Hydration Characteristics of Autoclaved Cement Kiln Dust-Sludge-Silica Fume Pastes

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Abstract: Autoclaved cement kiln dust (CKD) and sludge pastes made with and without silica fume were hydrothermally hardened at a pressure of 8 atm. of saturated steam for different autoclaving ages. Hydration characteristics of the autoclaved CKD-sludge-silica fume pastes were studied by the determination of compressive strength and chemically combined water contents at different autoclaving ages. The phase composition and morphology of the formed hydrates were studied using x-ray diffraction analysis and scanning electron microscope. The replacement of silica fume in CKD-sludge mixtures results in a marked increase in strength values of the autoclaved specimens at all stages of the hydrothermal process. The results of x-ray diffraction analysis and SEM-micrographs of autoclaved specimens for various mixtures indicated that the main hydration products identified are calcium silicates hydrated and minor amounts of $CaCO_3$. [Journal of American Science 2010;6(8):19-26]. (ISSN: 1545-1003).

Key words: cement kiln dust, sludge, silica fume, hydrothermal treatment.

1. Introduction

Autoclaving building products possesses several advantages including the marked development at shorter times of autoclaving at relatively high steam pressures. In addition, the utilization of industrial solid wastes in the production of high strength building products is of prim importance for environmental protection and development.

Industrial solid wastes such as cement kiln dust and other silica and alumina bearing materials are widely used for the production of blended cement and various cementations products. In this work we studied the usage of three wastes which can act as cementations materials as new building materials namely; cement kiln dust, sludge and silica fume. Hydrothermal treatment of these wastes is almost associated with building products having improved binding characteristics. The properties of these autoclaved products are always governed by the chemical composition and physical state of the formed hydration products which act as the main binding centers [1-3]. Cement kiln dust (CKD), is produced in relatively large quantities during the production of Portland cement. Various methods for utilizing CKD in industrial applications, including existing or proposed methods for alkali removal, are reported in the literature. Bhatty [4] provides a general review of these methods. Because of the generally high lime content of CKD and subsequent ability to harden upon exposure to moisture, CKD has been used as a binder in soil stabilization suitable for a sub-base in streets and high way construction. It is commonly used as a mixture with different solid-waste materials such as waste glass, fly ash, waste water sludge with the addition of cement or other admixtures if necessary [5]. Recently, there has been a trend of utilizing it in cement products [6-10].

Sludge is a byproduct produced in electrical stations in large quantities. Many attempted of sludge disposal alternatives such as agricultural use, land filling, marine disposal and incineration, etc, have adverse environmental impacts. There is a resulting increase of interest in reuse of sludge by incorporation into construction materials [11-12].

Silica fume is a byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. Silica Fume is also collected as a byproduct in the production of other silicon alloys such as ferrochromium, ferromanganese, Ferro magnesium, and calcium silicon. Silica fume consists primarily of amorphous (non-crystalline) silicon dioxide (SiO_2). The individual particles are extremely small, approximately 1/100th the size of an average cement particle. Because of its fine particles, large surface area, and the high SiO_2 content, silica fume is a very reactive pozzolana when used as a blend in cement and concrete [13-15]. The quality of silica fume is specified by ASTM C 1240 and AASHTO M 307. Toutanji et al [16] studied the effect of silica fume on the compressive and uniaxial direct tensile strength of Portland cement pastes and mortars. Many authors studied the durability of OPC blended with silica fume against sulfate ions [17-18], fire [19-20] and acid solutions [21-23].

The object of this investigation is to study the hydration characteristics of autoclaved specimens made with cement kiln dust- sludge and cement kiln dust -sludge- silica fume. The phase composition and the morphology of the formed hydrates were studied using x-ray diffraction analysis and scanning electron microscope.

2. Material and Methods

a Materials:

The starting materials used in this investigation are:
-Cement Kiln Dust (CKD) of Blain surface area about 2500 cm2/g collected during the manufacture of cement by the dry process from Suez cement company, Suez, Egypt. The chemical oxide composition was given in Table (1).
-Condensed silica fume is a byproduct of silicon or ferrosilicon alloys industries. It is obtained from ferro-silicon Co; Kom-Ombo, Egypt. It is amorphous silica with specific surface area 20 m2/g.
-Lime free sludge was obtained from West-Cairo power station , sakeel-Giza, Egypt. The chemical oxide composition was given in Table (1).

