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Impact of Elevated Temperature on Properties of Limestone Concrete

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Abstract: ***Limestone is normally less expensive than portland cement and can cost effectively replace a part of the powder content in most concretes. For this suppose, the scope of this work is to provide experimental data on the residual mechanical and physical properties of concrete containing limestone powder as a replacement or additive of cement content by mass subjected to heat. For this goal, five mixtures were casted, one as a control mixture and the others were with 10 and 15% limestone fines as a replacement and additive of cement content by mass. Reductions in both compressive and flexural strength results along with the extent of weight loss were examined. The mineralogy in unheated and preheated concrete at 20, 200, 400 and 600ºC was identified by means of thermogravimetry (TGA/DTG). Finally the scanning electron microscope (SEM) was done to study the microstructure of the hardened concrete. According to the results, limestone fines had a considerable effect on the properties of the concrete. The results indicated that, the residual compressive and flexural strength of 10 and15 % limestone fines as additive to cement content by mass are generally higher than those of convention concrete. In other words, elevated fire temperature is more damaging to the traditional concrete compared with additive limestone concrete. It has been established that limestone replacement causes reduce the compressive and flexural strength due to the dilution effect. The presence of limestone fines generally reduces the weight loss of heated concrete. TGA/DTG curves of unheated and preheated specimens can be used to estimate the degree of temperature which may the concrete exposed in accidental building fire as a practical part. Based on SEM images, no obvious cracks in limestone concrete whether as limestone replacement or additive up to 600ºC and the CaCO3 clearly observed without decomposition.***

Keywords: fire resistance, limestone fines, (TGA/DTG) and SEM.

I. INTRODUCTION

Concrete has excellent fire resistance properties and maintains its integrity and strength in very high temperatures. It is non-combustible (i.e. it does not burn) and has a slow rate of heat transfer. On the other hand, it does not mean that fire as well as higher temperatures does not affect the concrete. Characteristics such as color, compressive strength, concrete density and surface appearance are affected by high temperature **[1].** Therefore, improving concrete's fire resistance is a field of interest for this researcher. It is possible to improve fire resistance of concrete in many ways. One of the very efficient methods is cement replacement with pozzolanic. Concrete containing different types of mineral admixtures is used extensively throughout the world for their good performance and for ecological and economic reason **[2, 3].** The most used common mineral materials are fly ash, ground granulated blast furnace slag, silicafume and limestone powder. The aim of this study are carefully selected to study the effect of using limestone fines (L.F) as a replacement and additive to cement content by mass on the fire resistance of conventional concrete in terms of mechanical properties (compressive and flexural strength), weight loss, surface cracks, (TGA/DTG) and scanning electron microscope (SEM). Limestone is calcareous sedimentary rock mainly consisting of calcium carbonate ($CaCO_3$), commonly called calcite. Limestone is used in cement and concrete for various purposes, namely, as a raw material for clinker production and as coarse or fine aggregate. Limestone fines are produced by finely grinding limestone in quarrying operations and have been suggested for use as an additive in portland cement. Replacing of limestone into portland cement has been widely studied for several years **[4]**. Nowadays limestone has been widely used to add or replace a part of ordinary portland cement (CEM I) to produce portland limestone cement and portland composite cement. Using limestone can decrease the cost due to the less demand of gypsum content and produce almost zero associate CO_2 emissions **[5]**. Therefore, development of L.F-filled ternary composite cement is meaningful. The aim of this study are carefully selected to study the effect of using L.F as a replacement and additive to cement content by mass on the fire resistance of conventional concrete in terms of mechanical properties (compressive and flexural strength), weight loss, (TGA/DTG) and SEM. To this end, experiments were carried out on a series of mixtures as control mix without limestone fines, 10 and 15%limestone fines as replacement and additive to CEM I by mass.

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II. MATERIALS AND TESTING PROCEDURES.

A. Materials

In this investigation, Portland cement (CEM-I 42.5N) meets the ESS 4756-1/2006 requirements. The chemical analysis of CEM-I was carried out and the results are given in Table 1. Natural siliceous sand has been used as fine aggregate in concrete with specific gravity 2.5 and fineness modulus (F.M.) of 2.54 and pink limestone as a coarse aggregate with specific gravity and nominal maximum size (N.M.S.) of 2.56 and 1" respectively. The physical properties of fine and coarse aggregate are given in Table 2.

Lime stone powder was used as additive and cement replacement by mass. The physical properties and XRD analysis of used limestone powder are presented in Table 3 and Fig.1 respectively. One type of Superplasticiser Type F admixture was used to obtain a constant slump of 10 ± 2.5 cm. The admixture complies with the ASTM C 494/82 and B.S. 5075 Part 3 requirements.

Table 1 Chemical Analysis of CEM I Cement

	CEM-I
(SiO_2) %	17.8
(Al_2O_3) %	4.82
(Fe_2O_3) %	1
(MgO)%	3
(So_3)%	2.7
(CaO)%	60.9
Loss in ignition %	4.65
Insoluble residue%	4.34
Calculated compound composition	
(C_3S)%	59.73
(C_2S) %	6
(C_3A)%	11
(C4AF) %	3.043

Table 2 Physical Properties of Fine and Coarse Aggregate

Property	Bulk Specific gravity	Absorp. %	U.W t/m³	Material Finer than 75µm, %	L.A abrasion value, %
Sand	2.50	2.4	1.71	0.8	-
L.S Agg.	2.56	1.8	1.40	0.4	21
Allowable limit	-	3%	-	Less than 3%	Less than 30%

Table 3 Physical Properties of Limestone Fines (L.F)

Properties	Value
Blaine	3400 cm^2/gm
Specific gravity	2.55
Bulk density (kg/m³)	550

