

Durability of high –belite sulfate resisting cement pastes in MgSO_4 solution

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ABSTRACT

The influence of 4% MgSO_4 solution on the durability of the sulfate resisting cement (SRC) pastes with different ratios of belite up to 9 months was studied. The relative resistance of hardened cement pastes against the aggressive solution was assessed by determining the compressive strength, free lime, bulk density, apparent porosity, total sulphate and the hydration products with the aid of TGA, XRD, SEM and IR spectroscopy. It was found that the chemically combined water, free lime and total sulphate contents decrease with increasing belite content. The SEM shows that, SRC pastes with higher ratio of belite showed good resistance in aggressive media compared to other cements.

Keywords: Sulfate resistance cement, Belite, Alite, Durability

INTRODUCTION

The Portland cement industry consumes large amounts of energy and produces huge quantities of CO_2 ^[1]. So, the authors made industrial trials for the production of belite cements at lower temperatures and lime saturation factors than for OPC. It was found that, the energy consumed during the production of the belite cement clinkers was less than that of OPC. Compared with the production of OPC less limestone was consumed and less CO_2 evolved. Such low energy cements provide a cheap alternative to Portland cement with properties that are acceptable for many applications and the additional benefit of possible improved durability [1].¹

The belite cement has the advantages in comparison with Portland cement as follows:

- [1]. It requires less water demand for normal consistency, and possesses higher mortar flow ability, more compatible with concrete admixture, and therefore offers better workability to concrete,
- [2]. Its strength increase more rapidly at later ages in spite of its much lower early strength [2]. The strength of high belite cement at 90 and 180 days is higher than those of OPC at the same ages,
- [3]. It has lower heat of hydration and adiabatic temperature rise, less drying shrinkage and better resistance to chemical corrosion and to abrasion, which implies that it offers durability better than OPC.

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The resistant to sulphate attack of Portland cement with similar fineness and different chemical composition was investigated [3]. It was observed that, under the SEM the cement with higher C_3S content gypsum led to form in large veins parallel to the surfaces exposed to solution. However, in the low C_3S cement gypsum was located throughout the sample. Ettringite was found in all cements. The authors concluded that lowering the C_3S and C_3A contents of cement improves its resistant to sulphate attack. Cement with low C_3S (39%) and low C_3A content (4.6%) had the best performance in sulphate environments. It exhibited the lowest strength drop and expansion.

The manufacture of high strength SRC was studied [4]. It was found that the sulphate resistant character of cement is obtained by suitably adjusting the component of minerals in the clinker, lowering the C_3S and C_3A contents, promoting the C_2S content and decreasing the gypsum addition improved physical-chemical properties of the cement.

Mixtuers of SRCs, (with 40 % and 74 % C_3S content) and blended cements containing natural pozzolana or limestone filler were investigated [5]. Expansions, flexural and compressive strength of mortar immersed until 1 year in sodium sulphate solution were measured. The sulphate resistance of Portland cement with high C_3S content is very poor compared with low C_3S cement. Addition of natural pozzolana provides the maximum sulphate resistant while the addition of 20% limestone filler declining sulphate resistant of low C_3A cements. This behavior can be attributed to the reaction between SO_4 and CH in the paste.

The aim of the present work is to study the durability of the prepared sulphate resisting cements having different belite contents in 4 % $MgOS_4$ solution. The kinetics of hydration and mechanical properties of cement paste were determined. The hydration products were also identified by using SEM, XRD, TGA, and IR techniques.

MATERIALS AND METHODS

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

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 $1450^{\circ}C$ for two hours soaking time using B_2O_3 (0.5%) as stabilizer to complete formation of belite phase. The belite phase was 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. The samples were kept in airtight containers. Two cements B & C were prepared by mixing different amounts of belite with SRC. The phase composition of the prepared cements is shown in Table (2).

