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Pozzolanic Activity Evaluation of the Fired Drinking Water Treatment Sludge

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Abstract- **Drinking water treatment sludge (DWTS) is a type of by-product waste removed with huge amounts from water treatment plants. The sludge was collected and fired at 850°C then used as pozzolanic material. Different mixes from fired sludge and ordinary Portland cement were paste and hydrated up to 90 days. At the same time a ternary system formed from Portland cement, sludge and silica fume (SF) was also evaluated. The pozzolanic activity of these cement pastes has been evaluated by the determination of the chemically combined water and free lime contents at different times intervals; 1, 3, 7, 28 and 90 days. The hydration products of the cement pastes were also identified using XRD, FTIR and DSC. It was found that fired DWTS showed a pozzolanic activity but still lower than silica fume. The results of chemical analysis are in a good agreement with those of XRD, DSC and FTIR analyses.**

Keywords-**Recycling, Drinking Water Treatment Sludge, Silica Fume, Pozzolanic Activity.**

I. INTRODUCTION

Portland cement is the most widely used construction material. However, the production of cement consumes massive amounts of limestone, clay, sand and blast furnace slag, as it takes 1.7t of raw materials to manufacture 1t of clinker [1]. Global cement production has been expected to increase 2.5 times between 2005 and 2025, with the majority of this growth occurring in developing countries [2]. Eventually, this will result in a negative effect due to the depletion of natural mineral resources.

The rising cost and depletion of raw materials have forced the cement industry to review the logistics of raw material supply. Therefore, looking for other new, more economical raw materials are also becoming an immediate concern. Consequently, further research is necessary to illustrate the economic, environmental, and structural benefits to their use. Therefore, there is currently great interest in exploiting the pozzolanic and cementitious properties of these materials by incorporating in building products.

According to ASTM C595, a pozzolana is defined as "a siliceous or siliceous and aluminous materials which in itself possess little or no cementitious value. On the other side, in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds with cementitious properties" [3]. These compounds are calcium silicate hydrate (CSH) and calcium aluminosilicate hydrate (CASH). The rate of reaction of pozzolana with hydrated lime is termed pozzolanic activity. So, it is an index of the extent of the lime-pozzolan reaction [4]. The effect of many pozzolanas depends not only on reactive silica but also on the presence of reactive alumina which forms CASH as well as CSH. The reactive constituents of colloidal compounds resembling those formed from the hydration of Portland cement but with slow rate [5].

During the process of drinking water treatment a huge amount of sludge usually obtained. This sludge (DWTS), could be recycled in some useful industrial applications to reduce its risk to the environment [6,7]. Water treatment chemicals are aluminum salts ($Al_2(SO_4)_3.18H_2O$), ferric salts (e.g., $FeCl_3.6H_2O$), and ferrous salts (e.g., $FeCl_2$, $FeSO_4.7H_2O$). The addition of these chemicals during the water treatment process forming a sludge which rich in iron or aluminum as well as silica. This sludge may also contain other heavy metals from raw water or its contaminants after reaction with coagulant additives [8]. Many attempts were conducted to dispose this sludge such as in agriculture, landfill, marine and incineration applications. Moreover, there is an increase of the interest in recycling such sludge into construction materials [9].

The purpose of or recycling solid wastes is to make full use of raw materials and minimize the problem of pollution and their treatment. The reuse of DWTS in the construction materials has been thoroughly investigated. Recently, many studies have been carried out to investigate the use of sludge as cement raw material [7,9,10-13]. El-Didamony et al., [14] studied the hydration and the mechanical properties of the blended cement pastes containing OPC, fired DWTS and anhydrite gypsum.

Pozzolanic activity of fired clay bricks (Homra) was studied using hydrated lime as an activator [15]. Different mixes of Homra/hydrated lime were paste hydrated up to 90 days. The results of thermal analysis of the hydration products were related as much as possible to the pozzolanic activity as determined by chemical analysis. It was concluded that Homra, as a waste product of clay bricks industry can be used in the preparation of low cost pozzolanic cement.

The artificial pozzolanas are mainly products obtained by the heat treatment of clays, shales, sludge, silica fume, rice husk ash and pulverized fly ash. Homra is a cheaper material than Portland cement with low rate of pozzolanic reaction which is a source of active silica and alumina. The recycling of this waste product is widely used because it reduces cost, energy and pollution. The results revealed that the free lime contents increase up to 7 days then decrease up to 90 days. The blended cement composed of 80/20 mass% Portland cement/Homra respectively is the optimum mix composition which gives suitable properties.

The pozzolanic activity of amorphous silica fume was studied by mixing different ratios of silica fume and CaO [16]. The pozzolanic activity of the mixed pastes was followed using DTA and the quantitative determination of free lime, free silica and combined water contents. The results show that the activity of silica fume increases with lime content up to 70/30 mass% silica fume/lime, respectively. At higher lime contents up to 50 mass% the hydration products are characterized by a higher CaO/SiO_2 ratio and the rate of reaction decreases.

