Durability Performance of Blended Cements Incorporating Egyptian SRC and GBFS in Aggressive Water

H. El-Didamony, S. Abd El-Aleem Mohamed, H. Gouda

Abstract: The durability of concrete has been a major concern of civil engineering professionals over the last few decades. Durability is the capacity of concrete to resist deterioration caused by aggressive environments. An experimental investigation was carried out to evaluate the durability properties of blended cements prepared from substitution of SRC with different percentages of GGBFS up to 75 mass, %. The ingredients of each dry mix were homogenized, and then hydrated with the water of standard consistency. The specimens were cured under tap water for 28 days (zero time), then immersed in marine environment up to 12 months. The hydration products were analyzed using DTA, IR and XRD techniques. The durability properties were determined by measuring: free lime, combined water, bulk density, compressive strength, total sulfate and total chloride contents for each mix at different immersing ages. The results revealed that, GGBFS decreases the accessibility of SO_4^{2-} and Cl^- to penetrate into the pore system. Hence the total sulfate and total chloride contents decrease. Therefore, the durability performance of SRC is greatly enhanced by the use of high GGBFS contents. The composite cements containing 45-55 mass, % of GGBFS are comparable to or outperform SRC up to one year of immersion in aggressive water.

Keywords: Blended Cements; GGBFS; SRC; Durability; Bulk density and Compressive strength

I. INTRODUCTION

Concrete is the most widely used construction material today. It is termed durable or high performance concrete (HPC) when it keeps its form and shape within the allowable limits in different environmental conditions. The applications of HPC in power, gas, oil and nuclear industries are increasing with the time, due to its superior structural performance, environmental friendliness and low impact on energy utilization [1], [2]. The durability of concrete has been a major concern of civil engineering professionals. In addition, it has been of considerable scientific and technological interest over the last few decades. The durability normally refers to the duration or life span of the concrete and is directly affected by concrete performance in aggressive environments [3], [4]. Chemical attack due to aggressive water is one of the many factors that cause damage to concrete. The effect of seawater on concrete deserves special attention, because sea structures are exposed to the simultaneous action of destructive ions.

The penetration of aggressive ions into concrete primarily governs the physical and chemical deterioration processes [5]. Calcium, sodium, magnesium and ammonium salts constitute hazards to concrete as they react with hydrated cement paste leading to expansion, spalling, cracking and loss of strength. The most aggressive anions that affect the long-term durability of concrete structures are the chlorides and sulfates. Sulfate attack is generally attributed to the formation of expansive ettringite and gypsum [6], which is known to precipitate by a through-solution mechanism. The $CaCl_2$, which is formed from the reaction of $MgCl_2$ with the liberated Portlandite (CH) increases the solubility of $Ca(OH)_2$, which permits leaching of lime and thus increases the porosity of concrete, and leads to loss of strength. $Mg(OH)_2$ dissociates calcium silicate hydrate (C–S–H) producing $Ca(OH)_2$ and silica gel. The latter may react with $Mg(OH)_2$ to form magnesium silicate hydrates. The C–S–H in hydrated cement is also decomposed by $MgSO_4$ in aggressive solutions to give gypsum, hydrated silica and magnesium silicate hydrates (Mg–S–H), but this, unlike silica gel, has little or no binding properties. All the above mentioned reactions are accompanied by a decrease in strength and durability properties [7-9]. For producing HPC, it is well recognized that, the use of supplementary cementitious materials (SCM), such as silica fume (SF), metakaolin (MK) granulated blast-furnace slag (GBFS) and fly ash (FA), are necessary. SCMs are actually cheaper and more ''sustainable'' than cement [10, 11]. When they are used as a partial replacement of cement, suited replacement levels can improve the economic, physico-chemical, mechanical, durability and sustainability properties of concrete [12-14]. The chemical resistance of blended cements results mainly from the pozzolanic reaction leading to the consumption of free CH and formation of additional amounts of calcium silicate and aluminosilicate hydrates. These products fill up some of open pores forming more homogeneous and compact microstructure. Therefore, the blended cement pastes show good resistivity for sulphate and chloride attack. GBFS is a green construction material and one of the most widely used pozzlanic materials in concrete, for its unique property of improving the rheology of fresh concrete, and its ultimate mechanical and durability properties [15-17]. GBFS-blended concrete is more environmentally friendly concrete compared to OPC concrete. High replacement level of PC with slag leads to the development of concrete, which not only utilizes the industrial wastes but also saves significant natural resources and energy [18, 19],

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because the manufacture of one tonne of OPC would require approximately 1.5 tonnes of mineral extractions together with 5000 MJ of energy, and would generate 0.95 tonne of CO_2 equivalent. But, the production of one tonne of GGBFS would generate only about 0.07 tons of CO_2 equivalents and consume only about 1300 MJ of energy [20]. BFS is a by-product of iron manufacturing industry. Iron ore, coke and limestone are fed into the furnace, and the resulting molten slag floats above the molten iron at a temperature of about 1500 to 1600^oC. The molten slag has a composition of 30% to 40% SiO_2 and approximately 40% CaO, which is close to the chemical composition of Portland cement. After the molten iron is tapped off, the remaining molten slag, which mainly consists of siliceous and aluminous residues, is then rapidly water-quenched, resulting in the formation of a glassy granulate. This granulate is dried and ground to the required size which is known as ground granulated blast furnace slag (GGBFS) [21, 22]. GBFS is widely used around the world as SCM, due to its vitreous structure. It shows both cementitious behavior and pozzolanic characteristics in presence of the proper activator [23, 24]. Owing to difficulties in cooling the BFS very quickly, its cementitious minerals, such as C_3S and C_2S, are relatively inert to react with water compared with those of cement clinker, which leads to relatively low early strengths of blended cements containing steel slag. Therefore, GBFS has rarely been used for reinforced concrete buildings [25, 26]. The hydraulic reactivity of slag as a cementitious material is influenced by (i) its chemical composition [27], (ii) its particle fineness, (iii) its glass content, (iv) the alkali concentration "pH" of the reacting system, and (v) the temperature during the early hydration ages [28, 29]. Compounds that increase its hydraulic activity include: CaO, MgO and Al_2O_3 while SiO_2 reduces its hydraulicity [30]. These compounds (CaO, MgO, Al_2O_3 and SiO_2) are used to assess the suitability of a slag as a partial cement replacing material in concrete [31]. Ultrafine GGBFS (UFGGBFS) has increased surface area, which increases the apparent rate of hydration, pozzolanic reaction and has a better filling effect. Concrete with UFGGBS has a higher early strength, lower permeability and improved durability even at 3 days of curing [32]. Partial replacement of PC with UFGGBS has been shown to lead to significant reduction in chloride ion penetrability by densification of concrete microstructure [33]. In GBFS hydration, it reacts not only with free Portlandite but also with water to form hydrated calcium aluminates and C–S–H [34]. The latter product, additional to that formed by PC hydration, contributes to refinement of pores and blocking of chloride diffusing paths [35]. Therefore, the partial replacement of PC with GGBS can significantly reduce the risk of sulfate attack, alkali–silica reactions and chloride penetration [36]. An optimum slag replacement level to maximize concrete resistance to chloride penetration has so far not been established. The commonly used replacement level of 50 mass, % is based solely on compressive strength considerations[37], and some studies have reported increased chloride resistance as the slag replacement level increases from 40-65 mass, % of total cementitious material[38].The presence of slag in concrete also influences the chemical chloride binding capacity of the hardened cement paste[39]. This affects chloride transport in concrete through (i) partial blocking of pores in concrete, which results from the formation of calcium chloro-aluminates (Friedel's salt), or (ii) demobilization of chloride ions, or (iii) both [40]. The main compounds in cement which take part in chloride binding are tricalcium-aluminate (C_3A) and tetracalcium-aluminoferrite (C_4AF) [41]. In seawater, well-cured concretes containing large amounts of GGBFS usually outperform reference concrete containing only PC, because the former contains less free lime. Aggressive sulfate attack is one of the reasonable factors for deterioration and damage of concrete [42]. The compressive strength of slag rich cements at different curing times (3, 180, and 360 days) in seawater were measured and compared to their strengths at 6 months. Strength loss and expansion of those cements are mainly due to the lime leaching and the ettringite formation [43]. Gutierrez et al. [44] measured the compressive strength, water adsorption and chloride permeability of blended cements containing 60-80 mass, % GGBFS. The results showed that, the addition of slag increased the compressive strength and reduced the diffusion rate of chloride ions. Yilidrim et al. [45] studied the effect of cement type on the resistance of concrete against chloride penetration for given compressive strength classes. These cements including two different slag cements containing 37 and 65 mass, % of slag. SRC and OPC were used as references. In addition to these cements, the OPC blended with FA was also included in the study. It was concluded that, the slag cements have the highest resistance against chloride penetration, while SRC and OPC have the lowest resistance. This work aims to study the performance of composite cements containing Egyptian SRC and GBFS in aggressive water. Different blended cements were prepared from partial substitution of SRC with equal amounts of GBFS up to 75 mass, %. The extent of durability was investigated by chemical determination of combined water, free lime, total chloride and total sulfate contents. The physico-mechanical characteristics were studied by measuring of bulk density and compressive strength at different immersing ages (1, 3, 6, 9 and 12 months). Also, the effect of this aggressive medium was investigated by the aid of DTA, IR, and XRD techniques.