Table (1): The chemical oxide composition of CKD and sludge.

Oxide	%	
	CKD	sludge
SiO_2	15.4	60.25
Al_2O_3	3.76	2.06
Fe_2O_3	2.69	1.25
CaO	49.6	3.28
MgO	1.95	1.23
SO_3^{--}	5.23	1.28
K_2O	2.19	0.31
Na_2O	2.68	0.49
L.O.I	15.6	29.0
Free CaO	21.85	-
Free Cl^-	5.84	-

b Preparation of Mixes

Seven Mixes were prepared using different weight composition ratios of CKD, sludge and silica fume as shown in Table (2). The dry mixtures showed in Table (2) were first mixed using ethanol for one hour in order to ascertain a complete homogeneity of the mixture. After evaporation of ethanol, each dry mixture was mixed with distilled water for 3 minutes at a water/solid ratio of 0.45. From the paste produced, cylindrical specimens of 3.14 cm2 cross-section area and 2 cm height were molded at a pressure of 50 kg/cm2. The specimens were first cured at 100% humidity for 6 hours in order to attain the initial setting. The specimens of each mix were autoclaved at 8 atmosphere of saturated steam for 0.5, 2, 6, 12 and 24 hours. At the end of each autoclaving period, the specimens were dried, after being removed from the autoclave, in CO2 free atmosphere at 105°C for 24 hours to remove the free water.

At each autoclaving period, compressive strength test was carried out on the dried specimens. Then, chemically combined water contents were carried out on the crushed specimens. The phase composition of the formed hydrates is investigated using x-ray diffraction analysis. The morphology and microstructure of hydrated phases were identified using scanning electron microscopy (SEM).

Table (2): Composition percentage (w/w) of various dry mixtures and their notation.

Sample notation	Composition percentage(w/w)		
	CKD	Sludge	Silica fume
I	60	40	-
II	50	50	-
III	40	60	-
IV	50	45	5
V	50	40	10
VI	40	55	5
VII	40	50	10

3. Results and Discussion

1. Compressive Strength

The results of the compressive strength of autoclaved mixes made of weight percentage ratios 60/40, 50/50 and 40/60 of CKD / sludge (Mixes I, II and III) are shown in Fig.(1). The strength values increases with increasing age of autoclaving for all autoclaved Mixes (I –III) up to 18 hours. This mainly attributed to the hydrothermal interaction between the lime released from CKD with sludge to give calcium silicate hydrates which contribute considerably to the compressive strength of these autoclaving specimens. In addition, the presence of some alkali in CKD activates the hydrothermal reaction [1, 6]. However, the compressive strength values decrease after 24 hours of autoclaving, these results can be attributed to the stabilization of the initially formed hydrates via crystallization. Fig. (1) Shows also that the autoclaved specimens made of Mixes II and III possess the higher strength values compared to Mix I. This indicates these ratios of CKD to sludge in these Mixes possess the best hydrothermal reaction that led to the formation of hydration products having considerable hydraulic character.

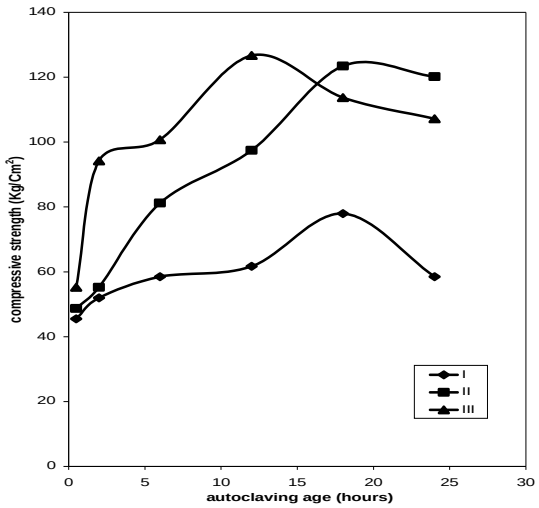


Fig.(1): Compressive strength (Kg/cm^2) of Mixes I,II and III at various autoclaving ages.

