Microstructural Development in Fly Ash-Lime-Metakaolin Mix

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Abstract— Microstructural developments of fly ash stabilized with lime and modified with small percentages of metakaolin were studied through X-ray diffraction and scanning electron microscopy tests.Specimens were cured using jute bag method for 7, 14 and 28 days. X-ray diffraction test results showed the appearance of new peaks, some of which are not so important.The graphs revealed that extension of curing period leads to an increase in intensity peaks of ettringite and CSH which leads to enhancement of strength of mix. The addition of metakaolin enhances the early strength of mix that promotes the pozzolanic reaction leading to early formation of calcium silicate hydrate. The scanning electron micrographs of the mix provide the conformation of the formation of calcium silicate hydrate (CSH). The micrographs reveal the fact that as the curing period increases the bond between the particles increases, which is developed by the formation of CSH due to pozzolanic activity.

Index Terms- Metakaolin, X-ray diffraction test, Scanning electron microscopy, Ettringite, Calcium silicate hydrate, Pozzolanic reactions, Jute bag method.

1 INTRODUCTION

In recent years the demand of electricity has increased tremendously due to rapid growth in urbanisation and industrialisation. One of the main forms of electricity generation in India is thermal power plants. Large quantities of fly ash are produced by thermal power plants as a by-product. Only 60% of the fly ash is utlilsed for some purposes and rest 40% causes disposal problems. So it is necessary to utilise the waste generated effectively in order to reduce the disposal problems. For several decades there is high growth in construction activities. So an intrest was created to use the waste product fly ash in construction activities.

Some additives like lime and metakaolin are added to fly ash for the improvisation of its self properties. Lime is a calcium containing material. It predominately consists of oxides, hydroxides and carbonates. Metakaolin is generally categorised as a supplementary cementing material or mineral admixture that complements the properties of concrete when it is used with cement. Metakaolin is a fine aluminosilicate having pozzolanic activity. It is manufactured by the calcination process of Kaolinite clays at a temperature of 650^{o}c to 750^{o}c.

In the present investigation an attempt has been made to study the increase in rate of strength gain in lime-fly ash mixes with the addition of a small percentage of metakaolin. A series of non destructive methods like X-ray diffraction and scanning electron microscopy tests are conducted to investigate microlevel analysis of fly ash-lime-metakaolin mix.

2 LITERATURE REVIEW

2.1 STUDIES ON FLY ASH

McLaren R J and Digionia A.M,“The typical Engineering Properties of Fly ash”

A good knowledge on physical and engineering properties of coal fly ash is required for better planning, design and construction of both disposal and utilisation projects.This study was conducted to find out the typical values or range of values of physical and engineering properties of fly ash. Data on 131 class F fly ash samples and 26 class C fly ash samples were taken and then database was analysed to determine the typical values or range of values for physical and engineering parameters.

N.K.Mishra, “Strength Characteristics of Clayey Subgrade Soil Stabilised with Fly ash and Lime for Road Works”

In this study writer makes an attempt to improve the strength properties of clayey soil to be used as sub grade by using locally available fly ashes as admixtures with lime. The results concluded that addition of lime to the fly ash increase the maximum dry density and decrease the optimum moisture content. This is due to the light weight of lime and fly ash.

Gray D H and Lin Y K, "Engineering properties of Compacted Fly Ash"
In this paper typical engineering properties of fly ash in compacted condition were studied. Standard proctor compaction tests were conducted on the samples as per code specifications. This study concluded that the rate of gain in strength and the peak strength of lime treated fly ash were sensitive to curing temperature.

2.2 STUDIES ON XRD ANALYSIS

B V Venkatarama Reddy and K Gourav, "Strength of Lime-Fly Ash Compacts Using Different Curing Techniques and Gypsum Additives"
This paper examines the improvements in the strength development in lime-fly ash-gypsum compacts through low temperature steam curing. The XRD patterns of lime-fly ash mixture are studied to understand the type and nature of products formed during curing process. Main peak represents quartz, presence of calcium hydroxide and unreacted mullite was also clear in XRD patterns.

