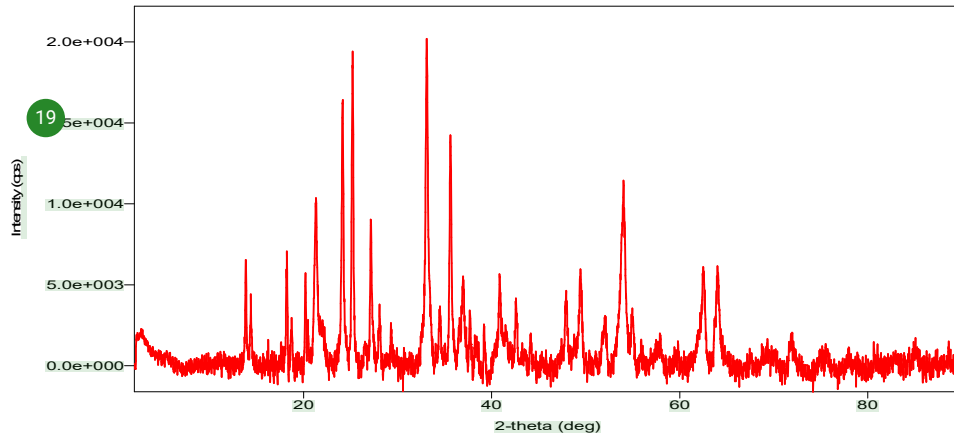


Figure 3.8 XRD image of red mud

(ii) **Sleeper cement** : OPC 53-S conforming to IS:269 [11] was used. The Tricalcium silicate content of such cements has to be minimum 45% whereas the tricalcium aluminate content is restricted to a maximum limit of 9% with minimum fineness of 370 m²/kg. Chemical and physical requirements of sleeper cement are given in Tables 3.9 and 3.10 respectively while laser diffraction analysis and x-ray diffraction graph of it are shown in Figs. 3.9 and 3.10 respectively.

Table 3.9 Chemical properties of sleeper cement

S.No.	Chemical property	Value
1.	$\text{CaO}-0.7 \text{SO}_3 / 2.8 \text{SiO}_2 + 1.2 \text{Al}_2\text{O}_3 + 0.65 \text{Fe}_2\text{O}_3$	0.91
2.	$\text{Al}_2\text{O}_3 / \text{Fe}_2\text{O}_3$	1.23
3.	Insoluble residue	0.98%
4.	MgO	1.62%
5.	SO ₃	3.18%
6.	LOI	1.52%
7.	Cl	0.03%
8.	C ₃ S	51.61%
9.	C ₃ A	5.85%

Table 3.10 Physical properties of sleeper cement

S.No.	Physical property	Value
1.	Fineness (m^2/kg)	408.4
2.	Standard consistency	29.0
3.	Setting time (minutes)	
	Initial Setting time	90
	Final Setting time	140
4.	Soundness	
	Le- chatelier expansion (mm)	1.0
	Autoclave expansion (%)	0.05
5.	Compressive strength (MPa)	
	3 Days (72 \pm 1Hrs.)	40

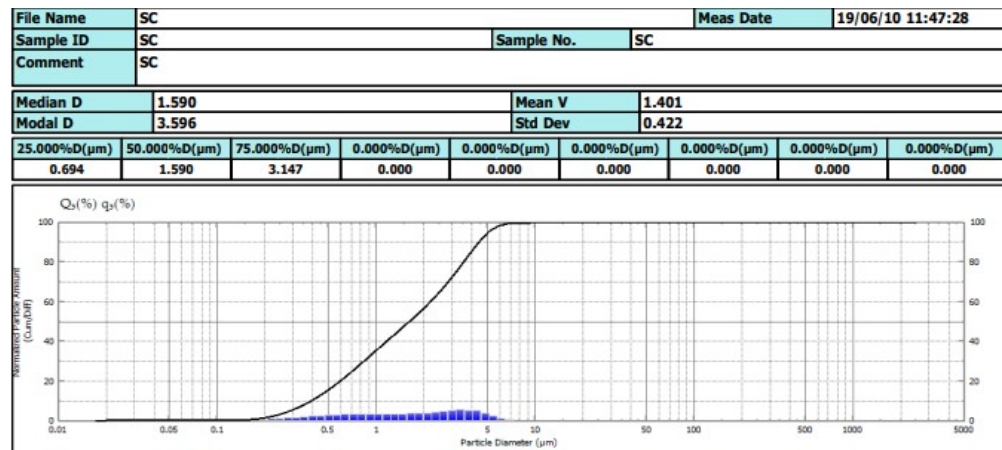


Figure 3.9: Laser diffraction analysis of Sleeper cement (OPC 53S)

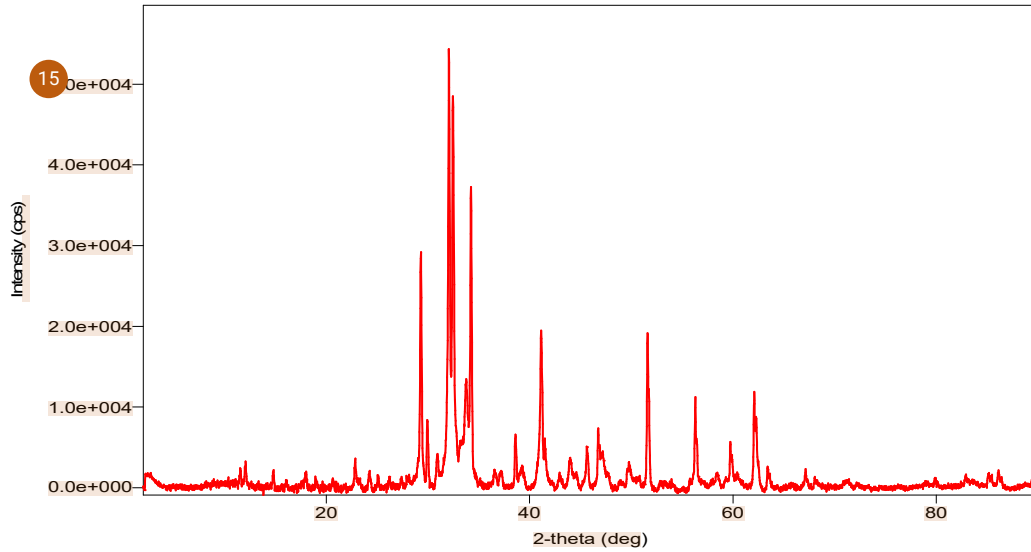


Figure 3.10 XRD image of Sleeper cement (OPC 53S)

3.2.3 Plasticizer: Commercially available superplasticiser based on second generation polycarboxylic ether polymers which has test certification /approvals of ASTM C94 Types G [34] and IS 9103 [35]. Its performance test results (as provided by the manufacturer) are given in Table 3.11 :

Table 3.11 Performance test results of plasticizer

S.No.	Property/Specification	Value
1	Colour	Light brown liquid
2	Relative density	1.07 ± 0.02 at 25 ⁰ C
3	pH	≥ 6
4	Chloride ion content	< 0.2%

3.3 SCHEME OF EXPERIMENTAL INVESTIGATION

In order to accomplish the aforementioned objectives, research work was performed on design control mix, binary and ternary mixes of cement with different pozzolans having high aluminous and silicious contents. All the pozzolans were used as a replacement of cement on weight basis. Metakaolin (MK) mixed with OPC in 10, 13 and 16% alongwith 15% flyash. Two mixes (ALC5 and ALC10) of OPC with 5% and 10% of High Alumina Cement (HAC) were also prepared containing 5% and 10% of flyash respectively. Another two mixes (ALC5S and ALC30S) of 53-Sgrade OPC with 5% and 30% HAC containing 15% and 10% of flyash respectively, were also studied. Redmud (RM) was mixed at 10%, 15% and 20% with OPC in last three (RM10, RM15 and RM20) mixes. The following mix design was adopted :

