

AGGRESSIVE ATTACK OF SEA WATER ON COMPOSITES CONTAINING METAKAOLIN

H. Abu-El-Naga¹, M. M. Elwan² and E. A. El-Alfi¹

¹Department of Refractories, Ceramics and Building Materials, National Research Centre, Dokki, Cairo, Egypt ²Department of Chemical Engineering, Tabbin Institute Metlurgical Studies, Tabbin, Helwan, Egypt E-Mail: halahossein@yahoo.com

ABSTRACT

Due to the presence of metakaolin in composite cement that consists of Portland Cement and blended cement containing granulated blast furnace slag 0, 45% at constant percent at all mix, with OPC 100, 55, 51, 47 and 43 percent and finally metakaolin 0, 0, 4, 8 and 12 % in sea water up to 12 months was investigated. The composite cement pastes which contains cement, granulated blast furnace slag and metakaolin possess higher value of physical properties at 4 and 8% metakaolin such as compressive strength and bulk density than those of OPC and blended cement but opposite direction on apparent porosity and portlandite. By X-ray diffraction indicated that calcium aluminate hydrate and calcium silicate hydrate leading to strengthening the durability of the hardened composite cement pastes.

Keywords: composite cement, metakaolin, granulated slag, sea water, blended cement.

1. INTRODUCTION

Cement clinker production causes the global man made CO₂ emissions, resulting from release of CO₂ from limestone in the pyro-processing of clinker [1-3]. With the urgent need to reduce the amount of energy consumed and CO₂ released in air, numerous studies on suitable materials to partially replace the clinker in blended cement called supplementary cementitious materials (SCMs) [4-12]. The most popular active additions (SCMs) are ground granulated blast furnace slag (GGBS), flying ash (FA), silica fume (SF) and metakaolin to improve the performance of concrete capable of withstanding serious environmental conditions [13]. Moreover, these active additions can react with water or with Portlandite that has been produced as a product of hydration reactions of clinker and form new hydrated products that boost the cement-based materials' properties to improve the microstructure development and increase the durability [14-16].

Metakaolin (MK) becomes obvious alternatives and was first incorporated in concrete in 1962, in the construction of Jupia dam, in Brazil.MK is a highly reactive pozzolanic material obtained by calcinations of kaolinitic clay at temperature 650-800 ⁶C depending on the crystalinity and purity of precursor clays [17].

MK is obtained at 500 °C, then transforms to silicon-spinel at 925 °C and at temperature above 1400 0C, mullite is forms, both silicon-spinel and mullite have low activity. The exothermal dehydroxylation reactions are presented in equations (1-3).

~ 500
0
C :AL₂O₃.2SiO₂.2H₂O = AL₂O₃.2SiO₂+ 2H₂O (1)
Metakaolin

925
$${}^{0}C: 2[AL_{2}O_{3}.2SiO_{2}] = 2AL_{2}O_{3}.3SiO_{2} + SiO_{2}$$
 (2)
Silicon-spinel

>1400
0
C : 3[AL₂O₃. SiO₂] = 3AL₂O₃.2SiO₂ + SiO₂ (3)
3:2 mullite

Meta kaolin has a high specific surface and it is a very fine material, with 99.9% of particles with size less than 16 µm and an average size of about 3 µm. So, the use of MK in cement pastes leads to a refinement of the pore structure [18-20]. The incorporation of "superfine" MK particles leads to a micro-filler effect and improves the cement matrix packaging.

Ground granulated blast furnace slag is a supplementary cementitious material can be used either a mineral admixture or a component in blended cements [21, 22]. GBFS is a by-product in the iron manufacturing industry. Iron ore, coke and limestone are fed in to the furnace, and the molten slag floats above the molten iron at a temperature of about 1500 to 1600°C, and then molten slag containing siliceous and aluminous residues. The molten slag is separated from liquid metal cooled. There are three types of slag depending on the ways of cooling, namely aircooled, expanded and granulated which is rapidly water-quenched, leading to the formation of a glassy (amorphous) granulated slag [23-25].

The entry of sulphate (a common aggressive substance present in soil and ground water) and chloride ions in concrete resulting in dissolution of CH, precipitation of gypsum, sulfoaluminates hydrates (ettringite and monosulfate) and chloroaluminate hydrate causing expansion and softening of concrete [26]. Moreover, these products produce microcraching and a loss of pore refinement leading to a reduction of mechanical properties and loss of durability [27-30]. Reactions produced by the sulphate attack are presented in (4) and (5) Equations.

 $Ca(OH)_{2} + Na_{2}SO_{4} + 2H_{2}O = CaSO_{4} - 2H_{2}O + 2NaOH$ (4)

$$3CaO.Al_2O_3 + 3CaSO_4.2H_2O + 26H_2O$$

= $3CaO.Al_2O_3.3CaSO_4.32H_2O$ (5)

MgCL₂ reacts with portlandite producing CaCL₂ which increases the porosity and leads to strength loss.



