Recycle of wastes of clay brick industry for producing Eco- cement

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ABSTRACT

This work aims at recycling of the solid wastes of clay brick industry (WCB) in the manufacture of blended cement. The various characteristics of collected samples of the waste were determined. WCB was ground to different surface areas. Different mixes were designed from the WCB and ordinary Portland cement (OPC). After adding the required amount of water for each mix, the pastes were moulded in 5x5x5cm^3 mould. The initial and final setting time were measured. The moulded specimens were cured at room temperature for 24hr, then demoulded and cured at water for the required testing time. The compressive strength for the hardened specimens was measured. The kinetic of the reaction was followed by determining free lime and chemically combined water contents. The obtained results were compared with OPC and different types of blended cement already existing in the market. The results clearly illustrate the suitability of WCB for the production of series of different types of blended cement (green products) having great impact on the energy saving moreover decreasing carbon dioxide content released during cement industry .

1-Introduction

Nowadays, energy and global warming are the most important crises. All the trends of the research activities and industrial technologists are dealing with the above two topics i.e. more saving for energy and decreasing the amount of gases evolved during industrial process and human activities. The main gases produce are Carbon dioxide gas (55%), Methane (14%) and Florien (14%). Cement industry is one of the most important industries in the construction sector. It can be considered as a good example representing the above challenge. Since, a lot of carbon dioxide gases is released during its process, also it consumes large amount of energy. Pozzolanic or blended cement is one of the proposed topics in the field of cement technology that can decrease both energy and CO2 gases. Pozzolana is defined simply (1) as any siliceous material having amorphous structure and can react with alkalis specially calcium hydroxide. The idea of blended cement depends upon using pozzlana to produce phases similar to that produced by cement when it subjected to water(2-3). The reaction depends upon many factors as type, degree of crystallinty, and fineness of the used pozzolana in addition to the curing conditions (4). There are many types of blended cement in the market now; slag cement is the most famous one. In general blended cements have many advantages, plus it can be considered as eco-cement. It decreases heat of hydration of concrete and increases durability of the concrete against aggressive attack (5).

Metakaoline (fired clay at700^{o}C) is considered as pozzolanic materials (6). Clay brick is made from clay and sand in certain ratio and fired at around 800^{0}C. In most of the red clay brick t factories,there are huge amount of waste clay brick (WCB), broken either during firing or handling. Up till now there are not valuable complite make use of this waste material; in addition it represents as an environmental and polluting problems. This investigation aims at making use of this waste material in producing blended cement. The latter were designed by partial replacement of Ordinary Portland Cement (OPC) with WCB in different ratios. The various characteristic of the new products were evaluated and compared with the already produced cements. Also, the impact of the blended cement on the amount of carbon dioxide released and energy were calculated.

2- Experimental work

The materials used in this study are different types of cements and waste of clay brick. The latter was collected from a factory very near to OPC factory. The collected sample was ground to different surface areas and the chemical and mineralogical properties were determined Table (1) and Fig (1) respectively. OPC is used in addition to two commercially produce blended cement know as Slag and Karank cements. The various properties of the collected samples of cement are given in Table (1).

Different mixes were designed from OPC and WCB as shown in Table (2). The standard amount of mixing water, initial and final setting was determined for each mix. The mixing water is added to each sample and mixed well then molded in one inch cub mould then cured in 100% humidity chamber for 24hr. After that, the specimens were demoulded and cured in water tank tell the testing time (1, 3,7and 28 days). The mechanical properties were determined for the tested specimens. The kinetic of reaction were monitored by determining free lime and chemically combined water for the hardened specimens. The same work was carried out on net OPC cement, Slag cement and Karnak cement for comparison. All the tested of this investigation was carried out according to A.M. Amin et al (7).

3-Results and discussion

As mentioned above the WCB was ground to different surface areas and mixed with OPC in different ratios. Thus, the discussion will be based upon each defined surface area as follows:-

3-1 Mixes with WCB Blain= 3300cm^{2}.gm^{-1}

Table (3) shows the amount of standard mixing water, initial and finial setting times for the hardened mixes designed in Table(2) in comparison with OPC, Slag and Karank cements. The results clearly show that mixing water increases with increasing waste material content. The setting time of the mixes containing waste material is a little bit higher than OPC and equal to the blended cements. This may be attributed to the addition of WCB may coat some of the OPC particles and decreases rate of penetration of water hence reaction of gypsum and calcium aluminates which are responsible for setting time (8).

