

CHAPTER 1 INTRODUCTION

1.1 GENERAL

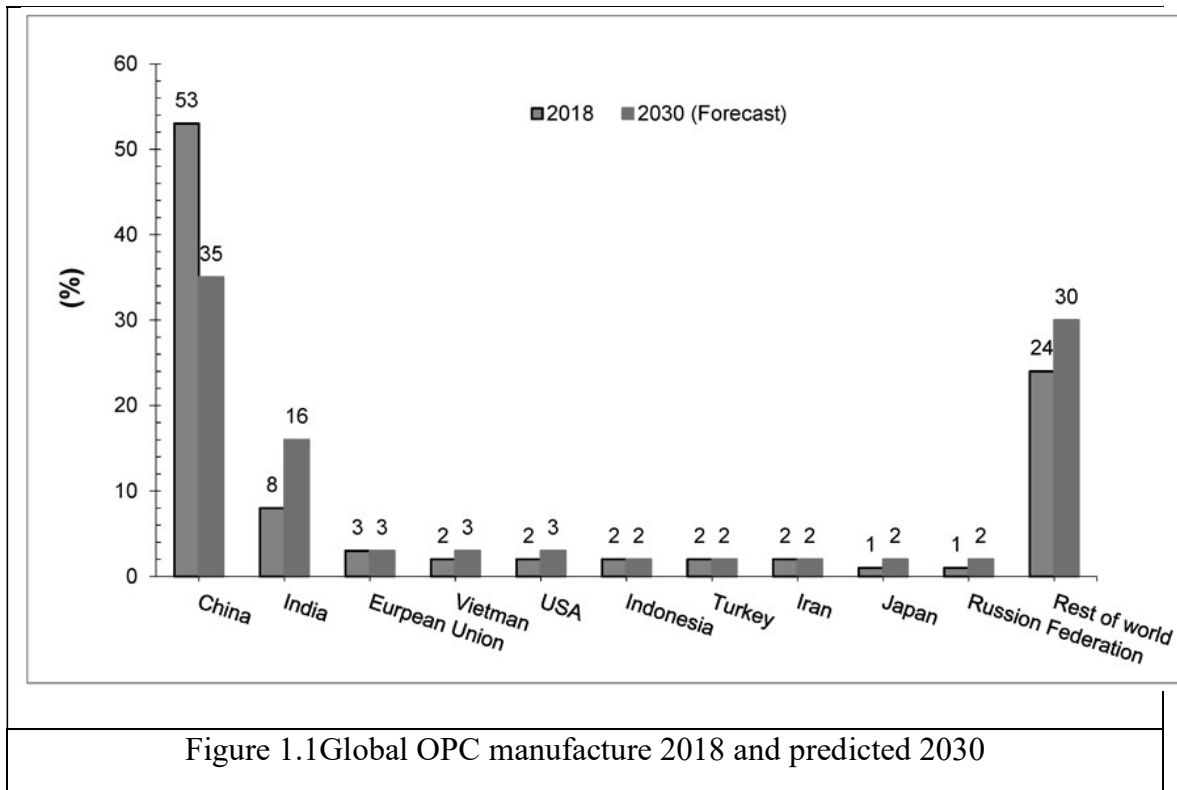
The construction industry has played a vital role in the process of urbanization and industrialization in recent times. It is responsible for generating 5-10% of the total employment opportunities available worldwide and contributes 5-15% to the GDP of nations [1]. The building industry is responsible for a significant share of global energy consumption, accounting for about 40% of the total usage. Additionally, this industry also contributes to 30% of natural resource depletion, 40% of carbon dioxide emissions, and about 30% of waste production. Moreover, the manufacturing process of hydraulic cement used in construction is accountable for around 7-9% of global carbon dioxide emissions. [2]. The global carbon dioxide emissions from cement factories currently make up more than 5% of total emissions. [3]. To mitigate these emissions, alternative binding materials can be used instead of Ordinary Portland Cement (OPC), as suggested by studies[4]–[6]. Several byproducts of the construction industry can be utilized in producing multicomponent binder materials for various purposes[7]. Studies have explored the use of supplementary components in building concrete to reduce the cost and scarcity of conventional materials[8]. Concrete is the most commonly used human-made construction material in the industry, and hydraulic cement is an essential ingredient in its production. Annually, over 4 billion tons of hydraulic cement are manufactured worldwide, resulting in the production of more than 30 billion tons of concrete in 2015.[9]. The World Cement Association Conference illustrates the global cement production rate in Figure 1.1, indicating a sustained increase in cement demand from 1990 to 2030. The escalating need for cement in modern buildings and

infrastructure, especially in emerging countries like China, India, Russia, and Japan, has fueled significant growth in manufacturing [10].

