INFLUENCE OF METAKOLIN ON RESISTIVTY OF CEMENT MORTAR TO MAGNESIUM CHLORIDE SOLUTION

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Introduction

Metakaolin (MK) was studied because of its high pozzolanic properties [1-2]. It is well known that MK is a reactive aluminosilicate, which is formed by the dehydroxylation of kaolin precursor upon heating in the temperature range of 700–800 °C [3-4]. The effects of MK on the durability and mechanical properties of mortar or concrete have been widely reported [5-8]. Recent works showed that MK is effective as a supplementary cementitious material on improving the durability of concrete, for example, alkali–silica reaction [9] and resistance to chloride ingress [10].The influence of chloride is either chemical by interaction with liberated lime from the hydration reaction forming what is known as Friedel's salt or hydrocalumite ($C_3A.CaCl_2.10H_2O$) causing softening to the composition. While the other most dangerous role is the free chloride ions that cause corrosion for the reinforcement steel in concrete leaving it damaged. Metakaolin (MK) recently was added to the list of pozzolanic materials [11], as it is silica based products that, on reaction with CH, produces C-S-H gel at ambient temperature so that prevent free lime from reaction with tricalcium aluminates forming hydrocalumite as represented by the latter equation. MK also contains alumina that, on reaction with CH, produces additional alumina containing phases, including C_4AH_{13}, C_2ASH_8, and C_3AH_6 [12].

The present article reports our findings of the effects of incorporating Metakaolin on cement mortar resistance to magnesium chloride attack as indicated from microstructarl properties immersed in magnesium chloride solution (5%) up to 360 days after water curing up to 28 days (zero time).

Starting materials

The materials used in this investigation are ordinary Portland cement (OPC) obtained from Suez Cement Company (Tourah plant), Egypt. Kaolin with high kaolinite content, provided from Al Dehesa, Sinai governorate, Egypt, was thermally treated at 820°C for 2 hrs with a heating rate of 5°C/min., to produce metakaolin (Mk). This temperature was chosen on the basis of an earlier research work (13). The results of chemical analyses of the starting materials are shown in Table (1). The calcinations below 700° C results in a less reactive metakaolinite with more residual kaolinite, above 850°C crystallization occurs and reactivity declines (14).

Table (1): Chemical composition of starting materials. (Mass, %)

Experimental procedures

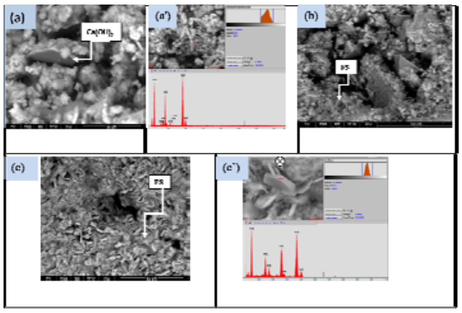
Six different blended cement mortar mixtures were prepared. OPC was partially substituted with 0%, 10%, 15%, 20%, 25% and 30% of Mk by mass. The water-binder material ratio (w/b) was 0.60 by mass. The cementitious material/fine sand (< 1.0 mm) was in the ratio of (1:3) in all mortar mixtures, mixed in a standard planetary mixer for 5 min continuously, poured in one inch cubic steel moulds, left at 100% relative humidity for 24 hours, demoulded and water cured up to 28 days (as zero time) in tape water after then removed from the tape water container and immersed in magnesium chloride solution (5%) for one year. The solution was renewed every month to keep the concentration as much as possible constant. After curing, the cubes were then dried well at 80°C for 24hr at each age and then the cubes were exposed to the compressive strength measurements and then subjected to stopping of the hydration process using stopping solution to prevent further hydration and for further analysis.

Chemical analysis was carried out using XRF Spectrometer PW1400. The removal of free water was accomplished by using alcohol/acetone method as recommended by different investigators (15). Compressive strength tests were carried out using five tones German Brüf pressing machine with a loading rate of 100 kg/min determined according to the ASTM (16). The microstructure of the hardened blended cement mortars was studied using SEM Inspect S (FEI Company, Holland) equipped with an energy dispersive X-ray analyzer (EDX).

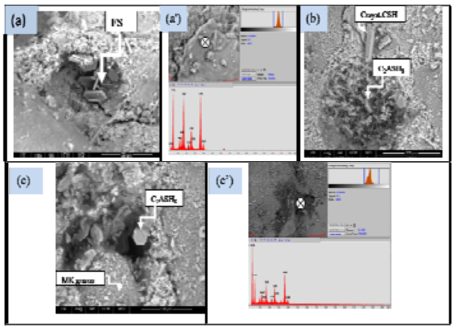
Scanning electron microscopy (SEM)

