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Study on Micro Structural Behavior and Strength Characteristics of Ultra Fine Fly Ash as a Secondary Cementitious Material with Portland Cement

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Abstract: This study presents an experimental investigation of the replacement of the modified cementitious material as a Ultra Fine Fly Ash (UFFA ~200 nm) on strength development of cement mortars. The Fly ash is classified into high calcium class C fly ash, which is used as partial replacement of cement. The cement was replaced with four different weight percentage of Raw Fly Ash (RFA) and UFFA by 15, 30, 45 and 60 mass %. The strength results of mortar cubes prepared with cement, cement with various percentage replacement of RFA and UFFA were compared. The water to binder ratio (w/b) of 0.485 was used for all the blended cement mortar mixes. Ball milling was carried out for a total duration of 5 hours to obtain UFFA and sample characterization was done to study various properties of the RFA and UFFA. Crystallite phase and grain size of RFA and UFFA were determined by using X-ray diffraction test. The shape and texture was studied using SEM analysis for RFA and UFFA.

The specimens used to determine the compressive strength of mortar are prepared in accordance with ASTM C 109 / IS :1727 (1999) and tested at the age of 3, 7, 14 and 28 days. The test results shows that strength increases with increase of RFA up to an optimum value, beyond which, strength is start to decreasing with further replacement of RFA. It may be due to the crystalline silica present in it which has low reactivity. It was observed that the smooth and inert surface of RFA was transformed to more reactive one by ball milling process, which is one of the top down approach to down scale of RFA. The UFFA shows much improved material characteristics compared to the RFA in terms of morphology, mineralogy, workability and compressive strength of fly ash cement mortars.

Key words: Material characterization, Ultra fine fly ash, Pozzolancement mortar, Compressive strength.

Introduction

Concrete is one of the most widely used materials in construction. The service life and durability of a concrete structure strongly depend on its material transport properties, such as permeability, which are controlled by the micro structural characteristics of concrete. It is known that the porosity and pore size distribution are the critical components of the microstructure of hydrated cement paste and influence durability. In order to achieve high strength, low permeability and durable concrete, it is therefore necessary to reduce the

porosity of cement paste. This can be achieved by incorporation of pozzolanic materials as partial replacement of cement¹. Reuse of waste materials plays a very important ecological and economic role in cement production, significantly reducing use of natural raw materials, energy needed for cement, CO₂ emissions in cement production and the final cement price at the market^{2,3}.

Fly ash is pozzolanic active material that are very often used as replacement additions to cement/concrete⁴. Pozzolanic active parts of minerals additions (amorphous and metastable aluminosilicates) chemically react with calcium hydroxide (CH) and form a new C-S-H phase. The C-S-H phase is the primary hydration product of OPC and is responsible for setting and hardening of cement and cement composites⁵. The start of the pozzolanic reaction, formation of new C-S-H phase, is reflected as an increased quantity of chemically bound water and as quantity of portlandite formed by hydration decreases, mechanical properties of cement composites materials are improved. The newly formed C-S-H phase fills the pores in developed microstructure of the cement composites, thereby making the microstructure more even and less porous, which directly increases the durability of the composites. The fineness of used pozzolanic addition is an important factor that, beside the physical effect of occupying the pores, determine the beginning of the pozzolanic reaction. According to studies made so far, the generally accepted rule is: "The greater the specific surface area of the materials the pozzolanic reaction starts earlier"⁶⁻⁸.

For maximization of fly ash reactivity there were developed several methods. Basically it is possible to divide these methods into four groups i) chemical activation focused on modification on the chemical surface ii) mechanical activation-in some studies this activation meant as a grinding process but as a mechanical activation can be account sieving and air separation too iii) thermal activation, such as slow or rapid cooling, producing changes in vitreous/crystalline ratio iv) combination of previous^{9,10}.

The objective of this study is to investigate the compressive strength of fly ash mortars due to packing effect and pozzolanic reaction when fly ash with different particle size is used to reduce Portland cement 43 grade at rate of different percentage of RFA and UFFA by weight of cementitious materials.