The mixing of the paste was done as described in a previous work ^[6]. The pastes were moulded in 0.5 inch cubic moulds, cured in humidity chamber at $23 \pm 1^{\circ}C$ for 24 hours, then demoulded and immersed in tap water up to 28 days (zero time). The samples were immersed in 4% magnesium sulfate solution as aggressive medium for 1, 3, 6, and 9 months. Three cubes representing each mix were tested for the compressive strength, free lime ⁽⁷⁾, apparent porosity and total sulfate. The hydration products of immersed sample were identified with the aid of TGA, XRD, SEM and IR spectroscopy.

RESULT AND DISCUSSION

The determined values of chemically combined water of the hardened cement pastes are graphically represented as a function of curing time in Figure (1). The combined water content increases with time and alite content for all cement pastes due to the increase of the hydration products. This is due to the higher activity of alite than belite. MgSO_4 reacts with either C_3AH_6 , $\text{C}_3(\text{AF})\text{H}_6$ and the librated lime from the hydration of alite as wall as belite. The alite phase librates 3 moles of $\text{Ca}(\text{OH})_2$ in comparison to one mole of belite. Therefore, the hydration products increase with the alite content in SRC pastes.

The free lime contents of the cement pastes immersed in 4 % MgSO_4 solution up to 9 months are graphically plotted in Figure (2). The results indicate that the free lime of (Cement A) and (Cement B) decreases with time up to 6 months and then increases due to the reaction of $\text{Ca}(\text{OH})_2$ with MgSO_4 to give gypsum and $\text{Mg}(\text{OH})_2$. The increase of free lime contents after 6 months may be ascribed to the decomposition of calcium silicate hydrate by $\text{Mg}(\text{OH})_2$ giving $\text{Ca}(\text{OH})_2$ and magnesium silicate hydrate. Therefore, the free lime content increases at latter ages. On the other side (Cement C) has lower values of free lime, which decrease up to 9 months. This means that as the belite content increases the librated $\text{Mg}(\text{OH})_2$ can not decompose the formed CSH to give $\text{Ca}(\text{OH})_2$.

The total sulphate contents of the cement pastes immersed in 4 % MgSO_4 solution up to 9 months are given in Figure (3). The total sulphate content increases for all cement pastes up to 9 months. This is mainly due to the migration of the sulphate ions from the aggressive medium (MgSO_4 solution) to the cement pastes which react with C_3A and $\text{Ca}(\text{OH})_2$ forming ettringite and /or calcium monosulphoaluminate hydrate⁽⁸⁾. On the other hand, C_3S -content was considered as an important parameter on sea water resistance of Portland cement. The increase of the alite content implies an increase of the $\text{Ca}(\text{OH})_2$ librated during the hydration of Portland cement which can convert to gypsum leading to surface damage and strength retrogression. The SRC with high belite content (Cement C) shows lower values of sulphate due to the low amount of the librated lime and consequently the total sulphate decreases. It can be concluded that the SRC with high ratio of belite is more durable in sulphate solution than that with high content of alite.

The apparent porosity of SRC pastes cured up to 9 months is plotted in Figure (4). It decreases with curing time due to the precipitation of hydration products in the open pores that leads to decrease the porosity. Also, the apparent porosity of cement pastes increases with belite content at early ages due to its low hydraulic properties in comparison with alite. After 6 months, SRC with high ratio of belite phase (Cement C) shows lower values of apparent porosity due to the decrease of librated $\text{Ca}(\text{OH})_2$ which reacts with MgSO_4 forming gypsum and then ettringite. This indicates that SRC with high ratio of belite is more durable in sulphate medium than this of lower values of belite.

