

# THE EFFECT OF SUPPLEMENTARY CEMENTITIOUS MATERIALS ON TRANSPORT PROPERTIES OF CEMENTITIOUS MATERIALS - STATE-OF-THE-ART



<https://doi.org/10.32970/CS.2021.1.4>

Zaid Ali Abdulhussein – Katalin Kopecskó

*The supplementary cementitious materials (SCMs) have recognized many of the beneficial influences on concrete ability to resist the penetration of chloride ions, such as fly ash, slag, silica fume, metakaolin, and other natural pozzolans; this benefit has primarily been ascribed to the refined pore structure that results from the appropriate use of SCMs, which, in turn, results in reduced permeability and ionic diffusivity. The paper illustrates the state-of-the-art research findings on; (1) the classification of the SCMs and physico-chemical properties; (2) the influences of SCMs on cement binder and the pore structure under chloride ion permeability; (3) the influences of the SCMs on the carbonation process of the cement binder that aims to determine the optimum relationship between SCMs and concrete transport properties. The interesting experimental investigations of the combined influence of chloride and carbonate permeation in cement binder that implement the latest methods in different curing conditions, types, and level contents of the SCMs will yield new scientific results and proposals for the industrial applications auxiliary materials.*

**Keywords:** supplementary cementitious materials, cement, transport properties, chloride migration, chloride diffusion, carbonation

## 1. INTRODUCTION

Supplementary cementitious materials (SCMs) are essential for producing high-performance concrete and preserving the environment (Ramezaniapour, 2014; Thomas, 2013). The main benefits of supplementary cementitious materials utilization in the cement and construction industry are threefold. First is the economic gain by replacing a substantial part of the Portland cement with cheaper natural pozzolans or industrial by-products. The second is lowering the blended cement environmental cost associated with the greenhouse gases emitted during Portland cement production. The third advantage is the durability improvement of the product. Additionally, even though the extensive blending of the SCMs with Portland cement is limited interference in conventional manufacturing, it provides the capability to take advantage, exploit of and immobilize considerable amounts of business and societal waste into construction substances (Snellings, 2012).

One of the most influencing factors on reinforced concrete structure's durability is the penetration of chloride ions to the steel reinforcement. De-icing roads with rock salt results in significant stress affected by the capillary pore system of concrete. Chlorides are well-known aggressive species for rebars of reinforced concrete (RC) structures. Therefore, the liquid water permeability and the chloride ion diffusion coefficient are involved as crucial parameters in governing equations of transport-related durability of concrete. Hence, it predicts the service life of RC structures. More precisely, the liquid water permeability is involved in the non-linear diffusion-type moisture transport equation

(Baroghel-Bouny, 2007). Likewise, the apparent chloride ion diffusion coefficient is engaged in the non-linear diffusion-type equation of the penetration of chloride ions in concrete (Fick's second law) (Baroghel-Bouny, 2007). Thus, it ensures the theoretical relevance of these properties as regards the durability of RC structures.

## 2. SUPPLEMENTARY CEMENTITIOUS MATERIALS (SCMS) CLASSIFICATION

The general definition of supplementary cementitious material embraces many materials that vary widely in origin, chemical and mineralogical composition, and typical particle characteristics. However, it was generally accepted that the hydraulic or pozzolanic activity of SCMs depends primarily on their physicochemical properties rather than their origin (Snellings, 2012). On the one hand, two broad categories can be distinguished: (i) natural origin and (ii) materials of human-made or artificial origin. The former group consists of materials that can be used as SCM in their naturally occurring form. In most cases, they only need conditioning of particle characteristics by grinding and sieving processes. Typical natural SCMs are pyroclastic rocks, e.g., tuffs, either diagenetically altered or not, and highly siliceous sedimentary stones such as diatomaceous piles of earth. The group of artificial SCMs includes materials that have undergone structural modifications due to manufacturing or production processes. Artificial SCMs can be produced,

for instance, by thermal activation of kaolin-clays to obtain metakaolin; or can be obtained as waste or by-products from high-temperature processes such as blast furnace slags, fly ashes, or silica fume (Snellings, 2012).

## 2.1 Sources of SCMs

A wide variety of materials are available for use as SCMs, including raw and calcined natural minerals, biomass ashes, and industrial by-products. Some of these materials are described in Table 1, intended to showcase SCM resources' variety and availability (Snellings, 2016).

