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Properties of Concrete Containing a New Cement-Grade Metakaolin

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ABSTRACT

The supply of economical good quality supplementary cementing materials (SCMs) such as fly ash is increasingly being challenged due to availability issues, transportation costs, and technical problems. The use of processed natural pozzolans, such as metakaolin in the production of concrete has engineering, economic, and ecological benefits to the construction industry.

This paper presents the results of a study on the suitability for new cement grade metakaolin called Whitemud^{MK} (WM). The chemical and physical characteristics of this material are determined in comparison with traditional metakaolinite (MK). The effect of cement replacement by WM on the hydration properties as well as the engineering characteristics of selected samples are investigated by means of XRD, TGA, SEM, strength measurements and chlorides penetrability. The results demonstrate comparable engineering properties to MK when cement is replaced by WM for up to 15%.

INTRODUCTION

The environmental features involved in the production and use of cement, concrete and other building materials are of growing significance. Portland cement, the most important component of concrete, is very energy intensive and its production accounts for 5% of the world's carbon dioxide in the atmosphere [WBSD 2005; Environment Canada 2005]. CO_2 emission, for example, is 0.8-1.3 ton per ton of cement production in the dry process [Chandra 1997]. Thus, replacing part of Portland cement by industrial by-products such as fly ash and ground granulated blast-furnace slag in concrete can contribute significantly to the reduction of CO_2 released into the atmosphere.

The partial replacement of ordinary Portland cement (OPC) by supplementary cementing materials (SCMs) reduces the amount of carbon dioxide produced compared to normal OPC production and cuts back on the amount of limestone and other raw materials used. Moreover, it can also improve concrete properties and increase the service life of structures [Lounis 2004]. The SCMs generally well accepted by the construction industry are fly ash, ground granulated blast furnace slag, and silica fume. However, their use is sometimes limited by availability issues, transportation costs, and technical problems. As a result there is pressure to find new sources. Increasing waste volumes and escalating disposal costs have forced a reassessment of public attitudes regarding the way society handles its wastes. This expanding awareness has given a definite trend toward recycling or use of a wide variety of solid waste materials. Many of the modern industrialized societies have reached their intended capacities, and much of the industry waste materials are shipped to landfills. A number of major environmental protection and pollution reduction initiatives underway are affecting the sustainability of concrete materials. These initiatives are established by commitments made at the local, regional, national and international stage.

The use of waste materials from other industries as raw material has a tremendous prospect for the cement industry to reduce its environmental impact. There is increasing demand for the inclusion of new and unique materials in concrete mixes, such as new types of pozzolans [Rehan 2004; Moura et *al* 2007; Sobolev et *al* 2007]. However, the existing efforts are fragmented and are at the embryonic stage. Some isolated studies showed the potential use of local industrial by-products and their contribution in reducing GHG emissions [Phair 2006].

This paper presents a preliminary study on the characterization of a new source of low cost metakaolin called Whitemud^{MK} (WM). WM is made from kaolin, a naturally occurring clay that is mined in southern Saskatchewan, Canada, and processed into a “cement-grade” metakaolin. Whitemud’s process is unique in that it does not involve additional processing that is often required to make standard and paper grade metakaolin. The hydration properties as well as the engineering characteristics of selected samples are studied and compared to metakaolinite (MK). The effect of this new SCM is expressed in terms of hydration products, strength development and chloride penetrability at different ages of hydration. The results demonstrate a potential replacement of cement by up to 15% of Whitemud^{MK} while keeping good engineering properties of concrete.

EXPERIMENTAL INVESTIGATION

Materials

The cement used was a Lafarge GU from the Woodstock plant. The fine aggregate used was a manufactured sand from Spratt Aggregates which was air dried before use. The coarse aggregate was a crushed stone sourced from Karson Kartage (Huntley Quarry, Carp, Ontario), which had a maximum size of 19 mm and was also air dried before use. Glenium 3000 FC from BASF was used as a superplasticizer. Whitemud^{MK} (WM) from Whitemud Resources Inc. Calgary, Alberta; and metakaolinite (MK) from Stochem Inc. Lachine, Quebec; were used in this study. For comparison purposes, silica fume (SF) from SKW Canada, St-Laurent, Quebec, was added to the experimental program. Table 1 presents the oxides content in the raw materials.