The microstructure and the morphology of the hardened OPC-Mk mortar pastes containing no metakaolin content immersed in 5%$MgCl_2$ (water cured up to 28 days) at 1,7, 90 days are shown in Fig.(1). The scanning electron micrographs (SEM) of the neat OPC mortar paste after one day of hydration Fig.(1a), showed the spreading of the hydration products all over the surface as well as the presence of massive layer of calcium hydroxide that covered also with the hydration materials. The EDX analysis confirms the presence of honeycomb CSH (II) that contains high calcium content than the silica. After 7 days, the micrograph indicates the growth of hydration products with the increase of ill-crystallized CSH phases and hexagonal crystals of $Ca(OH)_2$ as well as little plates of Friedel's salt that appear within the matrix (Fig. 1b).Whilst at 90 days, the hydration went steadily indicating the presence of ill-crystalline FS, demonstrated from the EDX analysis, overlapping with most of the hydration products and filling the pores resulting in a more compaction at these ages (Fig. 1c). As, the attack of magnesium chloride producing brucite ($Mg(OH)_2$), that has low solubility, assumed to envelop the remainder of the cement gel and protect it against further deterioration **[Cohen, and Bentur(1988)]**.

After 360 days, the microstructure seems different where a noticeable pore is filled with FS (thin hexagonal crystals) that appears to be crystalline in nature (Fig.2a). The EDX analysis for this age also indicate the presence of Ca,Si,Al and Cl where It's possible that those values of EDX incorporate calcium and silicon from hydrated cement matrix (Fig.2a').Also, Cl-ions seems to be fused within the hydration materials leading to an enhancement in the Physico-mechanical properties. With an increased substitution of OPC by Mk up to 25 wt. % at 360 days (Fig. 2b), the SEM micrograph indicates a relatively dense and compact structure where the cement binder exhibited a relatively low porosity. The content of CSH gel phases increases with the co-existence of the two types of CSH phases; these are CSH (II) which has a platy (honeycomb) type structure and CSH(I) with its fiber-like structure. We can notice the presence of well crystalline CSH allover the matrix structure and fibrous one within the pores with slight crystals of gehlenite hydrate. Whereas at 30% Mk, the micrograph consisted primarily of poorly crystalline structure as the cement content, was decreased sharply producing low content of hydrated lime compared with the last mentioned structure of 25%MK.Whilst, the gehlenite hydrates become a predominant as Mk is in excess also higher content of metakaolin grains dispersed on the matrix surface acting mainly as a filler Fig. (2c).



Fig(1):SEM micrograph of the neat OPC blended cement mortar specimens without metakaolin addition at W/C=0.60, magnesium chloride at (a) one day, (b) 7 days and (c) 90 days.



Fig(2):SEM micrograph of the neat OPC blended cement mortar specimens without metakaolin addition at W/C=0.60, magnesium chloride at 360 days (a) 0%MK (b) 25%MK and (c) 30%MK.

Compressive strength

The Figure of compressive strength with metakaolin content and curing time up to 360 days are represented in Fig.(3), where the compressive strength increases at any metakaolin addition with curing time, exceeding that of the reference mortar pastes at all curing time as result of binder formation and accumulation in the open pores caused by cement hydration as well as the pozzolanic reaction of metakaolin with CH.

From 0 up to 25 % replacement of PC with Mk, the increase of relative strength is mainly attributed to the filler effect leading to an initial acceleration of PC hydration and the increase of CSH binder phases caused by the reaction of CH liberated from cement hydration and metakaolin's SiO_2 component, while the decrease of the relative strength beyond 25%, may be due to the cessation of the pozzolanic reaction and the filler effect is surpassed by the dilution effect leading to low of the relative strength than that observed at 25% metakaolin or overcoming the filling effect over the pozzolanic one as the source of liberated lime (PC) decreases. The increase of metakaolin content up to 30%; decrease the strength as portlandite decrease which is one of the main pozzolanic reactants.

The conclusions elucidated from SEM emphasize compressive strength behavior, where the CSH increase with time (Fig.1).Where the microstructure exhibit a pronounced increase in ill-crystalline CSH with time, whereas the FS that formed at later ages (90day),spread all over the surface so that strengthen the structure. a different performance was noticed at later age of 360 days (Fig.2)., where EDX analysis interpret the inclusion of chloride ions within hydration materials preventing them from further formation of FS and improving the microstructure and chloride binding behavior **[Dhir and Jones (1999)]**. At 25% MK, the CSH (I) fill the pores with the presence of crystalline CSH leading to higher compressive strength. The sharp reduction in the strength values is apparent at 30% Mk content of OPC-Mk blend is related to the detection of unreacted Mk grains in the SEM micrographs **[Ambroise et al. (1994) and Klimesch and Ray, (1997)]**, as well as the presence of excess amount of gehlenite hydrate instead of FS that has lower binding properties.

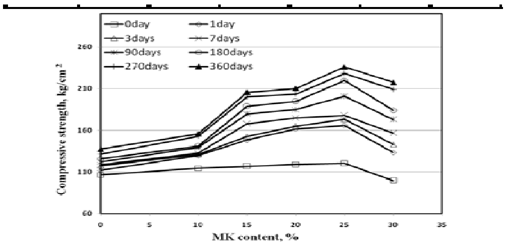


Fig (3): Compressive strength of the various blended cement (OPC-Mk) mortar pastes at different hydration ages in magnesium chloride (water/binder of 0.6%).

