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Review Paper

Effect of Different Supplementary Cementitious Materials on Mechanical and Durability Properties of Concrete

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ABSTRACT

Concrete is the most widely used composite in the world. Ordinary Portland cement (OPC) is the most commonly used binding material but the energy required for its production is large and its production leads to release of green house gases in the atmosphere therefore, the need for supplementary cementitious material is real. The utilization of Fly Ash (FA), Silica Fume (SF), Metakaolin (MK) and Ground Granulated Blast Furnace Slag (GGBS), as a pozzolanic material for concrete has received considerable attention in the recent years. This interest is a part of the widely spread attention directed towards the utilization of wastes and industrial byproducts in order to minimize the Portland cement consumption, the manufacture of which is being environment damaging. The paper reviews were carried out on the use of FA, SF, MK and GGBS as partial pozzolanic replacement for cement in concrete. The literature demonstrates that GGBS was found to increase the mechanical and durability properties at later age depending upon replacement level. Silica fume concrete performed better than OPC concrete even at early period for production of high strength concrete and high performance concrete. Fly ash increases the later age strength due to slow rate of pozzolanic reaction. Metakaolin was found to improve early age strength as well as long term strength but had poor workability.

1 Introduction

Cement production is one of the major sources of CO₂ emissions in the world. High cement content leads to an increase in greenhouse gases emission, which is highly relevant to global warming. Every ton of cement produced liberates about 1 ton of carbon dioxide [1], and the cement industry is responsible for almost 5% of the total global industrial energy consumption [2]. A reasonable solution for these problems is via the substitution of larger portions of the cement by supplementary cementitious materials without sacrificing its mechanical and durability properties [3]. Industrial wastes, such as blast furnace slag, fly ash and silica fume are being used as supplementary cement replacement materials. In addition to these, agricultural wastes such as rice husk ash, wheat straw ash, and sugarcane bagasse ash are also being used

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pozzolanic materials as partial cement replacement material [4,5]. Depending on the type of SCM, their use as partial cement replacement materials or as mineral additives have different effects on the properties of concrete. This is because they possess different chemical and mineralogical compositions, as well as different particle characteristics, which determine their water requirement, packing ability, as well as reactivity when used as part of binder for concrete. In general, the use of these materials in concrete has been associated with the refinement of the concrete pore structure. This in turn could affect the properties of concrete in the fresh and hardened states, including strength, deformation and durability performance [6–10]. Effect of different SCM on relative compressive strength of (HSC) high strength concrete with respect to OPC is shown in Fig.1-4[11]. However, concretes containing SCMs tend to have slower strength development especially at high cement replacement rates, since the Portland cement reaction (hydraulic) is much faster than the SCM reaction (primarily pozzolanic) [4].

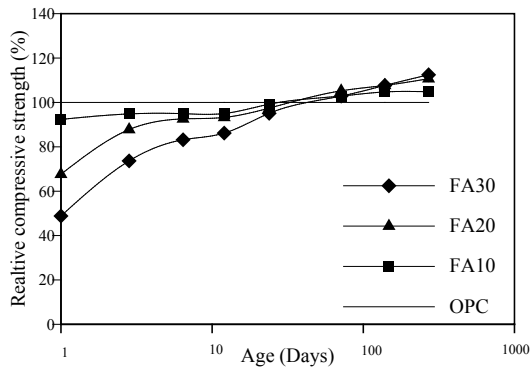


Fig. 1 – Effect of FA on relative compressive strength of HSC [11]

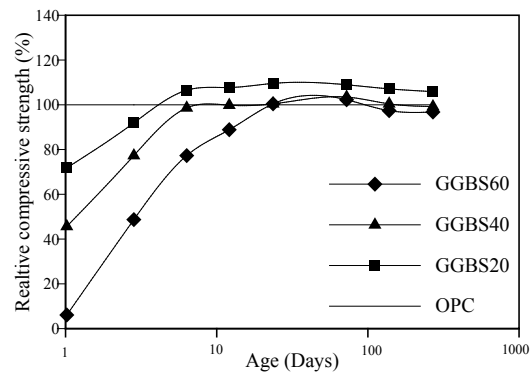


Fig. 2 – Effect of GGBS on relative compressive strength of HSC [11]

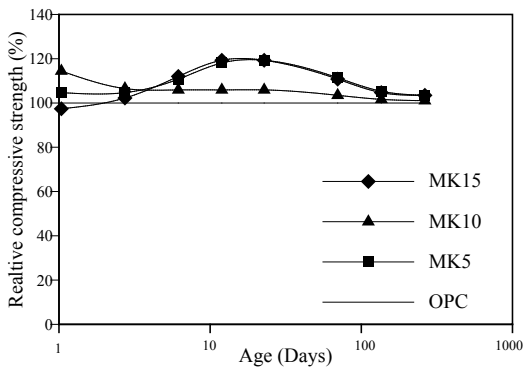


Fig. 3 – Effect of MK on relative compressive strength of HSC [11]

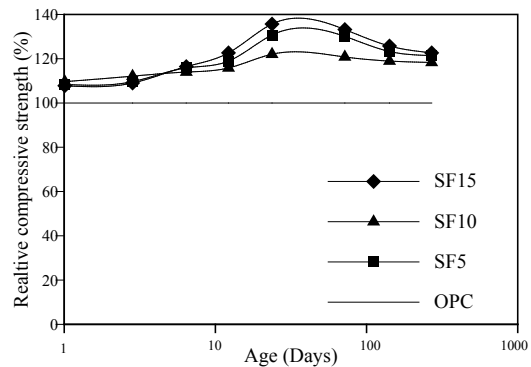


Fig. 4 – Effect of SF on relative compressive strength of HSC [11]

The pozzolanic reaction can only take place if there is available calcium hydroxide, a by-product of the hydraulic reaction. Therefore, a careful balance between the cement and SCM volumes is needed to ensure both reactions contribute to the strength. Achieving this balance requires a quantification of all the salient binder materials and their role in both hydraulic and pozzolanic reactions. A further challenge to using large volumes of SCMs is the inherent variability of the waste materials. Significant variation in performance is seen, a function of the source and type of SCM [12]. The concept of utilizing industrial and agricultural waste material or byproduct for production of concrete has a long and successful history, which includes fly ash, slag, metakaolin and silica fume. These once problematic, land filled waste materials are now considered valuable commodities for use in enhancing certain properties of concrete [13]. The objective of this paper is to review strengths and durability aspects of the use of silica fume, ground granulated blast furnace slag, fly ash and metakaolin as supplementary cementitious materials for concrete and mortar and to find out their viability to replace the OPC in concrete.

2 Research significance

As it has been reported in the introduction part that production of cement generates huge amount of CO₂ in the atmosphere and many researchers have recommended using supplementary cementitious material as substitute to cement in minimizing the CO₂ content and to reduce the cost of concrete. This study elucidates to understand the behaviour of SCMs as partial replacement of cement in the concrete. The main focus of this review work is to know the optimum content of different SCMs which includes silica fume, fly ash, metakaolin, ground granulated blast furnace slag and their influence on fresh, strength and durability properties. This investigation also demonstrates how these SCMs can be blended in adequate proportions for better performance of concrete.

3 Materials

3.1 Silica Fume (SF)

Silica fume is a by-product of silicon metal and ferro-silicon alloy industry instead of a waste product and its utilization in concrete technology has increased recently. It is an ultrafine powder collected as a by-product of the silicon and ferrosilicon alloy production and consists of spherical particles with an average particle diameter of 150 nm. This makes it approximately 100 times smaller than the average cement particle [14]. The bulk density of silica fume depends on the degree of densification in the silo and varies from 130 (undensified) to 600 kg/m³. The specific gravity of silica fume is generally in the range of 2.2 to 2.3. The specific surface area of silica fume can be measured with the BET method or nitrogen adsorption method. It typically ranges from 15,000 to 30,000 m²/kg [15]. Physical and chemical properties of silica fume are shown in Table 1. Silica fume is often used in two different ways: as a cement replacement, in order to reduce the cement content (usually for economic reasons); and as an additive to improve concrete properties (in both fresh and hardened states) [16,17].