Experimental Program

Materials and mortar preparation

Materials used in this investigation consisted of ordinary Portland cement 43 grade (OPC) conforms with ASTM C 150, standard ENNORE sand (sand) and distilled water and class C Fly ash according to ASTM C 618. The class C Fly ash obtained from Neyveli Lignite Corporation, Neyveli, Tamil Nadu. The sub-bituminous fly ash from Neyveli designated as Raw Fly Ash (RFA). The RFA was ground by ball mill to reduce its size into ultrafine particles, as in the case of UltraFine Fly Ash (UFFA). The RFA and UFFA were used to replace OPC at replacement levels of 0%, 15%, 30%, 45% and 60% by mass of binder. A binder to sand ratio of 1-2.75 was used. A constant water to binder ratio (w/b) of 0.485 was used throughout the investigation for all mortar mixes as described in ASTM C109.

All mortars mixes are prepared by using Hobart mixer machine accordance with IS:1727. After preparation of samples were cast in 50 mm standard cube moulds. After 24 hours the moulds are demoulded, then kept in water until the date of testing. The mortar cubes were tested to determine the compressive strength at curing ages 3, 7, 14, 28 days in accordance with ASTM C109, IS:1727, IS:4037. The averaging of three cubes results were considered for Compressive strength of mortars specimens.

Results and Discussion

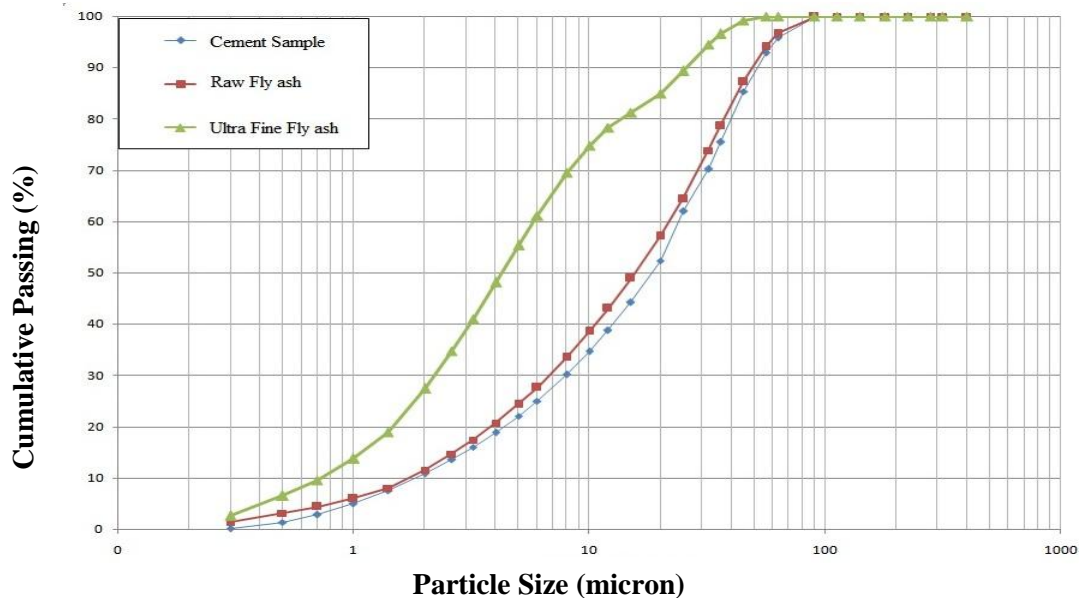
Physical properties of material

The major materials used in this instigation consisted of OPC, RFA and UFFA materials were studied the physical properties Table 1. show the physical properties of OPC, RFA and UFFA materials.

Table 1. Physical properties of material

Type of sample	Specific gravity	Retained on 45 micron sieve (%)	Blaine's fineness (cm ² /g)	Median article size (µm)
Cement	3.15	86.32	2630	23.28
Raw Fly Ash	2.62	87.21	3717	21.35
Ultrafine Fly Ash	2.56	99.12	7277	8.68

It is seen that OPC has particles retained on sieve No. 325 of 13.6% while the specific gravity and median particle size are 3.15 and 23.28 μm respectively. The weight retained on sieve No. 325 of RFA is 12.7% while UFFA is 0.8%. The median particle sizes of RFA is 21.35 μm while UFFA is 8.68 μm . The specific gravity of RFA and UFFA is 2.62 and 2.56 respectively. The particle size distribution of OPC and RFA and UFFA samples are shown in Figure 1. and their median particle sizes are tabulated in Table 1. The UFFA samples showed a very high Blaine fineness of 7277 cm^2 / g while retained 2.88% on 45 micron sieve and the median particle size was 8.68 μm .