2.2 STUDIES ON METAKAOLIN

Shaik Jabiulla and Dr.D Neeraja ,"Performance Evaluation of Metakaolin and Fly Ash Based Geo-polymer concrete"
In this paper the use of metakaolin based Geo Polymer Concrete (GPC) containing different proportions of alkaline activator and its effect on mechanical properties of GPC was studied. Two different concrete mixes containing different combinations with fly ash and metakaolin content varying between 0% and 100% were prepared and used for the experiments. The author concluded that molarity concentration is directly proportional to the compressive strength of the geo polymer concrete. The compressive strength of geo polymer depends on curing temperature and age. The mix with 50% of fly ash and 50% of metakaolin shows better compressive strength than other mixes.

Alexey Brykov, Svetlana Krasnobaeva and Maxim Mokeev, "Hydration of Portland Cement in the Presence of Highly Reactive Metakaolin".
In this the degree of conversion of highly reactive metakaolin in Portland cement metakaolin paste at different ages as well as the influence of metakaolin on the degree of hydration of Portland cement and composition of CSH is studied. At high dosage (30%), metakaolin promotes the hydration of PC, but possesses no promoting activity when taken at moderate dosage(10%).. At the age of 1-3 months, the degree of PC hydration in the presence of metakaolin is of 15-20% less than without it, due to deficit of water.CSH formed in cement paste in the presence of metakaolin is characterised by higher content of Q2 and Q2 species in comparison with the reference cement paste and hence has longer aluminosilicate chains as well.

Clovis Nita, Vanderley M John,Cleber M R Dias,Holmer Savastano, "Effect of Metakaolin on the Performance of PVA and Cellulose Fibers Reinforced Cement"
In this comparative study of behaviour of cellulose and PVA fibers reinforced cement made with different pozzolanic materials was studied. Up to 15% of the total cement was partially substituted by silica fume and metakaolin. The effect of cement substitution on hydration phases, pore size distribution, mechanical properties, water diffusion and hygroscopic expansion were evaluated.

3 METHODOLOGY

3.1 MATERIALS

The fly ash used in the experiment was collected from Hindustan Newsprint Limited, Vellor, Kerala. The specific gravity of fly ash was obtained as 2.24 and the liquid limit was obtained as 34.179%.The maximum dry unit weight and optimum moisture content of fly ash selected was obtained by standard proctor test as 0.99g/cm^3 and 54% respectively. The XRD and SEM of fly ash are shown in Fig.3.1 and Fig.3.2 respectively.Fig.3.1 indicates prominent silica peaks along with a few mullite peaks.Fig.3.2 shows that particles of fly ash do not have a specific shape and it contains both larger and smaller particles.

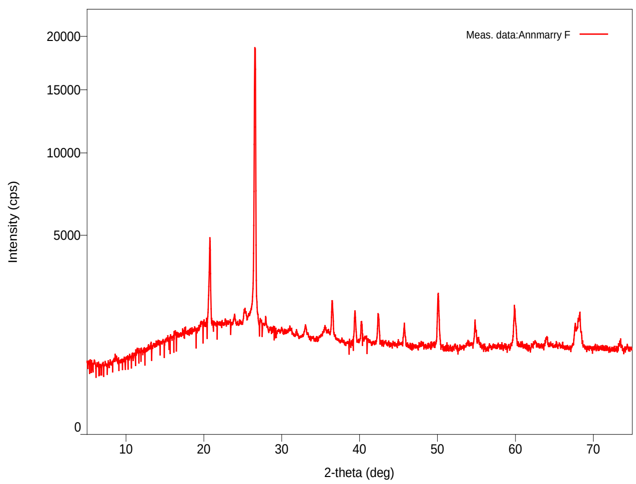

Fig.3.1: XRD of Fly Ash

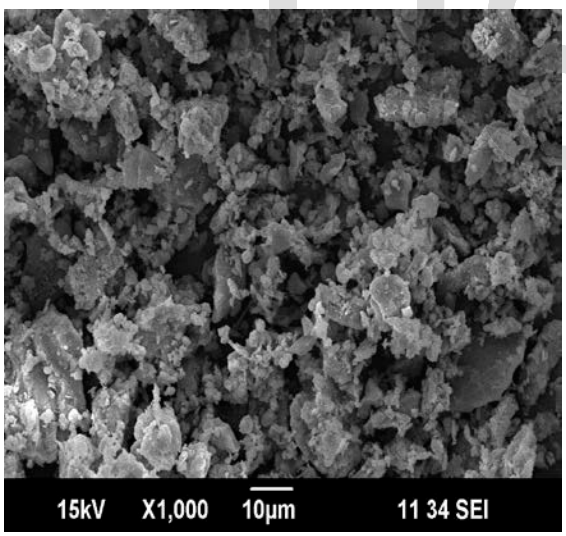

Fig.3.2: SEM of Fly ash

Commercially available lime in the market was adopted in the study. The specific gravity of lime is obtained as 2.15.The XRD and SEM of lime are shown in Fig.3.3 and Fig.3.4 respectively.Fig.3.3 indicates prominent calcium hydroxide peaks along with a few calcite and quartz peaks.Fig.3.4 indicates that lime does not have a definite structure it can be round, tubular or spherical.

