COMBINED EFFECT OF MGO AND SO_3 CONTENTS IN CEMENT ON COMPRESSIVE STRENGTH OF CONCRETE

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Abstract

Some oxides in cement such as MgO, free CaO and SO_3 may cause expansive reactions with time that lead to a decrease in concrete compressive strength. If such oxides were presented in high percentages, they may cause ultimate destruction of concrete. The present study was carried out to investigate the combined effect of MgO and SO_3 contents in cement on compressive strength of concrete. Concrete mixes, with different MgO and SO_3 percentages in type I and V cements, were cast. The results showed that there is a considerable effect of MgO content on concrete strength and on the optimum gypsum content in cement. The increase in MgO content results in a decrease in the compressive strength and a reduction in the optimum gypsum content. Type V cement appears to be more sensitive to the increase in MgO and SO_3 contents than Type I.

Keywords; MgO; SO_3; compressive strength; optimum gypsum content; ettringite.

التاثير المشترك لمحتوى MgO و SO_3 في الاسمنت على مقاومة الانضغاط للخرسانة

الخلاصة

هناك بعض الاكاسيد في الاسمنت مثل MgO و CaO الحر و SO_3 قد تسبب تفاعلات تؤدي الى تمدد كبير مع الوقت والتي بدورها تؤدي الى نقصان في مقاومة الانضغاط للخرسانة. اذا تواجدت هذه الاكاسيد بنسب عاليه فانها قد تكون سببا في انهيار الخرسانة الكلي. في الدراسة الحالية تم بحث التاثير المشترك للاكاسيد MgO و SO_3 في الاسمنت الاعتيادي والاسمنت المقاوم للكبريتات على مقاومة الانضغاط للخرسانة. تم عمل خلطات خرسانية بنسب مختلفة من هذه الاوكسيدات وكانت النتاذج تشير الى ان هناك تاثر واضح على مقاومة الانضغاط والمحتوى الأمثل للجبس في الاسمنت. اشارت النتائج أيضا الى ان زيادة محتوى MgO يؤدي الى انخفاض مقاومة الانضغاط للخرسانة وانخفاض قيمة المحتوى الأمثل للجبس في الاسمنت. أن تاثير هذه الاوكسيدات كان اكثر وضوحا في الاسمنت المقاوم للكبريتات مقارنة بنتائج الاسمنت الاعتيادي.

Introduction

Strength of concrete depends on many factors such as mix proportions and the qualities of its components, curing time and curing method, size of specimens, loading conditions…etc. Most factors affecting the quality of concrete components were thoroughly investigated. However, some other factors need further investigations, especially cement constituents, such as; free lime (calcium oxide), magnesia (magnesium oxide) and sulfates. These components have a significant influence on concrete durability; they are capable of causing cracks in concrete if their concentrations are too high. High concentrations of MgO and free lime are either due to its high percentages in raw materials or to inadequate burning during manufacture of cement (in case of free lime). It is well known that raw materials in Portland cement manufacture are burned at temperature of up to 1430 ^{o}C, in order to complete the reactions that give the known cement constituents. Tricalcium silicate (C_3S) starts to form between 1200 ^{o}C and 1300 ^{o}C (when C_2S reacts with free CaO), and by 1430 ^{o}C the reaction products formed are C_3S, C_2S, C_3A and C_4AF [1] If the burning is inadequate, some CaO does not react with C_2S and remains as free lime. CaO hydrates slowly and produces $Ca(OH)_2$ which is accompanied with an increase in volume. This may become a risk on concrete durability with time.

Magnesia is another minor constituent in cement. It exists in raw materials in the form of magnesium carbonate ($MgCO_3$) which decomposes to MgO and carbon dioxide at about 600-700 ^{o}C [2]. A large percentage of it remains free during burning. Only magnesia in form of periclase will be reactive. MgO reacts with water slower than free lime, and this is also accompanied by an increase in volume due to formation of $Mg(OH)_2$. This leads to delayed expansion in concrete.

