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CHARCTERISTICS OF SULPHATE RESISTING CEMENT PASTES CONTAINING DIFFERENT RATIOS OF BELITE PHASE

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ABSTRACT

The influence of tricalcium silicate (alite) content on the properties of the sulphate resisting cement (SRC) was studied. Three types of SRC with various ratios of alite/belite were prepared. The water of consistency, initial, and final setting time of these cements as well as the kinetics of hydration and physico-mechanical properties of the cement pastes were determined. Some of the hydrated cement pastes were investigated using DTA, TGA, XRD and IR techniques. The results show that the increase of alite content enhance the rate of hydration, and hence the early strength development, at the expense of the ultimate strength. One reason for this is that the microstructure formed during the accelerated hydration is usually coarser and less favorable for strength development. Contrary to this, slow hydration with increasing belite content cement paste allows the formation of a microcrystalline or gel-like structure of large surface area, which results in an ultimate good strength.

Keywords: Sulphate resistance cement, Belite phases, Hydration properties

INTRODUCTION

Calcium silicate phases are the main constituents in Portland cement, which to a great extent controls its hardening and strength development. In a simplistic way, the hydration reaction of C_3S (alite) and β-C_2S (belite)can be represented as follows:

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH, \quad \Delta H = 1114 \text{ Kj mol}^{-1} \quad (1)$$

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH, \quad \Delta H = 43 \text{ Kj mol}^{-1} \quad (2)$$

It is well known that these reactions do not describe exactly the stoichiometry of hydration. This is due to that the main hydration product CSH does not have the exact composition $C_3S_2H_3$; it is usually non-crystalline at even has a gel–like character and variable composition. The hydration product of β-C_2S is apparently stoichiometry similar to that of alite but with much lower evolution of heat and produces smaller quantities of CH [1].[1]

Conzalez et al [2] prepared four SRCs with low C_3A contents (0.1%) but having different ratios of C_3S between 40 and 74%. These were utilized for the preparation of cement samples which stored for two years in Na_2SO_4 solution. The sulphate attack mechanism was investigated by measuring expansion and flexural strength, while the micro-structural changes were studied by XRD and SEM using X-ray microanalysis. It was found that great expansion was measured for high C_3S-content and formation of the expansive ettringite was attributed to localized gypsum formation at interfaces of aggregate-paste that disrupts the samples and the attack increases. The deterioration of low C_3A cements by sulphate attack is possible and the C_3S content plays a decisive role in the potential damage of these cements.

The manufacture of high strength SRC was studied [3]. It was found that the sulphate resistivity of the cement is obtained by suitably adjusting the mineral component in the clinker, lowering the C_3S and C_3A contents, increasing the C_2S percent, and decreasing the gypsum addition. This led to improve physico-chemical properties of the cement pastes.

Recently, because of the harmful role of Ca $(OH)_2$ in aggressive attack , the researchers look for production of SRC with low C_3S (alite) contents. This cement not only has a good durability in aggressive attack but also has the advantages of belite cement which contains a higher proportion of belite (β-C_2S). Belite-rich cements have several potential advantages over Portland cement:

- The amount of energy required to manufacture belite cements is lower than that of OPC.
- The alite (C_3S) which is the main component of Portland cement formed at temperatures of about 1450°C while belite (β-C_2S) is formed at temperature around 1250°C.
- The level of CO_2 emitted during the manufacturing of belite cement is lower than for Portland cement by up to 10 % [4].

The present work aims to study the influence of increasing belite contents on the expense of alite on the physico-mechanical properties of sulfate resisting cement pastes. The water of consistency, as well as initial and final setting time of cement pastes were determined. The kinetics of hydration [2]in tap water as free lime and combined water contents of the cement pastes up to 90 days were studied. The mechanical properties of the cement pastes such as bulk density, total porosity and compressive strength were also determined. Some of the hydrated cement pastes investigated by using DTA, XRD, TGA and IR techniques.

MATERIALS AND METHODS

The materials used in this investigation were sulphate resistant cement (SRC) provided from El-Masria Cement Company and the belite phase prepared from pure chemicals. The chemical compositions of starting material are shown in Table 1.