Table 3.12 Details of mix design for concrete mixes

Mix designation	Water /binder ratio	OPC kg/m ³	Aluminous product		Flyash		Water kg/m ³	Fine aggregate kg/m ³	Coarse aggregate kg/m ³	SP kg/m ³
			%	kg/m ³	%	kg/m ³				
Control	0.32	466	-	00	00	00	149	643	1266	9.32
MK10	0.32	350	10(MK)	46	10	70	149	643	1266	9.32
MK13	0.32	336	13(MK)	60	15	70	149	643	1266	9.32
MK16	0.32	321	16(MK)	75	15	70	149	643	1266	9.32
ALC5	0.32	416	5(HAC)	25	5	25	149	643	1266	9.32
ALC5S	0.32	371	5(HAC)	25	15	70	149	643	1266	9.32
ALC10	0.32	374	10(HAC)	46	10	46	149	643	1266	9.32
ALC30S	0.32	280	30(HAC)	140	10	46	149	643	1266	9.32
RM10	0.32	420	10(RM)	46	00	--	149	643	1266	9.32
RM15	0.32	396	15(RM)	70	00	--	149	643	1266	9.32
RM20	0.32	374	20(RM)	92	00	--	149	643	1266	9.32

Chapter 4

Early Age Strength Test Results and Their Discussion

4.1 General

This chapter describes details of test procedures and discussion of the test results obtained from the experimental studies on various blends of pozzolan and OPC on early age strengths and their comparison with the control mix. High early age strengths are important criteria for concrete as they regulate removal of formwork and thereby the speed of construction as well as facilitate early use of concrete structures. In order to select suitable blends of OPC and pozzolans which could give early age strengths equal to pure OPC products, three key strengths of some blends were determined. The tests for compressive strength, flexural strength and splitting tensile strength on all the blends and control mix were conducted at 7 days and 28 days in accordance with relevant Indian Standards. The average of the strengths of three specimens have been reported as the final value for each case [36].

4.2 Preparation and Curing of Test Specimens

The procedure for preparation and curing the test specimens for all the tests i.e. ⁵⁹ compressive strength test, flexural strength test and splitting tensile strength test, complied in all respects with the requirements given in IS 516 [37]. Before starting the test, it was ensured that all the materials of concrete mix were at room temperature, $27^0 \pm 3^0\text{C}$ and in air-dried condition. For each batch of concrete mix the quantities of all the constituents were taken by weight as per the design mix. The binding materials, including OPC, pozzolanic materials, and other major components of concrete such as coarse and fine aggregates, water, and superplasticizer, were meticulously measured with an accuracy of 0.1% relative to the total batch weight. The test specimens were made soon after uniform mixing of all the materials, to achieve complete ³⁴ compaction of the concrete without having

segregation or excessive laitance. The concrete was poured into the mold in three layers, each approximately 5 cm deep, and subsequently vibrated using an appropriate vibrating table. The test specimens were kept in a location devoid of vibrations, wrapped in moist hessian cloth to maintain 90 percent relative humidity, and at a temperature of $27^{\circ} \pm 2^{\circ}\text{C}$ for a duration of 24 hours \pm 1 hour, starting from the moment water was added to the dry ingredients. Following this duration, the specimens were marked with identification, taken out of the molds, and promptly immersed in clean, fresh water. The water was refreshed every seven days and maintained at a temperature of $27^{\circ} \pm 2^{\circ}\text{C}$. Specimens stored in water were promptly tested upon removal, while still in their wet condition. Surface water and grit were wiped off the specimens, and any projections beyond the edges were removed before placing the specimen in position.

4.3 Compressive strength test

The cubic specimens of 150 mm size were placed in the machine so that the force was exerted to the sides of the cubes which were in vertical orientation at the time of casting. The faces of the specimens were kept in direct contact, i.e. without any packing material in between, on the steel plates of the testing machine. The load was applied without sudden impact, continuously increasing at a rate of approximately $13.73 \text{ N/mm}^2/\text{minute}$ ($140\text{kg/cm}^2/\text{minute}$) until the specimen's resistance to the escalating load ceased and no further increase in load could be sustained. The compressive strength of the specimen was determined by dividing this maximum load applied during the test by the cross-sectional area. Average of the three test results was calculated and adopted as the representative value of the batch if no individual test result vary more than $\pm 15\%$ beyond this value [37].

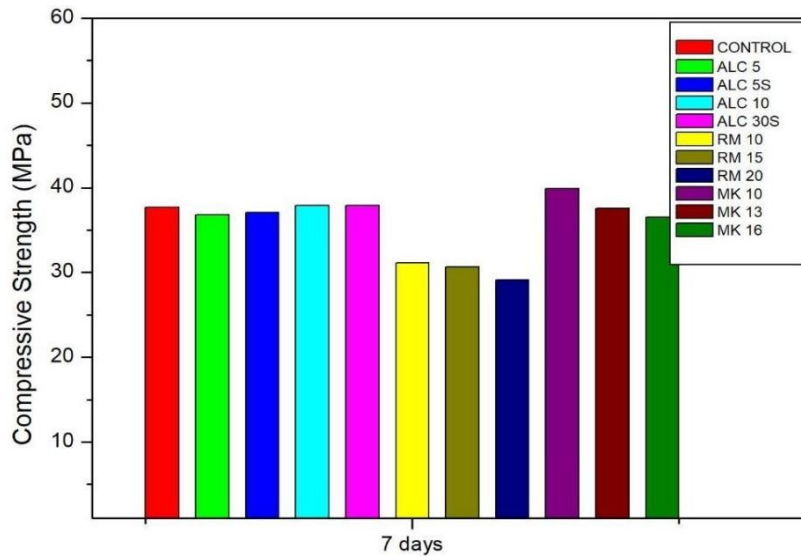


Figure 4.1 Arrangement for compressive strength test

The cubic specimens were tested at the ages of 7 days and 28 days. The results of these tests and average of three test results for each mix are presented in Table 4.1 and 4.2 respectively.

Table 4.1 Test results of compressive strength at 7 days

S.No.	Mix Designation	Compressive strength (MPa)			
		Specimen No.1	Specimen No.2	Specimen No.3	Average value
1	Control	37.69	35.97	39.33	37.66
2	ALC5	36.88	34.98	38.43	36.76
3	ALC5S	36.66	36.87	37.63	37.05
4	ALC10	38.12	39.45	36.08	37.88
5	ALC30S	37.69	37.78	38.20	37.89
6	RM10	31.01	32.21	30.12	31.11
7	RM15	28.67	31.50	31.85	30.67
8	RM20	28.04	30.07	29.23	29.11
9	MK10	40.64	41.18	37.87	39.90
10	MK13	34.79	39.54	38.31	37.55
11	MK16	38.29	35.59	35.66	36.51



8 Fig. 4.2 Average compressive strength of various mixes at 7 days

Table 4.2 Test results of compressive strength at 28 days

S. No.	Mix Designation	Compressive strength (MPa)			
		Specimen No.1	Specimen No.2	Specimen No.3	Average value
1	Control	47.46	48.87	50.77	49.03
2	ALC5	49.46	50.56	54.66	51.56
3	ALC5S	54.45	51.64	49.23	51.77
4	ALC10	51.47	51.34	50.11	50.97
5	ALC30S	52.78	49.4	55.52	52.57
6	RM10	47.54	40.44	44.48	44.15
7	RM15	45.88	43.43	36.91	42.07
8	RM20	36.37	42.34	42.38	40.36
9	MK10	55.46	52.32	60.88	56.22
10	MK13	44.13	46.56	54.33	48.34
11	MK16	59.07	52.15	50.1	53.77

Average compressive strength test results at 7 days, are shown in Fig.4.2 where MK10 achieved highest compressive strength. MK13, MK16 and all the ALC mixes gained compressive strength almost equal to the control mix, while RM mixes did not perform so well.

