An overview on the Influence of Pozzolanic Materials on Properties of Concrete

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ABSTRACT: Concrete is the most normally used material for construction. The worldwide production of cement has significantly increased since 1990.Production of cement results in a lot of environmental toxic waste as it involves the emission of CO2 gas. Complementary cementitious materials are finely ground solid materials that are used to replace a portion of the cement in a concrete mixture. These complementary materials may be naturally occurring, manufactured or natural waste. Various types of pozzolanic materials that improve cement properties have been used in cement industry for a long time. This paper reviews the use of pozzolanic material in concrete. A detailed literature review is carried.

Keywords: Fresh properties, Hardened properties, Portland cement, Pozzolanic materials.

INTRODUCTION

The most often used mineral admixture in the concrete industry is pozzolan. A "pozzolan" is defined as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementing property, but will in a finely divided form – and in the presence of moisture - chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (Malhotra and Mehta, 1996). Examples of pozzolanic materials are volcanic ash, pumice, opaline shales, burnt clay and fly ash. The silica in a pozzolana has to be amorphous, or glassy, to be reactive. Fly ash from a coal-fired power station is a pozzolana that results in low-permeability concrete, which is more durable and able to resist the ingress of deleterious chemicals. There are two types of pozzolan, namely natural pozzolan and man-made pozzolan. Natural pozzolans are of volcanic origin such as trass, certain pumicites, perlite, and Karoline. Man-made pozzolans include industrial by-products such as fly ash, blast furnace slag, and silica fume (Güneyisi, 2004). Figure 1. shows the percentages of the most commonly recycled materials used in concrete. Fly ash was very popular, with 20% of companies using it in concrete. Companies noted that FA is a great substitute for cement and it is cost effective. Some companies mentioned slag (12%) and silica fume (9%) for special projects, varying use according to the engineer from job to job bases. the physical and chemical analysis of mineral admixtures provided by the manufacturer are given in Table 1.
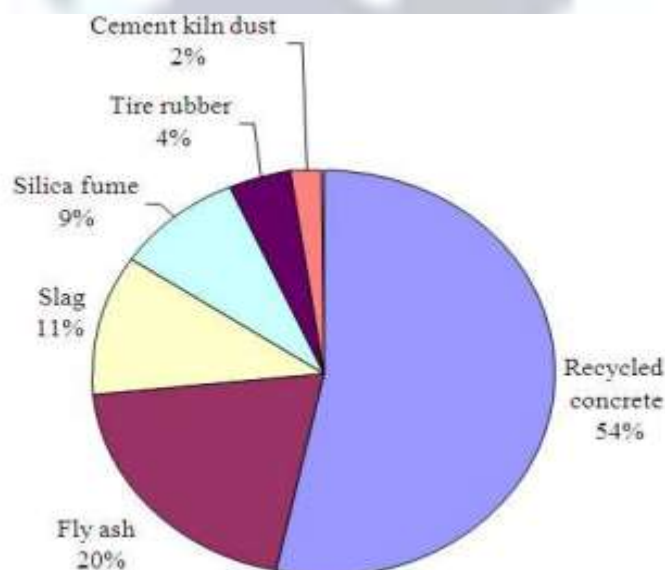

Fig 1. Most commonly used recycled material in concrete

Table 1. Physical and chemical analysis of mineral admixtures

Chemical analysis(%)	PC	FA	SF	GGBFS	MK
CaO	62.58	4.24	0.45	34.12	0.78
SiO_2	20.25	56.2	90.36	36.41	52.68
Al_2O_3	5.31	20.17	0.71	10.39	36.34
Fe_2O_3	4.04	6.69	1.31	0.69	2.14
MgO	2.82	1.92	-	10.26	0.16
SO_3	2.73	0.49	0.41	-	-
K2O	0.92	1.89	1.52	0.97	0.62
Na_2O	0.22	0.58	0.45	0.35	0.26
Loss of ignition	3.02	1.78	3.11	1.64	0.98
Physical Properties	**PC**	**FA**	**SF**	**GGBFS**	**MK**
Specific gravity	3.15	2.25	2.2	2.79	2.5
Blaine Fineness(m²/kg)	3260	287	21080	418	12000

1. Fly Ash (FA)

Fly ash is a by-product of the combustion of coal in thermal power plants, which is capable of reacting with Ca(OH)2 at room temperature. The pozzolanic activity of fly ash depends on the presence of SiO2 and Al2O3 in the amorphous form (Baker, 1984; Gesoglu, 2004). The use of fly ash in concrete technology dates back 1930s (Sengül, 2005). It is estimated that about 450 million tons of fly ash is produced worldwide annually, but only 6% of the total available is used as pozzolan in blended cements or in concrete mixtures (Baker, 1984). In Turkey, there are twelve active coal-burning power plants with annual fly ash production of about 15 millions tons. Fly ashes that comply with ASTM C 618 for mineral admixtures in portland cement concrete come in two classes: Class C is produced from burning sub-bituminous coal and has faster strength gain, while Class F is produced from burning bituminous coal and has higher ultimate strength. the chemical composition of types of FA is following in Table 2. according ASTM C 618.

In combination with portland cement, Class C fly ash can be used as a cement replacement, ranging from 20-35% of the mass of cementitious material. Class C fly ash must replace at least 25% of the portland cement to mitigate the effects of alkali silica reaction. In combination with portland cement, Class F fly ash can be used as a cement replacement ranging from 20-30% of the mass of cementitious material.

