India

Global Cement and Concrete
Association

BLENDED CEMENT
- GREEN, DURABLE & SUSTAINABLE

2022

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EXECUTIVE SUMMARY

Amongst the eight core industries of India, cement industry plays a vital role in the growth and economic development of our country because of its strong linkage to other sectors such as infrastructure, construction, housing, transportation, coal, power, etc. The installed capacity of cement industry in India is 537 million tonnes with cement production of around 334.37 million tonnes in 2019–20, which comprises 144 integrated large cement plants, 107 grinding units, 62 mini cement plants and 5 clinkerisation units. Cement is considered to be responsible for about 7% of global anthropogenic CO_2 emissions. Despite having the highest potential to reduce these emissions in an economically and technically feasible manner, the blending of mineral additions with cement is still significantly below its potential. This document addresses some of the misapprehensions about the use of blended cements that affect its acceptance and presents a comparison of these cements with Ordinary Portland Cement.

Blended cements are formulated by blending of portland clinker with other finely ground materials such as pozzolana and granulated blast furnace slag. The partial replacement of clinker, which is not only the more expensive component of cement, but also the most resource, energy and emission intensive, with mineral additives improve the sustainability of the material. Most importantly, as explained in this document, the performance of cements can be improved through this replacement, making blended cements the most attractive means to achieve sustainable infrastructure development.

The availability of fly-ash (from thermal power plants), blast furnace slag (from steel plants), use of advanced technology in the manufacturing of cement and simultaneous increase in market demand has increased the production of blended cement in the recent years. In India, the production of OPC is continuously declining, with simultaneous increase in production of blended cements like PPC, PSC, and Composite Cement based on granulated blast furnace slag and fly ash. Other cement formulations such as Portland limestone cement and limestone calcined clay cement are also at different stages of development in India. At present, blended cements have greater share (73%) in comparison to Ordinary Portland Cement (27%) of the total cement production. Blended cements provide the means to reduce the clinker factor even further in the near future, without a compromise on economy and safety.

TECHNICAL ADVANTAGES OF BLENDED CEMENTS

The fly ash – slag based composite cement is a relatively newly standardized type of cement and its specifications have only been formulated by the Bureau of Indian Standards in 2015. Its commercial production has already started in the country. The composite cement (conforming to IS: 16415–2015) can be produced either by inter-grinding of portland cement clinker (conforming to IS: 16353–2015), granulated slag (conforming to IS: 12089–1987) and fly ash (conforming to IS: 3812 (I) 2013) with the addition of natural/chemical gypsum or by an intimate and uniform blending of ordinary portland cement (conforming to IS: 269–2015), finely ground granulated slag and fly ash with the addition of ground gypsum. The composite cements are manufactured using 35–65% portland cement clinker/ ordinary portland cement along with 15–35% fly ash and 20–50% granulated blast furnace slag together as the blending component.

In this document, the advantages of different blended cements over OPC are discussed based on hydration, microstructure and permeability, rheology and workability, strength development, shrinkage (chemical, autogenous, drying etc.) and cracks, leaching, alkali aggregate reactivity, sulphate attack, reinforcement corrosion, long-term durability of construction and usage in preparation of high strength concrete.

The risk of thermal cracking is reduced in blended cements, compared to OPC due to the lower rate of heat evolution and the total amount of heat liberated during hydration. The temperature has a considerable effect on the total amount of heat evolution for a particular cement. The dormant period, the period during which the concrete can be safely transported, placed, finished, etc., is prolonged in blended cements due to the presence of the mineral additives such as fly ash and slag allowing easier working on the site and lesser wastage of the cement. The lower amount and rate of the heat of hydration for blended cement also makes them suitable for use in mass concrete structures such as dams and spillways.

In general, concrete made with cement blended with Supplementary Cementing Materials (SCMs), or where ordinary portland cement is partly replaced with SCMs, is more durable than concrete made with ordinary portland cement at the same water-to-binder ratio. The main reason is the formation of denser microstructure both due to improved particle packing initially and more Calcium Silicate Hydrates (CSH or CASH) formed from the conversion of calcium hydroxide (CH) due to what is known as the pozzolanic reaction. Improvements in the Interfacial Transition Zone (ITZ), which is usually regarded as a major feature governing the permeability of concrete, are seen to improve the durability and strength of concrete. The fine particles of the SCMs and the formation of the C-S-H gel from the pozzolanic reaction play an important role in the improvement of the ITZ.

Most research shows an improvement in the rheological properties of fresh concrete with the incorporation of SCMs. Since the workability of a freshly prepared concrete mix depends upon several factors such as the cement type, its fineness, a direct comparison of the ease with which various cements can be worked is difficult to compare. Even though some blended cements, due to their higher fineness can have a higher water demand than OPC, the presence of fine particles reduces the tendency to segregate and improves the flow of the concrete. The rounded particles of fly ash, even after distortion from grinding in the blended cements, offer a ball-bearing effect, improving flow. High-performance concrete mixes, such as self-compacting concretes, are difficult to produce without the use of SCMs.
Strength gain in blended cement is lower at early ages

but higher at later ages. With sufficient curing, the large potential of strength of concretes produced using blended cements can be tapped.

The shrinkage strains are comparable at early ages of the drying period for concrete made out of all types of cement blends. However, in the case of binary blends, use of PPC and PSC reduces the drying shrinkage of concrete in comparison to concrete made with OPC. Furthermore, in the case of ternary blends, shrinkage reduces with the higher replacement level of fly ash and slag in comparison to concrete made with OPC. This reduces the risk of cracking and improves the durability of structures.

The consumption of calcium hydroxide and the production of calcium silicate hydrate in the pozzolanic reaction refine the pore structure of cement matrix, thus enhancing the resistance of the cement-based materials against the transport of species from and into the concrete.

The use of SCMs/mineral admixture/blended cements in concrete significantly helps in mitigating the expansion due to alkali silica reaction (ASR), due to the reduction in the availability of alkalis in the pore solution and the refinement of the pore structure. Not only does this reduce maintenance costs of infrastructure such as dams and bridges, but also allows the consumption of local aggregates that may contain deleterious materials. The reduced expansion in SCM-blended systems reduces the risk of expansion and cracking.

This pozzolanic reaction also has the following beneficial impacts on sulphate attack:

a) The consumption of portlandite reduces the formation of gypsum, reducing the expansion and scaling of concrete

b) The replacement of part of the cement by a pozzolanic material dilutes the C3A content and hence all the aluminate bearing phases will accordingly be reduced;

c) The formation of secondary C–S–H also results in the densification of the hardened cement paste since it is deposited in the pores thereby making blended cements impermeable and, therefore, the sulphate ions cannot easily penetrate through the concrete matrix, as in the case of plain Portland cements.

Severe deterioration is however observed in all cements in the case of the rare exposure to high concentrations of magnesium sulphate, due to the reaction with portlandite to form gypsum and brucite (magnesium hydroxide). In the absence of portlandite, the C-S-H phases are attacked. This can lead to a disintegration of the hardened cement paste.

Chloride Induced Corrosion:

Concrete made with blended cements has very low chloride ion permeability or diffusivity as compared to OPC concrete, although it has a low chloride threshold value. The initiation period of concrete made with SCM will be higher in comparison to OPC concrete. The propagation period of concrete structure made with SCM significantly increases due to a lower corrosion rate in comparison to concrete made with OPC. This increases the service life of structures and reduces repair and maintenance costs.

Carbonation Induced Corrosion:

Due to the lower CO_2 emitted during the production process, blended cements also have a lower capacity to reabsorb CO_2. For this reason, concretes made with blended and composite cementitious material show a lower resistance against carbonation as compared to OPC. The carbonation depth of concrete made with blended cement is found higher in comparison to OPC at the same exposure period. As a result, the corrosion initiation period of concrete made with blended cements is likely to get reduced. Experience with fly ash based cements has shown that the long-term performance of blended cements is satisfactory as long as good construction practices are followed. While carbonation depths are increased in blended cement concretes, the resultant impact on corrosion propagation is still a subject of much research.

Performance of concrete or mortar is governed by mechanical and durability parameters. Both properties of concrete depend upon microstructural, chemical and physical characteristics. The chemical characteristics of concrete such as pH, reserve alkalinity and hydration products and physical characteristics such as permeability, shrinkage, etc. govern the concrete durability. Long term durability of concrete structure is directly related with the resistance of concrete against aggressive agencies like sulphate, chloride, carbonation, the heat of hydration, Alkali Silica Reaction (ASR), leaching etc. The effect of blended cement on mechanical and durability parameters have been tabulated on the next page.

Table: Performance of Blended cement concrete as compared to OPC concrete

S. No.	Parameter	Performance of Cement			
		OPC	PPC	PSC	CC
1	Heat of Hydration	High	Lesser	Lesser	Lower
2	Permeability	High	Lesser	Lesser	Lesser
3	Long term Strength	Normal	Higher	Higher	Higher
4	Shrinkage	High	Lesser	Lesser	Lesser
5	Alkali Aggregate Reaction	Less Resistance	Higher Resistance	Higher Resistance	Higher Resistance
6	Sulphate attack	Less Resistance	Higher Resistance	Significantly Higher Resistance	Higher Resistance
7.a	Chloride Induced Corrosion	Less Resistance	Higher Resistance	Higher Resistance	Higher Resistance
7.b	Carbonation Induced Corrosion **	High Resistance	Lower, but acceptable with good construction practices		

*In case of PPC, workability is enhanced when fly ash is mixed separately with OPC. But in case of intergrinding fly ash, water demand increases.

**The conclusion is drawn on the basis of the carbonation depth of concrete made with and without blended cements. However, the effect of CO_2 ingress on corrosion rate still requires comprehensive study in the propagation phase.

From the analysis of results of the above parameters, the performance of Blended Cement was observed better than OPC concretes excluding resistance against carbonation. So, concretes made with PPC, PSC and CC have a longer service life as compared to OPC concrete in aggressive environment.

Commercially available PSC in India has 50–60 % slag content whereas commercially available PPC in India has 30–35 % fly ash content. They are used for general purpose construction for a grade of concrete up to M50. For higher grade of concrete, customized PPC and PSC should be used with a lower % of fly ash and slag respectively. These blended cements thereafter may be used with the appropriate proportion of silica fume for the production of high strength concrete.

Indian standards and codes of practices recommend PPC and PSC in Plain, Reinforced and Prestressed Concrete construction and there are no constraints in their usage. Various circulars and specifications are given by CPWD, IRC, BIS and Ministry of railways. In the year 2009, the CPWD permitted the use of PPC vide their circular No. CDO/SE (RR)/Fly Ash (Main)/102 dated 09 April 2009 for concrete grade of M25 and above in RCC. Similarly, the use of PPC for prestressed concrete was earlier not recommended in different standards / specifications due to apprehension of late strength development, apprehension of low resistance towards carbonation induced corrosion of steel and lack of data on other critical properties of prestressed concrete like creep, shrinkage and fatigue. However, based on extensive research done at several R&D institutes of the country, Bureau of Indian Standard permitted the use of PPC in prestressed concrete by revising IS: 1343 in 2012.

The use of PPC and PSC is permitted by national and international Standards / Specifications including most government bodies. The use of Portland Pozzolana Cement conforming to requirements of IS: 1489 is already permitted by Ministry of Railways, Railway Board, Government of India, in substructures of bridges. As per "Guidelines for the Use of High-Performance Concrete Bridges" issued by the Ministry of Railways, Railway Board, Government of India, fly ash conforming to grade I of IS: 3812-2003 can be used where proportion should not be less than 20 percent and nor should exceed 35 percent by mass of cement. IRC: 112-2011 specifications "Unified code of Practice for Concrete Road Bridges provision for the use of blended cement" also permits the use of PPC in prestressed concrete structures. Internationally, PPC is permitted for use in prestressed concrete structures by Prestressed Concrete Institute (PCI) Manual, AASTHO specification, ASTM C-935 etc.

ENVIRONMENTAL ADVANTAGES OF BLENDED CEMENTS

MATERIAL COMPOSITION

OPC
95% Clinker
5% Gypsum

PPC
31% Fly Ash, 64% Clinker, 5% Gypsum

PSC
57% Slag, 38% Clinker, 5% Gypsum

CC
25% Granulated Slag, 45% Clinker
25 % Fly Ash, 5% Gypsum

REDUCTION IN CO_2 FOOTPRINT

OPC	PPC	PSC	CC
740	511	304	348

REDUCED ENERGY CONSUMPTION

Thermal energy in Kcal/Tonne

OPC	PPC	PSC	CC
724	495	305	343

Electrical energy in Kwh/Tonne

OPC	PPC	PSC	CC
87	64	59	57

INCREASED PRODUCTION CAPACITY

REDUCED LIMESTONE REQUIREMENT FOR PRODUCTION OF BLENDED CEMENT

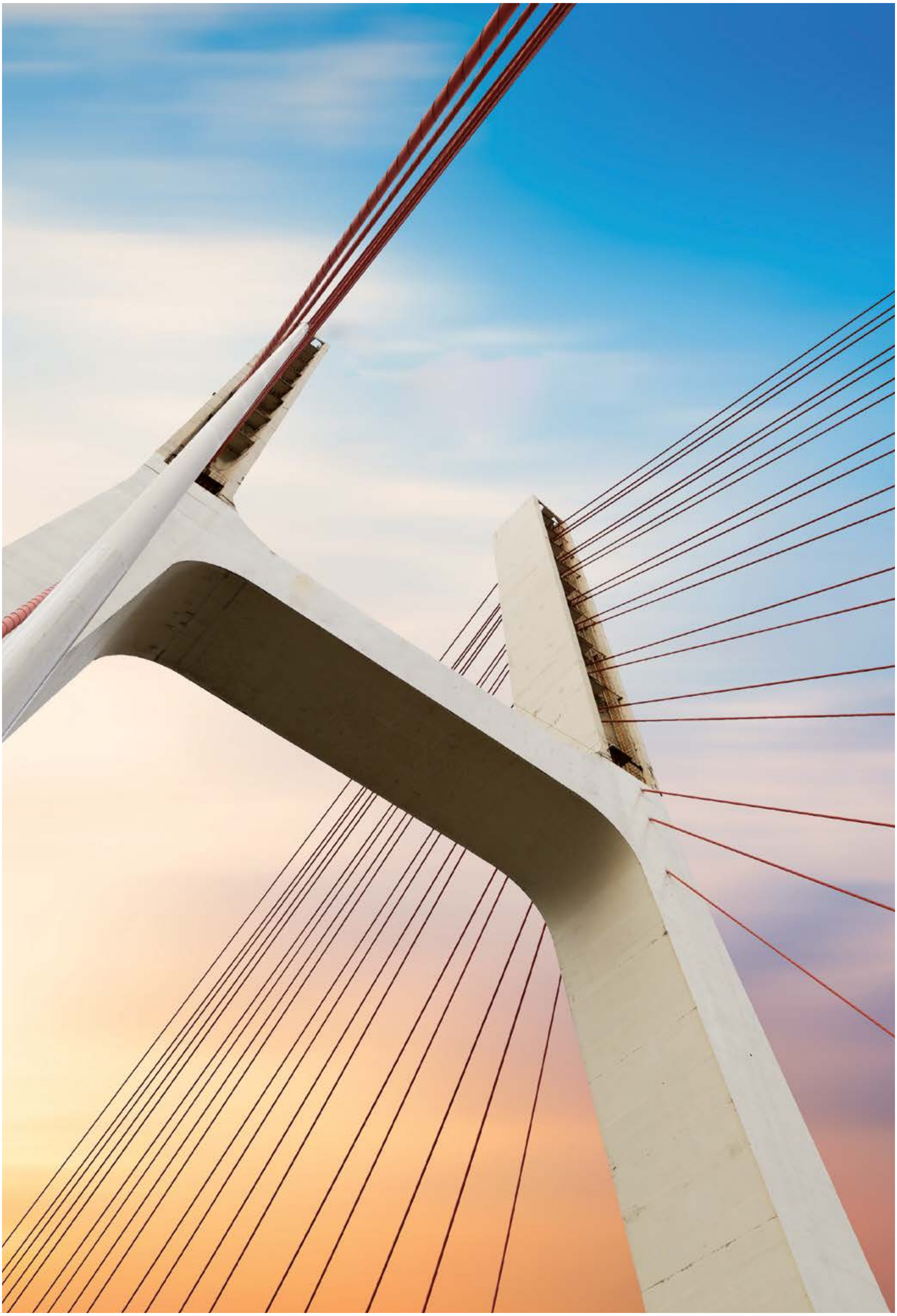
In India, there are only three blended cements approved by BIS, namely, PPC, PSC and Composite Cement. The other blended cements namely Portland Composite Cement based on both fly ash and limestone (PCC), Portland Limestone Cement (PLC), Portland Dolomitic Limestone Cement (PDC), Limestone Calcined Clay Cement (LC3) and multicomponent blended cements are at different stages of development in India. However, this report focuses on the performance of OPC, PPC and PSC mainly and upto some extent on composite cement for which the Indian standard is available.

The use of blended cements is widely internationally accepted and standardized. The European code 197–1–2011 gives specification of 27 distinct common cement products and their constituents. The code provides the proportions in which the constituents are to be combined to produce these distinct products in a range of six strength classes. The 27 common cements are grouped into five main cement types namely CEM-I, CEM-II, CEM-III, CEM-IV and CEM-V. Except for CEM-I which covers OPC rest for all the other cement groups i.e. CEM-II, CEM-III, CEM-IV and CEM-V consist of only blended cement. The blended cement covered in these cement groups CEM-II, CEM-III, CEM- IV and CEM-V are Portland slag cement, Portland fly ash cement, Portland silica fume cement, Portland limestone cement, composite cement, Portland burnt shale cement, blast furnace cement, pozzolanic cement. The latest European code 197–5–2021 also allows the production of cements with much lower clinker contents with various SCMs including fly ash, slag, calcined clay, limestone, etc.

The Canadian standard, A3001–13–2017, comprises 26 types of standardized cements. Out of which 20 are blended cements, which include Portland limestone cement, Portland slag cement, pozzolana cement and ternary/quaternary blended cements. The standard allows the use of upto 50% fly ash (both siliceous and calcareous) in pozzolana cement and up to 60% fly ash in ternary/quaternary blended cements.

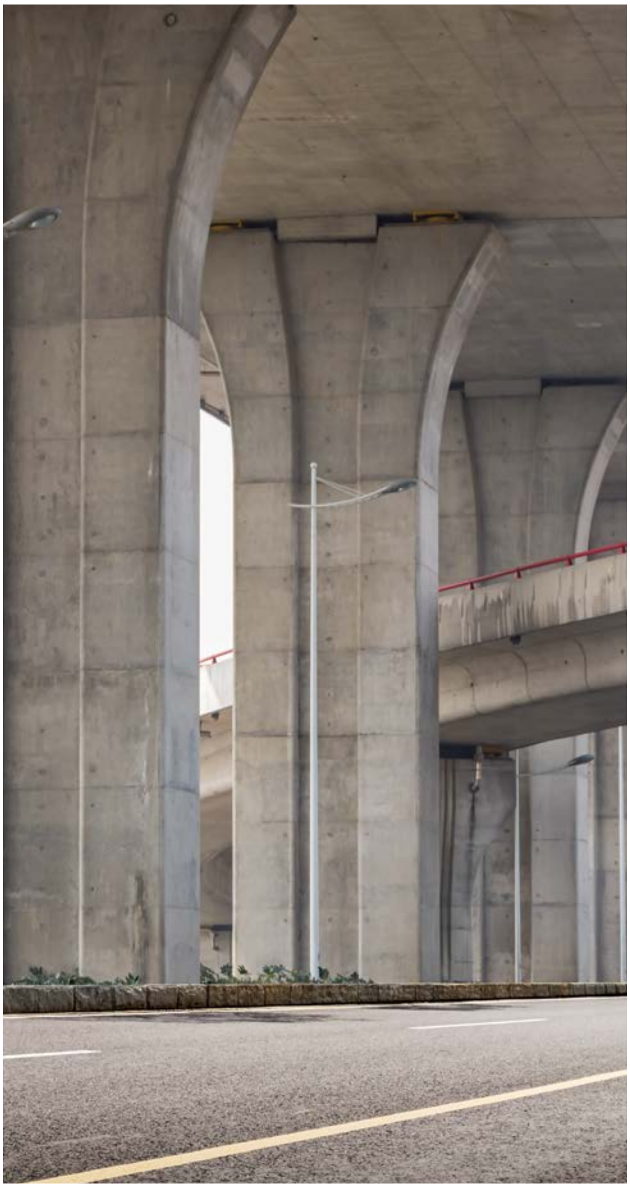
In comparison to the Indian standards, the European code covers a greater number of blended cements and it is also noted that cement group CEM-IV-B, Pozzolana cements, allows 36–55% of natural pozzolana and fly ash along with clinker and CEM-V-B, composite cements, allows the 31–49% of natural pozzolana and calcareous fly ash along with slag and clinker in it. On the other hand, in the Indian standards, both the Portland pozzolana cement and composite cement allow not more than 35% of fly ash usage. Also, there is a high need for the commercialization of new blended cements after getting due approval from BIS.

It can be seen in this report that blended cements demonstrate superior performance when compared to OPC. Not only do the blended cements offer a more sustainable solution for the CO_2 intensive industry, they also reduce the risk of cracking, allow easier construction, increase long-term strength and prolong the durability of structures in a wide range of environments from dams in the mountains to bridges on the open seas. Blended cements are a better replacement for Ordinary Portland Cement. In addition, both PPC and PSC are ideally suitable for mass concrete works, constructions in aggressive conditions such as marine, coastal and sub-coastal environments and chemically aggressive conditions. Even under normal conditions, they impart long term strength and improved durability. Considering the environmental and sustainability benefits of blended cements, state and central governments can incentivize these cements over OPC.



1.0

INTRODUCTION



Cement industry plays a key role in the growth of any nation. India has emerged as one of the fastest growing economy in the world and aimed to become a 5 trillion-dollar economies by the financial year 2024-25. Amongst the eight core industries of India, cement industry plays a vital role in the growth and economic development of our country because of its strong linkage to other sectors such as infrastructure, construction, housing, transportation, coal, power, etc. The concrete and cement industry is a key part of the construction sector – which accounts for 13% of global GDP.

India's cement production reached 334.37 million tonnes per annum (MTPA) in FY 2020. Due to the increasing demand in various sectors such as housing, commercial construction, industrial construction, GOI's aims for 100 smart cities, By expanding the capacity of railways for ease of transportation and achieving greater road connectivity road lengths, the cement industry is expected to reach 550-600 MTPA by 2025.

Cement manufacturing is an energy intensive process with high fuel and electricity consumption; energy costs account for 40-45% of the production costs of cement, so efforts are always being made to reduce the demand for fuels and electrical energy. Cement is considered to be responsible for about 7% of global anthropogenic CO_2 emissions. The cement manufacturing process releases carbon dioxide (CO_2) from the calcination process, fuel combustion and also indirectly from the usage of electricity. The manufacture of cements with mineral additions has been pursued as an alternative to reduce CO_2 emissions.

According to the IEA tracking report June 2020, global direct CO_2 intensity of cement in the Sustainable Development Scenario (SDS), 2014-2030, was 530 kg CO_2/t of cement in 2014, 540kg CO_2/t of cement in 2018 and should be 480kg CO_2/t of cement by 2030. From 2014 to 2018, globally the clinker-to-cement ratio increased at an average of 1.6% per year, reaching an estimated 0.70 in 2018; this rise was the main reason for the increase in direct CO_2 intensity of cement production over the period. In the SDS, globally the clinker-to-cement ratio should fall by 0.3% per year to a global average of 0.66 by 2030 by greater use of blended cements and clinker substitutes, including industrial by-products such as blast furnace slag and fly ash. The direct global CO_2 intensity of cement production increased 0.5% per year during 2014-18. To get on track with the SDS, a 0.8% annual decline is necessary till 2030.

The sharper focus is needed in two key areas: reducing the clinker-to-cement ratio (including through greater uptake of blended cements) and deploying innovative technologies (including CCUS). Governments can stimulate investment and innovation in these areas through funding R&D and adopting mandatory CO_2 emissions reduction policies. The current OPC cement is not a sustainable solution to meet increasing cement demand in emerging and developing activities.
To halt climate change and to reach the goals made at Paris Climate Agreement, it is necessary to increase the use of blended cement as viable alternative cement production.

The Global Cement and Concrete Association (GCCA)

on behalf of its member companies, which operate in almost every country of the world, recently unveiled a global industry 2050 Net Zero Roadmap – Concrete Future. The detailed roadmap sets out the path, milestones and levers that the cement and concrete industry will follow and implement to fully decarbonize by 2050, a target aligned with the Paris Agreement to limit global warming to 1.5°C.
The levers include:

- Increased clinker substitution – including fly ash, calcined clays, ground granulated blast furnace slag, and ground limestone
- Fossil fuel reduction and increased use of alternative fuels
- Improved efficiency in concrete production
- Improved efficiency in the design of concrete projects and use of concrete during construction, including recycling
- Alternatives to Portland clinker cement further developed
- CCUS and other breakthrough technologies
- Renewable energy

According to the Roadmap, blended cement has a key role to play in the future. At the cement plant or the concrete plant, fly ash, ggbs, ground limestone, and other materials such as calcined clays can be added to deliver concrete with reduced CO_2missions but which still deliver the required performance, and can even be enhanced. In the coming decade, there will be increased use of ground limestone and the introduction of calcined clays to both compensate for the reduced supply of fly ash and ggbs, and further reduce the clinker binder ratio.

The roadmap also highlights the policy asks and roles for governments and other stakeholders to help enable the transition.

Therefore, the utilization of blended cements becomes much more important, as these cements are environment-friendly and more cost-effective to produce due to lesser input of clinker and energy.

1.1

INTRODUCTION TO BLENDED CEMENTS

Blended cements are formulated by blending Portland clinker with other finely ground materials such as pozzolana and granulated blast furnace slag. Pozzolana is defined as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementing property, but will in a finely divided form – and the presence of moisture – chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. The availability of fly-ash (from thermal power plants), blast furnace slag (from steel plants), use of advanced technology in the manufacturing of cement and simultaneous increase in market demand have increased the production of blended cement in recent years.

The usage of blended cements in general imparts improved durability characteristics to concrete and provides higher resistance to chemical attack, higher impermeability of the concrete and improved resistance against alkali silica reaction. Use of fly ash and granulated blast furnace slag in the production of blended cements i.e. Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC) is also beneficial for conservation of natural resources, lowering in clinker factor in cement and reduction in CO_2 emissions leading to environmental sustainability. Bureau of Indian Standards (BIS) has brought a standard specification IS: 16415–2015 for composite cement in 2015. The standardization of Portland limestone cement and limestone calcined clay cement (LC3), which promise to further help in reducing emissions is in progress.

Blended cements are a better replacement for Ordinary Portland Cement. In addition, both PPC and PSC are ideally suitable for mass concrete works, constructions in aggressive conditions such as Marine, Coastal and Sub-coastal environments and chemically aggressive conditions. Even under normal conditions, they impart long term strength and improved durability.
The advantages of different blended cement as against OPC in terms of workability, strength development, durability, etc. are described in detail in Chapter 4.0. The environmental benefits due to blended cements are discussed in Chapter 5.0.

1.1.1

PORTLAND POZZOLANA CEMENT (PPC)

Portland Pozzolana Cement is manufactured either by inter-grinding Portland cement clinker (conforming to the requirements of IS: 16353–2015), gypsum and fly ash (conforming to Indian standard IS: 3812 (I)-2013, specification for Pulverized Fuel Ash) or by intimately blending OPC (Conforming to the requirement of IS: 269–2015) and fly ash. The percentage of fly ash in PPC permitted by IS: 1489 (I)-2015 is from 15 to 35%.

1.1.2

PORTLAND SLAG CEMENT (PSC)

Portland slag cement is manufactured by inter-grinding Portland cement clinker, gypsum and granulated slag (conforming to Indian standard IS: 12089–1987, specification for granulated slag for the manufacture of Portland Slag Cement) obtained from steel industries. PSC is also manufactured by blending OPC with ground granulated blast furnace slag (GGBFS). The slag constituent shall not be less than 25% and not more than 70% in PSC as specified in IS 455:2015. Since the slag is more easily available in Eastern part of India, production and availability of portland slag cement is greater in this part of the country.

1.1.3

COMPOSITE CEMENT

Composite cement is a new type of cement and its specifications have been formulated recently by the Bureau of Indian Standards. Its commercial production has already started in the country. The composite cement (conforming to IS: 16415–2015) can be produced either by inter-grinding of portland cement clinker (conforming to IS: 16353–2015), granulated slag (conforming to IS: 12089–1987) and fly ash (conforming to IS: 3812 (I) 2013) with the addition of natural/chemical gypsum or by an intimate and uniform blending of ordinary portland cement (conforming to IS: 269–2015), finely ground granulated slag and fly ash with the addition of ground gypsum. The composite cements are manufactured using 35–65% portland cement clinker/ordinary portland cement along with 15–35% fly ash and 20–50% granulated blast furnace slag together as the blending component.

1.2

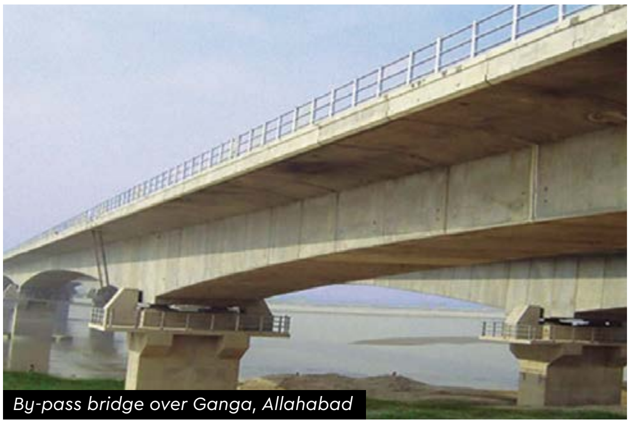
EXEMPLARY STRUCTURES USING BLENDED CEMENTS IN INDIA

Some exemplary uses of PPC in structures under most severe and extreme exposure conditions during the last three decades in India are:

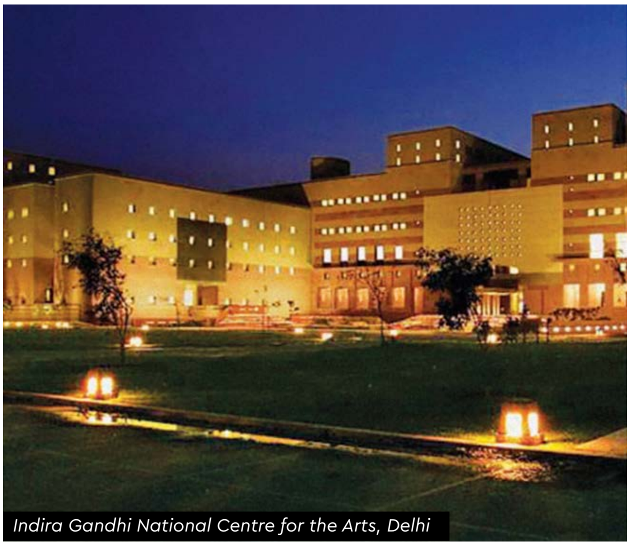
- Indira Gandhi national centre for the Arts, Delhi
- Several fly-overs on Ring road and outer Ring-Road in Delhi.
- By-pass bridge over Ganga, Allahabad
- Flyovers for municipal corporations, Mumbai and Ahmedabad.
- Delhi high court, Delhi
- Embassies in Delhi-USSR, Austrian and Turkish
- Computer Laboratory, Indian Agricultural Research Institute, Pusa, Delhi
- Mangalore Harbour project, Mangalore
- Naval Jetty, Cochin
- Pushpanjali shopping centre, Hyderabad
- Bongaigaon Refinery, Assam
- Salai project near Jammu
- 500 MW unit of Tata Electric Companies, Mumbai

Pushpanjali Shopping Centre, Hyderabad

Several flyovers on Ring Road and outer Ring Road in Delhi



By-pass bridge over Ganga, Allahabad



Indira Gandhi National Centre for the Arts, Delhi

Computer Laboratory, Indian Agricultural Research Institute, Pusa, Delhi

Delhi High Court, Delhi

Salal project near Jammu

Flyover in Mumbai

2.0

TYPES OF CEMENT IN INDIA

Different varieties of Portland cements, produced and marketed in India are under mandatory certification by the Bureau of Indian Standards (BIS). BIS has formulated standard specifications for different types of cements (Table 2.1).

Table 2.1: Types of cements and relevant Indian standard specifications

Sr. No.	Type of Cement	IS Code No.
1	Ordinary Portland Cement (OPC) (OPC33, 43, 43S, 53 & 53S)	IS 269:2015
2	Portland Pozzolana Cement (PPC)	IS:1489-2015 (Part-I): Fly ash
3	Portland Pozzolana Cement (PPC)	IS:1489-2015 (Part-II): Calcined Clay
4	Portland Slag Cement (PSC)	IS:455-2015
5	Composite Cement	IS:16415-2015
6	White Portland Cement	IS: 8042-2015
7	Sulphate Resisting Portland Cement	IS:12330-1988
8	Super Sulphated Cement	IS:6909-1990
9	Low Heat Portland Cement	IS:12600-1989
10	Hydrophobic Portland Cement	IS:8043-1991
11	Rapid Hardening Portland Cement	IS:8041-1990
12	Masonry Cement	IS:3466-1988
13	Oil Well Cement	IS:8229-1986
14	High Alumina Cement	IS:6452-1989

Among all these, the three most common cement types produced in India are Ordinary Portland Cement (OPC), Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC). OPC is produced in three grades; 33, 43 and 53 grade OPC. 43S & 53S grades of OPC are used in the production of railway sleepers. Besides, the types of cement produced in other top cement producing countries around the world indicate that these countries are also producing similar cements as those produced in India with variants in their nomenclature, purpose and performance due to specific climate conditions and conditions at the application scale but the material base remain largely similar.

In India, the production of OPC is constantly declining, with a simultaneous increases in the production of blended cements like PPC, PSC, and Composite Cement based on granulated blast furnace slag and fly ash. Presently, blended cements have a greater share (73%) in comparison to ordinary Portland cement (27%) of total cement production. Still, there is a potential to further reduce the clinker factor through increased use of composite cement and other future cement such as Portland limestone cement and limestone calcined clay cement.

The use of blended cements is widely internationally accepted and standardized. The type of cement production in various countries around the world is regulated either by standards set out by the regulating bodies of respective countries or by adopting standards of other countries. The European standards EN-197–1 is widely adopted and used by about 34 countries around the world. Further, major other cement producing countries like China, US, Turkey, Indonesia, Saudi Arabia, Korea, Russia, Iran, etc. have evolved their standards for types of cement to be produced in these countries.

European standard, EN-197–1 has specified 27 distinct common cements, 7 sulfate resisting common cements as well as 3 distinct low early strength blast furnace cements and 2 sulfate resisting low early strength blast furnace cements. The 27 common cements are grouped into five main cement types namely CEM-I, CEM-II, CEM-III, CEM-IV and CEM-V. Each cement type has different products like OPC, Portland slag cement, Portland fly ash cement, Portland silica fume cement, Portland limestone cement, composite cement, Portland burnt shale cement, blast furnace cement, pozzolanic cement. The standard permits different types of non-clinker constituents for the cement manufacture, such as ground granulated blast furnace slag, silica fume, siliceous and calcareous fly ash, natural pozzolana, industrial pozzolan, burnt shale, limestone (L & LL type) in different proportions, thus offering more flexibility of using various mineral constituents in the manufacture of blended cements compared to India. The latest European code 197–5-2021 also allows the production of cements with much lower clinker contents with various SCMs including fly ash, slag, calcined clay, limestone, etc.