3.2 Ground Granulated Blast Furnace Slag (GGBFS)

Ground granulated blast furnace slag (GGBS) is one of the ‘greenest’ of construction materials GGBS is obtained by quenching molten iron slag (a by-product of iron and steel-making) from a blast furnace in water or steam, to produce glassy, granular product that is then dried and ground into a fine powder. Physical and chemical properties of ground granulated blast furnace slag are shown in Table 1. The chemical composition of a slag varies considerably depending on the composition of the raw materials in the iron production process. To obtain a good slag reactivity or hydraulicity, the slag melt needs to be rapidly cooled or quenched below 800 °C in order to prevent the crystallization of merwinite and melilite.

3.3 Fly Ash (FA)

Fly ash is a by-product of the combustion of pulverised coal and is a pozzolanic material. When it is mixed with Portland cement and water, it generates a product similar to that formed by cement hydration but having a denser microstructure that is less permeable. Physical and chemical properties of fly ash are shown in Table 1. The fly ash replacement level as 15 - 25% is recommended for high strength concrete [18], while it can be used as more than 50% of total binder for normal strength concrete [19,20]. Two classes of fly ash are defined by ASTM C618: Class F fly ash and Class C fly ash [21]. The chief difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite). The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 20% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds. Fly ash produced from the burning of younger lignite or sub bituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime (CaO).

Table 1 Chemical compositions and physical properties of OPC and SCMs [11]

| Item | Cementitious materials, (%) | | | | |
|--------------------------------|-----------------------------|--------|--------|------|-------|
| | OPC | SF | MK | FA | GGBS |
| SiO ₂ | 20.69 | 94.02 | 51.6 | 47.8 | 35.84 |
| Al ₂ O ₃ | 4.72 | 0.43 | 41.3 | 24.9 | 14.00 |
| Fe ₂ O ₃ | 3.06 | 1.65 | 4.64 | 8.7 | 0.53 |
| CaO | 63.76 | 0.13 | 0.09 | 1.8 | 39.72 |
| MgO | 2.08 | 0.53 | 0.16 | 1.2 | 8.57 |
| MnO ₃ | - | - | - | - | 0.48 |
| TiO ₂ | - | 0.01 | 0.83 | 1.0 | 0.56 |
| SO ₃ | 2.92 | - | - | 0.9 | 0.15 |
| K ₂ O | 0.61 | 0.65 | 0.62 | 3.6 | - |
| Na ₂ O | 0.26 | 0.20 | 0.01 | 1.2 | - |
| LOI | 0.87 | 1.56 | - | 5.2 | 0.43 |
| <i>Compounds</i> | | | | | |
| C ₃ S | 53.9 | - | - | - | - |
| C ₂ S | 18.2 | - | - | - | - |
| C ₃ A | 7.2 | - | - | - | - |
| C ₄ AF | 9.2 | - | - | - | - |
| <i>Fineness</i> | | | | | |
| SSA (m ² /kg) | 380 | 20,000 | 15,000 | 380 | 426 |
| >45µm | - | - | - | 8.9 | - |

Note: OPC- Cement, SF- Silica Fume, MK- Metakaolin, FA- Fly Ash, GGBS- Ground Granulated Blast Furnace Slag

3.4 Rice Husk Ash (RHA)

Rice husk ash is an agro based material and obtained when rice husk, outer part of rice grain is burnt in controlled temperature below 700°C and the ash produced is amorphous in nature known as rice husk ash. Rice husk composes of organic constituents such as cellulose, lignin, fibre, and small amounts of protein and fat and certain range of minerals that include silica, alumina and iron oxides. It is estimated that 1,000 kg of rice grain produce 200 kg of Rice Husk; after Rice Husk is burnt, about 40 kg would become RHA. It contains about 80-85% silica which is highly reactive, depending upon the temperature of incineration [22].

3.5 Metakaolin (MK)

MK is an artificial pozzolan obtained from the calcination of kaolinitic clays at temperatures around 700–850 °C and its use in cementitious systems has been specified by ASTM C 618 [21]. The raw material input in the manufacture of Metakaolin (Al₂Si₂O₇) is kaolin. The high fineness of MK is expected to yield denser concretes and paste matrices, due to filling of the space between the cement particles [23]. Metakaolin on reaction with Ca(OH)₂, produces CSH gel at ambient temperature and reacts with CH to produce alumina containing phases, including C₄AH₁₃, C₂ASH₈, and C₃AH₆ [24,25]. The material is ground to a very fine particle size (1 to 2 µm) to increase its reactivity. Physical and chemical composition is shown in Table 1. Due to its high pozzolanic activity, the inclusion of MK improves the mechanical properties and durability of concrete.

4 Results and Discussions

4.1 Influence of Silica Fume (SF)

4.1.1 Workability of silica fume

Replacement of OPC with silica fume was found to decrease the workability and increase water demand for required slump due to being finer material. Bagheri [26] et.al observed increase in superplasticizer content of silica fume concrete compared to OPC concrete for required slump of 125 ± 25 mm with water binder ratio of 0.38. It was found that with increase in replacement level by silica fume, superplasticizer content also increase but combination of slag and silica fume decreases water demand compared to control mix. Sabet et.al [27] used superplasticizer content of 1.9% and 2.4% by mass of binder for 10% and 20 % silica fume respectively, which was more than control mix having superplasticizer content 1.4 % , for slump flow diameter of 600 ± 25 mm with constant w/b ratio of 0.32. Park [28] et.al found that high surface area of silica fume particles increases adsorption of superplasticizer (SP) and reduces the amount of SP available on the surface of cement particles resulting decrease in fluidity of the cementitious mixes. Mazloom et.al [29] showed that as replacement level of silica fume was increased from 6% to 15%, demand for superplasticiser also increases compared to control mix, to produce slump of 100 ± 25 mm with fixed water binder ratio 0.35. Khatri and Sirivivatnanon [30] reported that mixes incorporating high content of silica fume was found to be more cohesive compared to non-silica fume mixes. Shannag [31] found that using combination of constant 15% natural pozzolans and varied replacement level of silica fume from 5% to 20% with w/b ratio of 0.35, increase content of superplasticizer to obtain desirable workability. Concrete showed neither bleeding nor segregation because of the high total cementitious content and low water to cementitious ratios but density of most the concretes was found to be slightly lighter (about 4%) than normal weight concrete in the range of 2300 kg/m^3 . Koksai et.al [9] examined that addition of steel fibres in silica fume mix, decrease workability due to negative effect of steels fibres and increase in the content of silica fume as well as increase in volume fraction of steel fibres. In case of fibres, it was found that due to increase in volume fraction, number of fibres in unit concrete mixture becomes larger and the water absorbed on the surface becomes more, resulting in the obstructive effect of fibers on the flowability of fresh concrete [17].