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

Oxides%	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**Cl^-**	**I.L.**
SRC	**21.32**	**4.4**	**4.85**	**63.91**	**1.56**	**1.56**	**1.35**	**0.22**	**0.17**	**1.85**

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Belite phase	**35.18**	**0.13**	**0.12**	**62.50**	**0.27**	**0.04**	**0.02**	**0.18**	**0.07**	**1.34**

Belite (β-C_2S) was synthesized from reagent grade $CaCO_3$ and pure ground sand (more than 99.5 % SiO_2) in the proper molar ratio. The dry constituents of limestone and silica were mechanically mixed for 1/2 hour in a porcelain ball mill using two balls to attain complete homogeneity, then fired twice at 1450^0C for two hours soaking time using B_2O_3 (0.5%) as a stabilizer to complete the formation of belite phase and to keep it in the β- form. It was then ground and kept in airtight container

The dry constituents of SRC and belite phase were mechanically mixed for 30 minutes in a porcelain ball mill to attain complete homogeneity. Two cements B & C were prepared by mixing different amounts of belite with SRC. The prepared cements were ground to specific surface area 3250 g/cm^2.The phase composition (using Bogue equation) of the prepared cement is shown in Table 2.

The water of consistency [5] and setting times [6] were determined. The pastes were mixed with the required amount of water, and then moulded in 0.5 inch cubes and cured in a humidity cabinet for 24 hours. The sample cubes were then demoulded and immersed in tap-water for up to 90 days. The kinetics of hydration were followed by the determination of free lime [7] and combined water contents. The total porosity, bulk density and compressive strength were also measured up to 90 days. The mixing, moulding and stopping of hydration were described elsewhere [8].

Table 2: Phase Composition of the investigated SRCs, %

Cement	C_3S	β -C_2S	C_3A	C_4AF
Cement A	**57.17**	**18.07**	**3.46**	**14.77**
Cement B	**49.71**	**28.75**	**3.00**	**12.84**
Cement C	**43.97**	**36.97**	**2.66**	**11.36**

RESULT AND DISCUSSION

The results of water consistency as well as initial and final setting times for the prepared samples SRC are graphically represented in Figure 1. The water of consistency decreases with belite content due to its low heat of hydration. Also, as the amount of belite content increases the initial and final setting times elongated. This is also due to the setting and hardening of the cement pastes brought by the formation a CSH gel. The gel fills the space between the cement grains, bridges between them, and thereby causes stiffening of the paste and consequently hardening. Therefore, by increasing the belite phase on the expense of alite, the rate of formation of gel decreases due to lower reactivity of belite and consequently the setting time elongates.

The chemically combined water contents of the prepared SRC pastes cured in tap water for 3, 7, 28, 90 days are graphically represented as a function of curing time in Figure 2. The combined water content increases with curing time for all cement pastes due to the accumulation of hydration products by the progress of hydration. Also, as the belite content increases the combined water decreases, specially at early age (3-28 days), while the belite rich cement gives more hydration at later ages (90 days). This is concluded with the fact that the rate of hydration of the belite is slower than that of alite at early ages and consequently the amount of hydration products (CSH gel) decrease and the chemically combined water content is decreased.

The free lime contents of the prepard SRC pastes cured for 3, 7, 28, 90 days are shown in Figure 3. The free lime content of the cement pastes increases with curing time for all pastes. This is attributed to the continuous hydration of silicate phases liberating free lime. On the other side, the free lime content decreases with the belite content. The belite phase liberates less calcium hydroxide compared to that of alite, in addition to its slower rate of hydration during the early stages of curing, therefore, as the belite content increases the liberated lime contents decreases at all ages of hydration.

The apparent porosity of the hydrated pastes as a function of curing time is plotted in Figure 4. The apparent porosity of hardened cement pastes decreases with curing time for all cement pastes due to the continuous hydration of cement and the accumulation of hydration products within the pores of cement paste. Therefore, the apparent porosity decreases with time. Also, the apparent porosity increases with belite content which is attributed to its lower rate of hydration.

The compressive strength of the hardened cement pastes is graphically represented as a function of the curing time in Figure 5. The compressive strength of the cement pastes increases with time for all samples; this is mainly attributed to the increase of amounts of hydration products, in particular CSH (tobermorite- like gel) which is the main source of compressive strength. It can be seen that, the compressive strength of the low belite content cement pastes is higher than that of the rich belite cement. This is mainly due to the fact that, alite is responsible for most of the early strength of cement pastes, due to its high rate of hydration at early age. On the other hand, the belite rich cement contributes much more for the later strength of the cement pastes.

It is also clear that the strength of the cement with higher content of belite increases linearly up to 90 days. This is due to the higher rate of hydration at later ages. On the other side, the strength of the two other cements is gradually increased from 28 up to 90 days.