The measured compressive strength for the specimens cured for different periods are given in Table (4) and Figs. (2, 3 and 4). The results clearly show that the values of the compressive strength of the hardened specimens increases with curing time. In addition, specimens with 10% waste brick having compressive strength values higher than OPC. On the other hand, strength of the hardened specimens decreases with increasing waste material content in the mix. The continuous growth of the compressive strength is mainly due to the formation and accumulation of hydrated products having binding characteristics (6).

The kinetic of the reaction of the mixes under investigation were followed by determining chemically combined water and free lime. The results of free lime content are given in Table (5) and are also presented as a function of curing time as shown in Figs. (5, 6 & 7). The results show that free lime content decreases continuously with curing time. OPC reacts first with water to form different types of hydrated phases and free lime liberated (8). The latter reacts with WCB and water to form calcium hydrates in different forms and having binding properties as that produced from the hydration of OPC. The reactions resulted in more accumulation of binding materials with increasing curing time and more increase in the values of the compressive strength (6). The above findings are confirmed with the results of chemically combined water given in Table (6) and presented as a function of curing time as seen in Figs. (8,9 & 10). The results show that chemically combined water increases continuously with curing time. The chemically combined water content is a measure to the amount of the formed hydration products. It has to state that the values of compressive strength are not only determined by the amount of hydration products, but also with the type and crystalline materials of the formed hydrated phases. Many investigators (9&10) studied the relationship between mechanical properties and characteristic of the formed hydrated phases. It should be noticed that the amount of free lime decreases with the amount of OPC in the mix.

Generally, the results show that the compressive strength values (which is the most important property of cement) for hardened specimens of WCB are higher than slag cement and karank cement. Also, the results indicate that WCB ground to 3300 $cm^2. gm^{-1}$ can be used up to 15% to produce blended cement similar to OPC.

3-2Mixes with WCB Blain= 3600 $cm^2. gm^{-1}$

The reactivity of WCB is the most important factor determining its utilization hence, its amount in producing blended cement. The fineness of WCB was increased to 3600 $cm^2.gm^{-1}$ In order to increase its reactivity and can consume more quantity of the waste instead of OPC. The mixes in Table (2) were used with the new fineness of WCB. Table (7) show the results of standard amount of water necessary for mixing, initial and final setting. The results clearly illustrate that increasing fineness increases the amount of mixing water, final and initial setting time than OPC and mixes with lower fineness. The values of the measured compressive strength of the different hardened specimens are given in Table (8) and represented against curing time as shown in Figs. (11, 12 &13). The results show that the compressive strength increases with increasing fineness of the raw material used. The obtained results are confirmed with the results of chemical analysis for the hardened specimens indicating more consumption of free lime and higher values of chemical combined water. The last findings indicate that increase fineness means more reaction between WCB and free lime to form more binding material that can compensate the decrease in OPC content producing hardened specimens having higher compressive strength values.

3.3 Environment Impact of the new type of cement

3.3.1 Impact on the CO2 content

The sources of carbon dioxide polluting air are:-

1- Power Generation and Vehicles exhaust

2- Cement industry

3- Air craft

Thus, cement industry is considered as one of the most important source for carbon dioxide emission. The mechanism of this emission could be clarified as follows:

The raw materials used in cement industry are Limestone (80-85%) and siliceous materials (20-15%). The ingredients were mixed well and calcined at 1500^{o}c to produce calcium silicate and aluminates phases and carbon dioxide gas is evolved. Consequently, and based on the chemical reaction equation , during the production of one metric ton cement, about 0.55 MT CO2 gases liberated. In addition; about 0.40 MT CO2 gases produces from the used fuel. Thus for to produce one MT cement about one MT CO2 gases evolved. Nowadays, 1800 million ton cement is produced annually allover the world, which means 1800 million MT CO2 evolved annually as a result of the cement industry. It is expecting that the cement production will be increased to 3500 million ton at 2015 and more pollution by CO2 is expected to increase to 3500 million MT.