The compressive strength results of autoclaved pastes made of Mixes II, IV and V are shown in Fig.(2) indicate that the replacement of sludge in Mix II by 5 wt. % silica fume (Mix IV) or by 10 wt. % silica fume (Mix V) result in a marked increase in the strength values of the autoclaved specimens made of CKD- sludge- silica fume mixtures at all stages of the hydrothermal process. The results of Fig.(2) indicate also that the autoclaved pastes made of Mix V (containing 10 wt.% silica fume) possess relatively higher strength values compared with those of the autoclaved paste made of Mix IV (containing 5 wt. % silica fume). As the ratio of silica fume increased from 5 to 10 wt.%, the compressive strength increase, and reach a values of compressive strength in mix V (50 wt.% CKD + 40 wt.% sludge +10 wt.% silica fume) higher by 3 to 4 fold compared to mix II (50 wt.% CKD +50 wt. % sludge) at all the autoclaving times. Such results due to the high reactivity of silica fume to react with lime produced from CKD as compared to sludge in the hydrothermal reaction. At later autoclaved ages (24 hrs.) for Mix V, a slight decrease in strength values is observed, a result which is mainly associated with two factors, these are: (i) the well crystallization of the initially formed hydrates (mainly calcium silicate hydrates); the well crystallized CSH possess low hydraulic characteristics with relatively low strength and/ or (ii) the transformation of lime –rich CSH into low –lime CSH with a metastable state leads to lower mechanical properties.

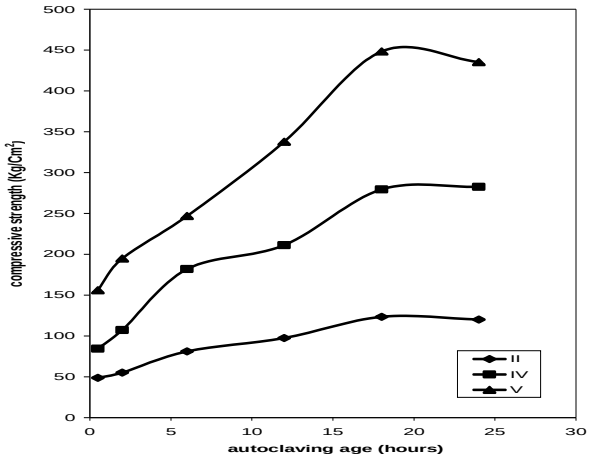


Fig.(2): Compressive strength (Kg/cm^2) of Mixes II, IV and V at various autoclaving ages.

Fig. (3) shows the compressive strength results of Mixes III, VI and VII in which a replacement of sludge in Mix III by 5 wt.% silica fume (Mix VI) or 10 wt.% silica fume (Mix VII) are made. Again, Fig. (3) shows the replacement of sludge by silica fume in the hydrothermal specimens results in a marked increase in the compressive strength at all stages of the hydrothermal process. However, the compressive strength values obtained here in these Mixes (VI and VII) are lower than those obtained in Mixes IV and V. Such results can be attributed to the weight ratios of CKD-sludge-silica fume in Mixes IV and V possess the best hydrothermal reaction compared to all autoclaving Mixes.

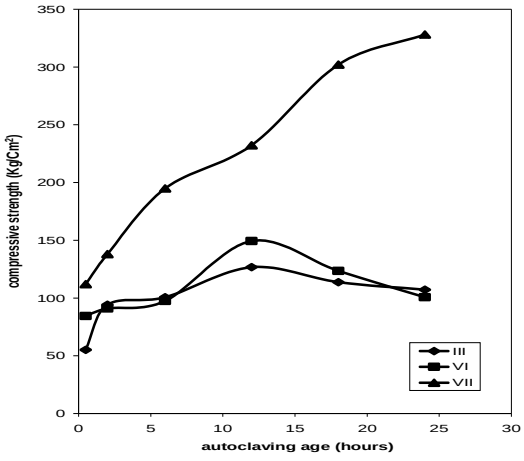


Fig.(3): Compressive strength (Kg/cm^2) of Mixes III, VI and VII at various autoclaving ages.