Over the past thirty years, the construction industry has taken several measures to minimize the emission of harmful gases associated with cement production, particularly in developed nations. These measures include using natural gas as an alternative to coal for calcination, employing carbon dioxide-absorbing chemicals, enhancing the grinding process for clinker, and promoting sustainable cement manufacturing practices. However, to significantly reduce greenhouse gas emissions, utilizing cementitious materials can be a practical and effective approach. Waste materials generated during production, such as ground granulated blast furnace slag (GGBS), micro silica (MS), metakaolin (MK), and fly ash (FA), can substitute Ordinary Portland Cement (OPC) and potentially decrease greenhouse gas emissions by a considerable amount. Table 1.1 shows the chemical composition of different cementitious materials (GGBS, silica fume, metakaolin and fly ash). ASTM [11], specifies that pozzolanic materials can be formed by accumulating chemicals such as silica, calcium, alumina, magnesia, and iron, to a concentration exceeding 70%. GGBS, MS, MK., and FA contain elements such as silica, calcium, alumina, magnesia, and iron, with a concentration greater than 70%. This makes them suitable candidates for use as pozzolanic materials, which can substitute OPC in concrete.

These days, many researchers are interested in using GGBS, MS, MK, and FA in cement blends due to their binding properties, which can help reduce the carbon footprint of the cement industry. Moreover, other types of industrial waste like waste marble, foundry sand, and rubber can also be utilized as binding materials to achieve the same goal. Several studies have shown that these pozzolanic materials, including the ones mentioned

earlier, are mostly waste materials resulting from various manufacturing processes.[12]–[16].



The ASTM C 595 defines pozzolana as a material that possesses little or no cementation value but can react with calcium hydroxide to form cementitious compounds in the presence of moisture. Calcium hydroxide is present in Portland cement as a hydration product, which can negatively impact concrete quality by creating voids due to its solubility in water and low strength. Mineral admixtures like pozzolanic materials can improve concrete quality by binding the calcium hydroxide, resulting in better performance. Hydrated cement paste consists of around 70% C-S-H, 20% calcium hydroxide, 7% sulpho-aluminate, and 3% secondary phases. [17]. [18], [19].

Table 1.1 Brief comparison of cementitious materials [20]

S.no.	Property	Portland Cement	Fly ash	GGBS	Micro silica
1	Surface area (m ² /kg)	350-500	300- 600	300-500	15000- 20000
2	Bulk Density (kg/m ³)	1300-1400	1000	1000- 1200	200-300
3	Specific gravity	3.12	2.30	2.90	2.20
Chemical composition					
4	SiO ₂	20	50	38	92
5	Fe ₂ O ₃	3.5	10.4	0.3	1.2
6	Al ₂ O ₃	5	28	11	0.7
7	CaO	65	3	40	0.2
8	MgO	0.1	2	7.5	0.2
9	Na ₂ O + K ₂ O	0.8	3.2	1.2	2.0

By partially replacing cement with SCMs, such as pozzolanic materials, a reaction occurs with the calcium hydroxide present in the Portland cement paste, resulting in the formation of calcium-silicate-hydrate gel. Some of the commonly used pozzolans or mineral admixtures include ground granulated blast furnace slag (GGBS), fly ash (FA), and micro silica (MS). A comparison between these mineral admixtures and Portland cement is provided in Table 1.1 and their particle size distribution is illustrated in Figure 1.1 [21]

Table 1.1, shows that the various mineral admixtures, such as GGBS, FA, and MS, have unique characteristics. When added to cement, they alter the composition of the paste,

affect the hydration process and microstructure of the paste and mortar, as well as the strength and permeability properties of concrete.