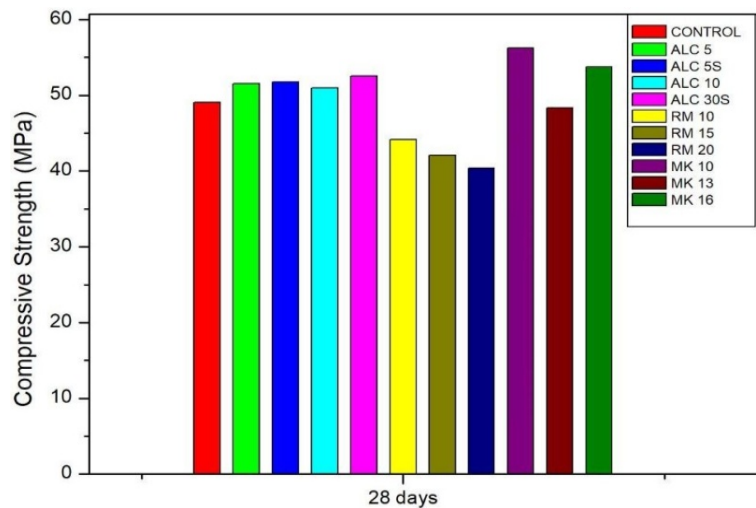


Figure 4.3 Average compressive strength of various mixes at 28days

Average compressive strength test results at 28 days are shown in Fig.4.3 which exhibit that all the mixes having good aluminous content achieved better compressive strength than the control mix except MK13 which shown comparable compressive strength to control mix. All the RM mixes have again performed poorly. The strength enhancement from the pozzolan occurs through multiple mechanisms, including ⁴⁶the filler effect, acceleration of Portland cement hydration, and the pozzolanic reaction between metakaolin (MK) and calcium hydroxide. The finer particles of pozzolan cause filler effect immediately after mixing which results in more efficient paste packing. The acceleration of cement hydration, and the pozzolanic reaction take place thereafter. High alumina content of MK and ALC mixes supported early strength gain of their binary as well as ternary blends.

4.4 Flexural strength test: The prismatic specimen was placed in the machine on two steel rollers, 38 mm in diameter and having centre to centre distance of 600 mm. The specimen will be positioned in the machine so that the load is applied along two lines which are 200 mm apart, to its top surface that was cast in the mold. The axis of the specimen and the axis of the loading device were carefully aligned. The force was applied steadily without sudden impact, incrementing continuously at a loading rate of 3923 N/min (400 kg/min). The load was raised until the specimen failed, and the ¹⁶ maximum load applied during the test was duly recorded. The flexural strength or modulus of rupture (f_b) is provided as

$$f_b = pl/bd^2$$

b = width of specimen (mm)

d = failure point depth (mm)

l = length of the span (mm)

p = maximum load applied (N)

Average of the three test results was calculated and adopted as the representative value of the batch if no individual test result vary more than $\pm 15\%$ beyond this value [37].



Figure 4.4 Arrangement for flexural strength test

The flexural strength test results of three specimens for all the mixes and their average values are shown in Table 4.3 and 4.4 respectively.

Table 4.3 Test results of flexural strength at 7 days

S.No.	Mix Designation	Flexural strength (MPa)			Average value
		Specimen No.1	Specimen No.2	Specimen No.3	
1	Control	7.11	7.45	6.66	7.07
2	ALC5	6.19	7.56	6.63	6.79
3	ALC5S	6.5	8.31	6.53	7.11
4	ALC10	7.34	6.42	7.34	7.03
5	ALC30S	7.75	6.92	6.7	7.12
6	RM10	6.52	6.21	7.39	6.71
7	RM15	5.56	6.57	6.59	6.24
8	RM20	6.77	6.32	5.59	6.23
9	MK10	6.77	7.29	7.33	7.13
10	MK13	7.08	6.67	6.87	6.87
11	MK16	6.83	6.51	6.72	6.69

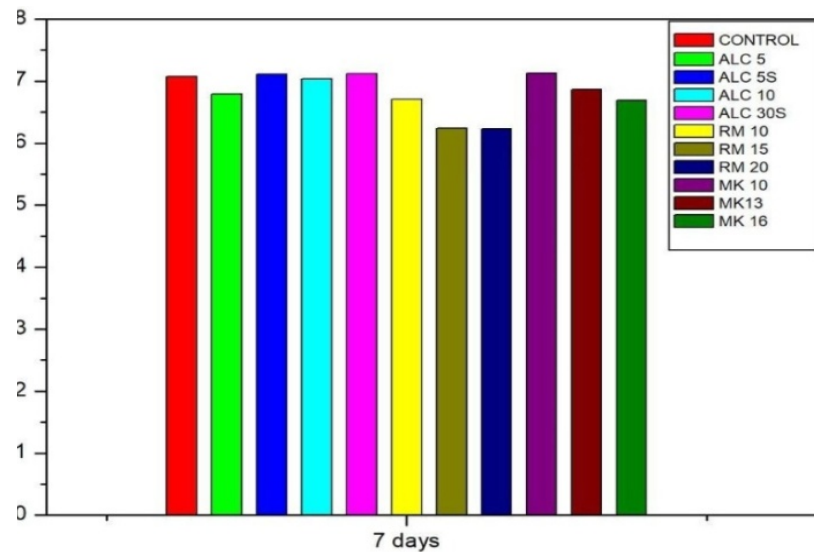


Figure 4.5 Average flexural strength of various mixes at 7 days

Average flexural strength of various mixes at 7 days are shown in Fig.4.5 where ALC mixes, MK mixes and RM10 gained 7 days flexural strength

almost equal to the control mix. Remaining mixes (i.e. RM15 and RM20) were having 7 days flexural strength less than the flexural strength of control mix. ALC and MK mixes have better flexural strength probably due to refinement in pore structure and denser, thinner interfacial transition zones.

Table 4.4 Test results of flexural strength at 28 days

S.No.	Mix Designation	Flexural strength (MPa)			
		Specimen No.1	Specimen No.2	Specimen No.3	Average value
1	Control	9.56	8.77	9.3	9.21
2	ALC5	9.11	8.72	8.85	8.89
3	ALC5S	8.87	10.06	8.27	9.07
4	ALC10	8.78	8.49	9.82	9.03
5	ALC30S	9.34	8.98	9.66	9.33
6	RM10	6.97	8.34	7.96	7.76
7	RM15	8.04	7.75	7.4	7.73
8	RM20	8.33	8.03	6.77	7.71
9	MK10	8.76	7.98	9.91	8.88
10	MK13	7.85	8.44	9.75	8.68
11	MK16	8.24	8.3	8.4	8.31

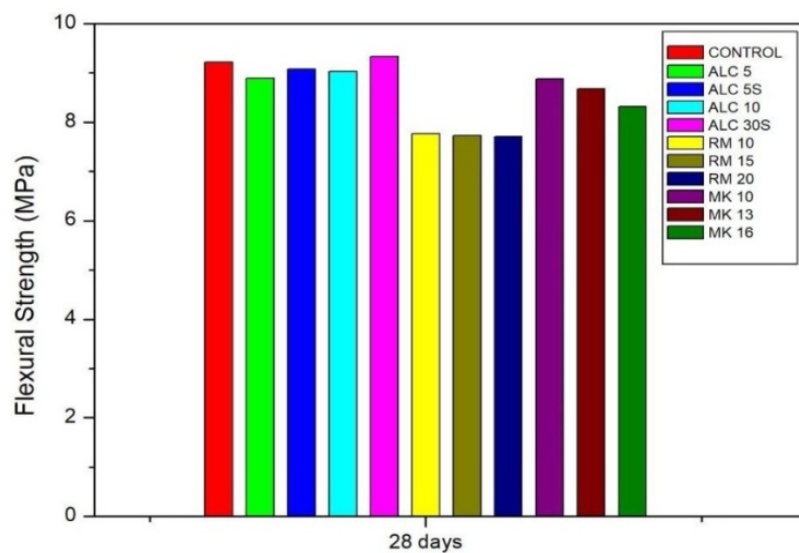


Fig.4.6, flexural strength of various mixes at 28 days

Results have shown that only ALC30S could perform better than the control mix, while other ALC and MK mixes are having flexural strength close to the control mix. RM mixes demonstrated flexural strength slower than the control mix.