2. Chemically Combined Water Content:

The result of combined (non evaporable) water content (Wn, %) of mixes containing different weight ratios of CKD and sludge (mixes I-III) are shown in Fig. (4). Obviously, the combined water contents values increases with increasing the autoclaving time up to 12 hours which indicate a progress of the hydrothermal reaction and formation of more hydrates. At the period 18-24 hours, the values of the chemically combined water contents slightly decrease in all Mixes. This can be explained to the transformation of lime–rich CSH into low –lime CSH with a metastable state leads to low water content and lower mechanical properties, and/or the stabilization of the initially formed hydrates via crystallization. Crystallized CSH characterized by low water content and low compressive strength.

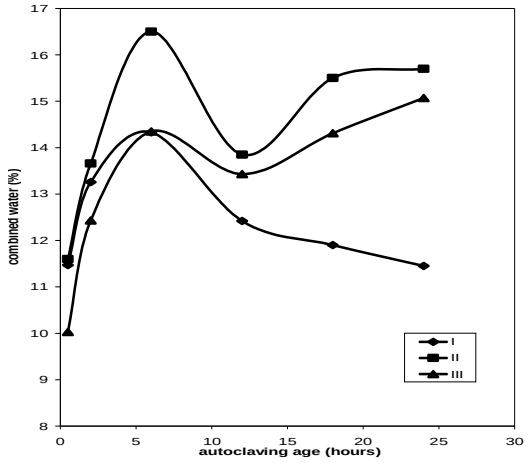


Fig.(4): Combined water contents of Mixes I, II and III at various autoclaving ages.

Combined water contents of autoclaved specimens made of Mix II, Mix IV (5 wt. % of sludge is replaced by silica fume) and Mix V (10 wt.% of sludge is replaced by silica fume) at different autoclaving times are shown in Fig.(5). Here, a similar trend of variation of chemically combined water contents of specimens containing silica fume (Mixes IV and V) to those free from silica fume (Mix II) was obtained but with relatively higher values. The increased values of chemically combined water contents indicate a formation of more hydrates and these confirm the compressive strength results. Mix (V) which composed of 50 wt. % CKD + 40 wt. % sludge and 10 wt. % silica fume shows the highest values of chemically combined water contents compared with the other investigated Mixes.

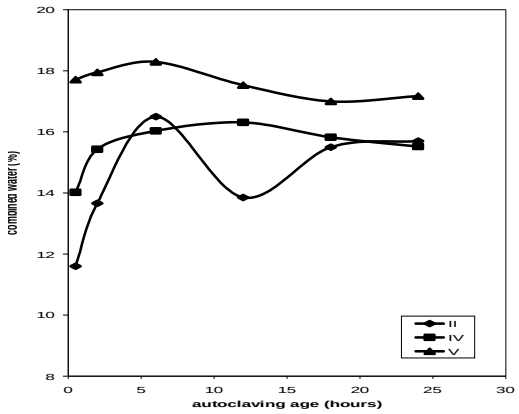


Fig.(5): Combined water contents of Mixes II, IV and V at various autoclaving ages.

Fig.(6) shows chemically combined water contents of autoclaved specimens of Mix III, Mix VI (5% of sludge is replaced by silica fume) and Mix VII (10 % of sludge is replaced by silica fume) at various autoclaving times. Again, in these specimens the replacement of sludge by silica fume led to an increase in the values of combined water contents at all the autoclaving times. These results confirm the results of compressive strength and indicate the high reactivity of silica fume compared to sludge in the hydrothermal reaction.

