



RESEARCH ARTICLE

HYDRATION REACTION OF METAKAOLIN BLENDED CEMENT IN THE PRESENCE OF SUPER PLASTICIZER

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ABSTRACT

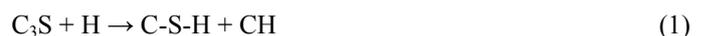
Blended Portland cements are hydraulic cements in which a well-defined fraction of the Portland cement clinker is replaced by other hydraulic, pozzolanic or non-hydraulic materials. Their general behaviour is similar to that of Portland cement since they harden when mixed with water and form the same calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H). The addition of supplementary cementitious materials (SCMs), such as metakaolin to cement generally improves workability, durability, and long-term strength. However, use of SCM concrete is sometimes limited due to a lack of understanding about material behaviors and a lack of proper specifications for its construction practice. In this paper the hydration of OPC in the presence of 30% metakaolin and 0.8% superplasticizer was monitored as a function of time with the help of heat evolution calorimeter, X-ray diffraction and SEM studies. Water consistency, setting time and compressive strengths were measured. Results have been discussed.

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INTRODUCTION

Concrete is the most important construction material in the world and perhaps its consumption is next to water. Portland cement is the binding material of concrete. Manufacturing of Portland cement (OPC) is a resource exhausting, energy intensive process and releases large amounts of the green house gas (CO<sub>2</sub>) into the atmosphere. Green house gases results in an increased temperature for the earth's troposphere. The intergovernmental panel on climatic change estimates that the average rise in temperature of the environment should reach between 1.9 and 5.3°C in the next 100 years. The need to reduce the consumption of energy and the release of carbon dioxide increased the emphasis on the use of blended cements. Blended Portland cements are hydraulic cements in which a well-defined fraction of the Portland cement clinker is replaced by other hydraulic, pozzolanic or non-hydraulic materials. Their general behavior is similar to that of Portland cement since they harden when mixed with water and form the same calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H). (Mukesh Kumar and Singh, 2015; Mukesh Kumar et al., 2012). Chemical reactions during the hydration of cement are given below



In order to reduce CO<sub>2</sub> emissions in the cement industry, a lot of efforts have been made. At present, efforts have been made to replace part of Portland cement (OPC) by supplementary cementitious materials (SCM) such as pozzolana and also replace OPC concrete by geopolymer concrete (Mukesh Kumar and Singh, 2015; Mukesh Kumar et al., 2012; Singh and Middendorf, 2009; Okoye et al., 2015; Singh et al., 2015). SCM can improve concrete properties such as compressive strength, durability and impermeability through hydraulic or pozzolanic activity. The main component of SCMs additive is usually an active amorphous SiO<sub>2</sub>. The availability of common used industrial by-products such as fly ash, blast furnace slag, rice husk ash, silica fume, and metakaolin (Sabir et al., 2001; Manjit Singh and Mridul Garg, 2006; Morsy et al., 2012; Mansour et al., 2011). The term pozzolana was defined as siliceous/aluminous materials, either natural or artificial, which react chemically with calcium hydroxide (CH) or with

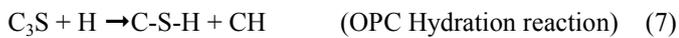
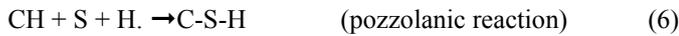
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materials that can release calcium hydroxide (Portland cement clinker) in the presence of water to form compounds that possess cementitious properties.

Pozzolanic reaction is a simple acid-based reaction between calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and Silicium acid.



The pozzolanic reaction is slow, so the rate of development of the strength and the heat of hydration associated with this reaction are low. On the other hand, the hydration of  $\text{C}_3\text{S}$  in Portland cement is relatively fast, so the development rate of the strength and the heat of hydration associated with it are high. It should also be noted that equation 6 (Singh *et al.*, 2015) is a CH consuming reaction, whereas equation 7 (Sabir *et al.*, 2001) is a CH producing reaction. When a mixture of Portland cement and pozzolana is allowed to hydrate, a gradual decrease of the free calcium hydroxide occurs with time as the pozzolanic reaction progresses.

formed CH compounds to produce supplementary calcium silicate hydrate (C-S-H).