4.5 Splitting tensile strength test: The cylindrical specimen of 150 mm diameter and 300 mm height was placed centrally so that load was applied across its diameter. In between the steel platens of the loading machine and the specimen contact surface two packing strips of hard board conforming to IS 1658 [38] with a width of 15 ± 2 mm, a nominal thickness of 4 mm, and a length greater than that of the specimen were interposed for even distribution of load along the line of contact. The strips were discarded after every single use. A continuous rate of loading without shock was maintained in the span of 1.2 to 2.4 N/(mm²/min). The splitting tensile strength of the specimen was determined with an accuracy of ± 0.05 N/mm² using the formula: $2P/\pi ld$, where P represents the maximum load in Newtons applied to the specimen, l is the length of the cylinder, and d is the diameter of the cylinder. Average of the three test results was calculated and adopted as the representative value of the batch if no individual test result vary more than $\pm 15\%$ beyond this value [39].

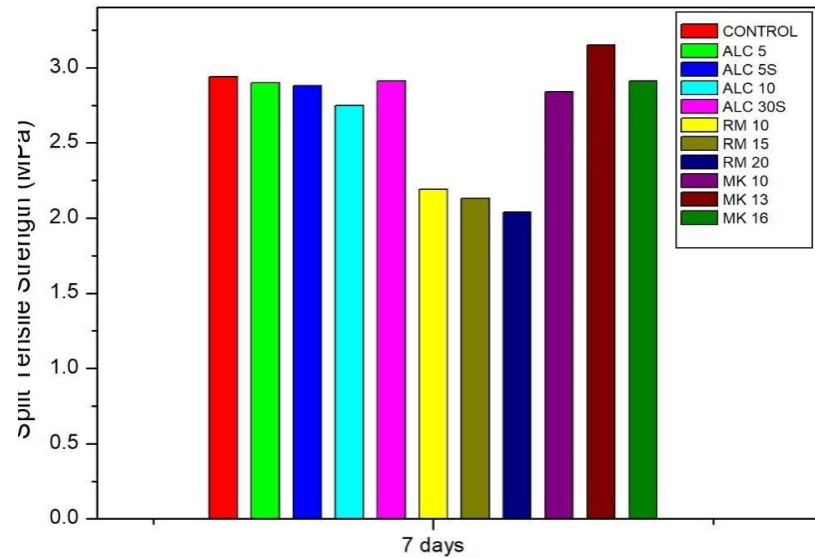


Figure 4.7 Arrangement for splitting tensile strength test

The splitting tensile strength tests on three cylindrical specimens of each mix were conducted after 7 days and 28 days. The test results alongwith their average values for all the eleven mixes are given in Table 4.5 and 4.6.

Table 4.5 Test results of splitting tensile strength at 7 days

S. No.	Mix Designation	Splitting tensile strength (MPa)			
		Specimen No.1	Specimen No.2	Specimen No.3	Average value
1	Control	2.77	2.96	3.10	2.94
2	ALC5	3.02	3.00	2.68	2.90
3	ALC5S	2.93	2.64	3.08	2.88
4	ALC10	2.86	2.65	2.74	2.75
5	ALC30S	2.78	2.97	2.99	2.91
6	RM10	2.26	2.23	2.07	2.19
7	RM15	1.98	2.31	2.10	2.13
8	RM20	2.11	1.96	2.04	2.04
9	MK10	3.02	2.80	2.71	2.84
10	MK13	3.13	3.07	3.26	3.15
11	MK16	2.74	3.03	2.97	2.91



8 Fig.4.8 Average splitting tensile strength of various mixes at 7 days

Fig. 4.8 demonstrates average splitting tensile strength of various mixes at 7 days in which all the mixes except MK13, and RM mixes, have split tensile strength nearly equal to the split tensile strength of control mix. While MK13 has demonstrated higher and RM mixes lower split tensile strengths than the split tensile strength of control mix.

Table 4.6 Test results of Splitting tensile strength at 28 days

S. No.	Mix Designation	Splitting tensile strength(MPa)			
		Specimen No.1	Specimen No.2	Specimen No.3	Average value
1	Control	3.07	2.87	3.5	3.15
2	ALC5	2.98	3.09	3.39	3.15
3	ALC5S	3.11	3.21	3.21	3.18
4	ALC10	3.04	3.15	2.75	2.98
5	ALC30S	2.88	3.21	3.29	3.13
6	RM10	2.2	2.33	2.76	2.43
7	RM15	2.61	2.46	2.32	2.46
8	RM20	2.35	2.67	2.33	2.45
9	MK10	2.81	3.06	3.25	3.04
10	MK13	3.82	3.04	3.8	3.55
11	MK16	3.61	3.12	2.89	3.21

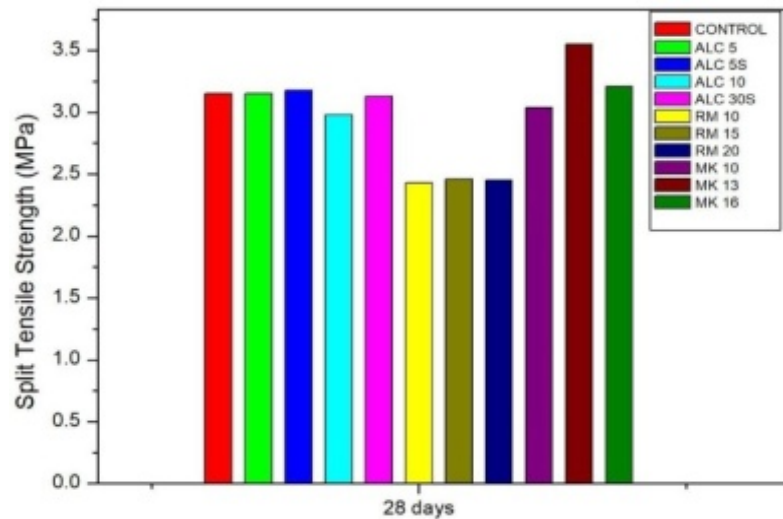


Figure 4.9 Average splitting tensile strength of various mixes at 28 days

Average splitting tensile strength of various mixes at 28 days shown in Fig.4.9 where all ALC mixes, MK10 and MK 16 have comparable split tensile strength to control mix. MK13 is having higher and RM mixes have splitting tensile strengths lower than splitting tensile strength the of control mix.

4.6 Discussion on strength test results:

The strength test results reveal that MK mixes specially MK10 has performed better than the control mix and hence can be used to replace the pure OPC mix for gain of early age as well as later age strengths. Similarly ALC mixes, MK13 and MK16 have also matched the performance of control mix at 7 days and 28 days, which may also be used in place of control mix. While other mixes (RM10, RM15 and RM20) have performed poorly at 7 days and 28 days.