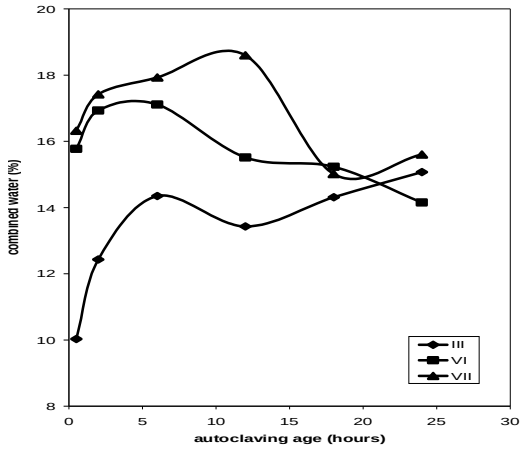


Fig.(6): Combined water contents of Mixes III, VI and VII at various autoclaving ages.

.3. X-ray diffraction analysis

The main hydration products formed as a result of hydrothermal reaction of the hardened specimens made from CKD, sludge and silica fume are identified by means of x-ray diffraction analysis.

X-ray diffraction patterns of the autoclaved CKD- sludge made of Mix II and autoclaved CKD-sludge –silica fume made of Mixes V at autoclaving ages of 0.5, 6, 18 and 24 hours are shown in Figs. (7 and 8) respectively. The distinct main hydration products identified were calcium silicate hydrates (CSH I, II) and minor amounts of $CaCO_3$. In addition, peaks characterized to unhydrated β-C2S and SiO2 were identified. At later autoclaving ages, 6, 18 and 24 hours, the intensities of the peaks characterized to CSH I,II were increased while the intensities characterized to unhydrated phases decreased. The formation of lime rich calcium silicate hydrates [mainly (CSH II] in autoclaved specimens made of Mix V (having high CKD content in dry mixture with 10 wt. % silica fume) is mainly responsible for the increased intensities characterized for hydrated phases (Fig. 8) of autoclaving of hardened CKD-sludge- silica fume pastes of Mix V compared to those of mix II. These results confirm the results of compressive strength.

4. Morphology and Microstructure

Fig.(9-a) shows the SEM micrograph of the hydration products formed after 6 hours of autoclaving of specimens made of Mix II (50 wt.% CKD + 50 wt. % sludge). The hydration products are mainly composed of semicrystalline calcium silicate hydrates beside minor amounts of CaCO3 and unhydrated phases β-C2S and SiO2. After 24 hours of the hydrothermal reaction a massive structure of calcium silicate hydrates appears as the minor hydration products (9-b).

Fig.(10-a) shows the SEM micrograph of the hydration products obtained after 6 hours of autoclaving specimens of Mix V ((50 wt.% CKD + 40 wt.% sludge +10 wt.% silica fume). The hydration products are mainly semicrystalline calcium silicate hydrates (CSH I,II). After 24 hours of autoclaving, crumpled foils with interlocking fibrous structure of calcium silicate hydrates appear in the SEM micrographs shown in Fig.(10-b).

4. Conclusion:

On the basis of the results obtained in our investigation we Concluded that:

1- Autoclaved cement kiln dust (CKD)-sludge pastes possess a considerably compressive strength at all different autoclaving ages. This mainly attributed to the hydrothermal interaction between the limes released from CKD with sludge to give calcium silicate hydrates.

2- The replacement of sludge by silica fume results in a marked increase in the compressive strength and the combined water contents of the formed hydrates at all the autoclaving ages. This mainly indicates the high reactivity of silica fume compared to sludge to react in the hydrothermal reaction.

3-X-ray diffraction analysis and SEM micrographs show the main hydration products are calcium silicate hydrates (CSH I,II) with a minor amounts of $CaCO_3$.