The results of the present investigation show 10-30% waste material can be used instead of OPC to produce blended cement having the same properties of the already used cement. This means that the waste can decrease the emitted CO2 content by this amount i.e. up to 600 million MT per year. This amount will be increases up to 1000 million MT at 2015. Thus, the produced cement can be called as eco- cement.

3.3.2 Impact on the energy♦

There are two type of energy for cement production; electricity and fuel. The impact of using the waste material on energy of the cement industry will be discussed in terms of the above two mentioned sources of energy:-

a- Electricity

The total amount of cement produced all over the world = 1800 million T/year

*Electricity needed to produce one ton cement	= 72kw
*The totals electricity for the production of cement all over the world	= 72X1800 million ton = 129million MW/year
*Electricity saving due to using 10% waste	= 13million MW/year
*Electricity saving due to using 30% waste	= 39 million MW/year

b- Fuel

*Fuel needed for producing one ton cement	= 80 Kg/T
*Fuel needed for producing cement all over the world	= 144 million T/y
*Fuel saving due to using 10% waste	= 14 million T/y
*Fuel saving due to using 30 % waste	= 42 million T/y

3.4 Impact on the durability of concrete

According to A.M Amin et al, (7) the durability of the blended cement made from WCB compared with sulfate resisting cement (SRC) in aggressive sulfate solution was studied. The change in the strength with curing time up to one year was followed as shown in Table(9). It clearly shows that the compressive strength increases up to 3month for both types of cements. This increase in the strength is mainly due to the acceleration effect of the sulfate ions to the hydration process which leads to more formation and accumulation of hydrated phases. As immersion time increases more penetration of sulfate ions occurs and reacts with the calcium hydrate phases forming ettrengite phase. The formed phase causes expansion

♦It should be noticed that the values stated in this study are approximated values, since it varies from one factory to another depending upon its condition.

in the hardened specimens and leads to decrease the strength. The latter reaction depends upon the penetration rate of sulfate through the hardened specimens. The diffusion rate of the aggressive ions through blended cement is lower than that for SRC. This is mainly due to the porosity of the blended cement specimens is lower than that for SRC (due to the precipitation of the hydration products of pozzolana with calcium hydroxide in the pore structure). Consequently, the SRC contaminates more aggressive ions and resulted in more deterioration. The results of SEM for the specimens cured for different times Figs (15&6) confirms the above findings. Its clearly illustrate the destructive action of sulfate ions on the structure of SRC compared with blended cement.

4- Conclusions

- WCB can be successfully used as pozzolanic material to produce blended cement having the same properties as OPC.
- More amount of the waste can be consumed to produce blended cement by increasing its fineness.
- Many types of blended cement using WCB can be produced analogous to the already existing cement in the market
- The new type of cement has great impact on the environmental and energy. It can save up to 30% of the energy used for the cement production. Also, it can decrease the amount of the released carbon dioxide up to 30%. In addition, wastes of clay brick can be recycled in cement manufacture.
- Durability of blended cement made from WCB in aggressive sulfate attack is higher than sulfate resisting cement.

5- References

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Table (1): Chemical analysis for the used raw materials.

Oxide	Ordinary Portland cement (%)	Karnak (%)	Portland Blast Furnace 35 (%)	Waste of Clay Brick
SiO_2	19.86	20.69	25.79	80.90
Al_2O_3	4.95	3.12	7.48	5.92
Fe_2O_3	4.15	3.39	3.55	4.46
CaO	62.12	43.88	56.32	3.82
MgO	2.36	1.12	2.73	1.37
SO_3	2.92	1.69	2.22	0.47
L.O.I	2.47	1.16	1.15	0.39
Ins. Res.	1.02	24.16	0.35	-
Na_2O	0.48	0.43	0.51	1.28
K_2O	0.14	0.15	0.34	0.96
Total	100.47	99.79	100.44	99.37

Table (2):Different mixes from OPC and WCB in different ratios.

Mix	OPC (% By wt)	WCB (% By wt)
1	90	10
2	80	20
3	70	30
OPC	100	-
Slag Cement	100	-
Karank Cement	100	-

Table (3): Results of Standard mixing water, initial and final setting time for samples made from WCB (Blaine = 3300 Cm^2 gm^{-1}) and in comparison with different types of cements.

