



## Effects of Calcium Chloride in Mixing and Curing Water on Strength of High-Performance Metakaolin Concrete

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### ABSTRACT

*This paper presents the results of an experimental investigation carried out to study the effect of aggressive chemical environment on High performance concrete with metakaolin in which Ordinary Portland cement is partially replaced by 20% of metakaolin by weight and aggressive chemical environment is simulated by subjecting the concrete to different concentrations of Calcium chloride ( $\text{CaCl}_2$ ) in deionised water during mixing and curing. Compressive strengths and split tensile strengths were determined at 7, 28 and 90 days. The results indicate that the compressive strength and split tensile strength increase with the increase in concentration of Calcium chloride when compared with concrete without Calcium chloride in mixing and curing water.*

**Keywords : Ordinary Portland cement, High-Performance concrete, Metakaolin, Compressive strength, Split tensile strength, Calcium chloride**

### Introduction

High-Performance-Concrete (HPC) has been defined as concrete that possesses high workability, high strength and high durability. ACI (American Concrete Institute) has defined HPC as a concrete in which certain characteristics are developed for a particular application and environment. In discussing the meaning of HPC, Neville and Aitcin [6] stated that "in practical application of this type of concrete, the emphasis has in many cases gradually shifted from the compressive strength to other properties of the material, such as a high modulus of elasticity, high density, low permeability, and resistance to some forms of attack." High-Performance-Concrete (HPC) is a concrete made with appropriate materials combined according to a selected mix design; properly mixed, transported, placed, consolidated and cured so that the resulting concrete will give excellent performance in the structure in which it is placed, in the environment to which it is exposed and with the loads to which it will be subject for its design life.

High-reactivity metakaolin (HRM) is a more recently developed supplementary cementitious material. It is a reactive aluminosilicate pozzolan formed by calcining purified kaolinite at a specific temperature change. Brooks et al. [4] studied about the effect of silica fume, Metakaolin, fly ash and ground granulated blast furnace slag on the setting times of high strength concrete. They observed that the general effect of silicon, metakaolin, fine aggregate and GGBS is to retard the setting time of high strength concrete. Metakaolin is a processed pozzolan that can be combined with calcium hydroxide in solution to form calcium silica hydrate. The modern use of metakaolin dates back to 1962 when it was used to supplement Portland cement during construction of the Jupia Dam in Brazil [7]. Metakaolin densifies and reduces the thickness of the interfacial zone, thus improving the adhesion between the hardened cement paste, sand and aggregate.

Sea water has a total salinity of about 3.5% (78% of the dissolved solids being  $\text{NaCl}$  and 15%  $\text{MgCl}_2$  and  $\text{MgSO}_4$ ) and produces a slightly higher early strength but a lower long term strength; the loss of strength is usually not more than 15% and can therefore often be tolerated [1]. However, in prac-

tice it is generally considered not advisable to use sea water for mixing unless this is unavoidable [5]. Natural waters that are slightly acidic are harmless, but water containing humic or other organic acids may adversely affect the hardening of concrete, such water, as well as highly alkaline water, should be tested. The effects of different ions vary, as shown by Steinhour [8].

Arunakanthi et al., studied the effect of Hydrochloric acid in mixing and curing water on strength of High-Performance Metakaolin concrete [2]. The present investigation presents the effect of  $\text{CaCl}_2$  on strength properties of HPC with and without metakaolin for various concentrations of  $\text{CaCl}_2$ .

### Experimental program

#### Materials Cement

Ordinary Portland (53 grade) cement of Ultratech brand was used. It was tested as per Indian Standards Specifications IS: 8112-1989. Its properties are specific gravity 3.1, normal-consistency of 33%, fineness of 5%, initial setting time is 105 minutes and final setting time is 350 minutes.

#### Fine aggregate

The locally available natural river sand was used as fine aggregate. It was tested as per Indian Standard Specification IS: 383-1970. Its fineness modulus is 2.69 and specific gravity is 2.7.

#### Metakaolin

Metakaolin obtained from KOAT manufacturing company, Vadodara, Gujarat, India is used in this investigation. The properties are Bulk Density (Gms / Ltr) 300 to 340, Average Particle Size 1.5 – 2.5 micron, Residue (> 45 micron) (max. %) 0.5 – 2%, Moisture content  $\leq$  1%, Specific Surface Area BET ( $\text{m}^2/\text{gm}$ ) 12 – 18.