Table 1: XRF analysis (based on 1 gram size calibration)

Major oxides (wt%)	OPC	MK	WM
Na_2O	0.08	0.13	0.14
MgO	3.23	0.05	0.42
Al_2O_3	4.74	45.04	30.70
SiO_2	19.74	51.87	63.79
P_2O_5	0.06	0.06	0.03
SO3	3.06	BDL*	0.13
K_2O	0.56	0.14	1.47
CaO	63.68	BLD*	0.24
TiO2	0.26	1.70	0.59
MnO	0.04	BDL	0.01

Fe_2O_3	**1.80**	**0.54**	**1.63**
Trace elements (ppm)			
Cr	**51**	**142**	**189**
Co	**BDL[*]**	**4**	**BDL[*]**
Ni	**47**	**49**	**91**
Zn	**24**	**9**	**12**
Sr	**369**	**37**	**18**
Zr	**70**	**121**	**149**
Ba	**178**	**93**	**375**
Pb	**BDL[*]**	**20**	**16**
LOI	**2.83**	**0.94**	**2.33**
Total	**1.00**	**100.52%**	**101.56%**

[*] BDL: below detection limit

Experimental techniques

X-ray diffractograms (XRD) were obtained using Scintag XDS 2000. Thermogravimetric analysis (TGA) was carried out in a TA Instruments, Q600. Scanning electron microscopy (SEM) analysis was performed using a Hitachi Field Emission Scanning Electron Microscope model S-4800. Compressive strength measurements and chloride penetrability tests were done according to the ASTM C39 [1984] and ASTM C 1202 [1997] standards, respectively.

Samples preparation

A series of mix designs for cement mortars and concrete samples were developed using different rate of cement replacement (Table 2). The mixes were prepared with water-cement ratios of 0.55. On completion of mixing the slump and air content of the mix were determined and 100 mm x200 mm concrete cylinders were cast. The cylinders were filled in three layers and vibrated on a vibrating table at each level. The cylinders were then placed in the curing room for 24 hours at which time they were de-moulded, labelled and returned to the wet room until required for testing.

Table 2. Concrete mixes

	Cement (kg)	**MK or WM (kg)**	**Water (kg)**	**Stone (kg)**	**Sand (kg)**	**Superpplasticizer (ml)**
Control (100%OPC)	18	0	9.9	45	36	0
OPC replacement 5%						
Whitemud^{MK}	17.1	0.9	9.9	45	36	0
Metakaolinite	17.1	0.9	9.9	45	36	0
OPC replacement 10%						
Whitemud^{MK}	16.2	1.8	9.9	45	36	0
Metakaolinite	16.2	1.8	9.9	45	36	15
OPC replacement 15%						
Whitemud^{MK}	15.3	2.7	9.9	45	36	30
Metakaolinite	15.3	2.7	9.9	45	36	50

RESULTS AND DISCUSSIONS

Chemical composition

The primary chemical requirement for an SCM to be a pozzolan is its content in vitreous siliceous material, eg. silica. This acts as the reactive entity in the material which, in a divided form and in the presence of moisture, will chemically react with calcium hydroxide at ambient temperatures to form compounds possessing cementitious properties. The extent of this reaction is primarily dependent on the amount and availability of silica in the pozzolan and in turn, depends on the raw material and the process of formation. The ASTM C618 standards [2005] suggests that a material may be pozzolanic if it possesses a minimum of 70% mass of silica (Si), aluminum (Al), and iron (Fe) oxides. Table 1 shows more than 70% for both MK and WM. CSA specifications A3001[2008] for the use of fly ashes classifies them into different types according to their CaO content: Type F less than 8%, Type CI between 8 and 20% and CH above 20%. The calcium oxide contents of the samples studied in this work are all under the 8% limit except for OPC. The average LOI values for all samples were less than the 6% maximum permitted by ASTM C618 [2005] for coal fly ash. Chapelle method (not included in this paper), a direct measure of calcium hydroxide consumed by activation at 90°C over a 18 hours) showed that MK had the highest pozzolanic activity followed by WM. The correlation between these chemical analysis and pozollanicity is confirmed for both samples.