II. MATERIALS AND EXPERIMENTAL TECHNIQUES

II (A). Materials

The starting materials used in this study were sulfate resisting cement (SRC) provided from Alexandria Cement Company and granulated blast furnace slag (GBFS) supplied from Iron and Steel Company, Helwan, Egypt. In addition, Caron's lake water, Fayoum, Egypt, was used as aggressive medium. The GBFS was finely ground in a laboratory steel ball mill having a capacity of five kilogram. The Blaine surface area of SRC and GGBFS were 3000±50 and 4000±50 cm2/g, respectively.

II (B). Experimental Techniques

The materials used were dried in an electric drier at 110^oC for 24 h to remove the moisture.

The chemical oxide analyses in mass, % of SRC and GBFS are listed in Table 1. In addition, the chemical analysis of Caron's lake water is shown in Fig.1. The pH of this water is 6.50 and its main salts are NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$ and $CaCl_2$. The amorphous structure of GBFS was confirmed by means of XRD technique as in Fig.2. It shows a hump between 30 and 40° indicating the presence of amorphous glassy phases. The mix compositions were prepared as show in Table 2. The ingredients of each mix were blended in a porcelain ball mill for 1h, using a mechanical roller mill to attain complete homogeneity. The hydration process was conducted on pastes using the required water of standard consistency (W/C, %). Both of W/C, % and setting times for each mix were determined according to ASTM specifications [46]. The mortars were prepared by mixing 1 part of cement and 2.75 parts of standard sand proportion by weighing with water content sufficient to obtain a flow of 110 ± 5 with 25 drops of the flowing table [47, 48]. The freshly prepared mortars were moulded into 50×50×50 mm cubic moulds. The specimens were cured for 24 h in 100% RH. at 23 ± 2^oC, then demoulded and cured under tap water for 28 days (zero time), and then immersed in Caron's lake water for the time of testing (1, 3, 6, 9 and 12 months) [7, 8]. The hydration of cement pastes were stopped by pulverizing 10 g of representative sample in a beaker containing 1:1 methanol-acetone, then mechanically stirred for 1h. The mixture was filtered through a gouch crucible, G4 and washed several times with the stopping solution and diethyl ether. The solid was dried at 700C for 1h, then collected in polyethylene bags; sealed and stored in desiccators for analysis [49, 50]. The aggressive attack was determined through the measurements of combined water, free lime, bulk density, compressive strength, total sulphate and total chloride at each time of testing. The chemically combined water content (Wn, %) of each mix was determined as the percent of ignition loss of the dried samples (on the ignited weight basis). The combined water contents were corrected for the water of free portlandite present in each sample [51, 52]. Free lime content (FL, %) was determined by an ammonium acetate method [53]. The bulk density was carried out before the specimens subjected to the compressive strength determination. Samples were weighed suspended in water and in air (saturated surface dry). Each measurement was conducted on at least three similar cubes of the same mix composition and curing time. The density was calculated using the following formulas [54]:

$$\text{Bulk density (dp)} = \frac{saturated \ \text{weight}}{\text{volume of sample}} \ \text{g/cm}^3$$

$$\text{Volume of sample} = \frac{saturated \ \text{weight - suspended weight}}{\text{density of liquid (water)}}$$

$$dp = \frac{saturated \ \text{weight}}{saturated \ \text{weight - suspended weight}} \times 1$$

For compressive strength determination according to ASTM specification [55], a set of three cubes was tested on a compressive strength machine of SEIDNER, Riedinger, Germany, with maximum capacity of 2000 KN force. The total sulphate content was gravimetrically estimated by using 1 g of powdered sample dissolved in 100 ml of distilled water with 5 m1 of concentrated HCl, then boiled for 5 min., filtered and washed several times with distilled water. 10 m1 of 10% $BaCl_2$ was added to the filtrate, which was digested, filtered and ignited for 30 minutes. The total sulfate content was calculated [7, 8]. The total chloride content was determined by weighing 2 g sample into a stopper conical flask. The specimen was dispersed with 25 ml water and then added 10 ml of nitric acid (sp. gr. 1.42). Fifty milliliters of hot water was added, heated to near boiling and kept warm for 10 to 15 min. If the supernatant liquid is turbid, it was filtered through a rapid paper (41 filter paper) and washed with hot water and then cooled to room temperature. An excess of standard 0.1 N $AgNO_3$ (16.98 g pure dry $AgNO_3$, in liter) was added, and 2–3 ml of nitrobenzene to stopple the flask, and was shaken vigorously to coagulate the precipitate, then 1 ml ammoumium ferric alum as indicator and titrate against standard 0.1 N ammonium thiocyanate [7, 8]. The powder method of XRD was adopted in the present study. For this, a Philips diffractometer PW 1730 with X-ray source of Cu kα radiation (λ=1.5418Å) was used. The scan step size was 2θ. The collection time 1s, and in the range of 2θ from 5 to 55°. The X-ray tube voltage and current were fixed at 40.0 KV and 40.0 mA respectively. An on-line search of a standard database (JCPDS database) for X-ray powder diffraction pattern enables phase identification for a large variety of crystalline phases in a sample [56]. The DTA was carried out in air using a DT-30 Thermal Analyzer Shimadzu Co., koyoto, Japan. Calcined alumina was used as inert material, about 50 mg (76μm) of each. The finely ground hydrated cement paste were housed in a small platinum-rhodium crucible. A uniform heating rate was adopted in all of the experiments at 20^oC/min [57]. For IR spectroscopic investigation, the samples were prepared using alkali halide KBr disks using Gensis FT-IR spectrometer in the range 400-4000 cm^{-1} after 256 scans at 2cm^{-1} resolution [58].