The compressive strength of cement pastes immersed up to 9 months in 4 % MgSO_4 solution is graphically plotted with time in Figure (5). The compressive strength increases up to 6 months then decreases for all cement pastes due to the increase of the amount of hydration products especially CSH which is the main source of the strength. The decrease of compressive strength after 6 months is due to that the magnesium sulphate reacts with calcium aluminate hydrate to give calcium sulphoaluminate hydrates and $\text{Mg}(\text{OH})_2$. It also attacks CSH to form gypsum, $\text{Mg}(\text{OH})_2$ and silica gel. Moreover, the resulting silica gel reacts very slowly with $\text{Mg}(\text{OH})_2$ to form hydrated magnesium silicate of an approximate composition $4\text{MgO} \cdot \text{SiO}_2 \cdot 8.5\text{H}_2\text{O}$ as a late-alteration product^[9]. The consequences of the attack are manifested in the forms of cracking, spelling, softening, mass loss and ultimately mechanical disintegration of the cementatious binder.

The change in compressive strength of the three types of SRC after 9 months is - 17.86 %, - 9.63 %, and + 13.67 for cements A & B and C respectively. This means that the durability of the cement pastes improves with the belite content.

Figure (6, a-b) shows the TG curves of the hydrated pastes of cements (A&C) immersed in 4 % magnesium sulphate solution up to 9 months. The endothermic peak of $\text{Ca}(\text{OH})_2$ in the range 450 °C decreases with belite content. Cements (A & C) give loss of 2.358 wt % and 1.963 wt % respectively. The loss is due to the decomposition of hydration products of the two cements A&C is 9.959 wt % and 8.343 wt %, respectively. This is also due to the higher rate of the hydration of alite in comparison with belite. On the other side (Cement C) has higher values of belite than (Cement A). Therefore the combined water content of (Cement C) is lower than that of (Cement A). This is in good agreement with the results of chemical analysis of free lime and combined water contents.

Figure (7) shows the infrared spectra of the hydrated samples of SRC with different ratios of belite immersed in magnesium sulphate solution up to 9 months. The band at 3468 cm^{-1} is attributed to stretching of hydroxyl groups associated with water in CSH and ettringite^[10]. In (Cement A) the bands at 3468 cm^{-1} and 978 cm^{-1} show higher intensity than (Cement C). This is attributed to the increase of alite phase which produces large amount of hydration products especially CSH during the hydration. The bands of calcium hydroxide and gypsum at 3646 cm^{-1} and 662 cm^{-1} respectively are strong in (Cement A) than (Cement C). This is attributed to the increase of alite content which liberates more calcium hydroxide. Band at 1119 cm^{-1} indicating the formation of ettringite^[10,11]. This band is clearly appeared in (Cement A) than (Cement C).

Figure (8) shows the XRD patterns of low belite content (Cement A) and high belite content (Cement C) cured in 4% magnesium sulphate solution up to 9 months. It is clear that, the intensity of $\text{Ca}(\text{OH})_2$ peak of (Cement C) is lower than of (Cement A). This is attributed to the decrease of free lime with belite content. The intensity of $\text{Mg}(\text{OH})_2$ peak (brucite) is also lower in (Cement C) than (Cement A) due to the decrease of calcium hydroxide liberated during the hydration of belite. $\text{Ca}(\text{OH})_2$ reacts with MgSO_4 giving gypsum and magnesium hydroxide. (Cement C) has high intensity of C_2S peak than (Cement A). High intensity of CaCO_3 peak appears in (Cement A) due to the carbonation.

SEM photographs of cement pastes A & C after 9 months exposed to magnesium sulphate solution are given in Figures (9, a-b-c), and (10, a-b-c). The figure illustrates that (Cement A) shows large amount of ettringite. There is no ettringite detected in (Cement C) this is due to the decrease of alite content which liberates much more calcium hydroxide that reacts with sulphate ions forming calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which reacts with calcium aluminate hydrate to form additional ettringite. From the figures it is clear that (Cement A) has large amount of ettringite and high porosity than (Cement C). This is in a good agreement with the bulk density and apparent porosity values.

CONCLUSION

Following conclusions may be reached on the basis of the above findings:

- 1- The deterioration of low C_3A sulfate resisting cement by sulfate attack is possible and the C_3S content plays a decisive role in the potential damage of these cements.
- 2- The great deterioration was observed for C_3S -content cement and the expansive formation of ettringite in this case was attributable to localized gypsum formation.
- 3- The sulfate resisting cement high in C_3S was attacked more severe than other with low one.
- 4- In SRC with low C_3S content, significantly less gypsum was found at the end of the test.