Mix	Standard Mining water (%)	Initial setting		Final setting	
		Hr	min	Hr	min
OPC	27	2	10	2	45
Karank Cement	25.75	2	05	3	15
Slag Cement	23.75	2	30	3	13
Mix A	28.50	2	20	3	05
Mix B	29.75	2	30	3	15
Mix C	30.50	2	35	3	15

Table (4): Compressive strength for the different hardened mixes (Blaine 3300cm^2.gm^{-1}), OPC, slag cement and karank cement.

Curing time (day)	OPC	Mix 1	Mix 2	Mix 3	Slag Cement	Karnak Cement
1	363	431	348	354	348	305
3	438	491	392	383	392	462
7	550	617	488	492	488	500
28	737	750	680	600	680	550
90	875	875	720	650	720	675

Table (5):Free lime content for the different hardned specimens (Blaine 3300cm^2.gm^{-1}).

Curing time (day)	OPC	Mix 1	Mix 2	Mix 3	Slag Cement	Karnak Cement
1	6.56	5.76	4.88	4.82	3.48	3.81
3	6.87	5.65	4.21	3.67	2.46	3.20
7	7.12	5.34	3.81	3.52	1.58	2.71
28	7.44	4.94	3.41	3.11	1.07	1.96
90	7.67	4.88	2.94	2.30	1.01	1.62

Table (6):Chemically combined water content for the different hardned specimens (Blaine 3300$cm^2$$gm^{-1}$).

Curing time (day)	OPC	Mix1	Mix 2	Mix 3	Slag Ceme nt	Karnak Cement
1	17.37	16.27	14.85	14.52	13.53	14.52
3	20.67	16.67	16.43	16.14	15.79	16.14
7	21.13	18.11	18.08	16.87	16.73	16.87
28	24.12	20.46	20.29	20.25	17.87	20.25
90	24.52	22.51	22.08	20.79	19.65	20.79

Table (7):Results of Standard mixing water, initial and final setting time for different specimens(Blaine = 3600 Cm^2 gm^{-1}).

Mix	Standard Mining water (%)	Initial setting		Final setting	
		Hr	min	Hr	min
OPC	27	2	10	2	45
Karank Cement	25.75	2	05	3	15
Slag Cement	23.75	2	30	3	13
Mix A	28.50	2	30	3	25
Mix B	29.75	2	40	3	45
Mix C	30.50	2	50	3	35

Table (8):Compressive strength for the different mixes (Blaine 3600cm^2.gm^{-1}), OPC, slag cement and karank cement.

Curing time (day)	OPC	Mix 1	Mix 2	Mix 3	Slag Cement	Karnak Cement
1	363	442	400	391	251	305
3	438	750	508	500	325	462
7	550	775	600	591	450	500
28	737	888	695	625	525	550
90	875	890	712	712	593	675

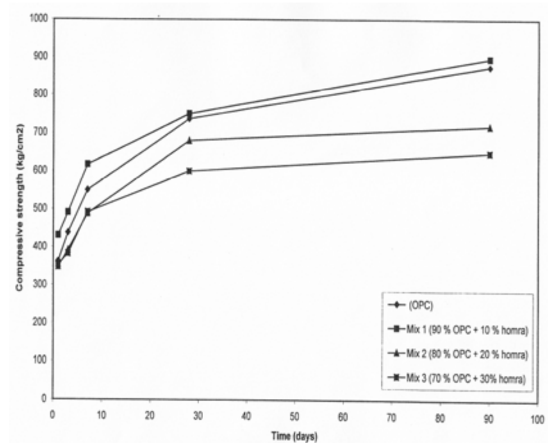

Fig. (2): Variation of compressive strength for the hardned specimens of blended cement (Blaine =3300 cm^2.gm^{-1}) in comparison with OPC as a function of curing time.

Table (9):Change in compressive strength values for the blended cement and sulphate resisting immersed in $MgSO_4$ solution up to one year.