4. Conclusions.

1. Metakaolin provide a good resistance to aggressive chloride solution as it consume liberated lime, so prevent the formation of Friedel's salt.
2. The maximum development of compressive strength was achieved for the specimens made from OPC-Mk blended cement mortars containing a metakaolin content of 25 wt. %
3. Microstructure of the MK-blended mortar exhibit a homogeneous and a compact structure, where the optimum mix of 25wt.%MK provide a pronounced development in the hydration materials as well as a relatively low porosity leading to an enhancement in the mechanical properties..

5. References.

1. **Janotka, I.; Puertas, F.; Palacios, M.; Kuliffayová, M. and Varga, C.,** " Metakaolin sand–blended-cement pastes: Rheology, hydration process and mechanical properties", Construction and Building Materials, **24(5)**, 791-802(2010).
2. **Cachim, P.; Velosa, A. L. and Rocha, F.,** "Effect of Portuguese metakaolin on hydraulic lime concrete using different curing conditions", Construction and Building Materials 24 (2010) 71–78.
3. **Badogiannis, E. and Tsivilis, S**., " Exploitation of poor Greek kaolins: Durability of metakaolin concrete", Cement and Concrete Composites, **31(2)**,128-133(2009).
4. **Siddique, R. and Klaus J.,**" Influence of metakaolin on the properties of mortar and concrete: A review", Applied Clay Science, **43,** 392–400(2009).
5. **Kim, H. S.; Lee, S. H. and Moon, H.Y.,** "Strength properties and durability aspects of high strength concrete using Korean metakaolin", Construction and Building Materials, **21,** 1229 – 1237(2007).
6. **Kim, H. S.; Lee, S. H. and Moon, H. Y.,** "Strength properties and durability aspects of high strength concrete using Korean metakaolin", Construction and Building Materials, **21,** 1229 – 1237(2007)
7. **Asbridge, A.H.; Page, C.L. and Page, M.M.**, "Effects of metakaolin, water/ binder ratio and interfacial transition zones on the microhardness of cement mortars", Cem. Concr. Res., **32 (9),** 1365– 1369 (2002).
8. **Asbridge, A.H.; Chadbourn, G.A. and Page, C.L.,** " Effects of metakaolin and the interfacial transition zone on the diffusion of chloride ions through cement mortars", Cem. Concr. Res., **31(11)**, 1567–1572(2001).
9. **Gruber, K.A.; Ramlochan, T.; Boddy, A.; Hooton, R.D. and Thomas, M.D.A.,** "Increasing concrete durability with high-reactive metakaolin", Cem. Concr. Compos., **23 (6)**, 479– 484(2001).
10. **Boddy, A.; Hooton, R.D. and Gruber, K.A.,** " Long-term testing of the chloride-penetration resistance of concrete containing high-reactive metakaolin", Cem. Concr. Res., **31 (5)**, 759–765(2001).
11. **Khatib, J.M.; Wild, S.,** " Pore Size Distribution of Metakaolin Paste", Cem. Concr. Res., **26**, 1545–1553(1996).
12. **Saikia, N., Kato,S., Kojima,T.,** " Thermogravimetric investigation on the chloride binding behaviour of MK–lime paste", Thermochimica Acta, **44** ,16–25(2006).
13. **Kakali,G.; Perraki, T.; Tsivilis, S. and Badogiannis E.,** "Thermal Treatment of Kaolin: The Effect of Mineralogy on The Pozzolanic Activity", Applied Clay Science, **20**, 73–80(2001).
14. **Ambroise, J.; Murat, M. and Pera, J.,** "Hydration Reaction and Hardening of Calcined Clays and Related Minerals: V. Extension of the Research and General Conclusions", Cement Concrete Research, **15**, 261-8(1985).
15. **Taha, A.S.; El-Didamony, H.;.Abo.EL-enein, S.A.; and.Amer, H.A.,** "Physicochemical properties of supersulphated cement pastes", Zement-Kalk-Gips, **34,** 351-353(1981).
16. **ASTM C109M-07**, "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars", (2007).
17. **Ambroise, J.; Maximilien, S. and Pera, J.,** "Properties of Metakaolin Blended Cements", Advanced Cement Based Materials, **1,** 161-168(1994).
18. **Cohen, M.D. and Bentur, A.,** "Durability of Portland cement–silica fume pastes in magnesium sulfate and sodium sulfate solutions", ACI Mater J. **85 (3)**,148– 157(1988).
19. **Klimesch, D.S. and Ray, A.,** "Use of the Second-Derivative Differential Thermal Curve in the Evaluation of Cement-Quartz Pastes with Metakaolin Addition Autoclaved at 180°C", Thermochimica Acta, 307, 167-176 (1997).
20. **Dhir, R.K. and Jones**, **M.R.,**" Development of chloride-resisting concrete using fly ash", Fuel, **78**, 137–142(1999).