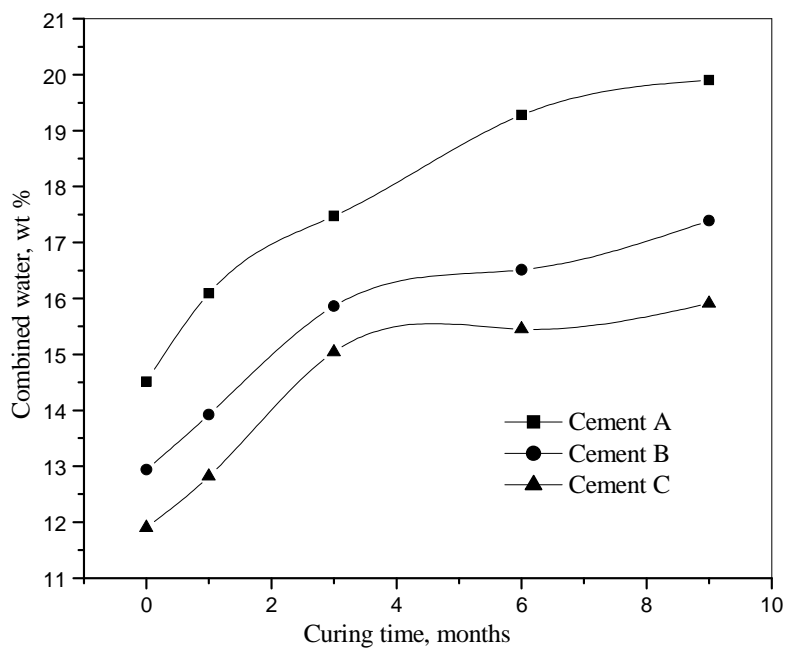


Figure (1): Chemically combined water content of SRC pastes immersed in magnesium sulphate solution up to 9 months

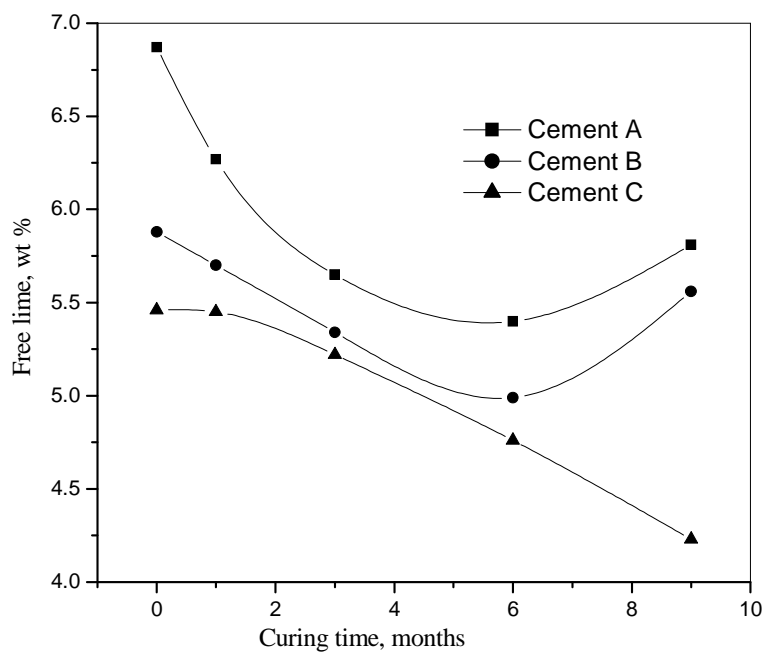


Figure (2): Free lime content of SRC pastes immersed in 4 % magnesium sulphate solution up to 9 months