3.0

INDIAN CEMENT INDUSTRY

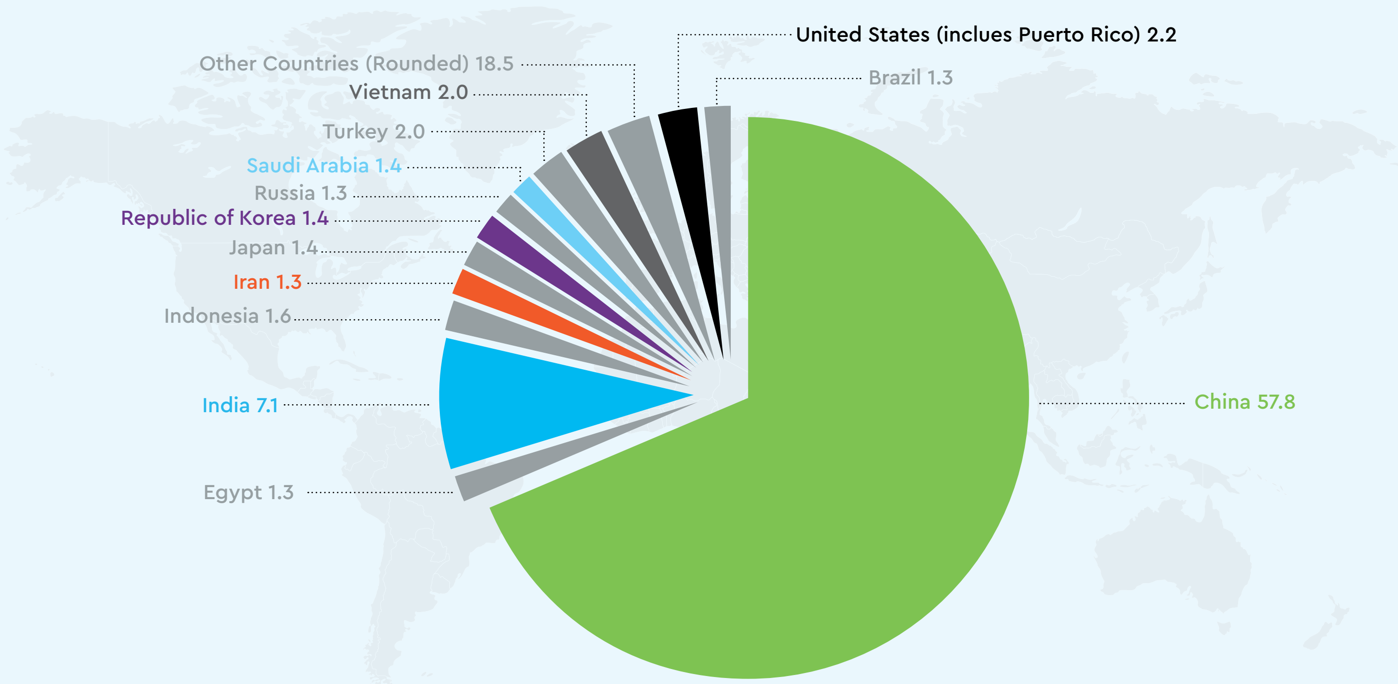
3.1

INSTALLED CEMENT CAPACITY AND PRODUCTION IN INDIA

In view of the rise in population coupled with infrastructural requirements, the annual global cement production is projected to reach around 4.8 billion tonnes by 2030 and 6.0 billion tonnes annually by 2050 (12–23% rise) from the current production level of more than 4.2 billion tonnes [4]. Back in 1995, the total global production of cement amounted to 1.39 billion tonnes which indicates the extent to which the construction industry has grown since then. Most of the increase in cement demand in the coming decades will be projected in emerging and developing countries, which already make up over 80% of global production. Some regions, such as China and the Middle East have excess cement production capacity, with cement production per capita levels well above the global average. Other regions, such as India and Africa are set to increase their domestic cement production capacity to fulfill their infrastructure development needs.

Today, India is the second largest cement producer in the world, after China as shown in figure 3.1 and it has evolved to become one of the best in terms of energy efficiency, quality control and environmental improvement. Indian cement industry has also been a strong contributor to employment, fiscal revenue, and community development while achieving manufacturing and technological advancement / excellence.

Figure 3.1: World Percentage share of Cement Production
(Source: Mineral Commodity Summaries 2018, USGS)



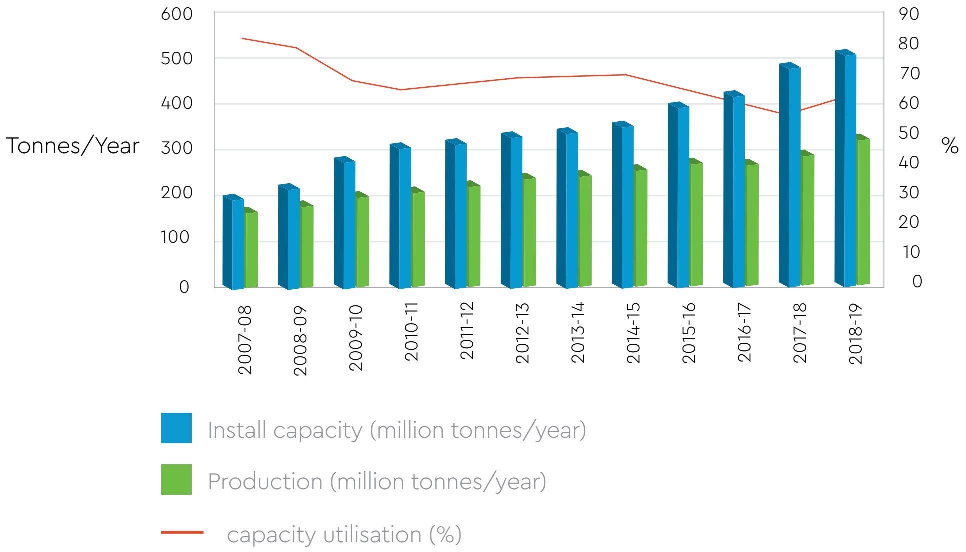
The installed capacity of the cement industry in India in 2018–19 is 537 million tonnes with cement production of around 334.37 million tonnes in 2019–20 (Source: Economic advisor, DPIIT), which comprises 144 integrated large cement plants, 107 grinding units, 62 mini cement plants and 5 clinkerisation units [1]. Cement consumption in India is still around 240 kg per capita against the global average of 530 kg per capita, which shows significant potential for the growth of the industry. Cement production and consumption are directly linked to the economic development of the country. The availability of cement is vital for infrastructure expansion, modern housing and urbanization. The capacity utilization of the Indian cement industry during the last ten years varied from around 60 % to 83 % as indicated in table 3.1 and figure 3.2. The continuous downward trend of capacity utilization is indicative of the idle capacity of over 200 million tonnes which is growing year by year.

Table 3.1: Installed Capacity, Production & Capacity Utilisation

Year	Installed Capacity (million tonnes / yr)	Production (million tonnes / yr)	Capacity Utilisation (%)
2007–08	209.20	174.31	83.32
2008–09	232.54	187.60	80.67
2009–10	294.32	217.44	73.88
2010–11	323.20	228.30	70.64
2011–12	336.10	246.70	73.40
2012–13	350.00	248.23	70.92
2013–14	360.00	255.60	71.00
2014–15	378.00	270.00	71.40
2015–16	420.00	283.45	67.40
2016–17	445.00	280.00	63.00
2017–18	509.00	297.50	58.44
2018–19	537.21	337.32	62.77
2019–20	537.21	334.37	62.21

Source: NCB, CMA, IBEF, Ministry of Commerce and Industry, https://ieconomics.com/i/Hkow7P0Zm1806 [1,2,3]

Figure 3.2: Cement Capacity and Production [1,2]

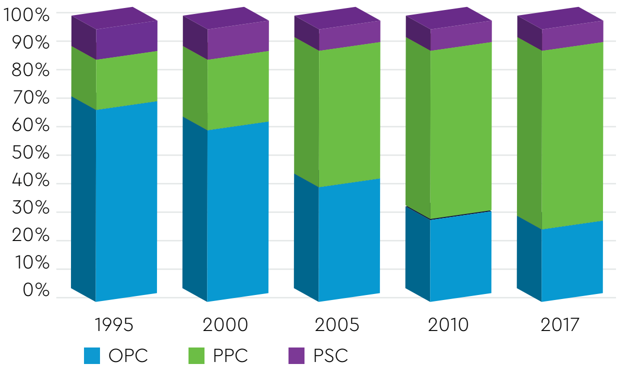


3.2

PRODUCTION OF DIFFERENT TYPES OF BLENDED CEMENTS IN INDIA

The share of blended cement production in total quantities of cement manufactured in India was 30% in 1995 which has increased to 73% of total cement production as shown in figure 3.3. PPC production in 2010 was 61%; this increased to 65% in 2017 as shown in figure 3.3. The share of PSC production has been almost flat, at less than 10%, although the absolute volume grew by about 40% in the last seven years. Increased acceptability by the market, growing awareness of sustainability concepts, the availability of fly ash from thermal power plants and the use of advanced technology triggered this rise.

Figure 3.3: Share of blended cement production in India [5]



The Indian cement industry has been gradually increasing the share of blended cements in its cement mix, resulting in an overall improvement in the clinker factor, which was 0.74 in 2010 and gradually decreased to 0.71 by 2017 as shown in table 3.2 [5]. The PPC clinker factor improved to 0.65 in 2017, compared to 0.68 in 2010. Fly ash consumption in 2017 was 31%, compared to 27% in 2010. The PSC clinker factor improved to 0.40 in 2017, compared to 0.55 in 2010, with an increase in PSC slag consumption to 57% in 2017 from 40% in 2010. The reduction in clinker factor has resulted in a reduction in the carbon footprint of cement industry, resource conservation due to lesser utilization of limestone per tonne of cement, reduction in thermal and electrical energy consumption and waste utilization.

Table 3.2: Clinker Factor for different types of Cement [5]

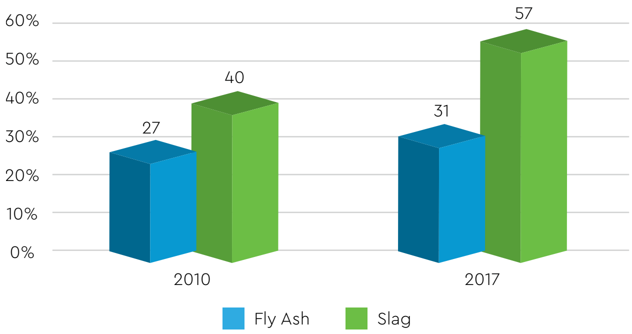
Type of Cement	2010	2017
OPC	0.95	0.94
PPC	0.68	0.65
PSC	0.55	0.40
Overall	0.74	0.71

3.3

INITIATIVES TAKEN BY CEMENT INDUSTRY FOR GREENING CEMENT INDUSTRY SUPPLY CHAIN

In 2019–20, 57.88 million tonnes of fly ash was utilized in the cement industry, which is 26 % of total fly ash utilization in the aforesaid year. In most of the Indian cement plants, 100% Fly ash generated in the captive power plants is utilized for manufacturing cement. The fly ash consumption in PPC has increased from 27% in 2010 to 31% in 2017 as shown in figure 3.4. Similarly, slag consumption in PSC has increased to 57% as compared to 40% in the year 2010.

Figure 3.4: Utilization of industrial by-products in manufacture of blended cements in Indian Cement Industry [5]



References:
1. Cement Compendium "The India Cement Industry – 2019", published by National Council for Cement and Building Materials, December 2019.
2. https://eaindustry.nic.in/ accessed on 4th October 2020
3. https://ieconomics.com/i/Hkow7P0Zm1806
4. IEA-WBCSD (2018), "Technology Roadmap: Low Carbon Transition in the Cement Industry", IEA & WBCSD-CSI
5. Low Carbon Technology Roadmap for the Indian Cement Sector: Status Review 2018, WBCSD, November 2018
6. Mineral Commodity Summaries 2018, USGS
7. Report on Fly Ash Generation and its utilization at coal/lignite based Thermal Power Stations in the country for the year 2018–19 published by Central Electricity Authority, January 2020

4.0

TECHNICAL ADVANTAGES OF DIFFERENT BLENDED CEMENTS OVER OPC

4.1

HYDRATION OF OPC, PPC, PSC AND COMPOSITE CEMENT

Primary compounds in Portland cement include calcium aluminates and calcium silicates. Compounds have the following notation: A = Al_2O_3, C = CaO, F = Fe_2O_3, H = H_2O, M = MgO, S = SiO_2, \$ = SO_3. Calcium aluminates include tricalcium aluminate (C_3A) and ferrite (C_4AF), while calcium silicates include alite (C_3S) and belite (C_2S). Both calcium silicates induce similar hydration reaction. The principal hydration products are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). Other major products are ettringite (C-A-\$-H) and Monosulphate. Ettringite is formed when sulfate and tricalcium aluminate react in an aqueous medium. Monosulphate is the result of reaction of the excess tricalcium aluminate with ettringite compounds [1].

Note: Mechanism of hydration and different chemical reactions occurring during the process of hydration of OPC and blended cement has been discussed in detail in Annexure A.

However, in cementitious systems such as PPC, PSC and composite cement which contain supplementary cementitious materials or pozzolanic materials, the portlandite produced during primary hydration reaction gets consumed by the pozzolanic materials present in blended cements during the additional secondary hydration reaction to form secondary CSH gel. Hence, in PPC, PSC, or composite cement systems, the $Ca(OH)_2$ content reduction occurs due to the secondary hydration reaction [2].

4.1.1

HEAT OF HYDRATION

The heat of hydration of cement depends upon its chemical composition and is approximately equal to the sum of heat of hydration of its individual pure compounds when their respective proportion by mass are hydrated separately. These values influence the risk of cracking of concrete at an early age. Typical values are given in table 4.1 below:

Table 4.1: Heat of hydration of pure compounds [3]

Compound	Heat of Hydration	
	J/g	Cal/g
C3S	502	120
C2S	260	62
C3A	867	207
C4AF	419	100

By reducing the proportions of C_3S and C_3A, the amount and rate of the heat of hydration can be controlled or reduced. Apart from reducing the relative proportions of C_3S and C_3A, if a certain fraction of clinker itself is replaced by suitable supplementary cementitious materials such as fly ash and slag, reduction in heat and rate of evolution of heat of hydration is observed.

Due to the possibility to reduce the carbon footprint of cement by blending it with cement replacing materials, supplementary cementitious materials (SCM) are becoming more and more important as mineral additions, especially in Portland cement-based composite cements. SCM affects the reaction of Portland cement by acting initially as (quasi-)inert addition and at a later stage due to their chemical reaction, which depends on the type, fineness and composition of the SCM. The presence of additional and different surface sites on the SCM can accelerate the hydration during the first hours as more surface for nucleation and growth of hydrates is present. This effect has been observed to be most distinct for calcite but is also generally observed if OPC is blended with quartz or blast furnace slag [3].

Blending Portland cement with fly ash can lead to retardation of hydration. This effect is caused by interactions of alumina from the fly ash and calcium from the pore solution or by chemisorption of calcium ions on the surface of the fly ash [4].

Slag, which is an amorphous calcium aluminosilicate material, has been considered to exhibit both pozzolanic and latent hydraulic activity. The reactivity of slag is controlled by chemical composition, glass content, fineness, and particle size distribution. Pure slag reacts with water at a very low rate or may not react at all.

Table 4.2: Heat of hydration values of OPC, PSC and PPC at different ages (NCB Studies)

Type of Cement	Heat of hydration (J/g)		
	3 days	7 days	28 days
OPC	202	275	323
PSC	224	239	287
PPC	204	226	261

Table 4.2 show the heat of hydration values of OPC, PSC and PSC at 3, 7 and 28 days in studies conducted at NCB. The heat of hydration of OPC at all ages is higher than PSC and PPC. The lower amount and rate of the heat of hydration for blended cement makes them suitable for use in mass concrete structures such as dams and spillways [5].

In the case of composite cement, around 50 to 60% clinker is replaced by GGBS and fly ash, the rate of evolution and the total amount of heat liberated during hydration is expected to remain below binary blended cements.

4.1.2

CONCLUSION

Based on the above discussion, the following observations can be made for the heat of hydration of blended cements:

- The rate of evolution and the total amount of heat liberated during hydration for blended cements i.e., PPC, PSC and composite cement is lesser in comparison to Ordinary Portland Cement.
- The temperature has a considerable effect on the release of the total amount of heat released for a particular cement.
- The dormant period is prolonged in blended cements due to the presence of the mineral additives such as fly ash and slag on the other hand it decreases with the temperature rise.
- Lower amount and rate of the heat of hydration for blended cement makes it a preferred cement in mass concrete structures such as dams and spillways.

4.2

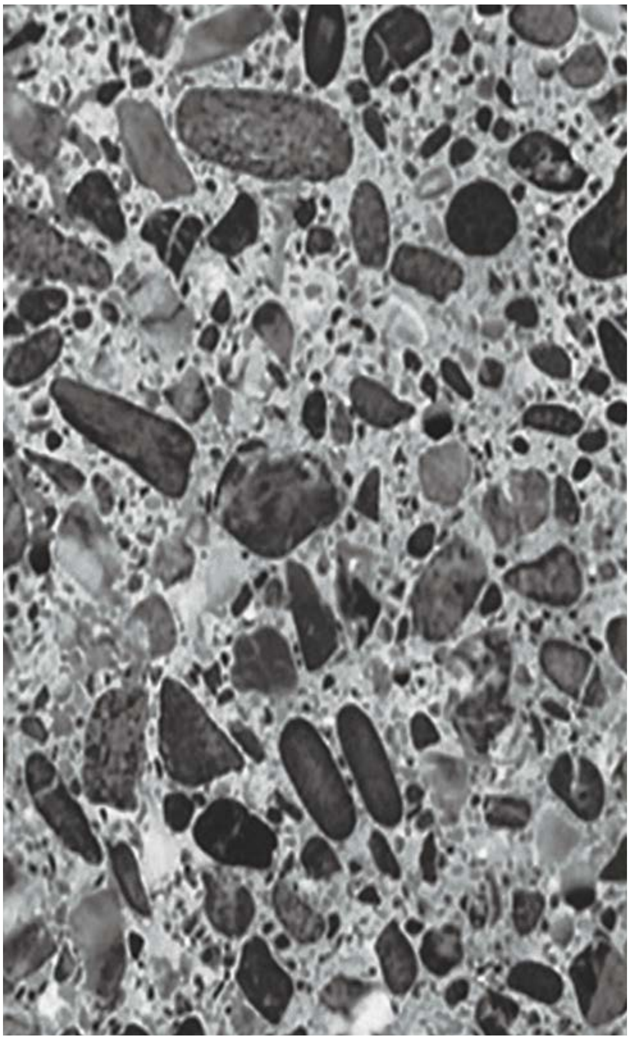
MICROSTRUCTURE AND PERMEABILITY

4.2.1

MICROSTRUCTURE

Cementitious construction materials are mainly used at a large scale and in huge quantities. The fundamental mechanical properties such as strength, ductility, creep, shrinkage, fracture behavior and fundamental durability properties such as permeability, etc. on macroscale depend to a great extent on its microstructure. The microstructural inhomogeneity as shown in figure 4.1 can lead to serious effects on strength and other related mechanical properties because these properties are controlled mainly by the microstructural extremes, not by the average microstructure.

Figure 4.1: Polished section of concrete specimen [6]



Concrete has a heterogeneous microstructure as shown in figure 4.2 and consists of mainly three phases, cement paste, aggregates, and the Interfacial Transition Zone (ITZ) between the cement paste and aggregate. Improving these three components enhances the mechanical strength and durability of hardened concrete [7]. The cement paste itself consists of unreacted cement grains, hydration products (crystals of calcium hydroxide, needles of ettringite, and fibrous layers of calcium silicate hydrate), and pores [8].

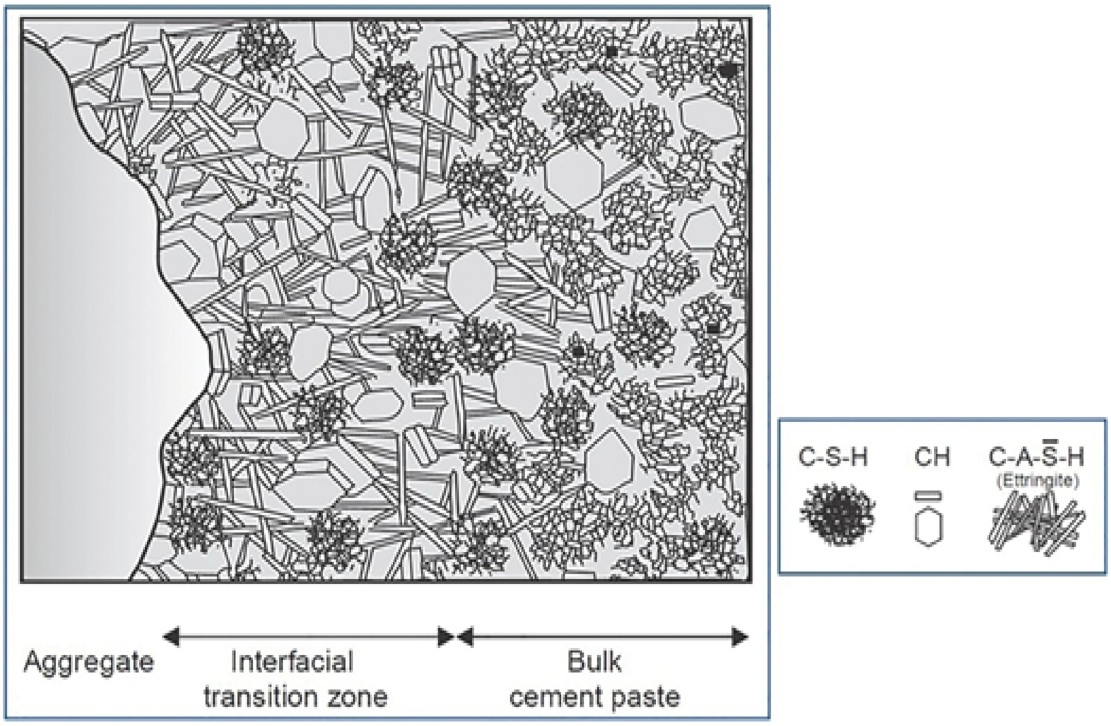


Figure 4.2: Schematic diagram of Microstructure of concrete [6]

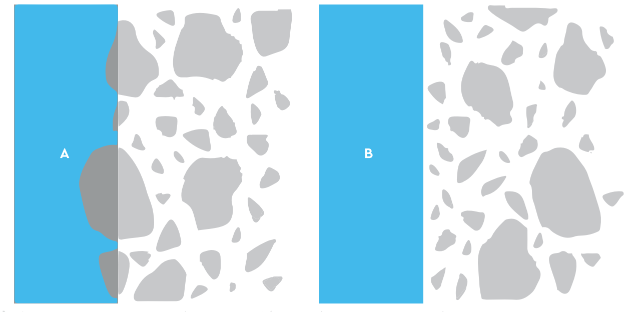
The interfacial transition zone (ITZ) is the region surrounding each aggregate particle, where the microstructure is modified by the presence of aggregate. The origin of this region lies in the so called "wall effects" by the packing of the anhydrous cement grains against the relatively flat surface of aggregates [9]. Because of this non-uniform distribution, there is an increase in the amount of porosity in ITZ [10–11]. The micro structural features can be described by the sequence of its development from the time concrete is placed as follows [11]:

(i) In freshly compacted concrete, water films form around the large aggregate particles. This would account for higher water to cement ratio closer to the aggregate than away from it.
(ii) In the same way as in the bulk cement matrix, calcium, sulfate, hydroxyl, and aluminate ions are produced by the dissolution of calcium sulfate and calcium aluminate compounds and are then combined to form ettringite and calcium hydroxide (CH). Owing to the higher water to cement ratio, these products in the vicinity consist of relatively larger crystals. Therefore, they form a more porous framework than in the bulk cement matrix.
(iii) With the progress of the hydration, poorly crystalline C-S-H, and the second generation of smaller crystals of ettringite and CH start filling the empty space that exists between the framework created by the large ettringite and CH crystals. Higher porosity and orientation deposition of crystals, and fewer cement particles than in the bulk cement matrix characterize ITZ as the weakest link in the cement-based composites [11], and should be taken as an important consideration for the investigation of overall performances of concrete.

The structure of the hardened cement in the ITZ is different from that of the bulk paste in terms of morphology, composition, and density. Compared to the bulk paste, the ITZ has less un-hydrated cement, large crystals of calcium hydroxide, greater concentration of ettringite, higher porosity (lower density) and less C-S-H [12]. As in the bulk paste, calcium, sulfate, hydroxyl, and aluminate ions are produced by the dissolution of calcium sulfate and calcium aluminate compounds. These ions combine to form ettringite and calcium hydroxide, which, due to the high w/c ratio, become larger in the vicinity of the aggregate resulting in a more porous framework than in the bulk cement paste matrix [6].

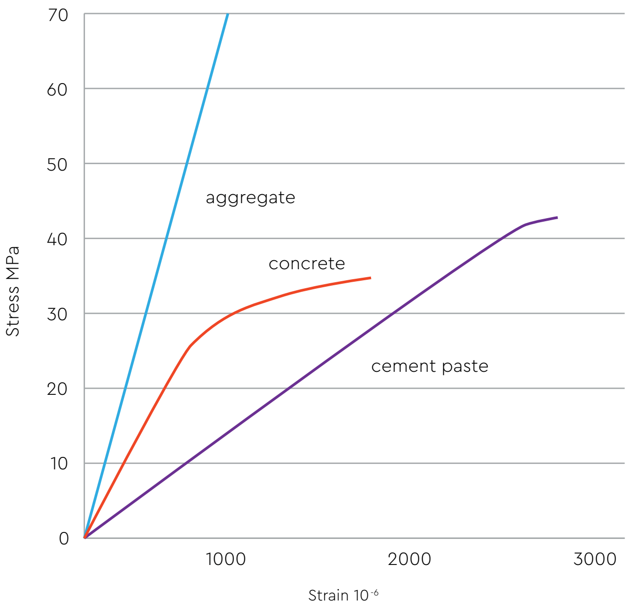
Quantitative characterization of the ITZ between the aggregate and the cement paste in concrete confirms that it arises due to the packing of cement grains (1–100 µm) against the larger aggregate particles. In other words, this difference in size means that each aggregate particle is a mini "wall," disrupting the normal packing of the cement grains and leading to the accumulation of smaller grains in the zone close to the aggregate while larger grains are found further out (Figure 4.3). This packing leads to a more porous zone, and the deposition of hydration products, especially calcium

Figure 4.3:
Schematic diagram showing "wall" effect of aggregate: (A) imaginary case and (B) real case [15]



hydroxide, tends to fill this zone [13]. The quality of the bond between the paste matrix and aggregates is influenced by the shape, size, mineralogical composition, surface roughness, surface moisture content, and porosity of aggregates as well as water/cement ratio [14]. From studies, it has been observed that the w/c ratio plays an important role in controlling the microstructure of the ITZ and its thickness.
The ITZ of the hardened concrete (about 10 to 50 µm thick), plays important role in its stiffness, strength, and permeability containing aggregate due to its generally, lower density and strength compared to bulk cement paste. When the concrete is subjected to loads, micro cracks may appear within the ITZ due to its weakness leading to the quasi-brittle nature of concrete [16] (Figure 4.4). This explains the phenomenon that the components of concrete (aggregates and hydrated cement paste) usually remain elastic until failure during a uniaxial compression test, while concrete shows inelastic behavior at levels higher than 40% of ultimate strength [6].

Figure 4.4: Effects of the ITZ on mechanical properties of concrete [15]



Concrete with superior properties such as high compressive strength and excellent durability can be produced by improvement in its ITZ taking into account the following:

- optimizing particle size distribution to obtain high density;
- using water reducing agents to reduce water/cement (w/c) ratio;
- adding pozzolanic admixtures to improve rheological properties, fill voids, and form additional calcium silicate hydrate; and
- preventing brittle failure by including steel fibers [17].

4.2.2

MICROSTRUCTURE OF CEMENT PASTE

The microstructure of cement paste is composed of three components i.e. solids, voids and water as shown in figure 4.5.

Figure 4.5: Constituents of microstructure of Cement paste

Solids	**Voids**	**Water**
C-S-H	Entrapped air	Capillary water
CH	Entrained air	Adsorbed water
Ettringite	Capillary pore	Interlayer water
Monosulphate hydrate	Gel pore	Chemically bound water
Residual unhydrated cement		

Tricalcium silicate and dicalcium silicate are the most important compounds responsible for the strength of hardened cement paste and together constitute around 70 to 80 percent volume. The average C_3S content in Indian cement is found in the range of 45–50 % and that of C_2S is about 18–28 %. The hydration products of C_3S and C_2S are the same, but the proportions of their hydration products are different. The hydration of C_2S and C_3S gives rise to calcium silicate hydrates forming a gel, known as C–S–H gel. The ratio between C–S–H and portlandite, resulting from the hydration of C_3S to that of C_2S changes from 61/39 to 82/18, and the amount of water required for hydration from 40% to 42% [18]. It is composed of extremely small particles with a layer structure that tends to aggregate in formations a few µm in dimension, characterized by interlayer spaces of small dimensions (<2 nm) and by a large surface area (100–700 m^2/g) [19]. Due to the high surface area as shown in figure 4.6, C–S–H can give considerable strength to the cement paste. Its chemical composition is not well defined since the ratio between the oxides may vary with the degree of hydration, water/cement ratio, and temperature (for instance the C/S ratio may vary from 1.5 to 2) [20]. However, upon complete hydration, it tends to correspond to the formula $C_3S_2H_3$ usually used in stoichiometric calculations. C–S–H occupies approximately 50–60% of the volume of completely hydrated cement paste [21]. Hydration of calcium silicates also produces hexagonal crystals of calcium hydroxide (Ca (OH)$_2$, portlandite). These have dimensions of the order of a few µm and occupy 20 to 25% of the total volume of solids [22].

The rate of hydration is much lower for C_2S compared with C_3S, and the strength of cement paste after 28 days of wet curing is mainly due to C_3S. Thus, the larger the amount of C_3S in a Portland cement, higher the rate of hydration and strength development of its cement paste at the early stage but C_2S provides higher ultimate strength to the cement paste by producing a higher amount of C–S–H. Increasing the fineness of cement particles can also increase the rate of hydration. As the reaction involving hydration of Portland cement are exothermic in nature, increasing the rate of hydration also increases the rate of generation of heat of hydration.

Figure 4.6: Feldman–Sereda model for C–S–H [6]

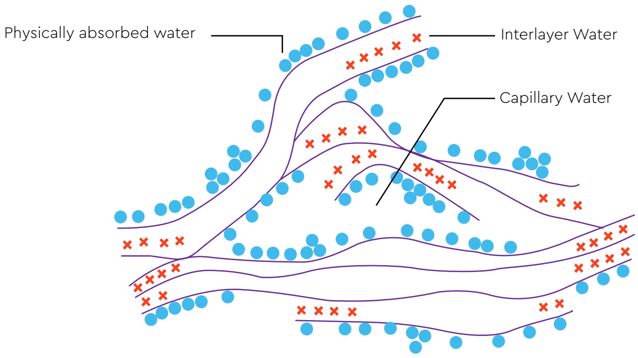


Figure 4.6, shows the simplified model for hydrated Portland cement proposed by Feldman and Sereda (1968), where water is trapped between calcium silicate mono layers and their distance and number of trapped water molecules are shown dramatically.

4.2.3

INFLUENCE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS ON MICROSTRUCTURE OF CEMENT PASTE

Part replacement of Portland cement by Supplementary Cementitious Materials (SCMs) may improve the microstructure and ultimately the durability of hardened cement paste. SCMs mainly influence the hydration and durability of blended cement paste in the cementitious materials by improving the particle packing, increasing pore refinement, making microstructure denser and reducing the connectivity of pores resulting from the reduction in the transport of aggressive agents into the concrete which plays a vital role in durability. SCMs have often a higher surface area and consist of smaller particles than Portland cement and also lower density. Hence, in the practical approach of just replacing cement with SCM by mass, there will be an increment in the volume of binder (cement + SCM + water) relative to the aggregate.

The hydration of pozzolanic materials or GGBS consumes lime and thus reduces its amount with respect to a cement paste obtained with Portland cement [23] (Figure 4.7 outlines the alterations of microstructures of hardened cement pastes made of Portland cement and blended cements) and hence the hydrated product of PPC and PSC (compared to that obtained with ordinary Portland cement) has a lower lime content and higher content of C–S–H. However, the reactions of pozzolanic materials or GGBS are slower than hydration of Portland cement, hence this effect can be achieved if the wet curing of the concrete is maintained long enough.

The amount of pozzolanic addition to Portland cement should be adjusted to the amount of lime produced in the hydration of Portland cement. Any excess of the pozzolanic addition will not react and thus, will behave as an inert addition ("filler").

In general, concrete made with cement blended with SCMs, or where ordinary cement is partly replaced with SCMs is more durable than concrete made with ordinary portland cement at the same water-to-binder ratio, when well cured and when the SCM is properly dispersed. The main reason is the formation of denser microstructure either due to improved particle packing initially or more binder (CSH or CAH) formed at the expense of calcium hydroxide (CH) either due to displacement of cement or pozzolanic reaction.

Also, from studies, it has been seen that the nature of the C-S-H gel forming in the pozzolanic reaction is quite different than the C-S-H gel formed by cement hydration. The general difference between C-S-H from pozzolanic reaction and which forms during Portland cement hydration is that the former C-S-H has a longer linear polysilicate anions and lower C/S-ratio than that of latter C-S-H [25].

4.2.4

PERMEABILITY

The permeability generally refers to the ease with which liquids or gases can enter and move through the concrete due to differential pressure. The usual range of permeability in a typical concrete material is of the order of 10^{-18} to 10^{-20} m^2 (water permeability), and 10^{-16} to 10^{-18} m^2 (gas permeability) [26]. The water to cement ratio and the curing time greatly influence the permeability of cement-based materials. These two parameters are more important regarding the control of permeability in hardened cementitious materials.

Permeability is an important characteristic of all concrete materials, which controls its durability against aggressive environments. The permeability of concrete is related to the proportion of CSH and CH produced in the hydrated cement paste. Due to the structure of CSH, it occupies a greater volume inside the hydrated paste, leading to lowering of the porosity and permeability so the higher the ratio of CSH and CH, the lower is the permeability of concrete. In concrete when fly ash or GGBS is used these materials react with CH and additional CSH is produced and hence improving the ratio of CSH and CH, which in turn reduces the permeability of concrete and hence increases its durability and mechanical properties as well.

As illustrated under para 4.2.1, concrete is a heterogeneous material consisting of, cement paste and ITZ. For normal aggregate concrete, the permeability of aggregates is neglected and the porosity of bulk cement paste mainly depends upon its voids, pore, pore size distribution and its interconnectivity within the paste. It also depends upon ITZ and its interconnectivity present in the hardened concrete. Details have been discussed subsequently under para 4.2.5, 4.2.6 and 4.2.7.

4.2.5

EFFECT OF POROSITY, PORE SIZE DISTRIBUTION AND ITS INTERCONNECTIVITY ON CONCRETE PERMEABILITY

The cement paste formed by the hydration reactions contains pores and voids of different sizes. The classification of concrete porosity is quite a complex matter. Pores in the hardened concrete can be roughly divided as illustrated in table 4.3:

Table: 4.3 Classification of pore sizes

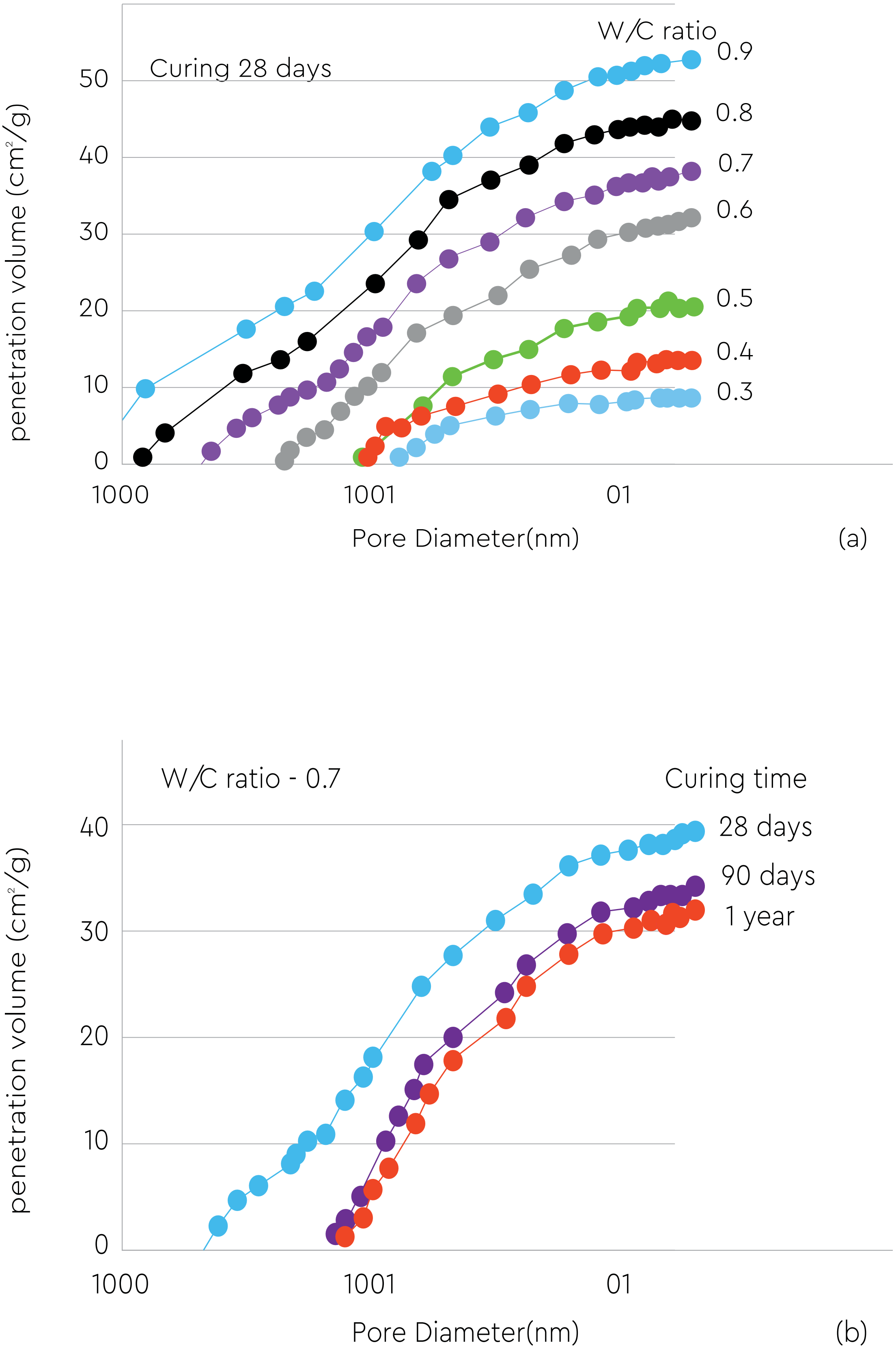
Types of pores	Description	Size	water	Properties affected
Capillary pores	large	10µm- 50nm	Evaporable bulk water	Permeability, strength
	Medium	50–10nm	Evaporable moderate menisci	Permeability, strength, shrinkage (high RH)
Gel pores	Small	10–2.5 nm	Evaporable strong menisci	Shrinkage (to 50% RH)
	Micropores	2.5–0.5nm	Non- Evaporable -no menisci - intermolecular interactions	Shrinkage creep (35–11% RH)
Interlayer spaces	Structural	< 0.5nm	Non – Evaporable-ionic/covalent bond	Shrinkage creep (<11% RH)
Other features	ITZ	20–50 µm	Bulk water	Permeability, strength
	Micro-cracks	50–200 µm	Bulk water	Permeability , strength

Gel pores essentially do not affect the durability of concrete as they are too small to allow significant transport of aggressive species but capillary pores, ITZ, and micro-cracks are relevant to the durability of concrete and the protection of embedded reinforcement since they determine the resistance to the penetration of aggressive species.