III. RESULTS AND DISCUSSION

III (A). The required water of standard consistency and setting times

The water of consistency (W/C, %) as well as initial and final setting times of the investigated cement pastes are plotted in Fig. 3. It is clear that, the substitution of 45 mass% of SRC with GBFS is accompanied by a sharp decrease of W/C, %. As the slag content increases up to 75 mass, % the water of consistency is slightly decreased. Also, setting times are elongated with slag content. This is attributed to the lower hydraulic properties of slag in comparison with SRC as a result of acidic oxide film formation on the outer most layer of slag [8], which renders the water penetration and the hydration progress.

III (B). Chemically combined water contents

The combined water contents (Wn %) of the hydrated SRC and blended slag cement mixes immersed in seawater up to one year are graphically represented as a function of immersing time in Fig. 4.

It is clear that, Wn,% increases with curing time for all hydrated cements [59], due to the continuous hydration of the main cement clinker phases as well as the slag portion, especially in the presence of $MgSO_4$, $MgCl_2$ and $NaCl$ that accelerate the hydration of cement phases leading to the formation of more hydrated products with high water contents. The liberated $Ca(OH)_2$ from the hydration of cement phases (C_3S and $\beta-C_2S$) can react with granulated slag to form additional hydration products. On the other side, Wn% decreases with slag content, due to its lower hydraulic properties in comparison with SRC. Generally, the presence of SO_4^{2-} and Cl^- enhances the hydration of cement phases. In addition, the blended slag cement mixes give hydrated products with low C/S and C/H ratios. Therefore, Wn% of blended slag cements is lower than that of pure SRC [60].

III (C). The free Portlandite contents and pH values

The free lime contents (FL, %) of SRC and blended slag cements immersed in sea- water up to one year are shown as a function of immersing time in Fig. 5. In case of the hydrated SRC mixes, FL, % decreases up to 3 months, then increases up to one year. This due to the reaction of $MgSO_4$ with $Ca(OH)_2$ to form $Mg(OH)_2$, which dissociates CSH to form magnesium silicate hydrate (MSH) and Portlandite [61]. The SRC mixes give higher free lime contents than those of blended slag cements, due to the higher percentages of C3S and $\beta-C_2S$ in SRC mixes comparing to the slag rich cement mixes. Those silicate phases are the main sources of free lime during the hydration of cement clinker. The FL, % of each blended slag cement decreases with immersing time up to 12 months in seawater. Also, as the GBFS mass % increases, the liberated Portlandite decreases. This is attributed to the following reasons: i) The pozzolanic reaction of slag with free lime to form additional amounts of calcium aluminate hydrate (CAH), calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (CASH), ii) The reaction of the liberated Portlandite with $MgSO_4$ and NaCl to form gypsum and $CaCl_2$, that produce sulphoaluminate as well as chloroaluminate hydrates and brucite, $Mg(OH)_2$. Also, $MgCl_2$ consumes another part of $Ca(OH)_2$ to form $Mg(OH)_2$.

III (D). Bulk density

The variation of bulk density (dp) of the hydrated SRC and blended slag cements with immersing time in seawater up to one year are graphically plotted in Fig. 6. In case of SRC, the bulk density increases up to 3 months, then decreases gradually with immersing time up to one year. The increase of dp at early ages of immersion is mainly due to the activation of SRC with the dissolved chlorides as well as sulfates forming calcium silicate, sulfoaluminate and chloroaluminate hydrates. These hydrates are precipitated in the open pores to give homogeneous and dense structure. But, at later ages, the continuous formation of excess hydrated sulfoaluminates [62] and chloroaluminate [15] leads to expansion and softening of the hydrated cement mortars. Therefore, the bulk density tends to decrease. On contrast, the bulk density of blended slag cements increases up to one year of immersion. With immersing time, the hydration of cement clinker in addition to the activation of slag portion increase, leading to formation of excessive

amounts of hydrated products. Those hydrates precipitate within the water filled pores to increase the bulk density. Also, the value of dp decreases with GGBFS mass, % in the blended cement, because the pozzolanic materials give hydrated products (CSH, CAH and CASH) with low C/S and C/H ratios.

III (E). Compressive strength

The compressive strength of the hardened SRC and blended slag cement mortars are plotted as a function of immersing time in Fig. 7. The results show that, the compressive strength of SRC mortars increases up to 6 months, then decreases up to 12 months. The increase of strength up to 6 months is due to the continuous activation of SRC by Cl^- and SO_4^{2-}, forming more CSH, CASH and hydrated sulfoaluminates. Whereas, the decrease of compressive strength of SRC after 6 months is mainly due to the presence of high C_3S and $\beta-C_2S$ contents, which liberate $Ca(OH)_2$, leading to the formation of ettringite and monosulfate [8] as well as Friedel's salt [15]. These phases expand or soften the cement mortars. By comparing the blended slag cements with SRC, it is found that, the compressive strength of slag containing cements increases linearly with immersing time up to 12 months. This due to the pozzolanic reaction of slag portion with the liberated lime, resulting in the formation of secondary CSH, which can coat the aluminate and other reactive phases, and then hindering the formation of secondary and lastly ettringite. Therefore, the slag rich cements outperform and more durable than SRC in aggressive water. It can be concluded that, the substitution of 45 to 55 mass, % of SRC with GGBFS gives a good durability than SRC in seawater. Also, as the slag content increases, the corresponding strength increases but with lower values.

III (F). Total sulfate

The total sulfate contents of the investigated cements are graphically represented as a function of immersing time up to one year in Fig. 8. The total sulfate contents for all cement mixes sharply increase up to one month, then slightly up to one year. This is attributed to the migration of sulfate ions (SO_4^{2-}) from the aggressive medium to the cement mixes. The SO_4^{2-} reacts fastly with C_3A and $Ca(OH)_2$, forming hydrated calcium sulfoaluminates as ettringite and/or monosulfate. In addition, $MgSO_4$ reacts with calcium silicate hydrate to produce gypsum, silica gel and brucite. It can be seen that, the blended cements containing higher GGBFS, % show lower total sulfate values and more resistant to sulfate attack than pure SRC. This is mainly due to their relative lower contents of clinker phases and $Ca(OH)_2$ in comparison with SRC.