The third factor which draws the researchers attention is the sulfates. Sulfates cause concrete or mortar deterioration when it exists in excessive amount. This phenomenon is called sulfate attack. The deterioration is caused either by internal sulfate attack or external sulfate attack depending on the source of the sulfates. Lerch [3] had done an interesting study about the effect of gypsum content on the hydration and properties of Portland cements mortar. He attributed the increase in strength with increase amount of gypsum content to its effect on accelerating the rate of hydration of Portland cement, particularly at early ages. The formation of sulfoaluminates in hardened cement paste may lead to lowered strength and undesirable expansion because the increase in volume within the structure of hardened cement paste causes large inner strains to develop [4]. These strains may result in the disintegration of cement paste. Sulfate attack on concrete causes the concrete to weaken and this is normally accompanied by expansion [5]

The effects of the gypsum explained above lead to the concept of the optimum gypsum content which was defined by Lerch [3] as that giving the highest compressive strength and lowest shrinkage in air without excessive expansion in water. This concept was also confirmed by many researchers [3,6].

The combined effect of these three oxides stated earlier on the properties of hardened concrete has not yet distinct. This paper is to study the effect of these oxides on compressive strength of concrete to extend the knowledge in this area. The effect of different MgO and SO3 content were investigated.

Experimantal work

Materials used:

Cement:

Two types of cement were studied; Type I Ordinary Portland Cement (OPC) and Type V Sulfate Resistance Portland Cement (SRPC). The two types of cement conformed to ASTM C150 / C150M – 15 and conformed to IQS (No.5-1984). Their physical characteristics and chemical analysis are listed in Tables 1and 2.

Aggregates:
Natural sand and crushed gravel with 20 mm maximum size were used. Its grading and other characteristics conformed to ASTM C33 / C33M - 13 and IQS (No.45-1984)as shown in Table 3.

Gypsum:
The gypsum was grinding to pass No.200 standard sieve, and added to the cement in different values to reach the required SO_3 content. Their chemical compositions are shown in Table 4.

Magnesia:
Periclase was prepared by burning magnesium oxide up to 1400 ^oC for one and a half hour, then cooled in air, grinded it to pass No.200 standard sieve and kept in glass container before using it in the mix. Table 4 shows the chemical analysis of the magnesia used.

Mix design:
ACI 211.1-91 method for mix design was followed to obtain (30) MPa concrete compressive strength, with 0.5 W/C ratio and 20 mm maximum size of aggregate. The slump for OPC was (95) mm and for SRPC was (120) mm. The quantities of the materials for the mixture in which OPC and SRPC were used are as follows: - Cement =360 kg/m^3, Gravel =950 kg/m^3, Sand =821 kg/m^3. The mix proportions are 1:2.28:2.64 (cement: sand: gravel) by weight of cement.

Compressive strength test:
(276) Cubes for compressive strength test with dimensions of (100×100×100) mm were cast. This test was conducted according to British standard specifications BS 1881-part 4-1983. The final compressive strength recorded was the average of the results obtained from three cubes tested for each age. The tests ages were; 7 days, 28 days, and 90 days. Two methods of curing were adopted; a) curing under water at an average temperature of 24 ^oC and b) curing in the air at laboratory temperature (an average of 28 ^oC).