Type of cement	Change in Compressive Strength %				Media
	Curing Time (Months)				
	1 M	3 M	6 M	12 M	
SRC	+5	+6	+7	-4	$MgSO_4$
Min1	+6	+7	+8	+7	

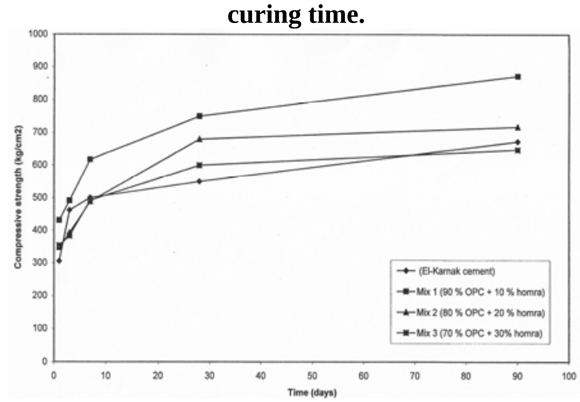

Fig. (3): Variation of compressive strength values for the different blended cement (Blaine =3300 cm^2.gm^{-1}) in comparison with karank cement, with curing time.

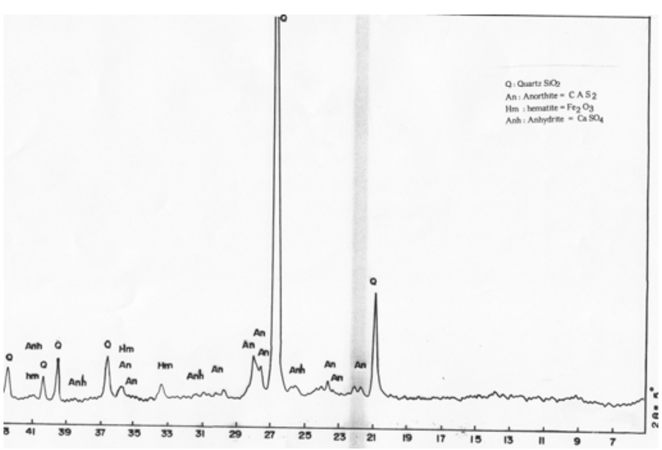

Fig. (1): XRD Pattern for sample of red clay brick.

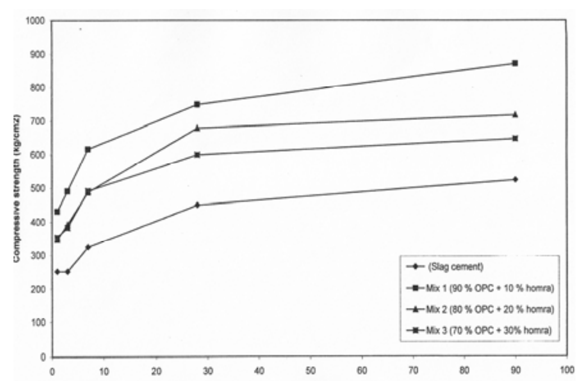

Fig. (4) vanation of compressive strength values for the hardened specimens of blended cement (Blaine =3300 cm^2.gm^{-1}) in comparison with slag cement with curing time.

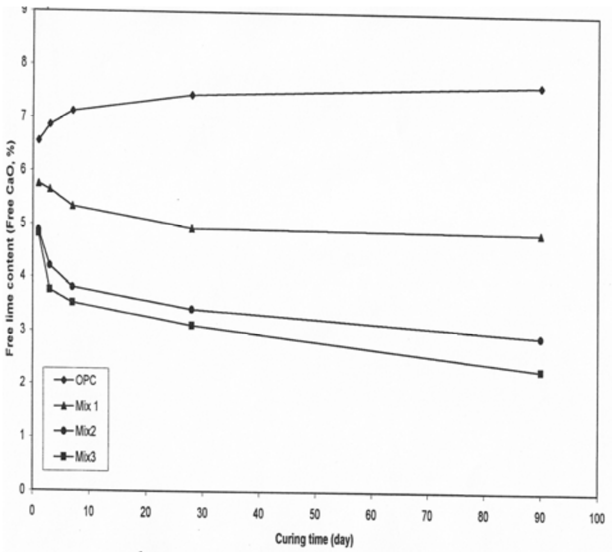

Fig. (5): Free lime content for the different mixes (Blaine =3300 $cm^2.gm^{-1}$) in comparison with OPC.