The influence of porosity on transport processes cannot be explained simply by the pore volume, the concept of connectivity or the degree of continuity of the pore system also has a great influence on the transport phenomenon. At higher porosity, the interconnected capillary pore system extends from the surface to the innermost portion of the cement paste and at this point, permeability remains high and transport processes like capillary suction of water (chloride-containing) can take place at rapid rate. With the decrease in the porosity, the capillary pore system loses its connectivity, and thus transport processes are controlled by the small gel pores mainly. As a result, water and ions will penetrate only to a short distance inside the cement paste. This influence of pore structure /geometry on transport properties can be described with the percolation theory. Various studies show, that below a critical porosity (ρ_c, the percolation threshold), the capillary pore system is not interconnected (only finite clusters are present) but above ρ_c the capillary pore system is continuous (infinite clusters). [9]

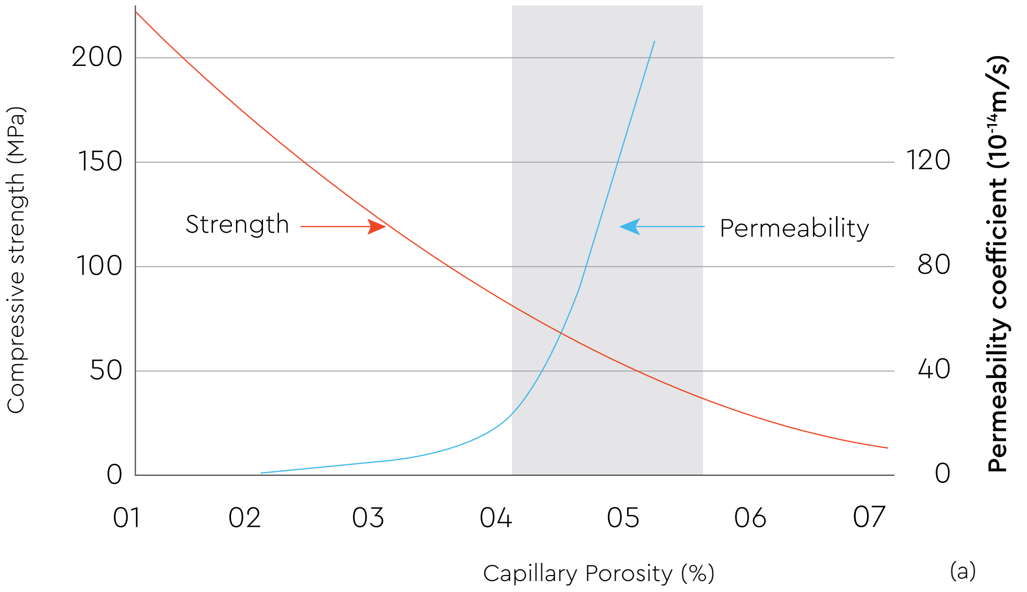
The main factors affecting the capillary porosity are, water/ cement ratio (Figure 4.8 a), curing (Figure 4.8 b) period, and type of binder used.

Figure 4.8: Influence of the (a) water / cement ratio and (b) curing on the distribution of pore size in hydrated cement pastes [24]

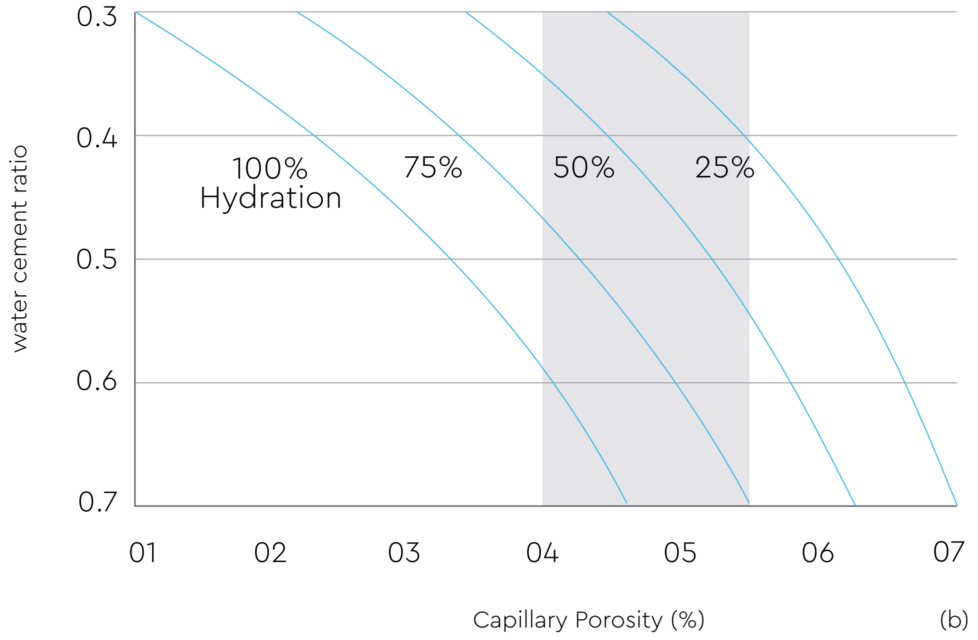


The decrease in capillary porosity ultimately increases the mechanical strength of cement paste and reduces the permeability of the hydrated cement paste (Figure no. 4.9). A distinction should be made between capillary pores of larger dimensions (e.g., >50 nm), or macropores, and micropores. The reduction in porosity resulting of both the macropores and the micropores play an essential role in increasing mechanical strength and durability of cementitious materials [24].

Figure 4.9 Relation between the transport properties of cement paste (expressed as coefficient of water permeability) and the compressive strength as a function of the w/c ratio and degree of hydration (a) Influence of capillary porosity on strength and permeability of cement paste. (b) Capillary porosity derives from a combination of water/cement ratio and degree of hydration [21]



(a)



(b)

4.2.6

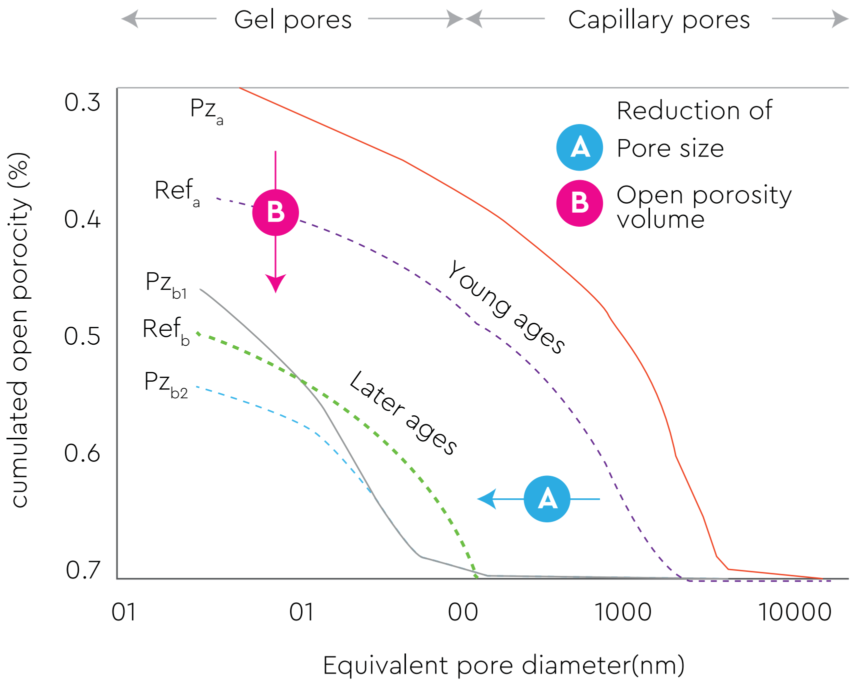
INFLUENCE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS (SCMS) ON CEMENT PASTE PERMEABILITY

The durability of cement-based materials is greatly influenced by the transport properties of the concrete, mainly by the difficulty with which aggressive agents (chlorides, sulphates, etc.) can penetrate the porous network of the cementitious materials. The durability of any concrete structure depends strongly on the external environment to which it is exposed and the porous structure of the material. The formulation of durable cementitious materials especially requires a reduction of the open porosity and permeability. A schematic representation of the effects of pozzolanic materials on the porosity of hardened cement pastes is briefly presented in Figure 4.10. In this figure, the pore size distribution is represented as a cumulative curve giving, for a particular equivalent diameter of pore, the total volume of pores having a dimension greater than or equal to this diameter. These cumulated curves highlight possible reductions of the maximum pore size and the open pores, as illustrated by arrows A and B respectively (Figure 4.10). These reductions are achieved for any paste with (Pz_a to Pz_b) or without (Ref_a to Ref_b) pozzolana by a decrease in the water–binder (w/b) ratio or by an increase in the paste curing time or degree of hydration. Specific effects of SCMs on the pore structure of hardened cement pastes, when compared to reference pastes of Portland cement only, can be described as follows:

- At young ages, SCMs lead to an increase in paste porosity and the pores size (Pz_a vs. Ref_a) because a smaller quantity of hydrates is formed in the paste. At that time, most pozzolans have not yet reacted to produce pozzolanic C-S-H and because of that the replacement of a fraction of cement by a mineral admixture has merely the effect of diluting the cement. With fly ash and GGBS, this situation can last for several days (more than 7 days for some fly ashes) and can even be prolonged if the SCMs are used at high doses or cured for particularly short periods of time [12]. For very active pozzolans such as silica fume, calcined clay and metakaolin, this state can be short, e.g. less than 3 days [27].

- At later ages, the pozzolanic reaction leads to the production of hydrates(C-S-H) in addition to those of Portland cement which leads to the refinement of pores in hardened cementitious materials.

Figure 4.10: Schematic representation of the pore size distribution of cement pastes with (Pz_a, Pz_{b1} and Pz_{b2}) and without (Ref_a and Ref_b) mineral admixture [15]



4.2.7

INFLUENCE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS (SCMS) ON CONCRETE PERMEABILITY

The presence of SCMs affects the porosity of cement-based materials by the action of refinement of the pore size distribution compared to control mixtures and by decreasing the thickness and porosity of the ITZ [28], which has porosity having a size comparable to that of capillary pores [14].

The beneficial effect of SCMs on the ITZ is attributed to the densification of the microstructure and the improvement in the mechanical properties of the bond by deposition of voluminous hydration products inside the ITZ region of the hardened concrete, resulting in the reduction of porosity and permeability, when SCMs are used [29].

The microstructure of ITZ plays a vital role in transport properties and hence the durability of concrete. From a transport point of view, it has been seen that the effective diffusion coefficient of chloride ion is 6–12 times greater in the ITZ than in the bulk cement matrix [30]. Therefore, it is very necessary to improve the quality of this weak region of hardened concrete.

Based on the microstructural features, modification of ITZ can be achieved by two main processes as classified below: (i) Coating aggregate surfaces with some chemical reagents or polymers before mixing [31]. However, the pre-treatment process of aggregates before concrete production will lead to a higher cost, and its practical potential may be limited. (ii) Using mineral admixtures such as silica fume, fly ash, metakaolin for partial replacement of cement. Such materials participate in the particle packing, latent-hydraulic reaction and pozzolanic reactions which helps in the densification of the ITZ [32, 33].

4.3

RHEOLOGY AND WORKABILITY

Caption:

4.3.1

RHEOLOGY

Rheology deals with the study of the flow and deformation behaviour of a material. Rheology of the cement paste governs the fresh properties of concrete and it is as important as hardened and durability properties. Rheology study basically comprises parameters like plastic viscosity and yield stress. Rheology of the cement paste is influenced by cement type, mineral admixtures/ SCM, chemical admixture, water content [34].

4.3.1.1

INFLUENCE OF BLENDED CEMENT ON RHEOLOGY

Most of the research shows improvement in the rheological properties of concrete with the incorporation of SCM. In one study done by Khayat et al. [35], the effect of various SCM like fly ash, slag and silica fume on the rheological properties and stability of high-performance grout containing a viscosity modifying admixture (VMA) in conjunction with high range water reducing admixture (HRWR) was studied. They concluded that in a well dispersed system, the use of binary and ternary binders exhibited lower yield stress and higher plastic viscosity and resistance to forced bleeding than grout made without any SCM.

4.3.2

WORKABILITY

Workability is the property of freshly mixed concrete or mortar which determines the ease and homogeneity with which it can be mixed, placed, consolidated and finished [36]. There are many factors that affect the workability of concrete such as water content in the concrete mix, type of cement, amount of cement and its properties, aggregate grading (size distribution), nature of aggregate particles (shape, surface texture, porosity etc.), the temperature of the concrete mix, the humidity of the environment, mode of compaction, etc.

4.3.2.1

INFLUENCE OF CEMENT TYPE ON WORKABILITY

The physical characteristics of cement that affect the workability of concrete are consistency and fineness. The consistency of cement represents the water demand to achieve a required flow. In table 4.4, the range of normal consistency and fineness for more than 120 market samples of OPC, PPC, PSC and CC for different cement brands tested at the NCB laboratory have been given. It is observed that consistency is in the order PPC>PSC ~ CC >OPC and fineness is in the order of CC>PPC ~ PSC>OPC.

Table 4.4: Range of Consistency and Fineness for OPC, PPC, PSC and CC

Sr. No.	Properties	OPC	PPC	PSC	CC
1.	Consistency, %	28.0 ± 2.4	32.0 ± 2.7	30.7 ± 2.0	30.1 ± 2.2
2.	Fineness, m^2/kg	298 ± 33	348 ± 26	341 ± 46	379 ± 36

It has been well established that the addition of fly ash leads to increase in workability because of its lubricating effect. Also, the replacement of clinker with SCM in blended cements lead to the dilution effects that leads to increase in a water-clinker ratio which in turn increases the workability of concrete. The spherical shape of fly ash helps in enhancement of workability of concrete. Hence, the water or dosage of superplasticizer required for the same level of workability in case of blended cements is less than OPC [37].

However, in blended cement production, fly ash can be introduced to the cement by separate grinding or inter-grinding process. These grinding methods provide different products from many aspects such as fineness and particle size distribution [38]. It has been observed that for a similar level of slumps, the concrete mixtures made with the blended cements produced using inter-grinding method require more dosage of superplasticizer than the concrete mixtures in which the unground fly ashes and the Portland cements have been added separately. The fineness of the cement produced due to the inter-grinding of the fly ash with the Portland cement results in the increase in fineness that will ultimately result in more dosage of superplasticizer. [39] Another reason for the increase in water demand or dosage of superplasticizer is distortion in the spherical shape of fly ash during inter grinding process that causes loss of its lubricating effect.

In a study at the NCB laboratory [40], the dosage of admixture required for a particular range of slump was investigated for OPC, PPC and PSC. The study was conducted at six different water cement ratios i.e., 0.36, 0.4, 0.45, 0.50, 0.55 & 0.60. The value of consistency, fineness and compressive strength for OPC, PPC and PSC used in the study are given in table 4.5.

Table 4.5: Physical properties of cements used in the NCB study

Sl. No.	Properties	OPC	PPC	PSC
1.	Blaine's fineness, m^2/kg	285	379	346
2.	Consistency, %	28	32	31
3.	Compressive strength, N/mm^2			
	3 days	34.5	30.0	26.5
	7 days	42.5	41.5	34.5
	28 days	57.5	55.5	49.0

Table 4.6: Dosage of Admixture required for different OPC, PPC and PSC

Sl.no.	w/c ratio	Type of cement	Mix Constituents		
			Cement (kg/m^3)	Water (kg/m^3)	Dose of admixture (% by Wt of Cement)
1	0.36	OPC-43	444	160	0.5
2		PPC	444	160	1
3		PSC	444	160	1
4	0.4	OPC-43	400	160	0.4
5		PPC	400	160	1
6		PSC	400	160	1
7	0.45	OPC-43	356	160	0.4
8		PPC	356	160	1
9		PSC	356	160	0.6
10	0.5	OPC-43	320	160	0.35
11		PPC	320	160	1
12		PSC	320	160	0.6
13	0.55	OPC-43	300	165	0.2
14		PPC	300	165	0.8
15		PSC	300	165	0.55
16	0.6	OPC-43	280	168	0
17		PPC	300	180	0.4
18		PSC	280	168	0

In table 4.6, the dosage of admixture required to obtain slump in the range of 50 – 75 mm for concrete made with OPC, PPC and PSC at different water cement ratios is provided. From the results, it was observed that the dosage of superplasticizer required for PPC is higher as compared to the other two cements. The reason for an increase in admixture dosage for concrete made with PPC may be due to the fact that the cement manufactured using inter grinding process leads to distortion of fly ash shape. In the case of PSC, the dosage of superplasticizer required for the same level of workability was found to be more than OPC.

4.3.1.1

CONCLUSION

The workability of a freshly prepared concrete mix depends upon the cement type and its properties, especially consistency and fineness. The slight increase in water demand that may be experienced due to the finer grinding of blended cements can be easily tackled through proper mixture design and the use of admixtures. In fact, the production of high-performance concretes, such as self-compacting concrete is difficult and uneconomical without the use of supplementary cementitious materials.

4.4

STRENGTH DEVELOPMENT

The strength of a material is defined as the ability to resist stress without failure. In concrete, strength is related to the stress required to cause failure and it is defined as the maximum stress the concrete sample can withstand [41]. Strength development of concrete is associated with compressive strength required at the age of 3, 7 and 28 days.

In multiphase materials such as concrete, the porosity of each component of the microstructure can become strength-limiting. Natural aggregates are generally dense and strong; therefore, it is the porosity of the cement paste matrix as well as the Interfacial Transition Zone (ITZ) between the matrix and coarse aggregate, which usually determines the strength characteristic of normal-weight concrete. Although the water-cement ratio is important in determining the porosity of both the matrix and the interfacial transition zone and hence the strength of concrete, factors such as compaction and curing conditions (degree of cement hydration), aggregate size and mineralogy, admixtures types, specimen geometry and moisture condition, type of stress, and rate of loading can also have an important effect on the development of strength [41].

4.4.1

INFLUENCE OF BLENDED CEMENT ON STRENGTH DEVELOPMENT

According to various concrete technologists across the globe, it is believed that even though early age strength (≤ 7 days) of concrete made with blended cement is low as compared to concrete prepared with OPC because of the slow pozzolanic reaction. The ultimate compressive strength for concrete made with blended cement is either equal or higher for concrete made with OPC [42], as long as sufficient curing is done. The reasons are firstly secondary pozzolanic reaction leads to the formation of CSH gel that has dense microstructure as compared to portlandite which forms during hydration reaction of clinker that leads to higher compressive strength. Secondly, the refinement of pore structure and filler effect of Supplementary Cementitious Materials (SCMs) like fly ash and GGBS leads to reduction in overall porosity of concrete and densification of microstructure of concrete. These two effects compensate for the dilution effect caused due to the addition of SCM as a part replacement of clinker in blended cement. Generally, it has been found that keeping factors such as water-cement ratio, cement content, aggregate quantity same, the rate of gain of compressive strength at later stages is higher for blended cement as compared to OPC but the value of ultimate compressive strength for concrete prepared with OPC is higher as compared to concrete made with blended cement.

In the case of PPC, while fly ash reacts at a relatively slower rate at the beginning, which leads to lower compressive strength during the first few days or weeks after mixing, higher strength is found in later ages [43, 44]. Fly ash particle size plays an important role in strength development. It has been observed that in the long-term, strength increases with the increase of fly ash up to a replacement rate of about 25 to 35%, beyond which strength values start to reduce with further addition of fly ash [42]. When fly ash is classified as reasonably fine fly ash, the rate of compressive strength gain of the blended cement pastes is significantly improved. [45]. This is the result of the packing effect of fine fly ash. The small and spherical shape of fly ash particles fills the voids and leads to the densification of microstructure [46]. The smaller particle size of fly ash with a higher surface area and glassy phase content also improves the pozzolanic reaction [47].

In the case of Composite Cement (CC), it has been observed that the early age strength of CC concrete is lower than that of OPC concrete. This may be due to the high level of clinker replacement. The pozzolanic activity of fly ash contributes to the strength gained at later stages because of continuous curing. However, at 28 days it is found that compressive strength made with PPC is almost comparable or just slightly less than concrete with OPC. This may be due to secondary pozzolanic reaction due to the presence of fly ash and GGBS that enhances the overall microstructure of concrete [48, 49].

In one of the studies conducted at NCB, the compressive strength of concrete mixes made with blended cement i.e., OPC 43G, PPC and PSC had been investigated at six different water-cement ratios i.e. 0.36, 0.40, 0.45, 0.5, 0.55 & 0.6. Some of the physical parameters of the cements used, i.e., fineness and compressive strength of OPC, PPC and PSC were previously provided in table 4.4 and 4.5.

Table 4.7: Rate of development of concrete compressive strength (%) in NCB study

Type of Cement	**Average % strength development at 28 days (w.r.t 7 days strength)**	**Average % strength development at later ages i.e., 90 days (w.r.t 28 days strength)**
OPC	21.34 ± 6.56	11.10 ± 2.16
PPC	42.56 ± 11.41	17.66 ± 6.91
PSC	33.73 ± 13.46	11.73 ± 4.6

From table 4.7, it is observed that for different water-cement ratios, the average rate of strength development between 7 and 28 days is maximum for concrete made with PPC and lowest for concrete with OPC cement. Between 28- and 90-days concrete with PPC has marginally higher rate of strength gain than concrete with the other two cements. However, for concrete prepared with PSC and OPC rate gain was almost equal. Although the blended cements have many advantages as discussed above, the development of compressive strength in case of blended cement is highly dependent on the curing of structures. Because of the slow pozzolanic reactions of fly ash, continuous wet curing and favorable curing temperatures are required for the proper development of strength. It has been observed by the researchers that in the field,, the drying ambient atmospheric conditions reduce the strength potential of blended cement concrete as compared to laboratory water cured specimens as the secondary pozzolanic reaction fails to contribute to the development of strength because of lack of curing [49, 50].

4.4.2

CONCLUSION

It can be concluded that strength gained in blended cement is lower at early ages but higher at later ages. However, sufficient curing is required to tap the potential of gain in strength in case of concrete made with blended cement.

4.5

SHRINKAGE (CHEMICAL, AUTOGENOUS, DRYING ETC.) AND CRACKS

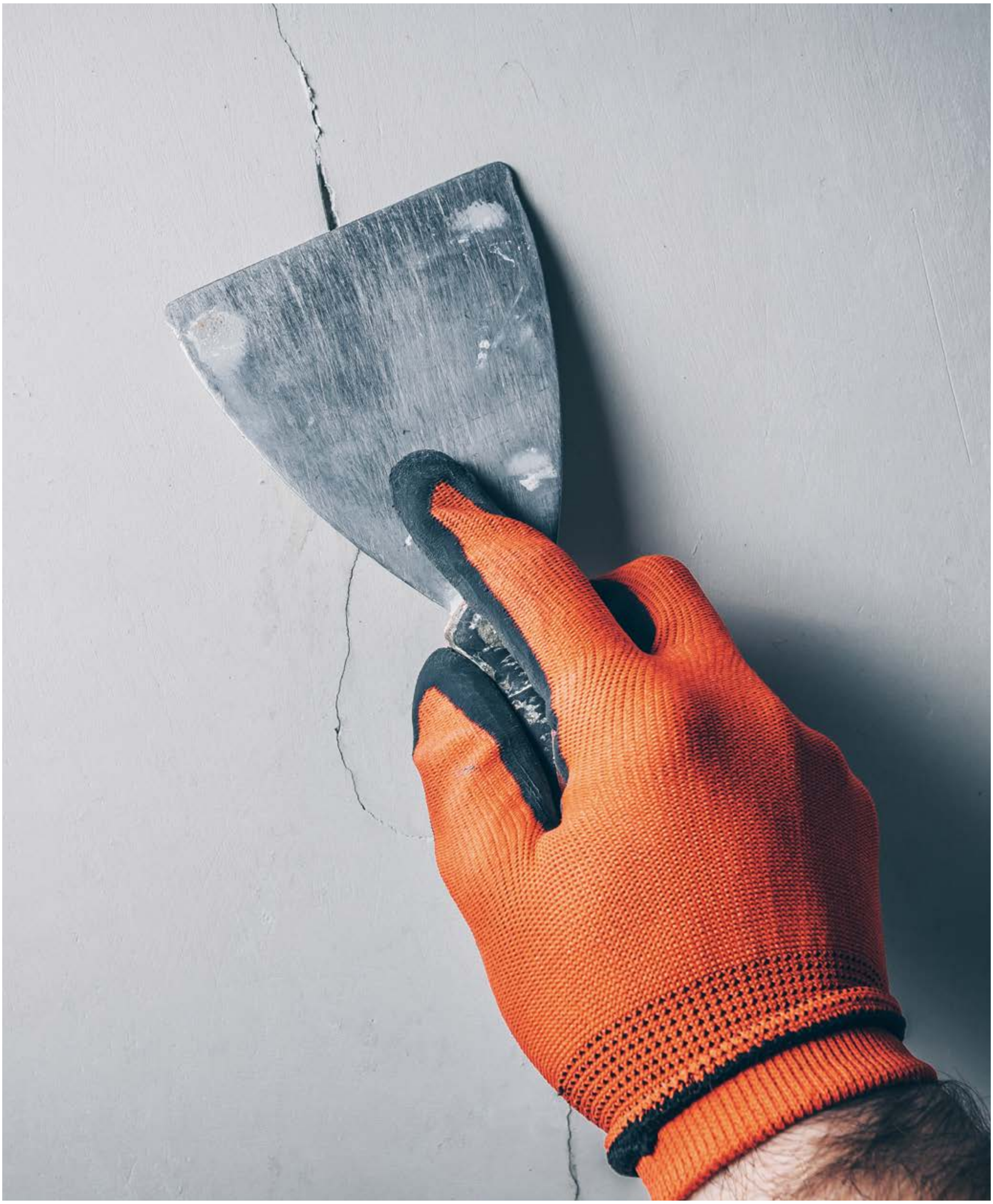
Shrinkage of concrete has been an area of increasing concern when focusing on maintaining durable structures. Over a period of time, shrinkage of concrete can induce cracks which can severely decrease concrete life expectancy. These volume changes in concrete are often attributed to the drying of the concrete over a long period, even though recent research observations have also focused on early age or plastic drying problems. At an early age, concrete is in a moist state and there are difficulties in measuring the fluid material. These difficulties in measuring the changes in concrete in its fluid stage have hindered comprehensive physical testing and understanding the factors associated to early age shrinkage. The most basic approach to minimize early age volume changes in concrete is to avoid drying of concrete by proper handling of the concrete during the initial few hours after placement. It is imperative that the concrete curing begins immediately and appropriate curing practices are adopted [51]. A supplementary problem to drying shrinkage at early ages is the change that occurs when no moisture transfer is permitted with the surrounding environment. Such reduction in volume of concrete is known as autogenous shrinkage and is generally attributed to chemistry of cementitious materials and internal structural changes. Autogenous shrinkage is mostly a concern in concrete having low water to cement ratio i.e. high strength concrete or high performance concrete mixes (having strength in excess of 40 MPa or 6000 psi). Overall, early age shrinkage in concrete is of increasing concern because it can lead to cracking when the concrete has not gained significant strength to withstand internal stresses [52].

Shrinkage of concrete occurs in two distinct stages: early and later ages. The early stage is usually defined as the period of around first 24 hours after casting, while the concrete is setting and beginning to harden. The term later ages refer to the concrete at an age of 24 hours and beyond. During this period, the concrete specimen is demolded and shrinkage measurements are conducted.

Shrinkage of concrete occurs due to the movement or loss of water. Tensile stresses are generated in concrete, when the water is lost from concrete due to either evaporation (drying shrinkage) or internal reactions (autogenous shrinkage). These stresses generated due to loss of water, pull the cement paste closer together which is registered as a volume reduction. During the initial period after casting shrinkage is even more critical since the concrete still has not gained much strength. Even the smallest shrinkage strains at early ages can result in stresses greater than the tensile capacity of the concrete, causing cracking [52].

Thus, shrinkage of concrete may be broadly classified into the following types:

- Autogenous shrinkage
- Plastic shrinkage
- Chemical shrinkage
- Hardened concrete drying shrinkage



4.5.1

PLASTIC SHRINKAGE

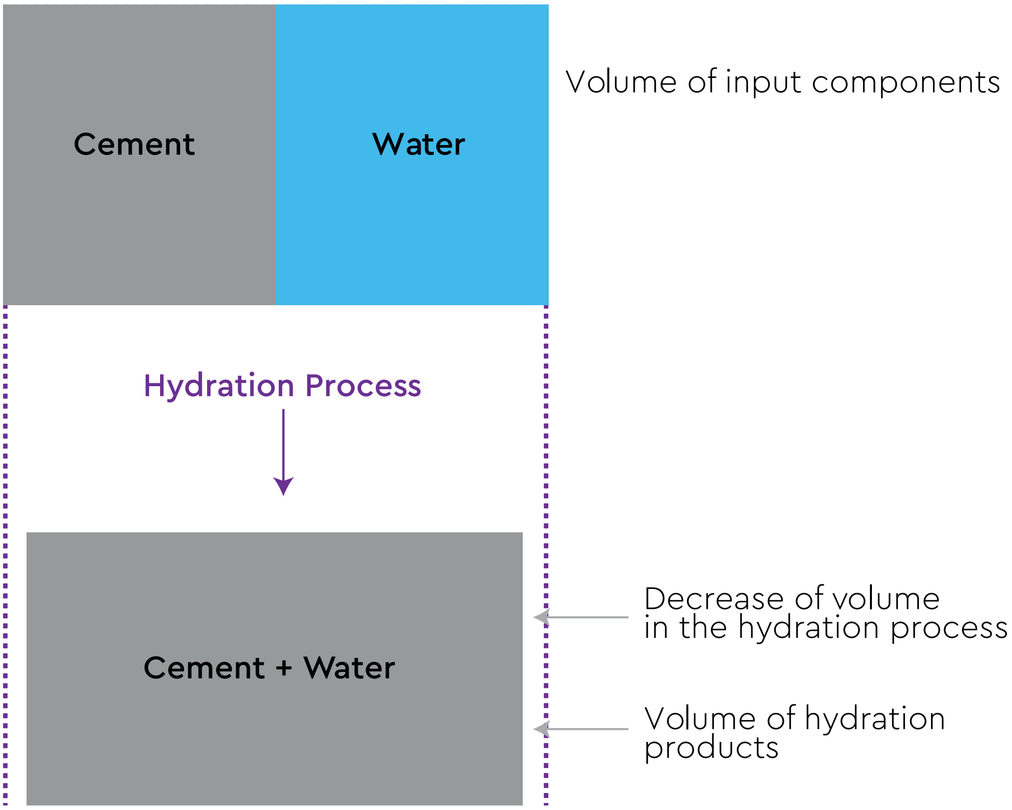
Plastic shrinkage is a consequence of water evaporation from the surface of fresh concrete and the absorption of water by the concrete formwork. Compared to other types of shrinkage (i.e. autogenous and drying shrinkages), volume change caused due to plastic shrinkage is highest and can range up to around 1 % of the cement volume. It occurs very rapidly in the first few hours and as such mainly remains unregistered. Typically, its effect is not significant in comparison to other stress conditions of construction because it occurs in the fluid mass of the fresh concrete. Surface layer shrinkage due to evaporation of water near surface is prevented by internal parts of concrete which do not shrink as much as a surface layer. This phenomenon leads to the occurrence of tensile stress in the surface layer. These stresses can be greater than the tensile strength of young concrete and thus leads to plastic cracks, shallow and wide. A higher amount of cement content in concrete mixes leads to an increase in the amount of plastic shrinkage. Detrimental effects of this plastic shrinkage can be effectively eliminated or countered through intensive and appropriate concrete curing practices i.e. by wetting of concrete elements (or covering with curing membranes) to retrieve water (or to prevent its evaporation) [53]

4.5.2

CHEMICAL SHRINKAGE

Chemical shrinkage of cement paste represents a decrease in volume of cement paste which occurs due to the chemical binding of water during the process of cement hydration. During the process of concrete hardening, several chemical transformations occur in the cement paste. The direct consequence of these chemical transformations is the reduction of cement paste volume. This phenomenon is clearly shown in figure 4.11. The volume of the hydration products, which are formed during the hydration of cement is smaller in comparison to the volume of input components, i.e. cement and water together. The main reason for a decrease in cement paste volume is the increased stiffness of chemically bound water in between cementitious hydration products in comparison to free water added in the mixture before binding. [54].

Figure 4.11: Schematic description of chemical shrinkage mechanism [54]

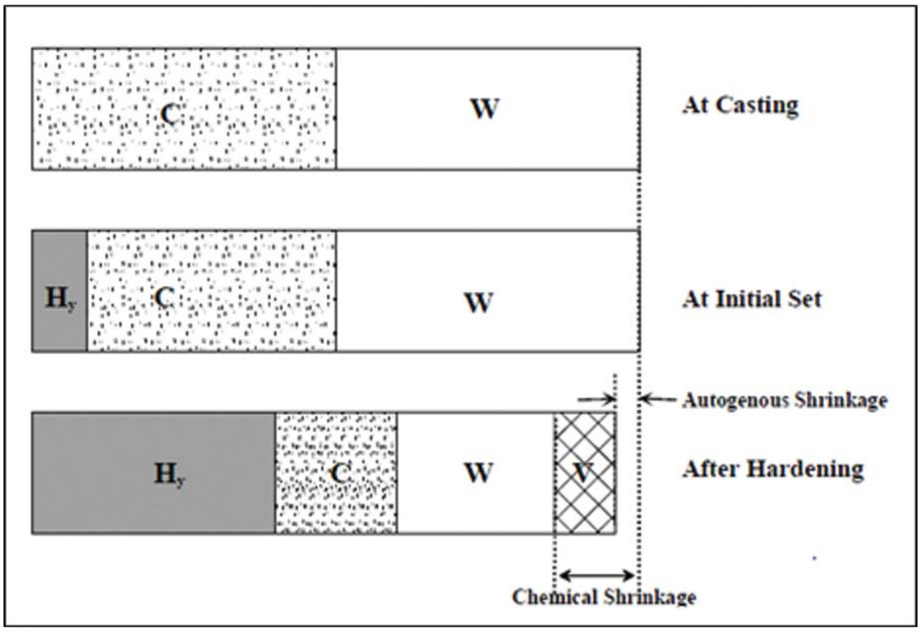


4.5.3

AUTOGENOUS SHRINKAGE

Autogenous shrinkage of concrete, which is also known as hydration shrinkage is a result of the chemical shrinkage process, that leads to the production of unsaturated pores [3]. This process, also known as self-desiccation, begins in those pores because of the process of hydration i.e. inside the cement structure all water is used for hydration and water cannot reach fast enough from the outside due to the reduced connectivity of the pores. When the shrinkage is restrained, it leads to tension and hence cracking in concrete. (Figure 4.12). Most of the autogenous shrinkage occurs during the first month and its rate and magnitude depend upon the constituents of the concrete mix. The component of concrete that shrinks is the cement paste when water is removed from the capillary pores. Water in the larger voids [>50 Nanometer (nm)] is considered to be "free water," because its removal does not result in volume change. However, water present inside small capillary voids (5 to 50 nm) may result in large shrinkage strains, when it is forced to leave the system [56]. The size and volume of the capillary voids are determined by the initial water-to-cement ratio and the degree of hydration of the mixture. The microstructure is also modified by the binder system used. Although it is generally reported that the use of SCMs reduces the risk of cracking due to shrinkage, the results vary between studies.