**Table 1:** Materials used or considered as SCMs (Snellings, 2016)

Material	Chemistry composition	Used as SCM (Mt/y)	Total volume est. (Mt/y)	Comments
Blast furnace slag	Ca-Si-Al	330	300–360	Nearly fully used, latent hydraulic
Coal fly ash	Si-Al	330–400	700–1100	Subject to limitations on carbon content, reactivity
Natural pozzolans	Si-Al	75	Large accessible reserves	Large variety/variability, often high water demand
Silica fume	Si	0.5–1	1–2.5	Used in high-performance concrete
Calcined clays	Si-Al	3	Large accessible reserves	Metakaolin performs best, often high-water demand

## 2.2 The Major Functions of SCMs Mechanisms

The result of the impact of SCMs is ruled via physics, chemistry, and thermodynamics. Dodson described that the effect of the SCMs on the properties of cement-based materials (Dodson, 2013) through:

- occur a reaction with the secondary product of cement hydration
- modify the kinetics of the hydration of cement in the mixture
- disperse cement particles in the mixture
- fill the pore spaces in cement paste.

## 2.3 Physical Properties and Chemical Compositions of the SCMs

The most widely used binder in concrete is the Ordinary Portland Cement (OPC), and the most effective SCMs used are fly ash, slag, silica fume, and metakaolin. Generally, the reactive components in SCMs are glassy or amorphous phases, and their intrinsic reactivity is determined primarily by the chemical composition and structure of these components. The main reactive phases for fly ashes and slags are aluminosilicate or calcium aluminosilicate glasses, respectively, with minor fractions of MgO, Na<sub>2</sub>O, K<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub> incorporated (Lothenbach, 2011).

The primary characteristics measured in powder-type materials are specific surface area, particle size distribution,

particle shape, and density from physical properties perspective. The specific surface area (defined on a mass basis) is the most common property used to describe Portland cement's fineness (Stark and Mueller, 2003). This surface area is an integral parameter that is of importance in defining concrete performance. The description of particle shape encompasses information about the angularity and sphericity, which affect workability and the physical phenomena utilized for particle size measurement (Naito, 1998). Tables 2 and 3, respectively, summarize the physical properties and chemical composition of common SCMs and OPC based on peer-reviewed publications (Panesar and Zhang, 2020; Sakir, 2020).

**Table 2:** Physical properties of cement replacing materials (Panesar and Zhang, 2020)

Characteristics	Low-calcium FA	High-calcium FA	GGBS	SF	MK
Shape	Spherical	Spherical	Angular	Spherical	Angular, platy
Mean size (mm)	5.0–73.5	2.0–73.5	13.8–22.2	0.1–0.3	1.0–20.0
Surface area (m <sup>2</sup> /kg)	300–500	300–500	350–650	13,000–30,000	-

FA = Fly Ash; GGBS = Ground Granulated Blast-Furnace Slag; MK = Metakaolin; SF = Silica Fume

**Table 3:** The chemical compositions of ordinary Portland cement (OPC) and different SCMs (Sakir, 2020)

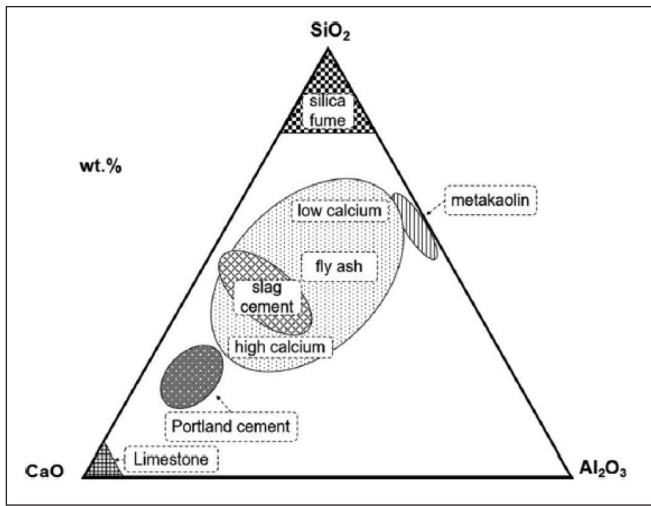
CC (wt.%)	FA	SF	GGBS	MK	OPC
SiO <sub>2</sub>	36–65	85–99	28–41	49–69	16–23
CaO	1–19	0–4	37–50	0–2	49–69
Al <sub>2</sub> O <sub>3</sub>	17–29	0–6	5–14	25–44	4–7
Fe <sub>2</sub> O <sub>3</sub>	4–31	0–3	0–1	0–3	2–7
MgO	0–7	0–5	4–10	0–3	0–5
SO <sub>3</sub>	0–3	0–2	0–3	0–1	0–1
Na <sub>2</sub> O	0–2	0–2	0–3	0–1	0–1
K <sub>2</sub> O	0–3	0–2	0–2	0–2	0–1
P <sub>2</sub> O <sub>5</sub>	0–2	0–1	–	0–1	–
LOI	0–5	0–6	1–2	0–4	–
Sp. gravity	2.26	2.24	2.88	2.51	3.15

CC (wt.%) = Chemical Composition weight percentage; FA = Fly Ash; SF = Silica Fume; GGBS = Ground Granulated Blast-Furnace Slag; MK = Metakaolin; OPC = Ordinary Portland Cement.