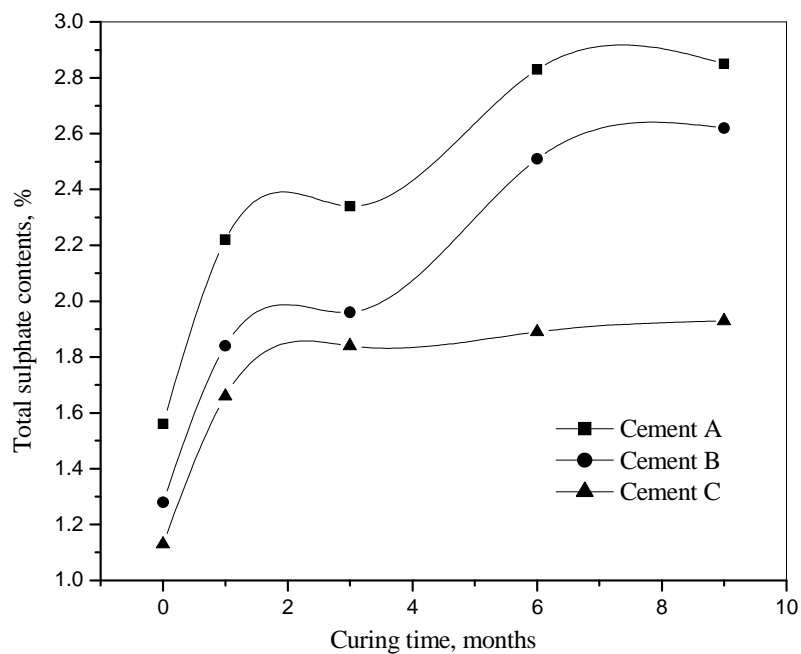


Figure (3): Total sulphate content of SRC pastes immersed in 4 % magnesium sulphate solution up to 9 months

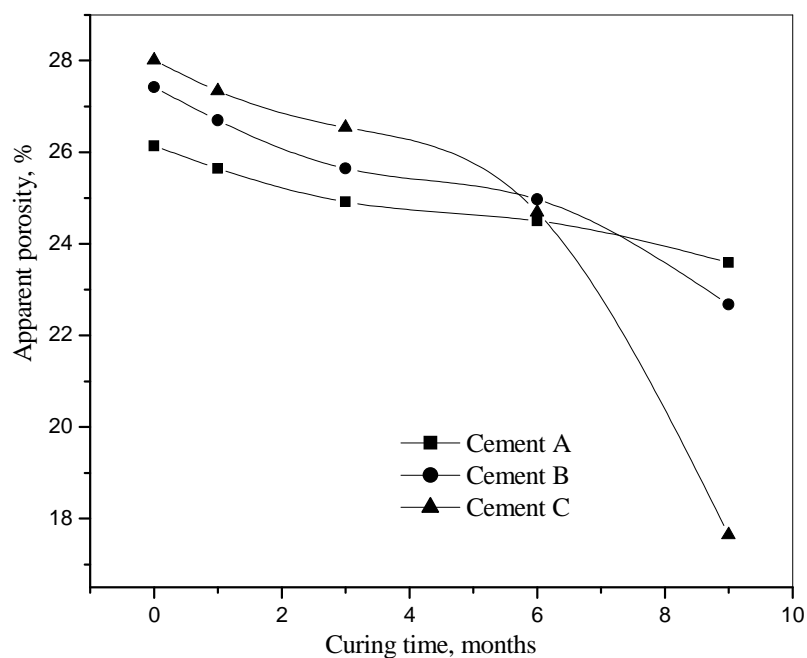


Figure (4): Apparent porosity of hardened SRC pastes immersed in 4 % magnesium sulphate solution up to 9 months