The use of pozzolanic materials can significantly enhance long term durability and improve the resistant to aggressive attack by sea water [17]. Durability of concrete has been a great concern of civil engineering professionals because of the exposure of sea structures to chemical deterioration of the harmful constituents of sea water on concrete. In a mixture containing MK, the binding capacity is a function of aluminates content [31] .Formation of Friedel's salt in mixtures of PC is due to reactive alumina in each pozzolan [32]. In addition, composites cements have a good effect in decreasing the permeability to chloride in concrete [33, 34] and reduce the corrosion problems of steel reinforcement [35-40].

This good performance is due to the pozzolanic reaction MK and GBFS consuming the portlandite liberate during the hydration of PC before it can react with sulphate and chloride ions [7, 41-44]. Moreover, we can deduce that lower availability of calcium hydroxide and much less expansive ettringite is produced. Many authors observed useful role of Na₂SO4 which acts as activator of pozzolanic materials leading to decreasing the portlandite existence in cementitious system [43, 44].

Furthermore, the chemical action of chloride ions, MK can present a physical protection mechanism by taking part the refinement of the pores of hardened cement pastes, so the pores become less interconnected making the penetration of chlorides more difficult [45] and good performance against reinforcement corrosion [46].

The present work aims to study the effect of different substitutions of Portland cement by metakaolin on the durability of Portland slag cement pastes in sea water to explain the improvement of the resistivity of the composite cement against sea water attack.

2. EXPERIMENTAL WORK

2.1 Materials and Mix Design

2.1.1 Ordinary Portland Cement:

The Portland cement was obtained from National Cement Company, Helwan, Egypt. The chemical analysis of Ordinary Portland Cement (was carried out using the XRF technique). The blain surface area of the Portland cement was $3.150 \text{ m}^2/\text{kg}$. The results are given in Table 1.

Table-1. Chemical analysis of the starting materials, (wt. %).

Materials	Oxides											
	SiO ₂	AL ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ 0	L.O.I	Total		
OPC	21.3	5.41	3.77	63.14	1.21	2.35	0.4	0.09	2.57	99.90		
GGBFS	39.89	13.72	2.56	26.38	3.47	1.22	1.00	1.06	1.98	99.97		
MK	46.68	35.75	1.49	0.10	0.19	0.03	0.05	2.96	12.18	99.82		

2.1.2 Granulated blast furnace slag

It was obtained from the Egyptian Iron and Steel Company, Helwan. It is usually obtained by water quenching of the molten slag. It was ground in steel ball mill to obtain a Blain surface area (4.560 m²/kg). In GGBFS, particles above $20\mu m$ in size react very slowly, despite, particles below $2\mu m$ react completely within 24 h in blended cement and alkali-activated systems (47-49). The results of chemical analysis of granulated slag were given in Table-1.

2.1.3 Metakaolin

It is a mineral material of aluminosilicate and was provided from Idfu, Aswan and Upper Egypt. The formula of metakaolin in the silicate chemistry is AS_2 (Al₂O₃.2SiO₂). Grain size of metakaolin is between cement and microsilica, and the specific surface is about 15 m²/kg. The MK is made from slow calcination of kaolinitic clay at 750 $^{\circ}$ C (50-52). The results of chemical analysis of metakaolin were given in Table-1.

2.2 Experimental Techniques

The dry constituents of OPC, metakaolin and slag were mechanically mixed for 30 minutes in a rotary mixer to attain homogeneity of the cement samples. The mix composition of different prepared cements is shown in Table-2.

Table-2. Mix composition of different preparedcements, wt, %.

Mix NO.	Α	В	С	D	Е
PC	100	55	51	47	43
MK	0	0	4	8	12
GGBFS	0	45	45	45	45

The prepared cement blends were mixed with the required water by continuous mixing by hand for 4 minutes by gauging trowels. The required water of standard consistency was determined according to ASTM specification [53-55]. Immediately, after mixing the cement paste was poured in one inch cubic moulds and pressed until homogeneous specimen was obtained. The molds were manually shaken to remove any air bubbles, and then smoothed by spatula. The moulds were curried in 100% saturated humidity chamber at 23 ± 2 °C for 24 hours, then remolded and cured under tap water for 28days (zero time), then immersed in sea water for 1, 3, 6, 9and 12 months. The aggressive solutions were renewed every month to keep the concentration of salt ions in sea water nearly constant. At the end of each period, three cubes representing each mix were tested for their physicmechanical properties.