Results and discussions

Effect of SO_3 content:
Table 5 shows the results obtained from the compressive strength tests of concrete made with OPC with the variations in SO_3 and MgO contents. It can be seen from the results illustrated in Figure 1 that generally there are two optimum SO_3 contents in cement. When MgO equal to (2.71%); there is a decrease in compressive strength with increasing SO_3 content followed by an increase at (4%) of SO_3, beyond this percentage the compressive strength decreases again. Similar behaviour is obtained at MgO content was (3.11%); first there is a decrease in compressive strength with increasing SO_3 below (2.8%) then the strength increased. It reached its maximum at the optimum SO_3 content of (3.6%). Beyond this percentage the strength decreased again. The compressive strength at (3.21%) MgO shows similar trend although the appearance of a second optimum SO_3 content is less clear.
The results of SRPC are shown in Figure 2 and Table 6. When MgO is equal to (1.58%) there are two optimum SO_3 content. These are (2.41% and 3.6%) of SO_3 content. Cement with (2%) MgO, generally shows the same trend, however, the appearance of the second optimum SO_3 content is less clear as in case of OPC stated earlier. In both cases it seems that with relatively high MgO content, the second optimum gypsum content tends to disappear. This may due to the negative effect of the combination of high MgO content with high SO_3 content in cement. The appearance of the two optimum gypsum content is in line with the results obtained by many researchers [7, 8, 9]. Al-Rawi et al. [9] interpreted these results in the light of the influence of gypsum upon the rate of heat liberation. The reaction of cement with water undergoes two cycles of increasing and decreasing rates. Sometimes a third cycle appears due to rapid hydration of C_3A when gypsum is consumed.

The development of concrete strength depends on the period between the second cycle, which refers to the increasing rate of hydration (i.e. increasing strength) and the third cycle, which can cause a decrease in strength due to destruction of some of the hydration products. If the third peak occurs immediately after the second peak, at low SO_3 content, or coincides with the second peak, the adverse effect of the third peak will be minimized, resulting in the first optimum gypsum content. With higher gypsum content, the third peak may occur a short time after the second peak. This causes a significant decrease in strength. On the other hand, if the third peak becomes too far from the second peak, the strength begins to increase and the second optimum gypsum content occurs.

Effect of MgO content:

The effect of increasing MgO is illustrated in Figure 3 for OPC and 4 for SRPC. It can be seen that generally at all percentages of SO_3 there is a decrease in compressive strength with increasing MgO content especially at later ages, except in the case of the appearance of the second peak of strength (at 3.6% SO_3 for OPC) explained earlier. This decrease in strength is due to the formation of $Mg(OH)_2$ which leads to inner stresses causing a reduction in compressive strength. It had been observed also that the increase in MgO content leads to a gradual decrease in optimum gypsum content in both OPC and SRPC. This due to combined effect of MgO and SO_3 when they hydrated.

Effect of curing age and curing method:

Figures 5 and 6 for OPC and SRPC respectively show the relationship between the curing time and compressive strength of concrete specimens cured under water. For all mixes, the specimens cured under water showed an increase in compressive strength with curing time in both OPC and SRPC except at high percentages of MgO (2.02, 2.2) in SRPC when there was a decrease in compressive strength at 90 days compared with the results in 28 days. It can be observed also that there is a reduction in the rate of gaining strength at later ages at high percentages of MgO mainly due to increase the formation of $Mg(OH)_2$. The specimens placed in air show, somewhat, a higher strength than those cured under water for OPC, while for SRPC there is a reduction in compressive strength when the specimens are placed in air compared with those cured under water. The increase in concrete strength in the case of OPC is mainly due to the limitation of the formation of $Mg(OH)_2$ and ettringite in the absence of water. Odler and Chen [10] observed that the final ettringite contents of samples cured entirely in air were distinctly lower than those found in the water cured materials. In SRPC, it appears that the early strength (at 7 days) is low; the presence of water will enhance the development of strength at later ages. Neville [1] reported that the effect of inadequate curing on strength is greater in concrete with lower rate of development of strength.

The difference in the curing method does not show a significant change in optimum gypsum content except at high percentages of MgO ; (3.21%) in OPC and (2 %) in SRPC, when the optimum gypsum content increased for the specimens placed in air compared with those cured under water. This supports the negative effect of hydrated MgO on optimum gypsum content of concrete stated earlier.

Conclusions

According to the results obtained in this study, from the autoclave and compressive strength tests, the following can be concluded: -

1- Increasing MgO content in cement generally results in a decrease in compressive strength of concrete especially at later ages (90days) in both OPC and SRPC, despite the fact that the fineness of the cements used are considerably greater than the minimum limits.
2- A significant effect of MgO content on optimum gypsum content in cement was observed. Increasing MgO content results in decreasing the optimum gypsum content.