Silica fume is known as a by-product of silicon manufacture. It contains more than 80–85% SiO_2 in amorphous form which is suitable to use in cement and concrete industries. The typical particle size of silica fume is 0.1–0.5 mm and the nitrogen BET surface area is 20,000 m^2/kg [17]. It is increasingly used as a mineral admixture to produce high-performance concrete (HPC). Silica fume has a low bulk density, which may cause difficulty in transporting and handling. Commercial suppliers have processed silica fume using different methods of densification and compaction in order to improve the handling and transport properties of material [18]. When silica fume is incorporated with Portland cement, the rate of cement hydration increases at early hours due to hydroxyl ions releasing and alkalis into the pore fluid. The increased rate of hydration may be attributable to the ability of silica fume to provide nucleating sites to precipitating hydration products like lime, calcium silicate hydrate tobermorite-like gel (C-S-H) and ettringite [19]. These good properties of silica fumes may have effects on (DWTS) and its presence in composite cement and may facilitate recycling of this type of sludge.

To help in consuming parts of this sludge its pozzolanic activity will be evaluated in order to judge the possibility of its recycling in cement industry. This was achieved by replacing parts of Portland cements with fired sludge and identifying its pozzolanic activity at different time intervals. The pozzolanic activity of this fired sludge can be evaluated from its reaction with the liberated portlandite during the hydration of Portland cement. Moreover, silica fume was incorporated in a triple system between sludge, silica fume and ordinary Portland cement. A little information is presently known about the properties of the waste product sludge - silica fume combination, such as their hydration and the rate of reaction of silica fume in the fired sludge systems.

II. MATERIALS AND METHODS

A. *Materials*

The drinking water treatment sludge (DWTS) was collected from one of the purification of drinking water stations at Hehia (Hehia station), Egypt. Condensed silica fume (SF) was obtained from Ferrosilicon Alloys Company, Edfo, Aswan. Ordinary Portland cement (OPC) was provided by Suez Cement Company, Egypt. The chemical composition of the starting materials was characterized by X-ray fluorescence and the loss on ignition after firing at 1000°C can be seen in Table 1.

Figure (1) illustrates the mineralogical composition of the fired sludge (DWTS) (burned at 850°C for 30 min.). It composes mainly of quartz as a main phase in addition to albite [Sod. aluminosilicate, ($NaAlSi_3O_8$)], hematite and small amount of anhydrite [14]. The hump in the XRD at 15-30 (2θ) is due to the presence of amorphous phase in the fired sludge. Particle size distribution was measured with laser scattering particle size distribution analyzer, Partica LA-950, allowing measuring range from 0.01 μm to 1000 μm, Table (2) and Fig. (2). The particle size distribution of fired sludge is about 91.35 mass% higher than 50 μm and the rest 8.65 mass% in the range from 50-500μm.

B. Specimen preparation

The mix composition of the investigated mixes is provided in Table (3). The ingredients were homogenized on a roller in a porcelain ball mill with four balls for one hour to assure complete homogeneity. The standard water of consistency [20,21] was used as mixing water of cement pastes followed by curing in desiccators saturated with water vapor (100% R.H.) at room temperature 23±2°C up to 90 days. The hydration of cement paste was stopped using acetone/methanol method [22,23]. The pastes were dried at 70°C for 6 hours then kept in airtight containers for further investigation. The rate of hydration was followed by the determination of free lime [5,24] as well as chemically combined water contents from the ignition loss of the dried cement pastes [25]. Some of the hydrated cement pastes were also investigated using XRD, DSC and FTIR techniques to show the formed hydration products.

C. Analysis

X-ray fluorescence (XRF) was performed using AXIOS, WD – XRF Sequential Spectrometer (PANalytical, 2005). X-Ray diffraction (XRD) analysis was carried using BRUKER apparatus. AXs, D8-ADVANCE (Germany 2001). DSC apparatus was used at a heating rate of 10°C min^{-1} from room temperature up to 1000°C. Some selected samples were investigated using a differential scanning calorimetry of the Type LABSYS TG-DSC 1600 rod, SETARAM, France, alumina crucible and argon atmosphere. FTIR analysis was recorded using KBr (2 mg of sample/198 mg KBr) discs with Genesis-II FT-IR spectrometer at frequencies in the range from 4000 to 400 cm^{-1}. The samples were prepared using alkali halide pressed disk technique as it gives a further reduction in scattering [26].

III. RESULTS AND DISCUSSION

A. *Portland Cement-Fired Sludge Blends*

Pozzolanic cements from OPC/fired sludge with the mass ratios 80/20, 70/30, 60/40 and 50/50 mass%, respectively denoting I, II, III and IV, were prepared and hydrated up to 90 days.

A.1. Chemically combined water contents

The chemically combined water contents of the Pozzolanic cement pastes containing different mass ratios of fired sludge (I–IV) up to 90 days are shown in Fig. (3). The combined water content increases gradually with curing time for all cement pastes due to the progress of hydration and formation of more hydrates. The chemically combined water content decreases with sludge contents, due to the low pozzolanic activity of fired sludge like pozzolana in comparison with OPC. The decrease of combined water content of mix (II) with 30 mass% fired sludge at 90 days is attributed to the release of water during polymerization of the CSH and/or transformation CSH lime with lower water content [27,28].

A.2. Free lime content

Figure (4) shows the free lime contents of all pozzolanic cement pastes (I-IV) as a function of curing time up to 90 days. It is clear that the free lime content increases up to 3 days then decreases up to 90 days. There are two different processes, one tending to increase the liberated lime and the other tending to decrease its content [29]. The increase of the free lime at early ages of hydration is due to that the rate of its liberation during the hydration of alite C_3S and belite β-C_2S of Portland cement is higher than it consumption by pozzolanic reaction [25,30]. The decrease of the free lime content from 3 up to 90 days is mainly due to the pozzolanic activity of fired sludge which consumes more liberated lime forming CSH, CAH or CASH. The decrease of free lime after 3 days gives an indication for a good pozzolanic activity of the fired sludge due to the presence of amorphous phase.