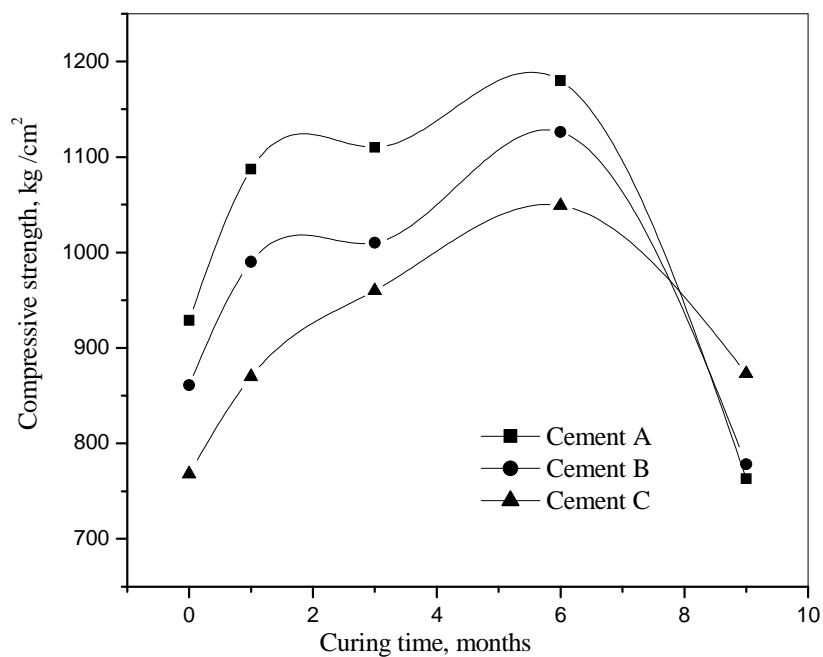


Figure (5): Compressive strength of hardened SRC pastes immersed in 4 % magnesium sulphate solution up to 9 months

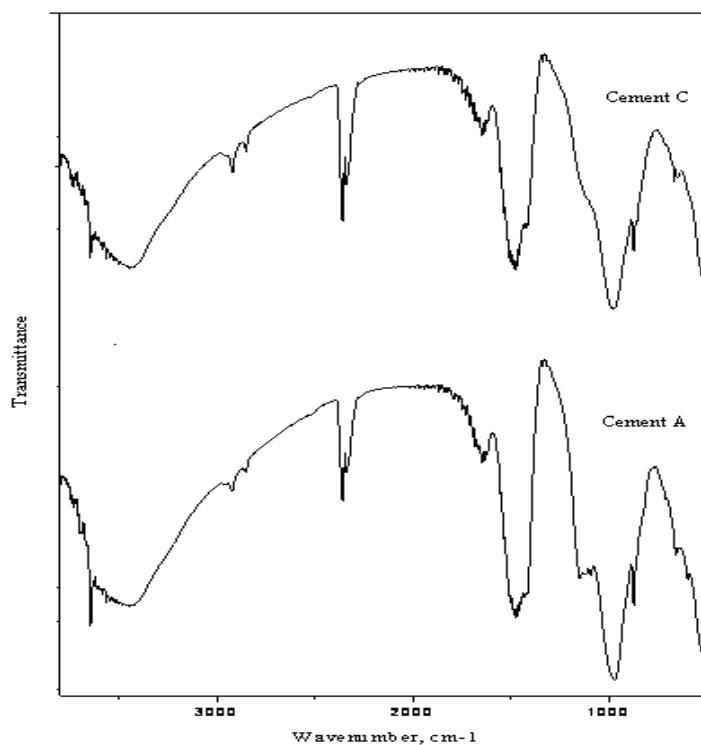


Figure (7): Infrared spectra of the hydrated sample of cements (A & C) immersed in 4 % magnesium sulphate solution up to 9 months