Thermal analysis

When cement is exposed to moisture, lime is produced as a result of the hydration of the alite, C_3S (and to a lesser extent, the belite, C_2S) clinker phase in Portland cement as described by the following reaction:

$$C_3S\ (C_2S) + a\ (b)\ H \longrightarrow C p S H_4 + q\ (r)\ CH \qquad (1)$$

Alite (belite) + water ⟶ Calcium silicate hydrates + Portlandite

A pozzolan is defined as a reactive aluminosilicate (A_xS_y), which can be either glassy such as fly ash and silica fume or semicrystalline such as metakaolinite. The most common and well-known pozzolanic process is the lime activation reaction induced by cement water reaction. This is based on the general reaction:

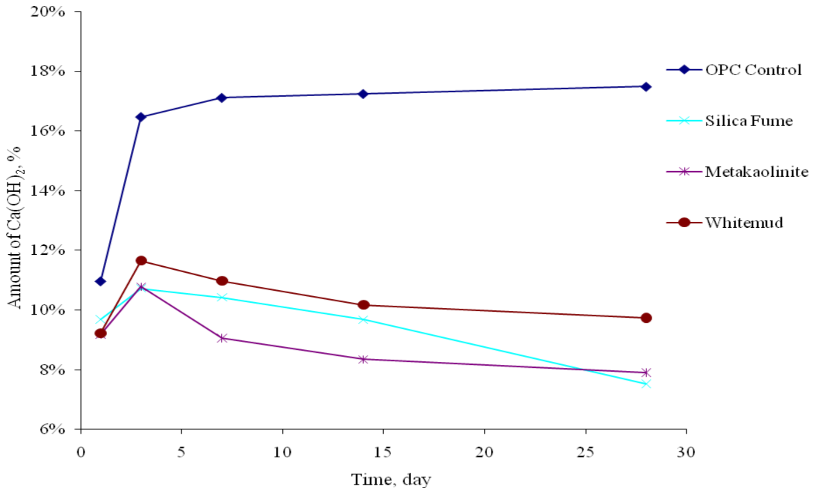
$$A_xS_y + mCH + nH \longrightarrow C\text{-}S\text{-}H + C\text{-}A\text{-}H \qquad (2)$$

Pozzolan+ Portlandite + water ⟶ Calcium silicate hydrates + Calcium aluminate hydrates

Blended cement pastes at 15% mass replacement were subjected to TG measurements after 1, 3, 7, 14 and 28 days hydration (Figure 1a). For comparison purpose samples including silica fume (SF) were added. In the case of the control sample, 100% OPC, the amount of $Ca(OH)_2$ increases with hydration time according to reaction (1). Cement systems with (SF), MK and WM show a significant decrease in the amount of $Ca(OH)_2$ indicating their considerable pozzolanicity. According to reactions (1) and (2), CH produced by C_3S (C_2S) reaction with water (1) is consumed by pozzolans to produce more C-S-H (reaction 2)

Figure 1b shows the evolution of $Ca(OH)_2$ amount at 28 days hydration as a function of substitution rate. The plot also includes the control samples (100% OPC) as a reference. Generally, all samples show a decrease in the $Ca(OH)_2$ produced when the replacement rate is increased from 5 to 15%. The figure clearly indicates that the pozzolanic reaction measured by the consumption of calcium hydroxide increases with the increase of cement replacement by MK, SF or WM. The thermogravimetric analysis confirms the pozzolanicity characteristics, as the calcium hydroxide produced is decreased when more hydrates are formed. Samples made with WM and MK all show similar behavior to those of silica fume.