3- The reduction in compressive strength of concrete and optimum gypsum content in cement due to increasing MgO content is greater in SRPC than OPC. This does not support the limits in some standard specifications that give the same upper limit of MgO for both OPC and SRPC.
4- There is an increase in compressive strength of concrete with curing time in both OPC and SRPC except at high percentages of MgO (2.02, 2.2) in SRPC and at (2.71) in OPC with very high SO_3 content (6%) when there was a decrease in compressive strength at (90days) compared with the results at (28 days). Also, the rate of increasing strength at later ages decreases at high percentages of MgO.
5- In most cases the specimens placed in air showed higher strength than those cured under water for OPC while for SRPC an adverse effect of air curing is observed.

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Table 1 Chemical composition and physical properties of OPC

Oxide composition	Oxide content %	Fineness (Blaine) cm^2/gm	290
CaO	62.11	Initial setting time (Vicat) (min)	95
SiO_2	22.02	Final setting time (Vicat) (Hrs:min)	3:35
Al_2O_3	5.27	Soundness (Autoclave method) %	0.1
Fe_2O_3	3.4	Compressive strength (MPa)	
MgO	2.71	3 days	16.53
SO_3	2.41	7 days	24.74
Free CaO	1.46	C_3S	45.17
L.O.I	1.47	C_2S	29.13
I.R	0.29	C_3A	7.97
L.S.F	0.86	C_4AF	10.35

Table 2 Chemical composition and physical properties of SRPC

Oxide composition	Oxide content %	Fineness (Blaine) cm^2/gm	375
CaO	62.58	Initial setting time (Vicat) (min)	115
SiO_2	21.76	Final setting time (Vicat) (Hrs:min)	3:45
Al_2O_3	4.17	Soundness (Autoclave method) %	0.04
Fe_2O_3	5.69	Compressive strength (MPa)	
MgO	1.58	3 days	15.62
SO_3	2.41	7 days	24.11
Free CaO	1.61	C_3S	53.2
L.O.I	1.53	C_2S	22.4
I.R	0.31	C_3A	1.2
L.S.F	1.58	C_4AF	17.3

Table 3 Grading of fine and coarse aggregates

Fine aggregate		**Coarse aggregate**	
Sieve opening size (mm)	Percentage passing %	Sieve opening size (mm)	Percentage passing %
10	100	37.5	100
4.75	96	20	97
2.36	83	10	54
1.18	57	5	2
0.60	32	-	-
0.30	13	-	-
0.15	3	-	-
SO_3 %	0.092	So3 %	0.035
Material finer than (75µ) %	3	Material finer than (75µ) %	0.5

Table 4 Chemical analysis of magnesia and gypsum

Material	Oxide Content %					
	CaO	MgO	SO_3	L.O.I	H_2O	I.R
Magnesia	1.4	97.8	0.07	0.01	__	__
Gypsum	33.6	__	41.0	4.22	17.89	1.86

Table 5 Compressive strength results for OPC

Mix symbol	MgO %	SO_3 %	Compressive strength of concrete(MPa)			
			7days	28days	90days water	90days air
M_0S_0	2.71	2.41	27.03	37.62	47.1	39.4
M_0S_1	2.71	2.8	24.88	36.832	38.21	41.6
M_0S_2	2.71	3.6	23.9	35.46	38.41	42.27
M_0S_3	2.71	4.0	23.7	37.32	43.87	44.0
M_0S_4	2.71	6.0	12.22	21.474	39.24	30.80
M_1S_0	3.11	2.41	27.66	37.765	40.43	37.76
M_1S_1	3.11	2.8	24.214	35.692	33.77	38.80
M_1S_2	3.11	3.6	23.4	37.54	41.02	45.54
M_1S_3	3.11	4.0	24.11	36.00	39.75	41.31
M_1S_4	3.11	4.5	20.48	29.33	34.68	35.69
M_2S_0	3.21	2.41	24.96	35.38	36.00	36.73
M_2S_1	3.21	2.80	24.44	32.88	39.7	38.35
M_2S_2	3.21	3.60	23.25	31.92	32.88	41.77
M_2S_3	3.21	4.50	19.40	28.00	34.43	30.36