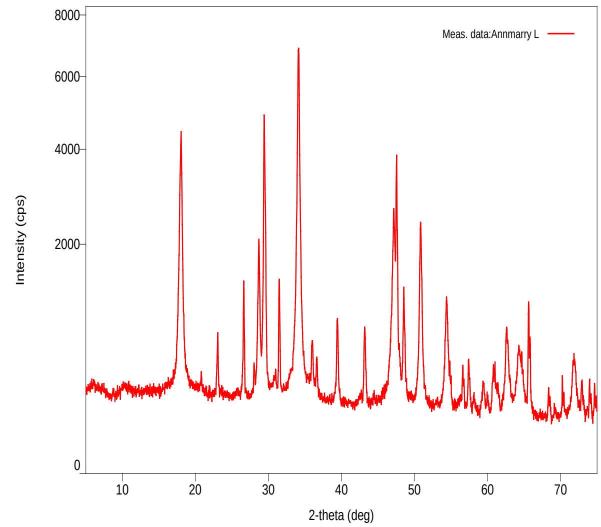

Fig.3.3: XRD of Lime

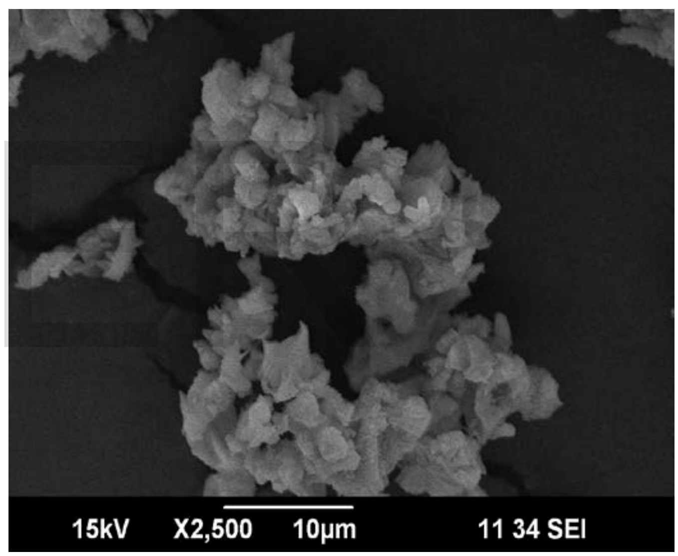

Fig.3.4: SEM of Lime

Metakaolin is a fine aluminosilicate material used as a supplementary cementing material. It is formed by a special process of calcination of Kaolinite clays at temperature in the range of 650°c -750°c.Metakaolin used in the study was collected from Ashirwaad Chemicals, Chennai. It had specific gravity of 2.42. The XRD and SEM of metakaolin are shown in Fig.3.5 and Fig.3.6 respectively.Fig.3.5 indicates prominent silicon dioxide peaks along with a few aluminium oxide peaks.Fig.3.6 indicates that metakaolin particles have oval and flake shape. Most of the particles are nano- sized particles ranging from 150nm to 300nm.