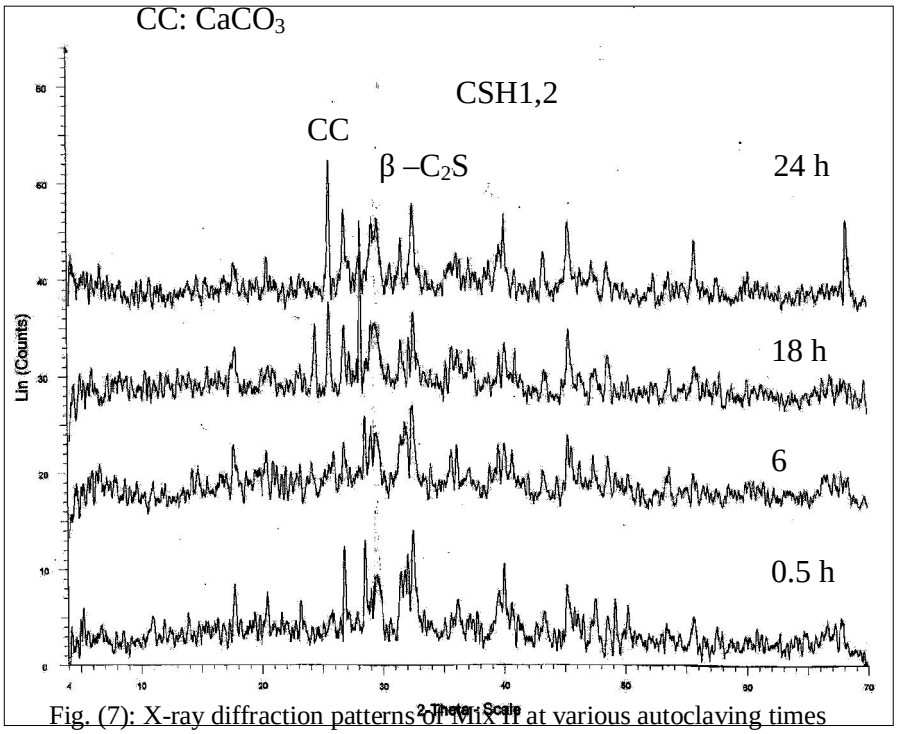


Fig. (7): X-ray diffraction patterns of Mix II at various autoclaving times

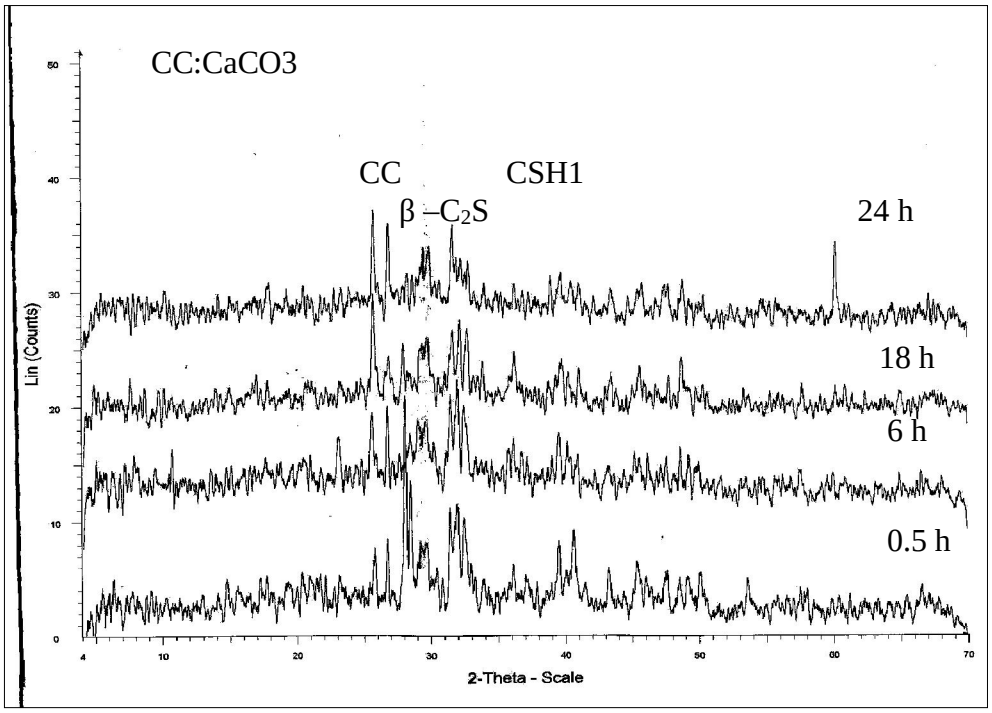
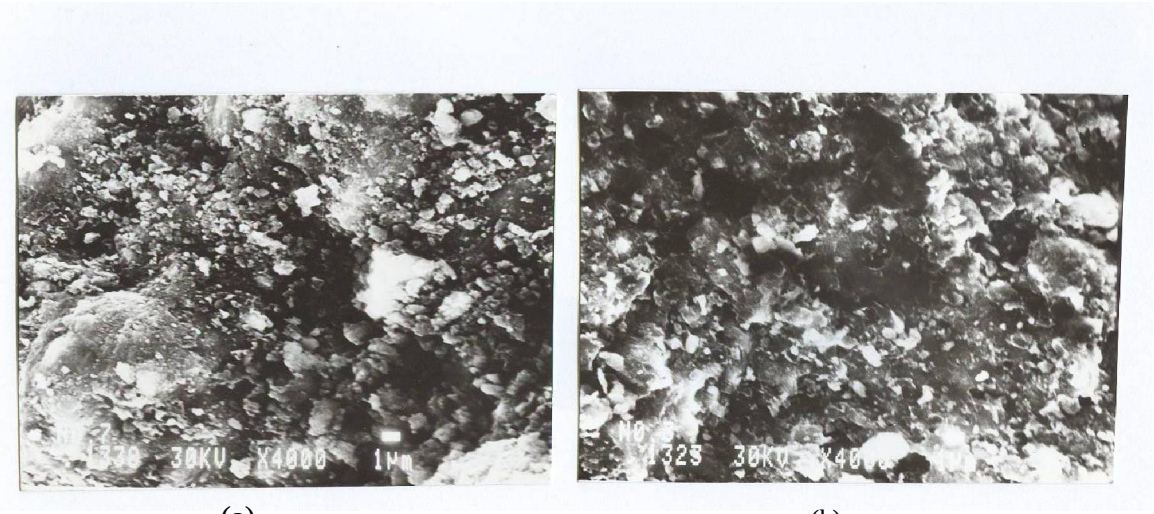
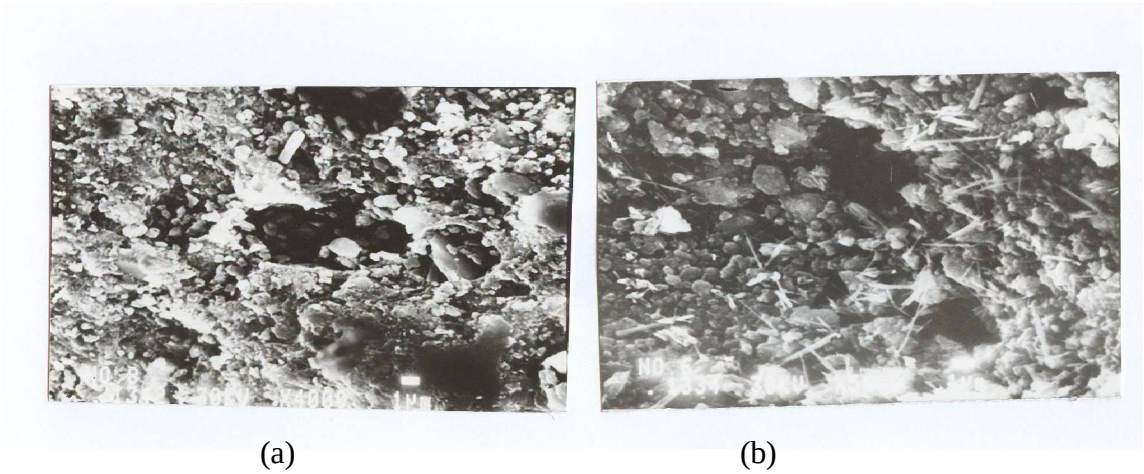


Fig.(8): X-ray diffraction patterns of Mix V at various autoclaving times



(a) (b)

Fig. (9): SEM micrographs of Mix II at at various autoclaving times
(a) after 6 hours (b)after 24 hours



(a) (b)

Fig.(10): SEM micrograph of Mix V at various autoclaving times
(a) after 6 hours (b)after 24 hours

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