Figure (6) illustrates the DTA thermograms of the hydrated cement pastes (A) and (C) cured for up to 90 days in tap water. The thermograms illustrate endotherms below 100°C, 484°C and 700°C. The first peak is due to the decomposition of calcium silicate and calcium aluminate hydrates. The second endotherm at 484°C represents the decomposition of calcium hydroxide. In addition, the third peak is due to the decomposition of calcium carbonate. The mean features of thermograms are characterized by the decrease in peak area of CSH, CAH and $Ca(OH)_2$ with belite contents. This is mainly due to the decrease in the amounts of alite which is proportional to the amount of liberated lime as well as the hydrated calcium silicates.

TG curves of the low belite content cement (A) as well as high belite cement (C) cured for up to 90 days in tap water are shown in Figure 7. It is clear that, the endothermic peak of $Ca(OH)_2$ in the range 450 ^{0}C decreases with the increase of belite content. Cements (A) & (C) give loss of 2.338 and 2.188 wt % respectively. The loss due to the dehydration of the two cements A&C up to 400^{0}C is 9.083 and 7.288 wt %, respectively. This is also due to the higher rate of the hydration of alite or the lower rate of belite. These results are in a good agreement with those of the chemical analysis.

Figure (8) shows the infrared spectra of the hydrated samples of cements (A) and (C) cured for up to 90 days in tap water. The band in the region 900-1000 cm^{-1} is due to silicate group (9), while that at 3460 cm^{-1} is attributed to stretching of hydroxyl groups associated with water in calcium-silicate-hydrates (10). The bands at 1430 and 870 cm^{-1} are due to carbonate. The very sharp band detected at ≅ 3646 cm^{-1}(11, 12) represents the free lime. The band appears at 976 cm^{-1} is due to the symmetric bending of bonds O–Si–O and O–Al–O which is in accordance with previous studies (13). It is clear that the bands at 3646 cm^{-1} and 3460 cm^{-1} which represent the hydration of free lime and hydration products respectively show higher intensity in cements (A) than (C). This is attributed to the increase of alite phase which has a higher rate of hydration.

The XRD patterns of the hydrated cement pastes A and C cured for 90 days in tap water are shown in Figure (9). It is clear that, the peak of calcium hydroxide shows higher intensity in Cement A than in cement C. This is attributed to the increase of alite content which produces higher amounts of calcium hydroxide than with belite. The peaks of unhydrated phases as C_3S and β-C_2S of cement (A) are lower than in cement (C). This is also due to the higher rate of hydration of alite. $CaCO_3$ is also detected in the two cements and the CSH is overlapped by the $CaCO_3$.

CONCLUSION

It can be concluded that;

1- Increasing the rate of hardening as well as that of hydration and hence the early strength development is done at the expense of the ultimate strength.

2- Increasing the belite content on the expense of alite gives rise to lower contents of $Ca(OH)_2$ in the hydrated cement which can improves the durability of the cement pastes in aggressive media.

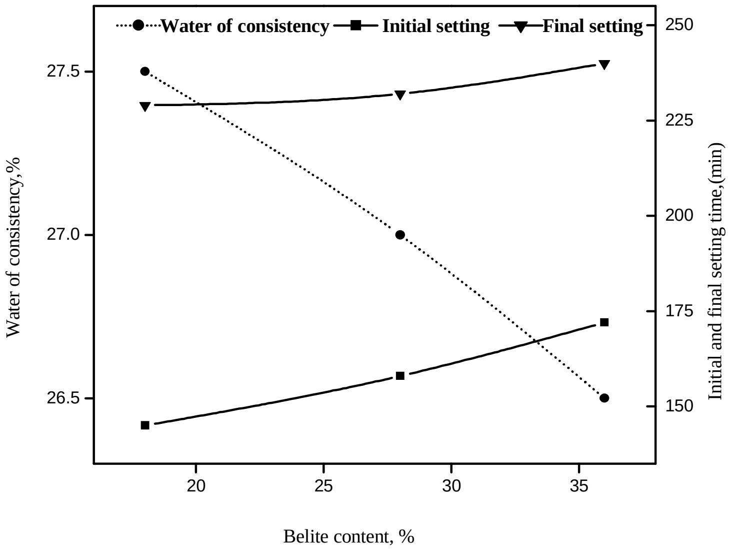

Figure (1): Water of consistency as well as initial and final setting times of SRC pastes