Chapter 5

Durability Test Results and Their Discussion

5.1 General

In this chapter methodology for accelerated sulphate attack on concrete mixes to assess the durability is elaborated alongwith the following :

- Durability of concrete
- Factors affecting durability of concrete
- Accelerated sulphate attack methodology
- Accelerated sulphate attack test results and their discussion

5.2 Durability of concrete

As per IS:456:2000 [18], concrete is deemed durable when it performs satisfactorily within its expected exposure during service in the working environment. Concrete is the most popular cementitious composite. Durability of concrete is a major concern for conserving resources, reducing wastes and the environmental impacts of its repair and replacement. Cement being an important ingredient of concrete, serious durability issues experienced by concrete structures further contribute to pressures of depletion of natural resources and environmental pollution due to cement industry.

In recent years, the durability of concrete structures has become a significant concern for concrete technologists. In some developed countries, it is not unusual to allocate a substantial portion of resources, ranging from 30 to 50% of the total infrastructure budget, for the repair and maintenance of existing structures. This has led to the need to codify the durability requirements world over. The American code ACI 318 [40], Australian code AS-3600 [41], Chinese code GB/T50476 [42], European code EN 206:2013+A1 [43] and ISO: 13823 [44] have addressed durability of concrete. In the latest revision of the Indian Standard code of practice

(IS: 456-2000)[18], to incorporate inherent protection against factors impacting a structure, the previous durability clause has been expanded, and a comprehensive clause addressing various aspects of designing a durable structure has been included. The durability clause has been augmented to provide detailed guidance on factors influencing durability. Changes have been made to the Environmental Exposure Conditions' table, now encompassing 'very severe' and 'extreme' exposure conditions. This provision outlines requirements regarding the dimensions and proportions of structural elements, the thickness of concrete covering, the quality of concrete, measures to protect against exposure to corrosive substances and sulfate aggression, minimum cement standards, the highest permissible water-cement ratio, restrictions on chloride levels, prevention of alkali-silica reactions, and underscores the importance of proper compaction, finishing, and curing techniques. The durability of concrete is very important due to following concerns:

Augmented Service Life: Buildings are typically designed with service lives ranging from 30 to 50 years, anticipating minimal maintenance needs for concrete elements within this timeframe. Monumental building structures, concrete bridges and other crucial civil engineering structures have greater service life requirements of typically 100 years or more. Durable concrete ensures prolonged service life of structure without any hindrance to the expected service requirements.

Enhanced Structural Performance: Improving the durability of concrete can yield advantages such as increased structural capacity and reduced deformations during service. This enables the creation of lighter and more stable structures while concurrently extending the service life of the construction. This approach allows for the engineering of buildings with optimized performance, moving away from more conservative deemed-to-satisfy principles in design.

Conservation of Resources: Durability can also play a significant role in environmental conservation. A durable concrete used in a structure reduces the

need for frequent replacement or repairs for several years. This, in turn, contributes to the conservation of natural and other resources that would otherwise be used in the replacement and repair processes.

5.3 Factors affecting durability of concrete

Apart from its physical and chemical properties, the durability of concrete is governed by the failure mechanism from various exposure conditions. A durable concrete is supposed to perform without any compromise to its serviceability requirements, at least for its designed life in the expected environmental conditions. The environmental and exposure conditions vary with time, place and position of the structural element which are inherent parts of the service life of any structure.

In order to ensure desired performance from durability concern, the following properties of concrete need to be focused: The physical characteristics of concrete play a crucial role in governing its permeability, controlling the ingress and egress of harmful substances, while its chemical properties are contingent upon the composition and volume of cement hydration byproducts. Physical properties that govern concrete's permeability, the entry and exit of aggressive substances and chemical properties on which the type and quantity of cement hydration products depend. The intricate interplay of these physical and chemical features is key to managing concrete permeability. While physical properties of concrete control rate of penetration of aggressive agents, interaction of these fluids and gases with the products of cement hydration, decides the severity of chemical attack [18].

The concrete durability may be affected by several forms of physical damages due to weathering such as , drying shrinkage cracking, frost action, cyclic wetting and drying. Moreover physical agents may cause abrasion, erosion or damage due to fire during service on the other hand concrete is prone to be deteriorated by the following harmful chemical actions [19]-[20]:

5.3.1 Carbonation: Carbonation occurs as carbon dioxide from the atmosphere penetrates concrete, dissolving within the pore solution. This dissolved carbon dioxide then reacts with hydroxides, converting them into carbonates and leading to a reduction in pH, typically below 9. As the pH of the pore solution nears 11, depassivation of steel occurs. The ongoing carbonation emanates from the concrete surface, creating an advancing front that extends across the structure's entire lifespan. The depth of carbonation (d) is directly proportional to the square root of time (t) and is represented by the equation:

$$d = C t^{0.5},$$

where C is denoted as the carbonation coefficient or the rate of carbonation, measured in $\text{mm}/\sqrt{\text{year}}$. Carbonation affects only the length of corrosion initiation stage of the reinforcement and as such carbonation is not a concern for plain concrete elements.



Fig. 5.1 Damage due to carbonation of concrete

5.3.2 Chloride Effect: Soluble chlorides, found in substances like seawater, groundwater, or de-icing salts, have the capacity to permeate concrete through capillary absorption or the diffusion of ions in water. Furthermore, chlorides may be introduced through chemical admixtures, tainted aggregates, or mixing water during the concrete preparation process. Depending on the concrete's quality and the environmental conditions it faces, chlorides have the potential to expedite the onset of corrosion reinforced concrete.



Fig. 5.2 Damage due to chloride attack on concrete

5.3.3 Alkali Silica Reaction: The reactive silica present in some aggregates, reacts with the hydroxides in pore water derived from the alkalis (Na_2O , K_2O) in the cement and cause damage to concrete. Alkali silica reaction (ASR) is the most common effect which generate map like cracking with gels coming through cracks on the concrete surface. During cement hydration, alkali ions are released and initiate an attack on the siliceous minerals present in the aggregate. This interaction leads to the creation of an alkali-silica gel, which can form either on the surface or within the pores of the aggregate particles.. Swelling of this gel due to water absorption cause disintegration of the aggregate and also destruction of the bond between the aggregate and the hydrated cement paste.



Fig. 5.3 Damage due to ASR on concrete

5.3.4 Sulfate Attack: Sulfate attack is a deterioration process involving the interaction of sulfate ions with the elements of cement paste, resulting in structural degradation. Sulfates are naturally present in soils, seawater, and groundwater, and they are also widely utilized in industrial processes and as fertilizers. These sources can lead to soil and groundwater contamination. Additionally, internal sources, such as sulfate release from the cement during service, contribute to sulfate-related issues. Sulfate attack can manifest in following forms:

5.3.4.1 Physical Attack: In some field conditions where the upper surface is exposed to dry surroundings, while the lower surface comes into contact with the ground containing solutions with salt the solutions ascend to the upper surface through capillary action. When surface evaporation surpasses the migration rate of the salt solution to the surface, salt crystallization takes place on the upper surface. The salt volume increases markedly when anhydrous Na_2SO_4 changes to $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. This increased volume creates pressure within the pores, leading to issues such as flaking, spalling and cracking which may manifest as surface scaling, and the loss of mass.