## 3. RECENT REGULATIONS AND CODES FOR SCMS USED IN CONCRETE TECHNOLOGY

Figure 1 presents the relative compositions of Portland cement, fly ash, slag cement, silica fume, and metakaolin on a ternary phase diagram (CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>); and Table 4 presents the maximum allowable usage of each cement replacing material according to international standards (Panesar and Zhang, 2020).

The maximum specified allowable percentages of cement replacing materials in the standards are based on the activity



**Fig. 1:** Ternary diagram supplementary cementing materials' composition (Panesar and Zhang, 2020)

index of the utilized materials. The activity index can be measured by standardized methods; however, the impact of SCMs on cement hydration needs to be understood (Skibsted and Snellings, 2019).

**Table 4:** Maximum specified allowable percentage of cement replacing materials based on national standards (contents in brackets indicate the cement type in each standard) (Panesar and Zhang, 2020)

SCMs	CSA A3000 (Canada)	ASTM C595; ASTM C150 (United States)	EN-197 BS-EN-197 (Europe and UK)	GB 175 (China)
GGBS	70%	95%	95% (CEM III/C)	20% (P.O) 50% (P.S.A) 70% (P.S.B)
Low/high-Ca FA	50%	40%	35% (CEM II/B-W) 35% (CEM II/B-V)	20% (P.O) 20% (P.S.A) 40% (P.F)
MK	40%	40%	35% (CEM II/B-Q)	Not specified
SF	15%	-	10% (CEM II/A-D)	Not specified

GGBS = Ground Granulated Blast-Furnace Slag; FA = Fly Ash; MK = Metakaolin; SF = Silica Fume; P.O= Ordinary Portland Cement; (P.S.A and P.S.B= Portland Slag Cement (A and B type)); P.F= Portland Fly ash Cement.

## 4. TRANSPORT PROPERTIES OF THE CEMENTITIOUS MATERIALS

The ingress rate of deleterious species (e.g., water, chlorides, sulfates) from the service environment into the cement-based structures and components throughout their service life is defined as the material's transport properties. They are intrinsic durability properties to be considered at the materials research and structural design stages (Han, 2013). Therefore, pore structure, tortuosity, and permeability are considered vital properties of porous materials such as cement pastes,

mortar or concrete, to understand their long-term durability performance. The chloride ion diffusion coefficient is considered a significant key parameter in governing equations of transport-related durability of concrete. As follows, a brief definition for this crucial parameter is given.

### 4.1 Chloride Diffusion Coefficients

Ollivier's study explains that two coefficients can be regarded as relevant durability indicators: (i) the effective chloride diffusion coefficient that appears in Fick's first law, and (ii) the apparent chloride diffusion coefficient can be derived from Fick's second law (Ollivier et al., 1998). The apparent chloride diffusion coefficients will be addressed, which can be regarded as more relevant for the (realistic) description of chloride ingress into concrete. This parameter also appears as a key parameter but may be more specific to the evaluation and prediction of RC structure's durability, hence the service life, concerning the risk of chloride-induced reinforcement corrosion. It is indeed Fick's second law, which is generally used to describe and predict the penetration of chlorides by "pure" diffusion in saturated concrete in non-steady-state (NSS) conditions (Baroghel-Bouny et al., 2007).

### 4.2 Influence of SCMs on Chloride Ion Permeability

Concrete permeability depends on multiple variables, such as combining composition quantities, compaction and curing, microcracks, and humidity conditions. The compressive strength and permeability of concrete are primarily influenced by capillary pores (El Mir et al., 2017; von Greve-Dierfeld et al., 2020). Based on the literature, with adequate curing, ground granulated blast furnace slag (GGBS), fly ash, and natural pozzolans generally reduce concrete permeability and absorption. The critical effect of SCMs, such as GGBS, on the concrete pore system is that large pores are minimized by blocking them with hydration products. The transform of continuous pores into discontinuous pores profoundly impacts concrete permeability (Kosmatka, Kerkhoff and Panarese, 2002). GGBS modifies the pore sizes and significantly decreases concrete permeability due to GGBS's reaction with calcium hydroxide and alkalis released during Portland cement hydration (Özbay, 2016). GGBS content a high level of aluminate, which is most likely responsible for the good binding characteristics. Additionally, the GGBS makes the cement matrix denser and diminishes the pore size. The ability of GGBS to protect against chloride-induced corrosion is attributed to the effective binding of free chloride ions (Kayali, 2012). Researchers showed that GGBS containing pastes have a higher chloride binding capacity than the PC control paste, which enhances C-S-H gel formation in concrete, hence providing larger surface areas available for adsorption (Kopeckó, 2006; Kopeckó and Balázs, 2017; Yuksel, 2018).