A.3. X-ray diffraction analysis

The principal hydration products in pozzolanic cement pastes are essentially similar to those resulting in OPC [5]. Figures (5-7) represent the XRD patterns of pozzolanic cement pastes (I, II, IV) as a function of curing time.

Figures (5,6) illustrate the XRD patterns of hydrated cement pastes (I & II) with curing time. It is clear that the anhydrous phases like alite and belite decrease with curing time up to 90 days. The portlandite peaks in mix II cement paste is nearly consumed at 90 days. On the other side, cement paste containing only 20 mass % sludge (I) illustrates the presence of portlandite at 90 days. This means that the 20 mass % of fired sludge is insufficient to consume all liberated portlandite during pozzolanic reaction. Moreover, formation of other type of CSH with higher silica content such as rosenhahnite ($Ca_3Si_3O_9H_2O$) was observed. This may be due to the reaction of Portlandite and/or CSH with amorphous silica of the fired sludge.

Figure (7) shows the XRD patterns of pozzolanic cement pastes denoted IV (50/50) after 3 and 90 days of hydration. The anhydrous cement clinker phases as alite and belite decrease with curing time. The portlandite is completely consumed at 90 days. This is mainly due to the pozzolanic activity of fired sludge and decrease of OPC portion. This result is in a good agreement with that of chemical analysis.

A.4. Differential scanning calorimetry (DSC)

Figure (8) illustrates the DSC curves of cement pastes (II, III and IV) hydrated for 90 days. The curves show four endothermic peaks. The broad endothermic peaks located up to 250°C. The first endotherm presents from 70 up to 150°C is due to the decomposition of CSH tobermorite gel like phase whereas the second endothermal effect from 150 up to 250°C is related to the decomposition calcium aluminosilicate hydrates (CASH). The third endotherm located at about 490°C is attributed to the hydroxylation of portlandite. The last endotherm or double endothermic peak is characteristic to the decomposition of $CaCO_3$ with different degrees of crystallinity [31-33]. The enthalpy of $Ca(OH)_2$ decreases with the sludge content [28]. In sample IV (50 mass% sludge) the peak of $Ca(OH)_2$ is completely disappeared due to high percentage of sludge which reacts with $Ca(OH)_2$ forming additional amounts of CSH and CASH. XRD analysis shows the absence of $Ca(OH)_2$ as well, which confirms this reaction. This result is in a good agreement with those of free lime contents determined by chemical methods as well as the XRD results.

A.5. FTIR spectra of hydrated cement pastes

Figure (9) shows the FTIR spectra of hydrated cement pastes (II) with 30 mass % sludge from one up to 90 days. The main characteristic features of these spectra can be summarized as follows: the absorption band at 3641cm^{-1} was attributed to the v_1 vibrations generated by the hydroxyl group coordinated to Ca^{2+} in the $Ca(OH)_2$ [34,35] while the wide band at 3441 cm^{-1} was assigned to the same vibrations generated by the O–H bonds in water bound in hydration prouducts [14,36]. The bending vibrations due to the H–O–H in the water appeared at 1649 cm^{-1}. The ν_3 and ν_2 stretching bands generated by C–O in the calcite appeared at 1430 cm^{-1} and 870 cm^{-1} [7]**.** The band in the region 1100-900 cm^{-1} is due to the presence of the silicate group [37]. The band for calcium silicate hydrate appears at 975 cm^{-1} [36,38] which is assigned to the asymmetrical SiO_4 stretching frequency. It indicates the polymerisation of silicate units, SiO_4, with the formation of CSH phase [35].

After 90 days the two bands at 1096 cm^{-1} and 997 cm^{-1} converted to one single band appears at 972 cm^{-1} for all cement pastes due to the symmetric bending of bonds O-Si-O and O-Al-O which is in accordance with the previous studies [28, 39]. This is due to the progress of hydration and formation of more hydration products.

B. Portland Cement-Fired Sludge-Silica Fume Blends

Composite cements were prepared by blending OPC/Fired Sludge/SF with the mass ratios 70/30/00, 70/25/5, 70/20/10 and 70/15/15, respectively denoting II, II-5, II-10 and II-15.

B.1. Chemically combined water contents

Figure (10) shows the chemically combined water contents of cement paste II with 30 mass% fired sludge which is replaced by 5, 10 and 15 mass% (II, II-5, II-10 and II-15) as a function of curing time up to 90 days. The replacement of fired sludge by silica fume leads to increase of the combined water contents at all curing times. This is due to the higher pozzolanic activity of silica fume in comparison with fired sludge which reacts with the librated $Ca(OH)_2$ forming additional amounts of CSH and CASH. The decrease of combined water content of cement pastes containing 10 and 15 mass% silica fume at 90 days is mainly due to a release of water during polymerization of the CSH [27,28,40]. This indicates that silica fume has higher pozzolanic activity than fired sludge.