5.3.4.2 External Chemical Sulfate attack: Due to permeability of concrete matrix, sulphate ions migrate from external sources and interact with products of

cement hydration. In the case of sodium sulfate, it specifically targets calcium hydroxide, leading to the formation of gypsum and NaOH. Gypsum then reacts with calcium aluminate hydrate to form ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$). The stability of C-S-H is maintained due to existence of NaOH which contributes to elevated alkalinity within the cement system. Calcium sulfate attacks the calcium aluminate hydrate only to form ettringite whereas magnesium sulfate has two-fold reaction with cement paste and hence is generally more aggressive, at the same concentration. Magnesium also reacts by replacing calcium in the solid phase, in addition to reacting with $Ca(OH)_2$ to produce brucite [$Mg(OH)_2$] and non-cementitious magnesium silicate hydrate (MSH). Like ettringite and gypsum, brucite is also an expansive mineral. Its formation within hardened cement paste induces mechanical stress. Another scarce common form of sulphate attack occurs under low temperatures and wet conditions when calcium silicate hydrate and calcium hydroxide undergo decomposition due to reactions with sulfate and carbonate, resulting in the formation of thaumasite. This process leads to significant weakening of concrete transforming it into a spongy white mass without any binding properties.

5.3.4.3 Internal Chemical Sulfate attack: This is a case of chemical attack where the source of sulfates is internally available in the concrete. Delayed ettringite formation (DEF) occurs in hardened concrete due to the delayed release of sulfate, leading to the formation of ettringite. This process induces expansion and subsequent cracking within the concrete structure. Contaminated aggregates containing gypsum or sulfur-rich clinker can serve as sources of sulfate, which may not be readily available during early hydration but can contribute to delayed ettringite formation (DEF) in the presence of moisture. Additionally, sulfates may become available due to the thermal decomposition of ettringite formed during early hydration in overheated concrete. When exposed to water, these sulfate and other reactant ions migrate, leading to the deposition of ettringite within existing micro cracks. Damage results from ettringite may be in the form of swelling or

crystal growth. The hydration of silicate phases of Portland cement releases $\text{Ca}(\text{OH})_2$. Sulfate ions react with calcium hydroxide to produce gypsum. This reaction product with a larger solid volume than the primary constituents, which can, in some instances, contribute to the degradation of the concrete.



Fig. 5.4 Damage due to sulphate attack on concrete

5.4 Accelerated sulphate attack methodology

There are many factors that may influence the sulphate attack on concrete. Accordingly variety of laboratory test regimes have been designed by researchers to study the effect of sulphate attack. Further, in order to evaluate the effect of sulphate attack several parameters are selected. Influence of these factors and their evaluation are discussed below:

Influencing factors for sulphate attack: The sulphate attack on concrete is studied varying the following factors which may affect the sulphate attack:

1. Sulphate solution: The effect of sulphate solution depends on its type, concentration, pH value and temperature. Na_2SO_4 , MgSO_4 and CaSO_4 solutions of 2% - 10% concentration are generally used. The leaching process may change the pH value of the immersion solution from neutral to higher values, hence pH value is to be maintained in order to simulate the

actual field conditions. Increased temperature of the solution accelerates the attack[45]

2. Immersion type: The specimens are kept either fully or partially immersed in the solution. In some tests compressive or flexural stresses (static/dynamic) are also applied during immersion period.[46]-[48]
3. Duration: Some tests are designed as rapid tests but it is generally accepted that a period of 1-2 years is essential for study of sulphate attack[49],[50].
4. Alternate wetting-drying cycles: In order to accelerate the sulphate attack which also simulates the actual conditions alternate wetting and drying cycles are adopted. These alternate cycles may be varied on the basis of ratio of wetting-drying periods, forced drying at high temperature or open air drying[51],[52].

Evaluation parameters : The evaluation of sulphate attack has been done on the basis of measurement/determination of various parameters such as expansion, weight change, loss of compressive strength, flexural strength, splitting tensile strength and microstructural study.

Adopted scheme for accelerated sulphate attack : ²or obtaining the experimental physical sulphate attack results in shorter duration, the artificial accelerated sulphate attack was designed as alternating wetting and drying in a 10% Na₂SO₄ solution. The wetting-drying cycles were set as alternate wetting and drying periods of 16 hours and 8 hours respectively [53]. Some other researchers have also found this wetting- drying cycle quite severe [54],[55]. ²Also, the monthly average day time temperatures in this region as well as in some other regions of the globe lies in the range of 20⁰C to 40⁰C (as shown in Fig 5.5), ²which is sufficient for drying of the outer layer where the sulphate ion concentration is significant [56]. Thus, full wetting by submerging the specimens in the solution and sun drying of the specimens to maximum extent has been achieved by keeping them in the open environment for explained duration.

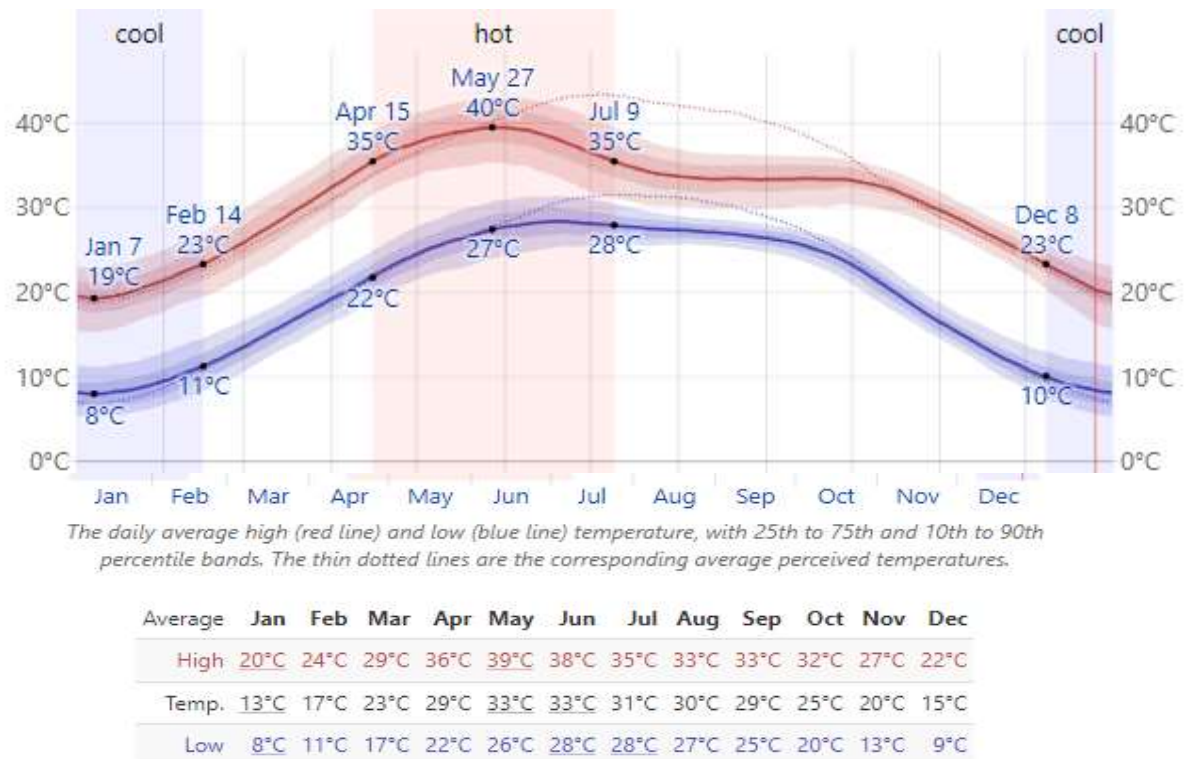


Fig. 5.5 Average high and low temperatures in New Delhi for 2020 [56]

After 28-day water curing, the specimens were transferred into 10% sodium sulphate solution for wetting-thereafter drying and such cycles were repeated at ambient temperatures. These specimens were tested for determination of three key strengths of concrete i.e. compressive strength, flexural strength and splitting tensile strength after 150 cycles, 300 cycles and 500 cycles. The average of values obtained for the three specimens for each test after specified number of cycles, has been considered as the residual strength of the mix. Each specimen was brought in saturated surface dry condition and weighed on electronic balance before testing.