In a study presented by Güneyisi and Gesoğlu, it reported that the decrease of the chloride ions permeability of GGBS-containing concrete was due to changes in the pore structure of the hydrated cement system (Güneyisi and Gesoğlu, 2008). Gesoğlu et al. investigated the chloride ion permeability and water permeability of concretes containing GGBS from 0% to 60% substitution ratio with a 20% increment rate. They pointed out that the highest total charge passed in OPC concrete is controlled and can be defined as medium chloride



ion permeability concrete; the chloride ion permeability was decreased by 20%, 40%, and 60% GGBS substitution of OPC concretes. However, with the use of mineral additives, chloride ions passed became less (Gesoglu, Güneyisi and Özbay, 2009). Therefore, GGBS improves the chloride resistivity of concrete made with the same water to cement ratio. A research study was investigated the chloride resistivity of concrete by performing a rapid chloride migration test (CTH-test; Tang and Nilsson, 1992). The result indicated that when the slag content of cement type is higher and the water to cement ratio remains constant, chloride penetration depths decrease. Concretes made with air-entraining agents and the same water to cement ratio, the chloride concentration at the same depth in the concrete increased; thereby the air-entraining agent increases the non-steady-state migration coefficient ( $D_{nssm}$ ). This chloride resistivity reduction is due to the increased porosity, which causes permeability to increase. Eventually, it can conclude that the chloride migration coefficient and penetration depth decrease by increasing slag content considering the same ratio of water to cement. The experimental results indicated the lowest chloride migration coefficient, hence the highest chloride resistivity for concrete samples made with cement CEM III/B 32,5 N among the tested cements (Kopeckó and Balázs, 2017).

Aghaeipour and Madhkhan investigated the effect of GGBS on reinforced cement concrete (RCC) durability; for a minimum permeability, they suggested a 40% substitution ratio of OPC, as the durability characteristics such as water absorption, permeability, and freeze-thaw cycles were considered (Aghaeipour and Madhkhan, 2017).

Silica fume (SF) and calcined clay such as metakaolin (MK) are especially effective in this regard. They can provide concrete with a chloride resistance of under 1000 coulombs using the ASTM C 1202 rapid chloride permeability test (Barger, 1997). Experimental investigations show that as the quantity of hydrated cementing materials increases, the permeability of concrete decreases, and the water to cementitious materials (w/b) ratio decreases.

Recently the sulfate resistant Portland cement (SRPC), high-ferrite Portland cement (HFPC) application in ultra-high-performance concrete (UHPC) and self-compacting concrete (SCC) have been widely attractive, and it was expected to be used in the marine environment. Although, the main issue is the low chloride resistance. Thus, the effect of SCMs on chloride migration in HFPC precast concrete was carried out briefly in a recent report. The study reported that two SCMs, silica fume (SF) and metakaolin (MK), can significantly improve the steam cured HFPC concrete resistance to chloride permeation. The SF enhanced mechanism is based on optimizing the pore structure to retard chloride migration, while the role of MK is based on promoting the chloride binding capacity. This research could provide insight into a new precast concrete configuration with excellent resistance to sulfate and chloride in the marine environment (Huang et al., 2019). Additionally, the combined effect of MK and SF is beneficial rather than MK alone in improving the durability properties of ultra-high-performance concrete (UHPC) (El Mir et al., 2017). In the case of the SCC mixture, silica fume was noticed to have a fast pozzolanic activity at an early age in comparison to metakaolin that has proved to possess a long-term effect on the improvement of chloride migration resistance. Furthermore, it observed at the highest bindery content (440 kg/m<sup>3</sup>) that SF tended to be more effective in resistance chloride migration between than MK at similar

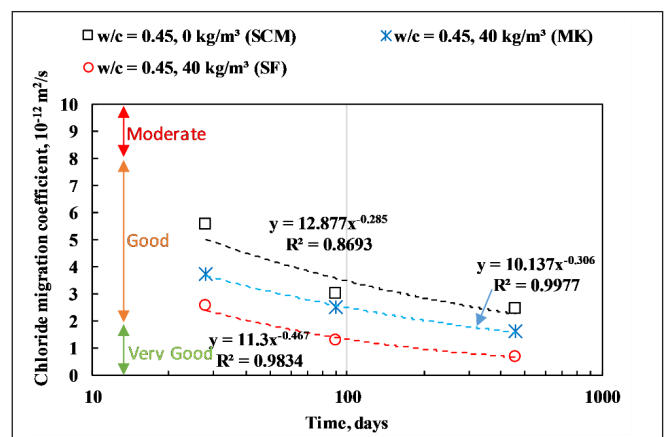


Fig.2: RCM for SCC mixtures incorporating MK at different levels of w/c as at 28, 90, and 460d (Courtesy of the author; El Mir, 2017).