In general, SCMs with higher alumina contents, such as MK, tend to have higher pozzolanic capacities because formation of C-A-H has a high CH demand. This is critical, as CH does not make a significant contribution to concrete strength and can be detrimental to durability. Its elimination or reduction by secondary reaction with MK can greatly enhance concrete performance (Mindess *et al.*, 2003). Addition of MK in mortar and concrete, increases water demand. This increases total porosity and as a result reduces strength. The mixing water can be reduced by adding suitable superplasticizer. The water reducing mechanism of superplasticizer is quite complex and the efficiency in reducing water demand depends on the adsorption rate and mineral composition of cement and MK. In this paper hydration of Portland cement in presence of metakaolin and superplasticizer has been studied.

**Table 1. Oxide composition of OPC**

Oxides	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SiO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cl	K <sub>2</sub> O	CaO
Composition (%)	0.460	2.460	5.520	19.98	3.170	3.480	0.019	0.880	61.62

**Table 2. Mineral composition of OPC**

Name	Chemical formula	Designation	Percentages
Alite (tri calcium silicate)	3CaO.SiO <sub>2</sub>	C <sub>3</sub> S	55-65%
Belite (di calcium silicate)	2CaO.SiO <sub>2</sub>	C <sub>2</sub> S	15-25%
Aluminate (tri calcium aluminate)	3CaO.Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A	8-14%
Ferrite (Tetracalcium alumino ferrite)	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	C <sub>4</sub> AF	8-12 %

ATPL- 410 as PC based superplasticizer (SP) from ATPL Ltd, New Delhi was used as superplasticizer.

This reaction can be accelerated by an increase in temperature and by using admixtures containing, for example, alkalis and sulfates. It is generally recognized that the incorporation of fly ashes as the partial replacement for Portland clinker in cement is effective means for improving the properties of cement. Due to its pozzolanic properties, ashes react with  $\text{Ca}(\text{OH})_2$  during hydration reaction and form calcium silicate hydrate. This can reduce the size of pores of crystalline hydration products, make the microstructure of cement paste more compact and consequently improve compressive strength and durability of cement. The major drawback is low early strength. While fly ash and ground-granulated blast furnace slag represent the majority of SCMs used, there is a shift to embrace other materials, which is driven by many factors, including supply-and-demand concerns (Maria C.G. Juenger and RafatSiddique, 2015). Calcined clay is one of the earliest known pozzolanic materials. It is even used today in places devoid of industrial wastes like fly ash, granulated blast furnace slag, etc. Kaolin is widely distributed in nature and the use of metakaolin (MK) in blended cement production has been well established (Saikia *et al.*, 2002). Siddique and Klaus (2009) found that MK as a partial substitution of cement enhances the early age mechanical properties including strengths as well as long term strength properties of cement paste/mortar/concrete. This is because when MK is introduced, it reacts rapidly with newly

## Experiments

### Materials

Portland cement OPC (IS : 3535- 1986) was taken from JK Lakshmi cement limited Haryana. The oxide and mineral compositions of OPC are given in Tables 1 & 2 respectively. Particle size distribution is given in Fig.1(a).

### Metakaolin

The oxide composition of Metakaolin (MK) used for making blended cement is given in Table 1 and particle size distribution is given in Fig.1(b).

**Table 3. Oxide composition of Metakaolin**

Oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O
Composition(%)	50.21	39.59	2.60	2.31	0.46	0.46	0.29

## Methods

### Preparation of Hydrated Sample

10 g each OPC and 30% MK blended OPC were mixed with 5.0 ml of distilled water or 0.8% super plasticizer solution in

polythene bags in order to have water/solid ration equal to 0.5. The mixtures were then mixed thoroughly and the air from the bags were removed and kept at room temperature (36°C). The hydration reactions were stopped at different intervals of time i.e. 1, 3, 7, 14 and 28 days with the help of isopropyl alcohol. The hydrated sample were then heated in an oven at 100°C for one hour, the samples were then kept in polythene bags and stored in a desiccator.