5.5 Accelerated sulphate attack test results and their discussion

The durability tests were conducted on specimens after subjecting them to wetting (16 hours) in 10% Na₂SO₄ solution and drying (8 hours) cycles. The

results are as shown in Table 5.7 to 5.10 and Figs. 7 to 10 for residual compressive strengths, residual splitting tensile strengths, residual splitting tensile strengths and percentage weight loss respectively after accelerated sulphate attack cycles.

Table 5.1 Average values of residual compressive strength after accelerated sulphate attack cycles

S.No.	Mix Designation	Residual average compressive strength (MPa)			
		0 cycles	150 cycles	300 cycles	500 cycles
1	Control	50.11	47.73	42.36	35.94
2	ALC5	51.89	46.56	42.48	38.22
3	ALC5S	51.05	46.32	42.04	37.55
4	ALC10	51.57	46.76	41.61	38.34
5	ALC30S	52.36	46.12	41.33	38.31
6	RM10	44.15	41.21	37.5	31.76
7	RM15	42.07	39.16	35.66	31.12
8	RM20	40.36	37.21	34.87	31.03
9	MK10	57.06	54.42	48.82	44.87
10	MK13	50.76	48.47	44.21	41.12
11	MK16	55.18	52.83	49.08	46.31

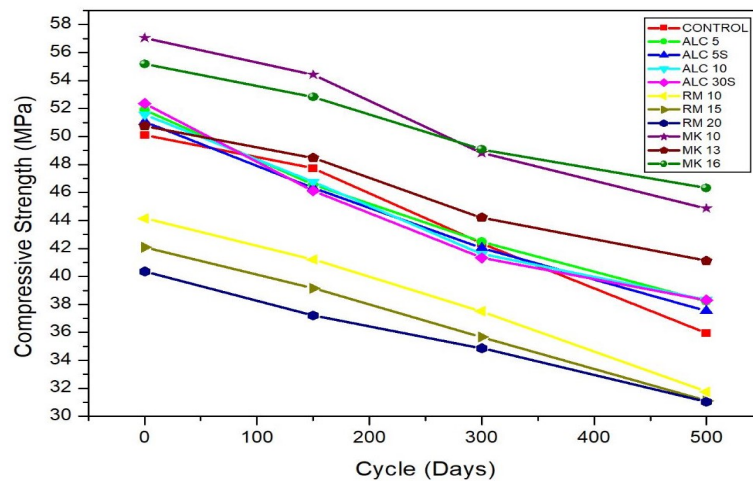


Fig. 5.6 Variation of residual average compressive strength of various mixes

Variation of residual average compressive strength after sulphate attack cycles shown in Fig.7 which reveal that control mix has maximum drop of about 28% in average compressive strength, after 500 cycles, whereas ALC mixes have a marginal lesser drop of about 26%. The MK mixes performed the best (i.e. significantly better) and demonstrated a loss of about 19% in average compressive strength. The RM mixes performed similar to control mix and had a loss (about 28%) in average compressive strength.

Table 5.2: Average values of residual flexural strength after accelerated sulphate attack cycles

S. No.	Mix Designation	Residual average flexural strength (MPa)			
		0 cycles	150 cycles	300 cycles	500 cycles
1	Control	9.37	8.68	7.56	6.1
2	ALC5	9.07	8.16	6.88	6.17
3	ALC5S	9.11	8.21	6.65	6.04
4	ALC10	8.88	7.87	6.45	6.11
5	ALC30S	9.11	7.76	6.46	5.98
6	RM10	7.76	6.84	6.28	5.17
7	RM15	7.73	6.73	6.07	5.12
8	RM20	7.71	6.75	6.14	5.15
9	MK10	8.88	8.24	7.38	6.31
10	MK13	8.72	8.07	7.11	6.07
11	MK16	8.43	7.84	7.1	6.08

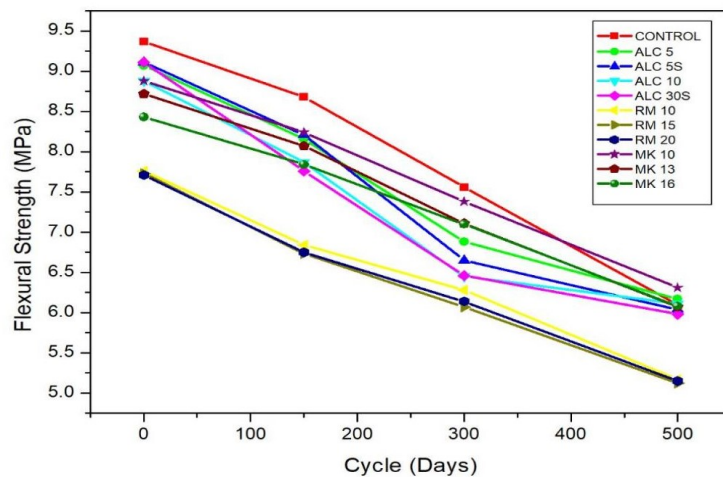


Fig. 5.7 Variation of residual avg. flexural strength of mixes

Fig.8 shows variation of residual average flexural strengths where the control mix has shown about 35% loss in flexural strength after 500 cycles, the loss of flexural strength in ALC mixes is a little lower i.e. 33%. The MK mixes performed even better and shown only 29% weight loss. The RM mixes performed almost similar to control mix and demonstrated a loss of about 34%.

Table 5.3: Average values of residual splitting tensile strength after accelerated sulphate attack cycles

S.No.	Mix Designation	Residual average splitting tensile (MPa)			
		0 cycles	150 cycles	300 cycles	500 cycles
1	Control	3.17	2.89	2.51	2.01
2	ALC5	3.15	2.73	2.52	2.19
3	ALC5S	3.18	2.66	2.47	2.22
4	ALC10	2.98	2.6	2.48	2.2
5	ALC30S	3.13	2.59	2.44	2.19
6	RM10	2.43	2.21	1.81	1.66
7	RM15	2.46	2.17	1.84	1.68
8	RM20	2.45	2.18	1.88	1.7
9	MK10	3.26	3.01	2.68	2.23
10	MK13	3.67	3.4	3.08	2.65
11	MK16	3.64	3.37	3.03	2.52

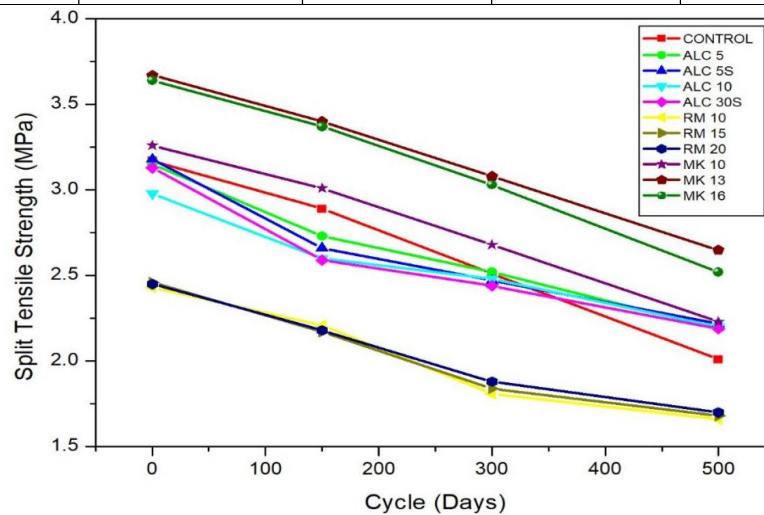


Fig. 5.8 Variation of residual average splitting tensile strength of various mixes

The loss of average splitting tensile strengths of various mixes after sulphate attack displayed in Fig.9 which revealed that after 500 cycles in control mix a loss of

37% is much higher than the loss in ALC mixes and MK mixes, which have about only 30%. The RM mixes have about 32% loss of average splitting tensile strength.