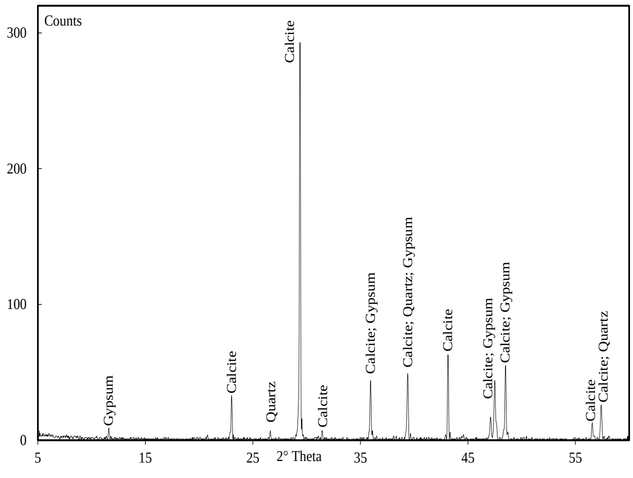

Fig. 1 XRD Analysis of used Limestone Fines

B. Mix Proportion

The experimental program was carried out as, 60 cubes 100 mm side lengths were casted to determine cube compressive strength and TGA/DTG for all mixtures; 12cubes were carried out for every mix. Ten beams of 500 mm x 100mm x 100mm were casted to study the flexure strength. The specimens are classified by the concrete mix design while limestone fines with a weight percentage of 10 and 15 % of the cementitious mass as a replacement and additive were used in the preparation of mixes as presented in Table 4. All concrete specimens have been cast according to ASTM C192-95. The moulds were oiled properly for easy demolding. After casting, moulds containing the specimens were covered with a plastic sheet and stored in the laboratory environment for 24 h. Then the paste specimens were demoulded and immersed in curing tank were then stripped and the specimens were placed in a temperature controlled curing tank at 20º C for a further 27 days, after that specimens were taken from the curing tank, wiped clean to remove any loose grit or extraneous material. The specimens were dried at 105º C for 24 hours then were weighed before exposed to the fire test. At the age of 28 days, the specimens were heated in an electric furnace at 200ºC, 400ºC and 600ºC as shown in Fig. 2. Each temperature was maintained for 2 hours to achieve the thermal steady state. The specimens were allowed to cool naturally to the room temperature. Clean tap water with a constant free water/binder ratio of 0.40 was used in concrete mixing.

Table 4 Details of Mix Proportion

Materials	M-C Control	M-L.F.10R	M-L.F.15R	M-L.F.10A	M-L.F. 15A
Cement, kg/m³	400	360	340	400	400
Coarse aggregate, kg/m³	1060	1055	1052	1021	997
Fine aggregate, kg/m³	713	710	708	681	665
Water, kg/m³	160	160	160	176	184
Superplasticizer, kg/m³	1.1	1.1	1.1	1.1	1.1
Limestone fines, kg/m³	-	40	60	40	60

Samples were taken from inside the cubes just about 1 mm from the surface and were analyzed by thermogravimetric analysis (TGA/DTG). TGA and DTG were done simultaneously. The maximum heating temperature was 1000°C with the heating rate 20°C/min using air as a medium under static condition. The thermogrevimetric analyzer was (Thass-TGA I 1000) as shown in Fig. 3. The mass of sample was about 40 mg. All results in the paper are given in terms of the ignited mass.

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Fig. 2 Electrical Furnance

Fig. 3 The Thermogrevimetric Analyzer (Thass-TGA I 1000)

III. TEST RESULTS AND DISSCUTION

The influence of the heating temperature on properties of control mix (M-C) and L.F concrete was investigated and the results were recorded as:

A. Compressive Strength

Compressive strength measurements were carried out at age of 28 days and reported in Table 5. The compressive strength of normal and limestone concrete was calculated from the average of three specimens and plotted as a function of limestone content**.** Fig. 4 shows the compressive strength of convention and limestone concrete using different content of limestone fines as replacement and additive of cement content. The compressive strength is obviously related to the limestone content.

Table 5 Compressive Strength of Concrete Specimens Exposed to 2 hr. Elevated Temperature after Cooling

MIX	Residual Compressive Strength (MPa)			
	Temperature (ºC)			
	20	**200**	**400**	**600**
M-C	36.2	30.1	27.9	20.2
M-L.F	35.5	28.5	24.7	16.7
M-L.F	32.0	23.3	18.5	13.2
M-L.F	45.3	36.4	33.5	25.0
M-L.F	47.1	36.5	34.5	26.4

At low fire temperature, at 200ºC the residual compressive strength of the control mix decreased by about 17% compared with its compressive strength at room temperature. Increasing the exposure temperature from 200 to 400°C and 600°C, caused a dramatic reduction in the compressive strength values by about 23 and 45 %respectively. Evidently, from Fig. 5 it is clear that the use of L.F as a cement replacement reduces the residual compressive strength of the specimens if it compared with control mix. The obtained percentages of reduction are about 2, 5, 11 and 18% for M-(L.F 10R) and about 12, 23, 34 and 35 % for M-(L.F 15R) comparing to M-C at different studied temperature. The replacement of portland cement by limestone powder caused a reduction in the compressive strength that can be explained as a result of cement dilution effect. It is indicated that the filler effect of limestone cannot compensate for the dilution effect of cement at all ages. On the other hand, the addition of limestone fines to the cement content increases the compressive strength by about 25,21,20 and 24% for M-(L.F 10A) and about 30,21,24 and 31% for M-(L.F 15A) at 20,200,400 and 600ºC respectively comparing to M-C at the same temperature. During hydration of portland cement some calcium carbonate reacts with the alumina phases of cement to form carboaluminates and delays or impedes the ettringite-monosulphate transformation **[6]**. This leads to the stabilisation of the ettringite and will result in an increase in the total volume of the hydration products, which might result in a decrease in porosity and thus an increase in strength. Also this increase in compressive strength may attribute to that the limestone fulfills the pores between cement particles.