Figure 4.12: Relations between autogenous and chemical shrinkage: C – unhydrated cement, W – unhydrated water, Hy – hydration products, and V – voids generated by hydration [55]



4.5.4

DRYING SHRINKAGE

Drying shrinkage is reflected from the surface towards the interior of the concrete mass. Drying shrinkage is the reduction in volume of concrete resulting from a loss of water from the concrete. Initially, free water escapes as bleed water from the concrete surface. Once the bleed water disappears due to evaporation, excess water will come out from the interior of the concrete mass [52]. Drying level varies according to the thickness of element, between its maximal value (on the surface) and its minimal value (in the core). Drying shrinkage depends on many parameters such as thickness of element, porosity or content of the free water in concrete, paste volume, binder fineness, temperature and relative humidity.

4.5.5

FACTORS AFFECTING CONCRETE SHRINKAGE

Factors affecting the shrinkage of concrete are usually interrelated although they can be grouped into two major categories:

- Characteristics of constituent materials
- Ambient environmental conditions [56].

On one hand, the first group covers the characteristic properties of constituent material itself, such as aggregate properties (i.e., size, gradation, content, and elastic properties), water to cement ratio, water content in concrete mix, air content, cementitious material content, characteristics of cement, characteristics of chemical and supplementary cementitious material admixtures. On the other hand, the environmental factors related to concrete comprise the external conditions such as relative humidity of the surrounding environment, ambient temperature and wind velocity [56]. Since, the drying process involves moisture loss from the surface, drying shrinkage mainly depends on the size and configuration of the element [57]. Usually, a concrete member of a larger size dries at a slower rate and thicker specimen has a lower rate of shrinkage in comparison to the thinner specimen. An inverse proportion between shrinkage and the ratio of specimen volume to its drying surface area is obtained from American Concrete Institute (ACI) [58]. Drying shrinkage decreases with increase in the volume-to-specimen surface area ratio of concrete member. The quantity of aggregate in the concrete mix is also a major factor affecting the potential of shrinkage. Shrinkage is basically related to the volume of aggregate content and higher content of aggregate has a lower shrinkage strain at the same w/c ratio.

ACI Committee 209 on "Factors affecting shrinkage and creep of hardened concrete" reports drying shrinkage of concrete decreases with an increase in the size of aggregate while decreasing the paste content as the quantity of cementitious paste in concrete is one of the major parameters affecting the shrinkage potential of a mixture. For a given water to cement ratio, decrease in paste content and subsequent increase in aggregate content leads to reduced shrinkage strain [59]. The elastic properties of the aggregate also affect concrete shrinkage – the lower the modulus of elasticity of aggregate, the higher will be the drying shrinkage of the concrete. Characteristics of cement, such as increased fineness and reduced sulfate content will reportedly increase drying shrinkage potential. Relative humidity around concrete can dramatically increase the shrinkage, especially when RH is lower than 10% [60]

4.5.6

EFFECT OF BLENDED CEMENTS AND SUPPLEMENTARY CEMENTITIOUS MATERIALS ON SHRINKAGE

Both mineral admixtures (supplementary cementitious materials) and chemical admixtures can have a significant impact on the shrinkage of a concrete mix. The research work in this area and relevant literature indicates that in comparison to OPC based concrete, the inclusion of slag cement has marginal effect on increasing shrinkage. High silica fume content in concrete mix may increase the short-term drying shrinkage. However, lower proportion of silica fume in mix may not lead to an increase in shrinkage over the long term (i.e., 365 days) [61]. The use of slag cement and silica fume in ternary mixes provides better performance compared to binary mixtures where slag cement and silica fume are used alone [62]. In comparison to plain Portland cement concrete, increased replacement dosages of Class F fly ash in binary mixes may reduce drying shrinkage [63]. Due to low alkali contents and higher Calcium to Silica ratio, class C fly ash reportedly causes more shrinkage than control concrete mixtures in comparison to class F fly ash. However, both types of fly ash combined with slag cement or silica fume in ternary blends diminish the adverse effects of silica fume or slag cement [62].

- Binary blends containing Portland cement and class F fly ash: Gesoğlu et al. replaced OPC by FFA at levels of 20%, 40%, and 60% and observed that the free shrinkage was reduced by using class F fly ash and this beneficial effect appeared to be more pronounced with increasing replacement levels [64]. In another study, class F fly ash was used to investigate the drying shrinkage behaviour in six mixtures cast with total cementitious contents of 400 and 500 kg/m^3. The use of the class F fly ash in mixes having 500 kg/m^3 cementitious content mixtures resulted in a nominal reduction in shrinkage strain [65].

- Binary blends containing Portland cement and slag: Reduction in shrinkage of concrete was observed when slag cement was used in a binary system in comparison to an OPC mixture. The shrinkage decreased with increased amounts of slag cement [63]. To assess the influence of slag cement on drying shrinkage behaviour, the Slag Cement Association (SCA) performed a critical review based on published shrinkage research. The authors concluded that given a similar mixture, slag cement appears to have a marginal effect on increasing drying shrinkage [67].

- Ternary blends containing Portland cement, slag cement, and class F fly ash: In comparison to control concrete mixes, reduction in shrinkage was observed by using 10% slag and 10% class F fly ash, 20% slag and 20% class F fly ash and 30% slag and 30% class F fly ash as a replacement to Portland cement in ternary blends [63]. Shrinkage in ternary blends containing calcined clay and limestone have been seen to present a similar shrinkage behaviour as OPC.

4.5.7

CONCLUSION

Based on the above, the following conclusions can be drawn:

- The shrinkage strains are almost comparable at very early ages of the drying period for concrete made from all types of cement blends. However, the shrinkage strains differed for concretes made with various cement blends at later ages.
- In case of binary blends, use of PPC and PSC reduces the drying shrinkage of concrete in comparison to concrete made with OPC.
- Furthermore, in case of ternary blends, shrinkage reduces with higher replacement level of fly ash and slag in ternary blends in comparison to concrete made with OPC.

4.6

LEACHING

Leaching of calcium ions, which is a rare phenomenon in the usual strength concretes today, increases the porosity of cement-based materials, consequently resulting in a detrimental effect on its durability since it facilitates the entry of aggressive harmful ions, causing damage to the structure. Under the attack of water environment, the dissolved calcium ions in pore solution from the cement hydration products Ca$(OH)_2$ and C-S-H gel in concrete flow into the water due to the great gradient of the calcium ion concentration, and this phenomenon leads to the reduction of the calcium content in concrete and decrease of alkalinity of the pore solution and the increase of porosity of concrete [68]. The increase in porosity results in degradation including damage to the pore structure and weakened matrix that leads to lower compressive strength of the cement-based material. [69, 70]

4.6.1

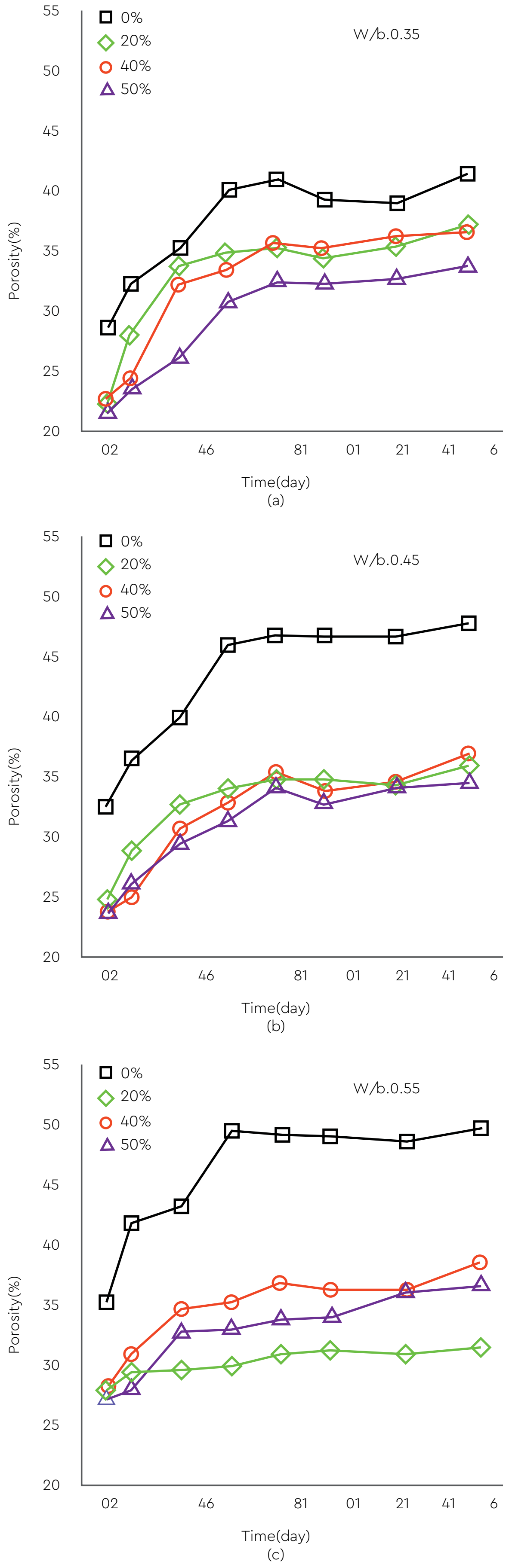
INFLUENCE OF BLENDED CEMENT/SCM'S ON LEACHING

Cheng et al. [72] investigated the effect of leaching behavior under the accelerated environment of ammonium nitrite. The effect of the leaching of calcium ions on the compressive strength and resistance against deterioration of cement-based materials was studied. The study focused on the influence of added SCM's (fly ash, slag and silica fume) on the leaching behavior of calcium ions. The solution of ammonium nitrate was used to accelerate the leaching process in this study. it was hence concluded that cement-based materials with SCM's can increase the resistance against the degradation process due to the formation of denser C–S–H gels. The leaching process of calcium ions decelerates, slowing the deterioration of compressive strength of the specimens. Therefore, adding appropriate SCM's into cement-based materials not only helps in increasing compressive strength, but also provides resistance to the leaching process.

Tang et al. [72] studied the impact of blast furnace slag and water-binder ratio on the leaching behavior of cement-based material and its corrosion resistance in water environments. This was investigated by analyzing the porosity, phase composition, microstructure morphology and Calcium-Silicon ratio of slag-cement pastes in the process of calcium leaching. The following conclusions were made from the study:

- The porosity of the cement pastes with no slag increases with the water-binder ratio, while the porosity, calcium hydroxide content and Ca/Si of the unleached slag cement pastes are less than that without slag.
- The higher slag content in slag-cement system results in lower calcium hydroxide content and Ca/Si in the slice specimen. The compactness, calcium hydroxide content and Ca/Si decrease with the increase of leaching time, and the reduction rate of the unleached matrix with slag is less than that without slag.
- The slag-cement pastes with 40% slag and low water-binder ratio, or with 50% slag and high water-binder ratio has the optimum calcium leaching resistance. Thus, from the results, as shown in figure 4.13, it was evident that appropriate slag content and water-binder ratio can slow down the microstructure deterioration of slag-cement pastes and calcium leaching process, and effectively improve its leaching resistance.

Figure 4.13: Change of porosity of slag-cement pastes with leaching time (a)water-binder ratio of 0.35, (b) water-binder ratio of 0.45, (c) water-binder ratio of 0.55 [72]



Rozière et.al [73] investigated the effect of compactness, in terms of water/binder ratio, between 0.3 and 0.6. and influence of the chemical composition of binder on the performance of concrete against leaching degradation. The authors used Fly ash, GGBS, and limestone as fillers in replacement of cement to show the influence. The damaged depths are assessed through a pH colorimetric indicator. One of the findings from the study was that blended cements or binder incorporating such pozzolanic materials actually produces less portlandite $Ca(OH)_2$, with equal or enhanced compactness of the matrix. 30% replacement of cement with fly ash improved the performance of the concrete mixtures exposed to leaching. The experimental results also confirmed the good resistance of binders including high proportions (more than 60% of the equivalent binder content) of GGBS, using either blended cement or adding as a mineral admixture as part replacement of Portland Cement.

However, Choi et.al [74] observed from their study that the residual strength of the leached part with OPC was in the range of 35–60%. Whereas in the case of mineral admixture replacement, upon blending with BFS, the residual strength of the degraded zone was in the range of 23–50%. And the residual strength of FA concrete was in the range of 25–30%. From results, it was concluded that the use of the mineral admixture did not show useful results. Therefore, a sufficient curing duration must be allowed for concrete blended with a mineral admixture to resist leaching degradation.

4.6.2

CONCLUSION

From the above statements, it can be concluded that the use of blended cements/mineral admixtures reduces the calcium hydroxide quantity and refine the pore structure of cement matrix via pozzolanic reaction, thus enhancing the resistance of the cement-based materials against leaching of calcium ions.

4.7

ALKALI AGGREGATE REACTIVITY

The chemical reaction between alkali hydroxides from Portland cement and a specific category of aggregates is known as an alkali aggregate reaction. The swelling and cracking due to aggregate alkali reaction appears after many years of construction. Even though the deterioration due to it is a slow process but is progressive and combined with other causes can lead to complete failure of the structure.

The AAR can be subdivided into two types viz, Alkali Silica Reaction (ASR) and Alkali Carbonate Reaction (ACR). The basic definition of the two as given by the American Concrete Institute [75] is:

- In ASR, the reaction is between alkalies and certain siliceous rocks or minerals, such as opaline chert, strained quartz, and acidic volcanic glass, present in some aggregates.

- In ACR, the reaction is between the alkalies (sodium and potassium) and certain carbonate rocks, particularly calcitic dolomite and dolomitic limestones, present in some aggregates.

4.7.1

ALKALI SILICA REACTION

The reaction between alkalies present in cement and silica found in aggregates results in the formation of soluble and viscous gel of sodium silicate or sodium silicate hydrate. This gel is hygroscopic in nature and expands on the absorption of moisture. This increase in volume and expansion stresses inside the siliceous aggregate which initiates cracking and fracture thereby leading to failure of the structure. Therefore, three essential factors for the propagation of ASR are shown in figure 4.14:

i) Reactive Silica
ii) Alkalies
iii)Moisture

Figure 4.14: Essential factors for propagation of ASR [76]

4.7.1.1

REACTIVE SILICA

The different types of aggregates used in concrete contain silica in a different form that can react. Aggregates containing silica that present large surface areas for reaction—poorly crystalline, many lattice defects, amorphous, glassy, microporous—are susceptible to reaction. [77] Silica in the form of microcrystalline and crypto-crystalline quartz, strained quartz in quartzite, opal, Chalcedony, Tridymite, Cristobalite are all reactive. The list of rocks with the reactive component is tabulated below in table 4.8 [78]

Table 4.8: Various reactive components in different rock types

MINERALS	
Opal.	
Chalcedony.	
Tridymite.	
Cristobalite.	
Cryptocrystalline, microcrystalline or glassy quartz.	
Coarse-grained quartz is intensely fractured, granulated and strained internally or filled with submicroscopic inclusions of which illite is one of the most common. Silicic, intermediate and basic volcanic glasses. Vein quartz	
ROCKS	
Rocks	Reactive component
Igneous rocks	
Granite, Granodiorites, Charnockites	More than 30 percent strained quartz as characterised by an undulatory extinction angle of 25° or more.
Pumice, Rhyolites, Andesites, Dacites, Latites, Perlites, Obsidians, Volcanic tuffs	Silicic to intermediate silica rich volcanic glasses; devitrified glass; tridymite.
Basalts	Chalcedony; cristobalite; palagonite; basic volcanic glass.
Metamorphic rocks	
Gneisses, Schists	More than 30 percent strained quartz as characterized by an undulatory extinction angle of 250 or more.
Quartzites	Strained quartz as above; 5 percent or more chert.
Hornfelses, Phillites, Argillites	Strained quartz as above; micros crystalline to cryptocrystalline quartz.
Sedimentary rocks	
Sandstones	Strained quartz as above; 5 percent or more chert; opal.
Greywackes	Strained quartz as above; microcrystalline to cryptocrystalline quartz.
Siltstones Shales	Strained quartz as above; microcrystalline to cryptocrystalline quartz; opal.
Tillite	Strained quartz as above; microcrystalline to cryptocrystalline quartz.
Chert Flint	Cryptocrystalline quartz; chalcedony; opal.
Diatomite	Opal; cryptocrystalline quartz.
Argillaceous dolomitic limestones Argillaceous calcitic dolostones Quartz-bearing argillaceous calcitic dolostones	Dolomite; phyllosilicates exposed by dedolomitisation .
OTHER SUBSTANCES	
Synthetic glass; silica gel	

4.7.1.2

ALKALIES

The alkalies present in concrete can be derived from Portland cement, supplementary cementing materials (e.g., fly ash, slag, silica fume), Chemical admixtures, etc. However, Portland cement is the main source of alkalies. The alkalies are present in the form of sodium and potassium salts but the alkali content is calculated in terms of sodium equivalent using the equation:

$$Na_2O \text{ equivalent} = Na_2O+0.658K_2O$$

The sodium and potassium are present in sulphate phase or is locked within the aluminate and silicate phase of the anhydrous cement. The alkalis which are not in sulphate form contribute to more than fifty percent and are found in C_3A, C_3S and ferrite in cement. [79] The swelling capacity of the gel is increased due to the presence of alkalis in the pore water solution. The hydroxyl ion concentration in the pore solution of concrete made with high alkali cement is maybe ten times higher than that made with low alkali cement. [80]

As per the Indian standards, the use of cement with alkali content below 0.6% expressed as sodium oxide equivalent is recommended in case when reactive aggregates are to be used. [81, 82]

4.7.1.3

MOISTURE

Water plays an important resource in the propagation of ASR. Portions of the structure exposed to moisture show higher damage as compared to other parts of structures. Hence, the hydraulic structures are more susceptible to expansion and swelling due to ASR. The relative humidity should be in the range of 80–90% for ASR development along with other probable conditions. [83]

4.7.2

MECHANISM OF ASR

The siliceous component from aggregate reacts with the OH- ion in the pore solution for the alkali silica reaction. However, the sodium and potassium components of alkalis do not react with the silica in aggregates, they only ensure the presence of OH- ions. The reaction can be subdivided into two phases. In the first phase, the alkali and silica combine to make alkali silica gel and in the second phase, this gel absorbs water and increases in volume. Since the gel is surrounded by water this increase in volume cause expansion thus leading to cracking.

Phase 1

$SiO_2 + 2NaOH + H_2O \longrightarrow Na_2SiO_3.2H_2O$

(2KOH can replace 2NaOH)

Phase 2

$Na_2SiO_3.2H_2O + H_2O \longrightarrow$ Expansion

4.7.3

RESISTANCE TO AAR USING DIFFERENT TYPE OF CEMENT

For resistance against AAR, the following means can be adopted:

- Use of inert aggregates
- Use of low alkali cement
- Addition of chemical additives
- Replacing cement with supplementary cementitious materials
- Use of blended cement

Out of the above-mentioned means, the use of SCMs and blended cement is most preferred as it is the most economical and viable method [85]. Even IS 456 recommends that fly ash when added by more than 25% or slag content at least 50 % as a part replacement to OPC are advantageous in preventing ASR in concrete.

The study of pore solution showed the effects on available alkalis due to the use of SCM to vary according to the composition of ash, percentage of replacement, sample age and alkali content of cement. [96] The presence of SCMs/mineral admixtures reduces the pH of the pore solution. Many researchers also believed the concentration of alkalis was reduced by the use of SCMs as they bind the free alkalis and as a result the expansion was delayed. Several studies proved that the use of alumina rich mineral admixtures like fly ash, slag or metakaolin are more effective against ASR as compared with silica rich additives like silica fume.

An experimental study was conducted using three types of mineral admixture viz, Fly ash, silica fume and GGBS with alkali contents of 0.53%, 1.37% and 0.56% respectively with OPC of 0.94%, 0.59% and 0.47% alkali content to study its effect in control of ASR. For reactive fine aggregate crushed quartz glass with an amorphous silica content of more than 90% was used. The pore solution analysis was done for potassium, sodium and hydroxyl ion. The degree of attack on the silica in aggregate is largely dependent on the concentration of hydroxyl ions. The composition of the resulting gel and its capacity to swell is dependent on the available potassium and sodium ion in the pore solution. The author reported that the mineral admixtures were able to control the expansion due to ASR. It was also stated that the use of a combination of mineral admixtures showed a better performance than a single type of admixture. A compounding effect to resistance against ASR was observed on using three mineral admixtures together. [87]

In this study, the authors experimented with twenty-two binary or ternary blends in different combinations using one high-alkali cement, metakaolin, low calcium fly ash, high-calcium fly ash and one slag cement with two different reactive aggregates. The two reactive aggregates, one natural river sand and one reclaimed glass–limestone blend where crushed glass and manufactured limestone were combined in the proportion 1:2, were used in the mortar mixtures. The effectiveness of mixes was checked by conducting a comparative study of modified mortar bar test method and ASTM C1260–14/C1567–13. Also, in the second phase of testing a modified version of ASTM C227–10 mortar-bar method was used where short bars (25×25×150 mm) were cast with the same blends. The authors concluded that high-calcium fly ash and slag did not perform well in both binary and ternary bends but metakaolin and low-calcium fly ash were able to mitigate the ASR effects. The use of a low dosage of metakolin (5%) with other SCMs showed good results in ternary blends. However, low dosage of metakaolin was not effective alone with both the reactive aggregates. However, a combination of 5% metakaolin and 35 % high calcium fly ash were effective with both the reactive aggregates. It was found that increasing low calcium fly ash content to 25 %, or combining 12.5 % of it with either 5 % metakaolin or 27.5 % high calcium fly ash, were both successful at suppressing ASR. [88]

The authors studied the outcomes of expansion tests on concrete prism and mortar bars. For this purpose, forty-two mixes were cast using two Portland cements (PC) with alkali contents, of 1.02% Na_2Oe (HAPC) and 0.60% Na_2Oe (LAPC) and eighteen types of fly ash at different levels. Also, for coarse aggregate siliceous limestone was used which is reactive in nature. The study concluded that all types of fly ash reduced expansion as compared to cement mix without fly ash. Also, the reduction in expansion increased with the increase in levels of replacement. The fly ash with higher alkali or calcium content is less effective in controlling expansion and hence higher percentage of replacement has to be used for preventing expansion. [89] This behaviour of high calcium fly ash can be attributed to the pore solution chemistry. A study on pore solution concluded that the fly ashes that reduce the hydroxyl ion concentration of the pore solution of pastes to less than 0.60 mol/l to 0.65 mol/l are much more effective in reducing expansion. [90,91]

Furthermore, the authors [89] concluded that the use of fly ash reduced expansion due to ASR. Generally, the expansion increases as the calcium or alkali content of the fly ash increases or silica content decreases at a given replacement level. As a result, the safe level of fly ash required to control the expansion within acceptable limits increases as the calcium or alkali content increases or silica content decreases. Their results showed that the low calcium fly ashes (ASTM Class F) were much more effective in reducing AAR expansion (at replacement levels of greater than 20%) than high calcium fly ash (ASTM class C). A ternary blend of 10% ASTM class F fly ash with 5% silica fume also showed good results in reducing the expansion.

High levels of replacement of fly ash may be required for highly reactive aggregates and high alkali content but this can hamper the early strength development. As per the study, the usage of fly ash led to reduction in compressive strength. The concrete produced with a higher level of fly ash replacement had very high electric resistivity thereby improving the overall durability. However, it showed an adverse effect on the early strength gain through 56 days due to reduction in hydration process but by the end of one year, the reduction in strength level dispersed. The authors suggested using a lower water/cement ratio while using fly ash for better early age strength development. [92]

The use of granulated blast furnace slag or fly ash replacement of OPC can be useful in reducing the alkali aggregate reaction provided fly ash content is at least 25% or slag content is at least 50% [93].

It was reported that the physicochemical properties of Rice Husk Ash (RHA) are similar to that of Silica Fume (SF), although RHA is more strongly pozzolanic than SF. It was concluded that 12–15% of RHA replacement levels shall be enough to control the expansion due to ASR[94]. In the study [95] it was concluded that the presence of RHA decreases the pH level of the pore solution by binding alkalis. However, a study done by another author concluded that RHA promotes ASR instead of mitigating it. They believed the RHA particles act as reactive aggregates and react with the hydroxyl ion to produce the gel and thus leading to expansion. [96].

4.7.4

CONCLUSION

It can be concluded that the use of SCMs/mineral admixture/blended cements in concrete greatly help in mitigating the expansion due to ASR due to:

- The reduction in the concentration of hydroxyl ion
- The concentration of alkalis in the pore solution of PPC, PSC and blended cement is less
- Refinement of pore structure binds the free alkalis thus reducing the the porosity and permeability thereby reducing the ionic mobility and hence less free alkalis are available to react with aggregates
- Reduction in calcium hydroxide due to pozzolanic reaction reduces the formation of gel
- Reduction of pH of pore water
- It is concluded that PPC having a minimum of 25% fly ash and PSC having a minimum 50% slag is beneficial in mitigating the ASR. The same provision has been made under IS 456:2000.

4.8

SULPHATE ATTACK

Sulphate attack is the most common chemical form of concrete deterioration. Sulphates are commonly found in soil, aggregates, seawater, and cements [97, 98]. Sulphate attack on concrete has been reported to be the cause of severe damage to concrete for over a century. Sulphate attack can lead to expansion, cracking, strength loss, and disintegration of the concrete, it is generally attributed to the reaction of sulphate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite [97, 98, 99]. The formation of ettringite leads to an increase in solid volume, resulting in expansion, cracking, and mass loss, particularly when restrained. The formation of gypsum can lead to softening and loss of mass and strength. In addition to the formation of ettringite and gypsum and its subsequent expansion, the deterioration due to sulphate attack is partially caused by the degradation of the calcium silicate hydrate through leaching calcium compounds. This process leads to a loss in calcium silicate hydrate gel stiffness and an overall deterioration of the cement paste matrix [100].

4.8.1

FORMS OF SULPHATE ATTACK

Sulphate attack can be divided majorly in two types [101]:

External Sulphate Attack (ESA)

Internal Sulphate Attack (ISA)

4.8.1.1

EXTERNAL SULPHATE ATTACK

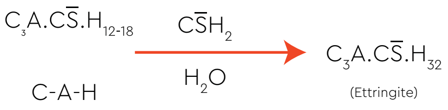
The ESA-induced damage, which is the traditional sulphate attack, is determined by the chemical interaction of a sulphate-rich soil or water with the cement paste. Soils containing sodium, potassium, magnesium, and calcium sulphate are the main sources of sulphate ions in groundwater. For ESA to occur, the following three conditions must be fulfilled:

- High permeability of concrete;
- Sulphate-rich environment;
- Presence of water.

In the absence of one of these elements, the ESA-related damage cannot occur. For instance, in porous and/or micro-cracked concrete not exposed to water, the ESA-related damage does not happen, even if sulphate ions are present in the environment because, in the absence of water, these ions — for instance in dry soil — cannot migrate through the interconnected pores of the concrete. The ESA-related damage manifests itself in several forms including cracking and spalling. The specific manifestation of the ESA-related damage depends on which one of the following three chemical processes are predominant:

a. Ettringite formation

The type of cement significantly affects all types of sulphate attack on concrete. Among the hydration products, calcium hydroxide and alumina-bearing phases are more vulnerable to attack by sulphate ions. On hydration, Portland cements with more than 5% tricalcium aluminate (C_3A) will contain most of the above alumina in the form of Monosolphate hydrate, ($C_3A.CS.H_{12\text{–}18}$) [102]. In the presence of calcium hydroxide, when the cement paste comes into contact with sulphate ions, both of the alumina-containing hydrates are converted to ettringite, as shown in $C_3A.CH.H_{18}$ or $C3A.CH.H_{12}$ below equations:



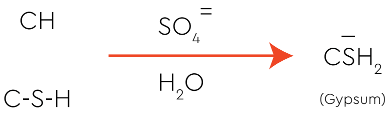
$$\begin{matrix} C_3A.C\bar{S}.H_{12\text{-}18} \\ C\text{-}A\text{-}H \end{matrix} \xrightarrow[H_2O]{C\bar{S}H_2} C_3A.C\bar{S}.H_{32}$$

(Ettringite)

This process is mainly responsible for cracking and spalling as a result of expansion produced by ettringite formation. This process may occur with all the sulphate salts including calcium sulphate, which acts directly on C-A-H and/or Monosolphate hydrate.

b. Gypsum Formation

An increase in the C_3S content of cement, generates a significantly higher quantity of calcium hydroxide. The produced calcium hydroxide may directly combine with the sulphate ions leading to the formation of gypsum. Gypsum formation from decalcification of CSH only occurs in case of magnesium sulphate attack.



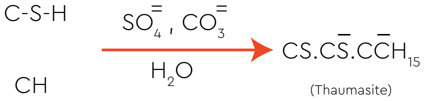
$$\begin{matrix}CH\\ C\text{-}S\text{-}H\end{matrix}\ \xrightarrow[H_2O]{SO_4^{=}}\ \underset{\text{(Gypsum)}}{C\bar{S}H_2}$$

This process may cause expansion, spalling and softening of hydrated cement paste. However, in the long term, another important feature is the loss of strength due to the loss of adhesion of the cement paste due to decalcification of C-S-H which is responsible for the binding capacity of the cement paste [103].

c. Thaumasite form of sulphate attack (TSA)

Thaumasite drew the attention of the concrete industry because it involves a unique form of sulphate attack, in which the formation of thaumasite alters the primary binder and causes concrete to progressively lose paste-aggregate bond, strength, coherence and eventually serviceability. Reactions involved in TSA are not limited by the amount of aluminate in cement (as is delayed ettringite formation, DEF) nor suppressed by the consumption or absence of portlandite. TSA can develop progressively and aggressively once it occurs, and the affected concrete may become "mushy" or even fluid as described in the technical literature [104]. Thus, there are sufficient reasons to call thaumasite the "true concrete cancer."[105]

In general, TSA is rare and only occurs at low temperatures (≤15 °C) with the availability of calcium silicate, sulphate and carbonate ions, and an abundance of moisture [106]. Incidental occurrence of thaumasite in fissures and voids of cementitious systems does not necessarily imply deterioration of the matrix; however, excessive formation of thaumasite within the microstructure of cementitious systems is an indication for TSA. Sulphate attack on C-S-H and CH in the presence of carbonate ions to form thaumasite:



$$\begin{matrix}C\text{-}S\text{-}H\\ CH\end{matrix}\ \xrightarrow[H_2O]{SO_4^{=},\ CO_3^{=}}\ \underset{\text{(Thaumasite)}}{CS.C\bar{S}.C\bar{C}H_{15}}$$

The thaumasite formation is accompanied by the most severe loss of strength and adhesion, which can transform hardened concrete into a pulpy mass, since a significant part of C-S-H can be destroyed according to reaction. This process may occur with every type of sulphate salts and is favoured by humid atmospheres and low temperature

d. Mechanism of Magnesium Sulphate attack

Magnesium sulphate attack starts by reacting with portlandite leading to the formation of magnesium hydroxide. However, unlike NaOH, the magnesium hydroxide ($Mg(OH)_2$) produced is insoluble and its saturated solution has a pH value of 10.5 (compared to a pH of 12.4 and 13.5 for CH and NaOH, respectively). Such a low pH destabilizes both ettringite and C–S–H [107].

Sulphate attack on C-S-H attack by magnesium sulphate ($MgSO_4$) is given by the below equation:

$$\begin{matrix}CH\\ C\text{-}S\text{-}H\end{matrix}\ \xrightarrow[H_2O]{MgSO_4}\ \underset{\text{(Gypsum)}}{C\bar{S}H_2}+\underset{\text{(Brucite)}}{Mg(OH)_2}+\underset{\text{(silica gel)}}{SiO_2.xH_2O}$$

The damaging attribute of $MgSO_4$ stems from the fact that reactions go on to completion thereby converting the C–S–H phase to M–S–H with no binding properties [108]. Even in this type of attack, without ettringite formation, there is a loss of strength and adhesion of the cement paste due to decalcification of C-S-H. This attack is, therefore, characterized by softening and deterioration of the surficial layers of the hardened cement paste and the profuse formation of gypsum and brucite, as elaborated in the above equation.

4.8.1.2

INTERNAL SULPHATE ATTACK (ISA)

ISA occurs in a sulphate free environment by the late sulphate ions released from either cement or gypsum-contaminated aggregates. Of these two internal sulphate sources, the latter is relatively rare because it can be prevented by controlling the sulphate content of the aggregates. One of the most famous forms of ISA is Delayed Ettringite Formation (DEF).

Delayed Ettringite formation (DEF)

Delayed ettringite formation (DEF) refers to the development of ettringite within the cement paste system of concrete after the concrete has hardened. In many ways, DEF is similar to other forms of sulphate attack; however, for DEF, the source of sulphate is internal, not external, and not the result of using a blend of gypsum or plaster with cement. Researchers have stated that the formation of DEF is related to many factors, including the environment, the cement, the aggregate type, and the curing conditions. DEF can be defined as the formation of ettringite (AFt) several months or years after the setting of cement, without the need for new external sulphates [109]. DEF is a consequence of significant heating of the concrete (>65 °C) after its casting, either due to a thermal treatment (e.g. steam curing in the precast industry) or to the exothermic reaction of the cement (e.g. mass concrete).

Consequences of DEF

DEF results in swelling and cracking of the concrete, which can happen after several years of humid conservation. It is believed that, since AFt is not a stable phase at high temperature, the initial heating of the concrete leads to the decomposition of primary ettringite. Some of the sulphate ions would then remain in the pore solution, while others would be adsorbed by C-S-H [110], which is a reversible process. Later with moist storage, their subsequent desorption would favour the reformation of ettringite in the hardened material, causing expansion and cracking in the concrete during its service life [111, 112].

4.8.2

INFLUENCE OF BLENDED CEMENT OR SCM ON SULPHATE ATTACK

During the pozzolanic reaction, portlandite is converted to additional C-S-H phases. Since portlandite is important for the formation of gypsum, the amount of gypsum that can be formed is decreased by the addition of pozzolanic materials [113, 114]. The content of clinker minerals whose reaction products are vulnerable to sulphate attack (e. g. aluminate and ferrite) is lowered by the addition of mineral admixtures due to dilution. Some very fine mineral admixtures serve as a surface on which additional C-S-H phases can grow. This leads to a higher relative degree of hydration of the clinker phases and therefore the impermeability of the hardened cement paste can be increased [115]. The aforementioned statements refer to exposure to sodium sulphate. If the concrete is exposed to magnesium sulphate, the addition of pozzolanic material can have a detrimental effect on sulphate resistance, as reported by accelerated studies on small scale specimens (in real scenarios, the large size of concrete members, and the impermeability effects may dominate). Magnesium sulphate reacts with portlandite to form gypsum and brucite (magnesium hydroxide). In the absence of portlandite, the C-S-H phases are attacked. This can lead to a disintegration of the hardened cement paste [108]. The higher reactivity, SiO_2-content, and added amount of the pozzolanic material and the lower the alite content in the cement, the more portlandite can be converted into C-S-H phases.

Latently hydraulic materials with a high CaO content such as blast furnace slag have a lower ability to reduce the portlandite content than pozzolanic materials with low CaO content such as coal fly ash and silica fume. A pre-hydration period of at least 4–6 weeks is recommended before exposure to sulphate attack if fly ash is used. During this period, a substantial degree of hydration of the fly ash can be gained. Also, the hydration of pozzolanic and latently hydraulic materials proceeds slower than the hydration of Portland cement. Due to the low rate of reaction, micro-cracks and large capillary pores can be sealed by the reaction product formed in the late stage.