It is noted that particle size distribution of OPC and RFA are not much different in sizes and also a coarser particles. The UFFA samples had a finer particle size distribution, which had an extremely predominant coarse peak. The reason for this change in frequency distribution behavior is probably associated with in homogeneity in the particle characteristics, which is greatly reduced by the ball milling process.

Grinding can be a possible solution to convert a RFA samples to UFFA samples. In the grinding process causes break up of large plerospheres and decreases the particle toughness¹⁰. Grinding process of cenospheres increases the specific gravity, fineness and consequently results in higher pozzolanic reactivity of the UFFA. The main effect of grinding is that coarse particles are crushed on smaller particles by grinding process. The smaller reactive particles which on the other hand can be increase the specific surface area and act as a good fillet materials.

Chemical composition of materials

The chemical compositions of OPC, RFA and UFFA are analyzed using an X-Ray fluorescence spectrometer and are tabulated in Table 2.

Table 2. Chemical composition of materials

Sample Type	Chemical composition (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LoI
Cement	21.41	5.54	4.47	62.32	1.23	2.83	1.05
Raw Fly Ash	35.2	27.4	6.83	19.2	1.73	4.21	2.74
Ultrafine Fly Ash	34.9	27.24	7.02	18.97	1.7	4.24	3.08

The amount of CaO of the RFA and UFFA varied between 19.2 and 18.97%. However, the Fly ashes sample were classified into class C as prescribed by ASTM C618 since the sum of the major components SiO₂, Al₂O₃ and Fe₂O₃ were less than 70% and CaO is more than 10%. The Loss on Ignition (LoI) of RFA and UFFA

was 2.74% and 3.08% respectively and within the limit of 6% as specified by ASTM C618. Many reports^{6,7,8,9,12,13,14} conclude that grinding and classifying do not have much effect on the chemical composition of the fly ash. The UFFA samples obtained by grinding may contain higher LoI has no relation to the increase of carbon content, which will act as a inert materials¹¹.

3.3. Setting time, Normal consistence (NC), Flow table value (FTV)of materials

The effect of RFA and UFFA on the start and end of settings of OPC samples by using Vicat instrument are showed in the Table3. The results indicate that the increase of the RFA addition shifts the start and end of settings to later hydration times and prolongs the setting time in comparison with the standard sample. However, when the fineness of fly ash was increased, the setting time were gradually reduced up to 30 mass % replacement of OPC by UFFA samples. It should be noted that the setting time of all OPC,RFA and UFFA paste were within the limit specified by ASTM C 150. In paste preparation it has been observed that the quantity of water needed to obtain normal paste consistency increases with the increase of the RFA addition.

Table 3. Setting time, NC, FTV for OPC,RFA and UFFA samples

Sample Type	% Replacement	Normal Consistency	Initial Setting Time in minutes	Final setting time in minutes	Flow Diameter in mm
OPC	0	0.3233	134	418	183
RFA15	15	0.3166	131	422	134
RFA30	30	0.3266	143	443	126
RFA45	45	0.3466	162	459	110
RFA60	60	0.3633	186	492	105
UFFA15	15	0.3033	120	416	151
UFFA30	30	0.3166	131	436	154
UFFA45	45	0.3233	142	452	161
UFFA60	60	0.3366	164	481	155

In addition of UFFA the w/b ratio decreases up to 30 mass %, then start to increases the w/b ratio while compare to OPC mortar. This can be attributed to the effect of increased quantity of spherical particle of UFFA samples.

3.4. Effect of UFFA in workability of mortars

The workability of mortar is measured in terms of flow diameter in mm according to ASTM C 1437. The effect of RFA and UFFA on workability of OPC mortar shown in Figure 2. The rate of decrease of flow values is higher in the case of RFA mortars than that of standard mortars. The UFFA mortars increases the flow value than that of RFA mortars.