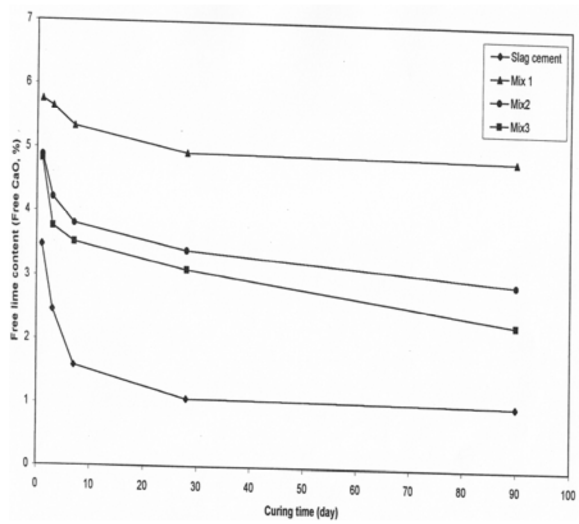

Fig. (7): Free lime content for the different mixes (Blaine =3300 $cm^2.gm^{-1}$) in comparison with slag cement.

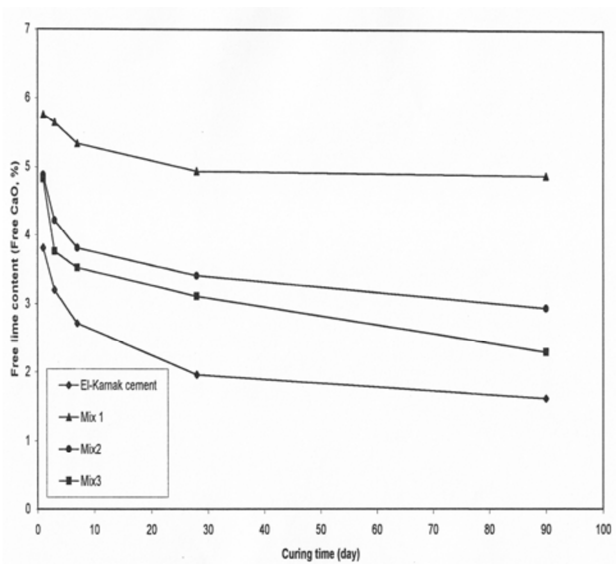

Fig. (6): Free lime content for the different mixes (Blaine =3300 $cm^2.gm^{-1}$) in comparison with karank cement.

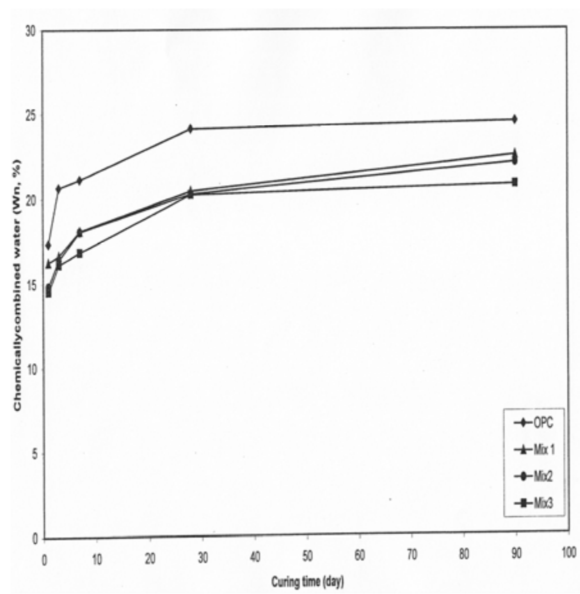

Fig. (8): Chemically combined water for blended cement in comparison with OPC (Blaine =3300 $cm^2.gm^{-1}$)

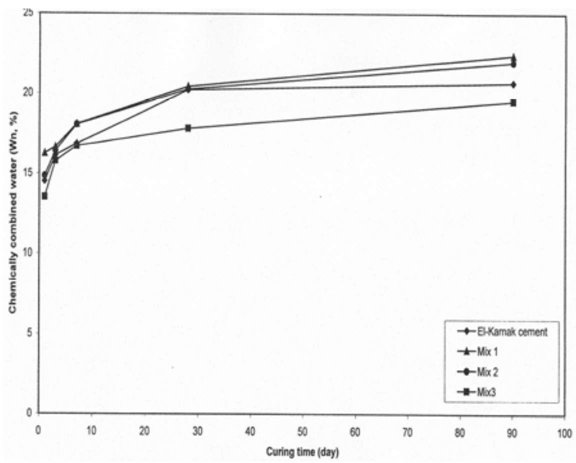

Fig. (8): Chemically combined water for blended cement in comparison with Karank cement (Blaine =3300 $cm^2.gm^{-1}$)