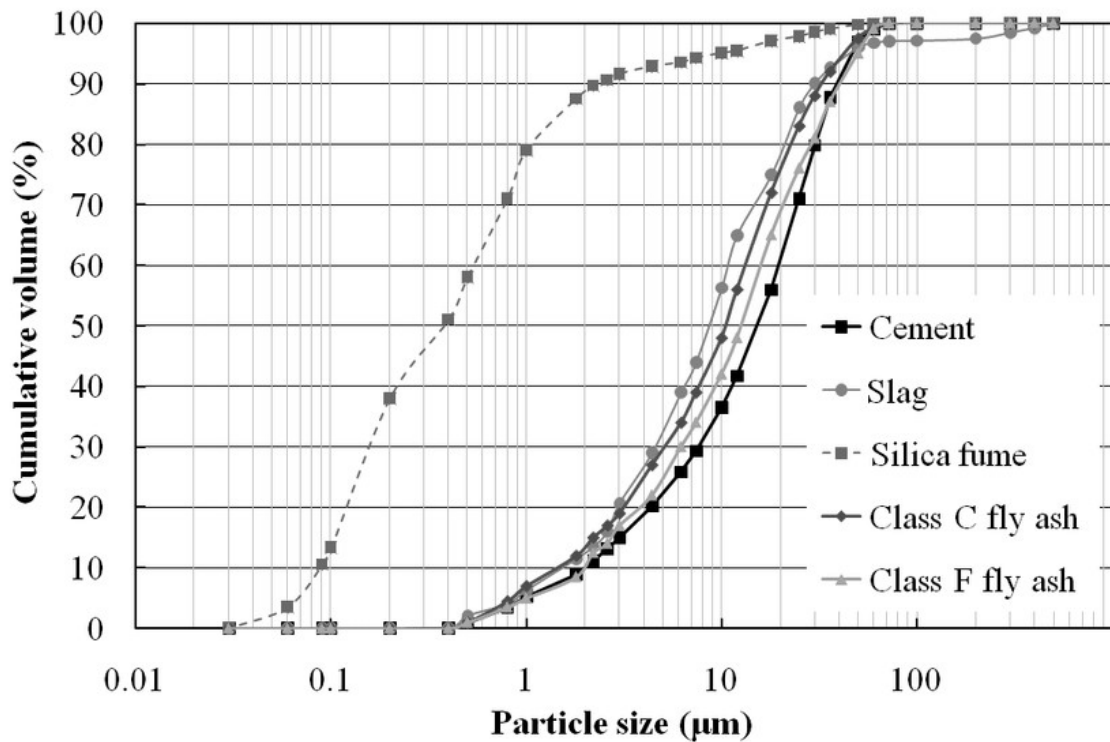


Figure 1.2 Particle size distribution of cementitious materials [21]

Using mineral admixtures in concrete provides a dual environmental benefit. Firstly, it reduces the amount of cement needed, which in turn reduces the amount of carbon dioxide produced during cement production. Thus, the use of supplementary cementitious materials leads to more sustainable concrete. Secondly, using mineral admixtures means that a product that would otherwise be discarded in landfills is being utilized. By using industrial byproducts in this manner, the use of mineral admixtures is seen as a highly effective way of addressing environmental concerns and reducing carbon dioxide emissions. Fly ash is commonly used in concrete because it is less expensive than Portland cement, but silica fume, which is more expensive, is typically not used except in cases where very high strength and low permeability concrete is required.[22][23].

The latest trend is to utilize more mineral admixtures as a direct replacement in the range of 5-70% by mass of total cementitious materials. In addition to reducing the use of cement, mineral admixtures also enhance the chemical, mechanical, and physical qualities [24][25]. The Concrete Admixture Handbook [26] describes that finely divided mineral admixture reduces the quantity of water required to achieve specific consistency of mortar or concrete; however, when the same is used in a large amount, water demand increases. In such cases, chemical additives like superplasticizers and air-entraining agents are used to maintain a particular consistency. The fine mineral admixtures do not lead to a denser granular packing of the cementitious matrix without SP [27].