Table 2. Chemical Composition of Class(C&F) Fly Ash

Substance or Property	Requirements (ASTM C 618) Class C Fly Ash %	Requirements (ASTM C 618) Class F Fly Ash %
SiO2 plus Al2O3 plus Fe2O3, min.	50	70
SO3, max.	5	5
Moisture content, max.	3	3
Loss on ignition1, max.	6	6

From a physical point of view, fly ash can also be very different from one another. They can appear in shapes such as spherical, rounded, irregular and angular. Fly ash is approximately half the price of cement, and in addition to its economical benefits, the use of fly ash in has been reduces permeability, bleeding, water demand and the heat of hydration. It also improves workability, however strength development is slower. From an environmental perspective, one of the benefits of fly ash is that the replacement of large portions of cement with fly ash serves to reduce CO2 emissions from manufacturing cement, thus making concrete an even greener material that it already is.

1.1. The Use of Fly Ash in the Fresh Concrete

The absolute volume of cement plus fly ash normally exceeds that of cement in similar concrete mixtures not containing fly ash. This is because the fly ash normally is of lower density and the mass of fly ash used is usually equal to or greater than the reduced mass of cement. While it depends on the proportions used, this increase in paste volume produces a concrete with improved plasticity and better cohesiveness. In addition, the increase in the volume of fines from fly ash can compensate for deficient aggregate fines. Fly ash changes the flow behavior of the cement paste; in

general spherical shape of fly ash particles normally results in a reduction in the water demand in the concrete for a given workability (ACI 232.2 R., 1996). (Bouzoubaa and Lachemi, 2001) produced self compacting concrete (SCC) with a cement replacement of 40%, 50%, and 60% by Class F fly ash. They demonstrated that incorporating fly ash improved the slump flow diameter and decreased the V -funnel flow time of SSCs. Besides, the temperature rise of the SCC was 5 to 10 Co lower than that of the control concrete and the setting times of SCCs were 3 to 4 hours longer than those of the control concrete. It was found in the study of (Sahmaran, 2006) that fly ash increased the setting time of the mortars, due to a spherical geometry and a coarse particle size, causing a reduction in the surface area to adsorb free water. (Sonebi, 2004) reported that the incorporation of pulverized fuel ash and limestone powder lessened the requirement of superplasticizer necessary to obtain the desired slump. The use of these materials also improved the rheological properties and reduced the risk of cracking of concrete due to the heat of hydration, thus led to more durable concrete.(Sekino and Narita, 2003) conducted a study to propose the mix design method for SCCs containing high volume fly ash, and to evaluate the effects of replacing cement by fly ash on the strength and durability of the SCCs. They concluded that SCC at 50% replacement level of FA had excellent workability and filling ability at the site of construction. (Xie et al., 2002) studied the preparation technology of high-strength self-compacting concrete (SCC) containing ultra-pulverized fly ash and superplasticizer. They found out that the effect of ultra-pulverized fly ash on fresh concrete is to improve the viscosity of fresh concrete, and the effect being the same as that of a viscosity agent. It does not decrease the flowability of fresh concrete.(Kim et al., 1996) studied the properties of super flowing concrete containing fly ash and reported that the replacement of cement by 30% fly ash resulted in excellent workability and flowability. (Sukumar et al., 2008). reported the relation between superplasticizer dosage and fly ash content existed in SCC mixes with 8~52% fly ash, slump flow of 742~793 mm, and W/P of 0.31~0.34. The superplasticizer dosage decreased with an increase in fly ash content up to 39%; higher fly ash incorporation however did not change the superplasticizer required, See Figure 2. Fly ash in SCC helps to reduce early-age cracking in SCC which decreases with an increase in strength. Low permeability, good freeze-thaw resistance and low drying shrinkage of SCC were achieved by incorporating 30~40% fly ash (Xie et al., 2002). SCC incorporating fly ash has long setting time because of slower reactivity of fly ash and the delaying effects of superplasticizer and VMA (Atis, 2003; Bouzoubaa and Lachemi, 2001).
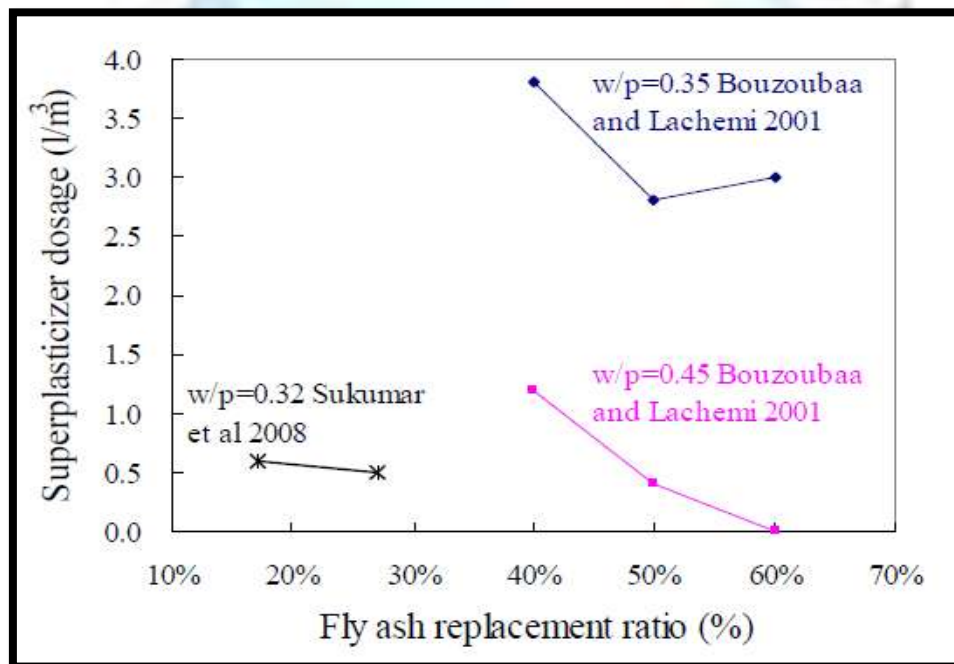