III (G). Total chloride

The variation of total chloride values of the hydrated SRC and blended slag cements with immersing time is shown in Fig. 9. The total chloride contents for all investigated cements increase gradually with time. It seems due to the chemical reaction between chloride ions and the hydrated products such as C_3AH_6 or C_4AFH_6 and $Ca(OH)_2$,

which lead to increase the chloroaluminate hydrates [15]. On the other side, the total chloride contents decrease with slag, %. This due to the decrease of cement clinker and $Ca(OH)_2$ contents with the increase of slag portion in cement blends. The results in hand reveal that, the blended cements containing higher GGBFS, % are more durable and give higher mechanical properties than SRC.

III (H). IR Spectroscopy

The infrared spectral analysis had been carried out on selected hydrated cement mixes. The IR spectra of some hydrated cement mixes immersed in seawater for 3 and 6 months are shown in Figs.10 and 11. It is clear that, the absorption band at 3448 cm^{-1} is related to the symmetrical stretching vibration of -OH bond in hydration H_2O [63]. The intensity of that band increases with curing time from 3 to 6 months. It seems due to the formation of additional amounts of hydrated products. The very sharp band at about 1162 cm^{-1} refers to the hydration of slag .Its intensity increases with immersing time, due to the formation of C-S-H [64]. The formed band at 985 cm^{-1} represents the formation of monosulfate phase, which results during the reaction of SO_4^{2-} with cement clinker phases, especially C_3A and C_4AF. However, the fundamental position of that peak was changed, due to the formation of ettringite at later age of hydration and the ettringite band appears at 961cm^{-1}. The appeared band at about 3622 cm^{-1} refers to free $Ca(OH)_2$ [65], which decreases with slag content and immersing time, due to its consumption during pozzolanic reaction with slag portion to form C-S-H . The observed band at 1446 cm^{-1} is the spectral band of Ca-O. Furthermore, this band is shifted to low frequency with time, due to the formation of ettringite and dissolution of free lime during the hydration process.

III (I). Differential thermal analysis (DTA)

The DTA thermograms of SRC and slag rich cements with 45, 55 and 75 wt, % slag immersed in seawater for 6 months are shown in Fig. 12. It is clear that, as the slag content increases, the Portlandite decreases. On the other side, SRC mixes show a relatively higher Portlandite endotherm. It seems due to the increase of $Ca(OH)_2$ content in SRC mixes in comparison with the blended cement mixes containing 45, 55 and 75 mass,% of slag. The endothermic peak located around 116°C increases at 45 mass, % GGBFS, due to the increase of the formed CSH. As the slag content increases, the endotherm is shifted to lower temperature. This is attributed the effect of Cl^- or SO_4^{2-} on the durability of CSH. The broad peak at 150°C refers to the decomposition of ettringite as well as chloroaluminate hydrate. The reaction of C_3A or C_4AF with $CaCl_2$ results in the formation of high and low forms of chloroaluminate hydrates. Under normal conditions of hydration, the low form ($C_3A.CaCl_2.12H_2O$) is obtained [56]. The DTA technique may be used to differentiate between the two forms. The low form causes endothermal effects of 190 and 350°C and the endotherm at 160°C is exhibited by the high form [66]. The DTA thermogram of cement mixes containing 75 wt., % of slag shows an intensive endotherm of $CaCO_3$. This may be due to the high total pore volume, which facilitates the penetration of CO_2 in the cement mix that causes carbonation.

III (J). Interpretation of XRD results

The X-ray diffractograms of pure SRC (M0) at different immersing times (0, 3, 6 and 12 months) in seawater are plotted in Fig. 13. All hydrated mixes show $Ca(OH)_2$ as the predominate phase with anhydrous β-C_2S and tobermorite like phase. The intensity of Portlandite peak decreases with immersing time up to 3 months, then increases up to one year and the difference is not sharp. This may be due to the formation of ill-crystalline Portlandite, which can not be found in the X-ray diffraction pattern, but the chemical method determines the crystalline and amorphous type. Tobermorite like phase has opposite manner to Portlandite phase at all ages of immersion. The peaks of anhydrous silicate phases superpose with those of the hydrated silicates and decrease with time, due to the hydration progress. The ettringite is not detected by XRD suggesting that, it was formed as very fine crystals [67]. The diffractograms of M$_2$ samples immersed in seawater for 3 and 6 month are graphically represented in Fig.14. It is clear that, the intensity of Portlandite peak decreases with the immersing time, due to the pozzolanic reaction with slag portion. But, the intensity of Portlandite peak at 6 months is actually higher than that at 3 months. This seems due to the decomposition of some of CSH with $MgSO_4$, giving excess $Ca(OH)_2$ The CSH peaks are present and increase with immersing time up to 6 months. Their intensities are higher than the corresponding peaks in case of SRC, due to the pozzolanic reaction of GGBFS with free $Ca(OH)_2$ to form additional CSH [8]. Also, the calcite peak increases with curing time.

IV. CONCLUSIONS

Based on the results of experimental program concerning the durability of composite slag rich cements prepared from substitution of different percentages of SRC by GGBFS up to 75 mass, % in aggressive water to one year comparing with pure SRC. The following conclusions and recommendations can be derived:

1- Substitution of SRC by GGBFS tends to decrease the mixing water and elongates the setting times, due to the lower hydraulicity of GGBFS in comparison with SRC.

2- The values of free lime (FL,%) and pH have the same trend and decrease with immersing time up to 3 months for hydrated SRC, then increases up to one year. The decrease is due to the reaction of chloride and sulfate ions with $Ca(OH)_2$, forming gypsum and $Mg(OH)_2$. But, after 3 months, $Mg(OH)_2$ reacts with CSH to form $Ca(OH)_2$. The slag rich cements show decrease of FL, % and pH values with time from 1 up to 12 months. It seems due to the pozzolanic reaction of slag with Portlandite.

3- $Ca(OH)_2$ reacts with slag portion to form more C–S–H gel and AFt, which intertwining with each other, filling the pores, forming a denser microstructures and significantly improving durability properties of cementitious materials.

4- The bulk density (dp) and compressive strength of the hardened composite slag cements increase with curing time and slag content, due to the increase of slag activation by SO_4^{2-} and Cl^-,

forming additional hydration products. On contrast, the dp values of SRC increases with time up to 3 months and then decreases up to one year. The increase is due to the activation of SRC in presence of SO_4^{2-} and Cl^-, producing hydration products. After 3 up to 12 months, the effect of ions enhances the formation of ettringite as well as Friedel's salt, leading to expansion and softening. Therefore, the strength properties significantly decrease.

5- The results of DTA, IR and XRD techniques are in a good agreement with each other and also with those of chemical and physico-mechanical properties.

6- In respect of aggressive water attack, the mechanical properties and durability of SRC is greatly enhanced by the use of high quantities of GGBFS. The blended slag cements containing 45-55wt., % GGBFS are comparable to or outperform SRC up to one year of immersion. It was evident that, these composite cements can be used to resist the durability threat.