The polycarboxylate (PC) SP has a high-water absorption rate and long-term slump retention at a low dosage. Still, its chemical structures determine its predominant mechanism and efficiency in cement-based materials [28].

1.2 ROLE OF FLY ASH IN CONCRETE

Fly ash is a combustion residue (coal mineral impurities) in coal burning electric power plants, which flies out with the flue gas stream and is collected by mechanical separators, electrostatic precipitators or big filters. Fly ash has been widely utilized in concrete since it reduces cost of concrete materials, conserves energy resources and reduces environmental problems. It has become an essential ingredient in concrete mixtures.

It mainly consists of SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO and some impurities. According to ASTM C 618, fly ash belongs to Class F if the sum of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) content is greater than 70 % and belongs to Class C if the sum of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) content varies from 50% to 70%. Usually, Class F fly ashes have a low content of CaO (<8%) and exhibit cementing properties, but Class C fly ash contain up to 20% CaO and exhibit no cementation properties. Class C fly ash is further divided into two types by Canadian

Standard Association (CSA) specifications for fly ash i.e., Type C I called intermediate calcium with 8% to 20% CaO and Type C II, i.e., high calcium if CaO is greater than 20%. Low calcium fly ash is produced by burning of anthracite or bituminous coal and high calcium fly ash is produced by burning of lignite or subbituminous coal. Most fly ashes, regardless of composition, improves the workability, tends to reduce the water demand of concrete and hence reduces the water reducing admixtures demand. It reduces cracking due to autogenous and plastic shrinkage. It increases the packing densities of cementitious system, thus creating a less permeable structure. It significantly reduces the permeability of resultant concrete to chloride, water and oxygen and increases concrete's resistance to alkali silica reaction, sulfate attack and other chemical attacks. In addition, it consumes calcium hydroxide and creates calcium-silicate-hydrate, thus making the concrete stronger [29] However, problems are also associated with using this material. Unlike silica fume, fly ash has relatively low surface area and accompanying pozzolanic activity. At normal temperatures, the pozzolanic reaction is slow to start and it does not progress to any significant degree until several weeks after the start of hydration. This results in slow strength development and inadequate strength at the normal age of loading, even though the concrete may have higher strength and durability in the longer term. It has been reported that at 28 days, the degree of fly ash reaction is just 10% [30], [31]. Although, at 91 days the strength of mixes incorporating fly ash was shown to outperform specimens without additives[32]. One explanation for the low activity of fly ash at room temperatures is that the pH of the solution is normally 13, which does not meet the pH requirements of activation of fly ash reaction that is found to be nearly 13.3. Due to its low strength development rate, fly ash concretes are more sensitive to poor curing than that of ordinary Portland cement concrete and thus requires more number of curing days [33]. Along with this, the performance of fly ash depends on its fineness too.

It is reported that fly ash exhibited low pozzolanic activity since it contained a high proportion of crystalline phases and thus cannot be used [34]. Compared to silica fume, fly ash mixes using excessive amounts of high range water reducing agents may cause segregation of different materials, resulting in lower strengths [35].

1.3 ROLE OF MICRO SILICA IN CONCRETE

Micro silica is a by-product of silicon or silicon alloy manufacturing, containing more than 80-85% SiO₂ in amorphous form, and is suitable for use in the cement and concrete industries. Its typical particle size is around 0.1-0.5 μm, with a nitrogen BET surface of 20,000 m²/kg. It is being used increasingly in the world as a mineral admixture to produce high performance concrete. Silica fume is light and has a low bulk density of 200 to 300 kg/m³. It was first utilized in 1970's as an additive in concrete in Norway [36]. The action of silica fume in concrete is physiochemical. The physical phase of this action is in the refinement of void system of cement paste; particularly the transition zone due to its extremely small size. This physical action provides a denser, more homogenous and uniform paste. A replacement of 15% of cement mass by silica fume will add approximately 20,00,000 particles to each cement grain, in such a way that the fine particles surround each cement grain, thus densifying the matrix, improving the bond with aggregate and reinforcing materials such as glass fibers [37]. The chemical phase consists of the pozzolanic reaction that transforms the weak calcium hydroxide crystals into the strong C-S-H gel. It affects the concrete properties by the following mechanisms:

- It eliminates the growth of calcium hydroxide at the cement – aggregate interface, or transforms calcium hydroxide into calcium silicate hydrate by the pozzolanic reaction between silica and lime.