#### Super-plasticizer

GLENIUM B233 is the super-plasticizer of BASF company. The properties are Aspect: Light brown liquid, Relative Density:  $1.08 \pm 0.01$  at  $25^\circ\text{C}$ , PH:  $>6$ , Chloride ion content:  $< 0.2\%$

**Variables studied:**

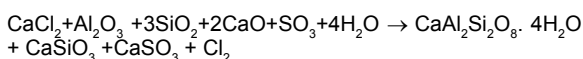
- (a) Concrete mix: The mix ratio of cement: sand: coarse aggregate is 1:0.76:1.8 with water/ binder ratio as 0.3. The dosage of superplasticizer is 1% by weight of cement. 20 % of Cement was replaced with of Metakaolin.
- (b) Mixing and curing environment: Four different concentrations of CaCl<sub>2</sub> (0.2 g/L, 0.5 g/L, 1g/L and 2 g/L) were adopted during the mixing in the deionised water and cured in same condition.
- (c) Exposure period: Specimens were tested periodically after the specified curing periods of 7, 28 and 90 days.
- (d) Size of specimens: 150mm x150mm x150mm size of cubes for compressive strength test and 150mm dia-300mm height of cylinders for split tensile strength test.
- (e) Samples for XRD and SEM testing: The cubes with maximum concentration of CaCl<sub>2</sub> after 90 days testing are collected and grinded and sieved under 40 micron sieve. This powder sample is sent for XRD testing and the broken pieces of cube samples are sent for SEM testing. A total of 135 cubes and 135 cylinders were cast in the laboratory. After 72 hours, all the specimens were demoulded and cured in water in a curing tank at room temperature. After specific exposure period, specimens were tested for compressive strength, split tensile strength in accordance with test procedure IS 516: 1959 [3].

**Results and discussion**

**Effect of CaCl<sub>2</sub> on compressive strength**

The effect of CaCl<sub>2</sub> concentration on the compressive strength and split tensile strength of HPC with and without metakaolin is presented in table: 1, 2, 3 and 4 and figures 1, 2, 3 and 4. Continuous increase in compressive strength and split tensile strength is observed with the increase in concentration of CaCl<sub>2</sub> for both HPCs. If the difference is less than 10% the change is considered to be negligible and if the difference is more than 10% the change is considered to be significant. It is observed that there is significant increase in both compressive strength and split tensile strength of both HPC's from 1 g/L concentration of CaCl<sub>2</sub>. The percentage change in compressive strength and split tensile strength of HPC with and without metakaolin increased with the increase in concentration of CaCl<sub>2</sub>. But the percentage change in compressive and split tensile strengths of HPC with metakaolin is less when compared with HPC without metakaolin. The XRD and SEM results show the formation of Calcium silicate hydrate (C-S-H gel) and Portlandite (Ca(OH)<sub>2</sub>) in both samples without CaCl<sub>2</sub>. But the intensities of C-S-H gel and Portlandite differ in two samples. The XRD patterns corresponding to HPC without metakaolin and HPC with metakaolin are shown in figures 3 and 5. By analyzing the XRD patterns of samples of two HPC's, the formation of C-S-H gel and Portlandite are formed at angles as shown in table 5 and 6. The intensity of C-S-H gel is more and the intensity of Portlandite is less for HPC with metakaolin when compared with HPC without metakaolin. This may be the cause for the strengths of HPC with metakaolin to be high under aggressive environment. The XRD tests are conducted for the two samples after 90 days with 2 g/L concentration (maximum) of CaCl<sub>2</sub>. It is observed that in addition to the compounds formed above, a compound named **Gismondine** (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>.4H<sub>2</sub>O) is formed in both HPC's with CaCl<sub>2</sub>. So the increase in strengths may be due to the formation of Gismondine. The angles at which the compounds are formed is shown in the table 4. The XRD patterns are shown in figures 5 and 6 respectively. The compound Gismondine has orthorhombic and dipyrimal structure. This is conchoidal and fractures look like fractures developed in brittle materials characterized by smoothly curving surfaces.