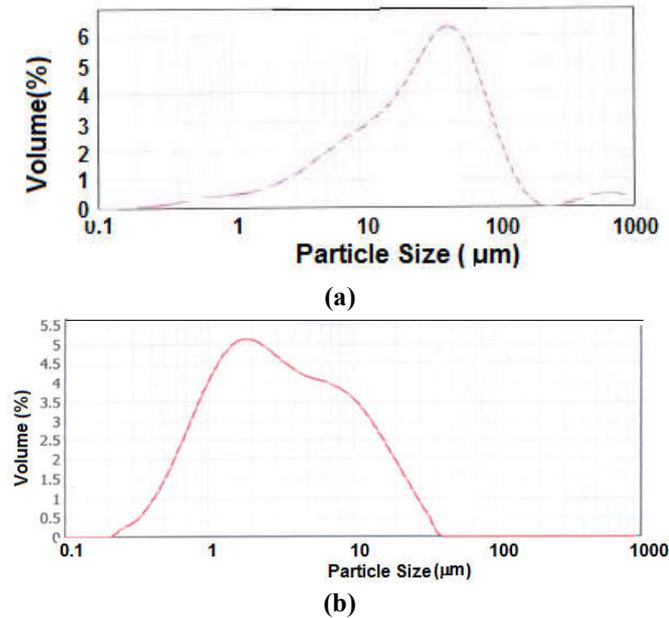


Fig.1. Particle size distribution of (a) OPC and (b) metakaolin



Fig.2. Vicat Apparatus

#### Determination of heat of hydration

2g each of OPC and 30% MK blended OPC were mixed with 1 ml of water or 2% superplasticizer solution in different plastic vials. Each vial was then vibrated for about 30 seconds and then placed into the calorimeter chamber immediately. The quartz powders were then mixed with water (w/quartz equal to 0.5) in plastic vial, which this was used as a reference. The rate of heat evolution and total heat evolved were determined as a function of time.

#### Determination of Water consistency

The water consistencies were determined with the help of Vicat apparatus (I S: 4031 part 4, 1988) (Fig.1).

#### Determination of setting time

Initial and final setting times were determined with the help of Vicat apparatus (I S: 4031 part 5, 1988) shown in Fig.2.

#### Determination of Compressive strength

Mortar cubes were prepared in 7.5 x 7.5 x 7.5 cm<sup>3</sup> moulds and compressive strengths in the absence and presence of MK and SP at different intervals of time were determined with the help of compressive strength testing machine. Mould and compressive strength testing machine are given in Fig.3.



a)



b)

Fig. 3 (a) Mould (b) Compressive strength Testing Machine

#### Determination of X- ray diffractions

Powder X-ray diffraction patterns of hydrated cements were recorded with X-ray diffractograph using CuK<sub>α</sub> radiations.

## RESULTS AND DISCUSSION

Hydration of OPC is a complex and highly exothermic reaction. As soon as cement content comes in contact to water, rapid heat evolutions takes place (Fig.4). This is a result of cement wetting, dissolution of alkalis, leaching of different ions in the solution, hydration of hemihydrates of gypsum and hydration of the aluminates phase. Soon after that the rate of heat evolution decreases and remains constant for some time, called the induction or the dormant period. During this period nuclei of critical size was formed and once it acquired the critical size, the hydration accelerated with time and reached to its maximum value at around 12 hours. This is due to the hydration of alite phase of cement. After the maximum rate of heat evolution, the rate of heat evolution started decreasing continuously. This continuous decrease is due to the formation of large amount of hydration product which covers the surface of unhydrated cement and the hydration reaction became diffusion controlled. In the presence of 30% MK, the shape of the rate of heat evolution curve remained the same but the maxima shifted to longer time with higher rate of heat evolution. The shifting of maxima to longer time may be due to dilution effect, whereas higher rate of heat evolution may be due to enhanced exothermic pozzolanic reaction between MK and CH. In the presence of superplasticizer, hydrations of both OPC and OPC-30%MK were retarded to a considerable extent. This may be due to adsorption of SP at the surfaces, which blocked the passage of water molecule towards fresh surface of cement. Total heat evolved as a function of time is shown in Fig.5. This has similar effect as in the case of rate of heat evolution (Fig.4).