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VI. TABLES AND FIGURES

Table 1: Chemical analyses of starting materials in mass, %

Oxides	SRC	Slag
SiO_2	19.35	41.79
Al_2O_3	4.19	8.77
Fe_2O_3	5.19	0.57
CaO	62.39	36.64
MgO	2.79	5.43
SO_3	2.18	1.21
K_2O	0.28	0.63
Na_2O	0.62	0.13

Table 2: Mix composition of blended cements in mass, %

Mix No.	GBFS	SRC
M0	0	100

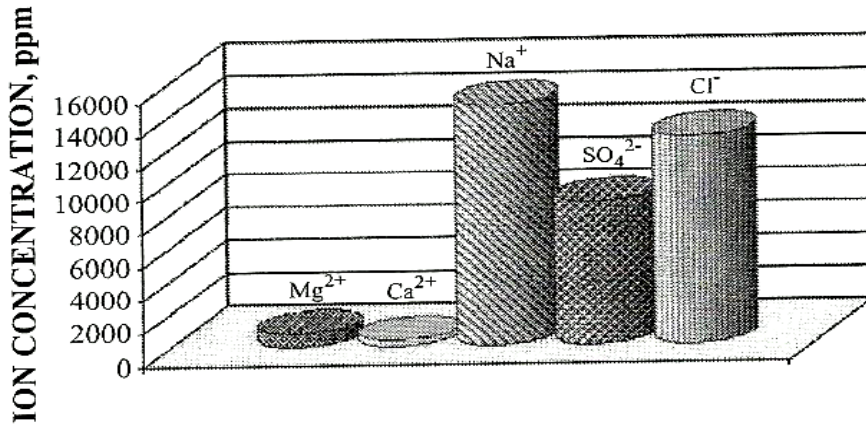|		
M1	45	55
M2	55	45
M3	65	35
M4	75	25

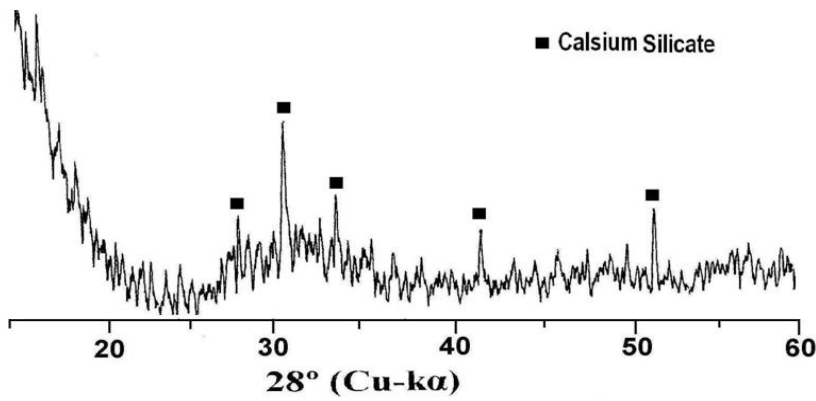Fig. 1. The chemical analysis of Caron's Lake water (ppm).
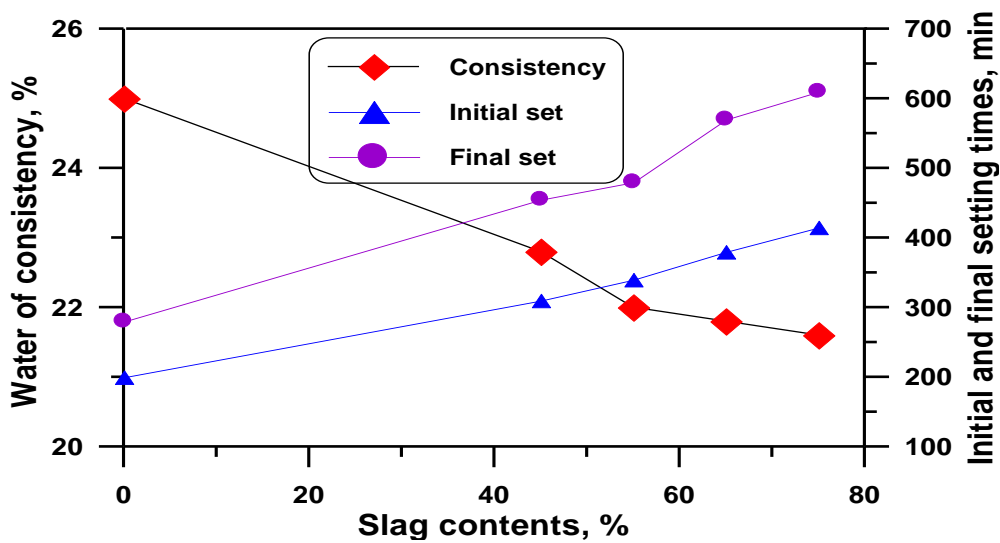

Fig. 2. XRD pattern of GGBFS

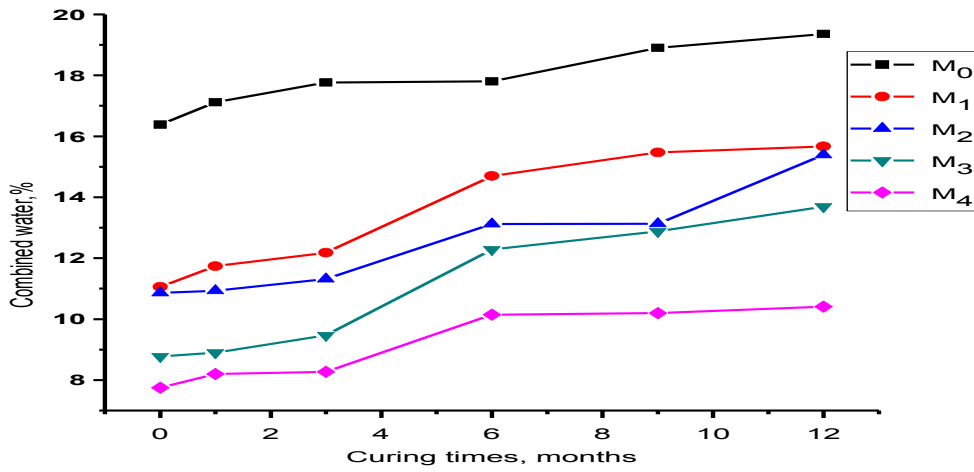**Fig. 3. Water of consistency and setting times of the investigated cement pastes**

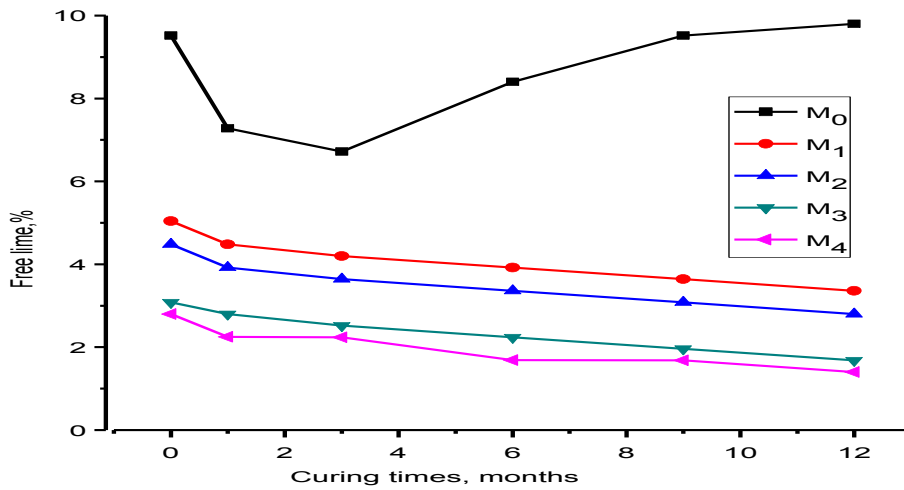**Fig. 4. Combined water contents of the hydrated mixes in aggressive water up to one year**