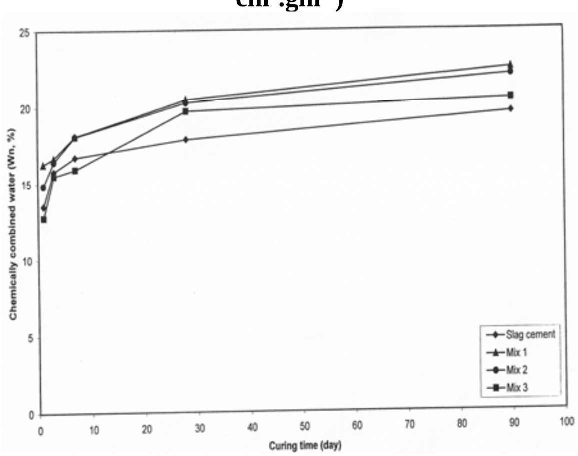

Fig. (10): Chemically combined water for blended cement in comparison with slag cement (Blaine =3300 $cm^2.gm^{-1}$)

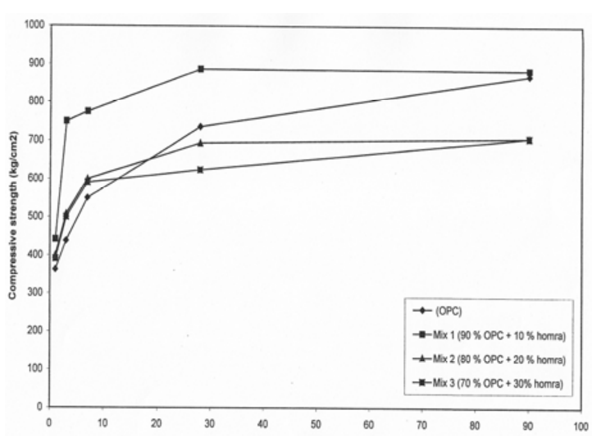

Fig. (11): Compressive strength of the different mixes (Blaine =3600 $cm^2.gm^{-1}$) in comparison with OPC.

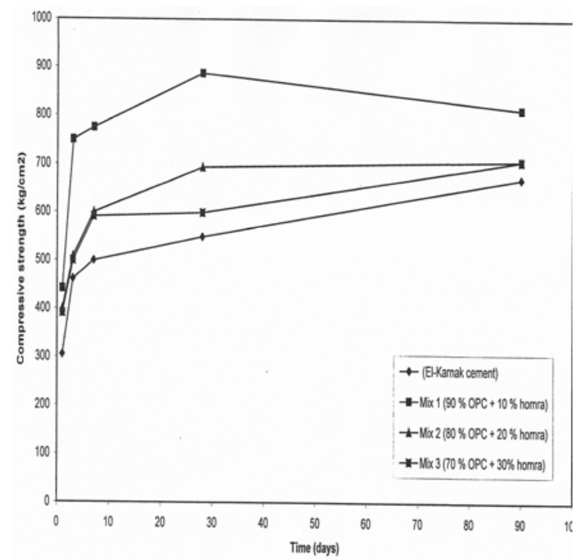

Fig. (12): Compressive strength of the different mixes (Blaine =3600 $cm^2.gm^{-1}$) in comparison with Karank cement.

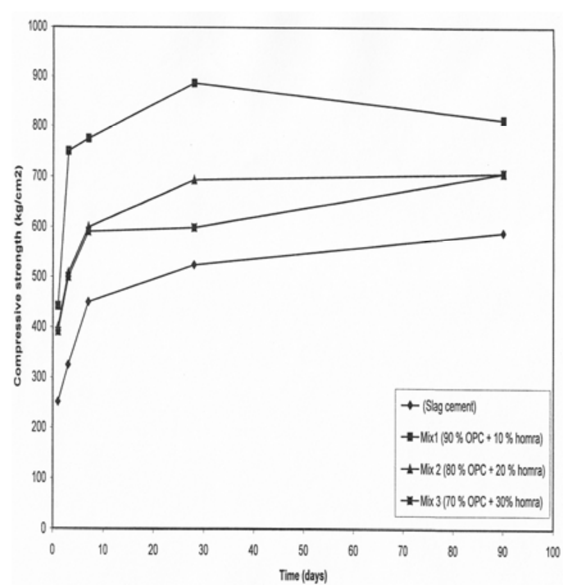

Fig. (13): Compressive strength of the different mxes (Blaine =3600 $cm^2.gm^{-1}$) in comparison with Slag cement.