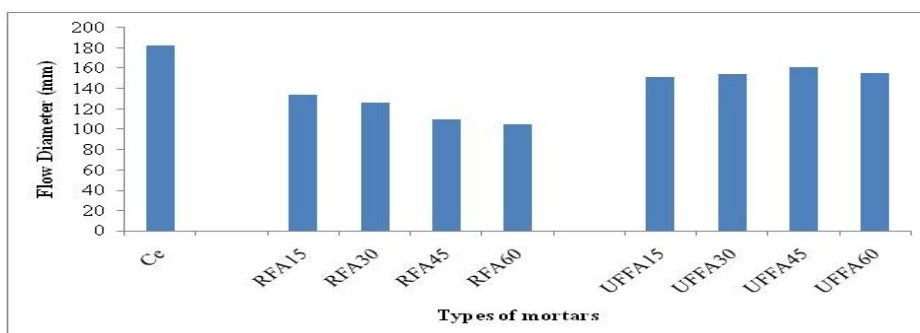


Figure 2. Workability of different mortar mixes

It is observed that addition of UFFA particles increases the flow value. This is due to finer particle size and spherical shape of UFFA samples.

3.5.Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was conducted to analyze the microstructure of OPC,RFA and UFFA samples.Figure 3.a&b shows the SEM micrographs of OPC with 30 μm and 5 μm magnitude. The spherical structure and the particle size of OPC was measured. Figure 3.c& d shows the SEM micrographs of RFA and Figure 3.e& fUFFA with 30 μm and 5 μm magnitudes.

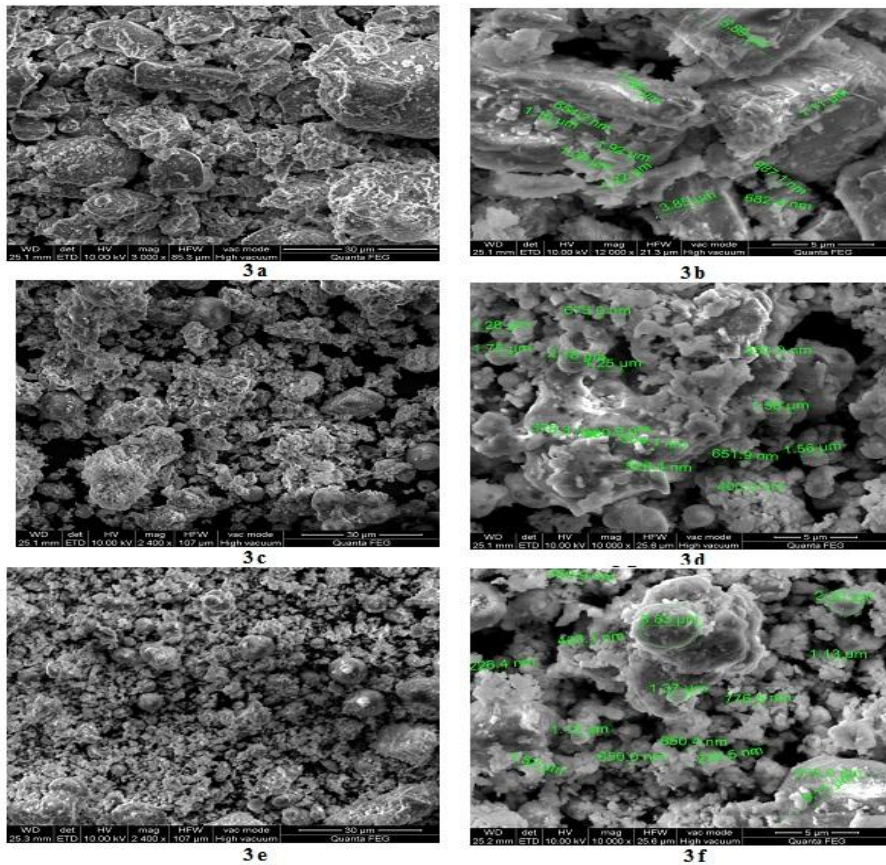


Figure 3.Particles shapes of OPC, RFA and UFFA samples by SEM with 30 μm and 5 μm magnitude.a& b OPC sample. c& d RFA sample. e& f UFFA sample images.