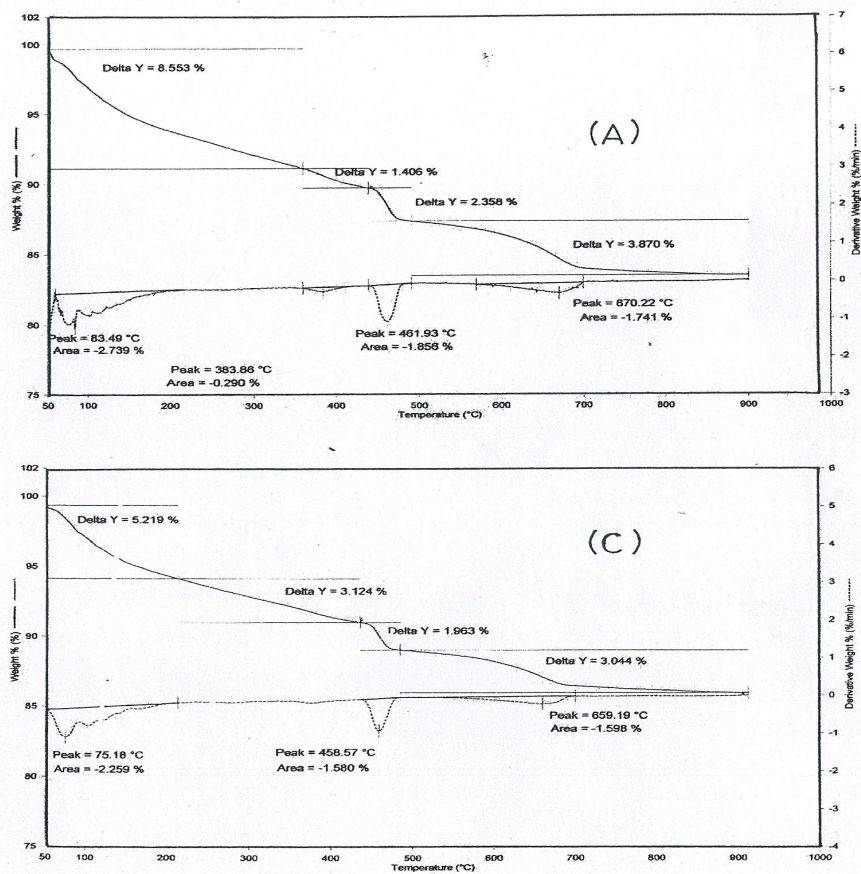


Figure (6) : TG patterns of hardened cement pastes (A) and (C) immersed in 4% magnesium sulphate solution up to 9 months

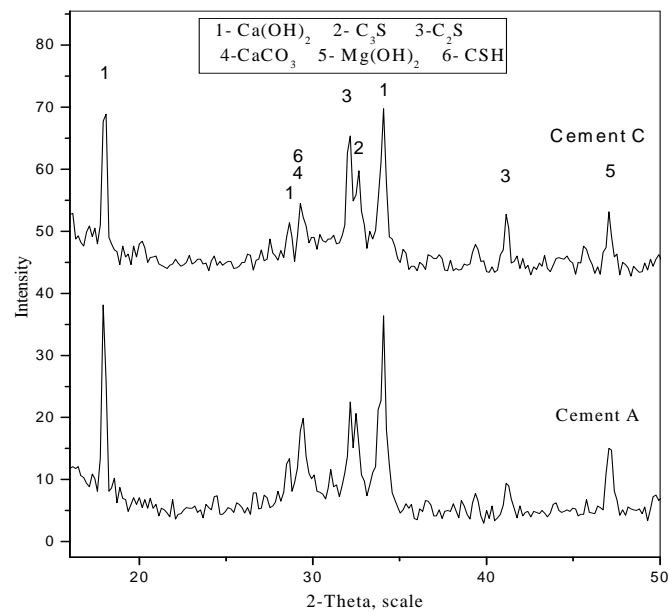
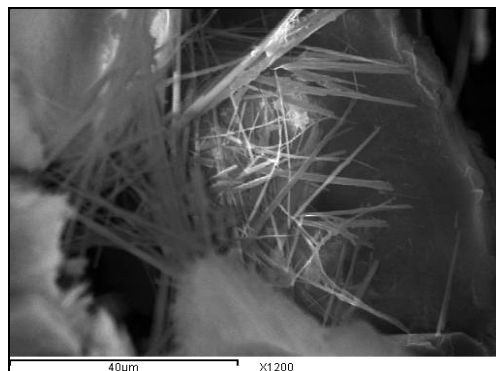
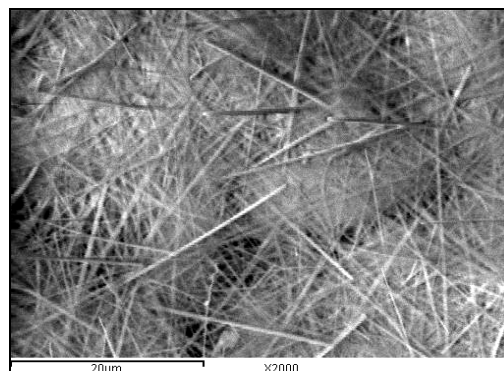