B.2. Free lime contents

The effect of substitution of equal amounts of fire sludge by silica fume can be seen from the free lime contents of composite cement pastes, denoting II, II-5, II-10 and II-15 up to 90 days in Fig. (11). The free lime of cement pastes II (70/30 mass % OPC - fired sludge) is slightly increased up to 3 days then decreased as explained before (Fig. 4). The substitution of fired sludge by silica fume tends to decrease the free lime content which is mainly due to the higher pozzolanic activity of silica fume in comparison with fire sludge. Increasing the amount of substituted fired sludge by silica fume decreases the free lime content at all ages of hydration.

B.3. X-ray diffraction analysis

Figures (12, 13) represent XRD patterns of composite cement pastes with 5, 15 mass% SF (II-5, II-15) hydrated for 1, 3 and 90 days. Composite cement pastes containing silica fume show the same trend of pozzolanic cement pastes but with the decrease of $Ca(OH)_2$ content after 3 days. This can be explained on the base that it has been completely consumed in the pozzolanic reaction of silica fume after 90 days due to its high reactivity. The rosenhahnite is also seen in cement paste with 15 mass% SF. This means that this phase is formed from the reaction of SF with portlandite or CSH. The blending of these additives with the cement causes important variations of the cement surface area, especially in case of silica fume. Consequently, composite cements containing silica fume has more hydraulic properties.

B.4. Differential scanning calorimetry (DSC)

The DSC curves of composite cement pastes with 5, 10 and 15 mass% SF (II-5, II-10 and II-15) are shown in Fig. (14). It is clear that by substituting sludge with silica fume the enthalpy of $Ca(OH)_2$ was decreased due to the ability of silica fume to reacted with Portlandite forming hydration products like CSH and ettringite [19]. The endothermic peak located at ≈ $100^{o}C$ increases due to the excess formation of rosenhahnite. The third peak is corresponding to the decarbonation of calcium carbonate, together with possible solid-solid phase transformations [41]. The exothermic peak at $870\text{-}940^{o}C$ corresponding to crystallization of wollastonite [42,43]. Differential scanning calorimetry is capable of identifying the low C/S ratios in CSH product by an exothermal peak in the vicinity of $900^{o}C$ and beyond.

B.5. FTIR spectra of hydrated cement pastes

Figures (15, 16) show the FTIR spectra of hydrated cement pastes (II-5 & II-15) with curing time up to 90 days. The spectra show the same bands of mix (II) cement pastes except the adsorption band at 3641 cm^{-1} due to the ν_1 vibration generated by the hydroxyl group coordinate to Ca^{2+} in the $Ca(OH)_2$ [34]. The substitution of fired sludge by silica fume with 5 and 15 mass% tends to decrease the free lime contents. In composite cement paste with 15 mass% SF the band of free lime is hardly detected after 90 days of hydration.

CONCLUSION:

The main conclusions of this paper can be summarized as:

- It can be seen that DWTS has a good pozzolanic activity but still lower than that of silica fume. It forms similar hydration products as silica fume such as CSH in addition to CASH. Moreover, by using such triple system (sludge, silica fume and cement) as a composite encourage applying such waste (DWTS) in cements industry which could help in reducing its production costs and decrease the pollution. Further efforts will be conducted to fully evaluate using this waste in cement production; data will be published in due course.
- The portlandite content decreases with the amount of fired DWTS. In cement pastes IV specimen (50%mass) DWTS there is no $Ca(OH)_2$ detected by X-ray, FTIR or DSC after 90 days due to the pozzolanic activity of fired sludge.
- Replacing fired sludge with SF increases the combined water and decreases the free lime due to the pozzolanic activity of SF which forming hydration products.

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Table (1): Chemical analysis of the starting materials, (mass, %)

Material Oxides	Ordinary Portland cement	Silica fume	Fired sludge
SiO_2	21.51	95.14	53.60
Al_2O_3	5.07	0.17	28.34
Fe_2O_3	4.39	0.46	9.42
CaO	64.21	0.28	3.10
MgO	2.00	0.81	0.64
SO_3	3.25	0.16	0.54
K_2O	0.29	1.99	0.75
Na_2O	0.23	0.58	0.30
TiO_2	--	--	1.28
*LI	2.40	0.04	1.51

*LI: loss on ignition at 1000°C.

Table (2): Particle size distribution of fired sludge

Particle size	Cumulative % passing
µm	Fired sludge
0.5 – 1.0	0.93
1.0 - 10.0	46.25
10.0 - 50.0	44.17
50.0 -100.0	6.16
100.0 -110.0	0.37
200.0 – 500.0	2.12
Total	100.0

Table (3): Mix composition of the investigated mixes, mass%:

Sample	I	II	III	IV	II-5	II-10	II-15
OPC	80	70	60	50	70	70	70
Sludge	20	30	40	50	25	20	15
Silica Fume	00	00	00	00	05	10	15

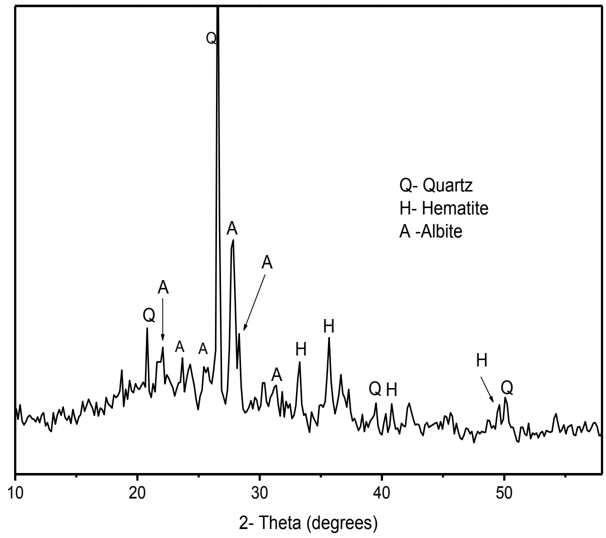

Fig. (1): XRD pattern of fired sludge from (DWTS)