Figure 2. Effect of fly ash on superplasticizer dosage of SCC (Bouzoubaa and Lachemi, 2001; Sukumar et al., 2008)

1.2. Fly Ash in the Hardened Concrete

Fly ash concretes generally have lower early strength due to the slow pozzolanic reaction of fly ash. This strength reduction depends on the content and properties of the fly ash used. In the 1980s, CANMET designed the so-called high-volume fly ash(HVFA) concrete in which 55–60% of the portland cement is replaced by Class F flyash and such concrete eventually demonstrated excellent mechanical and durability properties (Canada Energy Mines and Resources, 1986; Bilodeau and Malhotra,2000; Malhotra, 1986).(Yazıcı, 2007) performed a study to find out the effects of high volume FA replacement ratio on the properties of SCCs. In that study, cement was replaced by a Class C FA in various proportions from 30 to 60%. Similar tests were carried out with the incorporation of 10% SF to the same mixtures. The

results showed that the compressive strength decreased with the increasing FA content at all ages. The compressive strength of control (0% FA) and 60% FA mixtures were 61.8 MPa and28.4 MPa, respectively at 28 days. All mixes showed strength gain beyond 28 days and the control mixture reached to 72.5 MPa at 90 days while this value was 38 MPa for 60% FA content. However, it was possible to produce a SCC with a compressive strength value of 50 MPa with 30–40% FA replacement. 10% SF addition to the system positively affected the compressive strength and contributed to the production of SCC mixtures that develop high-mechanical properties incorporating high-volume of FA. At 30% and 40% FA replacement levels, compressive strength values even exceeded the compressive strength of the control specimens at 28 days. (Saraswathy et al., 2003) prepared concrete specimens with 10%, 20%, 30% and 40% of activated fly ash replacement levels and evaluated their compressive strength at 7, 14, 28 and 90 days and the results were compared with that the ordinary portland cement concrete (without fly ash). They also measured electrical resistivity and ultrasonic pulse velocity of the concretes to understand the quality of concrete. In that study, it was noted that, curing time increased the compressive strength of concrete, irrespective of amount of fly ash replaced. A decrease in compressive strength i.e. 1.5 times was observed as the percentage of fly ash replacement increased from 10 to 40%. (Saraswathy et al., 2003) also found that the electrical resistance of activated fly ash system showed less resistivity values than ordinary portland cement at replacement levels of 20% and above. This behaviour was observed due to the fact that, in activated fly ash the compatibility with hydrated cement phases and the remaining mineral phases act as more porous in the concrete formulation. With this result, the decrease in resistivity was observed. In addition, activated fly ash contains impurities like unburnt carbon, sulphur etc., increases the electrical conductivity and consequently decreases the resistivity values. Ultrasonic pulse velocity values observed for ordinary portland cement is found to be 4.35 km/s, whereas that for activated fly ash system ranged between 4.36 and 4.00 km/s.

1.3. Effects of Fly Ash on the Durability Properties of Concretes

Deterioration of concrete depends on the penetration of aggressive substances into concrete via micro cracks and interconnected pore system. Permeability of fly ash concretes at early ages can be significantly higher when compared to that of Portland cement concrete. At later ages, however, fly ash concretes can have much lower permeability depending on the content and characteristics of the fly ash used (Tasdemir, 2003). (Bilodeau et al., 1994) presented the results of investigations to determine the various durability aspects of high-volume fly ash concretes using eight fly ashes and two Portland cements obtained from US sources. Briefly, in high-volume fly ash concrete, the water and cement content were kept low at about 115 and 155 kg/m3 of concrete, respectively, and the proportion of fly ash in the total cementitious materials content ranged from 55 to 60%. The durability aspects investigated included resistance to the repeated cycles of freezing and thawing, deicing salt scaling resistance, resistance to the chloride-ion penetration, and determination of water permeability coefficient. Based upon the test results, it was concluded that regardless of the type of fly ash and the cement used, the air-entrained high-volume fly ash concrete exhibited excellent durability characteristics in the tests investigated. The only exception was the deicing salt-scaling test in which the performance of the concretes investigated was less than satisfactory. (McCarthy and Dhir, 2005) performed a study to examine the use of high levels of low-lime fly ash (high volume FA) as a cement component in concrete. Durability tests covering water absorption, water permeability, carbonation rates and chloride diffusion were carried out on the produced concretes. At the end of the experimental study, it was observed that water absorption, water permeability, and chloride diffusion tests indicated enhanced performance with high FA levels, while for carbonation rates similar performance to PC concrete was generally noted, although this may be slightly poorer at low design strength. (Malhotra, 2000) prepared a report on the resistance of concrete to the chloride ion penetration measured on 10 year old concretes so as to indicate the long term performance of the concretes with pozzolans. The charge passed through the concrete mixtures investigated in this study was less than 1000 coulombs at 10 years indicating very low chloride-ion penetrability. For the high volume fly ash concrete, the charge passed was 0, giving a chloride ion penetrability rating of these concretes as negligible. It is extremely rare to achieve values as low as this in portland cement concrete (Sengül, 2005).Scaling of concrete exposed to deicing salts occurs when immature or non air entrained concrete pavements are exposed to large quantities of deicing salts in a freezing and thawing environment. Concrete pavements containing fly ash that are exposed to deicing salts should be air entrained and allowed to reach a specified strength or maturity. There is some laboratory research that indicates concrete containing 40 percent fly ash, as a percentage of the total mass of cementitious material, may be more susceptible to scaling (ACI 232.2 R., 1996).