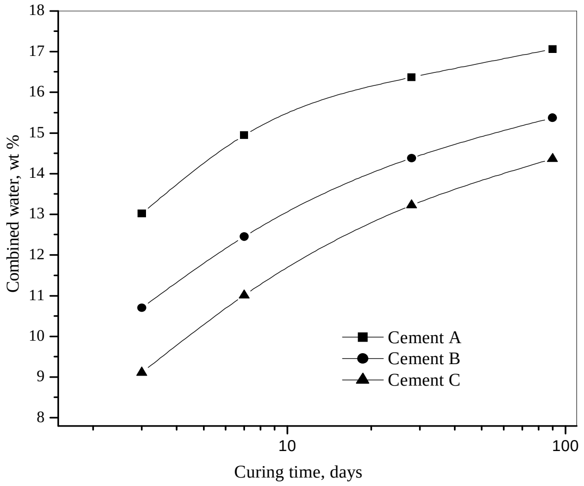

Figure (2): Chemically combined water content of SRC pastes as a function of curing time

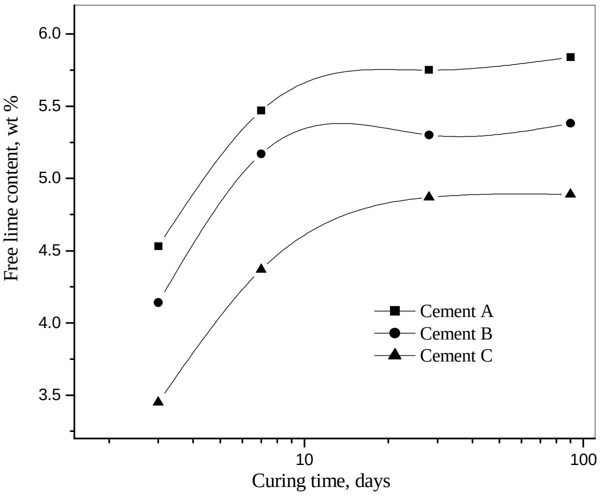

Figure (3): Free lime content of the SRC pastes as a function of curing time

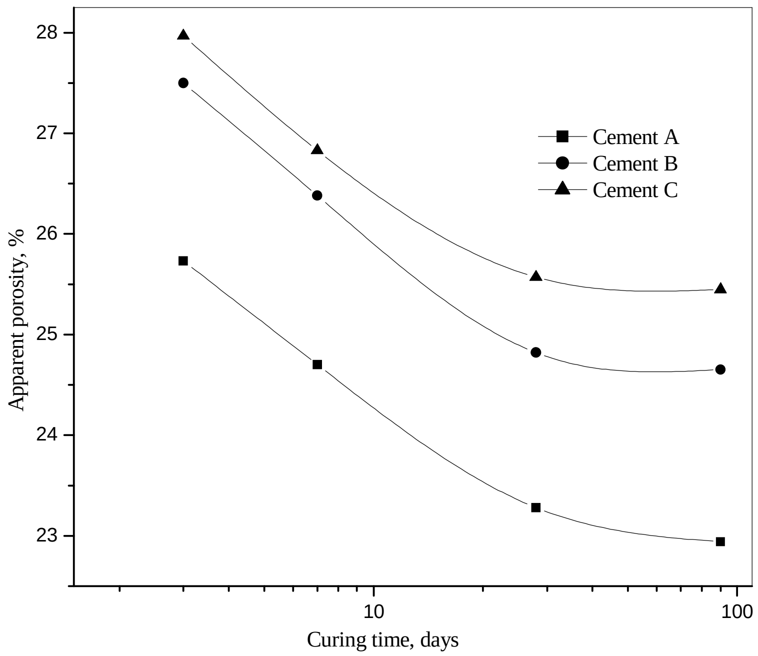

Figure (4): Apparent porosity of the hardened SRC pastes as a function of curing time