3 Month **12 Month**

(a)

(b)

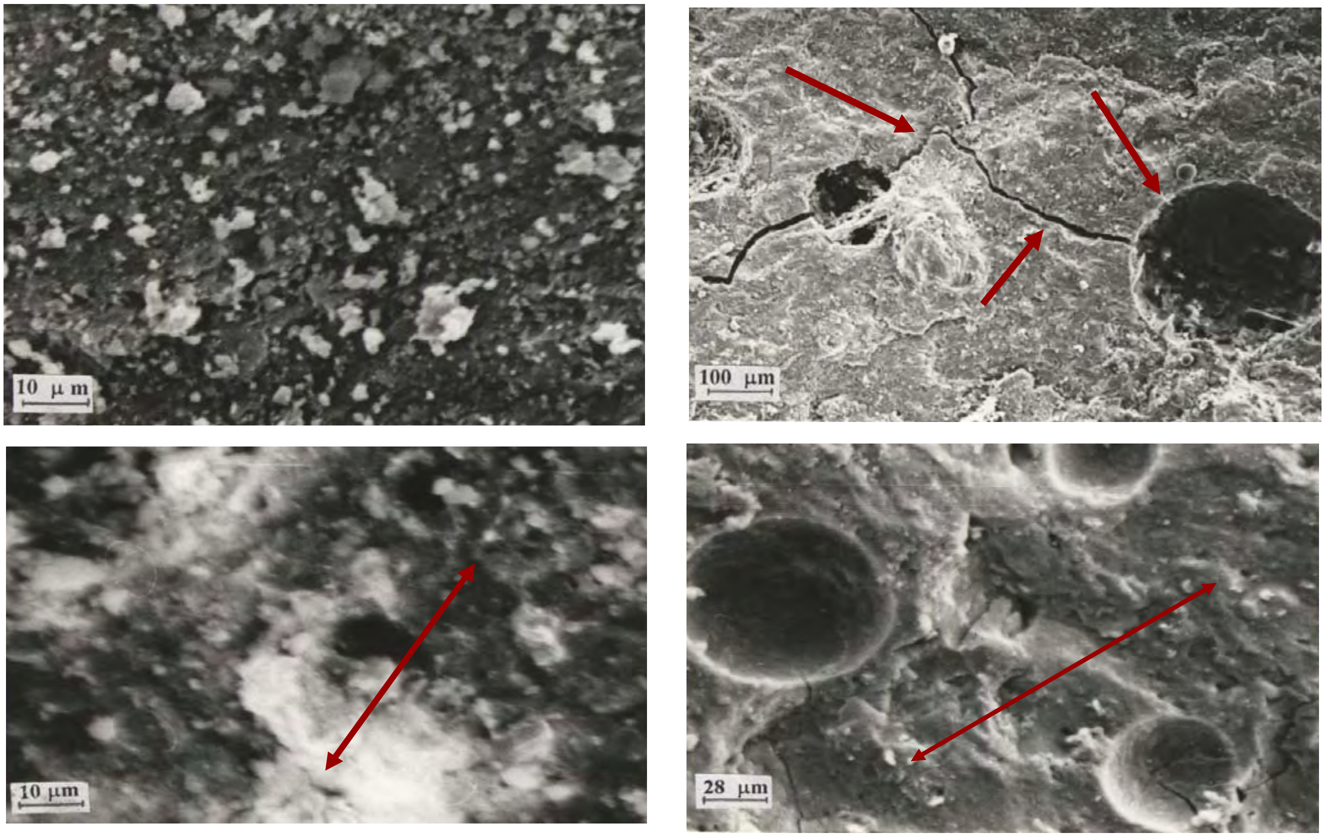

Fig. (14): SEM micrographs of Blended cement immersed in (4%) MgCl at 12 months (a = SRC & b = Blended cement)