4.1.2 Strength

Yan et.al [32] reported that use of silica fume as a replacement of OPC in concrete, improve interfacial zone because of the filler effect, crystallizing effect, and the pozzolanic effect of the silica fume. Jianyong and Pei [33] produced concrete by blend of silica fume and slag, which improve the compressive strength in later age but early age strength was less as compared to control mix. Yajun and Cahyadi [34] showed that concrete achieve significant strength at later ages i.e 56 and 90 days of curing with partial replacement of cement from 0% to 20% with water/binder ratio 0.4 but coarse silica fume agglomeration cannot react with $\text{Ca}(\text{OH})_2$ completely even at 90 days of curing age. Sabir [35] examined significant increase in strength at 7-day and 28-day for both the air-entrained and non-air-entrained samples for 5% and 10% replacement by condensed silica fume. This was due to two reasons, firstly high pozzolanicity, reacting with the calcium hydroxide to produce additional calcium silicate hydrate gel. Secondly due to extremely small particle size, acting as filler, reducing the porosity of the bulk cement matrix and resulting in a densified structure. Bagheri et.al [26] found improvement in rate of strength gain in ternary blends containing various dosages of silica fume to the mix containing 15% slag and in later ages shows improvements over control mix. It was also observed that ternary blends containing various dosages of silica fume to the mix containing 30% slag, decreases compressive strengths at all curing periods, however with progress of pozzolanic reactions at 90 and 180 days, the difference in strength became smaller. Sabet [27] et.al developed high performance self consolidating concrete (HPSCC) with 10% and 20% natural zeolite, fly ash and silica fume, which showed gain in strength continue over the 180 days of curing period. They reported that silica fume concrete exhibited higher strength than fly ash and natural zeolite at same replacement level. Guneyisi et.al [36] show that metakaolin and silica fume concrete had more compressive strength than control mix, with replacement level of 5% and 15% for w/b ratio of 0.25 and 0.35. It was observed that at low w/b ratio of 0.35, metakaolin concrete has more effect in strength gain than silica fume concrete. Poon et.al [37] also found similar results where silica fume and metakaolin increases the strength at or after 7 days and 3 days of curing respectively at low w/b ratio 0.50. Zaina et.al [38] examined the influence of high w/b ratios (0.45 and 0.50) on the strength development of high performance concrete (HPC). Concrete were cured in air dry and water curing condition. The concrete with water curing condition was found to have higher strength than air drying condition at all ages. This was due to continuous hydration of binding material. The authors [9, 32] showed that addition of

steel fibres into silica fume mix has maximum compressive, splitting and flexural tensile strength than all other mixes. Shannag [31] found that by using combination of natural pozzolan and silica fume, high to very high strength concrete can be produced, using total cementitious contents from 400 to 460 kg/m³, whose strength can be obtained from 69- 85 MPa at 28 days of curing.

4.1.3 Durability

4.2.3.1 Electrical resistivity

Electrical resistivity is important factor affecting corrosion in reinforced concrete regarding durability. According to ACI Committee 222, electrical resistivity of 20 kΩ cm is the minimum limit for corrosion propagation of steel rebar, above which corrosion will be low in concrete reinforcement [39]. Sabet et.al [27] observed that with 20% silica fume, concrete offered resistivity of 231 kΩ cm which was about 27 times the resistivity of control mix at 90 days of curing. This was due to higher pozzolanic reactivity of silica fume which results in denser structure of the paste. Bagheri et.al [26] examined binary and ternary blends containing silica fume and slag. They reported that ternary mixes had better performance than the binary mixes containing equal amounts of silica fume at 90 and 180 days. The effect of silica fume in increasing the electrical resistance was substantially higher than that of slag at all ages. This was attributed to the improvement in pore structure and reduction of (OH)⁻ in pore solution of concrete, which resulted increase in resistance of electrical resistivity.

4.1.3.2 Chloride penetrability and sorptivity

Poon et.al [37] investigated resistance of concrete against chloride ion penetration, which was expressed as total charge passed in coulombs during a test period of 6 hours. It was found that 5% SF replacement in concrete resulted in a lower total charge passed than a 5% MK replacement, but 10% MK replacement resulted in lower total charge passed than a 10% SF replacement, at both w/b ratios 0.3 and 0.5. However, silica fume and metakaolin indicate lower total charge passed through concrete compared to control mix. Guneyisi et.al [36] studied that concrete containing metakaolin and silica fume, at replacement level of 5% and 15% with water- binder ratio of 0.25 and 0.35, decreases gas permeability as well as water sorptivity compared to control mix as shown in Fig. 5 and 6 respectively. They observed that 15% MK incorporation provided 29% reduction in sorptivity values for both w/cm ratios, whereas, same level of SF replacement achieved 30% and 20% decrease in w/cm ratios of 0.25 and 0.35, respectively. This may be due to the pore refinement through filling and secondary hydration reaction of the mineral admixtures.

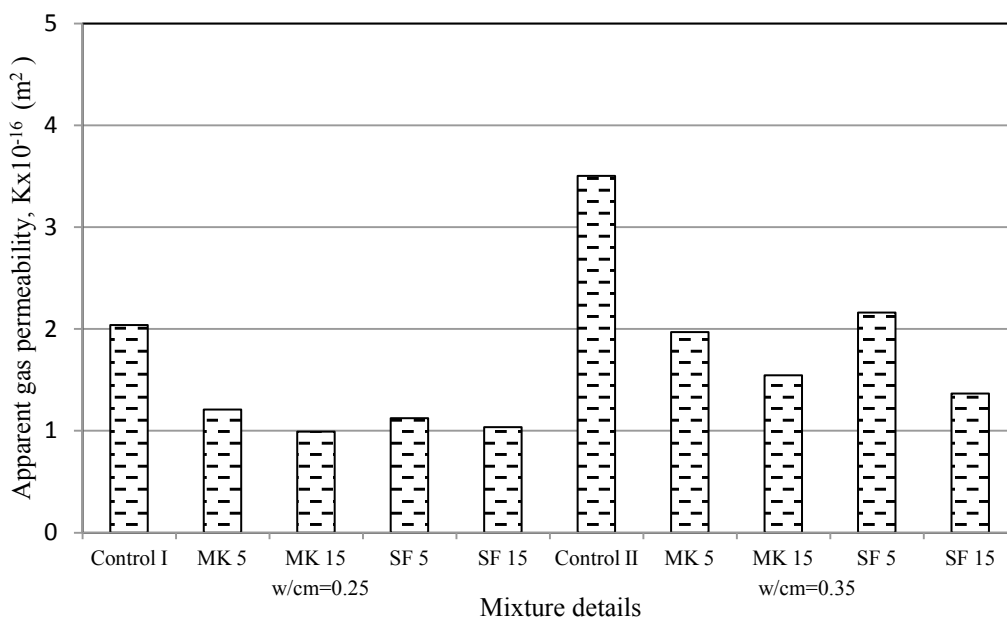


Fig. 5 - Effect of Silica Fume and Metakaolin on apparent gas permeability of concretes [36]

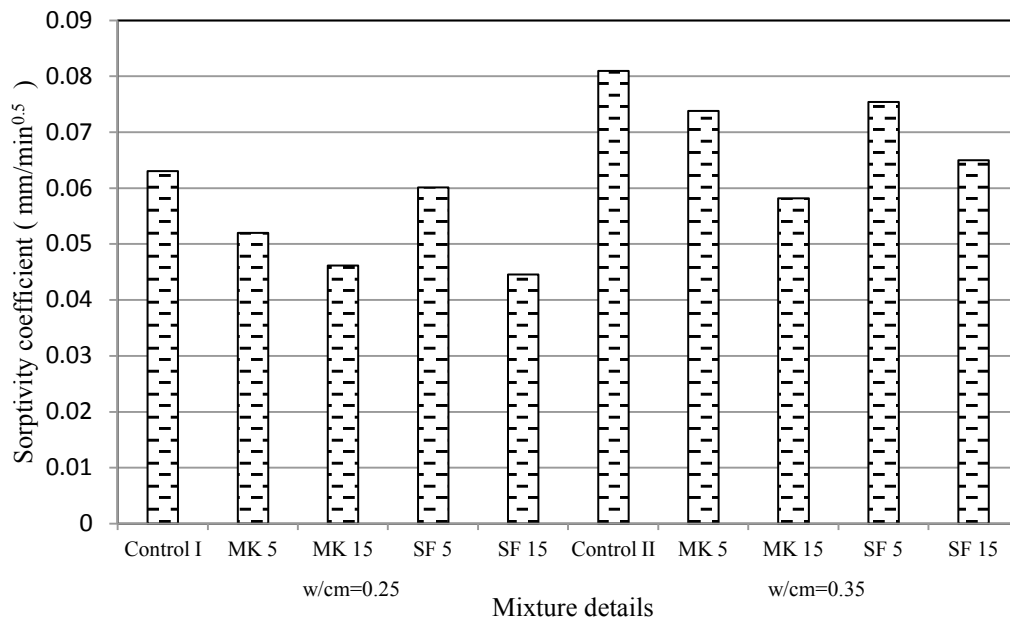


Fig. 6 - Effect of Silica Fume and Metakaolin on sorptivity coefficient of concretes [36]

Sabet et.al [27] found that with 10% and 20% natural zeolite, fly ash and silica fume, water absorption was less as compared to control mix. Replacement of cement by silica fume at 10% and 20%, reduced final absorption from 4.5% to 2.76% and 2.57% respectively which was better than natural zeolite and fly ash. They also discussed about chloride diffusion, by considering two parameters, effective diffusion coefficient (D_e) and surface chloride content. Silica fume was found to be most effective in reducing chloride penetration among three SCMs investigated. Chloride diffusion coefficient and surface chloride concentration of different concretes at 90 days of curing are shown in Fig 7.