- It eliminates large pores at the cement – aggregate interface, making it denser
- It is able to pack between the cement grains due to its extremely fine particle size, thus lowering the capillary pores, and increasing the density of the material.

As a result of these actions of silica fume, it provides significant improvement in mechanical properties and drastic improvement in durability and impermeability. While imparting significant contribution to concrete strength and durability, silica fume can create an increase in water demand to attain specific workability levels due to the increase in specific area. It has very low bulk density, which may cause difficulty in transporting and handling. If silica fume is densified and compacted in order to improve transporting and handling properties, high degree of agglomeration of silica fume takes place, which considerably decreases its chemical reactivity with calcium hydroxide [38]. Along with this, it can cause plastic shrinkage problems in concrete if not properly used. These factors, coupled with the higher cost of silica fume as compared to Portland cement and other pozzolans, has been barrier to its wider use in routine ‘day to day’ concreting jobs.

1.4 ROLE OF GGBS IN CONCRETE

Blast-furnace slag and its derivative GGBS are industrial byproducts commonly used as supplementary cementitious materials in cement and concrete production. GGBS has self-hydration properties in addition to its pozzolanic action, which distinguishes it from other compounds. This may be due to the presence of 30-40% calcium oxide, which contributes to its characteristic color. GGBS is a more environmentally friendly option for concrete materials as it utilizes a waste product that would otherwise need to be disposed of. Using GGBS can help reduce the depletion of traditional concrete components, such as OPC, fine and coarse aggregates, by incorporating them into the concrete mix. Numerous studies have demonstrated that substituting GGBS for cement does not lead to a reduction in concrete strength.

GGBS, or ground granulated blast-furnace slag, is a fine, granular, and glassy substance that is primarily produced as a byproduct of steel and iron production. The process involves melting a combination of limestone, iron ore, and coke in a blast furnace to create iron and slag, which is then rapidly cooled with water jets to form GGBS. The resulting material is composed mostly of silicates and aluminosilicates of molten calcium and has a high concentration of amorphous calcium, silica, and alumina, making it an excellent binder for cement concrete production. Its physical properties, including specific gravity, bulk density, and surface area, make it a viable supplement to traditional concrete components, despite impacting the flowability of concrete. Furthermore, GGBS offers several advantages over traditional concrete materials, including reduced risk of damage from alkali-silica reaction (ASR), higher resistance to chloride ingress, reduced risk of reinforcement corrosion, and increased resistance to sulfate and chemical attacks.[39][40][41].

1.5 ROLE OF CHEMICAL ADMIXTURE IN CONCRETE

High-range water-reducing admixtures or SPs are critical ingredients in modern concrete to improve flowability at low water content. SPs are commonly used in high-performance, self-consolidating, fiber-reinforced concrete, and other applications [42]. SPs are surface-active agents that change the surface charges of cement particles to disperse them into smaller agglomerates. The formation of such cement clusters during the initial mixing of Portland cement with water is due to relatively large Van der Waals forces of attraction, which work at inter-particle distances of 5 to 7 nanometers (nm). Plasticizers can overcome this force by exerting a strong repulsive force at the surface-liquid interface, allowing the trapped water to escape. The loosely entrapped water particles are associated with the clustered particles of the cement. This water is then used in the hydration process, thus decreasing the amount of water that is to be added

additionally otherwise [43]. The entrapped water between the cement particles is released when the SP is present; as a result, the fluidity or workability of concrete increases [44].

As a consequence, the ability to maintain consistency and flow is enhanced. These chemical admixtures are active for a certain amount of time before their effect wears off, and the cement paste starts to stiffen [45]. Since the dispersion of cement particles is the primary activity of SP, it is critical to investigate and comprehend dispersion behavior.