The probable chemical reaction upon the hydration of cement with mixing water containing CaCl<sub>2</sub> concentration is



In tables and graphs CHPC is HPC without metakaolin and

MHPC is HPC with metakaolin

**Table 1: Compressive strength in N/mm<sup>2</sup> for different concentrations of CaCl<sub>2</sub>**

S No	Dosage of CaCl <sub>2</sub> g/L	Compressive strength (N/mm <sup>2</sup> )					
		7 days		28days		90 days	
		CHPC	MHPC	CHPC	MHPC	CHPC	MHPC
1	0	39.5	60.0	58.0	78.0	63.5	80.0
2	0.2	39.8	61.2	59.3	79.9	65.4	82.3
3	0.5	40.4	64.1	60.5	84.9	68.4	87.5
4	1	44.4	70.9	67.6	95.4	75.7	102.6
5	2	46.0	74.8	69.4	101.9	77.6	106.1

**Table 2: %age change in compressive strength for different concentrations of CaCl<sub>2</sub>**

S No	Dosage of CaCl <sub>2</sub> g/L	Percentage change in Compressive strength					
		7 days		28days		90 days	
		CHPC	MHPC	CHPC	MHPC	CHPC	MHPC
1	0	0	0	0	0	0	0
2	0.2	0.75	2.01	2.25	2.55	3.05	2.89
3	0.5	2.28	6.85	4.36	8.89	7.59	9.36
4	1	12.41	18.24	16.56	22.31	19.26	28.23
5	2	16.46	24.63	19.62	30.62	22.23	32.64

**Table 3: Split tensile strength in N/mm<sup>2</sup> for different concentrations of CaCl<sub>2</sub>**

S No	Dosage of CaCl <sub>2</sub> g/L	Split tensile strength (N/mm <sup>2</sup> )					
		7 days		28days		90 days	
		CHPC	MHPC	CHPC	MHPC	CHPC	MHPC
1	0	4.19	5.3	5.35	6.05	5.67	6.15
2	0.2	4.26	5.43	5.47	6.22	5.85	6.34
3	0.5	4.33	5.67	5.6	6.59	6.1	6.75
4	1	4.76	6.29	6.24	7.43	6.79	7.91
5	2	4.94	6.63	6.4	7.91	6.94	8.16

**Table 4: %age change in split tensile strength for different concentrations of CaCl<sub>2</sub>**

S No	Dosage of CaCl <sub>2</sub> g/L	Percentage change in Split tensile strength					
		7 days		28days		90 days	
		CHPC	MHPC	CHPC	MHPC	CHPC	MHPC
1	0	0	0	0	0	0	0
2	0.2	1.68	2.36	2.34	2.75	3.15	3.13
3	0.5	3.32	6.92	4.72	9.04	7.62	9.82
4	1	13.59	18.84	16.68	22.74	19.72	28.56
5	2	18.01	25.02	19.64	30.72	22.36	32.75

**Table 5: Compounds and their intensities for samples of HPC's without CaCl<sub>2</sub>**

S NO	Angle in degrees	Compound	Intensity	
			CHPC	MHPC
1	12.58	C-S-H Gel	76	132
2	17.94	Portlandite	266	66
3	21.18	C-S-H Gel	32	86
4	24	Portlandite	110	72
5	34.34	C-S-H Gel	124	154
6	37.3	C-S-H Gel	34	72
7	42.24	Portlandite	64	38
8	50.76	C-S-H gel	90	120

**Table 6: Compounds and their intensities for samples of HPC's with CaCl<sub>2</sub>**

S NO	Angle in degrees	Compound	Intensity	
			CHPC	MHPC
1	11.78	Gismondine	68	76
2	15.92	C-S-H gel	48	58
3	16.38	Portlandite	48	34
4	20.9	Gismondine	230	244
5	24.34	C-S-H gel	106	134
6	27.74	Gismondine	160	164
7	30.58	C-S-H gel	98	100

8	34.56	Portlandite	78	70
9	35.32	Gismondine	72	78
10	41.4	Portlandite	74	66
11	47.24	Gismondine	118	146
12	50	C-S-H gel	70	74