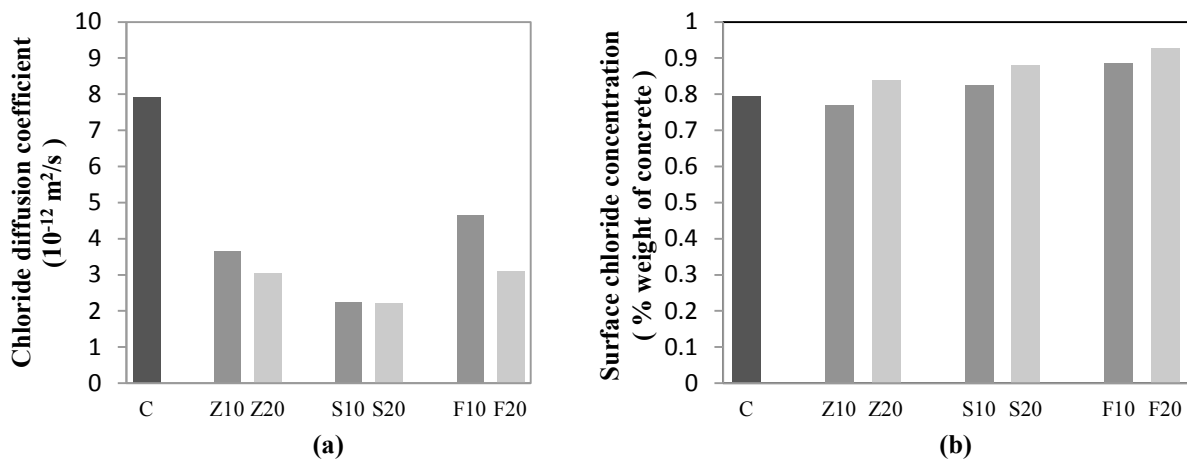


Fig. 7 - (a) Chloride diffusion coefficient and (b) surface chloride concentration of different concretes [27]

Elahi et.al [40] reported that, with 7.5% silica fume air permeability increases, whereas, 15% silica fume replacement decreases the air permeability at 44 days of curing compared to control mix. But at 91 days both 7.5% and 15% silica fume increases air permeability compared to control mix. This was found to be due two reasons, firstly, the sensitivity of the Autoclam may not be sufficient to pick up effects on air permeability at 91 days when the concrete is very dense. Secondly, the preconditioning prior to carrying out permeation tests may have created gradients of moisture through the concrete, which may have promoted micro structural modifications. They also reported that sorptivity results were found to be unchanged or slightly reduced for both replacements level than control mix at 44 and 91 days. The use of 7.5% SF was found to decrease the effective diffusion coefficient (D_e) by three times compared to the control mix but When the SF

content was increased from 7.5% to 15%, the associated decrease in D_c was only 5%. Therefore it could be considered that there is no real benefit in increasing the SF content beyond 7.5%.

4.2 Influence of Ground Granulated Blast Furnace Slag (GGBFS)

4.2.1 Workability of GGBS

The inclusion of GGBS in concrete increases workability in comparison to OPC concrete. Elahi et.al [40] examined that, with 50% and 70% slag at fixed w/b ratio of 0.30, increases the slump compared to control mix. It was reported that, to achieve the required slump of 60-90 mm, percentage of superplasticiser used was less in control mix than 50% and 70 % slag concrete but 50% slag concrete had more slump than 70% slag concrete. Johari et.al [11] observed increase in the slump from 110 to 200 mm, as OPC replacement was increased from 0% to 60% at constant superplasticizer content and w/b ratio 0.28. The improved workability exhibited by the concrete containing GGBS could be attributed to better cementitious particle dispersion and the surface characteristics of the GGBS particles, which are smooth and dense, and thus absorb little water during mixing [25]. Oner and Akyuz [41] concluded that, as GGBS content increases, water-to-binder ratio decreases for the same workability, and thus, indicating positive effect of GGBS on the workability. Boukendakji et.al [42] formed Self-compacting concrete (SCC), incorporating GGBS at 10%, 15%, 20% and 25% with two types of superplasticizer, based on polycarboxylate and naphthalene sulphonate, which increases the workability compared to control mix. Concrete with polycarboxylate based superplasticizer showed better workability than naphthalene sulphonate.

4.2.2 Strength

According to ASTM C 989, GGBS is classified into three grades – Grade 80, Grade 100, and Grade 120, depending on the relative compressive strength [43-45]. It is observed [46,47] that, increase in slag replacement by weight, decreases the strength of concretes in short term as compared to control concrete, but long term strength of concrete containing slag exhibits same or more than that of control mix. Boukendakji et.al [42] observed that, as replacement level was increase from 0% to 25% slag, there was decrease in early age strength although later age strength was comparable to control mix. Bilim et.al [46] studied three different cement dosages with three different water–binder ratios (0.30, 0.40 and 0.50) which shows that, slag replacement by weight decreases the strength of concretes at early ages compared to control mix. This was attributed to the relatively slower rate of pozzolanic hydration process. It was noted that at later age, slag undergoes hydration reactions in the presence of water with calcium hydroxide, resulting in C–S–H paste and exhibits an equivalent or greater final strength than that of control mix [48,49]. Elahi et.al [40] produced high performance concrete (HPC), with 50% and 70% GGBS, which shows reduction in the compressive strength at all ages. They reported that, with addition of 7.5% silica fume to the 50% GGBS has more strength than control mix at later age. Hannesson et.al [50] examined that at later age, strength exhibits beyond 60% replacement level of OPC by GGBS, whereas, early age strength was less for all replacement level from 20% to 100%. Li and Zhao [51] found that using combination of 25% FA and 15% GGBS had adequate early-age compressive strength, as well as maintaining long-term strength higher than PCC. Khatib and Hibbert [47] show that 80% replacement of cement by GGBS reduces strength at all ages but beyond 28 days of curing, with 40% and 60% GGBS, strength was greater than control mix. They also reported that combination of 10% metakaolin (MK) into GGBS mix, increases compressive strength during early age. This was due to higher reactivity of MK and faster rate of hydration process. Chen et.al [52] investigated compressive strength of high slag blast furnace cement (HBFC) by varying three parameters i.e. (W/B) ratios, curing environments, and curing durations. Curing condition was found to be more effective among three parameters. Seawater immersion and marine atmospheric curing were done to the concrete mixes. Results show that HBFC concrete was inferior to OPC concrete at all curing period under seawater. This was due to the slow hydration rate of the HBFC, although difference in strength decrease with increase of curing period. However in marine atmospheric curing, all HBFC concrete obtained superior strength than OPC concrete after 28 days except mix with w/b ratio of 0.36. Teng et.al [53] found that with 30% (UFGGBS) ultra fine ground granulated blast slag, compressive and flexural strength was more than control concrete even at 3 days of curing. They also reported that low w/c ratio has more enhancement in strength than high w/c ratio.