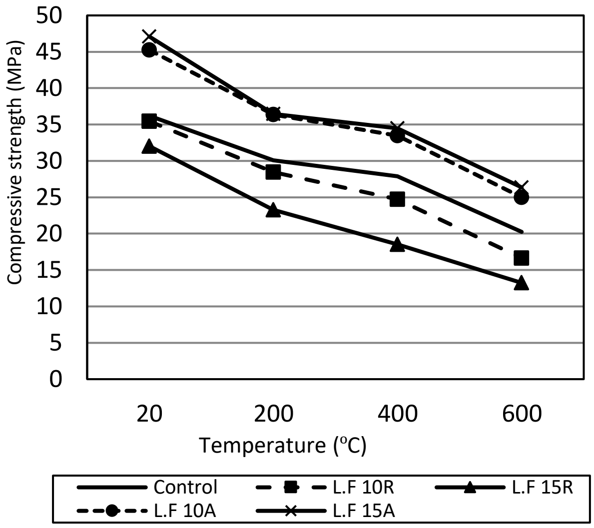

Fig. 4 Compressive Strength of all Mixtures after Exposed to Different Temperatures up to 600ºC.

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B. Flexural Strength

Experimental results of the effect of limestone fines, as a replacement and additive to cement content, on the flexural strength development are investigated in this study. Fig. 5 presents the 28-days flexural strength results and shows the reduction in the flexure strength of beams when exposed to elevated degree of temperature up to 600ºC. As shown in the Fig.5 it can be seen that the flexural strength decreases as limestone fines ratio is increased as a cement replacement by mass up to 15% at all the studied elevated temperature values. The performance of limestone fines as a cement additive is better than that of the convention concrete at all elevated degree of temperature up to 600ºC as illustrated in Fig.5. It can be seen that the addition of limestone fines to conventional concrete increase the flexure strength by about 24, 9, 40 and 40% for M-(L.F10A) and by about 34, 31, 52 and 60% for M-(L.F15A) at the same temperature, so as the limestone fines increase the flexural strength increase up to 15% as additive to cement content. This may be attributing to that the limestone particles fulfill the pores between the cement particles without any dilution on the cement content, so enhances the microstructure of the specimens.

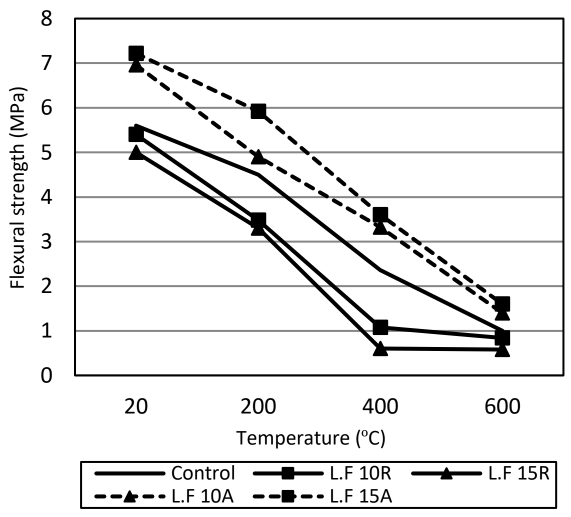

Fig. 5 Flexural Strength of Mixtures after Exposed to 20, 200, 400 and 600ºC for 2 hrs.

C. Spalling

Concrete spalling in fire is a complex topic and the influence of aging of concrete is not yet fully understood. In this study the spalling of the concrete is observed as a function of weight loss. Fig. 6 represents the weight loss of the specimens due to heating. It can be seen from the results of this study that the percentage of losses in the concrete mass of control mix are 4, 6.6, 7.9% at 200, 400 and 600ºC. From Fig. 6 it can be rendered that the addition of limestone fines generally reduces the weight loss of the concrete, whilst the replaces the cement content by limestone fines increases the weight loss up to 400ºC but at 600ºC it reduces the weight loss, this may attribute to that the limestone concrete mainly was constituted from CaCO3which decomposes at about 750ºC **[7]**. Clearly from Fig. 6 it can conclude that the extent of spalling of limestone concrete is slightly less than those of NC which reflects a better performance of L.F concrete over NC.

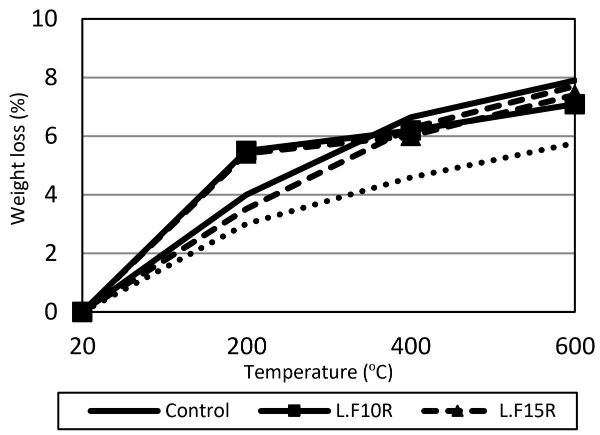

Fig. 6 % Weight loss of the mixtures at a) 200ºC b) 400ºC c) 600ºC

D. Thermogravimetric Analysis (TGA/DTG)

Thermogravimetric analysis (TGA) consists of finding change in weight of a material with increase in temperature. This plot is called a Thermogram. The loss of weight indicates decompostition or evaporation of the material. This technique allows finding out the temperature range in which a material will remain stable and the temperature at which it would undergo decomposition. The (TGA/DTG) curves as presented in Figs. [7, 8, 9, 10, 11] show three significant weight loss steps correspond to endothermic processes. The first at about 100ºC is attributed to surface water desorption as well as water loss from C-S-H gel layers and with the dehydration of ettringite, further mass loss up to approximate 400°C indicates continuous thermal decomposition of a complex mixture of hydrated silicate- and aluminate-type compounds. The second step at about 480ºC is due to the dehydration of Ca(OH)2 (portlandite) according to the following reaction:

$Ca(OH)_2 \longrightarrow CaO + H_2O$ and the its content drops rapidly. The third weight loss step, at about 790ºC, can be attributed to the decarbonation of $CaCO_3$which is correlated with the portlandite content and has tendency to increase toward the concrete **[8]**. The first step of weight loss is nearly completely hidden by the drying and dehydration processes of the ettringite and C-S-H gel for all the preheated samples at 200,400 and 600ºC. Total mass losses of unheated and preheated control samples at 20, 200, 400 and 600ºC after TGA test were about 25, 22, 14 and 8.5% respectively. Although TGA curves are similar in shape, significant differences can be observed in DTG profiles of portlandite and carbonated phase's decompositions. It can be obvious from Fig. 7-a that the loss weight at the second step of control mix reduces with the increasing of the elevated temperature of preheated concrete, which it means that the weight loss of the preheated sample to 400ºC is less than the weight loss of unheated sample. This is as a result to the difference in the amount of decomposed Ca(OH)2 before test, so these curves of TGA/DTG can be used to estimate the temperature which the buildings may be exposed in real fire.

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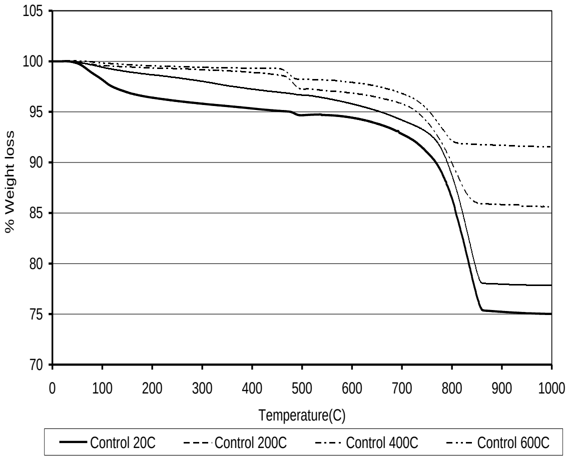
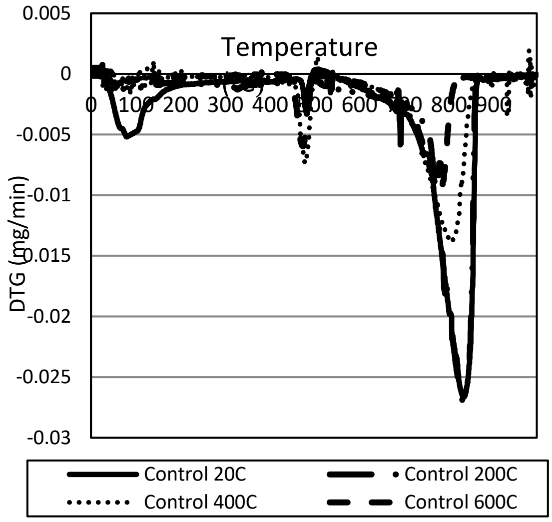
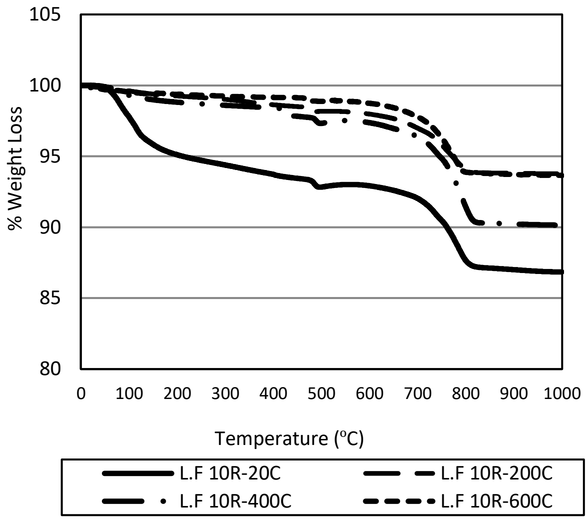
The limestone concrete also was investigated by (TGA/DTG) test. TGA/DTG curves for unheated and preheated limestone concrete are presented in Figs. [8, 9, 10, 11].Total mass losses for unheated concretes with 10 and 15% limestone as replacement and additive to cement content were 13.2, 13, 16.4 and 17.4 % respectively and less than the total weight loss of control mix which is 25%.**From** TGA/DTG curves it can be noticed that the weight losses for unheated concrete up to about 500ºC, were about 5.5, 7, 5, 9 and 8 % for M-C, M-(L.F 10R), M-(L.F 15R), M-(L.F 10A) and M-(L.F 15A). This result attributes to the carbonation of CaCo3 which products more Ca(OH)2.