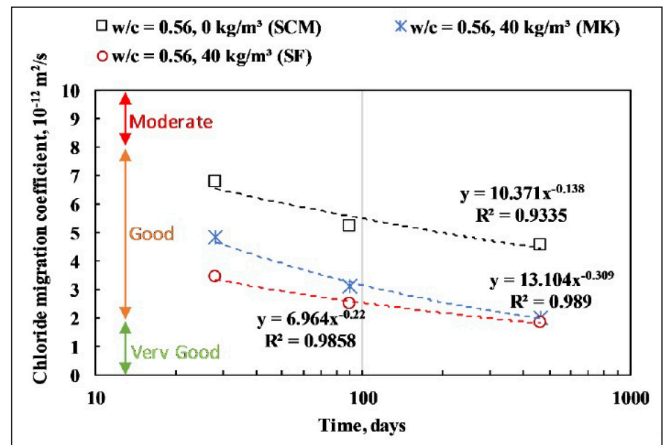
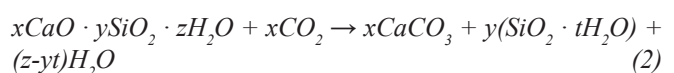
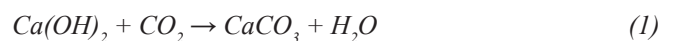


Fig.3: RCM for SCC mixtures incorporating MK at different levels of w/c as at 28, 90, and 460d (Courtesy of the author; El Mir, 2017).

percentages of mass replacement of cement; hence, SF is more effective in resistance chloride migration between 10-12.5% of mass replacement of cement, hence with the time progress, the further improvement on the chloride migration resistance of SCC containing SF is rather slight as compared to metakaolin at 460 days as shown in Figures 2 and 3 (El Mir, 2017).

## 5. CARBONATION REACTION

Concrete structures with reinforcing steel often face serious durability problems in the material's service that deteriorate with age progressively. The long-term ingress of environmental substances, such as seawater, marine aerosol, carbon dioxide (CO<sub>2</sub>), and sulfate; caused primarily the material's deterioration in the reinforced concrete structure. Among the aggressive substances, the CO<sub>2</sub> from the atmosphere can diffuse through the concrete pore structure, dissolving in the pore solution and reacting with the hydrated calcium compounds (Hussain, Bhunia, and Singh, 2017). This physicochemical phenomenon in cementitious materials is known as carbonation. The carbonation reaction takes place in cementitious materials with the governing reactions shown by Eqs. (1) and (2) (Papadakis, Vayenas and Fardis, 1991):



Ca(OH)<sub>2</sub> and C-S-H are the two primary hydration

compounds susceptible to  $\text{CO}_2$  in cementitious materials. The carbonation causes a reduction in the alkalinity of pore solution for concrete cover, which is thought of as a chemical degradation towards the RC structure with steel bars (Stefanoni, 2018). The development of a passive film of ferrous oxide at the surface of steel reinforcement that prevents the steel from aggressive corrosion requires a strongly alkaline environment within concrete (Zhang, 2017). When the carbonation front propagates, the alkalinity of the pore solution reduces. Thus, the initially formed passive film is gradually destroyed, and consequently, the time of initiating steel corrosion can be sharply shortened in RC structures. Additionally, the corrosion risk of steel reinforcement increases with exposure to moisture, oxygen, and even chloride ions; hence, steel corrosion induces rust expansion stress on the surrounding concrete, causing cracks in the concrete cover. This cracking situation further promotes the penetration of  $\text{CO}_2$  and other aggressive ions from the environment, which exacerbates RC structure's deterioration in the construction field. In addition to reducing alkalinity, carbonation significantly reduces the chloride binding capacity and increases the chloride ion diffusion rate in concrete (Zhang, 2017; Liu, 2017).

## 5.1 Influence of the SCMs on the Carbonation

Through the carbonation, a relatively high amount of calcium silicate hydrate (C-S-H) with a low Ca/Si ratio will carbonate in cement paste blended with SCMs. According to a study implemented by Schubert, pointed out that the action of SCMs is twofold since they are associated with the consumption of  $\text{Ca}(\text{OH})_2$  in the pozzolanic reaction, which reduces the pH and increases the rate of carbonation, while at the same time the formation of new C-S-H blocks capillary pores and decreasing carbonation (Schubert, 1987). Park found that the greater the amount of pozzolanic materials, the deeper the carbonation depth becomes (Park, 1995). A researcher stated that this phenomenon is primarily due to reducing the alkali content in cementitious materials. The calcium silicate hydrate formed from the pozzolanic reaction absorbs more alkali ions, hence, lowering the concrete's pH level (Mindess, Young and Darwin, 2003). A study has been conducted to determine the pore volume and size distribution of capillary pores using a Mercury Intrusion Porosimeter (MIP). Results reveal that carbonation of most of the species of C-S-H results in increasing porosity of cement paste. The total and effective capillary porosity of pastes blended with a high amount of GGBS increased after carbonation (Wu and Ye, 2017). Vineet has been investigated the carbonation resistance of cement that containing (SCMs) under the exposition of the carbon dioxide concentrations of 1% and 3%, relative humidity of 40%, 60%, and 80%, and temperature of 27 °C and 45 °C at two different water to binder ratio. The investigation reveals that the carbonation rate is dictated mainly by the degree of replacement of the clinker. Relatively to the percentage of water to binder and humidity, concrete made with cement-slag blends reveals more significant carbonation than mixtures containing other SCMs (Shah and Bishnoi, 2018). A study conducted by Bouikni mentions that concrete with 65% slag replacement always showed higher carbonation penetration than concrete with 50% slag and that water curing is a