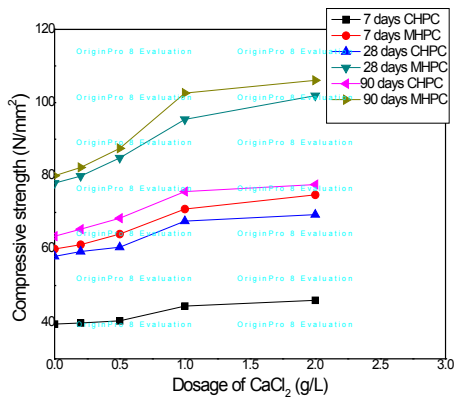


Figure 1: compressive strengths

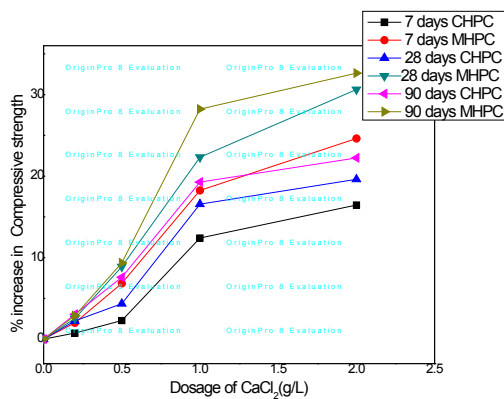


Figure 2: percentage increase of compressive strengths

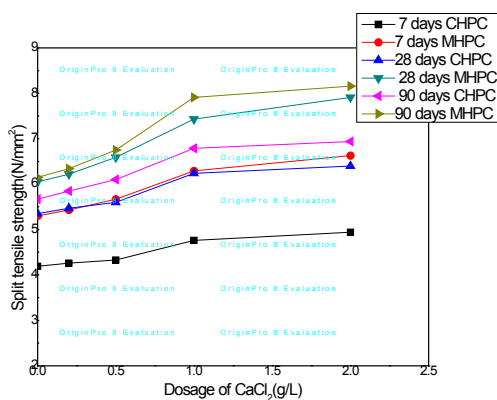


Figure 3: split tensile strengths

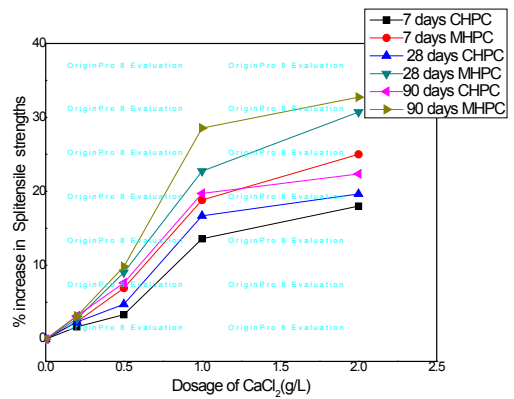


Figure 4: percentage increase of split tensile strengths

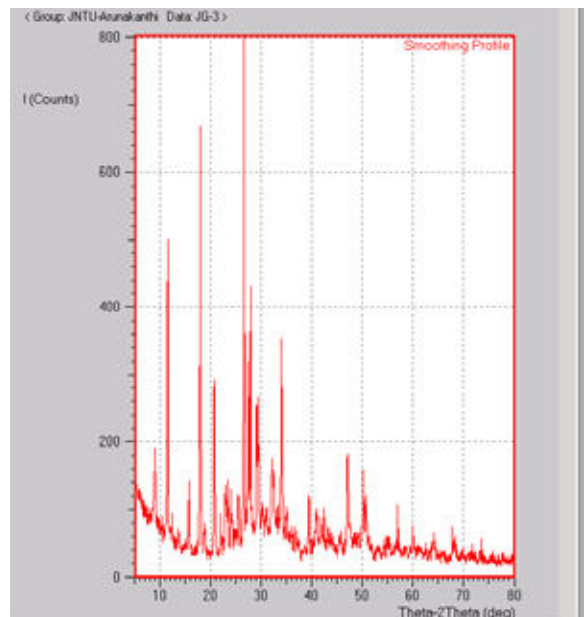
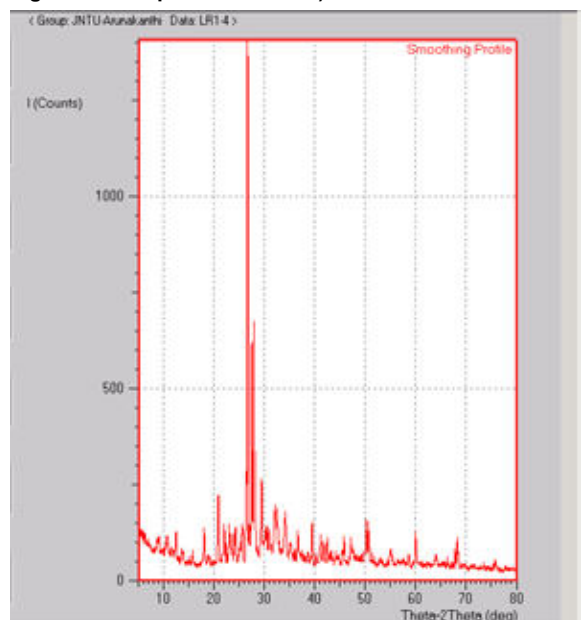