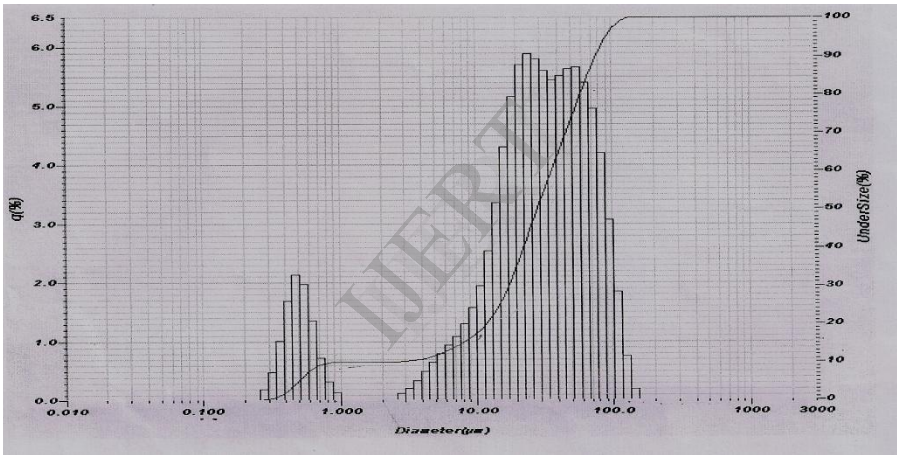

Fig. (2): The cumulative curve of the particle size distribution of fired sludge

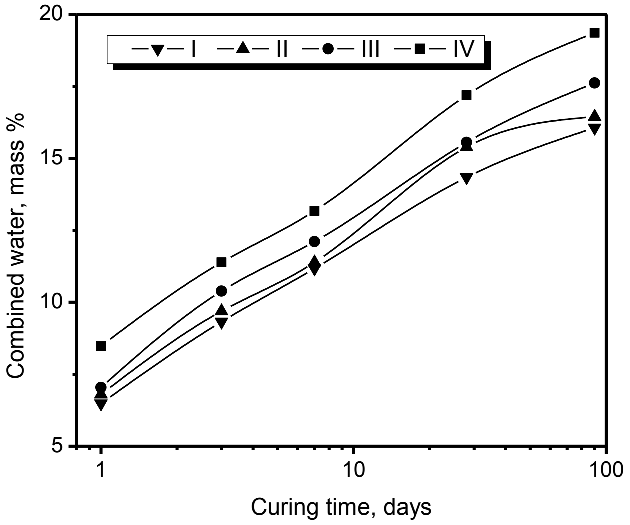

Fig. (3): Combined water contents of DWTS- OPC pastes as function of curing time

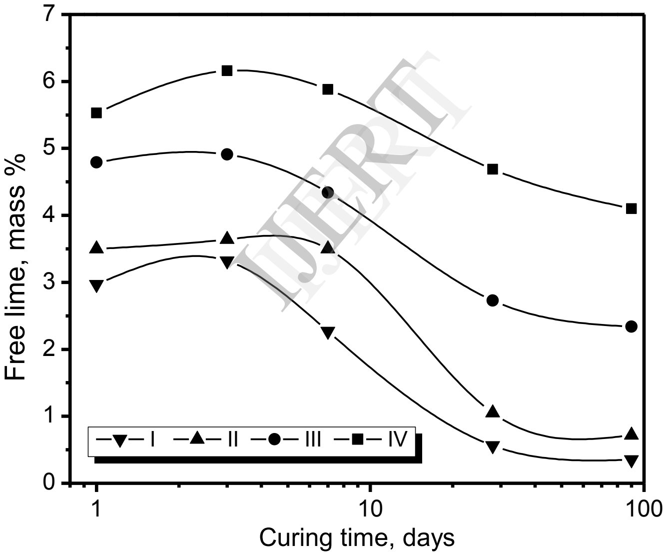

Fig. (4): Free lime contents of fired sludge-OPC pastes with curing time

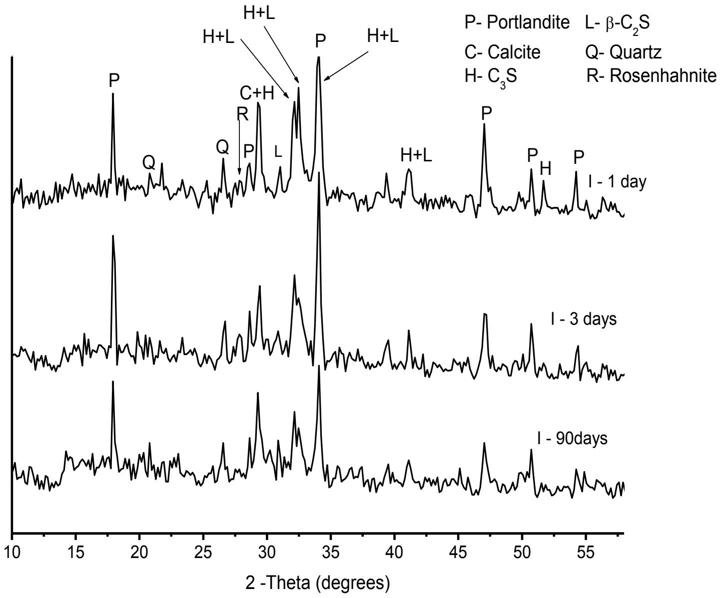

Fig. (5): XRD patterns of pozzolanic cement pastes with 20 mass % fired sludge with curing time