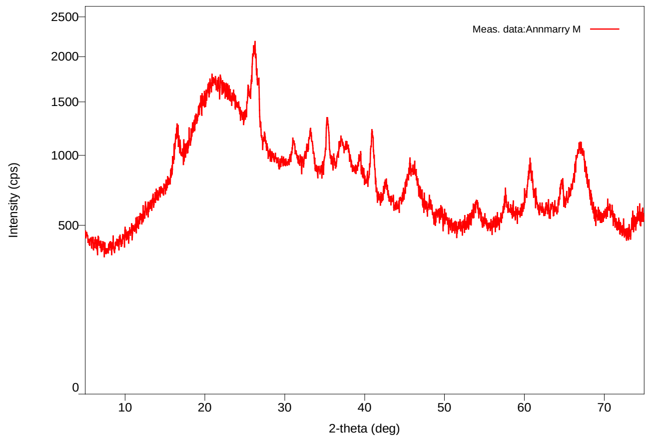

Fig.3.5: XRD of Metakaolin

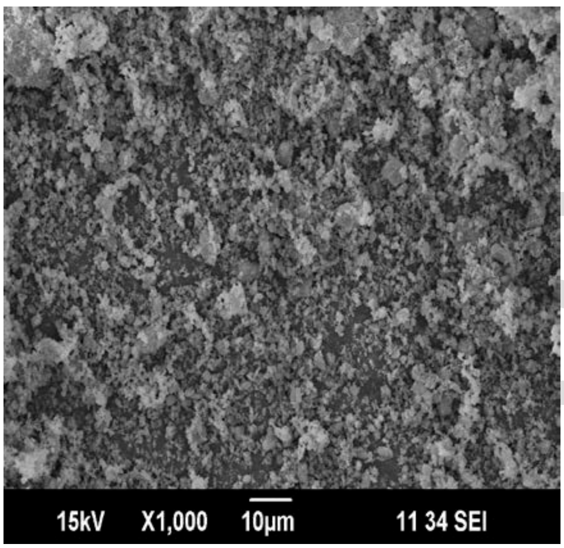

Fig.3.6: SEM of Metakaolin

3.2 SAMPLE PREPARATION PROCEDURES

3.2.1 Microscopic and Morphology Tests

Fly ash, lime and metakaolin are mixed with water uniformly. Then cylinderial samples of length 75mm and diameter 37.5 mm are made and it is allowed to cure for 7, 14 and 28 days.To conduct XRD and SEM tests the failed specimens after conducting unconsolidated undrained triaxial test were preserved in air tight polythene covers. Then the samples are oven dried and made into powdered form before conducting XRD and SEM tests.

3.3 TESTS CONDUCTED

3.3.1X Ray Diffraction Test

The X ray diffraction test (XRD) was performed using Rigaku Miniflex 600 diffractometer.To perform the test and to obtain best results a voltage of 40kv and current of 15 mA was selected. X ray is allowed to fall on the specimen at a diffraction angle of 2θ.The constant value of radiation used for proper resolution is Cukα=1.5425.

3.3.2Scanning Electron Microscopy Test

Scanning Electron Microscopy test was conducted using Jeol JSM-6490LA.It is a non-destructive test in which electron is allowed to pass through the specimen. Prior to testing specimen is coated with a gold layer of 5 mm. Scanning electron Microscopy test was conducted on the failed specimens from unconsolidated triaxial tests.

4 TEST RESULTS

4.1 MINERALOGY AND MORPHOLOGY TESTS

To study the micro level analysis of the reference mix XRD and SEM examination was carried out on the failed specimen cured for 7, 14 and 28 days.

4.1.1 X -Ray Diffraction (XRD) Analysis

The results of the XRD analysis of the reference mix cured for 7, 14 and 28 days are given in Fig.4.1.The Fig.4.1, 4.2 and 4.3 reveals the formation of calcium silicate hydrate (CSH) which is positioned at an angle 21°(2 Theta).The CSH peak shown in figures marks the early development of calcium silicate hydrate that enhances the strength characteristics of reference mix in the early stages due to the addition of metakaolin. The broad peak in the figures represents quartz (Q) that is positioned at 27 °. A new compound ettringite (Aft) is formed due to the reaction between calcium aluminate and calcium sulphate in the reference mix. The presence of ettringite (Aft) is shown by the new peaks positioned at about 29 °. Apart from these peaks, there are some other non-crystalline products that could not be identified in this study. This might be due to the presence of impurities present in fly ash caused by ignition of coal. From the Figures, it is clearly seen that the intensity of quartz peak increases negligibly as curing period increases but intensity of calcium silicate hydrate increases at an observable rate. The peak of ettringite is less during the initial stages of curing but peak increases when the curing period raises to 14 days. The diffractograms reveals that at 28 days of curing there is a further increase in intensity of CSH but the intensity of quartz is almost steady when compared to the mix cured for 7 days. It can be concluded from the figures that extension of curing period leads to an increase in intensity peaks of ettringite and CSH which leads to enhancement of strength of reference mix. The addition of metakaolin into the mix results in appearance and disappearance of peaks. The appearance is due to the formation of new crystals and disappearance is due to the transformation of gel structure into more crystalline form. The addition of metakaolin enhances the early strength of mix that promotes the pozzolanic reaction leading to early formation of calcium silicate hydrate**.**