Table 5.4 Average values of weight loss (%) after accelerated sulphate attack cycles

S.No.	Mix designation	Average weight loss (%)		
		150 cycles	300 cycles	500 cycles
1	Control	0.54	1.25	2.01
2	ALC5	0.51	1.18	1.96
3	ALC5S	0.52	1.16	1.97
4	ALC10	0.55	1.17	1.98
5	ALC30S	0.56	1.19	1.98
6	RM10	0.61	1.29	2.02
7	RM15	0.66	1.37	2.04
8	RM20	0.63	1.42	2.13
9	MK10	0.39	0.92	1.72
10	MK13	0.35	0.78	1.4
11	MK16	0.33	0.71	1.32

Average weight loss percentages of various mixes are shown in Fig.10 which demonstrate that RM mixes have more weight loss than the control mix. ALC mixes have weight loss little less than control mix, while MK mixes have significantly smaller weight loss than the control mix.

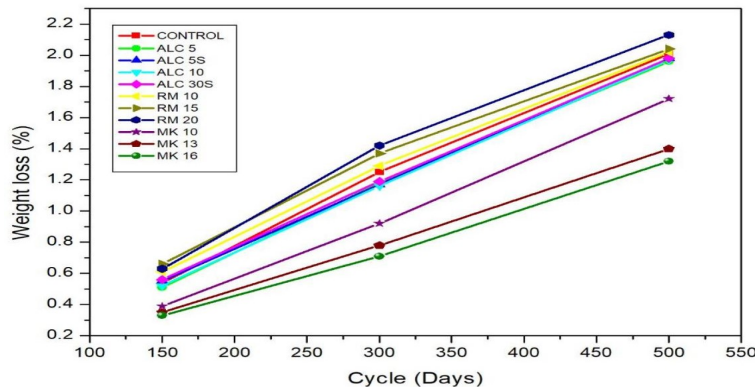


Fig. 5.9 Variation of avg. wt. loss (%) after accelerated sulphate attack cycles

5.6 Discussion on durability test results:

The test results under accelerated sulphate attack after 500 wetting -drying cycles indicate that addition of pozzolans has improved the sulphate attack resistance of the concrete. RM mixes proved comparable sulphate resistant to the control mix, while ALC mixes have shown marginally better sulphate attack resistance and MK mixes have demonstrated significantly better residual strengths than the control mix. With regards to weight loss, RM mixes have more, ALC mixes have comparable and MK mixes have significantly less than the control mix.

Chapter 6

Conclusion, Future Scope and Social Impact

6.1 General

The present study aimed for providing a feasible solution which attempted to reduce, to some extent, the effect of two perpetual problems i.e. ever growing pollution and depletion of natural resources. Both of these problems are byproducts of our developmental activities, of which construction is a major part.

All construction activities involve use of cement, hence to limit the above mentioned problems, reduction in use of cement is necessary. Pozzolanic materials when looked upon as alternative to OPC pose a limitation of slower rate of initial strength gain which is a hindrance in their use considering removal of formwork for speedy construction.

In this study a feasible solution is being suggested to overcome the limitation for the use of pozzolanic materials where ten binary/ternary blends of aluminous and silicious pozzolanic materials have been studied. These blends were prepared by replacing varying percentages of OPC in concrete mix. In order to select suitable blend(s), which could effectively enhance the gain of high early strength of cementitious composites, tests of compressive strengths, flexural strengths and splitting tensile strengths were conducted. The most suitable blends were suggested on the basis of their comparison with the control mix of OPC alone.

Another aspect of the study was to verify the use of these blends on durability aspect. For this purpose the durability tests were performed in an artificially accelerated sulfate attack environment over 150, 300 and 500 alternate wetting and drying cycles of 24 hours each. Some of the blends have performed quite satisfactorily in view of residual strength and percentage weight loss over these cycles.

The main conclusions of the study are summarized as under:

6.2 CONCLUSIONS

- All the redmud mixes (i.e. OPC blends with 10%, 15% and 20% of redmud) have performed poorly for strength gain with comparable durability performance to the control mix, so they are not recommended.

- Two High Alumina Cement mixes [1. OPC43 (90%) + High Alumina Cement (5%) + Fly ash (5%), 2. OPC 43(80%) + High Alumina Cement (10%)+Fly ash (10%)] and also the other two High Alumina Cement mixes [1.OPC 53S (80%)+ High Alumina Cement (5%) + Fly ash (15%), 2. OPC53S (60%)+ High Alumina Cement (30%)+Fly ash (10%)] were found to have comparable strengths at all ages and marginally better performance against sulphate attack than that of control mix.
- All the metakaolin mixes [1.OPC(75%)+Metakaolin (10%)+Fly ash (15%) 2.OPC (72%)+Metakaolin (13%)+Fly ash (15%) and 3. OPC (69%)+Metakaolin (16%)+Fly ash (15%)] performed well for gain of initial as well as later age strengths, except MK13 which shown 28 days compressive strength comparable to the control mix. MK10 has demonstrated the overall best performance for initial and later age strengths and second-best for resistance against sulphate attack among all the mixes, while the other two MK mixes (i.e. MK13 and MK 16) have also shown better sulphate resistance than the control mix. At 500 cycles MK16 has performed the best way, its residual strength has surpassed the residual strength of all other MK mixes.
- The pozzolanic admixtures of aluminous nature have been able to improve the initial and later age strengths as well as durability due to better particle packing, making additional cementitious products by consuming the calcium hydroxide made available by the hydration of complex oxides in cement. Only redmud mixes have failed to improve strengths with comparable durability performance.
- With regard to weight loss under sulphate attack, RM mixes have more, ALC mixes have little smaller and MK mixes have significantly smaller than the control mix.
- The results of various strengths and durability tests clearly reveal that incorporation of judicious blends of pozzolanic materials of aluminous nature can enhance the strengths beyond the control mix (prepared with OPC alone

i.e. without mineral admixtures) along with better durability performance. Use of MK10 mix (having 10% metakaolin and 15% flyash) can replace 25% OPC.

- Ample quantities of MK and flyash are available at reasonable costs and hence their blends can be used for replacement of OPC (by giving comparable/better strengths) and improved durability.

6.3 Future scope of the study

1. In line with the present study, blends of other pozzolanic materials may be studied for high early strength gain and durability.
2. The influence of pore size refinement of pozzolanic blends on strength development may be studied
3. In terms of durability, further data on long-term study is necessary to predict behavior of field structures made with these recommended blends and exposed to extreme exposure.
4. Microstructural study on products of hydration at various stages may be carried out for better understanding of the effects of pozzolans and their better proportioning.
5. A model may be developed for strength development of pozzolanic blends based on the particle size distribution of their aluminous and silicious contents.

6.4 Social Impact : This study has attempted to provide alternatives to pure OPC composites by using blends of siliceous and aluminous pozzolans with OPC. These pozzolans are abundantly available either as industrial waste or natural materials. Use of industrial waste reduce its environmental hazards and also due to its low cost prove to be an economic alternative to the highly processed material like OPC. Ever increasing consumption of cement is a great threat to environment due to high consumption of natural resources and energy involved in its production.

Also, cement production generates CO₂ and other harmful gases in large quantities. The social impacts of the study may be outlined as:

- Proper Utilization of industrial wastes which reduces their harmful effects.
- Reduction in OPC use which results in saving of natural resources, energy and protection from over burdening of environment pollution
- Providing safer and economic alternative to OPC.

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