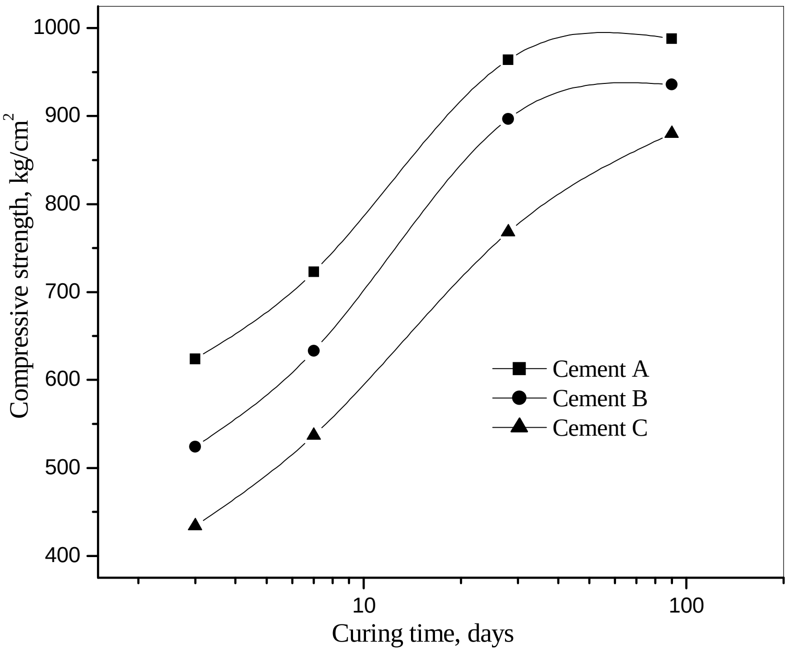

Figure (5): Compressive strength of the hardened SRC pastes as a function of curing time

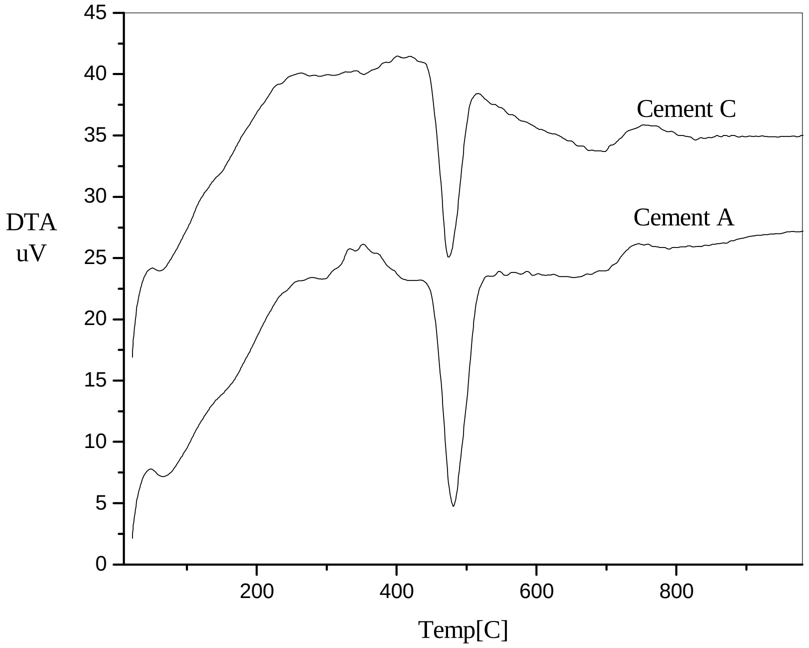

Figure (6): DTA thermograms of cement pastes (A) &(C) cured in tap water up to 90 days

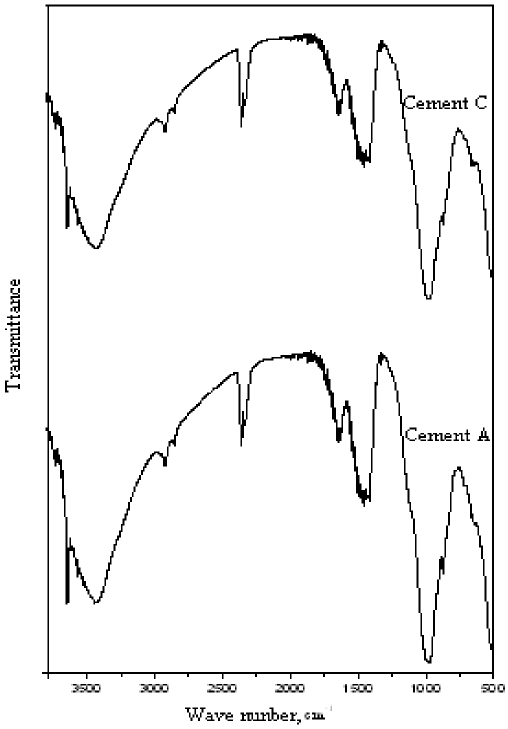

Figure (8): Infrared spectroscopy of hardened cement pastes (A) & (C) cured in tap water up to 90 days