4.2.3 Durability

4.2.3.1 Air permeability

Elahi et.al [40] observe increase in air permeability at all ages, with 50% and 70% GGBS compared to control mix. Further it was found that, 50% GGBS yielded lower value of sorptivity at 44 days compared to 91 days, whereas, increasing the GGBS content to 70% significantly increases the sorptivity at 44 days but considerably reduces the sorptivity at 91 days. Oner and Akyuz [41] showed that as the hydration of the portland cement occurs, production of portlandite crystal $[\text{Ca}(\text{OH})_2]$ and amorphous calcium silicate hydrate gel $[\text{C}_3\text{S}_2\text{H}_3]$ (C–S–H) take place in large amounts. The hydrated cement paste was found to have approximately 70% C–S–H, 20% $\text{Ca}(\text{OH})_2$; 7% sulpho-aluminates and 3% secondary phases. The $\text{Ca}(\text{OH})_2$ formed affects the quality of the concrete adversely by forming cavities as it is partly soluble in water and lacks enough strength but its strength can be increased by using GGBS which has positive binding effect with $\text{Ca}(\text{OH})_2$.

4.3.3.1 Chloride penetrability and electrical resistivity

Chloride diffusion coefficient is strongly dependent on the period of exposure of concrete to a chloride environment. Chen et.al [52] found that chloride diffusion coefficient of high slag blast furnace cement (HBFC) concretes was lower than OPC concretes, indicating low mobility of chloride ions due to reduction in the number of interconnected pores or the chemical binding with the cement hydrates. It was also found that air-cured specimens have lower chloride penetrability than seawater-cured specimens. Elahi et.al [40] found that value of effective diffusion coefficient (D_e) decreases three fold with the use of 50% GGBS and a further increase to 70% GGBS did not improve the chloride diffusivity substantially but addition of 7.5% SF to 50%GGBS resulted in the best performance for resisting chloride ion transport through HPCs. Teng et.al [53] studied that addition of 30% ultra fine ground granulated blast slag (UFGGBS) achieve lower chloride migration coefficient compared to the control mixes regardless of the curing age but inclusion of 30% UFGGBS was found to more beneficial than reducing the w/c ratio of concrete from 0.35 to 0.28. It was also observed that by using Wenner probe method electrical resistivity of UFGGBS concrete increase compared to control mix, resulting in low corrosion rate of UFGGBS concrete. Lubeck et.al [54] examined the increase in electrical resistivity of 50% and 70% slag concrete compared to concrete containing white and grey Portland cement and addition of activator accelerates electrical resistivity gains. However, addition of activator with 50% slag has more electrical resistivity than 50% slag without activator for white cement at 56 days but at 91 days 50% slag without activator has more resistivity. For grey cement, 50% slag without activator has lower resistivity than 50% slag with activator at all ages. Bagheri et.al [26] observed increase in electrical resistivity and chloride penetration of GGBS concrete compared to reference mix at 7 and 28 days of curing, as replacement but at 90 and 180 days shows improvement as replacement. Gao et.al [55] showed that pozzolanic reaction of GGBS consumes $\text{Ca}(\text{OH})_2$. GGBS significantly decrease the content of $\text{Ca}(\text{OH})_2$ crystals in the aggregate–mortar interfacial transition zone (ITZ) and reduce the mean size of $\text{Ca}(\text{OH})_2$ crystals. The reduction in mean size of $\text{Ca}(\text{OH})_2$ crystals make the microstructure of ITZ more dense. It [56–58] was found that C–S–H gel was produced due to the end reaction between slag and $\text{Ca}(\text{OH})_2$ which leads to enhancement in strength and durability of concrete.

4.3 Influence of Fly Ash (FA)

4.3.1 Workability of fly ash

Addition of fly ash as partial replacement of cement increases the workability of concrete. Khatib [59] developed SCC by replacement of OPC from 0% to 80% fly ash with fixed w/b ratio of 0.36. It was found that all mixes obtained slump flow of diameter greater than 700 mm except control mix, which indicates increase in workability with fly ash compared to control mix at same dosage of admixtures 0.7% by mass of binder. Siddique [60] investigated that incorporating high volumes of Class F fly ash with 40%, 45% and 50% partial replacement of OPC, shows increase in the slump varying from 85, 90 and 100 mm respectively. Toutanji et.al [61] observed decrease in the dosage of superplasticizer of fly ash concrete compared to reference mix, when replacement of OPC was increased from 0% to 30% by fly ash. Wei et.al [62] investigated the fluidity of mortars with high calcium fly ash and low calcium fly ash, as replacement of OPC from 30% to 70% at constant w/b ratio of 0.26. It was also reported that high calcium fly ash mortar reduce the required dosage of superplasticizer, with same water binder ratio to obtain similar flow compared to low calcium fly ash at all replacement levels. Low calcium fly ash was found to increase the dosage of superplasticizer, when replacement was increased from 45% to 70%. This was found to be due to difference in volcanic glass activity of high calcium and low calcium fly ash.

Hassan et.al [63] showed that 30% replacement of cement by fly ash, decrease the w/b ratio compared to reference mix. Sabet et.al [27] found that Self consolidating high performance concrete (SCHPC) decrease demand for superplasticizer as replacement of OPC by fly ash was increased upto 20% with constant w/b ratio 0.33. This was due to spherical geometry of fly ash particles which easily roll over one another and reduces friction at the aggregate-paste interface, which produces ball-bearing effect at the point of contact resulting in less demand of superplasticizer to reach target fluidity. Das and Pandey reported [64] that with increase in the replacement of fly ash, w/b ratio decrease compared to control mix for same compressive strength. W/B ratio was found to increase with increase in fineness of fly ash although w/b ratio was less than control mix for all types of fineness of fly ash.

4.3.2 *Strength*

Use of fly ash as partial replacement of cement decreases the early strength of concrete due to slower rate of pozzolanic reaction of concrete but attains strength equivalent or more than OPC concrete at later age. Calvo et.al [65] studied the influence of calcium nitrite (CNI) and fly ash on the long-term compressive strength of high performance concrete (HPC). Cement blended with 8% silica fume was replaced by fly ash from 0% to 40% at three different w/b ratios of 0.29, 0.37 and 0.45. Addition of CNI to concrete containing fly ash, compressive strength increased for all w/b ratios. Hassan et.al [63] showed that incorporation of 30% fly ash with w/b ratio of 0.29, decrease the compressive strength at early age compared to reference concrete and obtained similar strength at 28 days as OPC but increase strength after 1 year. Siddique [60] used three percentages of high volume class F fly ash at 40%, 45% and 50%, as replacement of cement, which shows decrease in compressive, tensile and flexural strength at all ages compared to reference mix. It was found that with increase in curing period upto 91 and 365 days, significant improvement was observed in strength due to pozzolanic reaction of fly ash. Shuang [66] investigated that incorporation of fly ash from 0% to 30%, as replacement of cement, decrease compressive and flexural tensile strength of concrete and mortar at 28 days of curing compared to control mix. Increase in strength of fly ash concrete and mortar was observed after 56 and 90 days of curing due to the pozzolanic reaction of fly ash. The optimum replacement level of fly ash was found to be 15%-20% for compressive strength and 20% for flexural strength. Toutanji et.al [61] found about 50% reduction in compressive strength with addition of 30% fly ash after the curing period of 14 days. The reduction in strength of concrete was attributed to the slow rate of pozzolanic reaction of fly ash, which require longer period of curing for gain of strength compared to OPC concrete. Kou et.al [67] observed that compressive strength of recycled aggregate concrete (RAC) decrease at 28 days, when fly ash was used from 0% to 35% as partial replacement of cement with w/b ratio of 0.45 and 0.55. However, gain in strength development of RAC was found between 28 and 90 days of curing, due to pozzolanic effects of fly ash at late ages and lower w/b ratio increase compressive strength compared to high w/b ratio. Sabet et.al [27] reported increase in Self consolidating high performance concrete (SCHPC) compared to control mix at 28 days of curing, which was due to pozzolanic reactivity and filling of voids between cement grains by small particles of fly ash.