2. Ground Granulated Blast Furnace Slag (BBBFS)

Slags are residues from metallurgical processes, either from production of metals from ore or refinement of impure metals. They are derived from lime-based inorganic fluxes used to extract impurities from metals which solidify on cooling. The slags used in concrete come from the blast furnace production of iron from ore. The iron ore is fed into the furnace with coke and limestone. The slag is formed at a temperature of 1300-1600 C° as a liquid layer floating on the top of liquid iron. It is then collected and cooled (Lee, 1974). The speed of cooling affects the properties of the slag. If allowed to cool slowly, it crystallizes to give a material having virtually no cementing materials. If cooled sufficiently rapidly to below 800 C°, it forms a glass which is latent hydraulic cement. This substance is then ground into a very

fine powder with a minimum of 80 percent less than 45 microns in size. This is the cementitious material called ground granulated blast furnace slag (GGBFS). GGBFS has been used for many years as a supplementary cementitious material in Portland cement concrete, either as a mineral admixture or as a component of blended cement. Blast furnace slag particles have mostly rough, sharp edged shapes.

2.1. Ground Granulated Blast Furnace Slag in the Fresh Concrete

(Wood, 1981) reported that the workability and placeability of concrete containing ground granulated blast furnace slag (GGBFS) yielded improved characteristics when compared with the concrete without GGBFS. This result was attributed to the surface characteristics of the GGBFS, which created smooth slip planes in the paste. The author also theorized that, due to the smooth, dense surfaces of the GGBFS particles, little if any water was absorbed by the GGBFS during initial mixing, unlike Portland cement. Cementitious matrix containing GGBFS had greater workability due to the increased paste content and increased cohesiveness of the paste. Pastes containing GGBFS exhibited different rheological properties compared to paste of Portland cements alone. The results indicated a better particle dispersion and higher fluidity of the pastes and mortars, both with and without water-reducing admixtures (ACI 233 R., 1995). Usually, an increase in setting time can be expected when GGBFS is used as a partially replacement of the Portland cement in concrete mixtures. The degree to which the setting time is affected is dependent on the initial temperature of the concrete, the proportion of the blend used, the water-cementitious materials ratio, and the characteristics of the Portland cement. Although significant retardation has been observed at low temperatures, the additions of conventional accelerators, such as calcium chloride or other accelerating admixtures, can greatly reduce or eliminate this effect. Since the amount of Portland cement in a mixture usually determines setting characteristics, changing the GGBFS proportions may be considered in cold weather. At higher temperatures, the slower rate of setting is desirable in most cases, but care may need to be taken to minimize plastic shrinkage cracking (ACI 233 R., 1995). GGBFS provides reactive fines with a low heat of hydration. A high proportion of GGBFS may affect stability of SCC resulting in reduced robustness with problems of consistence control while slower setting can also increase the risk of segregation (EFNARC, 2002).

2. 2. Ground Granulated Blast Furnace Slag in the Hardened Concretes

(ACI 233 R., 1995) provides for three strength grades of GGBFS, depending on their respective mortar strengths when blended with an equal mass of Portland cement. The classifications are grades 120, 100, and 80, based on the slag-activity index material; the early strength is inevitably lower than with the same content of cementitious materials consisting of Portland cement only. The incorporation of GGBFS in concrete does not alter significantly the usual relations between compressive strength and flexural strength or between the compressive strength and modulus of elasticity (Neville, 1996). Compressive and flexural strength-gain characteristics of concrete containing GGBFS can vary over a wide range. When compared to Portland cement concrete, use of grade 120 slag typically results in reduced strength at early ages (1 to 3 days) and increased strength at later ages (7 days and beyond) .Use of grade 100 results in lower strengths at early ages (1 to 21 days), but equal or greater strength at later ages. Grade 80 leads to lower strength at all ages. The extent to which GGBFS affect the strength is dependent on the slag activity index of the particular GGBFS and the ratio in which it is used in the mixture (ACI 233 R., 1995).

2.3. Effects of Ground Granulated Blast Furnace Slag in the Durability of Concretes

The beneficial effects of GGBFS arise from the denser microstructure of hydrated cement paste, more of the pore space being filled with C-S-H than in portland cement only paste. As a result of improved pore structure of hydrated paste of a Portland cement-GGBFS blend, and also because of low content of calcium hydroxide, the resistance to the sulphate attack is improved. Tests on concrete containing GGBFS have confirmed good resistance to penetration by chloride ions e.g. when the GGBFS content is at least 60% by mass of the cementitious materials and the water/cement ratio is 0.50, the diffusion coefficient of the concrete exposed to chloride ions is at least ten times smaller than when the cementitious materials consists entirely of Portland cement (Neville, 1996). The electrical resistivity of concrete is an important component of reinforcing steel corrosion cells, as high resistivity of the concrete reduces corrosion currents, and thus slowing the rate of corrosion. (Gesoglu and Özbay, 2007) investigated the effects of GGBFS on the electrical resistivity of the self compacting concretes. In that study GGBFS replaced Portland cement at 20%, 40% and 60% levels. Test results showed that the lowest electrical resistivity was obtained at normal Portland cement concrete with 12.8 k/ohm-cm and there was a gradual increase in the electrical resistivity of SCC with increasing GGBFS content. Although some laboratory tests with slag blended cement indicate less resistance to deicing salts, many researchers have found, in field exposure, little difference when compared to concrete not containing slag (ACI 233 R., 1995). Similar results were reported using blends of 50 percent GGBFS and 50 percent Portland cement, by(Hogan and Meusel, 1981). Most research indicates that scaling is usually found when the concrete has a high water-cementitious materials ratio associated with high amount of GGBFS (ACI 233 R., 1995).