(A)



(B)
Fig. 7 (TGA/DTG) Curves of Control Mix a) TGA b) DTG



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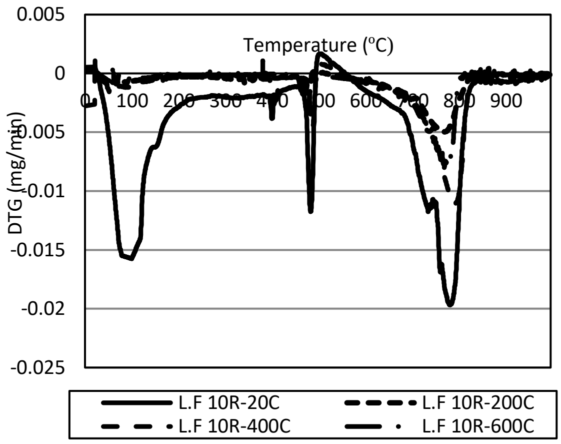
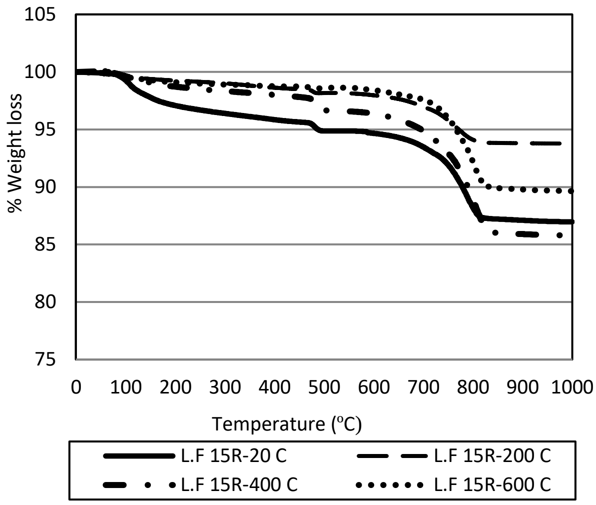


(B)
Fig. 8 (TGA/DTG) curves of concrete with 10% limestone fines as cement replacement by mass a) TGA b) DTG



(A)

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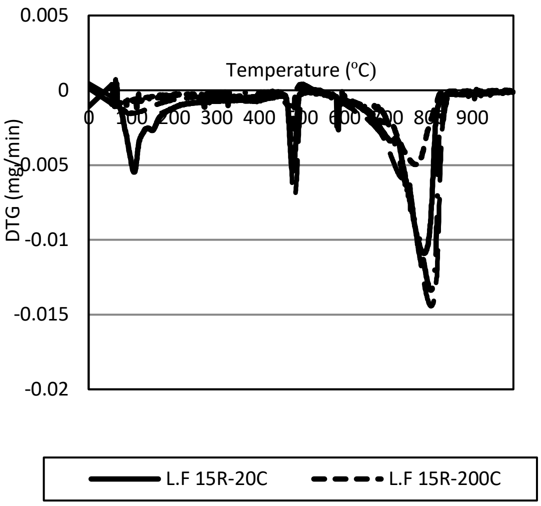
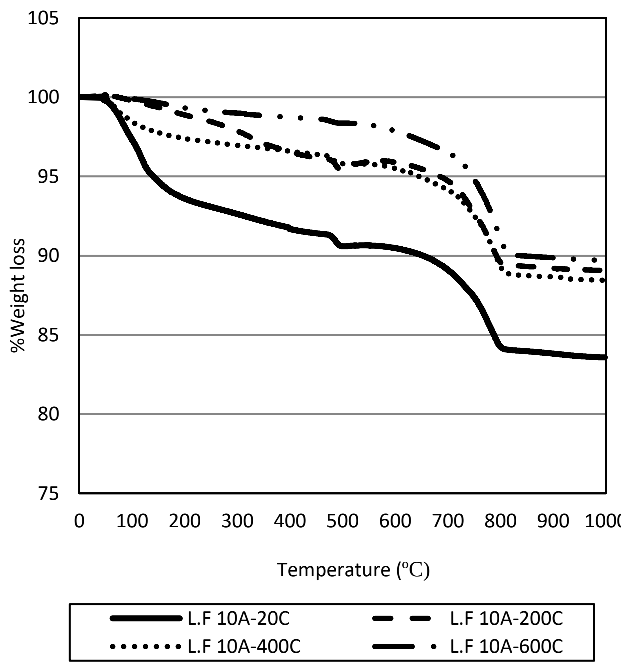


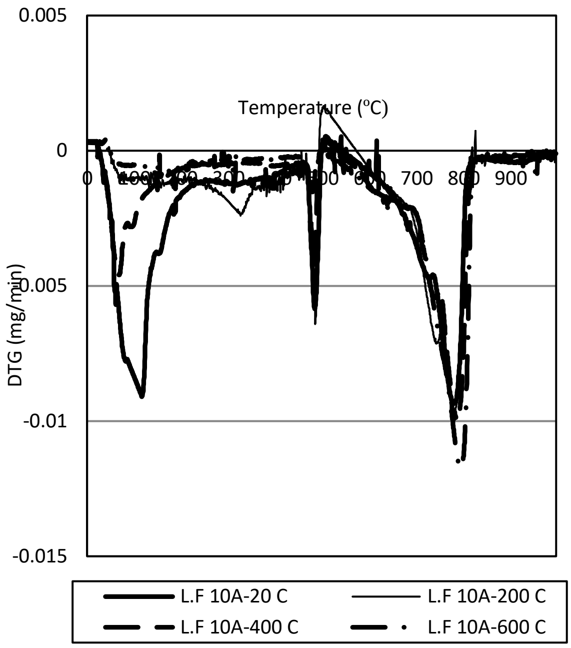
(B)

Fig. 9 (TGA/DTG) Curves of Concrete with 15% Limestone Fines as Cement Replacement by Mass a) TGA b) DTG

The thermograms show that hydrated C3A exhibits a small endothermal effect with a peak at about 320º C and additions of $CaCO_3$ suppress this peak specially as shown in Figs. 7-b, 10-b and 11-b for unheated and preheated concrete at 200ºC. In unheated samples of limestone concrete a little endothermic peaks appears at about 150ºC due to presence of monocarboaluminateas observed clearly in Figs. [8, 9, 10, 11](b) for unheated concrete **[9]**. By some implantation, Figs.[10,11] show, in unheated and in some cases of preheated specimens, a small endothermal peak at about 815ºC due to the CO_2 evolution.