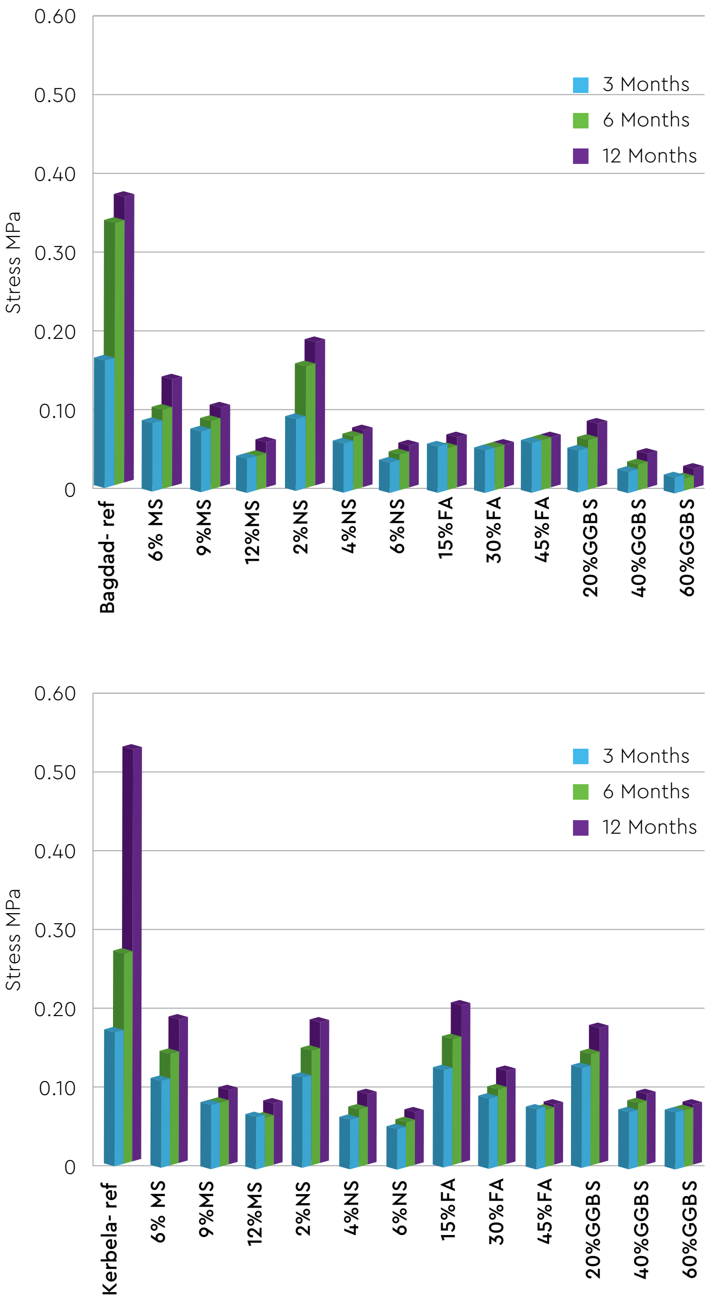
Omar S. Baghabra Al-Amoudi et al. [108] concluded from his study conducted to assess sulphate attack on plain and blended cements exposed to aggressive environments that Blended cements, particularly those prepared with silica fume (SF) and blast furnace slag (BFS), were observed to be highly resistant to Na_2SO_4 attack due to an interplay of various factors; the most important being the reduction in the portlandite (CH) produced by cement hydration and the densification of the microstructure of the hardened cement paste matrix. These factors mitigate the production of expansive ettringite.

Atahan et al. [116] investigated the effect of mineral admixtures such as nano silica, micro silica, fly ash and ground granulated blast furnace slag on the expansion of mortar bars caused by internal and external sulphate attack. It was observed from the study that compared to the reference samples without mineral admixture, irrespective of the mineral admixture type used, the expansion values for the mortar samples made with both sands were lowered by using mineral admixtures. Among the mineral additives considered, it can be concluded that GGBS replacement was the most effective one in limiting the expansions caused by internal sulphate attack. However, it should be pointed out that the selected replacement ratios for GGBS were quite high. A blend of Portland cement and GGBS contains more silica and less lime compared to Portland cement alone. As a consequence, because of higher replacement ratios, as well as the low calcium hydroxide content of the GGBS mortar, the resistance of sulphate attack is improved significantly. In below figure 4.15, the value of expansion obtained at 3, 6 and 12 months for mortar bars made with different compositions of cementitious materials with different sands are compared.

It can be observed that the formation of ettringite and gypsum at high sulphate concentrations can be avoided by the application of sulphate resisting Portland cement in combination with a mineral admixture having pozzolanic properties (e.g. fly ash or blast furnace slag). The low content of C_3A in the cement limits the amount of ettringite that can be formed during sulphate attacks. The pozzolanic reaction of the mineral admixture lowers the amount of portlandite in the microstructure and makes the hardened cement paste less vulnerable to the formation of gypsum. In agreement with this idea, mixtures containing sulphate resisting Portland cement and pozzolanic material showed the best performance under field conditions. In addition to the good chemical resistance, there is also good physical resistance against sulphate attack due to the late reaction of the pozzolanic or latently hydraulic admixtures.

Indian provisions on the prevention of sulphate attack

Figure 4.15 Expansion after 3, 6 and 12 months of mortars produced with: (a) Baghdad-sand, (b) Kerbela-sand



Sulphates from external sources:
IS 456 gives recommendations for the type of cement to be used, maximum free water/cement ratio and minimum cement content required at different sulphate concentrations in near-neutral groundwater having a pH of 6 to 9. Table 4.9 shows conditions as well as requirements to safeguard concrete against sulphate attack. In case of very high sulphate concentrations i.e. Class 5 conditions, use of lining such as polyethylene or polychloroprene sheet; or surface coating based on asphalt, chlorinated rubber, epoxy; or polyurethane materials have been recommended so as used to prevent access by the sulphate solution.

Table 4.9: IS 456 gives recommendations for Sulphate attack

Class	Concentration of Sulphates, Expressed as SO_3			Type of Cement	Dense, Fully Compacted Concrete (MSA 20 mm)	
	In Soil		In Ground Water (g/l)		Minimum Cement Content kg/m^3	Maximum Free Water-Cement Ratio
	Total SO_3 (%)	SO3 in 2:1 Water: Soil Extract (g/l)				
1	Traces(<0.2)	Less than 1.0	Less than 0.3	OPC or PSC or PPC	280	0.55
2	0.2 to 0.5	1.0 to 1.9	0.3 to 1.2	OPC or PPC or PSC Supersulphated cement or sulphate resisting cement	330 310	0.50 0.50
3	0.5 to 1.0	1.9 to 3.1	1.2 to 2.5	Supersulphated cement or sulphate resisting cement PPC or PSC	330 350	0.50 0.45
4	1.0 to 2.0	3.1 to 5.0	2.5 to 5.0	Supersulphated cement or sulphate resisting cement	370	0.45
5	More than 2.0	More than 5.0	More than 5.0	-DO-+ Protective coating	400	0.40

It should be noted that Portland slag cement with a slag content of more than 50 percent has been recommended by IS 456 as it exhibits better sulphate resisting properties. However, where chloride is encountered along with sulphates in soil or groundwater, ordinary Portland cement with C_3A content from 5 to 8 percent shall be desirable to be used in concrete, instead of sulphate resisting cement. Alternatively, Portland slag cement having more than 50 percent slag or a blend of ordinary Portland cement and slag may be used.

Sulphates in concrete

Sulphates are present in most of the cements and in some aggregates; excessive amounts of water-soluble sulphate from these or other mix constituents can cause expansion and disruption of concrete. To prevent this, the total water-soluble sulphate content of the concrete mix, expressed as SO_3 (where $SO_3 = 0.833\ SO_4$), should not exceed 4 percent by mass of the cement in the mix. The sulphate content should be calculated as the total from the various constituents of the mix.

4.8.3

CONCLUSION

When pozzolans are added to cement, they react with the calcium hydroxide, in the presence of moisture, to produce secondary calcium silicate hydrate (C–S–H). This pozzolanic reaction has the following beneficial impacts on sulphate attack:

(i) The consumption of portlandite reduces the formation of gypsum;

(ii) The replacement of part of the cement by a pozzolanic material entails a reduction in the C_3A content (i.e., dilution effect), hence, all the aluminate-bearing phases will accordingly be reduced;

(iii) The formation of secondary C–S–H also results in the densification of the hardened cement paste since it is deposited in the pores thereby making blended cements impermeable and, therefore, the sulphate ions cannot easily penetrate through the concrete matrix, as in the case of plain Portland cements.

4.9

REINFORCEMENT CORROSION

In general, corrosion can be defined as the process of any reaction of metal with its environment. This process is not always detrimental, for example, products of corrosion form passive layers in metals like aluminum, titanium, etc. which prevents further corrosion, while in case of iron/steel corrosion damages the reinforcement and reduces the operative area of rebar [17]. When the rebar/steel rod gets corroded, the product of corrosion Fe_2O_3 (rust) has more volume than the existing volume of steel as shown in figure 4.16. This reduces the operative area of the rebar [117].

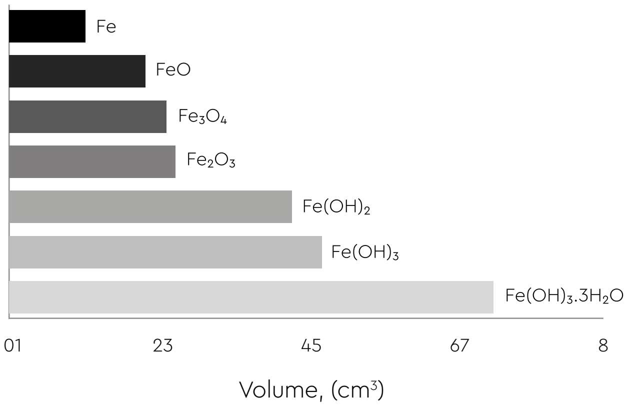


Figure 4.16: The relative volumes of iron and its reactive product[118]

Concrete acts as the environment for reinforcement in concrete structures. Concrete provide an alkaline medium (pH of 12–13) to reinforcement owing to the presence of calcium, sodium and potassium alkalis and hydroxide ($Ca(OH)_2$). A protective layer forms on the surface of the rebar and prevents Fe atoms from dissolving into the electrolyte. The protective layer is a film of the gamma ferrous oxides (γ-Fe_2O_3), iron oxide hydroxide [FeO(OH)] and magnetite (Fe_3O_4) which act as a barrier for Fe_2+ from entering into the solution as well as oxygen from diffusing to the steel surface [119]. The corrosion on reinforcement always initiates after the breakdown of this protective layer. This layer is broken by aggressive substances reaching the rebar level. These mostly ingress through the concrete cover from the external environment or sometimes from concrete ingredients such as water. These aggressive substances initiate the corrosion either by changing the alkaline nature of concrete or directly attacking the passive layer of reinforcement. Based on the attack of these substances on a passive layer, the corrosion-induced process is divided into two types [120]

- **Carbonation induced corrosion**
- **Chloride induced corrosion**

Due to a formation of a higher volume of rust than the material dissolving, corrosion causes tensile stress in concrete, which is undesirable. Corrosion also affects the load-bearing capacity of member and drastically decrease its strength and becomes a cause for the reduction in the lifespan of the structure. So, corrosion is the major governing factor that affects the service life of concrete structures [117]. Its rate of induction has become a widely researched subject. The rate of corrosion depends upon different factors such as type of binder, mix proportions of concrete, exposure condition, etc. Sometimes, it is not possible to avoid the exposure conditions and change the quantity of mix proportion of concrete to achieve specific requirements such as strength, workability, etc. In that scenario, the type of cement can be changed, or the water to cement ratio can be modified. These binders act as corrosion resistant without altering the mechanical properties of concrete [121].

Corrosion is an electrochemical process that signifies a physio-chemical phenomenon. Corrosion on reinforcement depends on the chemical and physical characteristics of concrete. For anticorrosive behavior, concrete should be alkaline and less permeable for aggressive agents. Concrete incorporating SCM from industrial wastes like fly ash, slag and silica fume are found to be more durable in an aggressive environment. The enhanced durability of concrete results from denser micro-structure strengthened aggregate-matrix interface, reduced micro-cracking and increased water-tightness [122].

4.9.1

CHLORIDE INDUCED CORROSION

Chloride is one of the most aggressive anions, which initiates corrosion by breaking the passive layer of reinforcement. Mostly chloride ions reach the rebar level, either through the concrete ingredients or from the external environment. The external source of chloride ions is found in coastal zones and deicing salts used in cold weather. The offshore structures are exposed to seawater and bridges, which are in the snowfall region, salt is sprinkled over the bridge for de-icing purposes.

4.9.1.1

CLASSIFICATION OF CHLORIDE ION IN CONCRETE

The chloride ion in the concrete is present in the different forms as follows

(a) Adsorbed chloride
It is adsorbed on the surface of the hydration product (C-S-H) of the binder [122].

(b) Bound chloride
It is the sum of chemically bound chloride with hydration products of the cement, such as the C_3A (tricalcium aluminate) or C_4AF (tetra calcium aluminoferrite) phases, and loosely bound chloride with C–S–H gel [124].

(c) Free or water-soluble chloride
It is the concentration of free chloride ions (Cl) within the pore solution of concrete, and is extractable in water under defined conditions.

Among these forms of chloride ions, 'free chloride' is responsible for inducing corrosion on the reinforcement. When the chloride ions concentration is increased, then the resistivity of concrete decreases and corrosion rate over reinforcement increases. However, any change in chloride ions in concrete does not alter the pH of the concrete medium [129].

4.9.1.2

CHLORIDE THRESHOLD VALUE (CTL)

The chloride threshold value can be defined as the content of chloride at the steel depth that is necessary to sustain local passive film breakdown and hence initiate the corrosion process. It is usually presented as the ratio of chloride to hydroxyl ions, the free chloride content ([Cl-]/[OH-]), or the percentage of the total chloride content relative to the weight of cement. So, CTL is an important parameter to predict the service life of concrete structure which is subjected to chloride-induced corrosion. However, the measured value of CTL possesses a large range due to adopting a different method of measurements and its value also depends upon several factors such as the condition of the steel-concrete interface, concrete mix proportion, type of binder, and environmental condition. Despite the importance of the CTL, conservative values such as 0.2% or 0.4% by weight of cement have been used in predicting the corrosion-free life, because of the uncertainty regarding the actual limits in various environments for chloride-induced corrosion [124, 125].

4.9.1.3

MECHANISM OF CHLORIDE INDUCED CORROSION

The steel reinforcement in concrete is protected from corrosion by a passive film formed due to the high alkalinity of concrete on the steel surface. This passive film is decomposed due to the attack of chloride ions (Cl-) or carbon dioxide (CO_2). Corrosion initiates when ferrous ions (Fe_2+) from rebars (acting as an anode) are dissolved in the electrolyte (concrete pore solution) and e- are free to move. These electrons drift from steel to another portion of the same or different rebar (acting as a cathode), where, together with the available water and oxygen, they form hydroxide (OH-) ions.

Anodic reaction $Fe \rightarrow Fe^{2+}+2^{e-}$
Cathodic reaction $4e^{-}+2H_2O+O_2 \rightarrow 4OH^{-}$

OH – travel through electrolyte and combine with ferrous ions to form ferric hydroxide which gets converted to rust by further oxidation.

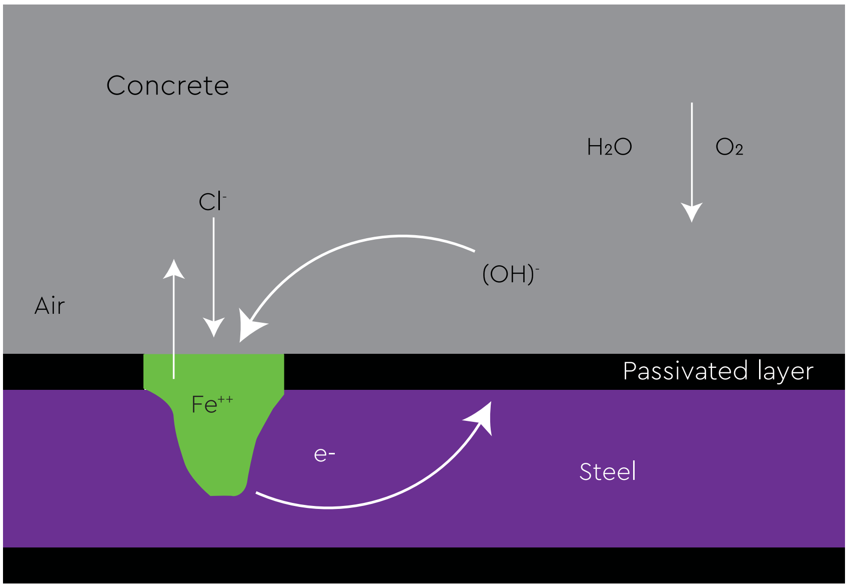
$Fe^{2+}+2OH^{-} \rightarrow Fe(OH)_2$ (Ferrous hydroxide)
$Fe(OH)_2+2H_2O+O_2 \rightarrow Fe(OH)_3$ (Ferric hydroxide)

Chloride ions activate the surface of the steel to form an anode, the passivated surface being the cathode. The reactions involved are as follows:

$Fe^{2+}+2Cl^{-}\rightarrow Fe(Cl)_2$ (Ferrous chloride)
$Fe(Cl)_2+2H_2O\rightarrow 4Fe(OH)_2+2HCl$

The chloride induced corrosion is highly localized at a small anode, pitting of the steel takes place [126]. Figure 4.17 shows the electro-chemical corrosion in the presence of chloride ions.

Figure 4.17: Schematic representation of electro-chemical corrosion in the presence of chloride ions [126]



4.9.1.4

BEHAVIOR OF BLENDED CEMENT AGAINST CHLORIDE INDUCED CORROSION

The time taken by chloride ions to reach the threshold value at the rebar level is called the initiation period. After corrosion initiation, the corrosion rate increases with time, and at a certain period corrosion level reach to an extent, that leads to the collapse of the structure, that period is called the propagation period. The service life of a concrete structure is the summation of the initiation period and propagation period [124]. The effect of blended cement on chloride ingress, CTL, and the corrosion rate is discussed in the following sections.

a) Effect of blended cement on chloride ion penetration

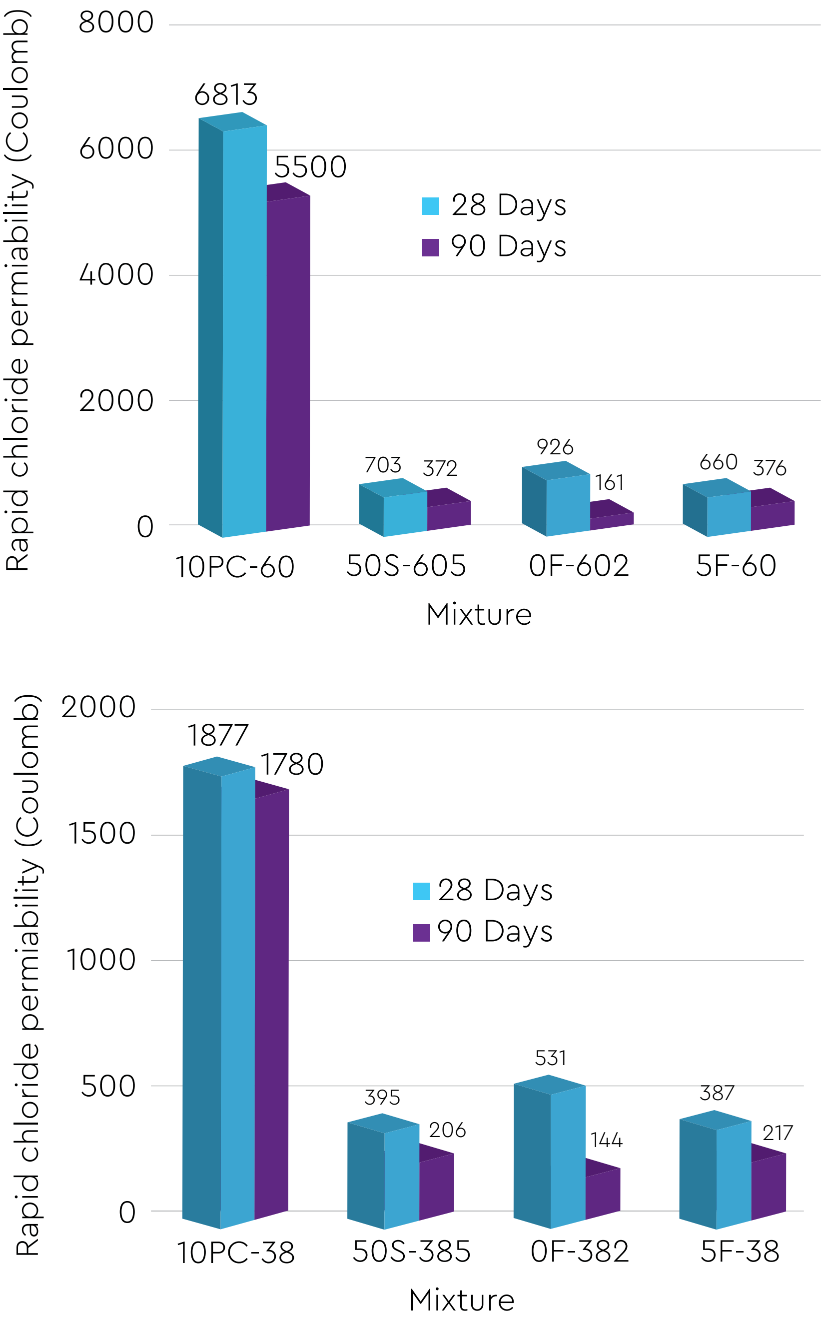
The penetrability of chloride ions can be evaluated by different tests such as Rapid Chloride Permeability Test (RCPT), NT Build 492, chloride diffusion coefficient, etc. The resistance of chloride ions depends on the w/c ratio, type of cement, age of concrete, concrete pore structures, curing, etc. Concrete made with PPC, PSC and CC show higher resistance than concrete made with OPC. The concrete made with blended cement at a lower water cement ratio possesses lower permeability and denser structure due to pozzolanic activity.

The RCPT results of concrete made with OPC and blended cement are shown in figure 4.18 [127]. RCPT value of concrete made with blended cement is compared with OPC concrete. The following conclusions are remarked.

- The effect of water/cement ratio was found to be prominent in OPC concrete as compared to concrete made with SCM.
- For w/c ratio 0.6 and 0.38, the RCPT value for concrete made with SCM decreased more than 85% and 60% respectively as compared to concrete made with OPC.

However, RCPT test results signify the effect of the chloride ion penetrability and the same cannot be used as an indicator for the rate of corrosion.

Figure 4.18: RCPT test results of concrete with water cement ratio of 0.6 and 0.38 [127]



The other test results like chloride diffusion, NT build 492, etc. also represent the higher resistance against chloride ions by PPC, PSC and CC as compared to OPC. Arora et al. [157] found the higher chloride diffusion coefficient OPC as compared to PPC and PSC. The concrete made with PSC possesses the lowest value of chloride diffusion coefficient in comparison to concrete made with OPC and PPC. The chloride diffusion coefficient of concrete made with SCM is found lower due to the higher fineness of SCM attributed to the lower permeability of concrete made with SCM. The pozzolanic reaction helps to lower the number of capillary pores and clogging the pores. The ITZ is improved by pozzolanic reaction, which reduced the penetration of chloride ions. GGBS and fly ash have high fineness, which may have contributed to obtaining lower chloride ion permeability. Pozzolanic material binds the hydroxyl ion in pore solution. The chloride ion penetration gets lowered by alkali binding in pore solution [128,129].

NCB has studied extensively, the application of blended cement against chloride ion ingress and chloride induced corrosion. The results are shown in Table 4.10.

Table 4.10: Results chloride ion ingress test on concrete made with different type of cement [130, 147]

Sl. No.	Cement	w/c	RCPT (Coulombs)	NT-Build 492 (mm^2/ year)	Non-steady state chloride diffusion in immersion (mm^2/ year)
1.	OPC	0.36-0.6	1500-5000	300-800	210–350
2.	PPC (30% fly ash)	0.36-0.6	500-1500	300-500	100–200
3.	PSC (45% slag)	0.36-0.6	<500	<200	20–70
4.	CC (15-35% fly ash +25-50% slag)	0.6	400-700	N.A.	N.A.

Note: N.A. – Not Available

RCPT test, NT-Build 492, chloride diffusion coefficient (as per ISO 1920 part 11) represents higher resistance of Concrete made with PPC, PSC and CC as compared to concrete made with OPC against chloride ingress. Water-cement ratio has a considerable effect on the long-term durability test and accelerated /short term test methods. The chloride diffusion coefficients values were obtained either from the chloride immersion test (Cd) or from NT build 492 (Cd (NT)) shows an increasing trend with an increase in w/c ratio. Dependency of chloride diffusion coefficient values on w/c are much less in case of PSC concrete as compared to OPC concrete. Non-steady state migration test RCPT shows a good trend with chloride diffusion coefficient generated from immersion test when plotted universally whereas fair correlation was found between chloride diffusion coefficient obtained from Chloride immersion test (Cd) and NT build 492 (Cd (NT)) [130, 147].

b) Effect of blended cement on chloride threshold value

The pH of concrete's pore solution made with SCM decreases due to pozzolanic activity and consumption of portlandite. The reduction of pH will result in a reduction in the concentration of OH- in pore solution. This will result in a lower threshold value of chloride ion as shown in table 4.11. A certain chloride concentration, which does not cause corrosion in Portland cement concrete, can thus suffice to initiate corrosion in a concrete with mineral additives of residual material [131]. Several investigators have identified the [Cl-]/[OH-] ratio as an important indicator to determine the initiation period of service life of the concrete structure. The use of SCMs in concrete, do not always increase the ratio of [Cl-]/[OH-] as some of the Cl– can be bound by hydration products. The binding capacity of C-S-H depend upon the ratio of Ca/Si, amount and type of SCMs [123]. SCMs such as fly ash and slag having alumina content produce calcium aluminate hydrates (C-A-H) by the pozzolanic reaction which binds the chloride ions [132]. Chlorides react with compounds of binder to give new hydrates product such as calcium chloroaluminates (e.g. Friedel salts – $CA_3.CaCl_2.10H_2O$).

Table 4.11 Chloride threshold value (%, by wt. of Binder) [133]

S. No.	Cement	Chloride threshold value		
		Total chloride (%, by wt. of Binder)	Free chloride (%, by wt. of Binder)	$[Cl^-]/[OH^-]$
1	OPC	0.78	0.11	0.26
2	70% OPC+ 30% Fly ash (PPC)	0.68	0.07	0.21
3	70% OPC +30% Slag (PSC)	0.97	0.13	0.23

Alumina containing SCMs such as fly ash, GGBS generally lead to an increase in chloride binding, due to the formation of more Friedel's salt [134]. In one hand, the use of SCMs decreases the chloride threshold value to break the passive layer and initiate corrosion. On the other hand, the chloride binding capacity is increased by fly ash and GGBS which counters the effect of lower chloride threshold value and increases the initiation time of corrosion. This will lead to a longer service life of the concrete structure [135].

c) Effect of blended cement on rate of chloride induced corrosion

After the destruction of passive layer, corrosion on reinforcement is initiated. The remaining service life of a corroding concrete structure depends upon the rate of corrosion. The corrosion rate is function of many variables such as cover thickness, quality of surrounding concrete (which depend upon type of cement, water-binder ratio, mix proportions etc.), exposure condition, type of induced corrosion etc. The corrosion is monitored by many techniques such as electrical resistivity, half-cell potential, linear polarization resistance, EIS etc. The concrete made with blended cement shows a higher resistance against the flow of ions due to its impermeable nature and binding effect of chemical compound.

The rate of chloride induced corrosion in concrete made with PPC and PSC shows significantly lowered as compared to OPC concrete. The concrete made with PSC possesses the lowest corrosion rate and its 8–20 times lower than OPC as shown in table 4.12. This may be due to higher resistance against the flow of ions due to the consumption of alkali content in pore solution, and high resistivity of these concretes which limits severely the corrosion by lowering the rate of corrosion [121, 136, 141, 147]. The resistivity of concrete made with OPC generally varies in the range of 5–20 kohm-cm, in case of concrete made with PPC varies in the range of

40–80 kohm-cm whereas in case of concrete made with PSC varies in the range of 40–60 kohm-cm [147].

Table 4.12: Corrosion rate and other related parameter for different cement concrete[141]

Type of cement	Grade	pH	Corrosion rate (mils per year)	
			Normal water immer-sion	Sea water immer-sion
OPC 1	M15	12.50	1.0	1.4
	M30	12.37	1.5	1.9
	M45	12.00	1.4	1.3
PPC1 (20% fly ash)	M15	12.06	0.8	0.8
	M30	11.90	0.7	0.9
	M45	12.10	0.7	0.9
OPC 3	M15	12.20	1.9	2.4
	M30	12.23	1.5	1.9
	M45	12.20	0.3	1.9
BFSC3 (50% slag)	M15	12.00	0.09	0.5
	M30	12.09	0.07	0.4
	M45	12.10	0.08	0.3

4.9.1.5

CONCLUSION

The service life of the concrete structure is the summation of initiation period and propagation period. The initiation period is the function of chloride ion permeability and chloride threshold value. Concrete made with SCM have very-very low chloride ion permeability or diffusivity as compared to OPC concrete, although it has low chloride threshold value. The initiation period of concrete made with SCM will be higher in comparison to OPC concrete [147]. The propagation period of concrete structures made with SCM significantly increases due to lower corrosion rate in comparison to concrete made with OPC. The overall service life of concrete made with SCM will be higher than concrete made with OPC against chloride ion attack.

4.9.2

CARBONATION INDUCED CORROSION

Carbonation induced corrosion is one of the major issues associated with reinforcement corrosion of RCC structures located in non-coastal areas. This phenomenon leads to premature failure of reinforced concrete structures before their intended service life [140].

4.9.2.1

MECHANISM

Carbonation is a physiochemical phenomenon that results in physical and chemical change in concrete properties. Carbonation of concrete is the chemical reaction between atmospheric carbon dioxide and the products of cement hydration particularly $Ca(OH)_2$ with the reaction :

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Carbon dioxide molecules that ingress into the concrete react with calcium hydroxide, with C-S-H gel, and with the alkali and calcium ions in the pore solution. The consequence of these reactions is drastic and could be analyzed by determining the pH of the system [137].

$$CSH + 3CO_2 \rightarrow 3CaCO_3\ 2SiO_2\ 3H_2O$$

4.9.2.2

FACTOR INFLUENCING CARBONATION

CO_2 ingress is controlled by the partial pressure of CO_2 in the surrounding environment and by the pore geometry of the concrete. In industrial environment, the partial pressure level of CO_2 is usually higher in comparison to the normal environment. The pore structure of the concrete is influenced by:

- Chemical composition of the cement used;
- w/c ratio;
- cohesiveness /richness of the mix;
- Effectiveness of the compaction;
- Curing methods employed;
- Duration of curing and
- Presence of mineral admixtures e.g. silica fume, GGBS, fly-ash etc.

The rate of CO_2 diffusion is also sensitive to the moisture content of the concrete. In saturated concrete, the ingress of CO_2 can take place only by the diffusion of

CO_2 that has been dissolved in the pore solution. As is common with that most gases, the solubility of CO_2 in aqueous solution is small, comparatively little CO_2 can diffuse through water-saturated concrete. In practice, the rate of diffusion of CO_2 into air-dry concrete can be more than an order of magnitude greater than the same concrete when saturated. In other words, the highest rates of carbonation occur when the relative humidity is maintained between 50 and 75%. Below 35% relative humidity, the degree of carbonation that takes place is considered insignificant. Above 75% relative humidity; moisture in the pores restricts CO_2 penetration [130, 137, 140].

4.9.2.3

EFFECT OF BLENDED CEMENT ON CARBONATION

It has been observed in many studies that the concrete made with SCM as partial replacement of OPC reduces the resistance of concrete against the carbonation in comparison to OPC concrete. This reduction in carbonation resistance of concrete made with SCM is due to following reasons:

- The lesser amount of the carbonate phases (i.e., $Ca(OH)_2$) present in concrete made using cement with pozzolanic replacements [137].

The amount of calcium hydroxide present in cementitious materials determines the durability of concrete structures against carbonation since it maintains a high pH of 12.6. It is accepted that the calcium hydroxide content has a significant impact on the carbonation rate, since higher total calcium hydroxide ($Ca(OH)_2$) has higher CO_2 binding capacity. In blended cements, pozzolanic reactions also consume $Ca(OH)_2$. As a result, less $Ca(OH)_2$ is available and the rate of carbonation is higher than in OPC which contains higher amount of $Ca(OH)_2$. Moreover, the lower $Ca(OH)_2$ availability results in more CSH carbonation. In contrast with $Ca(OH)_2$ carbonation, CSH carbonation does not densify the pore structure. The $Ca(OH)_2$ and CSH are the most susceptible phases to carbonation. The amount of $Ca(OH)_2$ and severity of CO_2 attack on CSH has been found to greatly affect the rate of carbonation process [138,139].

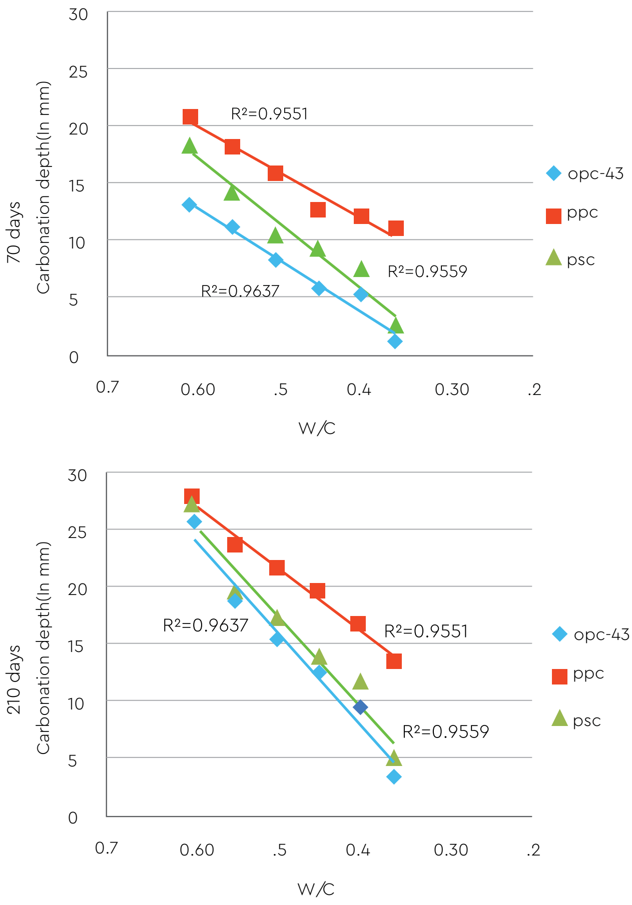
a) Carbonation depth

Carbonation depth signifies the ingress of CO_2 gas into a cementitious system and it's an important parameter to quantify the rate of carbonation. The phenolphthalein indicator method is the most adopted method to measure carbonation depth. Carbonation depth of concrete made with SCM is observed higher in comparison to OPC concrete, which signifies the lesser resistance against carbonation. The carbonation depth is found to be the function of time and it is given by the following equation [140].

$C(t) = kt^x$
$C(t)$ = depth of carbonation (in mm);
k = carbonation coefficient;
t = exposure period (in years);
x = exponent

To predict the depth of carbonation and ease of understanding, most of the researchers used 0.5 as an exponent(x) in the carbonation model. Based upon the correlation developed for quick determination of service life design, the value of carbonation depth and corresponding carbonation coefficient, K can be determined with the help of accelerated testing techniques like air permeability and electrical resistivity. However, for assessment with greater confidence, the suitable factor of safety needs to be considered [140]. The carbonation depth in concrete made with PPC and PSC was found to be approximately 2 times and 1.5 time higher than OPC concrete respectively as shown in figure 4.19. It decreases linearly with decreasing the w/c ratio for OPC, PPC and PSC concrete [130,140]. The carbonation depth in composite cement concrete was observed comparable with PPC concrete [140].

Figure 4.19: w/c vs Carbonation depth (70 days exposure period=15 years under normal exposure and 210 days exposure period = 45 years under normal exposure) [140]



b)Carbonation Induced Corrosion Rate

Carbonation is a major concern for low cementitious systems and blended cement. The carbonation depth is generally higher in the case of the blended cementitious system and reach at the rebar level in a shorter period as compared to OPC. Carbonation changes the alkaline nature of concrete due to formation of carbonic acid and leads to corrosion of reinforcement. In line to the carbonation depth, the rate of carbonation induced corrosion also depends upon type of cement. The rate of carbonation induced corrosion in blended cement concrete is also observed higher as compared to OPC concrete as shown in table 4.13.

Table 4.13: Mean icorr value as well as time needed to carbonate the four type of binder [142]

Type of cement	Time (Days) needed to Carbonate	I_{corr} ($\mu A/cm^2$)
CemA	5	0.33
CemC	3	0.47
CemC+ 15% Fly Ash	1	0.60
CemC + 70% Slag	0.9	3.16

The effect of carbonation induced corrosion rate for concrete made with composite blends is found to be higher in comparison to concrete made with 35% fly ash [130]. Corrosion rate of concrete made with PSC was also found to be higher as compared to concrete made with OPC and PPC [142–146]. However, the reason behind the higher corrosion rate was not explained in the present studies. So, a thorough investigation required that must include microstructure study to quantify the carbonation induced corrosion rate.

4.9.2.4

CONCLUSION

Concrete made with blended and composite cementitious systems shows lesser resistance against carbonation as compared to OPC. The carbonation depth of concrete made with blended cement was found higher in comparison to OPC at same exposure period. Due to this, the initiation period of concrete structures made with SCM will be reduced.