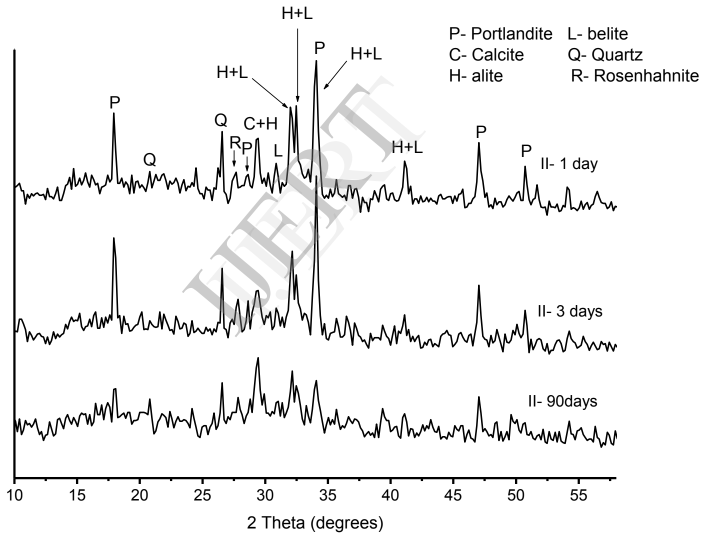

Fig. (6): XRD patterns of pozzolanic cement pastes with 30 mass% fired sludge as a function of curing time

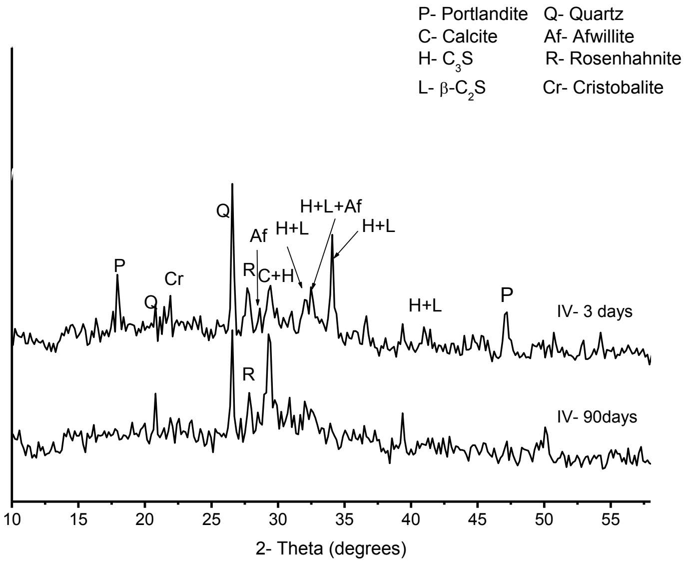

Fig. (7): XRD patterns of pozzolanic cement pastes with 50 mass% fired sludge after 3 and 90 days

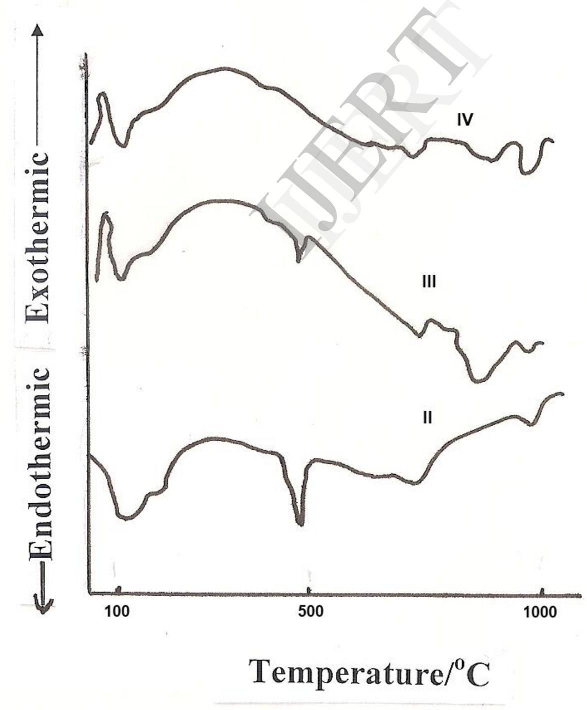

Fig. (8): DSC curves of cement pastes II, III, IV hydrated for 90 days

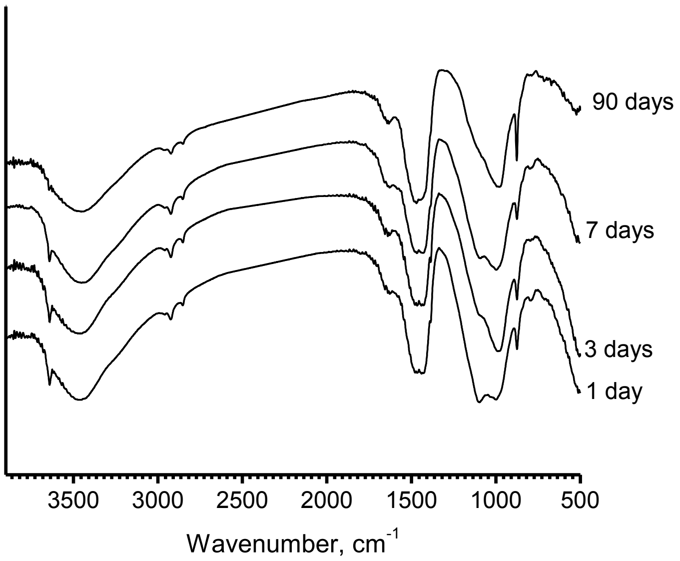

Fig. (9): FT-IR Spectroscopy of composite cement pastes with 30 mass% sludge as a function of curing time