The SEM images shows the OPC,RFA and UFFA particle sizes are 3.82 μm ,651 nm, 185 nm respectively.From the SEM images, the OPC and RFA samples images are shows irregular and non spherical shape of the particles. But the UFFA sample shows the spherical shape of particles compare with OPC sample SEM images.

Fourier Transform Infrared Spectroscopy Analysis (FT-IR)

The IR bandwidth and possible assignment are shown in Table 4.andFigure 4.The peak at 3450-3400 cm^{-1} was shown in all the three materials, which is O-H stretching of Si-OH group, the peaks are compared to RFA and UFFA samples.

The peak intensity of 3450-3400 cm^{-1} at this wave number is found to increase with decrease the particle size by grinding is an evidence for the breaking down of the Quartz structure and formation of Si-OH group.FT-IR spectroscopy reveals that the characteristic –OH stretching vibration peak intensity increase by reduction of particle size RFA to UFFA.

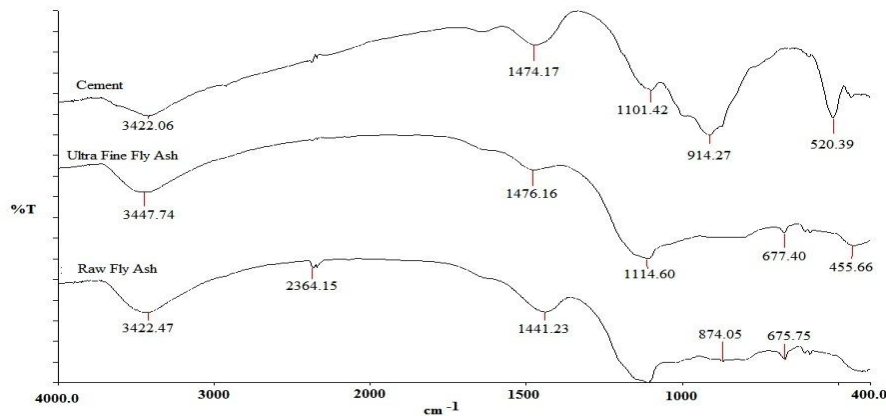


Figure 4.FT-IR spectra of OPC, RFA and UFFA samples

Table 4. IR bands of OPC, RFA and UFFA and their possible Assignments

Observed band (cm ⁻¹)	Band assignment
3450-3400cm ⁻¹	OH stretching of Si-OH group
1450-1400cm ⁻¹	OH stretching
1125-1100cm ⁻¹	Si-O-Si asymmetric stretching
675-670cm ⁻¹	Si-O-Si symmetric stretching
550-450cm ⁻¹	Si-O-Alstretching

X-Ray Diffraction Analysis

X-ray diffraction is a tool used to find the crystallite size of the phases of RFA and UFFA samples, with the help of a PANalytical ‘X’ Pert PRO diffractometer using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) at an accelerating voltage of 40 kV and a current of 30 mA. The results of XRD measurement is a diffractogram, showing phases present (peak position), phase concentrations (peak intensity), amorphous content (background hump) and crystallite size (peak width). By measuring and analyzing the positions and intensities of these peaks it is possible to determine the spatial characteristics of the grating. The samples were scanned at a step size of 0.017 ($^{\circ} 2\theta$) in the 2θ range from 5° to 100° . It works on the principle of Bragg’s law: $n\lambda = 2d \sin\theta$.