(a)



(b)

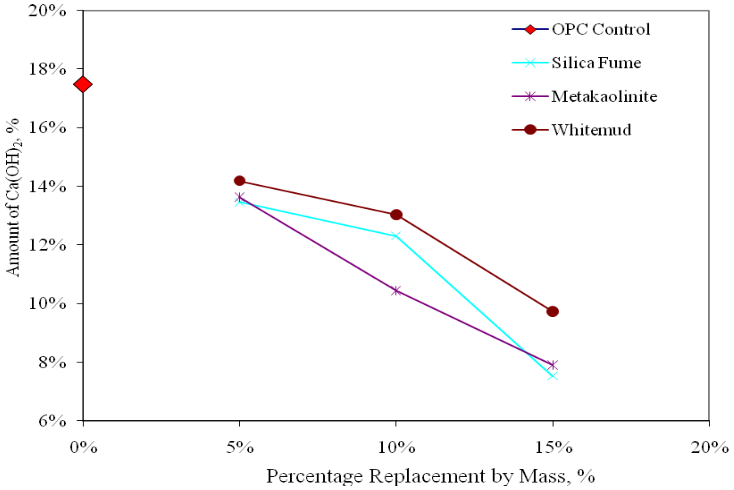


Figure 1. (a) Ammount of $Ca(OH)_2$ determined by TGA for paste samples made with control OPC and with 15% replacement of OPC by MK, WM and SF, (b) Amount of $Ca(OH)_2$ determined by TGA for different OPC pastes hydrated for 28 days at 0, 5, 10 and 15% OPC repalcement.

X-Ray diffraction analysis

The XRD patterns (Figures 2) not only confirm the TGA results, but also provide additional information about the mineral phases present in the starting materials as well as in the hydrated samples. The clinker phases (C_3S, C_2S, C_3A and C_4AF) of OPC as well as some peaks due to the presence of gypsum (G) are present. In the case of WM, the XRD profile contains a mixture of both amorphous and crystalline silica. In samples containing 15 % replacement of cement by WM, it can be seen that all hydrated samples (7, 14, 28 days) present typical hydration process profiles. At 1 day hydration, the sample indicates the presence of $Ca(OH)_2$ as well as peaks associated with unreacted clinker phases. The peak intensities of $Ca(OH)_2$ decrease with the hydration time. At 28 day-hydration, the peaks of $Ca(OH)_2$ become lower than those of OPC hydrated at the same age. This is an indication of the pozzolanic character of WM, as it is demonstrated by the TGA results. At 7 and 28 days hydration, the XRD profiles indicate the presence of a small peak representative of calcium aluminum oxide hydrate.

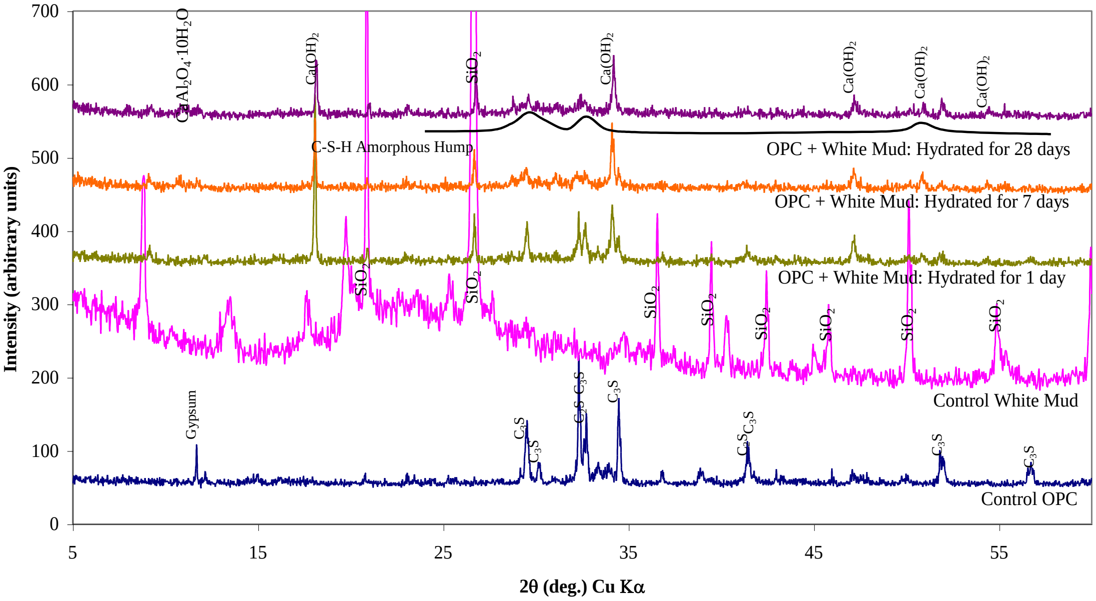


Figure 2: XRD patterns of anhydrous OPC and cement pastes containing 15 % cement replacement by WM at different ages of hydration