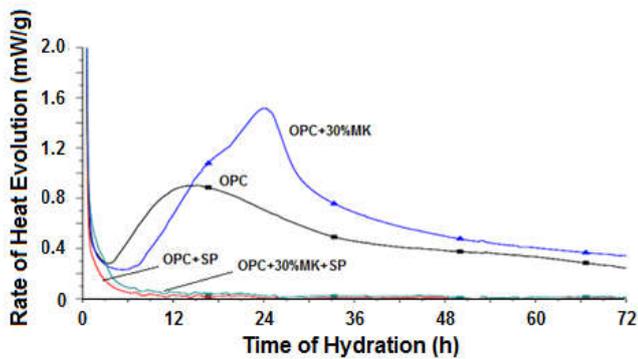


Fig.4. Rate of heat evolution as a function of time

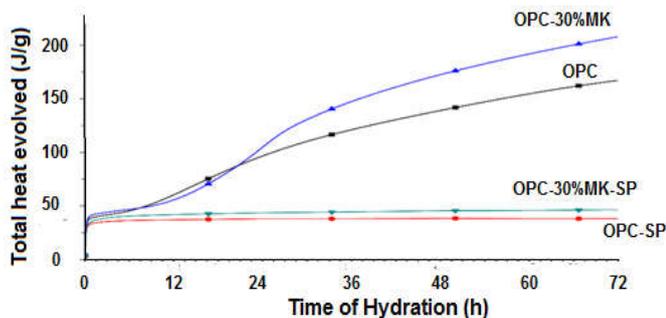


Fig.5. Total heat evolved as a function of time

Water consistencies are given in Table 4. The results showed that Metakaolin increases slightly the water consistency of the ordinary Portland cement. This is due to adsorption of water on

MK surfaces. On the other hand the water consistency decreased with the addition of super plasticizer. This indicated that addition of super plasticizer to the cement decreases the water requirement and as a result, compressive strength may increase.

Table 4. Water consistency

Cement Sample	OPC	OPC+30% M.K	OPC +0.8% SP	OPC+30%M K+0.8%SP
Water consistency	27	27.55	26.50	26.75

Initial and final setting times are given in Table 5. The result showed that both the initial and final setting time are increased in the presence of MK, which further increased in the presence of superplasticizer.

Table 5. Setting time (minute)

Cement sample	OPC	OPC +30% M.K	OPC+0.8 % SP	OPC+30%M. K+0.8% SP
IST(Min)	180	185	230	240
FST(Min)	220	230	290	300

Compressive strength values are given in Table 6 and its variation with time is shown in Fig.6.

Table 6. Compressive Strength (MPa) of different mix

Time (days)	OPC	OPC+30% MK	OPC+0.8% SP	OPC+30%M.K +0.8% SP
1	28.9	29.1	29.6	29.8
3	39.0	39.7	39.8	41.5
7	49.2	50.2	51.7	52.4
28	59.0	59.4	60.3	63.2

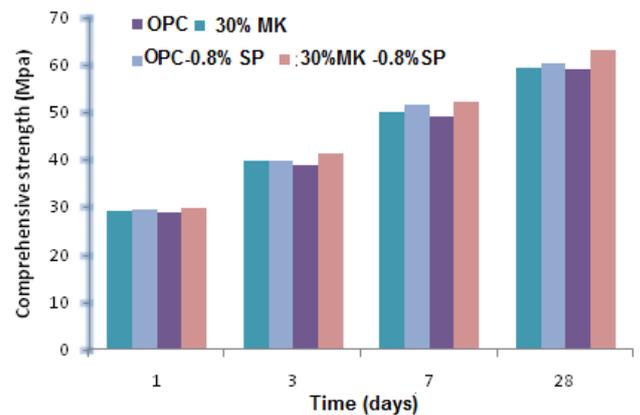


Fig.6. Variation of compressive strength with hydration time

Compressive strengths of OPC in the absence and presence of 30% MK, 0.8% SP and their combination increased with hydration time. This is as a result of increased amount of hydration products and decrease of porosity. The compressive strengths of OPC, OPC-0.8%SP, OPC-30%MK and OPC-30%MK- 0.8%SP were found to be comparable at all the times of hydration. However, OPC-30%MK- 0.8%SP gave highest compressive strengths at all the times. This may be due to early pozzolanic reaction of MK with CH, forming larger amounts of C-S-H and reduction of water due to SP. As a result compressive strength is increased. X-ray diffraction patterns of different cement system hydrated for 3 days are shown in

Fig.7. When OPC was allowed to hydrate an intense peak due to CH is obtained. However in the presence of MK and SP the intensities of different peaks were affected, indicating the hydration.