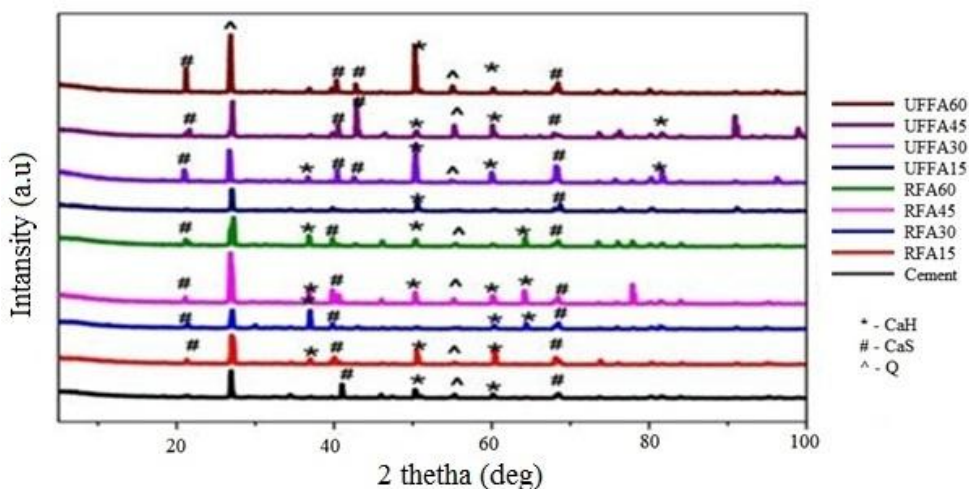


Figure 5. X-Ray diffractograms of different types of mortar mixes at age 28 days

The average crystallite size was determined by using Scherrer’s equation.

$$D = K\lambda / \beta \cos\theta \tag{1}$$

where D is the crystallite size, λ is the X-ray wavelength, β is the FWHM of the diffraction peak, θ is the diffraction angle and k is the Scherer's constant. The UFFA exhibits lower degree of crystalline, where the crystalline size reduced to 46nm due to the addition of UFFA. Calcium Hydroxide (CH) shows peaks at $50.30^\circ, 60.17^\circ$ at 2θ values (d spacing of 1.8 Å and 1.5 Å). The CH has a strong peak located at 2θ angle of 50.30° and it had been selected to be the measure of hydration performance in all samples. In the process of cement hydration, CH is able to react with SiO_2 in further cementing system and form additional C-S-H to improve the mechanical properties of mortars. Calcium silicate shows peak (CS) shows peaks at $21.14^\circ, 68.43^\circ$ at 2θ values (d spacing of 4.1 Å and 1.3 Å). The quartz exhibits peaks at $27.04^\circ, 55.02^\circ$ (d spacing of 3.3 Å and 1.6 Å) and its intensity increased with UFFA % increased. The average crystalline size of Quartz phase for OPC mortar mixture is 68.48nm. The average crystallite size of Quartz phase for 15, 30, 45 and 60 mass percent replacement of RFA and UFFA mortar mixture is 62.82nm and 46.50nm respectively. The reduction in crystallite size from 68.48 nm to 46.50 nm with increase in UFFA, thus increasing the unstructured realms. Due to the unstructured realm is very interesting as it may enhances compatibility with various polymeric matrices.

Comparisons of XRD powder pattern of the samples with RFA and UFFA after 28 days of hydration shows that this reduction in crystalline phases, the pozzolonically active amorphous phase of the UFFA is likely to be increased. This is, indeed, evident from the increased amorphous hump present below the crystalline peaks^{2,9}.

Compressive strength of mortar mixes

The compressive strength of standard mortar and mortar containing RFA and UFFA are presented in Figure 6.a&b. The results were compared 3,7,14 and 28 days for different types of mortar mixes.

At the age of 3 days, the compressive strength of RFA mortars were less than that of standard mortar. The compressive strength of standard mortar was 19.25 MPa compared with RFA Replacements 15, 30, 45 and 60 mass % are 17.13MPa,15.3MPa,13.89MPa and 12.18 MPa respectively. The compressive strength of OPC with RFA mortar were decreased while increase of cement replacement with RFA. This is due to RFA had irregular shape and porous particles.

The compressive strength of cement with UFFA mortar were compared to standard mortar, the results are UFFA replacement 15,30,45 and 60 mass % are 27.82,23.18,17.76 and 15.48 MPa respectively. It shows that 15 and 30 mass % of replacement of UFFA increases the compressive strength compare to standard mortar. However, the UFFA replacement 45 and 60 mass % results are lower compare to standard mortar but higher than the RFA mortar. At the age of 7 days and 14 days the RFA mortars mixes are less than to standard mortar. The UFFA mortar mixes are 15 and 30 % replacements increase the compressive strength compare to standard mortar. While 45 and 60 mass % of UFFA decrease the compressive strength compare to standard mortar.