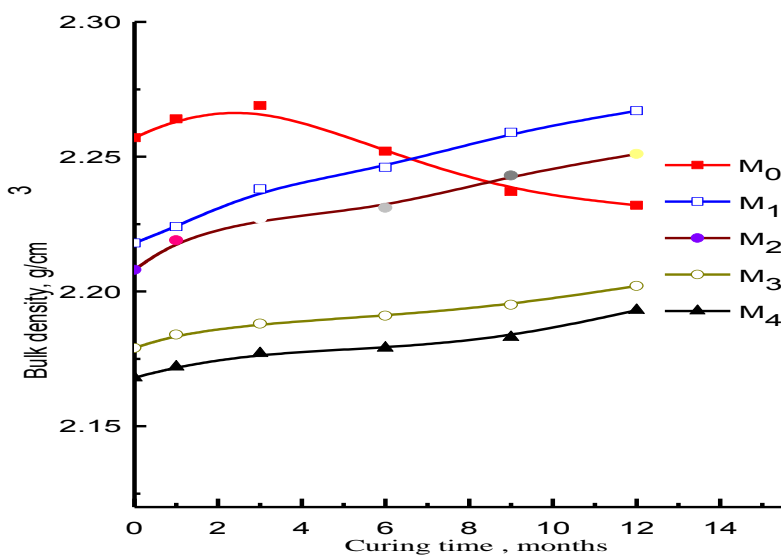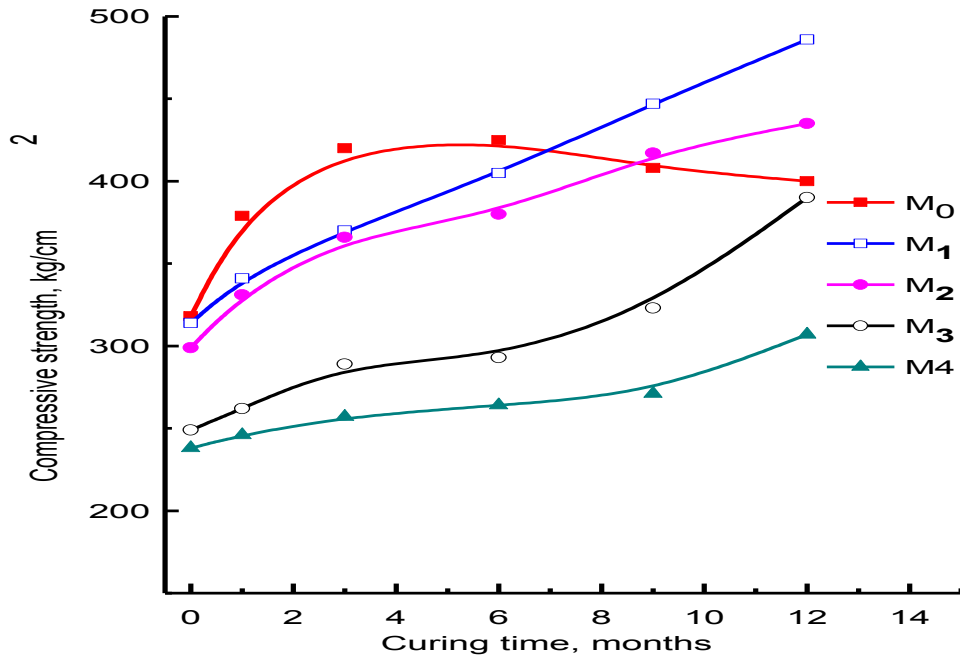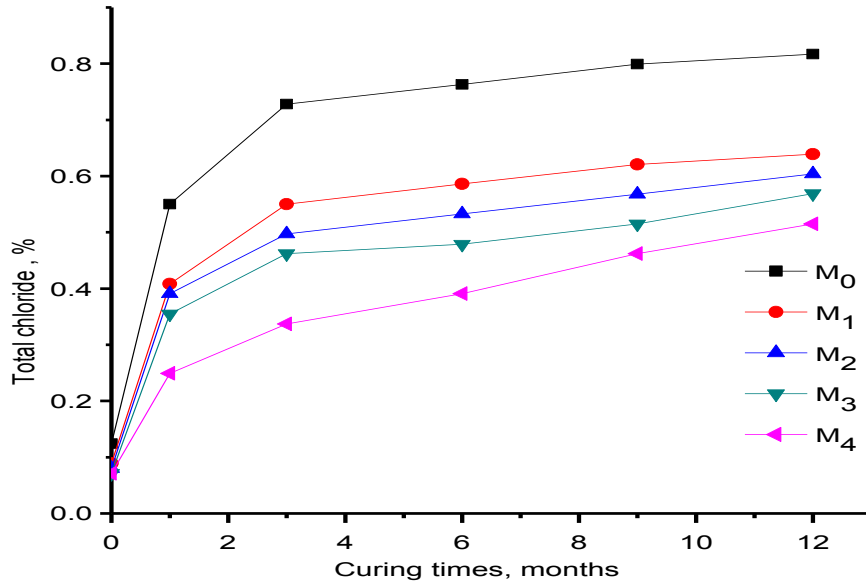**Fig. 5. Free lime contents of the hydrated mixes in aggressive water up to one year**

Fig. 6. Bulk density values of hydrated mixes in aggressive water up to 12 months

Fig. 7. Compressive strength values of the hardened mortars in aggressive water up to one year
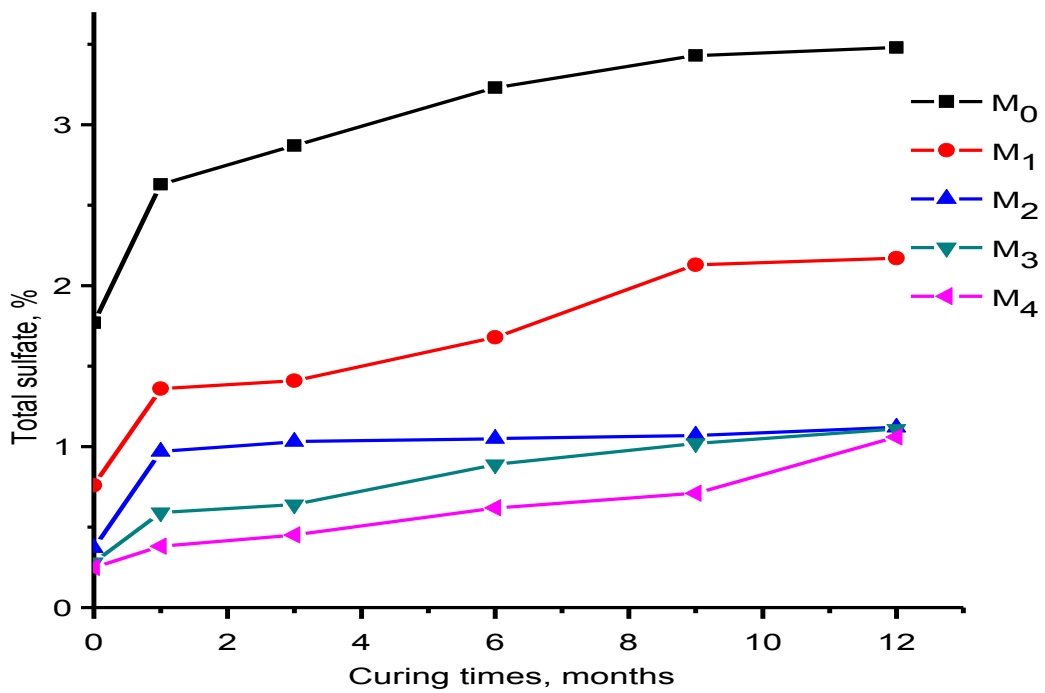
Fig. 8. Total sulfate contents of the hydrated cements in aggressive water up to one year