The kinetic of hydration was followed by the determination of free portlandite contents of hydrated cement pastes (ASTM 114) [56]. Bulk density and total porosity were determined before the specimens subjected to compressive strength determination during weighing the hardened specimens suspended in water and air, for at least three cubes of the same ages [56, 57]. After the compressive determined, the hydration of cement pastes was stopped using (1:1 v) methanol-acetone mixture, then mechanically stirred for 1 h, then filtered through a G_4 , washed two times with diethyl ether, dried at 70 °C for 1 h and stored in desiccators for analysis [44].

Some selected samples were examined by the powder method of X-ray diffraction (XRD) using Philis diffractometer PW 1730 with X-ray source of Cu Ka radiation was carried out The diffractometer was scanned from 5 ° to 65 ° (20) in step size of 0.015 and the counting time per step was 1.8 s. The X-ray tube voltage and current were fixed at 40 KV and 40 mA, respectively. An online search of a standard database (JCPDS database) for X-ray powder diffraction pattern enables phase identification for large variety of crystalline phases in the sample.

3. RESULTS AND DISCUSSIONS

3.1 Compressive Strength

The compressive strength of hardened composite cement pastes in comparison with OPC pastes immersed in seawater up to 12 months is plotted against curing time in Figure-1. The results indicate that the compressive strength of OPC pastes (A) increase up to 3 months due to the activation effect of chloride and sulphate ions and formation of CSH. In contrast, the compressive strength decreases after the first 3 months and up to 12 months due to the formation of sulphoaluminate , chloroaluminate hydrate and Friedel's salt having less binding properties and softening the

Cement pastes [58, 59].

Mix (B) has higher compressive strength than OPC pastes due to the pozzolanic effect of GGBF reacting with the liberated lime, resulting in formation of dense microstructure with additional amount of CSH. On the other hand, the decreasing of compressive strength after 6 months and up to 12 months is mainly attributed to the aggressive attack of sulphate and chloride ions in seawater.

The results illustrate that, the compressive strength of composite pastes (C), (D) and (E) increases with curing time due to higher reactivity of the reactive alumina present in MK. Moreover, the replacement of cement by MK initiates Friedel's salts formation in presence of chlorides results in formation of calcium aluminates. Calcium chloroaluminate is obtained during ionic exchange and the replacement of OH by CL ions; these ions changed chemically into stable compounds precipitated in cement pastes. Therefore, this is the best mechanism of protection by MK in pastes (17), meanwhile, the pozzolanic reaction of GGBFS leading to formation of denser CSH. The composite cement pastes (D) possess higher values of compressive strength than those of the OPC and composite cement pastes.

It is clear that, the replacement of cement by mineral admixtures decreases the $Ca(OH)_2$ contents liberating during hydration of OPC resulting in bridging the gap between cement particles by fine mineral admixture particles leading to improvement of compressive strength (60). Also, the addition of MK and GGBFS tends to improve the durability of OPC cement pastes because of not only as a reactive pozzolana but also as a filler leading to densifing the pore structure to enhance the resistance to sulphate and chloride attack.

3.2 Bulk Density

Figure-2 represents the bulk density of hardened composite cement pastes immersed in sea water for 1, 3, 6, 9 and 12 months. The bulk density of all composite cement pastes containing different percents of MK increase up to 12 months, due to the pozzolanic effect of MK and GGBFS leading to formation of dense structure of additional amount of CSH .The bulk density of OPC pastes (A) increases up to 3 months, while mix B increases up to 6 months, a result of acceleration effect of chloride and sulfate then decrease up to 12 months. Mix B has higher values of bulk density than those of OPC pastes. This is due to the pozzolanic reaction of GGBFS.

It is concluded that, composite cement pastes containing 8% MK (D) show higher values of bulk density, due to the higher reactivity of MK leading to formation of denser and high stiffness CSH and CAH and decreasing penetration of chloride and sulphate ions. So, mix D has the highest durability effect against sea water.

3.3 Apparent Porosity

Figure-3 represents he variations of apparent porosity of hardened composite cement pastes immersed in sea water for 1, 3, 6, 9 and 12 months. The apparent porosity values of the cement pastes containing MK and GGBFS decrease with curing time, while the cement pastes with GGBFS decrease up to 6 months then increase up to 12 months. The apparent porosity of cement pastes decreases at early ages of immersion due to the filling up of the available pores with the hydration products.

It is evident that, the cement pastes containing different percent of MK and 45% GGBFS represent lower values of porosity. This is due to micro filling and pozzolanic effect of GGBS and metakaolin. Moreover, the total pore volume of pastes decrease to small pore diameter portion as a result of compacting hydration product CAH and C-S-H gel forms and fine particles bridge the gap between cement particles [7].