Microstructural analysis

Hydrated cement pastes were subjected to an SEM analysis. Figure 3a shows a typical microstructure of OPC. The hydration at 28 days gives a microstructure that is dominated by the presence of the major hydrates: C-S-H, CH and in some cases ettringite (Et), as shown in Figure 3d. Both WM and MK contain reactive silica and aluminum oxide that produce C-S-H gel upon hydration. As a result of their pozzolanicity, more hydrates are formed and the microstructure becomes denser. SEM analysis of control WM and MK samples exhibit very similar microstructural features as shown in Figures 3b and c, respectively. Upon hydration (Figures 3e and f), the clinker phases in cement are replaced by fibrous C-S-H. Randomly oriented CH crystals are dispersed through the paste and small amount of Et needles are present in most samples because of the presence of gypsum in the anhydrous cement, as shown by the XRD analysis.

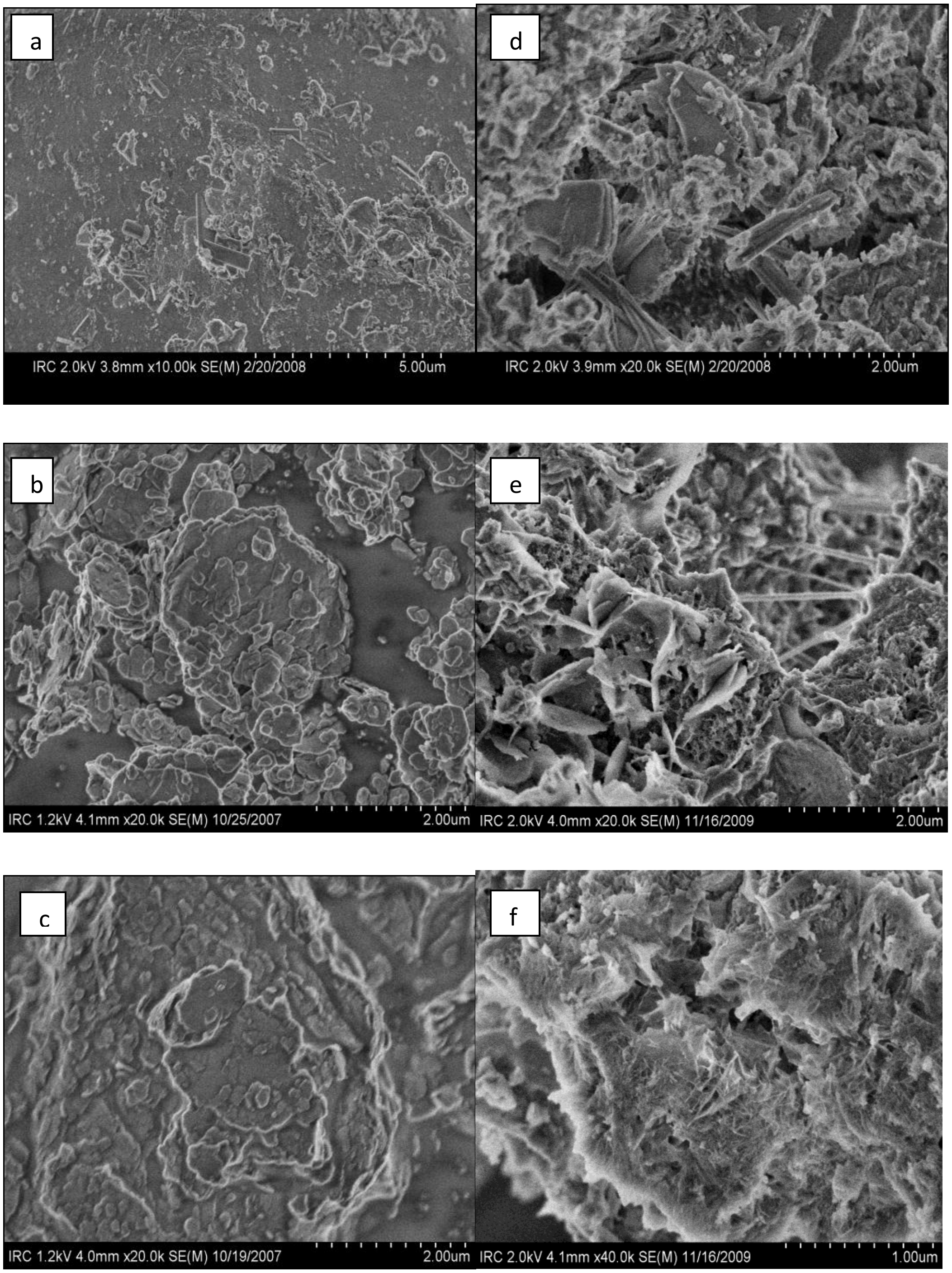


Figure 3. SEM images of: a) Control OPC, b) Control MK, c) control WM, 28 day-hydrated samples containing d) 100%OPC, e) 15%MK/85%OPC, and f) 15%WM/85%OPC**.**

Setting time

Figure 4 shows the results obtained with samples containing different proportions of WM and MK as replacements for cement at 0.55 w/c ratio. All samples exhibit an initial setting time within the allowable range compared to the control sample, as recommended by ASTM C403 [2006]. A decrease in both initial and final set time with the increase of the replacement rate of cement (5 to 15%) was observed for both WM and MK samples compared to the control. The setting of cement paste is recognized to be caused by the increasing volume of hydration products [Hewlett 2007]. It is obvious that the setting of cement pastes is closely related to the chemical and physical properties of the SCMs. At the early stage of hydration, very fine pozzolanic additives such as MK and WM simulate the hydration process by acting as “seed grains” for hydrates [Kuennen 1996]. Therefore, more hydrates are formed and the setting time is consequently shortened compared to the control sample. The pozzolanic reaction is then initiated after the setting of cement (~1day), which produces more hydrates and increased compressive strength at later ages of hydration.