Table 6 Compressive strength results for SRPC

Mix symbol	MgO %	SO_3 %	Compressive strength of concrete(MPa)			
			7days	28days	90days water	90days air
M_0S_0	1.58	2.41	20.44	39.09	51.55	37.02
M_0S_1	1.58	2.80	15.33	37.11	48.36	32.43
M_0S_2	1.58	3.60	20.87	37.77	49.70	39.84
M_0S_3	1.58	4.00	19.55	35.99	36.73	37.91
M_1S_0	2.0	2.41	19.10	37.25	43.24	34.58
M_1S_1	2.0	2.60	16.88	36.654	41.764	37.47
M_1S_2	2.0	2.80	20.44	38.21	38.65	34.21
M_1S_3	2.0	3.60	11.40	31.70	32.43	27.55
M_2S_0	2.02	2.41	19.70	36.73	34.80	34.65
M_3S_0	2.2	2.41	19.59	35.50	32.02	35.10

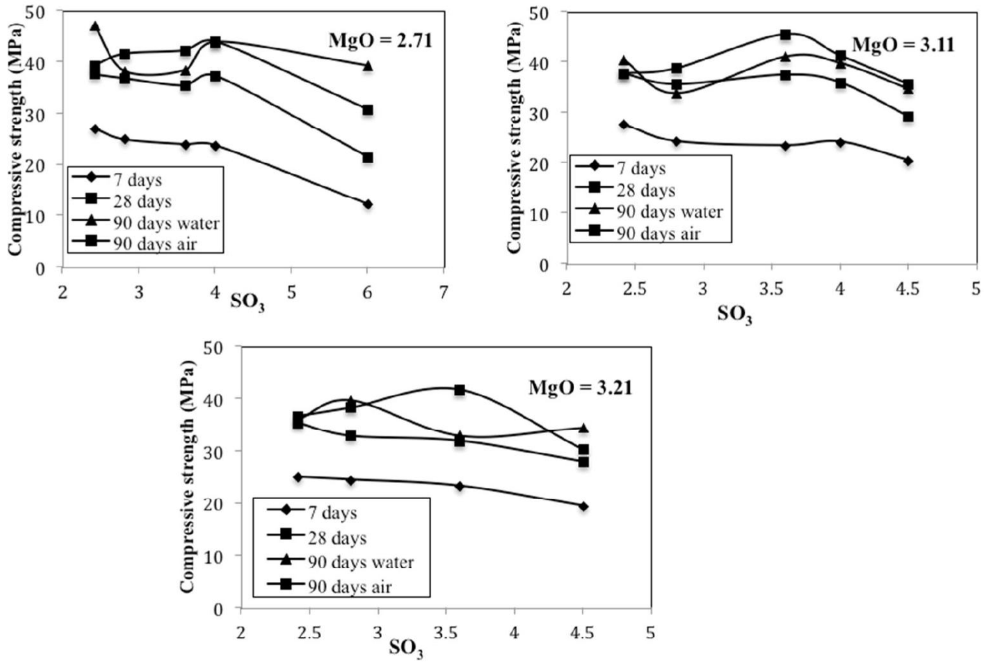


Figure 1 Compressive strength versus SO_3 content in OPC with different MgO percentage