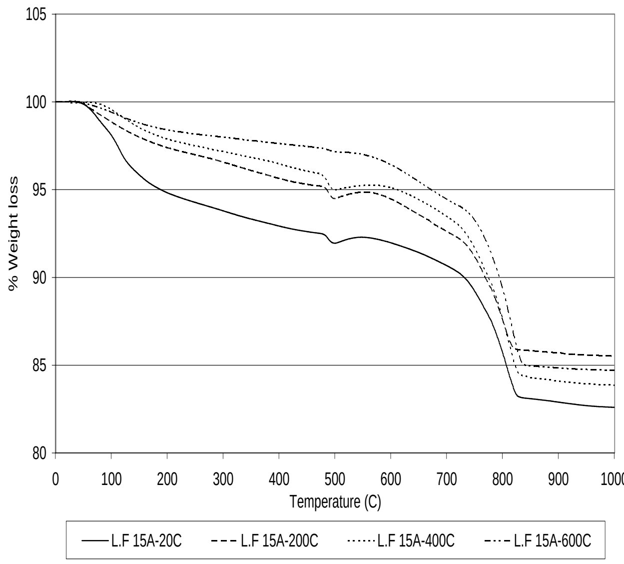


(A)



(B)

Fig. 10 (TGA/DTG) Curves of Concrete with 10% Limestone Fines as Cement Additive by Mass a) TGA b) DTG



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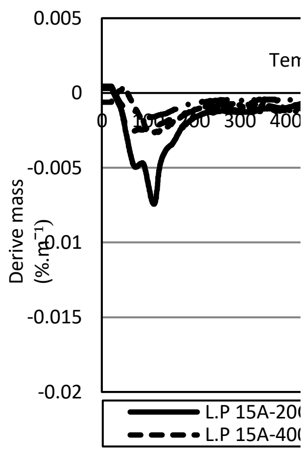


(B)

Fig. 11 (TGA/DTG) Curves of Concrete with 15% Limestone Fines as Cement Additive by Mass a) TGA b) DTG

Finally, it can be notice some disturbtion in DTG curves, this is due to explosive substances sometimes decompose so rapidly that the force of the recoil disturbs the TGA signal. This problem can be avoided by using smaller sample quantities or by diluting the sample with an inert substance.

E. Scanning Electron Microscopy

Scanning electron microscopy allows examination of microstructural details. At the beginning, SEM was carried out on raw materials of limestone fines as shown in Fig.12. replacement, this is as a result to that the limestone particles fulfill the pores between cement and the formation of monocarboaluminates. Also it can be observed a very good adhesion between the matrix and the fine aggregate as shown in Figs. 13-a. All mixtures at 200ºC exhibit plenty in all hydrated products and unreacted $CaCO_3$ (marked ''C'') large crystals are observed in limestone concrete as presented in Figs. 13-b. At 400ºC and from Figs. 13-c**,** the control specimen shows the cracks with about 0.30 µm width and the concrete start to be poor of hydration products, whilst the limestone concrete still without obvious cracks. Image of 15% limestone as additive renders wealth of $Ca(OH)_2$. Along with the increase in temperature, both the density and length of microcracks increased, and the porosity. The cracks of control mix were swollen and the crack width was about 0.60 µm at 600ºC as illustrated in Fig. 13-d. On the other hand the limestone particles became microcracks intermingled with voids due to the increasing more manifest in limestone concrete at 600ºC, whether M-L.F 15R or M-L.F15A as clearly obvious in Figs. 13-d.

In this study fragments of specimens broken off and SEM was carried out on M-C, M-(L.F 15R) and M-(L.F 15A) at 20, 200, 400 and 600ºC. Evidently, as shown in Figs. 13-a, the microstructure of all the mixtures concrete at 20ºC displayed the existence of microcrystalline and nearly amorphous, there is the calcium silicate hydrate (marked ''CSH'') as a main product together with the calcium hydroxide (marked ''CH'') which occurs as relatively crystalline plates and monosulpho-aluminate hydrate (ettringite) (marked ''AFt''). SEM of the concrete with 15% limestone as additive shows dense concrete if it compared with control mixture and 15% limestone concrete as cement