4.10

LONG-TERM DURABILITY OF CONSTRUCTION

Table 4.14: Performance of Blended cement concrete as compare to OPC concrete

		Performance of Cement			
S. No.	**Parameter**	**OPC**	**PPC**	**PSC**	**CC**
1	Heat of Hydration	High	Lesser	Lesser	Lower
2	Permeability	High	Lesser	Lesser	Lesser
3	Long term Strength	Normal	Higher	Higher	Higher
4	Shrinkage	High	Lesser	Lesser	Lesser
5	Alkali Aggregate Reaction	Less Resistance	Higher Resistance	Higher Resistance	Higher Resistance
6	Sulphate attack	Less Resistance	Higher Resistance	Significantly Higher Resistance	Higher Resistance
7.a	Chloride Induced Corrosion	Less Resistance	Higher Resistance	Higher Resistance	Higher Resistance
7.b	Carbonation Induced Corrosion **	High Resistance	Lower, but acceptable with good construction practices		

*In case of PPC, workability is enhanced when fly ash is mixed separately with OPC. But in case of intergrinding fly ash, water demand increases.

**The conclusion is drawn on the basis of carbonation depth of concrete made with and without blended cements. However, effect of CO_2 ingress on corrosion rate still requires comprehensive study in the propagation phase.

From the analysis of the results, it is observed that the performance of concrete made with the blended cement is better than concrete made with OPC cement, excluding resistance against the carbonation. However, concrete made with blended cement have longer service life in chloride aggressive environment as compared to OPC concrete.

4.11

USAGE IN PREPARATION OF HIGH STRENGTH CONCRETE

High Strength Concrete (HSC) when compared to normal strength concrete has benefits both in performance and cost efficiency. HSC has many advantages such as reduction in structural element size, reduction in amount of longitudinal reinforcement in flexural and compression members, increase in resistance to very aggressive environments and decrease in maintenance and repair costs [148].

4.11.1

CONSTITUENTS OF HIGH-STRENGTH CONCRETE

The highest percentage of concrete's volume is occupied by the aggregate and hence selection of the appropriate aggregate plays an important role while designing high-strength concrete. Use of best quality and the strongest aggregates are required so that the fracture plane should pass either through cement mortar or ITZ. Another main constitute of High strength concrete is the cementitious material used. Generally, all types of Portland cement proved to be suitable in production of concrete of compressive strength up to 60 MPa at the 28th day of age [149]. Cements with high compressive strength are suitable for production of high strength concrete. However, to achieve higher strength with respective increase in performance and workability it is necessary to design and study reactions between additional chemical and mineral admixture. The most common types used in preparation of high-strength concrete are fly ash, slag and silica fume, while less in use are ultra-fly ash, metakaolin and calcined natural pozzolans. Fly ash is the most common type of SCM and by-product of combustion of pulverized coal; it is spherically shaped and glassy residue. Fly ash improves the workability of plastic concrete, and the strength and durability of hardened concrete. Another common type of SCM used in concrete is slag; a by-product of steel plants. Slag improves the durability of the concrete. Silica fume is also very common mineral admixture used in high strength concrete. The principle of micro filling with silica fume benefited in strengthening the bond between coarse aggregate and concrete paste, with the ability to achieve compressive strength of over 105 MPa.

4.11.2

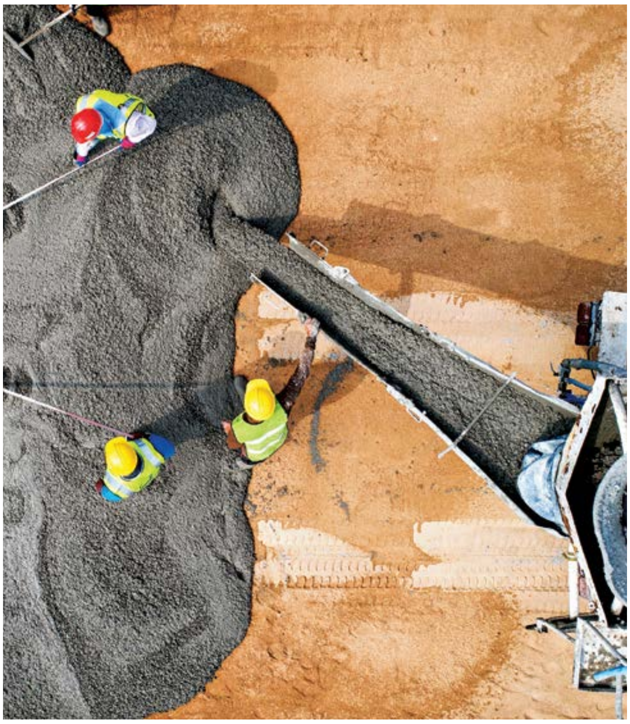
USE OF BLENDED CEMENTS SUCH AS PPC, PSC IN HSC

As mentioned, the production of high strength concrete needs addition of mineral admixture or supplementary cementitious materials, but more importantly the proportion of the mineral admixture is important when strength and overall performance of the high strength concrete is considered. Various studies in past have found that the fly ash up to 25% replacement of OPC in high strength concrete has shown positive effects while in case of silica fume only up to 10-15 % have shown positive effect. Similarly, in case of GGBS, replacement up to 40% is fruitful in enhancing the properties of the high strength concrete [150, 151]. The blends of OPC, fly ash or slag and silica fume gives the positive results in production of high strength concrete. Therefore, the dosage of fly ash and slag in PPC and PSC respectively should be tailored for the production of high strength concrete.

4.11.3

CONCLUSION

Commercially available PSC in India have 50-60 % slag content whereas commercially available PPC in India has 30-35 % fly ash content. They are used for general purpose construction for grade of concrete up to M50. For higher grade of concrete, customized PPC and PSC should be used with lower % of fly ash and slag respectively. These blended cements thereafter maybe used with the appropriate proportion of silica fume for the production of high strength concrete.



References:

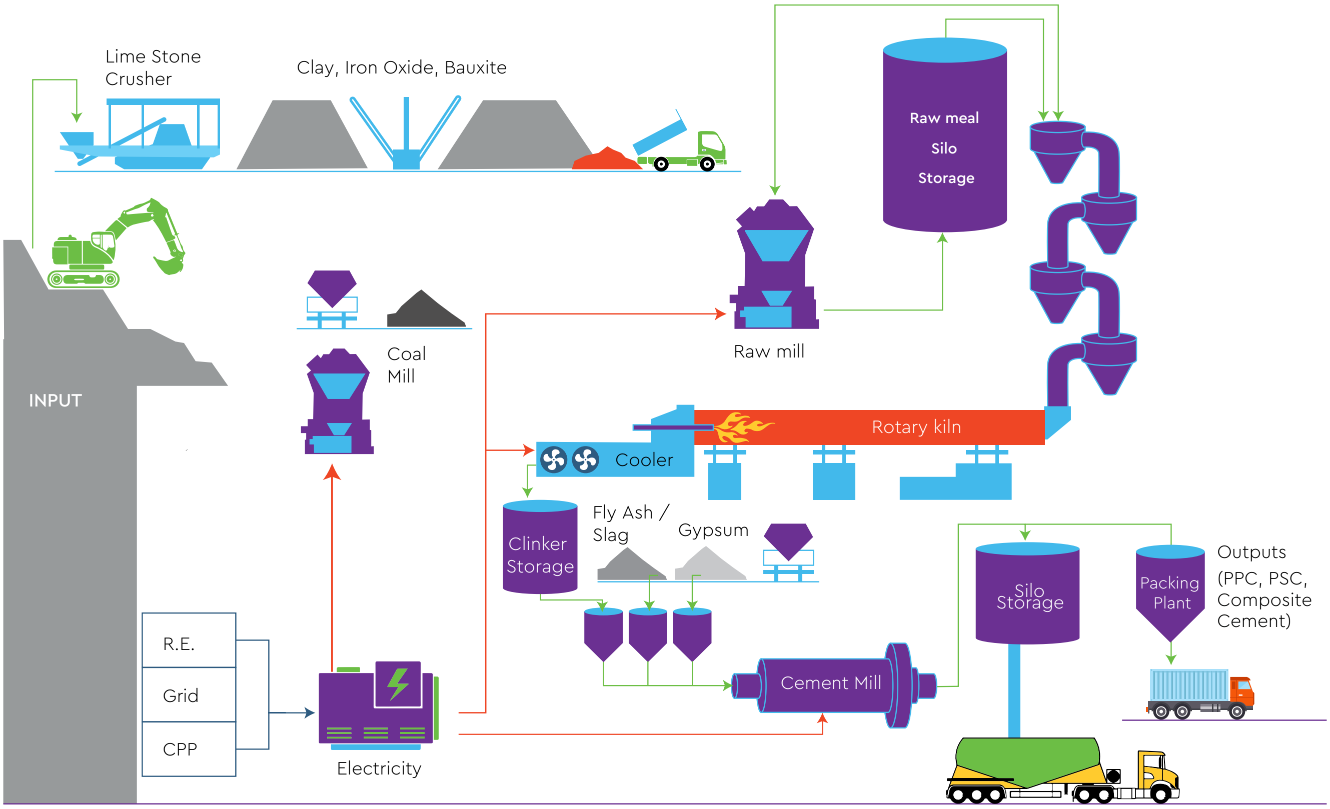
1. Li, Jinxin, "Predicting early-age thermal behavior of mass concrete for bridge foundation." Graduate Theses and Dissertations.12659 (2012).
2. B. N. Winter, "Understanding Cement: An Introduction to cement production, cement hydration and deleterious processes in concrete." Retrieved from: https://www.understanding-cement.com/hydration.html# (2012)
3. A. M. Neville & J. J. Brooks, "Concrete Technology" Second edition (2010).
4. A. Schöler, B. Lothenbach, F. Winnefeld, M. B. Haha, M. Zajac & H. M. Ludwig, "Early hydration of SCM-blended Portland cements: A pore solution and isothermal calorimetry study." Cement and Concrete Research, 93, pp. 71–82 (2016).
5. K. A. Paine, L. Zheng & R. K. Dhir, "Experimental study and modelling of heat evolution of blended cements." Advances in Cement Research 17, pp. 121–132 (2005).
6. D. Zampini, S.P. Shah, H.M. Jennings, Early age microstructure of the paste-aggregate interface and its evolution, J. Mater. Res. 13 (1998) 1888–1898.
7. Luca Bertolini, Bernhard Elsener, Pietro Pedeferri Elena Redaelli, and Rob Polder": Wiley-VCH Verlag GmbH & Co. KGaA,Boschstr. 12, 69469 Weinheim, Germany.]"corrosion of steel in concrete, Prevention, Diagnosis, Repair"
8. Mehtha, P.K. and Monteiro, P.J.M. (2006) Concrete: Microstructure, Properties, and Materials, 3rd edn, McGrawHill
9. K.L. Scrivener, A.K. Crumbie and Peter Laugesen, "The Interfacial Transition Zone (ITZ) Between Cement Paste and Aggregate in Concrete", INTERFACE SCIENCE 12, 411–421, 2004
10. B. Bourdette, E. Ringot, J.P. Ollivier, Modeling of the transition zone porosity, Cem. Concr. Res. 25 (1995) 741–751
11. K.Y. Liao, P.K. Chang, Y.N. Peng, C.C. Yang, A study on characteristics of interfacial transition zone in concrete, Cem. Concr. Res. 34 (2004) 977–989.
12. A.K. Crumbie, Characterization of the Microstructure of ConcretePhD thesis University of London, London, 1994
13. Influence of supplementary cementitious materials (SCMs) on concrete durability, M. CYR, University of Toulouse, France
14. Feldman (1983) and Uchikawa (1986) for GGBS, Feldman (1983), Nagataki and Ujike (1986) and Poon et al. (1999, 2001) for fly ash, Nagataki and Ujike (1986), Batrakov et al. (1992), Hooton (1993) and Poon et al. (1999, 2001, 2006) for silica fume, and Khatib and Wild (1996), Frias and Cabrera (2000), Poon et al. (2001, 2006), Güneyisi et al. (2008) and Badogiannis and Tsivilis (2009) for metakaolin
15. K.L. Scrivener, A.K. Crumbie and Peter Laugesen, "The Interfacial Transition Zone (ITZ) Between Cement Paste and Aggregate in Concrete", INTERFACE SCIENCE 12, 411–421, 2004
16. E.J. Garboczi, D.P. Bentz, Analytical formulas for interfacial transition zone properties, Adv. Cem. Mater. 6 (1997) 99–108.
17. Stauffer, D. (1985) Introduction to Percolation Theory, Taylor & Francis, London.
18. Powers, T.C. (1958) Structure and physical properties of hardened Portland cement paste. Journal of American Ceramic Society, 41
19. Neville, A.M. (1995) Properties of Concrete, 4th edn, Longman Group Limited,Harlow.
20. Taylor, H.F.W. (1990) Cement Chemistry, Academic Press Inc., London
21. Bensted, J. and Barnes, P. (eds) (2002) Structure and Performance of Cements, Spon Press, London
22. Diamond, S. (2007) Physical and chemical characteristics of cement composites, in Durability of Concrete and Cement Composites (eds C.L. Page and M.M. Page), Woodhead Publishing Limited, pp. 10–44.
23. Neville, A.M. (1995) Properties of Concrete,4th edn, Longman Group Limited, Harlow.
24. Schiessl, P. (ed.) (1988) Corrosion in Concrete, RILEM Technical Committee 60-CSC, Chapman and Hall, London.
25. Feldman (1983) (fly ash and GGBS), Gonen and Yazicioglu (2007) (fly ash), Cwirzen and Penttala (2005) (silica fume), Khan (2003) (silica fume), Khatib and Wild (1996) and Frias and Cabrera (2000) (metakaolin
26. M. CYR, University of Toulous, Influence of supplementary cementitious materials (SCMs) on concrete durability
27. Khatib J M and Wild S (1996), Pore size distribution of metakaolin paste, Cement and Concrete Research, 26, 1545–1553
28. Carles-Gibergues A (1981), Les ajouts dans les microbétons. Influence sur l'auréole de transition et sur les propriétés mécaniques, Ph.D. thesis, Université Paul Sabatier, Toulouse
29. Hooton, 1993, for silica fume, Poon et al., 1999, for silica fume and fly ash
30. D. Breton, J.P. Ollivier, G. Ballivy, Interfaces in cementitious composites, in: J.C. Maso(Ed.) CRC Press 1992, pp. 279–288.
31. P. Xie, J.J. Beaudoin, Modification of transition zone microstructure—silica fume coating of aggregate surfaces, Cem. Concr. Res. 22 (1992) 597–604.
32. R. Akcaoglu, M. Tokyay, T. Celik, Assessing the ITZ microcracking via scanning electron microscope and its effect on the failure behavior of concrete, Cem. Concr. Res. 35 (2005) 358–363.
33. S. Erdem, A.R. Dawson, N.H. Thom, Influence of the micro- and nanoscale local mechanical properties of the interfacial transition zone on impact behavior of concrete made with different aggregates, Cem. Concr. Res. 42 (2012) 447–458
34. Parth K Thaker and Narender K Arora, "Measuring Behavior of Fresh Cement Paste",71st RILEM Annual Week & ICACMS 2017, Chennai, India, 3rd – 8th September 2017
35. K. H. Khayat, A. Yahia, and M. Sayed, "Effect of Supplementary Cementitious Materials on Rheological Properties, Bleeding, and Strength of Structural Grout", ACI Materials Journal 105(6):585–593, November 2008.
36. American Concrete Institute (ACI) Standard 116R-90 (ACI 1990b)
37. Performance of blended cement concretes prepared with constant workability, Omar S. Baghabra Al-Amoudi, Mohammed Maslehuddin, M. Ibrahim, M. Shameem, M.H. Al-Mehthel, Cement & Concrete Composites 33 (2011) 90–102.
38. Comparison of intergrinding and separate grinding for the production of natural pozzolan and GBFS-incorporated blended cements, K. Erdogdu, M. Tokyay , P. Türker, Cement and Concrete Research 29 (1999) 743–746.
39. N. BouzoubaaA, M.H. Zhang, V.M. Malhotra, Laboratory-produced high-volume fly ash blended cements Compressive strength and resistance to the chloride-ion penetration of concrete, Cement and Concrete Research 30 (2000) 1037- 1046
40. V V Arora, and Puneet Kaura, "Suitability of Accelerated Test Methods as a Tool for Service Life Prediction for RC Structures Made of Ordinary Portland and Blended Cement",71st RILEM Annual Week & ICACMS 2017, Chennai, India, 3rd – 8th September 2017
41. "Concrete: Microstructure, Materials and Properties", Book by P. KUMAR MEHTA, PAULO J.M. MONTEIRO, published by McGraw-Hill, 2005.
42. N. BouzoubaaA, M.H. Zhang, V.M. Malhotra, Laboratory-produced high-volume fly ash blended cements Compressive strength and resistance to the chloride-ion penetration of concrete, Cement and Concrete Research 30 (2000) 1037- 1046
43. "Effect of the starting fly ash on the microstructure and mechanical properties of fly ash-belite cement mortars", A. Guerrero, S. Goni, A. Macias, M.P. Luxan, Cement and Concrete Research 30 (2000) 553–559
44. "Efficiency of mineral admixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with compressive strength", Martin Cyr, Philippe Lawrence, Erick Ringot, Cement and Concrete Research 36 (2006) 264 – 277
45. "Effect of fly ash fineness on compressive strength and pore size of blended cement paste", Prinya Chindaprasirt, Chai Jaturapitakkul, Theerawat Sinsiri, Cement & Concrete Composites 27 (2005) 425–428.
46. "Isaia GC, Gastaldini ALG, Moraes R. Physical and pozzolanic action of mineral additions on the mechanical strength of highperformance concrete." Cement and Concrete Research 2003;25:69–76.
47. "Slanicka S. The influence of fly ash fineness on the strength of concrete", Cement and Concrete Research 1991; 21(2/3):285–96.
48. Effect of supplementary cementitious materials on the compressive strength and durability of short-term cured concrete H. Toutanjia, N. Delattec , S. Aggounb , R. Duvalb , A. Dansona, Cement and Concrete Research 34 (2004) 311 – 319.
49. "Experimental Study on Strength Gaining Characteristics of Concrete using Portland Composite Cement", Md. Alhaz Uddin, Mohammed Jameel, Habibur Rahman Sobuz, Md. Shahinul Islam, and Noor Md. Sadiqul Hasan, KSCE Journal of Civil Engineering (2013) 17(4):789–796.
50. "High Performance Concrete", Book by Pierre-Claude Aïtcin published by E & FN SPON
51. E. Holt (2000). "Where did these cracks come from?" Concrete International, Vol. 22, No. 9, pp. 57 – 60
52. E. Holt (2001). "Early age autogenous shrinkage of concrete." Technical Research Centre of Finland, VTT Publications 446
53. M. S. Isović, G. Markovski & M. Ćećez (2012) "Shrinkage strain of concrete – causes and types." Gradevinar- 64, pp. 727–734
54. M. S. Isović (2010). "Influence of steel fibre reinforcement to the behaviour of reinforced concrete beams." University "St. Cyril and Methodius" of Skopje, Civil Engineering faculty, Doctoral thesis, pp. 38–59.
55. E. Tazawa (1998). "Autogenous Shrinkage of Concrete." Proceedings of the International Workshop organized by JCI (Japan Concrete Institute), E & FN Spon, London, Hiroshima, pp. 411
56. V. M. Malhotra & P. K. Mehta (1996). "Advances in Concrete Technology, Volume 1: Pozzolanic and Cementitious Materials." Gordon and Breach Publishers, Amsterdam, Netherlands
57. RILEM TC 107 (1995). "Guidelines for characterizing concrete creep and shrinkage in structural design codes or recommendations." Materials and structures 28, pp. 52–55
58. ACI (2005). "Report on factors affecting shrinkage and creep of hardened concrete." ACI Standards, ACI 209.1R-2005, Farmington Hills, MI: American Concrete Institute
59. G. Pickett (1956). "Effect of aggregate on shrinkage of concrete and hypothesis concerning shrinkage." Journal of the American Concrete Institute, Vol. 27, No. 5, pp. 581–590
60. G. E. Troxell, H. E. Davis & J. W. Kelly (1968). Composition and properties of concrete, 2nd. Edition., McGraw-Hill Book Co., New York
61. G. A. Rao (2000). "Long-term drying shrinkage of mortar – influence of silica fume and size of fine aggregate." Indian Institution of Science. Cement Concrete Research 31, pp. 171- 175
62. E. Guneyisi, M. Gesoglu, E. Ozbay (2010). "Strength and drying shrinkage properties of self-compacting concretes incorporating multi-system blended mineral admixtures." Construction and Building Materials, pp. 1878–1887.
63. M. Gesoğlu, E. Güneyisi & E. Őzbay (2009). "Properties of self-compacting concretes made with binary, ternary, and quaternary cementitious blends of fly ash, blast furnace slag, and silica fume." Construction and Building Materials, 23, pp. 1847–1854.
64. S. Deshpande, D. Darwin & J. Browning (2007). "Evaluating free shrinkage of concrete or control of cracking in bridge decks. Structural Engineering and Engineering Materials." SM Report No. 89. The University of Kansas Centre for Research, Inc. Lawrence, Kansas.
65. M. N. Haque & O. Kayali (1998) "Properties of high-strength concrete using a fine fly ash." Cement and Concrete Research, Vol. 28, No. 10, pp. 1445–1452
66. F. Collins & J. G. Sanjayan (2000). "Cracking tendency of alkali-activated slag concrete subjected to restrained shrinkage." Cement and Concrete Research 30, pp. 791–798.
67. D. A. Whiting, R. J. Detwiler & E. S. Lagergren (2000). "Cracking tendency and drying shrinkage of silica fume concrete for bridge deck applications." ACI Materials Journal. Title No. 96 M10
68. Agostini, F.; Lafhaj, Z.; Skoczylas, F.; Loodsveldt, H. "Experimental study of accelerated leaching on hollow cylinders of mortar", Cem. Concr. Res. 2007, 37, 71–78.
69. C. Garde, R. Franqois, T. Jean-Michel, Leaching of both calcium hydroxide and C-S-H from cement paste: modeling the mechanical behavior, Cem. Concr. Res. 28 (6) (1996) 1257–1268.
70. K. Haga, S. Sutou, M. Hironaga, S. Tanaka, S. Nagasaki, Effects of porosity on leaching of Ca from hardened ordinary Portland cement paste, Cem. Concr. Res. 35 (9) (2005) 1764–1775.
71. An Cheng, Sao-Jeng Chao, "Wei-Ting Lin, Effects of Leaching Behavior of Calcium Ions on Compression and Durability of Cement-Based Materials with Mineral Admixtures", Materials 2013, 6, 1851–1872
72. Yu-Juan Tang, Xiao-Bao Zuo, Shao-Li He, Olawale Ayinde, Guang-Ji Yin, "Influence of slag content and water-binder ratio on leaching behavior of cement pastes", Construction and Building Materials 129 (2016) 61–69.
73. E. Roziere, A. Loukili, Performance-based assessment of concrete resistance to leaching, Cem. Concr. Compos. 33 (4) (2011) 451–456.
74. Y.S. Choi, E.I. Yang, Effect of calcium leaching on the pore structure, strength, and chloride penetration resistance in concrete specimens, Nucl. Eng. Des. 259 (2013) 126–136.
75. www.concrete.org
76. Chapter 2, Guidelines for The Use of Lithium to Mitigate Or Prevent Alkali-Silica Reaction, Fedral Highway Administration, U.S. Department of Transportation

77. Fernandes, I., Broekmans, M.A.T.M. Alkali–Silica Reactions: An Overview. Part I. Metallogr. Microstruct. Anal. 2, 257–267 (2013). https://doi.org/10.1007/s13632-013-0085-5
78. Monogram on Alkali-aggregate reaction in concrete, Central soil & Materials Research Station, New Delhi, 2008
79. IS 1489(Part 1): 2015 Portland Pozzolana cement-Specifications
80. IS 269: 2015 Ordinary Portland cement-Specifications
81. C. Larive, A. Laplaud, O. Coussy, The role of water in alkali–silica reaction, in Proceedings of the 11th International Conference on Alkali–Aggregate Reaction in Concrete, Québec City, 2000, ed. by M.A. Bérubé, B. Fournier, B. Durand, pp. 61–69
82. Chapter 10,Petrographic Methods of Examining Hardened Concrete: A Petrographic Manual, Fedral Highway Administration, U.S. Department of Transportation, 2006
83. Swamy R N (1992), Role and effectiveness of mineral admixtures in relation to alkali–silica reaction, in Swamy, R. N. (Ed.) The Alkali–Silica Reaction in Concrete. London,
84. Blackie and Son Ltd. IS 456 : 2000 Plain and reinforced concrete – Code of practice (Fourth Revision)
85. Roland F. Bleszynski and Michael D.A. Thomas, Microstructural Studies of AlkaliSilica Reaction in Fly Ash Concrete Immersed in Alkaline Solution, Advanced Cement Based Materials 1998,7,66–78.
86. Della M. Roy, Paul J. Tikalsky, Barry E. Scheetz, James Rosenberger, Tara Cavalline, And Periaswamy Arjunan, Influence of Portland Cement Characteristics on Alkali Silica Reactivity. TRB 2003 Annual Meeting
87. Harald Justnes,2016, How SCMs Improve Concrete Durability – A Fundamental View, sustainable construction materials and technologies, Las Vegas, USA, August 7–11,2016
88. Ke-Liang LI, Guo-Hong Huang, Lin-Hua Jiang, Yue-Bo Cai, Jian Chen and Jian-Tong Ding, "Study on Abilities of Mineral Admixtures and Geopolymer to Restrain ASR," Trans Tech Publ., vol. 302–303, pp. 248–254, 2006.
89. Bektas, F., & Wang, X. (2017). Effectiveness of Ternary Blends in Mitigating ASR Demonstrated on the Modified Mortar-Bar Test. Journal of Testing and Evaluation, 45(3), 1099–1104.
90. M.H. Shehata, M.D.A. Thomas, R.F. Bleszynski, The effect of fly ash composition on the chemistry of pore solution, Cem Concr Res 29(1999) 1915–1920.
91. J. Duchesne, M.-A. Berube, The effectiveness of supplementary cementing materials in suppressing expansion due to ASR: Another look at reaction mechanisms: Part 2. Pore solution chemistry, Cem Concr, Res 24 (2) (1994) 22–230.
92. M.H. Shehata, M.D.A. Thomas, The effect of fly ash composition on the expansion of concrete due to Alkali silica reaction, Cement and Concrete Research 30 (2000) 106–1072
93. Lane, D. S., and C. Ozyildirim. "Preventive measures for alkali-silica reactions (binary and ternary systems)." Cement and concrete research 29.8 (1999): 1281-1288.
94. Hasparky, N.P., Monteiro, P.J.M. and Carasek, H. (2000), "Effect of Silica Fume and Rice Husk on Alkali-Silica Reaction", ACI Materials Journal Vol 97 No 4
95. Cao H T, Bucea A, Ray A, Yozghatlian S (1997), "The effect of cement composition and pH of environment on sulfate resistance of Portland cements and blended cements" Cement and Concrete Composites, 19(2), p.161–171 (https://doi.org/10.1016/S0958-9465(97)00011-5)
96. Le, Ha Thanh, et al. "The mix design for self-compacting high performance concrete containing various mineral admixtures." Materials & Design 72 (2015): 51–62.
97. ACI Committee 201: Durable Concrete, ACI Manual of Concrete Practice, Part 1, Detroit, Michigan, 1992, 39 p.
98. Collepardi, M.: Ettringite formation and sulphate attack on concrete. In: Malhotra, V. M. (editor): Proceedings of the Fifth CANMET/ACI International Conference on Recent Advances in Concrete Technology (ACI SP-200), 2001, p. 21–37.
99. Collepardi, M.: Thaumasite formation and deterioration in historic buildings. In: Cement and Concrete Composites, Volume 21 (1999), p. 147–154.
100. Developments in the Formulation and Reinforcement of Concrete, A volume in Woodhead Publishing Series in Civil and Structural Engineering Book • 2nd Edition • 2019
101. Brown, P. W.: Thaumasite formation and other forms of sulphate attack. In: Cement and Concrete Composites, Volume 24 (2002), p. 301–303.
102. Mehta PK. Mechanism of expansion associated with ettringite formation. Cem Concr Res 1973;3(1):1–6.
103. Mehta, P.K., "Sulphate Attack on Concrete – A Critical Review", Materials Science of Concrete III, The American Ceramic Society, 1993 pp. 105–130.
104. M.M. Rahman, M.T. Bassuoni, "Thaumasite sulphate attack on concrete: Mechanisms, influential factors and mitigation" Construction and Building Materials 73 (2014) 652–662
105. "Thaumasite Sulphate Attack: Case Studies And Implications", Hugh (Xiaoqiang) Hou, Laura J. Powers, John Lawler, Koray Tureyen, 37th international Conference on Cement Microscopy
106. Santhanam, M.; Cohen, M. D.; Olek, J.: Sulphate attack research- whither now. In: Cement and Concrete Research, Volume 31 (2001), p. 845–851.
107. Rasheeduzzafar, Al-Amoudi OSB, Abduljauwad SN, Maslehuddin M. Magnesium–sodium sulphate attack in plain and blended cements. ASCE J Mater Civil Eng 1994;6(2):201–22.
108. Attack on plain and blended cements exposed to aggressive sulphate environments Omar S. Baghabra Al-Amoudi, Cement & Concrete Composites 24 (2002) 305–316
109. A. Pavoine, X. Brunetaud b, L. Divet "The impact of cement parameters on Delayed Ettringite Formation", Cement & Concrete Composites 34 (2012) 521–528
110. Glasser F P, Damidot D and Atkins M (1995), Phase development in cement in relation to the secondary ettringite problem, Advances in Cement Research, 7, 57–68.
111. Ramlochan T, Zacarias P, Thomas M D A and Hooton R D (2003), the effect of pozzolans and slag on the expansion of mortars cured at elevated temperature: Part I: Expansive behaviour, Cement and Concrete Research, 33, 807–814.
112. Ramlochan T, Thomas M D A and Hooton R D (2004), The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature: Part II: Microstructural and microchemical investigations, Cement and Concrete Research, 34, 1341–1356.
113. Torii, K.; Taniguchi, K.; Kawamura, M.: Sulphate resistance of high fly ash content concrete. In: Cement and Concrete Research, Volume 25 (1995), p. 759–768.
114. Tian, B.; Cohen, M. D.: Does gypsum formation during sulphate attack on concrete lead to expansion? In: Cement and Concrete Research, Volume 30 (2000), p. 117–123.
115. Dhir, R. K.; Hubbard, F. H.; Munday, J. G. L.; Jones, M. R.; Duerden, S. L.: Contribution of pfa to concrete workability and strength development. In: Cement and Concrete Research, Volume 18 (1978), p. 277–289.
116. Use of mineral admixtures for enhanced resistance against sulphate attack, H.N. Atahan , D. Dikme, Construction and Building Materials 25 (2011) 3450–3457
117. Cabrera JG, G. P., "The Effect of Reinforcement Corrosion on the Strength of the Steel/Concrete Bond. International Conference on Bond in Concrete", 11–24, 1992.
118. ACI Committee 222-corrosion of metals in concrete. ACI Manual of Concrete Practice. Part-1, 1992.
119. Flitt, H. J., & Schweinsberg, D. P. A., "guide to polarisation curve interpretation : deconstruction of experimental curves typical of the Fe / H 2 O / H + / O 2 corrosion system". 47, 2125–2156, 2005. https://doi.org/10.1016/j.corsci.2004.10.002
120. Emmons, P. H.. Concrete Repair and Maintenance Illustrated: Problem Analysis, Repair Strategy, and Techniques. RSMeans, p. 314, 1996.
121. Velu Saraswathy, Subbiah Karthick, Han Seung Lee, Seung-Jun Kwon & Hyun-Min Yang, "Comparative Study of Strength and Corrosion Resistant Properties of Plain and Blended Cement Concrete Types" Advances in Materials Science and Engineering Volume, 2017
122. Mullick, A.K., "Performance of Concrete with Binary and Ternary Cement Blends", Indian Concrete Journal, Vol. 81, No. 1, pp. 15–22,2007.
123. Beaudoin, J. J., Ramachandran, V. S., & Feldman, R. F., "Interaction of chloride and C-S-H", Cement and Concrete Research, 20(6), 875–883, 1990.
124. Ahm-ad, S., "Reinforcement corrosion in concrete structures , its monitoring and service life prediction — a review". 25, 459–471, 2003. https://doi.org/10.1016/S0958-9465(02)00086-0
125. Ann, K. Y., & Song, H.-W., "Chloride threshold level for corrosion of steel in concrete", Corrosion Science, 49(11), 4113–4133 2007.
126. Neville, A., J.J. Brooks, Concrete Technology 2nd edition, 2009
127. Sengule O., Tasdemir, M. A., "Compressive Strength and Rapid Chloride Permeability of Concretes with Ground Fly Ash and Slag" Journal of Materials in Civil Engineering, 494–501 2009.
128. Li, S., and Roy, D. M., "Investigation of relations between porosity, pore structure and chloride diffusion of fly ash and blended cements." Cem. Concr. Res., 16 5, 749–75 1986.
129. Dhir, R. K., and Jones, M. R., "Development of chloride-resisting concrete using fly ash." Fuel, 78 2, 137–142 1999.
130. V V Arora, Puneet Kaura, Piyush Mital, Bikekananda Mohapatra, "Performance assessment of concrete made with ternary cementitious blends against chloride ingress and CO$_2$ attack". Civil Engineering and Construction Review, May 2020
131. Byfors, K., "Influence of silica fume and fly ash on chloride diffusion and pH values in cement paste", Cement and Concrete Research, 17(1), 115–130, 1987.
132. Jensen, H.-U., & Pratt, P. L., "The binding of chloride ions by pozzolanic product in fly ash cement blends", Advances in Cement Research, 2(7), 121–129, 1989.
133. Oh, B. H., Jang, S. Y., & Shin, Y. S., "Experimental investigation of the threshold chloride concentration for corrosion initiation in reinforced concrete structures", Magazine of Concrete Research, 55(2), 117–124, 2003.
134. Dhir, R. K., Jones, M. R., & McCarthy, M. J., "Binder content influences on chloride ingress in concrete. Cement and Concrete Research", 26(12), 1761–1766, 1996.
135. McNally, C., & Sheils, E., "Probability-based assessment of the durability characteristics of concretes manufactured using CEM II and GGBS binders", Construction and Building Materials, 30, 22–29, 2012.
136. Lübeck, A., Gastaldini, A. L. G., Barin, D. S., & Siqueira, H. C., "Compressive strength and electrical properties of concrete with white Portland cement and blast-furnace slag", Cement and Concrete Composites, 34(3), 392–399, 2012.
137. V.G. Papadakis, M.N. Fardis, C.G. Vayenas, "Hydration and carbonation of pozzolanic cements", ACI Mater. J. 119–130, 1993.
138. J. M. Marangu, J. K. Thiong'O, and J. M. Wachira, "Review of Carbonation Resistance in Hydrated Cement Based Materials," J. Chem., vol. 2019, 2019, doi: 10.1155/2019/8489671.
139. Visser, J. H. M., "Influence of the carbon dioxide concentration on the resistance to carbonation of concrete" Construction and Building Materials, 67, 8–13, 2014.
140. VV Arora, and Puneet Kaura, "Service life design of concrete structures subjected to carbonation", One day symposium on Durability and service life design of concrete structures 2017, NCB Ballabgarh.
141. Dinakar, P., Babu, K. G., & Santhanam, M., "Corrosion behaviour of blended cements in low and medium strength concrete", Cement and Concrete Composites, 29(2), 136–145, 2007.
142. Andrade, C., & Buják, R., "Effects of some mineral additions to Portland cement on reinforcement corrosion", Cement and Concrete Research, 53, 59–67, 2013.
143. Montemor, M.., Cunha, M.., Ferreira, M.., & Simões, A., "Corrosion behaviour of rebars in fly ash mortar exposed to carbon dioxide and chlorides. Cement and Concrete Composites, 24(1), 45–53 2002.
144. Alonso, C., Andrade, C., & González, J. A., "Relation between resistivity and corrosion rate of reinforcements in carbonated mortar made with several cement type, Cement and Concrete Research, 18(5), 687–698, 1988.
145. Alonso C. and Andrade C., "Effect of cement type and cement proportion in the corrosion rate of rebars embedded in carbonates mortar, Material's and Construction, 37 no 205 5 – 15, 1987.
146. Alonso, C., Andrade C., and González J. A., "Approach to the effect of concrete resistivity in the corrosion of rebars in concrete", Materiales de Construccion 37 no 207 5 – 12, 1987.
147. VV Arora and Puneet Kaura, "Suitability of accelerated test methods as a tool for service life prediction for RC structures made of ordinary portland and blended cement" ICACMS; 2017
148. Ilda Kovačević and Sanin Džidić, High-Strength Concrete (HSC) Material For High-Rise Buildings, 12th Scientific/Research Symposium with International Participation METALLIC AND NONMETALLIC MATERIALS "B&H, 19th-20th April 2018
149. İlker BekirTopçu, TayfunUygunoğlu and İsmailHocaoğlua, Electrical conductivity of setting cement paste with different mineral admixtures, Construction and Building Materials Volume 28, Issue 1, March 2012, Pages 414–420
150. Harun Mallisa, and Gidion Turuallo, The maximum percentage of fly ash to replace part of original Portland cement (OPC) in producing high strength concrete, AIP Conference Proceedings 1903, 030012 (2017)
151. Sreejith Haridas and Shaji M Jamal, "Study of properties of high strength concrete prepared by partial replacement of cement with GGBS," International Research Journal of Advanced Engineering and Science, Volume 2, Issue 2, pp. 127–130, 2017.