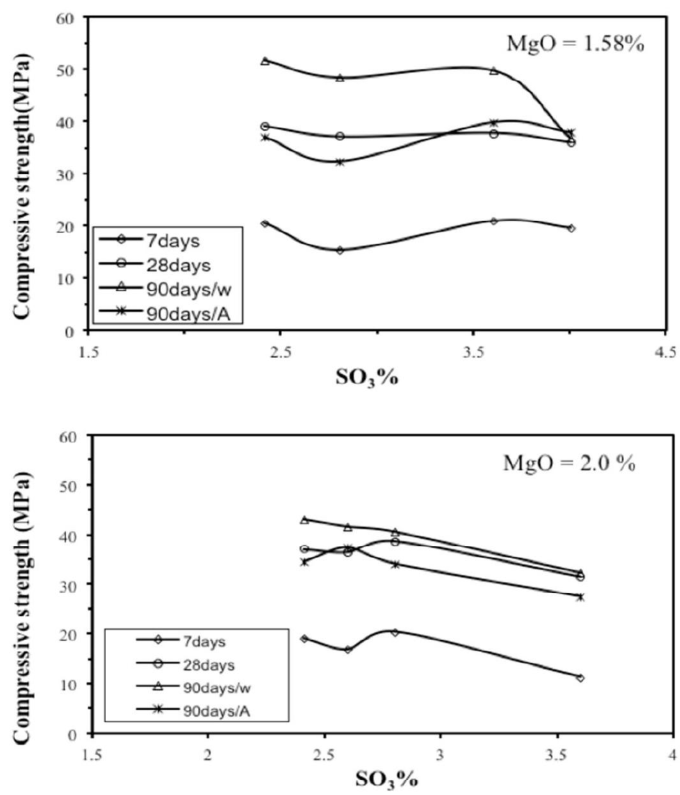


Figure 2 Compressive strength versus SO_3 content in SRPC with different MgO percentage

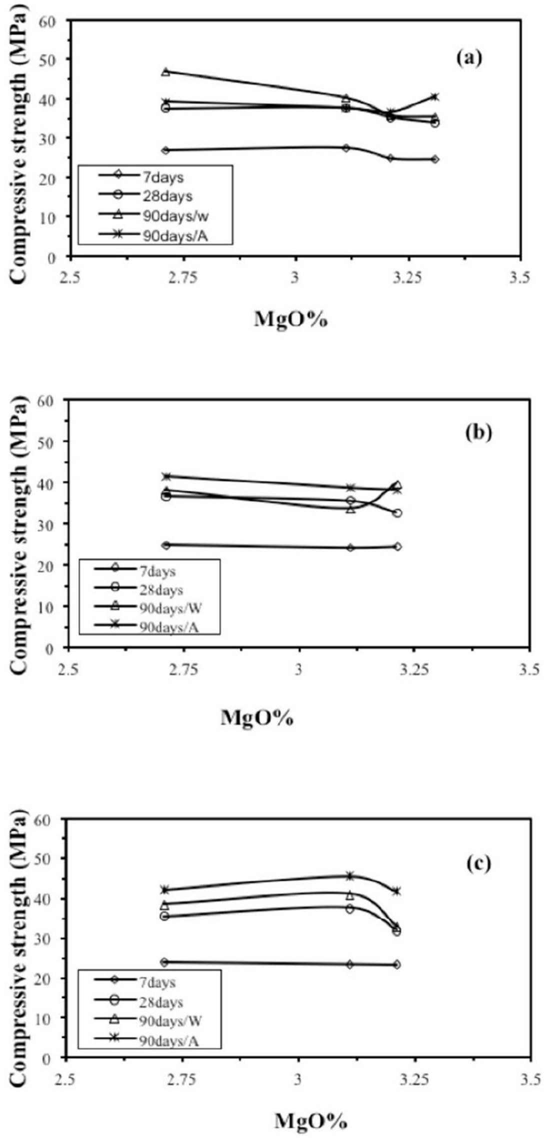


Figure 3 Compressive strength versus MgO content in OPC

a) SO_3 =2.41% b) SO_3=2.8% c)