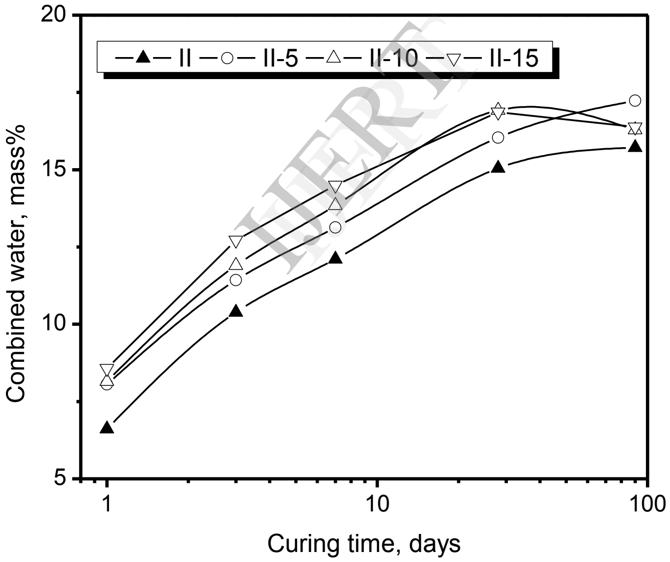

Fig. (10): Combined water contents of cement pastes with silica fume instead of fired sludge

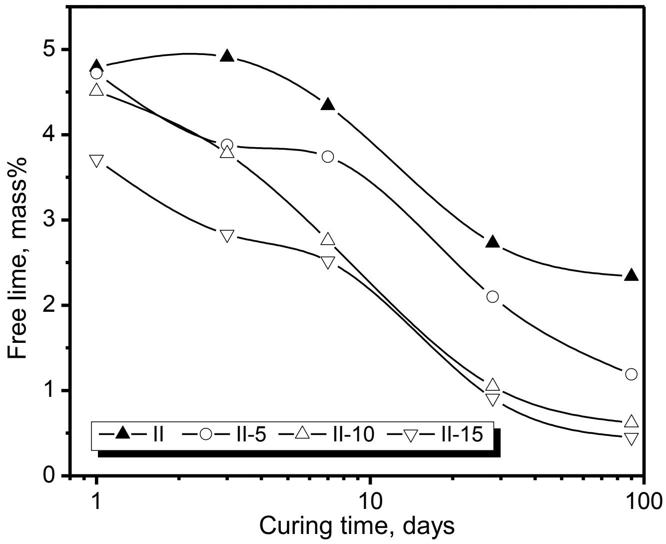

Fig. (11): Free lime contents of composite cement pastes containing Silica fume instead of fired sludge

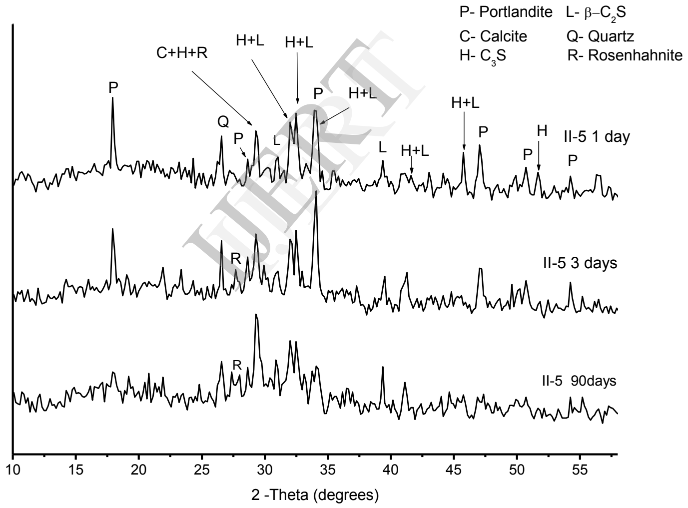

Fig. (12): XRD patterns of composite cement pastes with 25 sludge + 5 silica fume mass% with curing time