3. Silica Fume (SF)

Silica fume is a by-product resulting from the reduction of high-purity quartz with coal or coke and wood chips in an electric arc furnace during the production of silicon metal or ferrosilicon alloys. The silica fume, which condenses from the gases escaping from the furnaces, has a very high content of amorphous silicon dioxide and consists of very fine spherical particles. Ferrosilicon alloys are produced with nominal silicon contents of 61 to 98 percent. When the silicon content reaches 98 percent, the product is called silicon metal rather than ferrosilicon. As the silicon content increases in the alloy, the SiO2 content will increase in the silica fume. Limited applications have been made using silica fume from production of 50 percent ferrosilicon alloys (ACI 234 R., 1996).Most silica fumes range from light to dark grey in colour. Because SiO2 is colourless, the colour is determined by the non-silica components, which typically include carbon and iron oxide. In general, the higher the carbon content, the darker the colour of the silica fumes. The carbon content of silica fume is affected by many factors relating to the manufacturing process such as: wood chip composition, wood chip use versus coal use, furnace temperature, furnace exhaust temperature, and the type of product (metal alloy) being produced. The degree of compaction may also affect the colour. The average diameter of silica fume particles are 0.1 μm and their specific surface area is about 20000 m^2/kg, as compared to 250 to 450 m2/kg for an ordinary portland cement or a fly ash. Chemical composition of SF varies depending on the nature of the the manufacture process from which the SF is collected. The main constituent material in SF is silica (SiO2), the content of which is normally over 90%. (Delage and Aitcin, 1983).

3.1. Silica Fume in the Fresh Concretes

The water demand of concrete increases with increasing the amounts of silica fume used due primarily to its high surface area (Scali et al., 1987; Carette and Malhotra, 1983). Fresh concrete containing silica fume is more cohesive and less prone to segregation than concrete without silica fume. As the silica-fume content increases, the concrete may appear to become sticky. Concrete containing silica fume shows significantly reduced bleeding. This effect is caused primarily by the high surface area of the silica fume to be wetted; there is very little free water left in the mixture for bleeding. Additionally, the silica fume reduces bleeding by physically blocking the pores in the fresh concrete (ACI 234 R., 1996). Silica-fume concrete usually includes chemical admixtures that may affect the time of setting of the concrete. Previous experiences indicate that the setting time is not significantly affected by the use of silica fume alone. Practical control of the setting time may be achieved by using appropriate chemical admixtures. In the literature, there is a general agreement on the retardation of initial and final setting times of the concretes containing FA and GGBFS. The behaviour seen in the SF concretes was different from those with FA and GGBFS in that the addition of SF generally reduced the initial and final setting times of the concretes, especially at 10 and 15% replacement levels. No general agreement could be found in the literature considering the effect of SF content on the setting times of concretes (Gesoglu and Özbay, 2007). Some researchers (Brooks et al., 2000; Alshamsi et al., 1993; Khedr and Abou-Zeid, 1994) stated that SF has retarding effect while some others reported its accelerating effect on the setting times. According to (Pistilli et al., 1984 and De Almeida and Goncalves, 1990) for a lower water/binder ratio concrete containing a superplasticizer, the effect of SF was to reduce the setting times when compared to those of control concrete containing the same amount of superplasticizer. (Park et al., 2005) investigated the influence of the cementitious materials containing fine particles on the rheology of the pastes. The mineral admixtures used were finely GGBFS, FA, and SF. Cementitious pastes were designed as one component Portland cement (PC), two-components (PC-GGBFS, PC-FA, and PC-SF), and three components (PC-GGBFS-SF and PC-FA-SF) systems. It was found for the two component system that yield stress and viscosity decreased with replacing PC with GGBFS and FA. In the case of PC-SF system, however, yield stress and viscosity steeply increased with increasing SF. For both of the three-component systems the rheological properties of the cementitious pastes improved compared with the PC-SF binary systems.

3.2. Silica Fume in the Hardened Concretes

Since silica fume improves the bond between the paste and aggregate, the influence of the quality of the aggregate on the mechanical properties of concrete becomes more important in silica-fume concrete. (Bhanja and Sengupta, 2005) carried out an extensive experimental study over the water–binder ratios ranging from 0.26 to 0.42 and silica fume–binder ratios from 0.0to 0.3. They were determined, compressive, flexural and split-tensile strengths at 28days. The compressive, as well as the tensile strengths increased with silica fume incorporation, and the results indicated that the optimum content is not constant but depends on the water–cementitious material (w/cm) ratio of the mixture . When compared to splitting tensile strength, flexural strength has exhibited greater improvements. According to ACI committee report (ACI 234 R., 1996) the static elastic modulus of silica fume concretes is apparently similar to that of portland cement concrete of similar strength.(Helland et al., 1983) concluded that the stress-strain behaviour of silica-fume concrete was similar to that of portland-cement concrete. (Sellevold and Nilsen, 1987) found that the dynamic modulus of elasticity increases with increasing silica-fume content in pastes. (Mazloom et al., 2004) demonstrated that the compressive strength development of the concrete mixtures containing silica fume was negligible after the age of 90 days; however, there were 26% and 14% strength increase in the control concrete after one year compared to its 28 and 90 days strengths, respectively. At the age of 28 days, the strength of concrete containing 15% silica fume was about 21% higher than that of the control concrete. Therefore, the inclusion of silica fume in concrete mixture, mainly

affects short-term strength of concrete. The difference in strength development in ordinary Portland cement concrete and silica fume concrete can be attributed (Wild et al., 1995) to the rapid formation of an inhibiting layer of the reaction products preventing further reaction of SF with calcium hydroxide beyond 90 days. In the case of the control concrete, hydration is at a less advanced stage and strength still shows significant improvement.