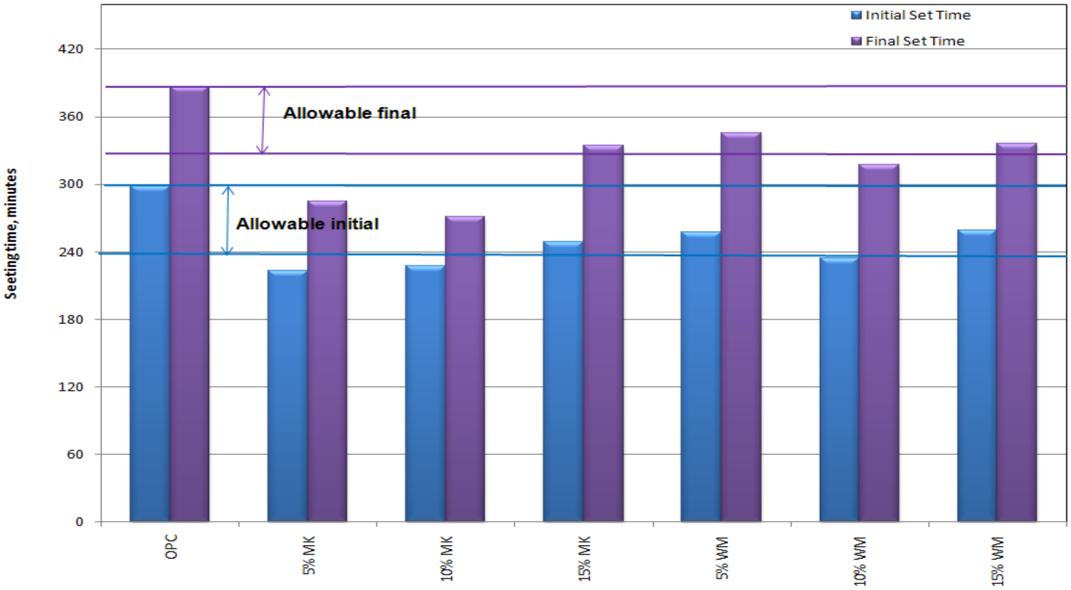


Figure 4. Setting time of OPC and OPC containing MK and WD at different ages of hydration

Compressive strength measurements

The compressive strength development of concrete at each age (3, 28, 56 and 91 days) is indicated in Figure 5. Compared to the control (OPC) sample, those made with WM and MK showed greater strength. The increased strength was observed at curing periods as early as 3 days. Improved strength development occurred at 28 days and 56 days for most samples containing WM and MK. 10% WM replacement and 15% MK replacement samples both reached 53 MPa at 91 days while 15% WM replacement and 15 % replacement of MK samples reached 52 and 47 MPa strength development respectively at 28 days.

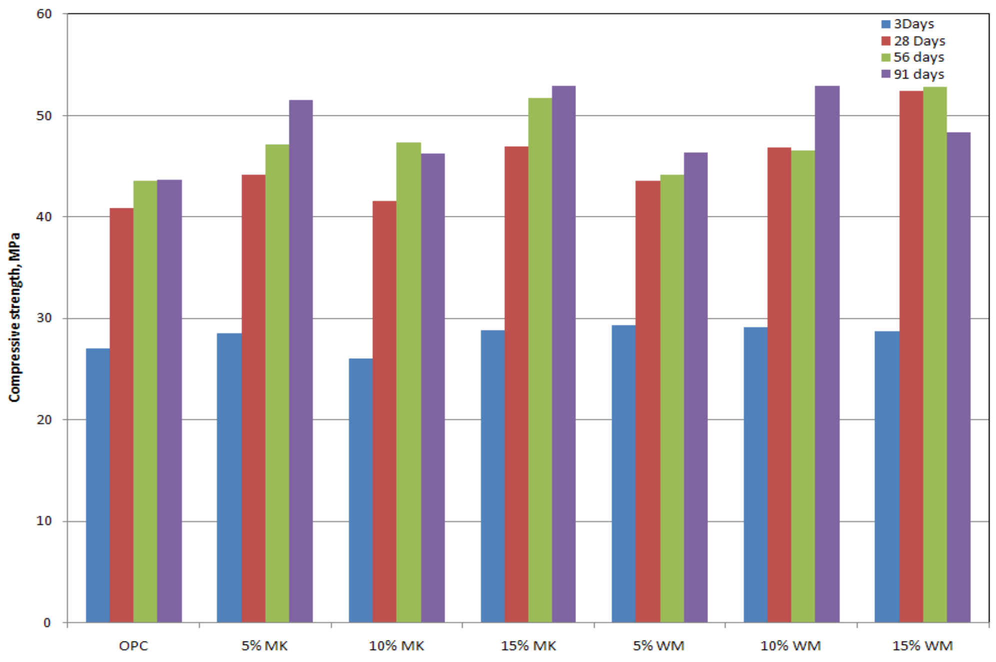


Figure 5: Compressive strength of OPC and OPC containing MK and WM at different ages of hydration

Chloride penetrability

Resistance to chloride ions penetration is a very important test used to assess the durability of concrete samples.. The test measures the total charge passed through a concrete sample in coulombs during a period of 6 hours. According to Feldman’s classification [Feldman et al 1999] the level of resistance to chloride penetration in traditional concrete is high when w/c > 0.6, moderate at w/c= 0.4-0.6, and low when w/c < 0.4. The tests were conducted in accordance with the ASTM C 1202 standard [1997]. The test method covers the determination of the electrical conductance of concrete by subjecting a saturated concrete specimen with a diameter of 4 in. (100 mm) and a thickness of 2 in. (50 mm) to 60 volts DC for six hours. One side of the specimen is immersed in a sodium chloride solution and the other side in a sodium hydroxide solution. The total charge passed is measured in coulombs (second.ampere). Higher values of coulombs represent the higher chloride ion penetrability. The preliminary evaluation was done for two samples cut from 100 mm diameter standard cylinders per mix. The standard cylinders were cast for each concrete mix, and were cured for 90 days according to the ASTM C 39 [1984].