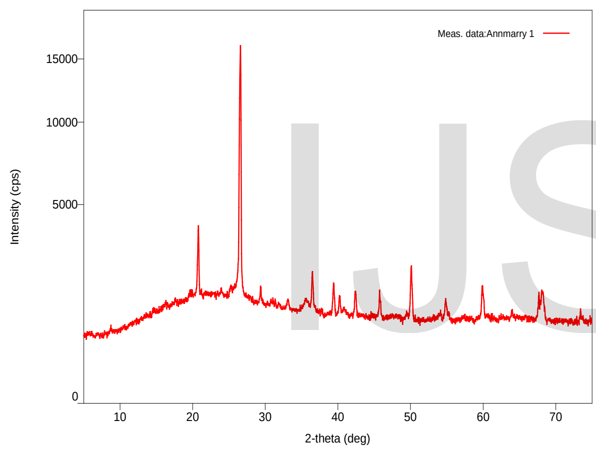

Fig.4.1:X-Ray Diffractogram of the Reference Mix at 7 Days of Curing

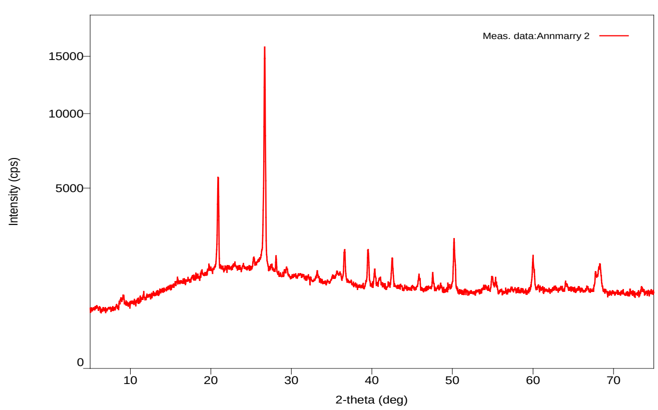

Fig.4.2:X-Ray Diffractogram of the Reference Mix at 14 Days of Curing

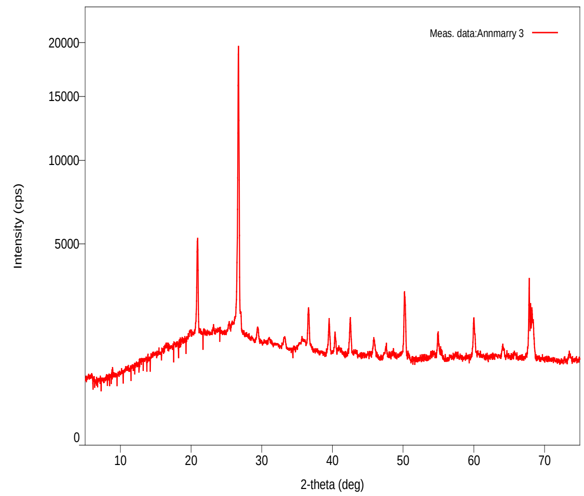

Fig.4.3:X-Ray Diffractogram of the Reference Mix at 28 Days of Curing

4.1.2 Scanning Electron Microscopy Test

Scanning Electron Microscopy analysis was conducted to confirm the mineralogical characteristics and crystalline structure. The scanning electron micrographs of the reference mix are shown in Fig.4.4, 4.5 and 4.6. This test provides the conformation of the formation of calcium silicate hydrate (CSH). The micrographs reveal the fact that as the curing period increases the bond between the particles increases, which is developed by the formation of CSH due to pozzolanic activity. This formation of bond enhances the strength characteristics of reference mix. There is no bonding among the fly ash particles in the SEM results shown in Fig.3.2. A new compound ettringite is formed as the curing period increases from 7 to 28 days which enhances the strength characteristics of reference mix. The development of ettringite filling the void spaces among fly ash particles appeared to be denser leading to enhance strength of reference mix.