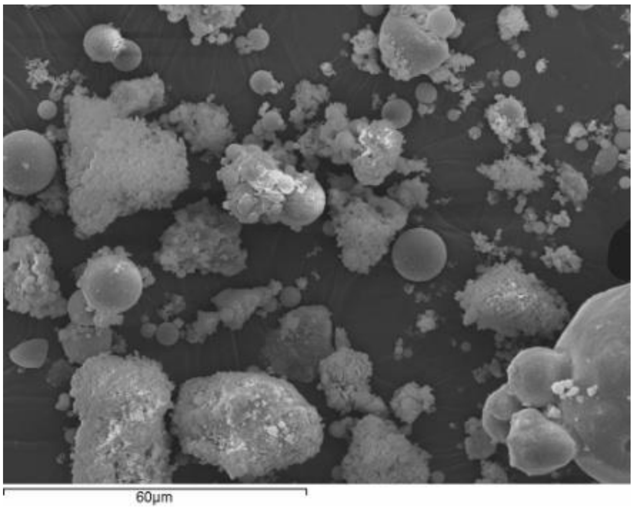
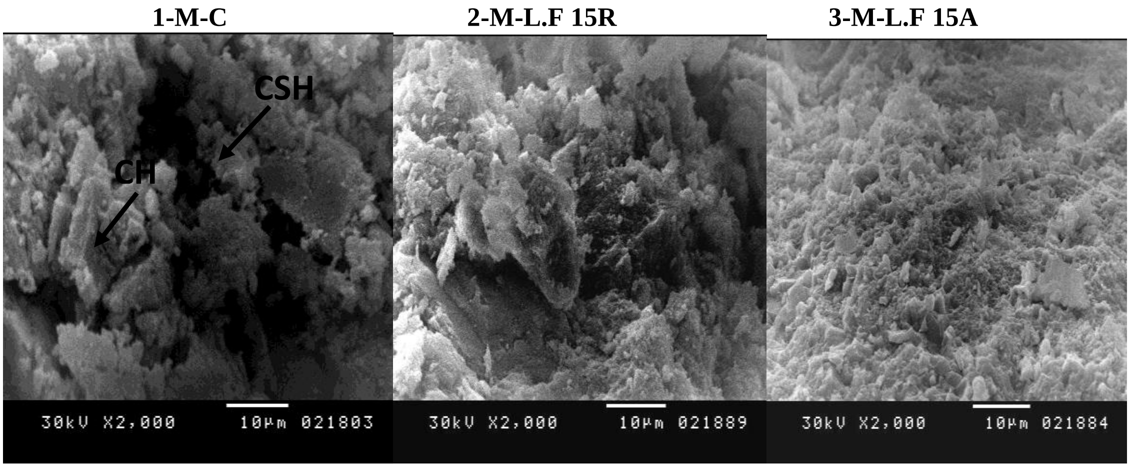


Fig. 12 Raw Material of Limestone Fines under SEM



(A) 20° C

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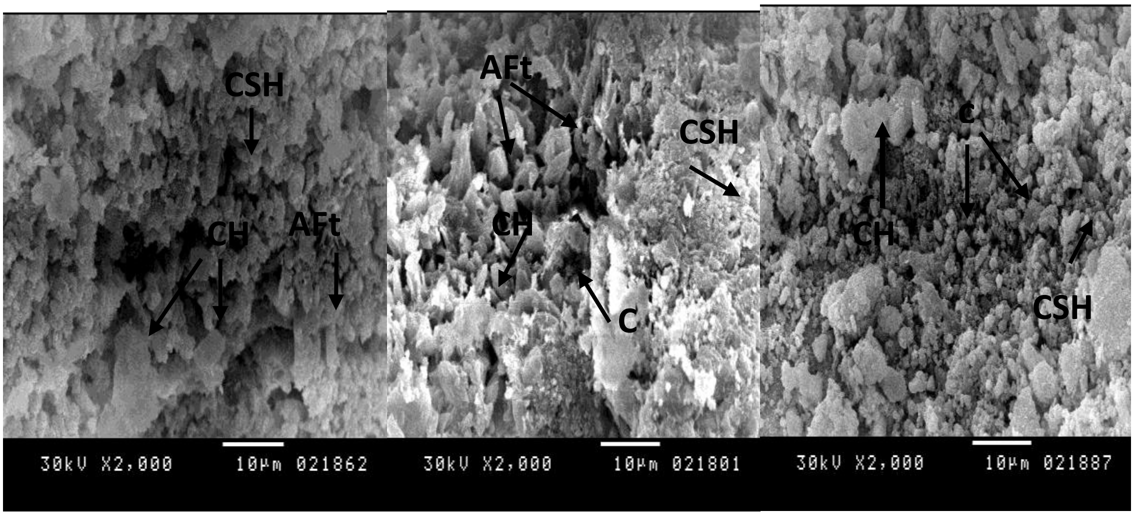
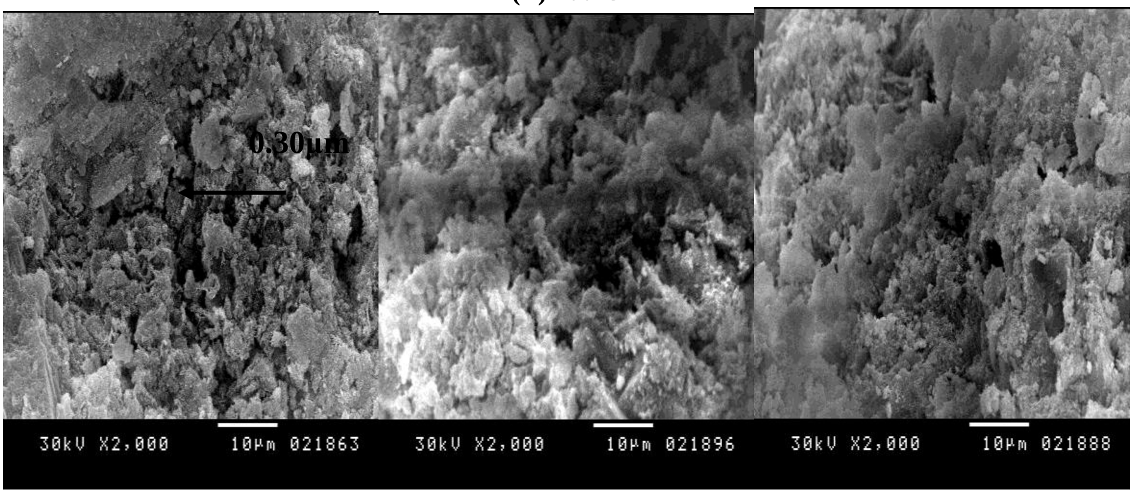
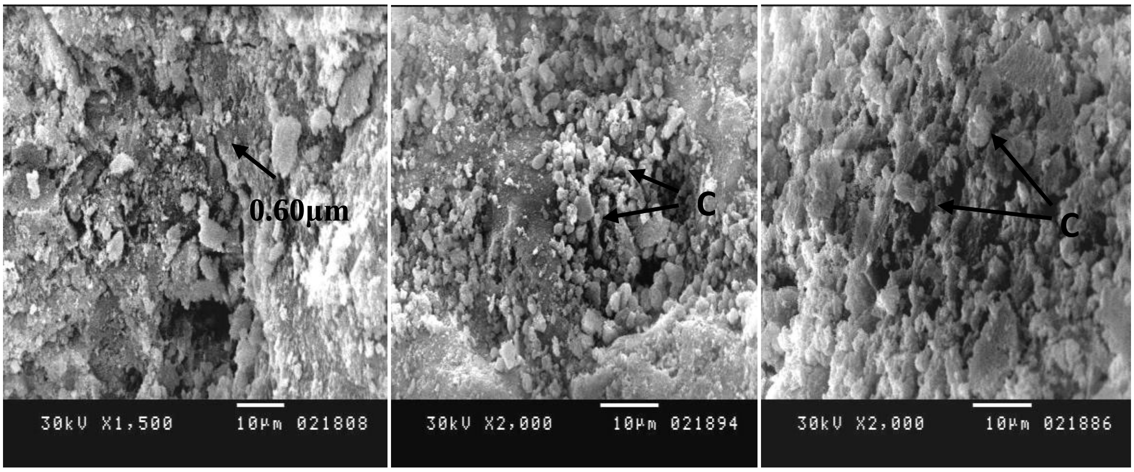