4.3.3 *Durability*

4.3.3.1 *Electrical resistivity and conductivity*

Das and Pandey [64] found that electrical conductivity of fly ash concrete decrease with increase in replacement and fineness of fly ash. Fineness of 305 m²/kg and replacement level of 35% fly ash shows lower electrical conductivity among all mixes, with 700 coulombs of current passing through it, which shows concrete of very low permeability. Sabet et.al [27] reported that incorporation of 10% and 20% fly ash increase electrical resistance of Self consolidating high performance concrete (SCHPC), which was about 3.5 and 6 times resistivity of control mix respectively.

4.3.3.2 *Carbonation and chloride penetrability*

Das and Pandey [64] studied the influence of three types of fly ash fineness on the carbonation of concrete. Cement was replaced by fly ash at 15%, 25% and 35% with Blaine's fineness of 200, 225 and 305 m²/kg for each replacement level. With increase in fineness of fly ash, carbonation depth of concrete was found to decrease compared to control mix. Fly ash with fineness of 305 m²/kg showed lower carbonation depth among mixes at all curing periods. Kou et.al [67] showed that recycled aggregate concrete (RAC) decrease resistance to chloride ion penetration compared to control mix, when recycled aggregate content was increased from 0% to 100% at w/b ratio of 0.45 and 0.55. Use of fly ash as partial replacement of cement from 0% to 35% in RAC was found to increase resistance to chloride ion penetration. Lower w/b ratio increase

resistance to chloride penetration due to decrease in volume pores of concrete resulting in impermeable concrete. Sabet et.al [27] found that fly ash concrete reduce chloride diffusion coefficient compared to control mix, which was due to pozzolanic effect and chloride binding by the aluminates phases during the ponding time. Sengul and Tasdemir [68] investigated that replacement of Portland cement by 50% fly ash improve resistance to chloride ion penetration (RCPT) compared to control mix at w/b ratio of 0.6 and 0.38. For w/b ratio of 0.60, reduction in rapid chloride permeability of fly ash concrete was about 86% and 97% for 28 and 90 days of curing respectively. For w/b ratio of 0.38, reduction in rapid chloride permeability of fly ash concrete was about 92% for 90 days of curing. It was also reported that inclusion of pozzolans was more effective than water/cement ratio in reducing rapid chloride permeability of concrete.

4.4 Influence of Metakaolin (MK)

4.4.1 Workability

Use of MK in concrete mix decrease workability which requires either increase in the amount of mixing water or the use of high range water reducing admixture (HRWRA). Paiva et.al [69] found that high range water reducing admixtures improve the workability at a given amount of mixing water or lead to the same workability with a great reduction in water content. Madandoust and Mousavi [70] observed slump flow values between 660 and 715 mm for SCC, by adjusting dosage of high range water reducing admixture (HRWRA) for varying w/b ratio from 0.32 to 0.45. Results show that lower amount of HRWRA was required for mixes with higher W/B ratio, at similar MK content, to maintain the slump flow in a desire range as shown in Fig. 8. This was attributed to the increase in the lubrication between the fine particles with increasing W/B ratio, which resulted in reducing the yielding stress and better flowability.

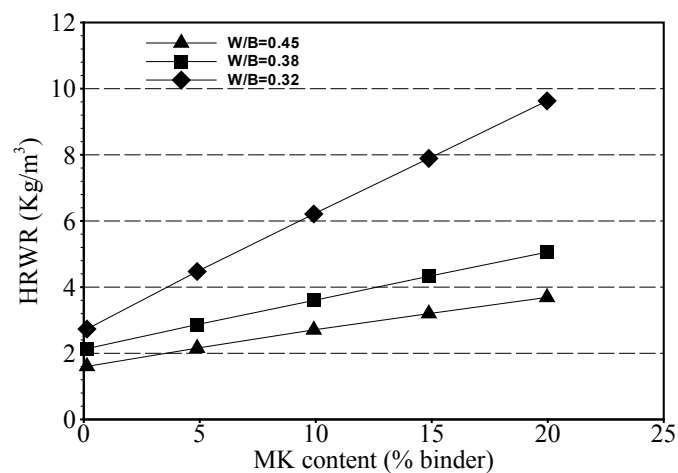


Fig. 8 - HRWR dosage for different w/b ratios [70]

Hassan et.al [63] examined that incorporation of MK increases the viscosity of SCC mixtures. When MK content was increased from 0% to 25% as partial replacement of OPC, the amount of HRWRA increases by 30% for desirable slump of 650 mm, which shows that addition of MK increases demand of HRWRA for SCC mixtures. Karahanet.al [71] showed that self consolidating lightweight concrete (SCLC) with w/b ratio 0.33 achieved the desired slump flow in the range of 700 ± 10 mm but HRWR amount increased from 0.38 to 1.63 kg/m^3 , as metakaolin content was increased from 0% to 15%. They also reported about filling and passing ability of SCLC mixtures, which shows decrease with the increase of metakaolin content. Authors found [72,73] that addition of (HRWRA) causes adsorption on the particle surface, which deflocculates, releasing water to lubricate the system and facilitate the air expulsion retained inside the particles agglomerates.

4.4.2 Strength

Incorporation of meta kaolin in concrete as partial replacement of OPC, increases early strength of concrete due to faster rate of pozzolanic reaction. Courard et.al [74] prepared mortar with partial replacement of cement from 5% to 20% MK which shows decrease in bending and compressive strength during first days compared to control mix but achieved

more strength in bending and compressive after 14 and 7 days respectively. Madandoust and Mousavi [70] shows that presence of MK improves early and long term, compressive strength as well as splitting tensile strength of SCC with three different w/b ratios 0.32, 0.38 and 0.45. They also reported that at same MK content, the compressive strength of the concrete specimens increases with a lower w/b ratio. Wild et.al [75] found that increase in compressive strength of metakaolin concrete due the filling effect of MK particles, accelerating the cement hydration and pozzolanic reaction of MK with calcium hydroxide. The optimum replacement level of 20% MK was found to give maximum long term strength. Masour et.al [76] studied the influence of metakaolin on compressive strength of mortar, which was obtained by calcining kaolin at 850°C or 3 hour. Mortar prepared with 10%, 20% and 30% MK as partial replacement of OPC shows increase upto 20% MK and further increase in replacement of MK to 30%, decreases compressive strength compared to reference mix. Among three replacement levels, 10% MK shows highest strength at all ages. Ramezaniapour and Jovein [77] observed that as w/b ratio decrease from 0.5 to 0.4 and 0.4 to 0.35 for 10%, 12.5% and 15% MK, compressive strength of MK concrete increases compared to control mix at all curing periods. When metakaolin content increases from 12.5 to 15% for w/b ratio 0.4 and 0.35, strength was found to decrease for 15% MK compared to 12.5% MK as shown in Fig.9. The reduction in compressive strength for 15% MK compared to 12.5% MK was due to clinker dilution effect. Parande et.al [78] examined compressive strength of mortar and concrete made with partial replacement of OPC by metakaolin from 0% to 20%. Concrete and mortar shows increase in compressive strength, with increase in replacement of MK compared to reference mix but more than 15% replacement decrease strength compared to other replacement levels. This decrease was found to be due to compounding effect. Hassan et.al [63] prepared SCC with metakaolin by partial replacement of OPC. Metakaolin was varied from 3% to 25%, with constant w/b ratio of 0.40, which shows increase in compressive strength after 28 days of curing except 3% MK compared to reference mix.