Figure 5: XRD pattern of HPC i) with out metakaolin



ii) with Metakaolin

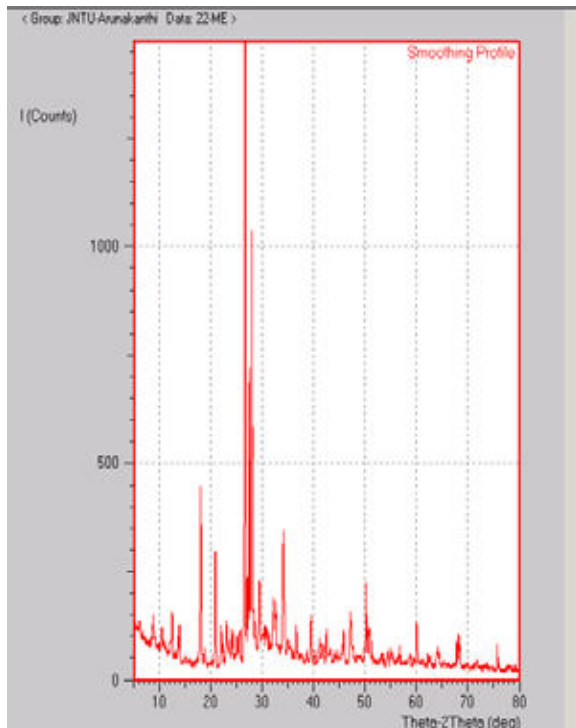
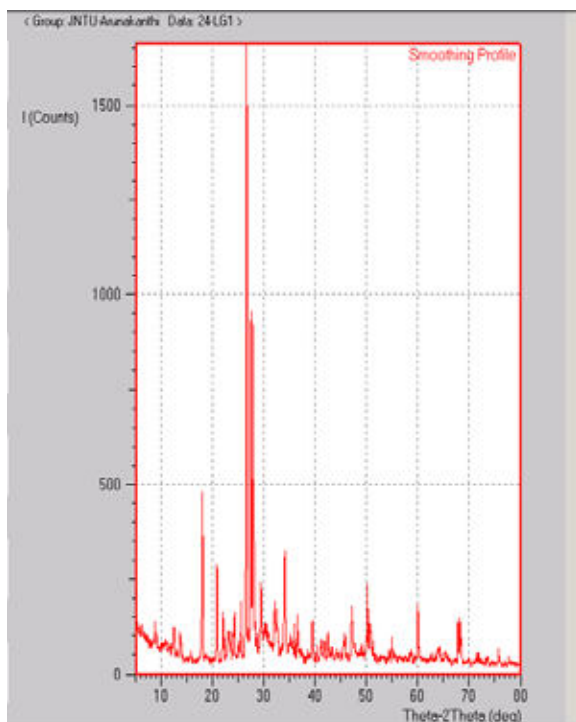


Figure 6: XRD pattern of HPC i) without metakaolin +  $\text{CaCl}_2$



ii) with Metakaolin +  $\text{CaCl}_2$

### Conclusions

Based on the above results of the investigation conducted on High-performance concrete with partial replacement of cement by 20% metakaolin and subjected to various concentrations of  $\text{CaCl}_2$ , the following conclusions can be drawn:

1. Compressive strength and split tensile strength of HPC increased with the replacement of cement by 20% metakaolin. And the strengths increased with the increase in concentration of  $\text{CaCl}_2$  in mixing and curing water.
2. Compressive strength and split tensile strength increase as the curing period increases for later ages of curing i.e., 7 days, 28 days and 90 days for 20% metakaolin and for all concentrations of  $\text{CaCl}_2$ .
3. From XRD studies it is concluded that the formation of C-S-H gel with more intensity and Portlandite with less intensity may be responsible for more strengths of HPC with metakaolin.
4. From XRD studies it is concluded that the formation of compound Gismondine may be responsible for increase in strengths with the increase in concentration of  $\text{CaCl}_2$ .

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