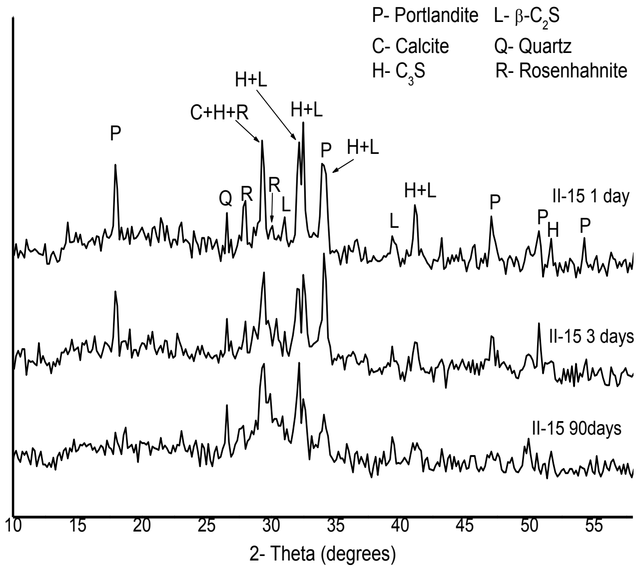

Fig. (13): XRD patterns of composite cement pastes with 15 sludge + 15 silica fume mass% as a function of curing time

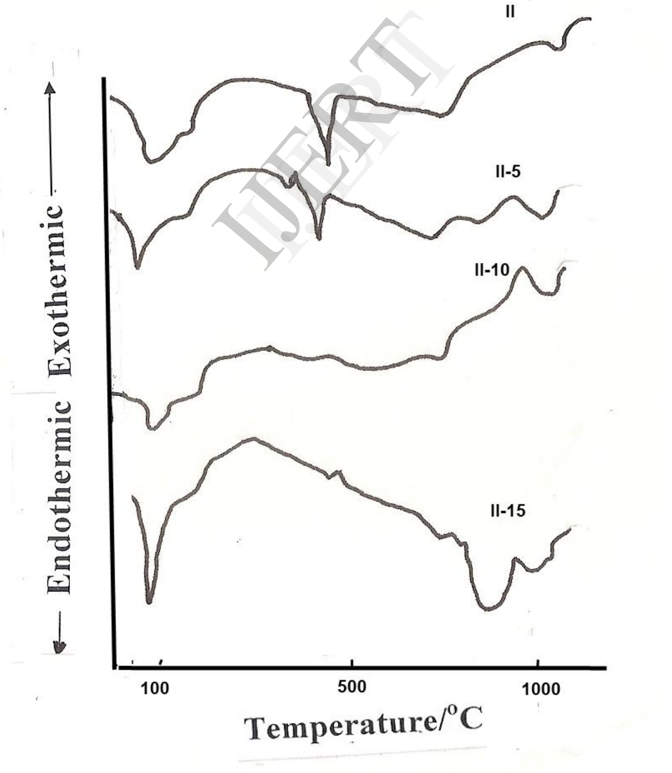

Fig. (14): DSC curves of cement pastes (II, II-5, II-10 and II-15) hydrated up to 90 days

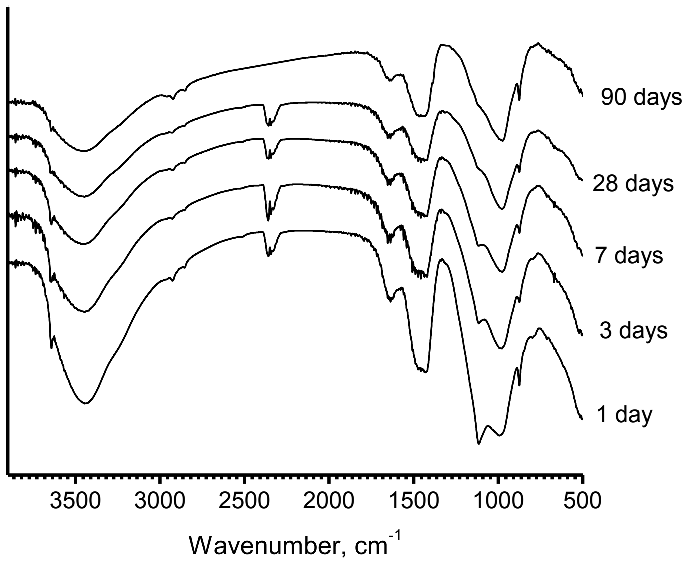

Fig. (15): FT-IR Spectroscopy of composite cement pastes with 25 sludge + 5 silica fume mass% with curing time

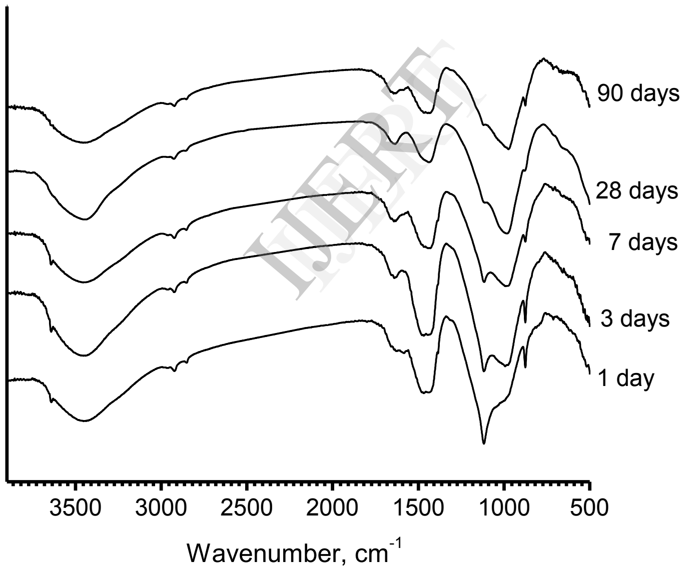

Fig. (16): FT-IR Spectroscopy of composite cement pastes with 15 sludge + 15 silica fume mass% as a function of curing time