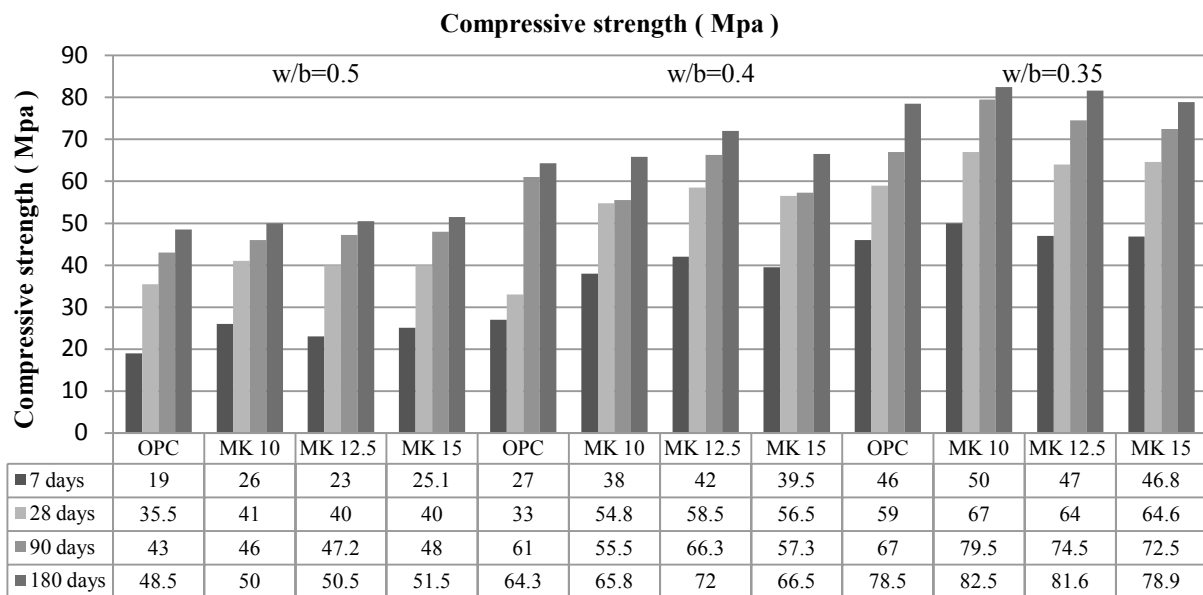


Fig. 9 - The effect of Metakaolin on the compressive strength at various ages [77]

4.4.3 Durability

4.4.3.1 Sulphate attack

Due to being very fine material, incorporation of metakaolin in concrete enhances microstructure and reduces porosity resulting improvement in durability properties. Courard et.al [74] found that OPC mortar exhibits expansion after only a few days and variation in length observed was 3.7% after 84 days. They reported that metakaolin has positive effect on mortar durability in the sulfate environment, by consuming $\text{Ca}(\text{OH})_2$ and metakaolin-modified mortar shows inhibition of sulfate attack, especially for more than 10% replacement of cement part. Khatib and wild [79] examined increase in resistance to sodium sulphate (Na_2SO_4) solution for mortar, prepared with partial replacement of high C_3A and intermediate C_3A cement by metakaolin from 5% to 25%. Decrease was observed in expansion of mortar with increase in MK content

for both types of cement. For mortars made with high C_3A cement, expansion in Na_2SO_4 solution is very rapid for compositions containing up to 10% MK but for mortars made with intermediate C_3A cement, expansion does not appear upto 300 days and only specimens with low MK levels actually expand. Sulphate resistance was found to increase as the replacement level of cement with MK increases, up to at least 25% replacement. Authors [80,81] showed that the initial hydration products of cement and MK are C-S-H gel, C_4AH_{13} and C_2ASH_8 which are less dense than hydrogarnet which appear later on.

4.4.3.2 Water absorption

Courard et.al [74] prepared mortar with 5% to 20% MK, as partial replacement of cement, which shows increase in water absorption at all replacement levels compared to reference mix. It was found that MK provides a denser structure to concrete due to microfilling and secondary pozzolanic reactions [37,75]. Madandoust and Mousavi [70] studied absorption characteristics of the SCC concrete, which shows decrease in water absorption with increase in metakaolin, as replacement of OPC from 5% to 20%, at varying w/b ratios. At lower w/b ratio, significant decrease was observed in absorption characteristics of concrete with inclusion of MK. Ramezani pour and Jovein [77] found decrease in sorptivity of MK concrete with the period of curing. They reported increase in sorptivity with increase in w/b ratio but replacement of 10% MK performed better compared to other replacement levels irrespective of w/b ratio and testing age as shown in Fig.10.

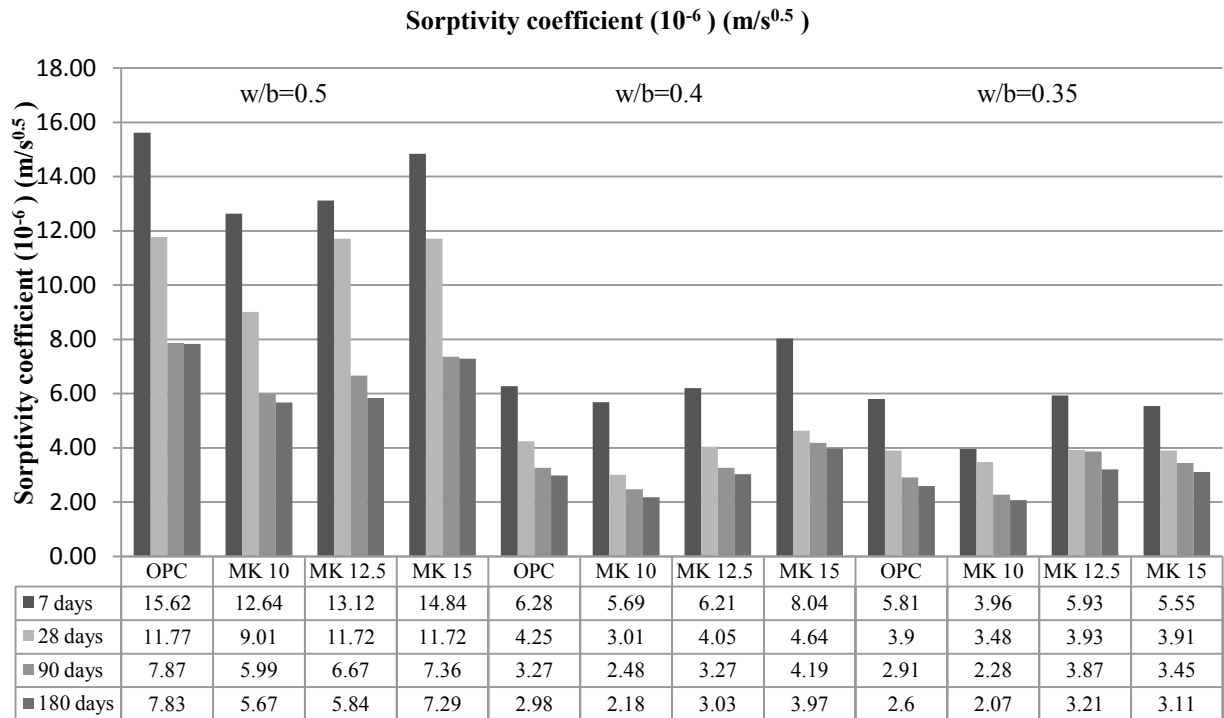


Fig. 10 - The effect of Metakaolin on the sorptivity coefficient (10^{-6}) ($m/s^{0.5}$) at various ages [77]

4.4.3.3 Chloride penetrability and electrical resistivity

Guneyisi et.al [82] formed chloride contaminated concrete by partial replacement of OPC with 5% and 15% MK. Concrete containing 0%, 1.5%, 3%, and 5% NaCl by weight of the total binder content, improve resistance against corrosion and electrical resistivity with inclusion of metakaolin as shown in Fig. 11. Electrical resistivity was found to decrease with increase in the level of chloride contamination and 15% MK concrete improve electrical resistivity followed by 5% MK compared to control mix.