3.3. Effects of Silica Fume on the Durability Properties of Concretes

(Alexander and Magee, 1999) examined the durability performance of various condensed silica fume (CSF) concretes in comparison to Portland cement (PC) and PC/GGBFS controls. Oxygen permeability index, water sorptivity, chloride conductivity tests were performed on the produced concrete samples and the test results indicated that durability performance was significantly improved when using CSF in all tests. (Pigeon et al., 1986) investigated the freeze-thaw durability of concrete with and without silica fume in accordance with the requirements of ASTM Tes Method for Resistance of Concrete to Rapid Freezing and Thawing (C 666 Procedure A). The water-cement ratio of all mixes was 0.5, and the silica-cement ratio of the silica fume mixes being 0.1. The test results showed that the critical value of the air-void spacing factor in these ASTM C 666 tests is significantly lower for the silica fume concretes. Such concretes therefore appeared to be more susceptible to internal cracking caused by rapid freeze-thaw cycles in water, even though the use of silica fume decreased the surface scaling of the test specimens. This confirms that scaling and internal cracking are two different forms of frost damage caused by rapid freeze-thaw cycles in water. The sulphate resistance of concrete containing silica fume is good, partly because of lower permeability, and partly in consequence of a lower content of calcium hydroxide and of alumina, which has become incorporated in C-S-H. Tests on mortar have shown also the beneficial effect of silica fume upon resistance to solutions magnesium, sodium, and calcium chlorides (Neville, 1996).

4. Metakaolin (MK)

The raw material input in the manufacture of metakaolin is kaolin clay. Kaolin is a fine, white, clay mineral that has been traditionally used in the manufacture of porcelain. It is thought that the term kaolin is derived from the Chinese Kaolin, which translates loosely to white hill and has been related to the name of a mountain in China. Kaolinite is the mineralogical term that is applicable to kaolin clays. (www.metakaolin.com, 2007). Metakaolin when used as a partial replacement substance for cement in concrete, it reacts with Ca(OH)2 one of the by-products of hydration reaction of cement and results in additional C-S-H gel which results in increased strength. Metakaolin is obtained by thermal activation of kaolin clay. This activation will cause a substantial loss of water in its constitution causing a rearrangement of its structure. To obtain an adequate thermal activation, the temperature range should be established between 600 to 750°C. Metakaolin is used in oil well cementing to improve the compressive and flexural strength of the hardened cement. Metakaolin also reduces the hardened cement permeability to liquids and gases. Chemical formula of Metakaolin is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.(Aiswarya. et al., 2013; Poon et al., 2006).

Calcium hydroxide is one of the by-products of hydration reaction of cement. When cement is partially replaced with Metakaolin, it reacts with calcium hydroxide and results in extra C-S-H gel. C-S-H gel is the sole cause for strength development in cement and cement based concrete. The chemical reaction is given below

Cement + Water = C-S-H gel + Ca $(OH)_2$
Ca $(OH)_2$ + Metakaolin = C-S-H gel
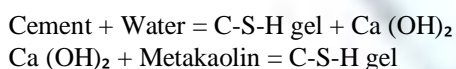
An important difference between MK and natural pozzolans or other types of artificial pozzolans is that MK is a primary product, while SF and FA are secondary products or byproducts. The key in producing metakaolin for use as a supplementary cementing material, or pozzolan is to achieve as near to complete dehydroxilization as possible without overheating. Successful processing results in a disordered, amorphous state, which is highly pozzolanic. Thermal exposure beyond a defined point will result in sintering and the formation of mullite, which is dead burnt and not reactive. In other words, kaolinite, to be optimally altered to a metakaolin state, requires that it is thoroughly roasted but never burnt (Kriven et al., 1994).

4.1. Metakaolin in the Fresh Concretes

It is well known that Metakaolin (MK) adversely affects the workability of concretes (Sabir et al., 2001). (Bai et al., 2002) reported that there was a systematic decrease in both slump and compacting factor and a systematic increase in Vebe time as the portland cement was partially replaced by MK with a level of 0 to 15%. Effects of MK on the setting time and consistency of mortars were determined by (Batis et al., 2005). The MK blended cements demand significantly more water than relatively pure cement owing to the high fineness of MK. The increase in the MK content causes a significant increase of the water demand compared with other blended cements. The initial and final setting times of metakaolin cements is higher than the setting time of pure cement.