significant factor in reducing carbonation (Bouikni, 2009).

An investigation of the influence of silica fume (SF) on the carbonation depth, reporting that higher carbonation depths are associated with the use of SF, some studies confirmed these results (Skjolsvold, 1986; Grimaldi, Carpio and Raharinaivo, 1989; Khan and Lynsdale, 2002). A researcher studied several SCMs (SF, low- and high-calcium fly-ash), noting that the carbonation depth decreases as the aggregate replacement by SCMs increases, the carbonation depth increases as cement replacement by SCMs increases (Papadakis, 2000). Kulakowski and Lewis mentioned an increase in concrete carbonation when fly-ash (FA) is used (Ho and Lewis, 1983). Gonen and Yazicioglu indicated that the depth of the carbonation of reference concrete mixes was slightly lower than that containing FA. Simultaneously, in concrete mixtures containing silica fume and fly-ash (SFAC), the carbonation depth was lower than that of other concrete mixes, where silica fume had little effect on carbonation. These authors attribute the lower depth of carbonation in SFAC to their lower porosity; they observe that the porosity of FA mixtures was double that of the SFAC concrete (Gonen and Yazicioglu, 2007).

Curing conditions has a significant influence on the carbonation depths in concrete mixtures. A study investigated in the case of fly-ash concrete mixes; the carbonation depths are about 20-50% higher in the case of air-curing than in the case of water-curing due to the diffusion of  $\text{CO}_2$ , which is affected by the water saturation degree in the mixture. Thus, the drier the porosity, the higher the  $\text{CO}_2$  diffusion, and as a consequence, the faster and higher carbonation depth occur (Younsi, 2011). Bai has been studied the PC-PFA-MK concrete mixes, revealing two major trends: (i) increasing PC replacement with PFA raises the depth of carbonation, and (ii) systematically replacing PFA (pulverized fly ash) with increasing MK levels decreases the depth of carbonation. A strong correlation between reduced carbonation depth and reduced sorptivity was also recorded (Bai, 2002). The resistance of compound mixtures of PC-MK, PC-GGBS, and PC-GGBS-MK against the chloride ion penetration and carbonation depth, shows the mix proportion of 10% GGBS and 10% MK shows an evident influence on decreasing the chloride ion migration coefficient and carbonation depth; PC-MK was more effective than PC-GGBS. Among all the specimens, the compound mixture of GGBS and MK (PC-GGBS-MK) presented the most beneficial influence to improve the chloride penetration resistance and to enhance concrete carbonation resistance (Duan, 2013).

According to the summarized literature of the report that RILEM TC 281-CCC recently conducted, indicated that with the reduced portlandite content in SCM containing systems, rapidly the carbonation will happen in the main  $\text{CO}_2$ -binding phases, C-S-H in the case of using SF, and C-A-S-H phases in the case of using GGBS, FA, MK, and other Al-containing SCMs. It seems to be that the carbonation of these hydrates is a significant contributor to carbonation shrinkage (polymerization shrinkage), especially at low Ca/Si ratio C(-A)-S-H, and induces coarsening of pore structure upon carbonation and reduce the mechanical strength. Additionally, upon the carbonation, the porosity of cementitious materials increases with increasing SCMs replacements ratio (von Greve-Dierfeld et al., 2020).

## 5.2 Combined Effect of the Carbonation and SCMs on Chloride Permeability

The durability of concrete structures is a frequent significant investigating issue, and it considerably impacts the service life of the concrete structures. Since the actual structures are more likely to experience deterioration due to the combination of more than two factors rather than the action of a unique factor, researchers in advanced countries recently attempted actively to investigate the chloride ions penetration under the combined action of carbonation, freezing-thawing, and salt attack. The penetration depth of chloride ion and carbonation depth was investigated in an environment subjected simultaneously to salt attack and carbonation (Tumidajski and Chan, 1996). The most crucial degradation among the multiple deterioration processes could be seen to be the corrosion of reinforcement due to chloride ions penetration, especially in the case of nuclear power plant (NPP) structures located in a coastal area.