5.0

ENVIRONMENTAL ADVANTAGES

Figure 5.1: Production Process of Blended Cement



In order To analyze the environmental impacts of blended cement like PPC, PSC and Composite Cement vis-à-vis other types of cement like OPC, the typical composition considered is given in table 5.1. The composition of OPC is taken as 95% Clinker and 5% gypsum. For comparison of blended cement with OPC in terms of environmental advantages, the typical composition of blended cements is taken based on the average fly ash and slag consumption in India. Therefore, for PPC and PSC, it is considered that clinker is substituted by 31% and 57% respectively. The composition of composite cement is taken as 45% clinker, 25% granulated slag, 25% fly ash and remaining 5% gypsum. The production process of blended cement is shown in figure 5.1.

Table 5.1: Composition of typical OPC, PPC, PSC and Composite Cement
(Functional Unit: 1 tonne of product)

S.NO.	Type of Cement	Composition of Cement			
		Clinker	Fly Ash	Granulated Slag	Gypsum
1.	OPC	95%	-	-	5%
2.	PPC	65%	31%	-	4%
3.	PSC	40%	-	57%	3%
4.	Composite Cement	45%	25%	25%	5%

A comparative inventory data sheet of typical input materials/energy and outputs based on NCB studies, associated with production of 1 tonne of clinker, OPC, PPC, PSC and composite cement as per the composition given in table 5.1, are compiled and shown in table 5.2. The composition for production of 1 tonne of clinker, it is considered that 1.5 tonnes of kiln feed are required. Limestone requirement is taken as 95% of kiln feed and rest are additives like bauxite, iron ore and clay. The thermal energy requirement is taken as 762 kcal/kg of clinker and coal requirement is 152 kg/tonne of clinker with a GCV of 5000 kcal/kg clinker. Based on NCB studies, electrical energy requirement is taken as 60 kWh per tonne of clinker and an additional 30 kWh and 25 kWh for grinding energy in cement mill for OPC and PPC respectively. Hence, total electricity consumption per tonne of OPC comes out to be 87 kWh/tonne of cement. The electricity consumption for PSC grinding will be higher as compared to OPC as slag is difficult to grind and is taken as 35 kWh/tonne as compared to 30 kWh per tonne required for OPC and PPC. However, for grinding energy in cement mill for composite cement, the electricity consumption for composite cement is taken as weighted average of energy requirements of grinding of OPC, PPC and PSC. The total electricity consumption required per tonne of composite cement is approximated as 57 kWh in comparison to 87 kWh required for OPC production.

Table 5.2: Inventory data for production of Clinker, OPC, PPC, PSC and Composite Cement (Functional Unit: 1 tonne of product)

Parameter	**Clinker**	**OPC**	**PPC**	**PSC**	**Composite Cement**	**Unit** (per tonne)
INPUTS						
Raw Materials						
Lime stone	1420	1349	923	568	639	kg
Fly ash	-	-	310	-	250	kg
Slag	-	-	-	570	250	kg
Bauxite	20	19	13	8	9	kg
Iron ore	30	28.5	19.5	12	13.5	kg
Clay	30	28.5	19.5	12	13.5	kg
Gypsum	-	50	40	30	50	kg
Energy resouces						
Electricity	60	87	64	59	57	kWh
Thermal Energy	762	724	495	305	343	('000) kcal
OUTPUTS						
Emission to air						
Direct Carbon dioxide (CO_2)	779	740	507	312	351	kg
Indirect Carbon dioxide (CO_2)	70.4	102	75	69	67	kg
Nitrogen Oxides (NOx)	1.6	1.52	1.04	0.64	0.72	kg
Sulphur dioxide (SO_2)	0.1	0.10	0.07	0.04	0.05	kg
Particulates (PM)	0.3	0.285	0.20	0.12	0.14	kg
Waste						
-		-	-	-	-	-

(The values given in above table are typical values used for comparison based on NCB studies)

In blended cement, as clinker factor is reduced, the corresponding requirements of limestone, additives, coal, and electrical energy for production of blended cement will get reduced proportionately. In PPC, PSC and composite cement, the clinker factor is reduced to 65%, 40% and 45% respectively. However, the grinding energy required for production of PSC is higher than that of OPC and PPC as slag is harder to grind.

5.1

REDUCTION IN CARBON FOOTPRINT

Indian cement industry has been working on the issue of its GHG emissions and has brought down the CO_2 emission intensity (tCO_2 /t cement) from 1.12 t of CO_2/t of cement in 1996 to 0.719 t of CO_2/t of cement in 2010. Moreover, in the last 7 years, the CO_2 emissions intensity (including onsite/captive power plant (CPP) power generation) was around 0.67 tCO_2/t cement in 2017, which was 49 $kgCO_2$/t cement i.e. 6.8% lower as compared to 2010. For Indian Cement Industry, the direct CO_2 emission intensity (from calcination process and combustion of fuel) is around 0.588 tCO_2/t cement in 2017, which was 32 $kgCO_2$/t cement i.e. 5% lower compared to 2010 [8]. The reduction of 32 $kgCO_2$/t cement in direct CO_2 footprint is mainly due to increased usage of alternative fuel, reductions in clinker factor and increases in blended cement production as shown in table 5.3 below. The cement sector will need to make significant efforts to achieve the 40% reduction required to meet the 2050 objectives of 0.35 tCO_2/t.

Table 5.3: CO_2 emission intensity reduction [8]

Lever	Emission intensity contribution ($kgCO_2$/t of cement)
Clinker substitution	-33.3
Alternative fuel use	-4.39
Thermal energy efficiency	+5.33
Net reduction	-32.4

Based on the composition of cements given in table 5.1 and inventory given in table 5.2, the direct CO_2 emissions for producing OPC cement is around 740 kg CO_2/t OPC whereas, in case of PPC there is a 31% reduction of CO_2 emissions, in case of PSC there is a 59% CO_2 reduction and in case of composite cement, there is a reduction of 53% in CO_2 emission as compared to OPC. The direct and total CO_2 emission scenarios for different types of Cements are shown in figures 5.2 and 5.3 respectively.

Figure 5.2: Direct CO_2 emission scenario for different types of cement

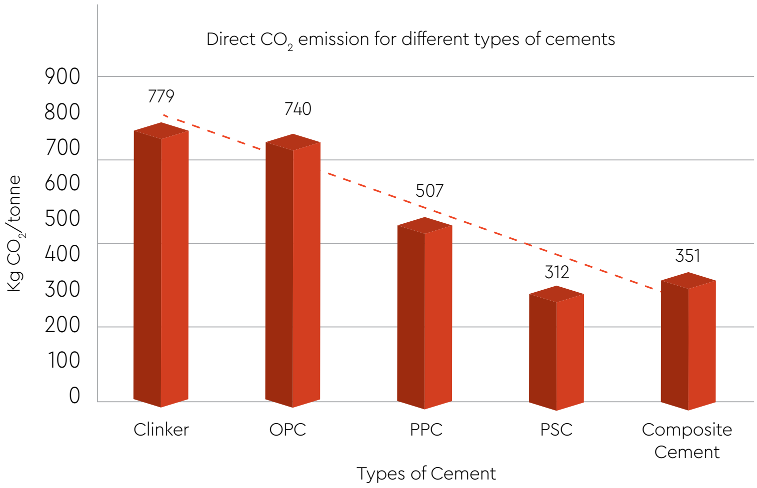
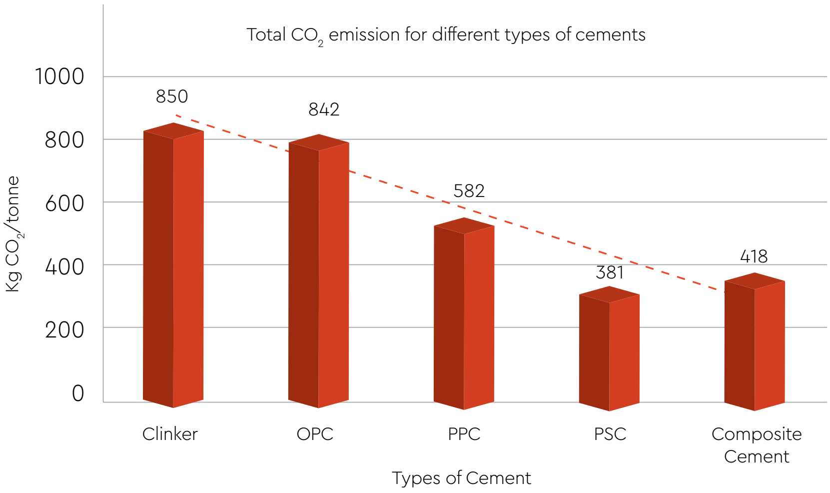


Figure 5.3: Total CO_2 emission scenario for different types of cement



Embodied CO_2 with generation and transportation of fly ash and slag are not considered while calculating the direct and total CO_2 emissions associated with different types of cement.

5.2

REDUCED ENERGY CONSUMPTION

The Indian cement industry's estimated average specific thermal and electrical energy consumption is 762 kcal/kg clinker (excluding VSK based) and 82.5 kWh/t cement respectively. However, the estimated average specific electrical energy consumption for grinding units is 35 kWh/t cement. The energy costs increase or decrease based upon fuel price as well as power unit cost. The analysis for average percent energy cost showed that total energy cost accounted for around 40–45% of the total production cost of cement (packed cement), out of which, fuel cost accounted for 25-30% and power cost accounted for 15–20%. The use of blended cements will help in reducing thermal and electrical energy consumption.

For comparison of specific heat consumption, based on composition of cement given in table 5.1 and inventory is given in table 5.2, the average thermal energy consumption required for producing clinker is around 762 kcal/kg clinker. Based on the clinker content in OPC and blended cements like PPC, PSC and composite cement, the thermal energy consumption is around 724 kcal/kg OPC, 495 kcal/kg PPC, 305 kcal/kg PSC and 343 kcal/kg CC respectively as shown in figure 5.4. Similarly, the average electrical energy consumption for producing OPC is around 87 kWh/t OPC whereas, in case of blended cements like PPC, PSC and composite cement, the electrical energy consumption is around 64 kWh/t PPC, 59 kWh/t PSC and 57 kWh/t CC respectively as shown in figure 5.5.

Figure 5.4: Thermal energy consumption pattern for different types of cement (NCB Studies)

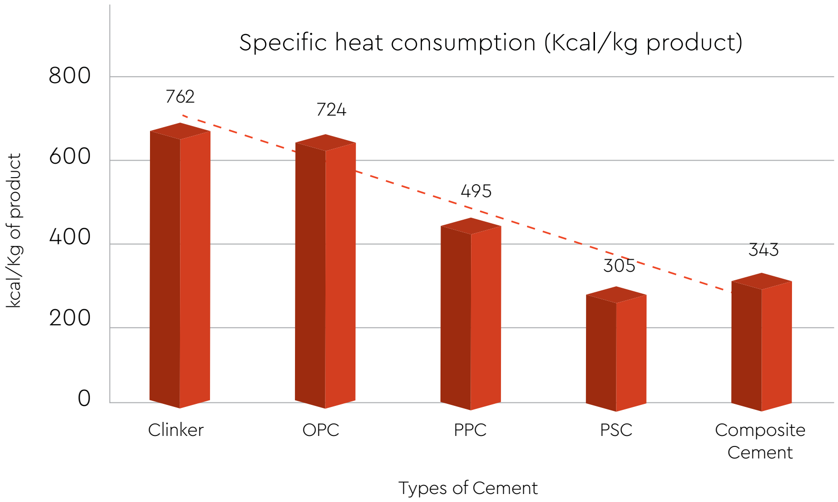
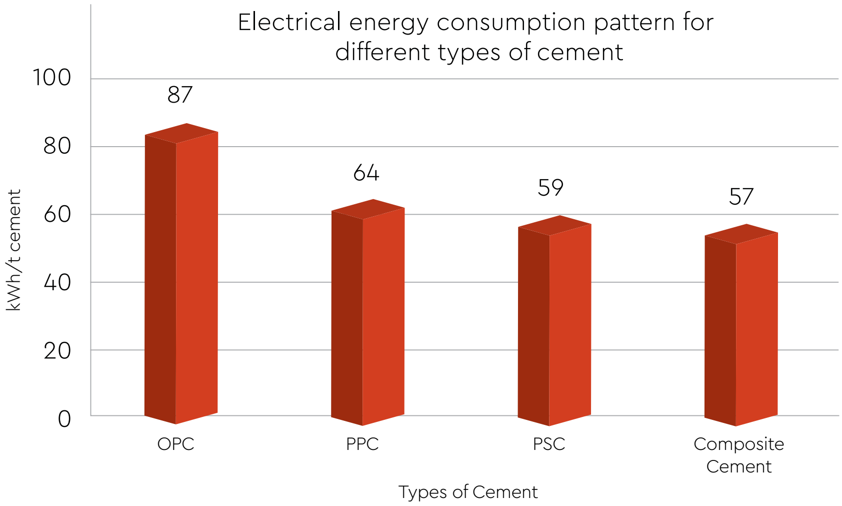


Figure 5.5: Electrical energy consumption pattern for different types of cement (NCB Studies)

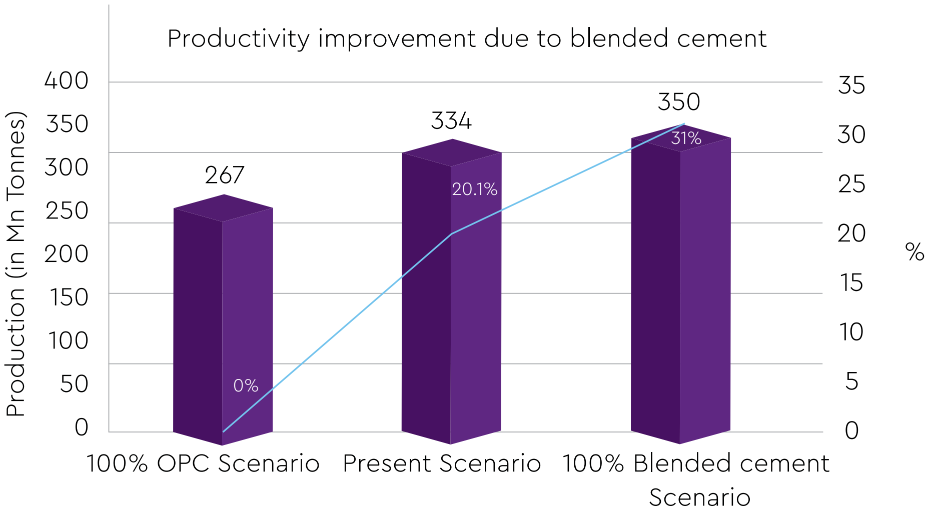


5.3

INCREASED PRODUCTION CAPACITY

In the present scenario (27% OPC, 65% PPC, 7% PSC & 1% other product), with existing clinker production having same plant capacity utilization, there is an improvement in productivity to the tune of 20.1% as compared to 100% OPC scenario. Similarly, for a 100% blended cement scenario with same clinker production, there can be a further increase of 31% in cement productivity as shown in Figure 5.6.

Figure 5.6: Increased production Capacity due to Blended Cement (NCB Studies)



5.4

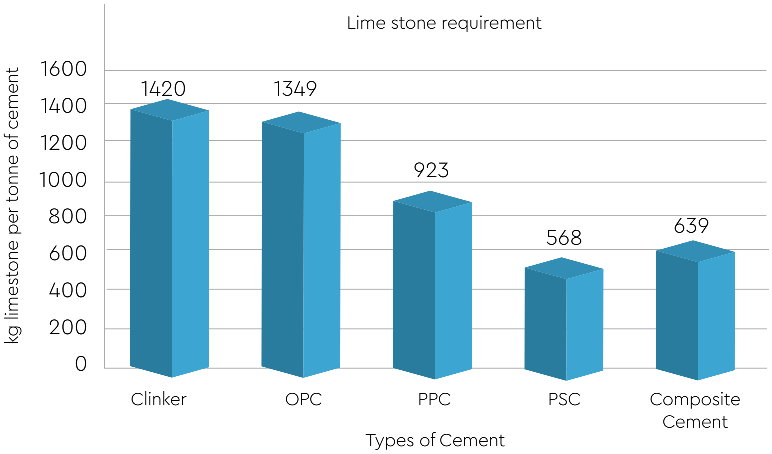
CONSERVATION OF LIMESTONE RESERVES

The use of mineral admixtures such as Granulated Blast Furnace slag, fly ash etc. led to broadened raw material base resulting in the conservation of natural resources, particularly limestone. Limestone reserves and resources available in India for future requirements as per the Indian Bureau of Mines (IBM) are shown in table 5.4. It is also expected in the future that low-grade limestones that are not suitable for clinker production will be used in cements like Portland limestone cement and limestone calcined clay cement.

Table 5.4: Limestone reserves and resources available in India [1]

Discription	**In million tons**
Cement Grade Limestone Reserves	**13,616**
Remaining Resources	128,138
Resources Restricted: Under Forest (22.5%)	28,831
CRZ & Other Regulated Areas (7.5%)	9,610
Sub Total	38,441
Net Available remaining resources for future growth	**89,697**
Total Available Limestone Reserves & Resources	**103,313**

Figure 5.7: Limestone Requirement for different types of Cement (NCB Studies)



The limestone requirement for clinker and different types of cement including blended cements like PPC, PSC and composite cement is shown in figure 5.7. The limestone requirement is calculated based on the cement composition given in table 5.1.

5.5

UTILIZATION OF INDUSTRIAL BY- PRODUCTS

5.5.1

FLY ASH

In India, Central Electricity Authority (CEA) on behalf of Ministry of Power has been monitoring the fly ash generation and its utilization at coal/ lignite based thermal power stations in the country since 1996. Data on fly ash generation and utilization including modes of utilization are obtained from thermal power stations on half yearly as well as on yearly basis. Fly ash utilization for the Year 2019-20 is given in figure 5.8 [7].

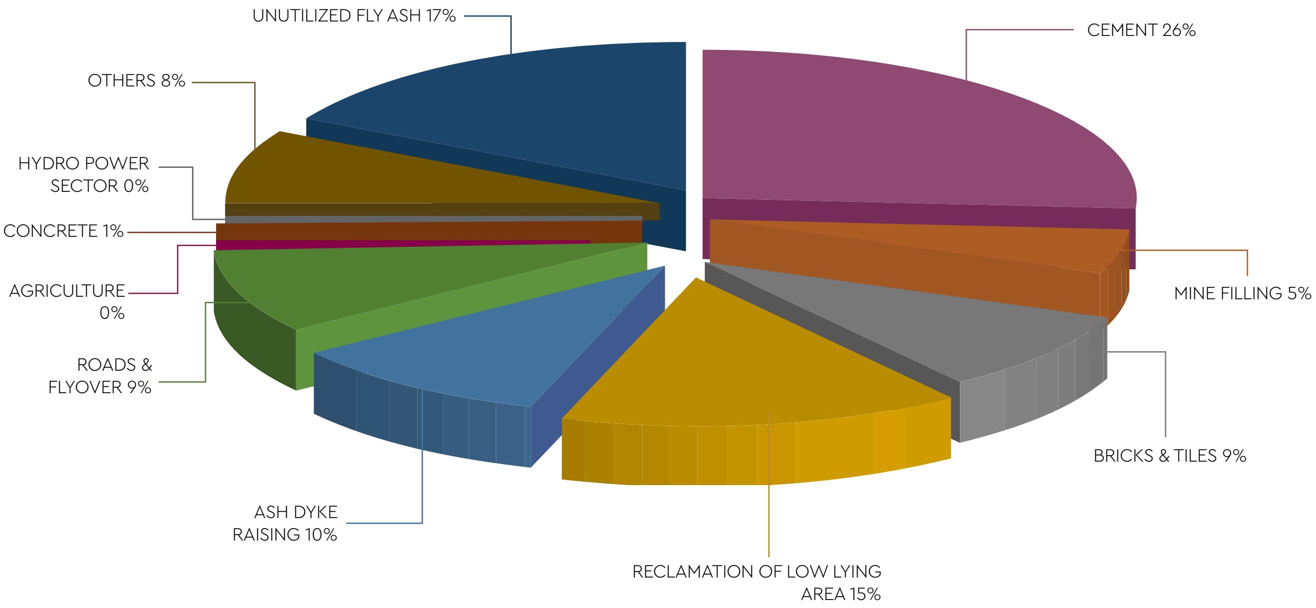


Figure 5.8: Modes of utilization of fly ash for the year 2019-20 [7]

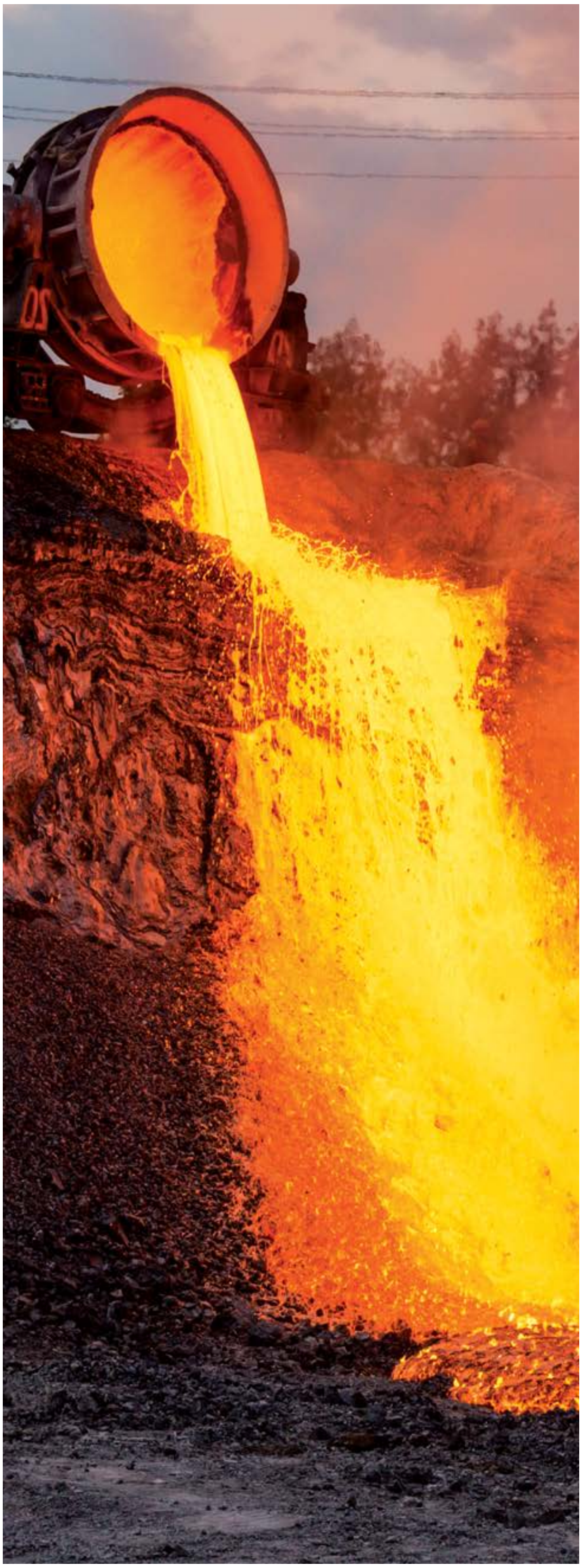
Fly ash is being used by Cement Industry as a pozzolanic material in manufacturing of Portland Pozzolana Cement. It saves both precious limestone and coal. The utilization of fly ash in manufacturing of cement is a high value added use. Fly ash conforming to standard IS: 3812 (1) 2013 can be used (up to 35% maximum) in the manufacture of PPC as per IS: 1489 (part 1) 2015. The enhanced use of fly ash in Portland Pozzolana Cement (PPC) results in the reduction of clinker factor in cement (clinker factor: percentage (%) of clinker content by cement mass), followed by lessened CO_2 emissions through decreased fuel combustion and limestone calcination. In 2019-20, quantity of fly ash consumed is around 57.88 million tonnes in cement industry as shown in table 5.5. Quality of the fly ash samples varies depending on their glass content. Percentage of glass content in Indian fly ashes varies between 15 and 45% and the Lime Reactivity (LR) between 2.0 and 7.0 mpa.

Table 5.5: Utilization of industrial by products by cement companies in India [1,7]

Cement Company	Quantity of Fly Ash consumed (Million Tonnes)	Quantity of Slag consumed (Million Tonnes)
Total Consumption in cement industry in India	57.88	~22

5.5.2

GROUND GRANULATED BLAST FURNACE SLAG (GGBFS)



The increased use of Ground Blast Furnace Slag (GBFS) as specified in IS: 12809- 1987 for the manufacture of Portland Slag Cement (PSC) has a direct impact on reducing CO_2 emissions, by decreasing specific fuel consumption and reducing limestone calcination. Blast furnace slag is a non-metallic product consisting essentially of glass containing silicates and aluminosilicates of lime and other bases, which is developed simultaneously with an iron blast furnace. Granulated Blast Furnace Slag (GBFS) is obtained by further processing of the molten slag by rapidly chilling or quenching with water or stream. Ground Granulated Blast Furnace Slag (GGBFS) is obtained by duly grounding granulated blast furnace slag as specified in IS: 16714–2018 for the use in cement, mortar and concrete.

Generally, approximately 0.45–0.50 tonne of granulated blast furnace slag (GBFS) is generated with every tonne of hot metal produced. Currently, India produced approx. 25 million tonnes of blast furnace slag out of which 22 million tonnes of slag is granulated. At present, an average of 57% (by weight) of GBFS is used in PSC in India.

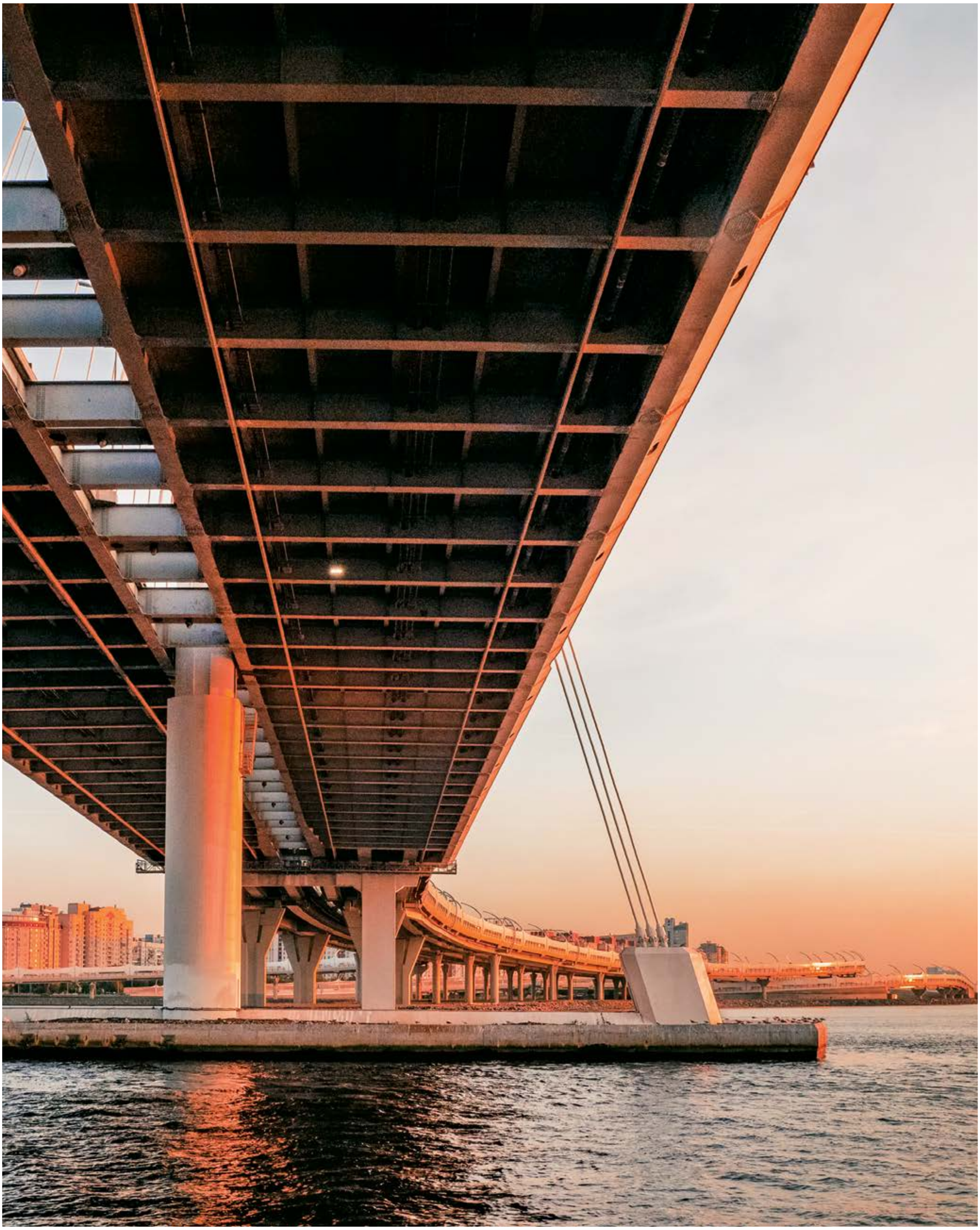
As per Indian standard specification IS: 455–2015, GBFS can be used in the range of 25–70% in the Portland Slag Cement (PSC). On contrary, the European standard (EN-197) for blast furnace slag cement type III/B and III/C allows the addition of ground GBFS in the range of 66-80% and 81–95% respectively. Indian cement industries utilize about 92% of granulated slag generated by the different steel plants.

References:

1. Cement Compendium "The India Cement Industry – 2019", published by National Council for Cement and Building Materials, December 2019.
2.Sustainability Report, UltraTech Cement Ltd., 2019–20
3.Sustainability Report, Ambuja Cement Ltd., 2019
4.Sustainability Report, ACC Ltd., 2018
5.Corporate Sustainability Report, Shree Cement Ltd., 2018–19
6.https://eaindustry.nic.in/ accessed on 4th October 2020
7.Report on Fly Ash Generation and its utilization at coal/lignite based Thermal Power Stations in the country for the year 2019–20 published by Central Electricity Authority, January 2021
8.Low Carbon Technology Roadmap for the Indian Cement Sector: Status Review 2018, WBCSD, November 2018
9.https://ieconomics.com/i/Hkow7P0Zm1806

6.0

CONSTRAINTS IN USING BLENDED CEMENT IN CONSTRUCTION



There is a rapid growth in production of blended cements such as Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC) over the last decade. The Indian standards and codes of practices recommend PPC and PSC in Plain, Reinforced and Prestressed Concrete construction. The PSC is used against the aggressive environments of chlorides and sulphates in soil and groundwater.

Some apprehension of late strength development and durability performance against carbonation induced corrosion earlier delayed the full-fledged usage of PPC in Reinforced Cement Concrete (RCC) construction. Fly ash was being used mainly in small proportions in mass concreting for dams and other hydraulic structures especially in coastal areas. In year 2009 the CPWD permitted the use of PPC vide their circular No. CDO/ SE (RR)/Fly Ash (Main)/102 dated 09 April 2009 for concrete grade of M25 and above in RCC. Similarly, the use of PPC for prestressed concrete was earlier not recommended in different standards / specifications due to apprehension of late strength development, apprehension of low resistance towards carbonation induced corrosion of steel and lack of data on other critical properties of prestressed concrete like creep, shrinkage and fatigue. However, based on extensive research was done at several R&D institutes in the country, Bureau of Indian Standard permitted the used of PPC in prestressed concrete by revising IS: 1343 in 2012.

Now, the use of PPC and PSC is permitted by national and international Standards / Specifications including most government bodies discussed here under:

- The use of Portland Pozzolana Cement conforming to requirements of IS: 1489 are already permitted by Ministry of Railways, Railway Board, Government of India, in substructures of bridges.

- As per "Guidelines for the Use of High-Performance Concrete Bridges" issued by the Ministry of Railways, Railway Board, Government of India, fly ash conforming to grade I of IS: 3812–2003 can be used where proportion should not be less than 20 percent and nor should exceed 35 percent by mass of cement.

- IRC: 112–2011 specifications "Unified code of Practice for Concrete Road Bridges provision for the use of blended cement" also permits the use of PPC in prestressed concrete structures.

- Internationally, PPC is permitted for use in prestressed concrete structures for example in Prestressed Concrete Institute (PCI) Manual, AASTHO specification, ASTM C-935 etc.

The use of PPC and PSC is generally preferred in structures where chloride ingress is likely an example in coastal areas owing to higher chloride penetration resistance of PPC and PSC. In case of PPC usage in non-coastal environment, the points to be taken care of will be early age strength, curing period and little extra cover to take care of carbonation. Therefore, PPC and PSC are already permitted in Indian Standards and presently, there are no constraints on their usage.

In the year 2015, a new Indian standard IS: 16415–2015 has come on composite cement. The Indian standards and codes of practices recommend usage of composite cement only in plain cement concrete and not in reinforced cement concrete due to lack of experimental data on application and durability performance of composite cement. Preliminary durability studies and literature has indicated that composite cement similar to PPC is beneficial in coastal environment prone to corrosion due to chloride ingress. Like in PPC, in Composite cement, there is apprehension on durability of reinforced concrete structures with respect to carbonation induced corrosion owing to higher clinker substitution. The detailed R&D work on evaluating durability performance of concrete with composite cement has been taken up by many R&D institutes across the country and the outcome of the same is expected in about two to three years'.

7.0

HOW THE GOVERNMENT CAN INCENTIVIZE BLENDED CEMENT OVER OPC

Considering the environmental and sustainability benefits of blended cements, state and central governments can incentivize these cements over OPC by:

- Ensuring fly ash supply sustainability: Thermal power companies need to sign Long-Term Agreements for fly ash sale to cement plants, instead of yearly tenders
- Government to mandate the utilization of Blended cement in Infrastructure projects
- **"Polluters to Pay"** concept to be implemented to avoid an increase in price for fly ash and GGBS. Blended cements consume the wastes from other essential industrial activities and save significant land degradation, water and air pollution. As an essential service to the nation towards permanent disposal of fly ash and GGBS, central and state government must consider "Polluter to pay" principle to change the existing process where waste disposer is being charged
- Development of concrete standard for using triple blend (Cement + Fly Ash + Slag) Concrete
- Government recognitions, like awards and subsidies (e.g. GST rebate) to promote blended cement usage

Green Certification:

- The Government can start providing carbon credit points to the projects using blended cement as it will reduce the embodied CO_2 footprint of the project
- CII –IGBC (Confederation of Indian Industry – Indian Green Building Council) has 'GreenPro' and 'GreenCo' certification process for cement plants & products that are fulfilling the criteria for products having a lower CO_2 footprint and protect the environment
- Linking the usage of these products to LEED (Leadership in Energy & Environmental Design) certification process or Green building certification process with tangible benefits, for building & infrastructure construction companies, will help promote blended cement over OPC

Linking other government schemes to promote usage of fly ash e.g. Ujjwal DISCOM Assurance Yojna (UDAY) is the scheme for financial turnaround and revival package for electricity distribution companies. It can be linked to the usage of fly ash generated out of power companies from which these DISCOMs are buying the required power

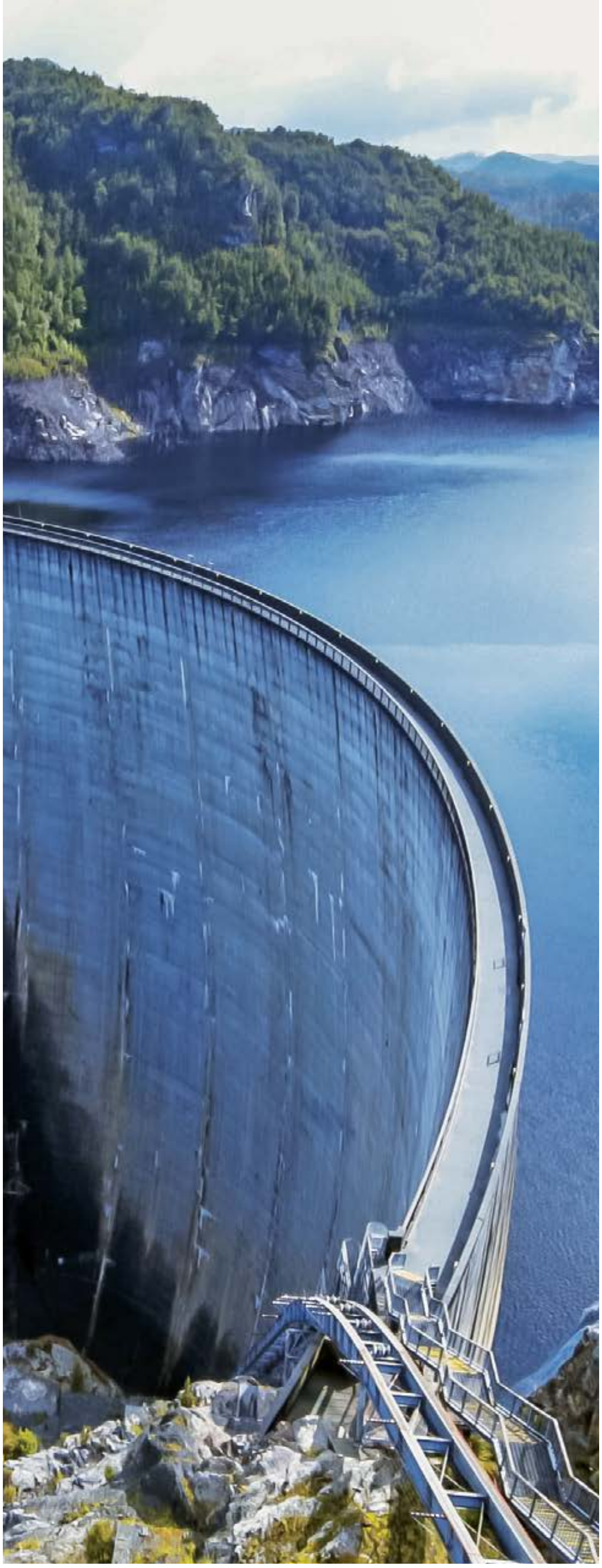
8.0

SUSTAINABILITY PRACTICES RELATED TO BLENDED CEMENT IN GLOBAL SCENARIO

The amount of clinker used is directly proportional to the CO_2 emissions generated in cement manufacturing due to both the combustion of fuels and the decomposition of limestone in the process. While global cement production will continue to grow at an average annual rate of 0.2% until 2030, it is important that the clinker-to-cement ratio declined to the global average of 0.64 by 2030. This can be done through increased use of blended cements and clinker substitutes, including industrial byproducts such as blast furnace slag or fly ash. Blended cement is a sustainable alternative to traditional cement. With the use of blended cement, GHG emissions can be reduced by almost 40% depending on the ratio of the mixture.