1.6 SYNERGIC EFFECTS OF MINERAL AND CHEMICAL ADMIXTURE

From the above discussion, it can be said that there are definite benefits of using chemical and mineral admixture like FA, GGBS, MS, etc. in concrete as partial replacement of cement. However, both mineral and chemical admixture has certain shortfalls, and neither could be described as a panacea for all concrete problems. However, using a combination of mineral and chemical admixture along with cement as a ternary system should result in several synergistic effects. Some of the possibilities can be the following:

1. Chemical admixture compensates for the low early strength of concrete with mineral admixture.
2. Mineral admixture increases long-term strength development
3. Chemical admixture offsets the increased water demand of mineral admixture concrete
4. Chemical admixture reduces the total quantity of binding material
5. Incorporating the chemical admixture with mineral admixture makes concrete more compact, resulting in lesser permeability and enhanced durability.

1.7 OBJECTIVES OF RESEARCH WORK

Based on the literature review discussed in Chapter 2, it has been identified that the efficiency of SP has been incorrectly calculated using the original water content, which can lead to inaccurate conclusions about its effectiveness [46][47]. As a result, the current study proposes a new approach to evaluate the efficiency of SP, which can save time and costs associated with finding the proper workability.

In addition to evaluating the efficiency of SP, the new approach proposed in this study also takes into account the effect of other factors, such as cement type and water-cement ratio, which can affect the workability of concrete. By considering these factors, the study aims to provide a more comprehensive and accurate evaluation of SP efficiency.

Although various studies have investigated the use of chemical and mineral admixtures for durability analysis, very few have compared the results of concrete mixed with both chemical and mineral admixtures with plain concrete containing FA, GGBS, and MS [48]–[50]. This study aims to fill this research gap and provide a comprehensive analysis of the effects of chemical and mineral admixtures on concrete durability.

The comparison of concrete mixed with both chemical and mineral admixtures with plain concrete containing FA, GGBS, and MS is particularly important because it allows for a better understanding of the synergistic effects of these admixtures on concrete durability. This can have significant practical implications, as it can help engineers and construction professionals to choose the most appropriate admixtures for their specific applications.

The problem of acid rain has attracted attention from environmentalists and researchers worldwide since its first observation by British chemist R.A. Smith in 1852. The issue has become increasingly severe in recent decades[51][52], with at least one-third of Chinese territory being covered by acid rain. Previous studies have simulated acid rain

but have not considered the impact of environmental air with water droplets [53] [54]. In this study, a scenario has been simulated to better understand the impact of acids in naturally occurring rainfall.

The simulation of naturally occurring acidic rain is important because it provides a more realistic representation of the conditions under which concrete is exposed to acidic environments. This can help to better understand the long-term effects of acid rain on concrete durability, and inform the development of more effective measures to mitigate its impact.

Very few data sets have been considered for forecasting compressive strength and other concrete properties, or research has used data from the literature, which will not produce highly accurate results. In this study, we used a variety of machine learning techniques to forecast compressive strength using more than 1000 actual laboratory data.

The use of machine learning techniques for predicting compressive strength and other concrete properties is particularly important because it allows for more accurate and efficient predictions, which can save time and costs associated with laboratory testing. This can have significant practical implications, as it can help to optimize concrete mix designs and improve the overall quality of concrete structures.

1.8 ORGANIZATION OF THE DISSERTATION

The thesis presentation has been organized into eight chapters, as detailed below: **Chapter 1** introduces the thrust area and the need for research on the synergistic action of mineral and chemical admixture, and the objectives of the study have been briefly discussed.

Chapter 2 presents a comprehensive review of relevant literature based on the research work carried out by various investigators.

Chapter 3 describes the research methodology adopted for study on the material used including their chemical, microstructural and mineralogical analysis. It also describes the sample preparation of paste, mortar and concrete for investigations of their various properties

Chapter 4 deals with discussions about the properties of the material used and presents the results and discussion of the study on the physical properties of paste and mortars of OPC admixed with FA, MS, and GGBS. It also deals with saturation dosage of SP and its efficiency

Chapter 5 Shows the effects of admixing FA, GGBS, and MS with and without SP on mechanical properties of concrete.

Chapter 6 presents the durability aspects of concrete systems. It also deals with the mineralogical and microstructural analysis of the admixed concrete.

Chapter 7 deals with the mathematical modeling and predicted model using experimental laboratory data

Chapter 8 presents the key finding of the study. The recommendation based on the results of this study and the future scope of the work is also described.