The impacts of chloride content on carbonation in concretes has frequently considered; in comparison, the investigations of the carbonation influence on the progress of chloride penetration is limited. With the utilization of the replacement of supplementary cementitious materials (SCMs), the results of the carbonation depth of GGBS and PFA samples are higher than of mixes without these materials by using phenolphthalein indicator and XRD analysis. The results of the depth of the carbonation for the mixtures incorporating SCMs (PFA and GGBS) have less  $\text{Ca}(\text{OH})_2$  than the OPC mixtures at a different depth. Hence, at a deep depth, the relative intensities of  $\text{Ca}(\text{OH})_2$  remain low, but the concentration of  $\text{CaCO}_3$  stays high (Al-Ameeri, 2018). An investigated study points out the carbonation effect on the chloride penetration and replacing OPC by GGBS and PFA in cracked concrete samples. The depth of chloride ( $\text{DoCl}$ ) and carbonation ( $\text{DoC}$ ) was explored by using an accelerated environment test programmed ( $\text{CO}_2$  and  $\text{Cl}^-$ ). The depth of carbonation was determined by the phenolphthalein indicator, whereas the  $\text{DoCl}$  was measured by  $\text{AgNO}_3$  spraying. Two series of concrete samples were tested for chloride penetration. The series differences are that the first was exposed to an accelerated  $\text{CO}_2$  environment, while the second was exposed to a typical  $\text{CO}_2$  environment and exposure time to  $\text{CO}_2$  for both was five weeks. Results for the two series for different crack widths and w/c ratios are presented in Tables 5 and 6.

**Table 5:** Chloride penetration depth ( $\text{DoCl}$ ) mm for samples used in (series 1) (Al-Ameeri et al., 2021)

Sample - w/c ratio	Un-cracked	Cracked width 0.1 mm	Cracked width 0.2 mm	Cracked width 0.3 mm	Cracked width 0.4 mm
M 0.4	24	30	30	29	35
M 0.5	35	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$
M 0.6	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$
M 0.5 +GGBS	15	25	29	30	33
M 0.5 + PFA	14	23	22	25	27

**Table 6:** Chloride penetration depth ( $\text{DoCl}$ ) mm for samples used in (series 2) (Al-Ameeri et al., 2021)

Sample - w/c ratio	Un-cracked	Cracked width 0.1 mm	Cracked width 0.2 mm	Cracked width 0.3 mm	Cracked width 0.4 mm
M 0.4	27	33	31	34	39
M 0.5	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$
M 0.6	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$	$\geq 40$
M 0.5 +GGBS	15	29	31	31	31
M 0.5 + PFA	20	25	26	27	30

The chloride ion penetration increases significantly within the concrete samples exposed to the  $\text{CO}_2$  environment for all mixes used in the study. There is a significant decrease of chloride ions penetration in carbonated and uncarbonated concretes incorporating SCMs when compared to the reference concretes. Additionally, for concrete specimens exposed to carbonation and chlorides, crack widths affect the penetration of chloride and, therefore, must be taken into consideration in service life prediction models (Al-Ameeri et al., 2021).

Generally, the pozzolanic materials improve the durability of the concrete, especially for chloride penetration (Chindapasirt, Rukzon and Sirivivatnanon, 2007), such as silica fume (SF), metakaolin (MK), ground palm oil fuel ash (POA), ground rice husk ash (RHA) and fly ash (FA). A study had been conducted on the influence of carbon dioxide on the chloride ion penetration and diffusion coefficient in OPC mortar containing partial replacement of (RHA, POA and FA) with constant water-cement ratio and under a testing environment with 5% of  $\text{CO}_2$  and 30 days of immersion in 3% of  $\text{NaCl}$  solution. From the test, it can be concluded that in normal circumstances, the incorporation of pozzolans such as POA, RHA and FA are very beneficial to the performance of mortar in terms of chloride resistance. In terms of exposure to a high level of carbon dioxide concentration, the resistance to chloride penetration of mortar containing pozzolans is lowered and renders the mortar susceptible to chloride attack depending on the type and level of replacement. Eventually, mortars with RHA show the best performance in terms of chloride penetration resistance. FA and POA and the blend of these pozzolans produce mortars with reduced resistance to chloride penetration as a result of exposure to carbon dioxide (Chindapasirt, 2008).

The corrosion of concrete structures has received significant attention related to the deterioration of sea-side structures, such as new airports, bridges, and nuclear power plants. In this regard, many studies have done on the chloride attack in concrete structures. However, an investigation study explored the influences of carbonation to chloride attack in concrete structures by utilizing fly ash as a partial cement substitute. The major test variables considered in this study are fly ash and w/c ratio to examine the chloride ion penetration effects in concrete for the case where the carbonation was exerting. Eventually, the investigation result showed that the admixing of fly ash is highly efficient in preventing the penetration of chloride ions under a single condition when carbonation is exerting combined action, the concentration of chloride ion tends to be high until an actual depth, but the concentration of



chloride ion decreases suddenly beyond a certain limit depth, which minimizes its effect on the corrosion of reinforcement according to the admixing of fly ash even under the combined action of the carbonation (Oh, Lee, Lee and Jung, 2003).