8.1

GLOBAL SCENARIO OF BLENDED CEMENT



The global blended cement industry was valued approximately at USD 295.4 billion in 2017 and is anticipated to grow with a healthy growth rate of more than 7% over the forecast period 2019–2025 [3]. Rising investments by governments considering smart city projects, surging urbanizations in both the developed and developing countries and escalating disposable income of the individuals are the substantial drivers of the industry across the globe. In terms of region, the global blended cement market can be divided into North America, Europe, The Asia Pacific, Latin America, and the Middle East and Africa. Asia Pacific is a major consumer of blended cement. Government funding for the construction of smart city projects, coupled with rapid urbanization in China and India are the factors driving building and construction sectors in the region. In addition, rise in disposable income of the middle-class population in Asia Pacific is likely to augment the construction sector in the region. Expansion of the building and construction sector due to rise of building permits across the U.S in North America and increasing urbanization in Nordic Countries of Europe is projected to drive the blended cement market in these regions. In UK & USA, the usage of blended cement is nearly 90% of the total production. Economic growth coupled with the need for housing facilities in Middle East and Africa is projected to boost market in the near future. The global blended cement market can be categorized as follows:

- Global blended cement market, by type-fly ash, blast furnace slag and silica fume
- Global blended cement market, by application residential and commercial, dams, marine structure, roads and flyovers and others
- Global blended cement market, by region-
  - North America: USA, Canada
  - Europe: Germany, France, UK,Italy, Spain, Russia & CIS, Rest of Europe
  - Asia Pacific:China, Japan, India, ASEAN, Rest of Asia Pacific
  - Latin America: Brazil, Mexico, Rest of Latin America
  - Middle East & Africa: GCC, South Africa Rest of Middle East & Africa

The global blended cement market is dominated by few key manufacturers. These manufacturers are primarily focused on new product launches and increasing their production capacity to gain market share. Key players operating in the global blended cement market include; ACC Limited, Lafarge Holcim North America Inc., CEMEX S.A.B.de.C.V, Lafarge Holcim Philippines, Inc, HeidelbergCement AG, Taiheiyo Cement Group, Buzzi Unicem USA Inc., Ultratech Cement, JSW Cement and others.

The Canadian standard, A3001–13–2017, comprises 26 types of standardized cements. Out of which 20 are blended cements, which include Portland limestone cement, Portland slag cement, pozzolana cement and ternary/quaternary blended cements. The standard allows the use of upto 50% fly ash (both siliceous and calcareous) in pozzolana cement and upto 60% fly ash in ternary/quaternary blended cements.

The regional spread of clinker to cement ratio observed currently is almost halved in 2DS by 2030. China remains the region with the lowest clinker to cement ratio (0.58) compared to the highest 0.72 average level shared by Eurasia and another Asia Pacific (Figure 8.1). About 8% to 19% reduction in clinker to cement ratio in relative terms are considered across different regions by 2030 compared to current levels. Reduction in clinker content in cement is highly dependent on the local availability of cement constituents, as well as on the required properties of finished products, which are dictated by local standards and technical requirements of end-use applications. Because of the cost economy and technical suitability of these cementing materials, the blended cement market is expected to be driven off in near future in comparison to traditional cement and would have a lion's share in estimated global cement production of 6.0 billion tonnes by 2050. In global research scenario, clinker substitution is proved to be the most innovative approach and patenting around the reduction in clinker content in cement continues to rise. Not only has the number of patent filings related to this area increased rapidly in recent years, but the growth in such filings has outpaced that in other cement sub-sectors i.e., low carbon technologies (Figure 8.2). Therefore, manufacture of blended cements could play a greater role in achieving an average global clinker ratio of 0.60 by 2050, as set out by the 2018 Technology Roadmap, and has the potential to mitigate 0.29 gigatonnes (GT) of CO_2 in 2050 in the 2DS compared to RTS [4]. This is equivalent to 128% of current direct CO_2 emissions of global cement production.

Figure 8.1: Regional clinker to cement ratio in 2DS, low variability case

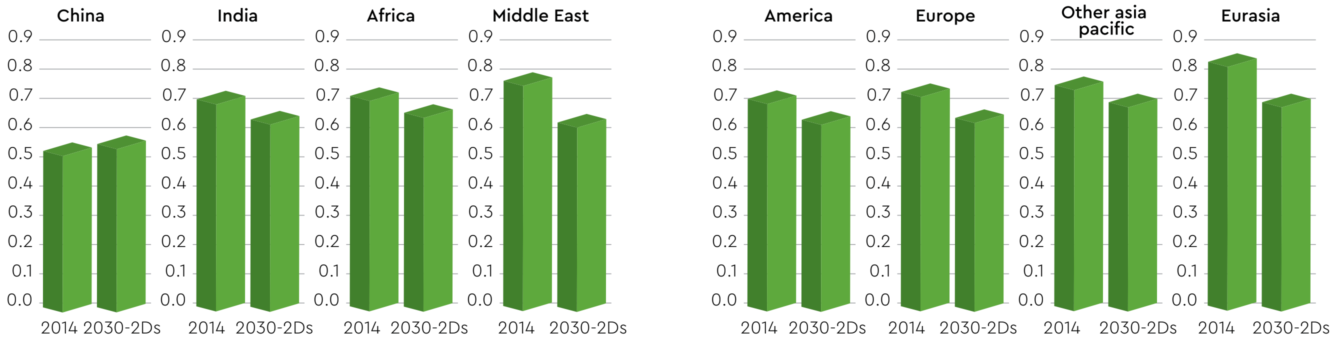
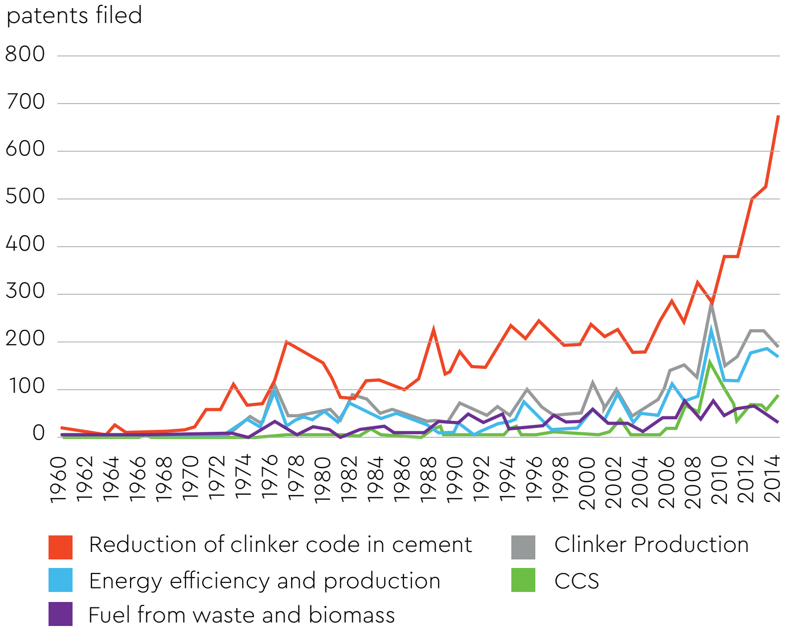


Figure 8.2: Patenting trends of low carbon technologies



8.2

STATUS OF SUPPLEMENTARY CEMENTITIOUS MATERIALS

Blast furnace slag and fly ash are the most proven material worldwide owing to their respective cementing and pozzolanic properties. IEA estimates that 480–560 MT blast furnace slag and steel slag were produced worldwide annually in 2014 and more than 675 MT fly ash is available globally, but highly variable quality of fly ash drives down the amount of fly ash used in cement, which is estimated at around 5% of global cement production [2]. The worldwide amount of slag available only around 5% of the total clinker production, whereas fly ash, although available in large amounts and not available in some countries (30% of the worldwide clinker) [6], is limited to 25–30% on mass basis in cements for technical performance reasons [2].

Silica fume, the third important industrial waste of relevance to the cement and concrete industry, is of limited availability, perhaps not exceeding 2.5 million tonne per year, and is used to make concretes for special applications.

Natural materials, such as clay and limestone are abundantly available but are used in smaller quantities at present. Limestone can also be used instead of clinker in cement. Limestone-containing cements typically have a reduced water demand, which results in better workability for concrete. It is estimated that cements using limestone as a filler currently represent 25–30% of the global cement production, and that the share will increase by up to 48% by 2050.

Cements based on calcined clay and ground limestone are considered to penetrate the market, reaching 27% of the global cement production by 2050. Recent developments benefit from optimized combinations of calcined clay and ground limestone as cement constituents, potentially enabling up to 50% clinker displacement without affecting cement properties.

With the above trends of availability and use of SCMs, it may be tentatively estimated that the production of blended cements could not have exceeded one billion tonne per year or about one-fourth of the total global production of cements. The most worrying tendency, however, is the flattening tendency of the clinker substitution trend in the subsequent years [WBCSD, 2015], particularly from 2010 onwards.

Extensive research is also going on in the area of multicomponent cement CEM-VI. The CEM VI are low-emission binders with very low CO_2 emissions in the range of 350–450 kgCO_2/T cement . The characteristic feature of these ternary composite cements is a higher concentration of a mixture of the two non-clinker main components in their composition. In this new group of composite cements CEM VI, the content of Portland clinker would not exceed 50% and the non-clinker component may be used from 50–65% maximum. Multi-component Cem-II cement, containing at least 50% clinker, is also standardized under EN-195–5–2021.

References:

1. CSI (Cement Sustainability Initiatives) (2017), "Global Cement Database on CO_2 and Energy Information", www.wbcsdcement. org/GNR, assessed January 2017, WBCSD, Geneva
2. ECRA-CSI (2017), European Cement Research Academy-Cement Sustainability Initiative (eds.), "Development of State of Art Techniques in Cement Manufacturing: Trying to Look Ahead", ECRA, Düsseldorf & Geneva (www.wbcsdcement.org/Technology)
3. Global Reports Store (2019), "Blended Cement Market Size, by Type (Grey Blended Cement, White Blended Cement), by Application (residential, non-residential, infr structure)-Global Opportunity Analysis and Industry Forecast 2019–25, Category: Building & Construction, Published on 2019.09.25.
4. IEA-WBCSD (2018), "Technology Roadmap: Low Carbon Transition in the Cement Industry", IEA & WBCSD-CSI
5. Lehne J and Preston F (2018), "Making Concrete Change Innovation in Low Carbon Cement and Concrete" (Chatham House Report), London,UK.
6. Scrivener K (2014), "Options for the future of cements", Special Issue: Future Cements, The Indian Concrete Journal, 88(7), p.11–21.
7. WBCSD (2015), Getting the Numbers Right: Project Emissions Report

9.0

WAY FORWARD FOR BLENDED CEMENTS AS A SUSTAINABLE BUILDING MATERIAL

9.1

INNOVATIVE CEMENTING MATERIALS AND CEMENT SYSTEMS

The iron and steel industry shift away from widely used blast furnace route towards scrap-based electric arc furnaces, which are less energy and carbon intensive. The coal-fired power plants significantly reduced their carbon footprint by switching over to renewable non-fossil sources, thus affecting the availability of fly ash in future. Because of a scarcity of these materials in future, it is estimated that the production of blast furnace slag and fly ash are projected to be around 16% of cement production in 2050 [17] and also increases the need to explore alternative cement constituents to avoid an increase in clinker to cement ratio and even to support its reduction. According to IEA-CSI, 2018, limestone (18%) and calcined clay (8%) could be the potential materials in future in the manufacture of blended cements by 2050 (2DS) in comparison to 2014 status where a major share goes to proven materials; granulated BF slag (13%) and fly ash (6%) (Figure 9.1). [12]

Figure 9.1: Global cement composition (Source: IEA-CSI, 2018)

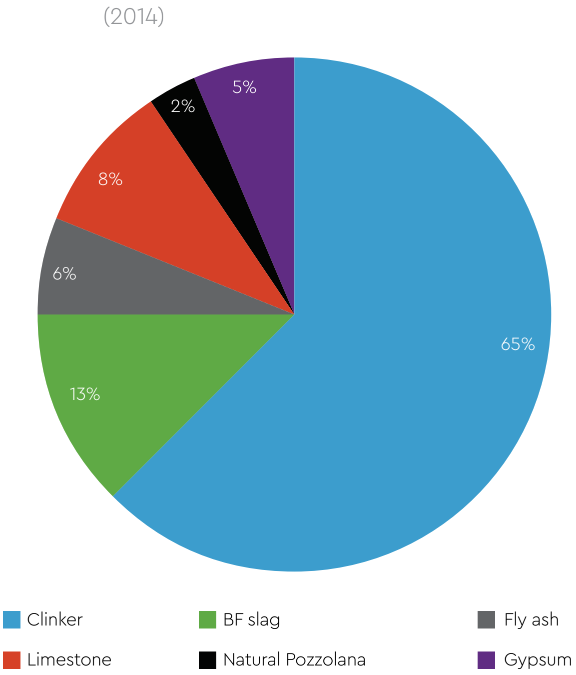
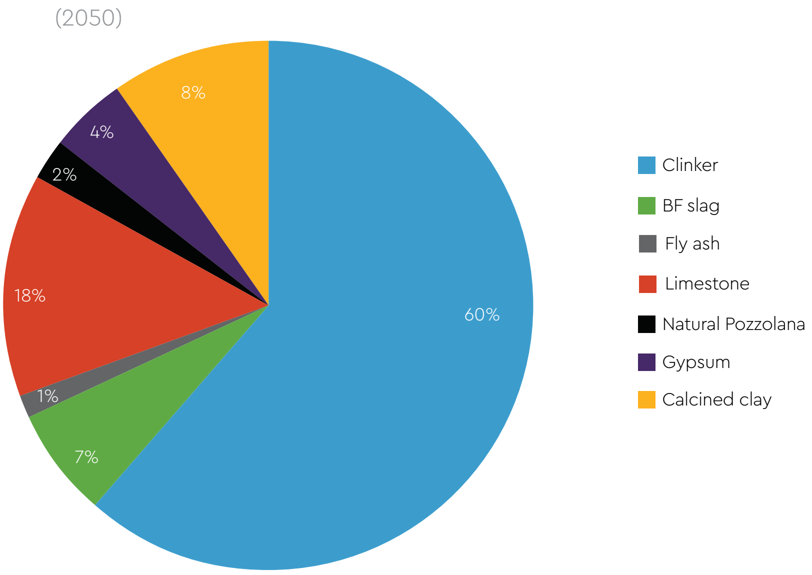


Figure 9.1: Global cement composition
(Source: IEA-CSI, 2018)



Limestone can be used as mineral constituent in manufacture of Portland Limestone Cement (PLC). Typically, the mass content of limestone in such cements is up to 35% [8]. Many studies reported the use of dolomite limestone [16, 19, 23], marble waste [1] as mineral constituents in development of Portland Dolomite Cement (PDC).

Presently, studies are going on in development of Portland Limestone Cement (PLC), Portland Dolomite Limestone Cement (PDC) and fly ash-limestone based composite cement by exploiting the synergy between aluminates from clinker/fly ash and carbonates from limestone.

PLC was initially developed in France and was later adopted by European standard allows up to 35% of limestone. At present, the production of these types of cements substantially increased around the world. Portland limestone cement is a potential cement; which India could also produce in near future. NCB is also carrying out extensive research on Portland Limestone Cement considering locally available raw materials and climate conditions. Initial results in this subject are encouraging and the codal formation of PLC is under consideration.

Calcined clay has been used in cement production from long time, with Brazil systematically producing about 2.0-million-tonne calcined clay annually, since 1970s [24]. Early strength decreases with higher proportion of calcined clay, but recent developments benefit from optimized combination of calcined clay and ground limestone as cement constituents, potentially enabling up to 50% clinker replacement (LC3) without affecting cement properties [24]. The global reserves of raw clays are considered effectively unlimited compared to global cement production volume, and cement based on ground limestone and calcined clay are considered to penetrate the market in a 2-degree scenario (2DS), reaching 27% of global cement production by 2050 [12]. Thermally treated red mud to the extent of 20% - 30 wt.% [11; 20] and construction and demolition (C&D) wastes could also be used as potential blending component in cement manufacture.

Jauffret and Glasser, 2016 observed that the substitution of up to 20–25 mass% of cement by half-burnt dolomite (thermally activated dolomite, under specific conditions to form a product composed of an intimate mixture of periclase (MgO) and calcite ($CaCO_3$) and acts as a supplementary cementitious material) was found to preserve the 28-days compressive strength of cement pastes, with maximum values being obtained for a substitution level around 10–15 mass% half-burnt dolomite. [14]

Research on cement replacement containing agro-based materials have shown great potential for their utilization as partial replacement for cement and aggregates in concrete production. The use of these wastes offer novel sustainable materials and contribute to greener construction, provided these wastes are burnt under controlled temperature and time to impart pozzolanic properties [15], including rice husk ash [2; 9; 18], sugarcane bagasse ash (SCBA), sintered in between 500–700°C [7; 10], palm oil fuel ash (POFA) [3; 4; 13], cassava waste ash (CWA) [21], corn cob ash [5], vegetable ashes [15], bamboo leaf ash (BLA) at 600°C [25], rice straw ash [22] etc.

9.2

R&D NEEDS FOR FUTURE

The Research & Developmet needs can be described as follows.

- Identify the availability of cement blending materials globally

- Need to continuously assess their properties on a global scale taking into account the varying nature of most cement blending materials and analyzing their carbon footprint, in addition to cement strength and durability.

- The availability of current materials and shifts in industrial process routes make it imperative that research efforts also focus on identifying and developing new cement blending materials. Calcined clay and red mud are possible candidates, and ongoing research is expected to provide critical information on their performance and durability.
- Need to investigate the use of non-conforming fly ashes, weathered steel slags, various non-conforming other steel slags like Basic Oxygen Furnace (BOF), Laddle Heat Furnace (LHF), Argon Oxygen Decarborised (AOD) and Electric Arc Furnace (EAF) slags etc. in cement manufacture.

- In the same context, similar benefits may be realized from valorizing other cementing materials, including electric arc furnace slag, vegetable ashes, agro-based products ash, animal wastes ash, bauxite residue, tailings from mining operations, municipal sludge waste etc.

9.3

NEWER DEVELOPMENTS IN BLENDED CEMENTS IN INDIA

In India, there are only three blended cements approved by BIS, namely, PPC, PSC and Composite Cement. The other blended cements namely Portland Composite Cement is based on both fly ash and limestone (PCC), Portland Limestone Cement (PLC), Portland Dolomitic Limestone Cement (PDC), Limestone Calcined Clay Cement (LC3) and multicomponent blended cements are at different stages of development in India. There is high need for commercialization of new blended cements after getting due approval from BIS.

Extensive research is also being carried out in the areas of new blended cements at NCB. In the project on preparation of Portland composite cement, blends are prepared with four types of clinker from different regions of India along with the regionally available fly ash and limestone. Performance evaluation of various mixes of limestone-fly ash, cement mortars were performed to investigate the effects of using different percentages of lime and fly ash as a replacement of cement on the compressive strength of such mortars at various ages. The blends were prepared using 15–35% fly ash and 5–10% of limestone samples. The results depicted that the clinker quality plays an important role on the performance of limestone and fly ash based composite cements.

Studies also taken up to investigate the feasibility of using different grades of limestone in the development of Portland Limestone Cement and to formulate new Indian standard for its commercialization. Different Portland Limestone Cement blends were prepared by inter-grinding as well as separate grinding & blending of 10, 15, 20, 25, 30 and 35 wt. % of cement grade, dolomitic, and low-grade limestone with clinker and gypsum. Long term durability studies are in progress for the prepared PLC blends.

Several types of research have been undertaken in India with respect to multi component blended cement (Limestone-calcined clay cement, Fly ash-calcined clay cement, marble dust-calcined clay cement, limestone-fly ash- granulated BF slag and dolomitic limestone-fly ash-granulated BF slag) at varying clinker factors (0.40 to 0.60). These multi component cements show a good potential concerning strength and durability.

Research is also ongoing in the area of High volume fly ash cement (HVFAC) enhancing the percentage of fly ash in PPC beyond the limit specified in the Indian standard codes. The fly ash content used in HVFAC blends is ranging from 35 to 55 wt%. These cement blends were prepared at Blaine's fineness of 350, 400 and 450 m^2/kg. The HVFAC is also prepared with fly ash mechanically and chemically activated. The above prepared high volume fly ash cement blends were evaluated for their oxide constituents, particle size distribution and physical characteristics such as Blaine's fineness, consistency, setting time, compressive strength at different ages, soundness and drying shrinkage according to different Indian standard test procedures. The cement blends which were investigated showed their performance at par with the Indian standard specification for fly ash based blended cements.

9.4

POLICY PRIORITIES AND REGULATORY FRAMEWORK

To encourage and facilitate reduction of clinker to cement ratio:

- Independent organizations to develop cement and concrete standards and codes that allow widespread use of blended cements while ensuring product reliability and durability at final applications to promote the use of blended cements.

- Government to promote the use of blended cements in sourcing and public procurement policies.
- Governments and industry to ensure traceability /labeling/ethical and responsible sourcing of construction materials.

- Industry and universities to conduct R&D into processing techniques for potential cement blending materials that cannot be used due to quality constraints.

- Industry to promote international training events with national standardization bodies and accreditation institutes, to exchange experience on reducing the clinker to cement ratio, cement and concrete standards and environmental and economic impact.

- Adopting the policy of **"Polluter has to Pay"**.

- Incentives to the users of industrial wastes and byproducts in manufacture of value-added products.

- Need to enhance market awareness and acceptability, because in some regions, users are reluctant to select blended cement over Portland cement.

- Need to introduce a freight subsidy for allowing the transportation of SCMs from surplus areas to cement clusters, where SCM availability is limited.

References:

1. Agarwal S K, Chaturvedi, S K, Saxena A (2018), "Investigation into the role of marble dust as mineral additive in cement manufacture", World Cement, March, p. 49–60.
2. Alex, Josephin, J. Dhanalakshmi, B. Ambedkar (2016), "Experimental investigation on rice husk ash as cement replacement on concrete production", Construction and Building Materials, 127, 353–362.
3. Al-mulali MZ, Awang H, Khalil HA, Aljoumaily ZS (2015), "The incorporation of oil palm ash in concrete as a means of recycling: A review", Cem. Concr. Compos., 55, 129–138.
4. Alsubari, Belal, Payam Shafigh, and Mohd Zamin Jumaat (2016), "Utilization of high vol ume treated palm oil fuel ash to produce sustainable self-compacting concrete", Journal of Cleaner Production, 137, 982–996.
5. Aprianti E, Shafigh P, Bahri S, Farahani J N (2015), "Supplementary cementitious materials origin from agricultural wastes", Construction and Building Materials, 74, 176–187.
6. Armstrong T (2018), "A review of global cement industry trends", International Cement Review, International Cement Review, CONCREATECH, New Delhi, November 2018.
7. Bahurudeen A, et al. (2015) "Assessment of pozzolanic performance of sugarcane bagasse ash", Journal of Materials in Civil Engineering, 28(2), 04015095.
8. ECRA-CSI (2017), European Cement Research Academy-Cement Sustainability Initiative (eds.), "Development of State of Art Techniques in Cement Manufacturing: Trying to Look Ahead", ECRA, Düsseldorf & Geneva (www.wbcsdcement.org/Technology)
9. Ferraro, R M and Nanni A (2012) "Effect of off-white rice husk ash on strength, porosity, and conductivity and corrosion resistance of white concrete." Construction and Building Materials, 31, 220–225.
10. Ganesan K, Rajagopal K, Thangavel K (2007): "Evaluation of bagasse ash as supplementary cementitious material." Cement and concrete composites 29 (6), 515–524.
11. Govindrajan D and Jayalakshmi G (2012), "Investigation on the influence of calcined red mud on cement hydration", International Journal of Recent Scientific Research, 3(12), p.1039–1041.
12. IEA-WBCSD (2018), "Technology Roadmap: Low Carbon Transition in the Cement Industry", IEA & WBCSD-CSI
13. Islam, Mohammad Momeen Ul, et al. (2016) "Mechanical and fresh properties of sustain able oil palm shell lightweight concrete incorporating palm oil fuel ash", Journal of Cleaner Production, 115, 307–314.
14. Jauffret G and Glasser F P (2016), "Thermally activated dolomite as pozzolanic addition to Portland cement", Advances in Cement Research, 28(6), 378–386 (https://doi.org/10.1680/jadcr.15.00110)
15. Martirena F and Monzò J (2018), "Vegetable ashes as supplementary cementitious materials" Cem.Concr.Res., 114, 57–64.
16. Mikhailova O, Yakavlev G, Maeva I, Senkev S (2013), "Effect of dolomite limestone powder on the compressive strength of concrete", Procedia Engineering, 57, 775–780.
17. Miller S A, John V M, Pacca S A, Horvarth A (2018), "CO_2 reduction potential in the global cement industry by 2050", Cem.Concr.Res., 114, 115–124
18. Naji G A et al. (2010) "Assessment of the effects of rice husk ash particle size on strength, water permeability and workability of binary blended concrete." Construction and Building Materials 24 (11), 2145–2150.
19. Preethi G and Arulraj G (2015), "Effect of replacement of cement with dolomite powder on the mechanical properties of concrete", IJISET – International Journal of Innovative Science, Engineering & Technology, 2(4)
20. Rebeiro DV, Labrincha JA, Morelli MR (2011a), "Effect of calcined red mud addition on the hydration of Portland cement", Material Science Forum, 727–728, p.1408–1411.
21. Salau M A, Efe E I, Olonade K A. (2012) "Structural strength characteristics of cement-cassava peel ash blended concrete." Civil and Environmental Research, 2.2
22. Surajit M and Sharma R P (2016), "Experimental investigation on strength and water permeability of mortar incorporates with rice straw ash", Advances in Materials Science and Engineering.
23. Szybilski M and Nocuń-Wczelik W (2015), "The effect of dolomite addition on cement hydration", Procedia Engineering, 108, 193–198.
24. UNEP (United Nations Environment Programme) (2016), "Eco-Efficient Cements: Potential, Economically Viable Solutions for a Low-CO2 Cement based Materials Industry", UNEP, Paris
25. Villar-cociña E, Morales E V, Santos S F, Savastano Jr H, Frias M (2011), "Pozzolanic be haviour of bamboo leaf ash: characterization and determination of the kinetic parameters", Cem.Concr.Comp., 33, 68–73

ANNEXURE 'A'

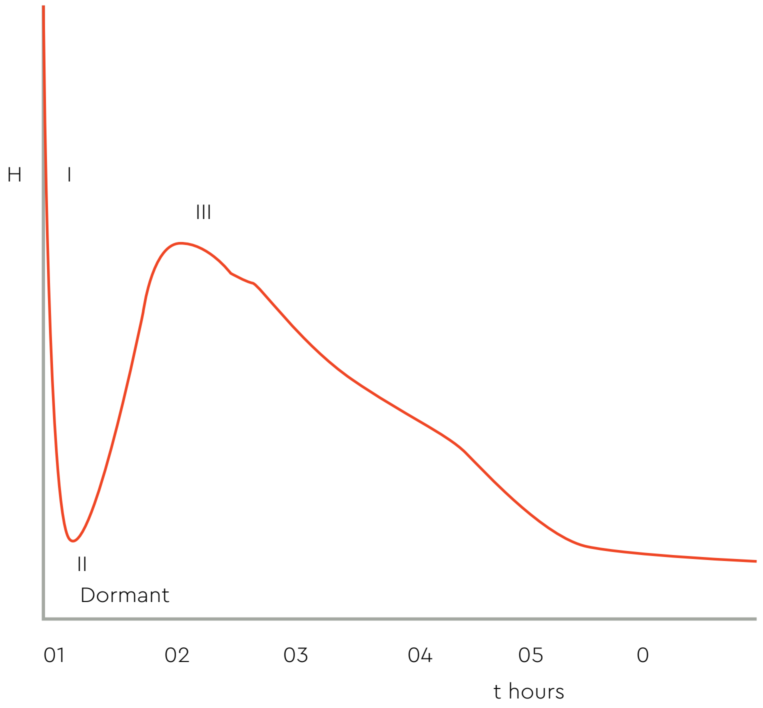
A.1

HYDRATION OF OPC, PPC, PSC AND COMPOSITE CEMENT

Primary compounds in Portland cement include calcium aluminates and calcium silicates. Compounds have the following notation: A=Al_2O_3, C=CaO, F=Fe_2O_3, H=H_2O, M=MgO, S=SiO_2, \$=SO_3. Calcium aluminates include tricalcium aluminate (C_3A) and ferrite (C_4AF), while calcium silicates include alite (C_3S) and belite (C_2S). Both calcium silicates induce similar hydration reactions. The principal hydration products are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). Other major products are ettringite (C-A-\$-H) and Monosulphate. Ettringite is formed when sulfate and tricalcium aluminate react in an aqueous medium. Monosulphate is the result of reaction of the excess tricalcium aluminate with ettringite compounds. When water is added to cement, the reactions which take place are mostly exothermic, that is, these reactions generate heat [1]. Almost immediately after the additionof water, some amount of the clinker Sulphates and gypsum dissolve and produce an alkaline, sulphate-rich solution. Soon after mixing, C_3A reacts with the water to form an aluminate-rich gel (Stage I on the heat of hydration curve, figure A.1). This gel reacts with Sulphates present in the solution to form small rod-like crystals called Ettringite. the Reaction of C_3A with water is highly exothermic but does not last long, only a few minutes, and is followed by a few hours of comparatively low heat evolution. This is known as the induction, or dormant period (Stage-II).

At the end of this dormant period, C_3S and C_2S present in the cement start to react, which leads to the formation of calcium silicate hydrate gel and calcium hydroxide. This represents the main period of hydration (Stage III), during which time concrete begins to gain strength. The period of maximum heat of hydration occurs typically between about 10 to 20 hours after mixing and then slowly tails off. In a mix that contains OPC only, most of the strength gain occurs within about a month. When PC gets partly replaced by other materials such as fly ash, strength gain occurs at a slower rate and may continue for several months or even up to a year. Ferrite reaction also starts immediately as water is added, but then gets slowed down, probably because a layer of iron hydroxide gel gets formed which coats the ferrite and acts as a barrier, preventing further reaction [1].

Figure A.1: Typical heat of hydration curve [2]



A.1.1

REACTIONS INVOLVED IN PROCESS OF HYDRATION OF OPC

Clinker contains silicates, C_3S and C_2S, aluminates C_3A and C_4AF.
Hydration of Alite and Belite is given by the following equations-

$$C_3S + 5.3H \rightarrow C_{1.7}SH_4 + 1.3CH$$
$$C_2S + 4.3H \rightarrow C_{1.7}SH_4 + 0.3CH$$

Hydration reactions of aluminates and ferrites in the absence and presence of gypsum is shown below:
Without gypsum, aluminate reacts with water to form hydro garnet.

$$C_3A + 6H \rightarrow C_3AH_6$$

In the presence of gypsum, aluminate reacts with gypsum and produces Ettringite

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$$

Once entire gypsum present in the system is consumed, Ettringite reacts with the remaining aluminate to form Monosulphate.

$$2C_3A + C_6AS_3H_{32} + 4H \rightarrow 3C_4ASH_{32}$$

Hydration reactions of Ferrite are similar to that of aluminate, as given below:

$$C_4AF + 10H \rightarrow C_3AH_6 + CH + FH_3$$
$$C_4AF + 3CSH_2 + 30H \rightarrow C_6AS_3H_{32} + CH + FH_3$$
$$2C_4AF + C_6AS_3H_{32} + 12H \rightarrow 3C_4ASH_{12} + 2CH + 2FH_3$$

However, in cementitious systems such as PPC, PSC and composite cement which contains supplementary cementitious materials or pozzolanic materials, the portlandite produced during primary hydration reaction gets consumed by the pozzolanic materials present in blended cements during the additional secondary hydration reaction to form secondary CSH gel as given below:

$$3CH + 2S \rightarrow C_3S_2H_3$$

Hence, in PPC, PSC or composite cement systems, the Ca(OH)2 content reduction occurs due to the secondary hydration reaction.

References for Annexure 'A'

1. Li, Jinxin, "Predicting early-age thermal behavior of mass concrete for bridge foundation." Graduate Theses and Dissertations.12659 (2012).

2.B. N. Winter, "Understanding Cement: An Introduction to cement production, cement hydration and deleterious processes in concrete." Retrieved from: https://www.understanding-cement.com/hydration.html#(2012)

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ACRONYMS

2DS	2-degree Scenario
AAR	Alkali Aggregate Reaction
ACI	American Concrete Institute
ACR	Alkali Carbonate Reaction
ASR	Alkali Silica Reaction
BIS	Bureau of Indian Standards
CC	Composite Cement
CEA	Central Electricity Authority
CH	Calcium Hydroxide
CSH	Calcium Silicate Hydrate
CSI	Cement Sustainability Initiative
DEF	Delayed Ettringite Formation
ECRA	European Cement Research Association
EN	European Standards
ESA	External Sulphate Attack
GBFS	Granulated Blast Furnace Slag
GCCA	Global Cement and Concrete Association
GGBFS/GGBS	Ground Granulated Blast Furnace Slag
HSC	High Strength Concrete
IEA	International Energy Agency
ISA	Internal Sulphate Attack
ITZ	Interfacial Transition Zone
LC3	Limestone Calcined Clay Cement
MT	Million Tonnes
NCB/NCCBM	National Council for Cement and Building Materials
OPC	Ordinary Portland Cement
PCC	Portland Composite Cement
PLC	Portland Limestone Cement
PPC	Portland Pozzolona Cement
PSC	Portland Slag Cement
R&D	Research & Development
RCC	Reinforced Cement Concrete
RCPT	Rapid Chloride Permeability Test
RHA	Rice Husk Ash
SCM	Supplementary Cementitious Materials
SF	Silica Fumes
WBCSD	World Business Council for Sustainable Development

About GCCA India

Global Cement & Concrete Association (GCCA) India launched in July 2019 to work with the Indian cement & concrete sector on Climate Change, Circular Economy, Health & Safety, SDGs, and Advocacy. It currently has 13 member companies, aggregating more than 65% of India's cement production capacity.

The GCCA exists to drive advances in sustainable construction to demonstrate industrial-sustainable leadership in cement and concrete manufacturing. It is working hard to enhance the cement and concrete industry's contribution to many important global, social and developmental challenges.

Sustainable development of the cement & concrete industry is at the very core of the GCCA's work and has five pillars: health & safety, climate change & energy, social responsibility, environment & nature, and circular economy.

The GCCA gathers and publishes data on the industry's sustainability commitments, guidelines, and initiating research. The GCCA 2050 Cement and Concrete Industry Roadmap for Net Zero Concrete is the collective commitment of the world's leading cement and concrete companies to fully contribute to building the sustainable world of tomorrow. More information about the 2050 roadmap and GCCA is available at https://gccassociation.org/.

GCCA INDIA MEMBER COMPANIES

ACC

Ambuja Cement
Giant Compressive Strength

MP BIRLA GROUP
BIRLA CORPORATION LIMITED

Dalmia Bharat

HEIDELBERGCEMENT

JK Cement LTD.

JSW Cement

NUVOCO
Shaping a new world

ORIENT CEMENT
CK BIRLA GROUP

Shree Cement

KAMAL CEMENT
SHREE DIGVIJAY CEMENT CO. LTD

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