(B) 200ºC



(C) 400ºC



(D) 600ºC

Fig. 13 SEM Images of 1-M-C 2-M-L.F15R 3-M-L.F15Aat a) 20 b) 200 c) 400 and d) 600ºC

IV. CONCLUSIONS

In this study, effect of limestone powder content on compressive strength, flexure strength, weight loss, TGA/DTG and SEM of hardened convention concrete specimens that exposed to high temperature up to 600ºC gradually was investigated. The experimental results obtained lead to the following conclusions:

1- In view of the above, it can be concluded that the mechanical properties of conventional and limestone concrete (compressive and flexural strength) decreased with an increasing in the exposed temperature.

2- Limestone fines, as a cement replacement by mass, have influence on the observed compressive and flexural strength values. It was confirmed that compressive and flexural strength reduced with the increase of amount of limestone fines due to the dilution effect of cement.

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3- On contrary, the use of limestone fine as additive to cement content increased the compressive and flexural strength considerably up to 15% of cement content, this could be ascribed more to the filling effect of unreacted LF and due to formation of new hydrated compounds such as the carboaluminates that fulfilled the big capillary pores of cementitious system.
4- The weight loss of the limestone concrete is less than convention concrete and the TGA sustain this result for the studied degree of temperatures, even the limestone fines were as a replacement or additive.
5- This study has a TGA/DTG curves for unheated and preheated concrete up to 600ºC, from which it can be identify the temperature that the buildings may be exposed in a real fire depending on the total weight loss or even the trend of TGA/DTG curves.
6- According to SEM, the limestone reduces the cracks of concrete at 400 and 600ºC. Also $CaCO_3$ particles appeared clearly for heated limestone concrete up to 600ºC. Concrete with 15% limestone as additive to cement content showed the densest concrete and were reached with $Ca(OH)_2$ plates.

V. FUTURE WORK

Further work is required to get data for other structural properties of the limestone concrete and the optimum dosage. Also the use of limestone as additive to cement concrete must be take its´ right in the future researches because concrete can gained more strength and durability by using limestone without any additional cement content which will reduce the inconvenience. The chemical effect of limestone fines needs to be investigated in the long term standpoint due to the probable transformation of monocarboaluminate into ettringite.

REFERENCES

1. Morsy M.S. Rashad A.M., Shebl, S.S., (2008), “Effect of Elevated Temperature on Compressive Strength of Blended Cement mortar,” Building Research Journal, 56, pp. 173-185.
2. Xiao J., Falkner, H., (2006), “On residual strength of high-performance concrete with and without polypropylene fibres at elevated temperature,” Fire Safety Journal, 41, pp. 115-121.
3. Kalifa, P. Chene G., Galle, C., (2001), “High-temperature behavior of HPC with polypropylene fibers: from spalling to microstructure,” Cement and Concrete Research, 31, pp. 1487-1499.
4. D J Harrison, British geological survey, Technical report w/g/92/29. Industrial minerals laboratory manual of limestone.
5. Weerdt, K. De, Haha, M. Ben., Saout, G. Le., Kjellsen, K.O., Justnes, H. andLothenbach, B. (2011a). “Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash.”*Cement and Concrete Research* 41: 279–291.
6. G. Menendez, V. Bonavetti and E.F. Irassar, Strength development of ternary blended cement with limestone filler and blast-furnace slag, Cement & Concrete Composites 25 (2003) 61-67.
7. Z. Sauman, Carbonization of porous concrete and its main binding components,
Cem. Concr. Res. 1 (1971) 645–662.
8. V.S. Ramachandran, J.J. Beaudoin, Handbook of Analytical Techniques in Concrete Science and Technology, William Andrew Publishing/Noyes, 2001.
9. Handoo, SK, Agarwal S, Agarwal SK, Physiochemical, Mineralogical, and Morphological Characteristics of Concrete Exposed to Elevated Temperatures, Cement and Concrete Research, 32, 1009-1018, 2002.

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