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Fig. 9. Total chloride contents of the hydrated cements up to one year in aggressive water
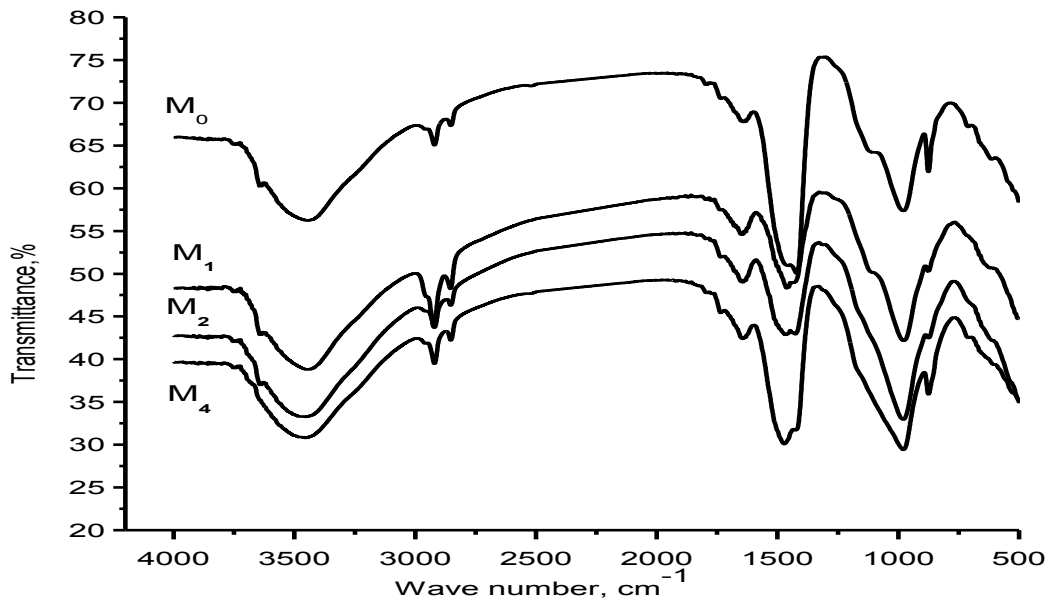
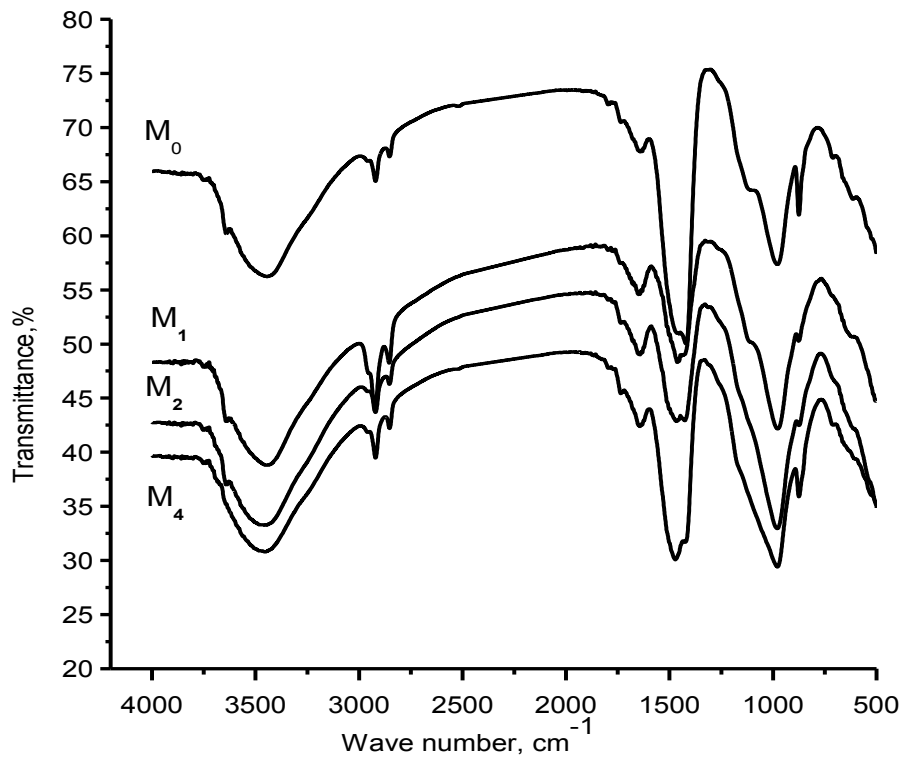**Fig. 10. IR-spectra of M0, M1 and M2 at 3 months in aggressive water**

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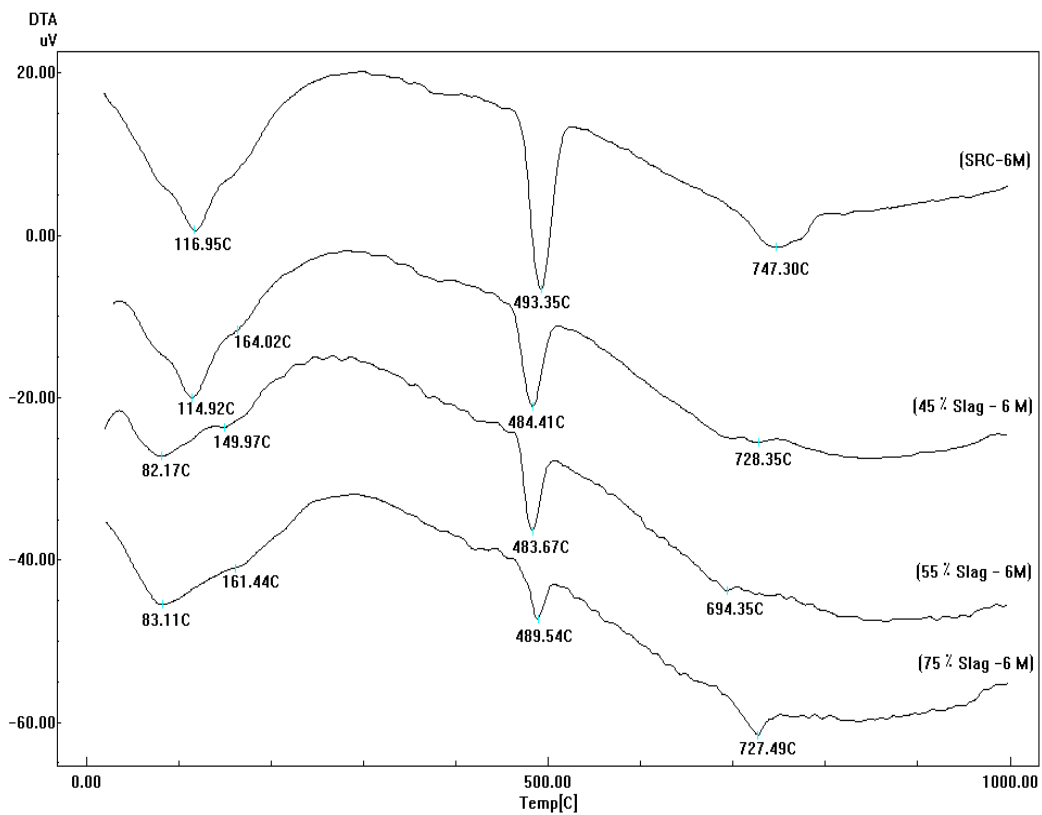**Fig. 11. IR spectra of M0, M1, M2 and M4 at 6 months in aggressive water**