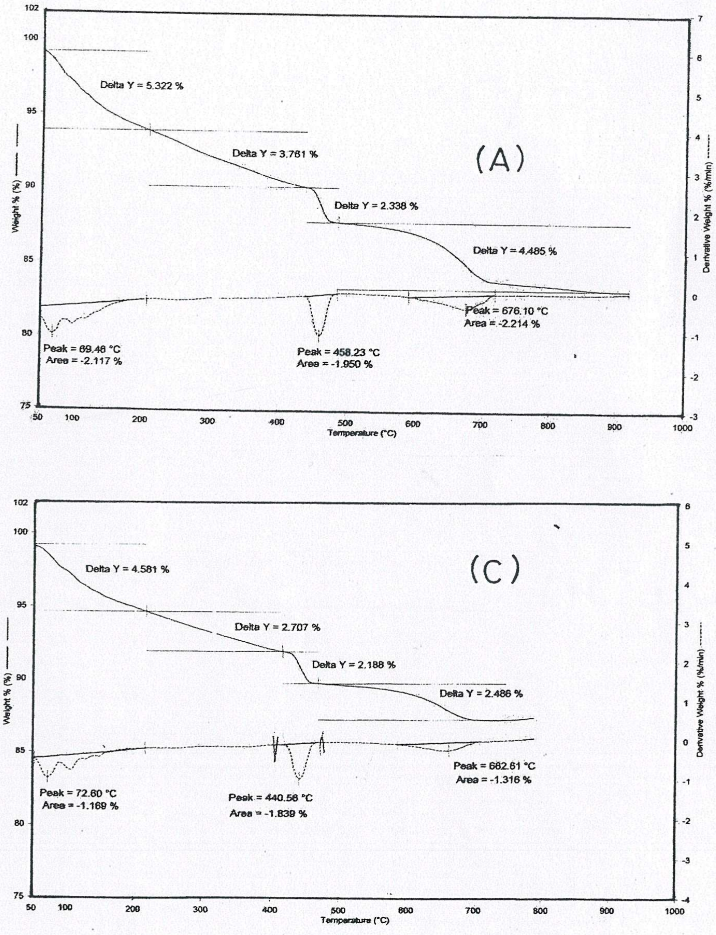

Figure (7) TG patterns of hardened cements (A) and (C) cured in tap water up to 90 days

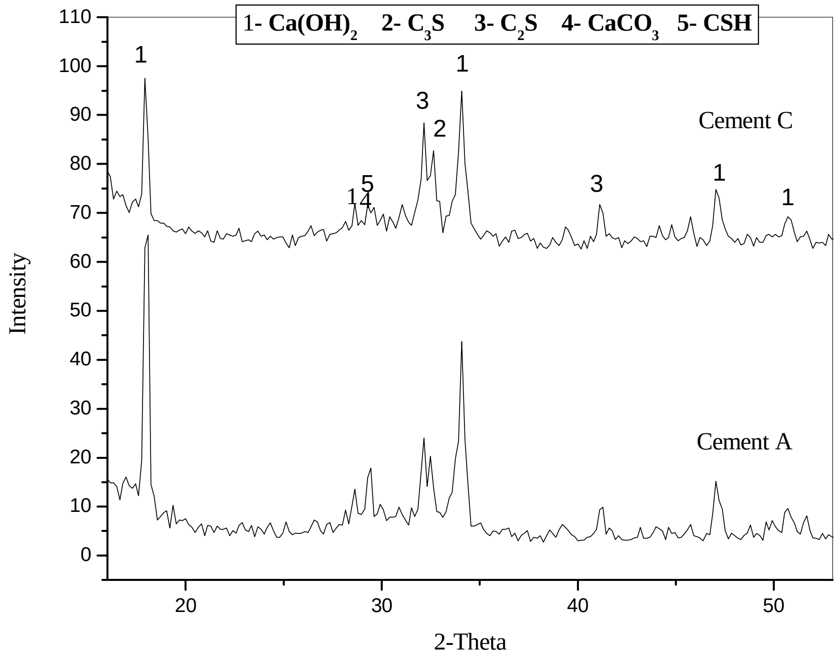

Figure (9): XRD patterns of hardened paste of Cements (A) & (C) cured in tap water up to 90 days

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