## 6. CONCLUSIONS

The article is an attempt to summarize the current state of the SCMs performance in cement composites and their advanced influences on chloride ion permeability and carbonation behaviour. Various influencing factors have been considered, including curing conditions, mixture proportion, temperatures and w/b ratio. Overall, the interesting experimental results would significantly contribute to developing a more systematic, comprehensive, and accurate mathematical model for describing the behaviour of the materials. Based on the literature research, the main conclusions are as follows:

- The supplementary cementitious materials, as SF, GGBS, and MK, show a significant impact on permeability and sorption characteristics of concrete, specifically on the pore structure of the concrete and chloride ion's binding capacity. The GGBS and MK have beneficial effects on promoting the effective binding capacity of free chloride ions, while the SF's enhancement mechanism is based on the optimization of the pore structure to retard the chloride ion migration.
- The carbonation system of cementitious materials containing SCMs is different from the Portland cement system due to the different pore structures and pore solution chemistry. The carbonation will happen rapidly by reducing the content of the non-consumed portlandite in the SCMs containing system.
- The porosity of concrete in terms of chloride ion permeability and carbonation resistance is sensitive to material factors, such as w/b ratio, curing type, humidity, and level of replacement of the clinker, which is directly influencing.
- The binary and ternary mixtures of SCMs show a beneficial improvement in the carbonation depth due to their lower porosity; it shows a correlation between reduced carbonation and reduced sorptivity, the concrete's carbonation resistance improving with substantial and sufficient curing periods.
- Among the most effective common SCMs, metakaolin (MK) shows a beneficial effect on the concrete's durability. It improves the resistance against chloride penetration (decreases the chloride ion permeability) by enhancing the chloride ion binding capacity and also reduces the carbonation depth of concrete in the case of mono (one kind of SCMs used as cement substitution in mixture), binary and ternary mixes.
- Pozzolanic materials improve the durability of the concrete, especially for chloride penetration; in the case of the combined effects of carbonation on chloride penetration resistance in concrete, the levels and types of SCMs replacement effects the ability of concrete to resist the penetration of chloride ions. Therefore, the crack widths affect the penetration of chloride, hence, must be taken into consideration in service life prediction models.
- The high level of the SCMs replacement in concrete may show a lower effect on the carbonation resistance due to their consumption of  $\text{Ca}(\text{OH})_2$  in pozzolanic reaction, which reduces the pH level in concrete, consequently,

increase the carbonation depth and reduce the ability of these materials to resist other forms of deterioration, determination of the influence of high SCMs on carbonation resistance; long-term experiments are needed, respectively.

## ACKNOWLEDGEMENTS

The scholarship support provided for the PhD study and research work to the first author by *Stipendium Hungaricum* Scholarship Program is gratefully acknowledged.

The authors acknowledge the support by the Hungarian Research Grant NVKP\_16-1-2016-0019 "Development of Concrete Products with Improved Resistance to Chemical Corrosion, Fire or Freeze-Thaw".

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**Zaid Ali Abdulhussein:** PhD student in Civil Engineering in the Department of Construction Materials and Technologies at the Budapest University of Technology and Economics in Hungary (Supervisor: Katalin Kopecskó PhD). He graduated in Civil Engineering from the National University of Malaysia (2018). His main research fields are the durability of concrete and other materials, supplementary cementitious materials, transport properties of cementitious materials, and construction materials' deterioration processes. Email: [zaid.abdullhussein695@edu.bme.hu](mailto:zaid.abdullhussein695@edu.bme.hu)

**Katalin Kopecskó:** Associate Professor at the Budapest University of Technology and Economics in Hungary. Graduated in Chemical Engineering (1990) and has postgraduate studies in Concrete Technology (2004). She has PhD degree since 2006. She teaches Chemistry for Civil Engineers (BSc), Material Science for Civil Engineers (MSc), and Alkali activated materials in Civil Engineering (PhD) subjects. Her research fields are deterioration processes of construction materials, the durability of concrete and other materials, cement hydration, diagnostics, mineralogical and microstructural analysis, X-ray diffraction (XRD), thermal analyses (TG/DTG/DTA), scanning electron microscopy (SEM). She is a member of the Hungarian Group of *fib* and the Technical Committee MSZT/MB 102 (Cement and Lime) in the Hungarian Standards Institution. Email: [kopecsko.katalin@emk.bme.hu](mailto:kopecsko.katalin@emk.bme.hu)