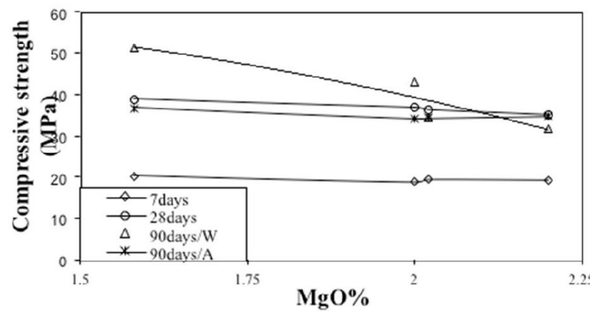
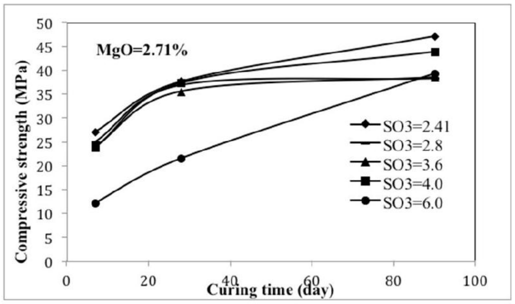
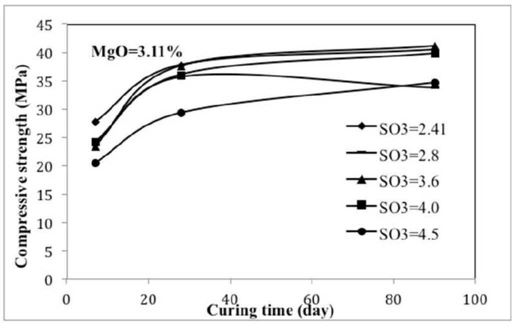


Figure 4 Compressive strength versus MgO content in SRPC (SO_3=2.41%)





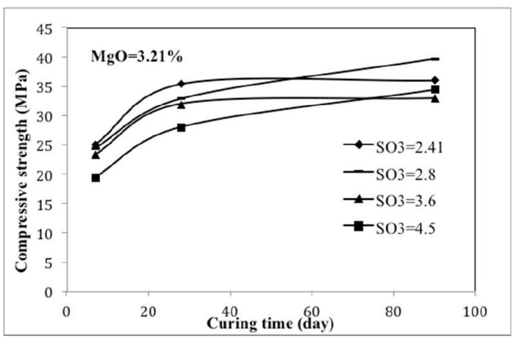
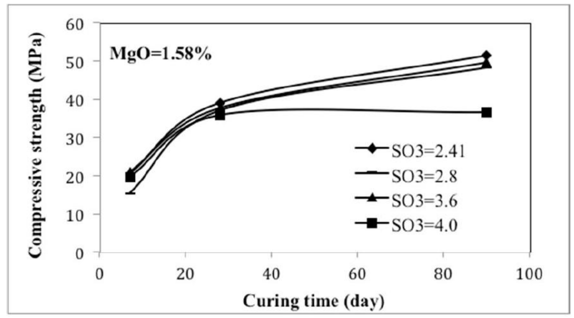


Figure 5 Compressive strength versus curing time with difference MgO and SO_3 contents in OPC



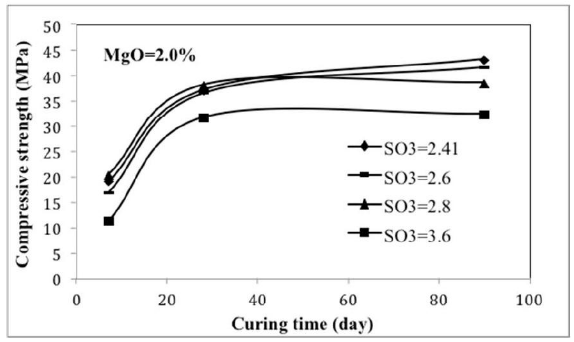


Figure 6 Compressive strength versus curing time with difference MgO and SO_3 contents in SRPC