The data on the resistance of concrete mixtures to chloride ions penetration determined according to the ASTM C 1202 for ages 56 and 91 days are presented in Figure 6. The graphs summarize the results of the tests performed on different cement systems containing 5, 10, and 15% replacement of cement by MK and WM. At both ages, the concrete samples containing WM and MK show very similar behavior and exhibit much higher resistance to chloride penetration compared to the control sample. It is noted that the resistance increases as the replacement rate changes from 5 to 15% in all samples. It is also noted that chloride penetrability is further decreased with increase of sample age. As the concrete samples hydrated longer, the microstructure of the pastes become denser. This behavior is attributed mainly to enhanced pozzolanic reactions induced by the presence of WM and MK. As a result, concrete becomes less permeable and the chloride ions ingress decreases accordingly.

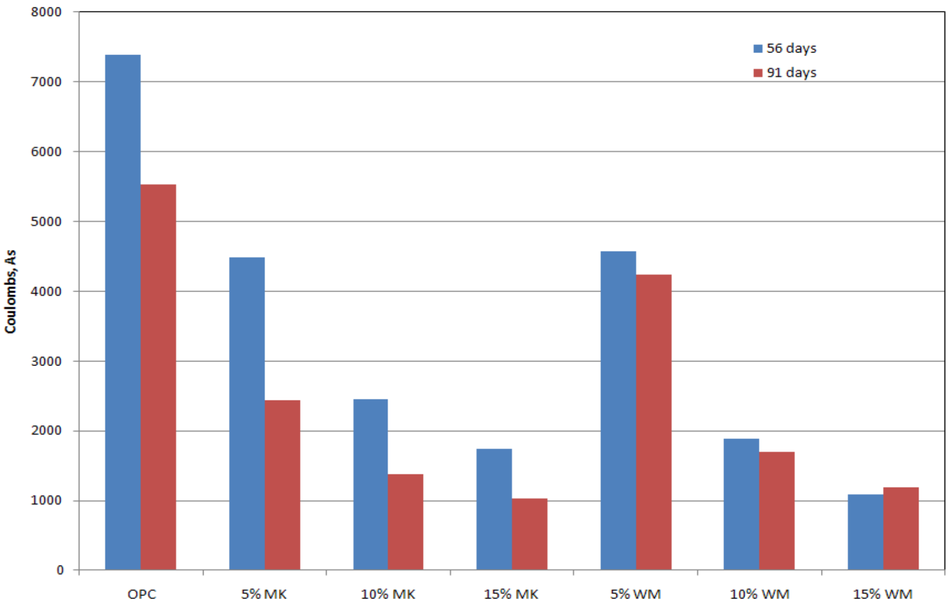


Figure 6. Chloride penetrability tests on selected concrete samples at 56 and 91 days

CONCLUSIONS

From the findings of this work, it was observed that WM characteristics and properties in concrete samples were comparable to those with MK. The conclusions can be summarized as follows.

- Due to its remarkably high pozzolanic activity, as demonstrated by TGA analysis, WM performs comparably to MK.
- With the partial replacement of OPC with WM and MK, the setting time of the paste is shortened. This behavior may be due to the presence of "nucleation sites" that promotes the early formation of a large amount of hydrates.
- The partial replacement of OPC with WM and MK increased the compressive strength of concrete samples at different ages of hydration. In some instances, it was much higher than that of the reference specimen.
- The increased compressive strength in samples containing WM and MK is due to an improved microstructure as a result of the pozzolanic properties of WM and MK.
- The chloride penetrability resistance of concrete materials containing WM outperformed samples made with control OPC. The production of more hydrates contributed to the densification of the pore structure, thus blocking the path to chloride ingress.

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