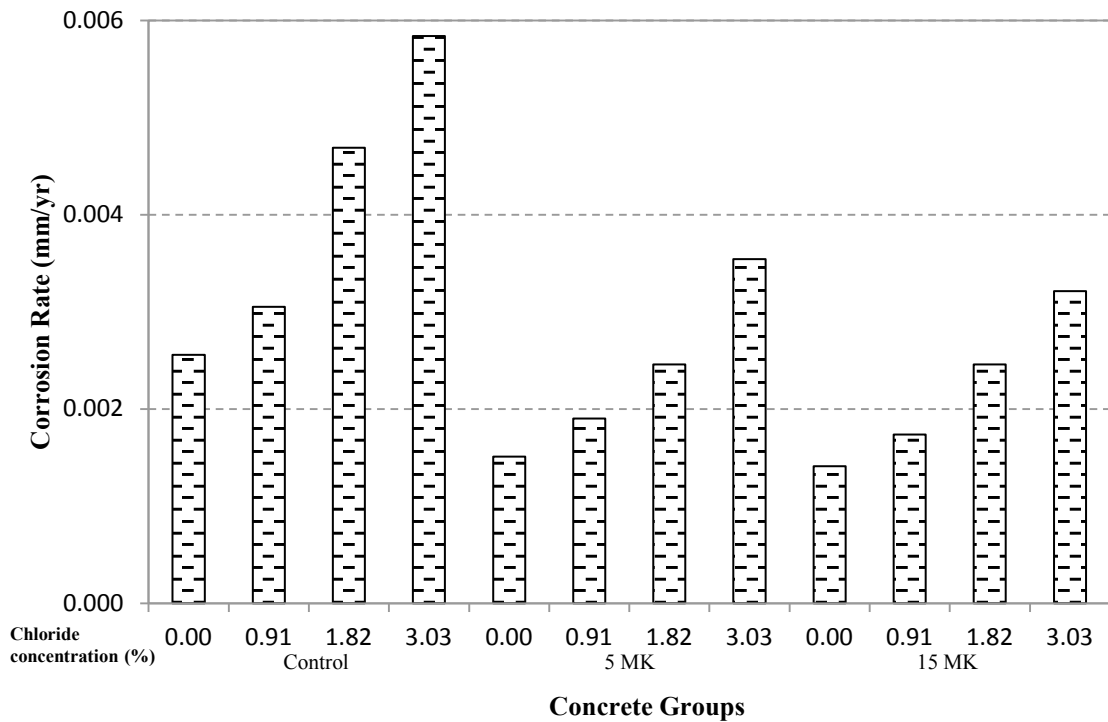


Fig. 11 - Corrosion rates of the concretes with respect to the level of MK used and the chloride contamination level [82]

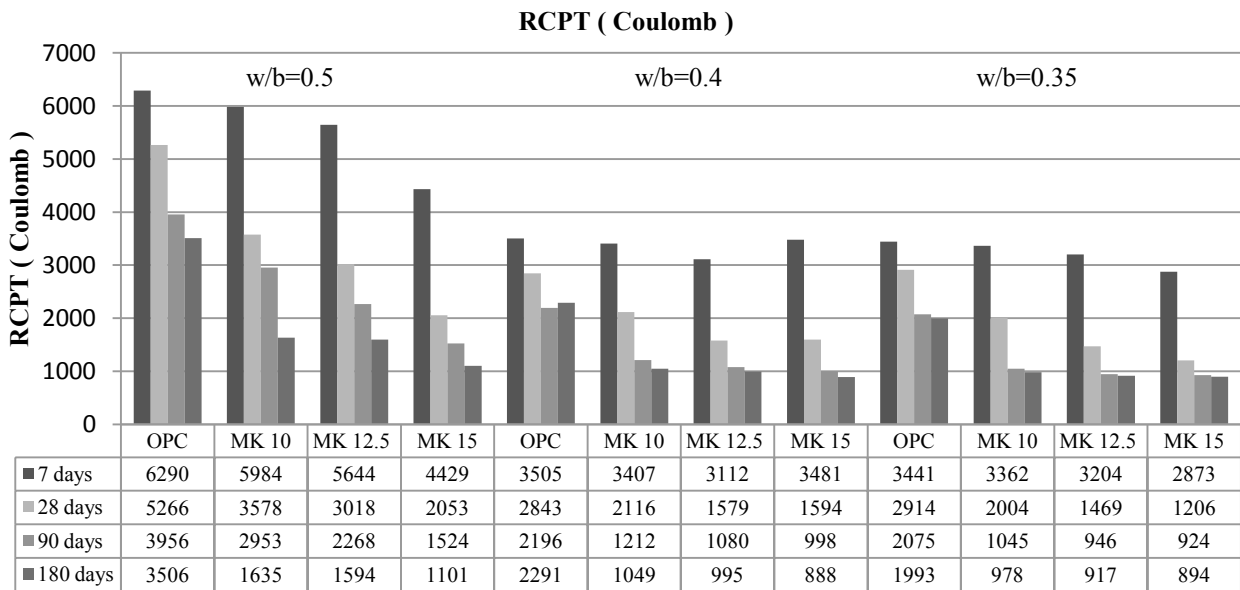


Fig. 12 - The effect of Metakaolin on the rapid chloride ions permeability (Coulomb) at various ages [77].

Ramezaniapour and Jovein [77] found that resistances to chloride penetration improve, when replacement of OPC by metakaolin increases from 0% to 15% at different w/b ratios as shown in Fig. 12. It was also observed that MK drastically enhance the electrical resistivity compared to OPC concrete, which was about 2-4 times higher for the 15% MK. Poon et.al [37] observed increase in resistance to chloride penetration for HPC, when OPC was replaced by metakaolin from 5% to 20%, at w/b ratios of 0.3 and 0.5. At the w/b of 0.3 the concrete with a 10% MK replacement showed the best performance, while at the w/b of 0.5 the concrete with a 20% replacement was the best. Gruber [83] showed that with 8% and 12% high reactivity metakaolin (HRM), decrease was found in chloride ion penetration of HRM concrete compared to reference mix

at w/b ratio of 0.3 and 0.4. About 50% and 60% reduction was observed for concrete with 8% and 12% HRM respectively compared to reference mix but best performance at all ages was exhibited by 12% HRM at w/b ratio of 0.3.

5 Conclusion

SCMs being finer material than OPC, improves microstructure by filler effect making the concrete structure dense resulting in better performance in term of durability properties. SCMs should be used in proper proportion to improve fresh, strength and durability properties depending upon the type of concrete required. When SCM are added to the mix, they react with $\text{Ca}(\text{OH})_2$, formed by hydration of OPC. The reaction between $\text{Ca}(\text{OH})_2$ and SCMs results into C-S-H gel, responsible for gain of strength. Silica fume concrete is mostly used for high performance concrete. Early age strength of silica fume concrete was found to be more than OPC concrete, even after 7 days of curing due to improvement in interfacial transition zone which further leads to enhanced durability properties. Use of silica fume was found to decrease workability of concrete and to overcome this problem, it should be blended with some admixture or SCM which may improve its workability. GGBS concrete was found to have less early strength due to slow rate of pozzanlic reaction but at later age attains strength equivalent to OPC concrete and further curing leads to increase in strength. Durability of GGBS concrete was better than OPC concrete due to filler effect which makes the microstructure dense. GGBS should be blended with some other SCM so that its initial strength can be improved. Generally, GGBS increases workability of concrete in comparison to control mix. Use of fly ash increase the workability and improves the mechanical properties at later age but early age strength was less than control mix where as attains strength equivalent to OPC concrete at 28 day. Fly ash was also found to reduce heat of hydration and help in preventing shrinkage and cracking. Durability of fly ash concrete was better than OPC concrete with low w/b ratio and enhances with age as pozzolanic reaction is slow. Optimum replacement level of fly ash concrete was 30% for attaining strength. Metakaolin increases the early age strength due to high rate of pozzlanic reaction and also increases long term strength but rate of strength gain becomes slow at later age. Addition of metakaolin in the concrete mix decreases workability, so high range water reducing admixtures are required or w/b ratio is to be increased to obtain desirable workability. Due to fine material it increases micro pore structure resulting into enhanced durability properties.

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