Figure (8): XRD patterns of hardened cement pastes (A & C) immersed in 4% magnesium sulphate solution up to 9 months

(a)



(b)



(c)

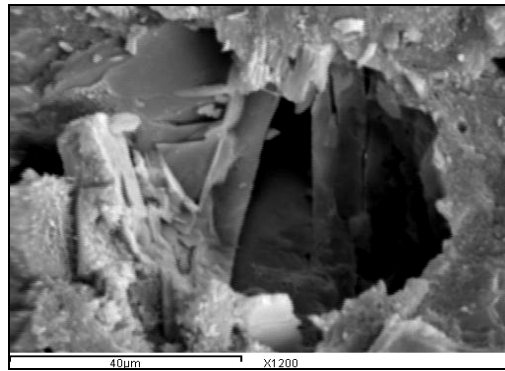
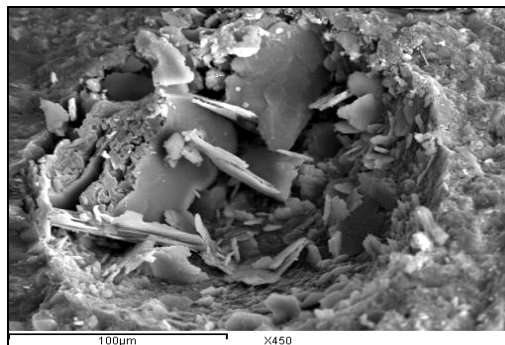
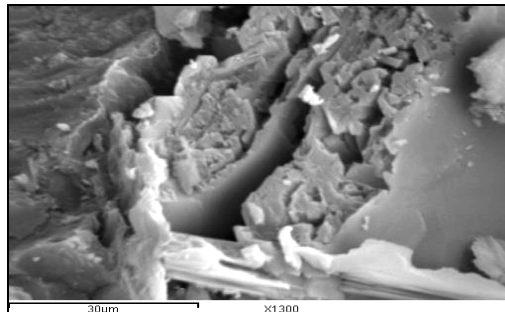


Figure (9, a- b- c): SEM photographs of cement paste (A) immersed in 4 % magnesium sulphate solution up to 9 months

(a)



(b)



(c)

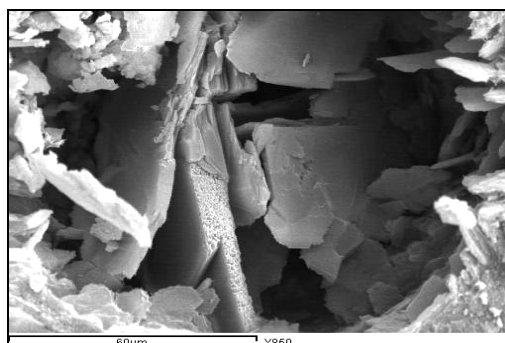


Figure (10, a-b-c): SEM photographs of cement paste (C) immersed in 4 % magnesium sulphate solution up to 9 months

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