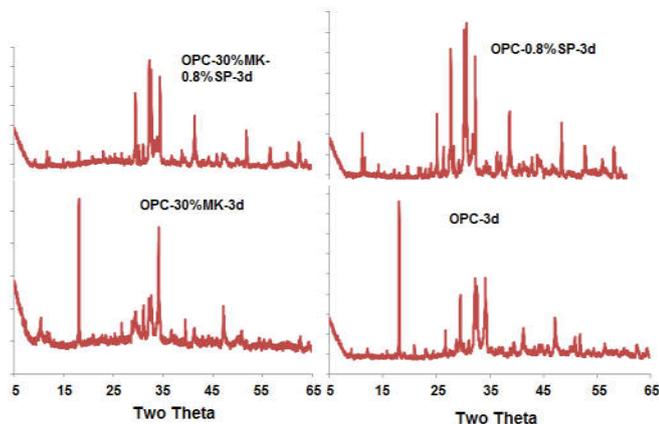


Fig.7. X-ray diffraction patterns

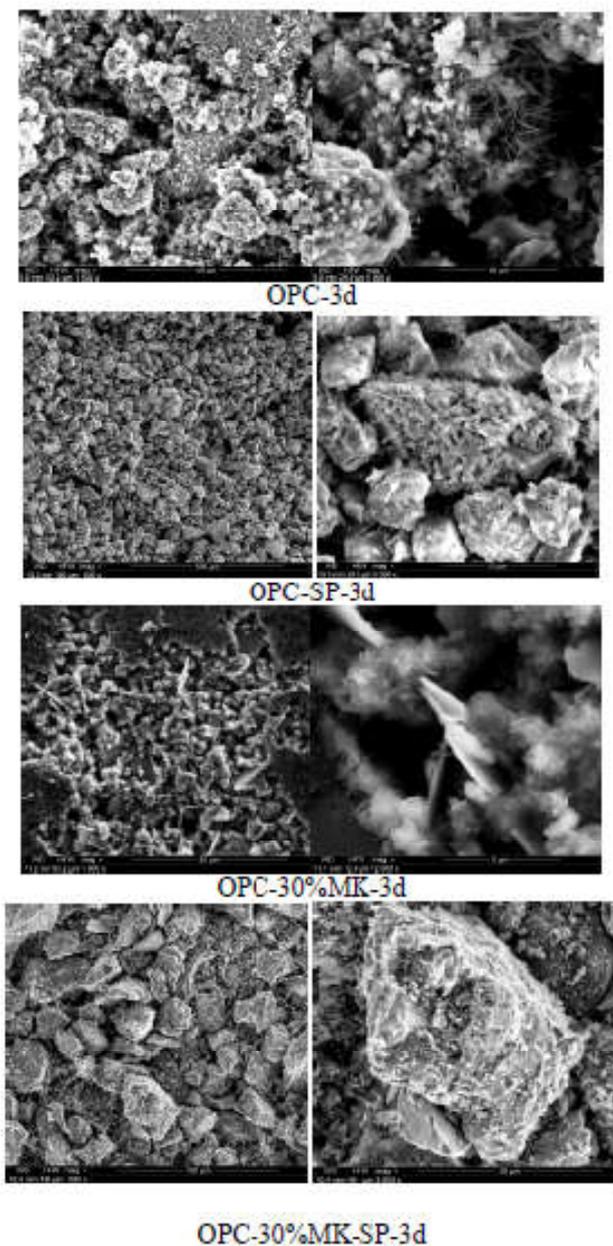


Fig.8. SEM pictures

SEM micrographs of different systems hydrated for 3 days are shown in Fig.8. The pictures clearly indicate that during hydration morphologies are changed. Both MK and SP modified the morphology in different ways. The morphology of OPC-30%MK-0.8%SP hydrated for 3 days was much more compact and as a result the compressive strength values were higher.

### Conclusion

From the results it is concluded that in the presence of 30 % Metakaloin and 0.8%SP, the hydration products were very compact with a dense structure. This reduced the pore size and pore size distribution. As a result the compressive strength at all the times was higher. Use of MK with SP might minimise the deficiencies of blended cements at early hours.

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