4.2. Metakaolin in the Hardened Concretes

In metakaolin blended cement concretes, metakaolin contributes to the strength of concrete not only at early ages mainly by the filling effect, but also at later ages due to the fast pozzolanic reaction (Poon et al., 2006). (Naveen et al., 2006) presented the results of experimental studies wherein fly ash, metakaolin and their blends were used as fillers in SCC. The results showed that SCC can be produced with cement content, as low as 200 kg/m3 of concrete together with rest of the powder coming from fly ash. High strength SCC can be obtained through incorporation of metakaolin. The use of MK is reported to increase the concrete strength especially during the early ages of hydration (Zhang and Malhotra, 1995). After 14 days of curing the contribution that MK provides to concrete strength is reduced (Wild et al., 1996). The increase in compressive strength of MK concrete is thought to be due to the filling effect where MK particles fill the space between cement particles, acceleration of cement hydration and pozzolanic reaction of MK. This effect is similar to that of silica fume. Although the pore volume slightly increases in pastes containing MK, the pore structure of paste, however, is found to be refined (Khatib and Wild, 1996). The improvement in pore structure of the paste is increased when the amount of MK increases up to at least 20% as partial substitution of PC (Khatib and Hibbert, 2005). The incorporation of up to at least 30% MK increases the sulphate resistance of mortar (Khatib and Wild, 1998). The portlandite content in MK paste and mortar is reduced due to the reaction between PC hydration products and MK (Wild and Khatib, 1997). In order to evaluate and compare the mechanical properties of the concrete having metakaolin, (Kim et al., 2007) conducted compressive, splitting tensile and flexural strength tests on the concrete specimens using various replacements of silica fume and metakaolin. The compressive strengths obtained at 1, 3, 7, 28, 56, and 91 days mentioned study. This demonstrated that the level of compressive strength developed according to the replacement ratio of the binder by MK and SF, from 5% to 20%. A replacement ratio of 15% was seen to improve the development of compressive strength, but such effect appears to reduce for 20%. In other words, the most remarkable strengths were developed for replacement ratios from 10 to 15%, with poor improvement effect for a replacement ratio of 15% compared to 20%. It was observed that the level of splitting tensile strength developed dependent mainly on the replacement ratio of the binder by MK and SF, from 5% to 20%. For a replacement ratio ranging between 10% and 15%, it was observed that the strength enhanced as the replacement ratio increased, while there was strength reduction at 20%. It was also detected that the values of splitting tensile strength reached about 6% of the compressive strength. The flexural strengths measured at 1, 3, 7, 28, 56 and 91 days are to verify the level of flexural strength developed depending on the binder replacement ratios. Test results revealed that the strength increases with increasing the replacement ratio of the binder employed. It can be verified that the values of the flexural strength reach about 10% of the compressive strength. (Murali.G and Sruthee.P, 2012) experimentally studied the use of Metakaolin as a partial replacement substance for cement in concrete. The use of Metakaolin in concrete effectively enhanced the strength properties. The optimum level of replacement was reported as 7.5%. The result showed that 7.5% of Metakaolin increased the compressive strength of concrete by 14.2%, the split tensile strength by 7.9% and flexural strength by 9.3%.

4.3. Effects of Metakaolin on the Durability Properties of Concretes

There is a strong evidence that metakaolin greatly influence the pore structure in the paste and the mortars and produces substantial pore refinement. This leads to significant modification to the water transport properties and diffusion rates of harmful ions (Sabir et al., 2001). It has been reported that MK reduces the volume of capillary pores of sizes (0.05-10_m) normally associated with increased permeability. Rate of water absorption of mortar is halved by replacing 20% of the cement by MK (ECC International Document Product, 1996). (Coleman and Page, 1997) have shown that cement paste blended with 10% or 20% MK exhibited higher capacities than PC pastes, to chloride ions introduced by contamination of the mix water, thus reducing Cl- concentration in pore solution. (Kostuch et al., 1993) showed that expansion in concrete due to alkali silica reaction is completely eliminated by replacing the standard portland cement used by 15% MK. (Pera et al., 1998) examined the influence of MK on the resistance of concrete to solutions of lactic acid and ammonium sulphate simulating and aggressive agricultural environment. The result of this research showed that the presence of 10% MK limited the damage caused by exposure to lactic acid.

5. Rice Husk Ash (RHA)

Rice husk ash is produced by incinerating the husks of rice paddy. Rice husk is a by-product of rice milling industry. Controlled incineration of rice husks between 500^0 C and $800C^0$ produces non-crystalline amorphous RHA (Mehta and Monteiro, 1993; Mehta and Folliard, 1995). RHA is whitish or gray in color. The particles of RHA occur in cellular structure with a very high surface fineness. They have 90% to 95% amorphous silica (Mehta and Folliard, 1995). Due to high silica content, RHA possesses excellent pozzolanic activity. The physical properties of RHA largely depend on burning conditions. Particularly, the period and temperature of burning affect the microstructure and characteristics of RHA (Nagataki, 1994). The partial burning of rice husks produces black RHA whereas the complete burning results in either white or grey RHA (Ismail and Waliuddin, 1996).The burning condition also affects the relative density of RHA. The relative density of grey RHA obtained from complete burning is generally 2.05 to 2.11 (Ismail and Waliuddin, 1996, ; Nehdi et al., 2003b). The RHA particles are mostly in the size range of 4 to 75 µm .The majority of the particles pass 45-µm (No. 325) sieve. (Mehta, 2002), which is larger than that of silica fume. However, unlike silica fume, the

RHA particles are porous and possess a honeycomb microstructure (Zhang and Malhotra, 1996). Therefore, the specific surface area of RHA is extremely high. The specific surface area of silica fume is typically 20 m^2/g whereas that of non-crystalline RHA can be in the range of 50 to 100 m^2/g (Mehta, 1992). The typical chemical composition of RHA is given in Table 3.