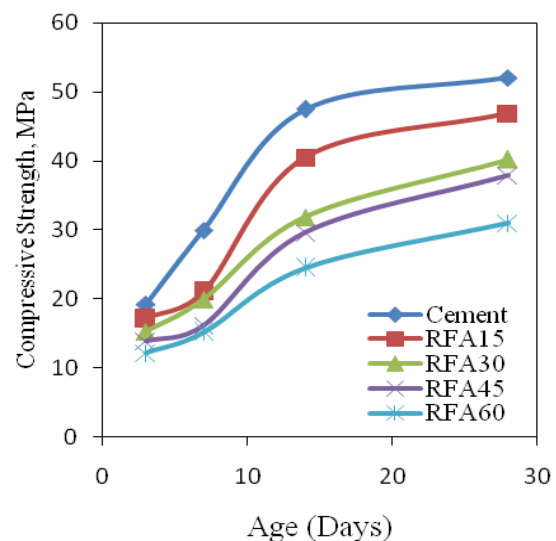
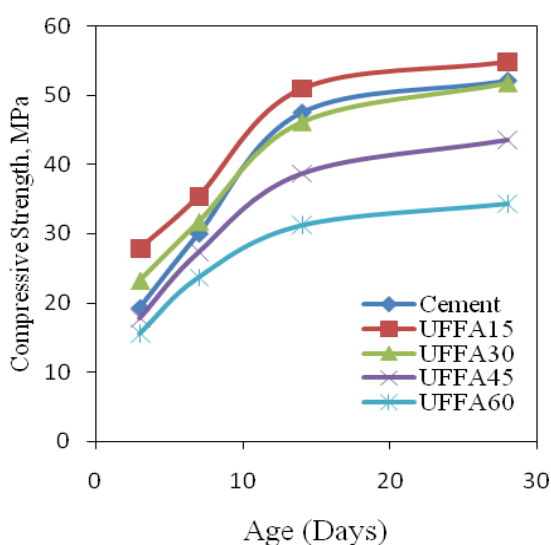


Figure 6a. Compressive strength of UFFA mortar Figure 6b. Compressive strength of RFA mortar

At 28 days, the compressive strength of standard mortar was 52.08 MPa while the compressive strength of the RFA mortars of replacement of 15,30,45 and 60 mass % were 46.87,40.24,37.92 and 31.03 MPa respectively. The UFFA cement mortar of replacement of 15 mass % are 54.86 MPa compare with standard mortar. The UFFA cement mortar of replacement of 30,45 and 60 mass % are 51.79,43.58 and 34.28 MPa respectively. From this results, the Optimum replacement of UFFA is 30 mass % in cementitious materials. However, when RFA was processed to obtain UFFA, the rate of strength gain of mortar was improved significantly with increases of fineness. It was noted that all RFA cement mortars still gave lower compressive strength than that of the standard mortar. It can be concluded from the results that the strength development rate of UFFA mortars depends on the fineness of Fly ash particles^{3,6,7}.

Conclusion

An experimental study was conducted to investigation the influence of chemical and physical properties of RFA and UFFA on the compressive strength of OPC mortar. The following conclusion can be drawn:

1. The flow table value (FTV) of the mortar mixes shows, the coarser fractions sized RFA mortar mixes gave the less FTV than standard mortar and UFFA mortar mixes. This is due to finer particle size and spherical shape of UFFA samples. The UFFA mortar provided significance improvements in the fresh behavior and compressive strength of mortars with compare to the RFA and Standard mortars. It can be concluded from the results that the strength development rate of UFFA mortars depends on its fineness and packing effect of UFFA particles.
2. The RFA and UFFA mortar samples of XRD powder pattern shows that this reduction in crystalline phases. This is, indeed, evident from the increased amorphous hump present below the crystalline peaks. In this process of cement hydration, CH is able to react with SiO₂ in further cementing system and form additional C-S-H to improve the compressive strength of mortars.

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