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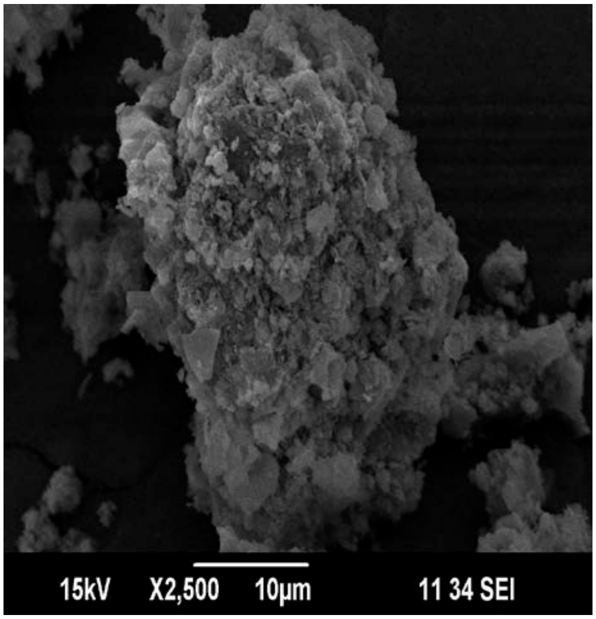

Fig.4.4: SEM Result of Reference Mix Cured at 7 Days

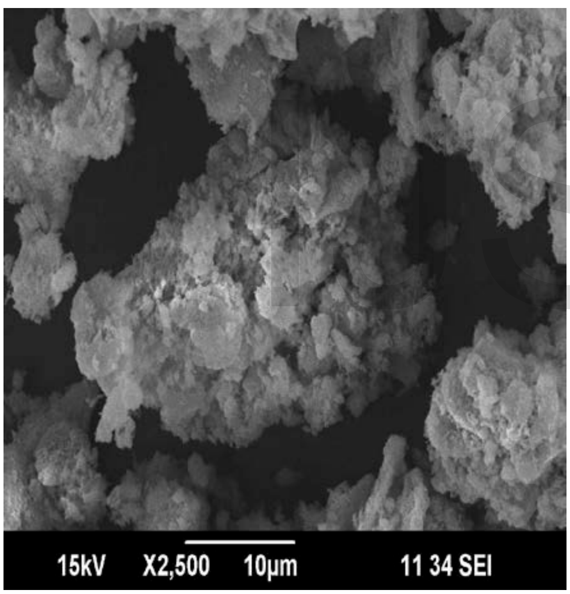

Fig.4.5: SEM Result of Reference Mix Cured at 14 Days

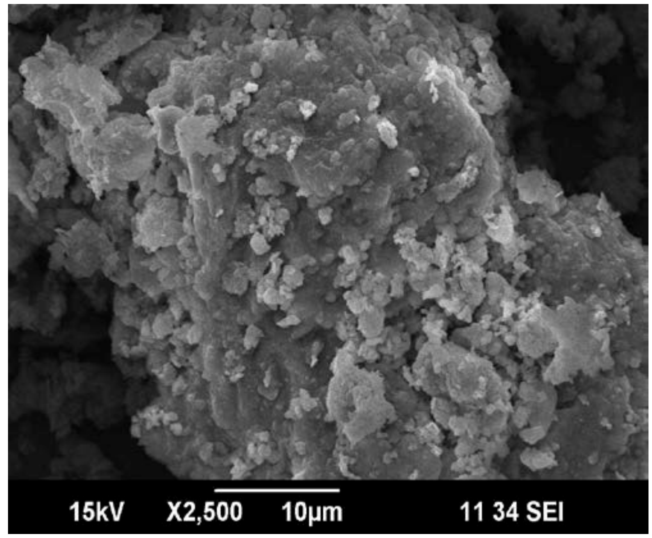

Fig.4.6: SEM Result of Reference Mix Cured at 28 Days

5 CONCLUSIONS

The CSH peak shown in figures marks the early development of calcium silicate hydrate that enhances the strength characteristics of reference mix in the early stages due to the addition of metakaolin. The extension of curing period leads to an increase in intensity peaks of ettringite and CSH which leads to enhancement of strength of reference mix. The addition of metakaolin into the mix results in appearance and disappearance of peaks. The appearance is due to the formation of new crystals and disappearance is due to the transformation of gel structure into more crystalline form. The addition of metakaolin enhances the early strength of mix that promotes the pozzolanic reaction leading to early formation of calcium silicate hydrate. Scanning electron microscopy test provides the conformation of the formation of calcium silicate hydrate (CSH). The micrographs reveal the fact that as the curing period increases the bond between the particles increases, which is developed by the formation of CSH due to pozzolanic activity. This formation of bond enhances the strength characteristics of reference mix.

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