Table 3: Typical chemical composition of rice husk ash (Mehta 2002)

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	Igneous Loss
%	94.37	0.06	0.04	0.48	0.13	0.08	1.97	1.19	1.18

5.1. Rice Husk Ash in Concrete

The use of RHA in concrete was accelerated after Mehta's findings in 1973 (Mehta ,1992). During the last two decades, RHA has been used to produce high strength and high performance concretes in many countries including Canada (Mahmud et al., 2004; Mehta, 1992; Zhang and Malhotra, 1996). In USA and Canada, RHA has been competently used to protect concrete structures from chloride attack (Mehta, 1992; Zhang et al., 1996). Also, it has been used recently in Canada, as a part of composite cement to produce normal-strength self compacting concrete (Nehdi et al., 2004).

However, In concrete, the RHA mainly serves as a microfiller, pozzolan, and viscosity modifier. The RHA particles can fill the voids between the larger cement grains because of their smaller size, as shown in Figure 3. However, the microfilling ability of RHA is not as effective as silica fume. This is because the RHA particles are much larger than the silica fume particles. (Mehta, 1994, ;Zhang and Malhotra, 1996). Although RHA is not very fine in particle size, it behaves as a very reactive pozzolanic material because of its extreme surface fineness and high silica content (Mehta, 1992, ; Mehta, 1994). In the presence of water, the RHA actively reacts with

$Ca(OH)_2$ liberated during cement hydration (pozzolanic reaction) and produces additional calcium silicate hydrate (CSH), as shown in Equation 1. And Equation 2.
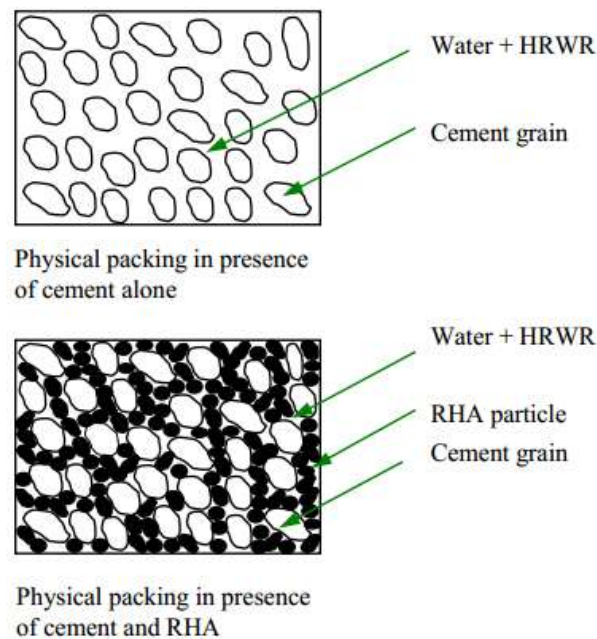

Figure 3. Microfilling effect of RHA

Hydration reaction: C_2S or $C_3S + H_2O \rightarrow$ Primary CSH + $Ca(OH)_2$ Eq.1
Pozzolanic reaction: $Ca(OH)_2 +$ RHA $(SiO_2) + H_2O \rightarrow$ Secondary CSH   Eq.2

The pozzolanic reaction product fills the pores existing between cement grains and results in dense calcium silicate hydrate, as shown in Figure 4. Both micro filling and pozzolanic effects of RHA play an important role to refine the pore structure in bulk paste matrix and interfacial transition zone of concrete. As a result, the strength, transport properties and durability of concrete are improved.
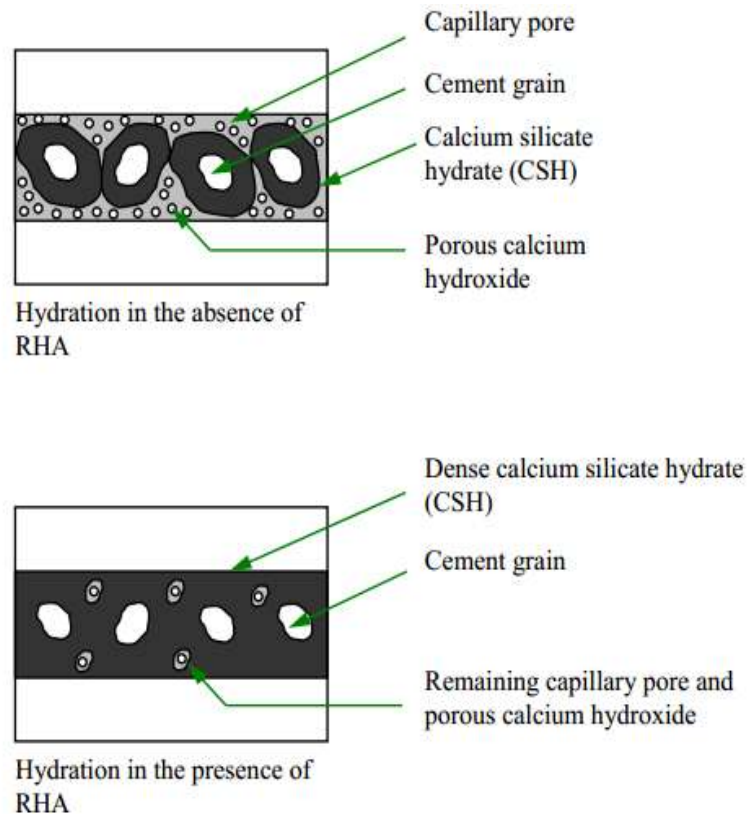
Figure 4. Pozzolanic effect of RHA

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