Fig. 12. DTA thermograms of M0, M1, and M2 after 6 months in aggressive water

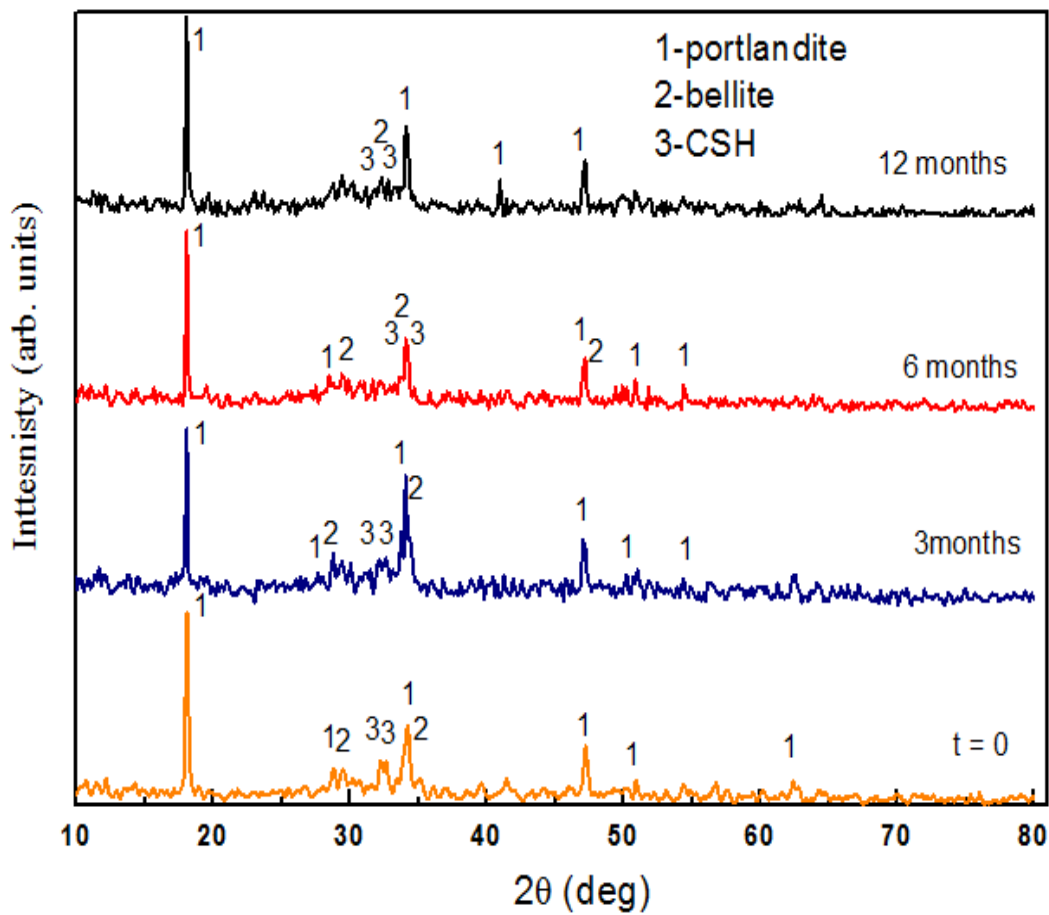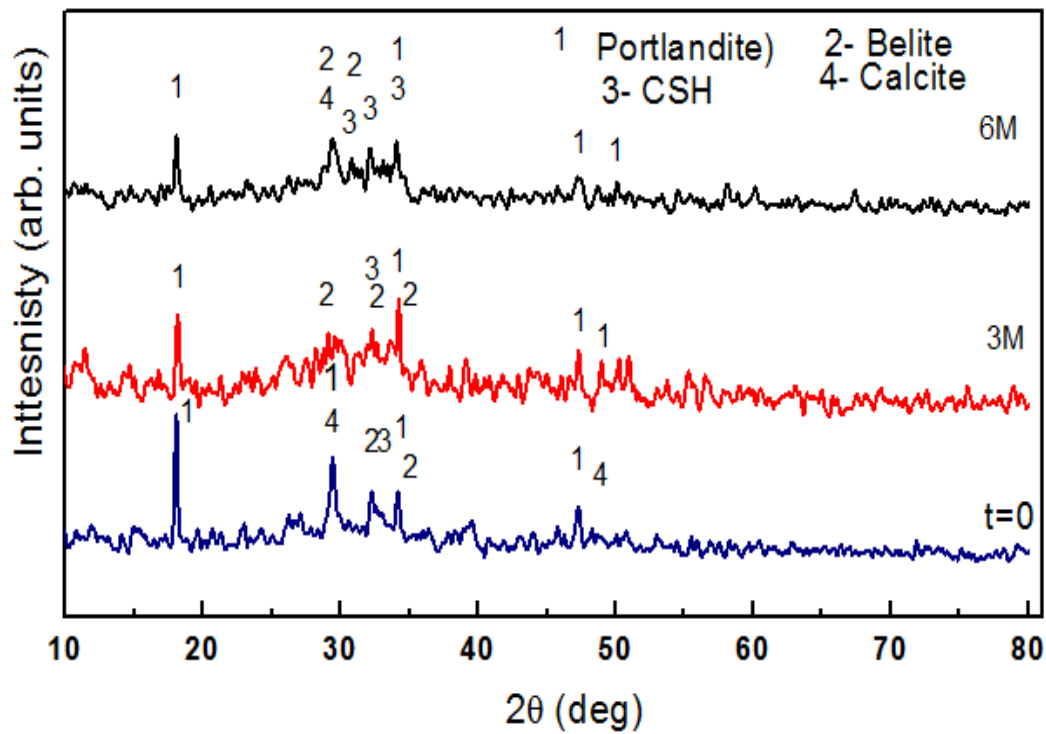**Fig. 13. XRD patterns of SRC (M0) immersed in aggressive water up to one year**

Fig. 14. XRD patterns of M2 immersed in aggressive water up to 6 months