3.4 Free Portlandite Contents

Free portlandite contents values of hardened composite cement pastes containing MK immersed in sea water up to 12 months are plotted as a function of curing time in Figure-4. The results indicate that, the free portlandite contents of composite cement pastes decrease with curing time up to one year due to highly pozzolanic effect of MK as well as GGBFS that react with Ca(OH)₂

(C)

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liberated during the hydration of OPC leading to formation of additional hydration products. Moreover, as MK content increases, the portlandite contents decrease due to the higher reactivity and surface area of MK. It should be mentioned that, the cement composite pastes containing MK and GGBFS is proved to be a promising way to improve the durability of cement pastes.

It can be seen that, OPC pastes have the highest values of the free portlandite contents where, that portlandite contents decrease up to 3 months due to the reaction with chloride and sulphate ions forming CaCL₂, $Mg(OH)_2$ and $CaSO_4$ leading to formation of chloroaluminate hydrate and sulphoaluminate. Magnesium ions react with free portlandite released from hydration forming brucite layer at the exposed cement particles surface. Magnesium ions penetration under the brucite layer into the interior of the cement paste is forbidden because of low solubility of brucite layer. After 3 months, the brucite becomes a protective layer around cement particles which prevents the Mg²⁺ ions penetration resulting in the increase of free portlandite contents after 3 months up to 12 months.

3.5 X-Ray Diffraction Patterns

Figure-5 illustrates XRD patterns of A, B, C, D and E hardened samples immersed in seawater for 12 months. In sample A, It could be seen that, portlandite (the most important phase due to its good-crystallinity) is presented with an increasing amount. As well as the hydration of clinker minerals are still working (the hydration of silicate phases showed by growing the intensity of portlandite). In case of composite samples, this is appeared that, by increasing the amount of MK, the intensity of Portlandite peak as well as the intensity of clinker minerals decrease. This is owing to the pozzolanic reaction between metakaolin, granulated slag and portlandite. Moreover, quartz peaks were detected as a main content of slag cement. The anhydrous silicate phases(β -C₂S and C₃S) peaks superpose with the hydrated silicates peaks and then decrease by increasing MK percents, due to the hydration progress forming additional amount of calcium aluminates hydrates and calcium silicates hydrates [13]. These additional hydration products fill the available open pores forming compact microstructure of hydration products which forbidden the penetration of chloride and sulphate ions leading to strengthening the durability of the hardened composite cement pastes. The present of sulphoaluminate, calcium carbonate, and gypsum were detected with different intensity for all immersing samples. The ettringite peaks is not discovered by XRD because, it was thought to be a very fine crystals [61].

Figure-6 shows the XRD results of composite cement pastes containing 8% MK D (showed the best mechanical properties) immersed in seawater for 1, 3 and 12 months. The results show the presence of diffraction lines corresponding to sulphoaluminate, quartz, calcium carbonate as well as C₄AH₁₃. The results illustrate that, the deleterious products of sulphoaluminate and gypsum decrease with increasing the curing time of immersion in seawater. Moreover, the intensity of these peaks decreased with increasing curing time. Also, the $Ca(OH)_2$ peaks disappeared in the composite cement pastes and additional amount of calcium silicates hydrates and calcium aluminates hydrates appeared. So, MK plays an important role for enhancing the durability of the composite cement pastes. These results completely agree with the physicomechanical results.

CONCLUSIONS

- The metakaolin made from slow calcinations of kaolinitic clay at 750 ° c with specific surface area is about 15m²/kg but granulated blast furnace slage 4.56m²/kgin blended cement is bigger than metakaolin.
- The sea water is affecting on cement, blended cement and composite cement.
- Composite cement containing cement, granulated slag and metakaolin with 8% percent give better physical properties such as compressive strength, bulk density, finally portlandite and opposite direction on apparent porosity
- composite cement had a relatively good sea water resistance performance which contains OPC, granulated slag and metakaolin due to:-
- The presence of calcium aluminate hydrates and calcium silicate hydrates.
- XRD of composite cement pastes containing 8% metakaolin showed the best mechanical properties immersed in sea water for 1, 3and 12 months.

(ACC)



Figure-1. Compressive strength of hardened composite cement pastes containing 45% granulated slag and different percents of metakaolin immersed in sea water up to 12 months.



Figure-2. Bulk Density of hardened composite cement pastes containing 45% granulated slag and different percent of metakaolin immersed in sea water up to one year.



Figure-3. Apparent porosity of hardened composite cement pastes containing 45% granulated slag with different percents of metakaolin immersed in sea water up to 12 months.



Figure-4. Free Portlandite Contents of hardened composite cement pastes containing 45% granulated slag with different percents of metakaolin immersed in sea water up to 12 months.



Figure-5. XRD patterns of hardened A, B, C, D and E immersed in sea water up to 12 months.



Figure-6. XRD patterns of hardened M immersed in sea water for 1, 3 and 12 months.

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