SOUNDNESS OF CEMENT PASTE DUE TO COMBINED EFFECT OF MGO AND SO_3 CONTENTS IN CEMENT

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Abstract
This study was carried out to investigate the combined effect of MgO and SO_3 content in cement on soundness of the cement paste throughout their effect on autoclave expansion tests. Cement paste, 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 autoclave expansion tests and on the optimum gypsum content in cement. The increase in MgO content results in an increase in the autoclave expansion and a reduction in the optimum gypsum content. The autoclave test is not sensitive to the variation in SO_3 content in cement at low MgO value. The sensitivity is increased with increase MgO content. Type V cement appears to be more sensitive to the increase in MgO and SO_3 contents than Type I. The X- ray diffraction analysis was also conducted to examine the microstructure and phase distribution of cement paste after autoclave treatment.

Keywords; MgO; SO_3; soundness of concrete; autoclave expansion.

ثبات العجينة الاسمنتية نتيجة للتاثير المشترك لمحتوى MgO و SO_3 في الاسمنت

في هذا البحث تم دراسة التاثير المشترك لمحتوى المركبين MgO و SO_3 في الاسمنت على نتائج فحص الثبات للعجينة الاسمنتية بطريقة المحمم. تم عمل خلطات بنسب مختلفة من هذه الاوكسيدات وتم استخدام نوعين من الاسمنت هما الاسمنت البورتلاندي الاعتيادي والاسمنت المقاوم للكبريتات. اضهرت النتائج ان هناك تاثر هام لهذه الاوكسيدات على التمدد الطولي والنسبة المثلى للجبس في الاسمنت حيث اشارت النتائج الى ان زيادة محتوى MgO يؤدي الى زيادة التمدد الطولي للعجينة الاسمنية وانخفاض قيمة المحتوى الأمثل للجبس في الاسمنت. لوحظ أيضا من النتائج ان فحص التمدد بطريقة المحمم غير حساس للتغير في محتوى SO_3 في الاسمنت عند النسب الواطئة من الاوكسيد MgO ويزداد التحسس بزيادة نسبة MgO. أن تاثير هذه الاوكسيدات كان اكثر وضوحا في الاسمنت المقاوم للكبريتات مقارنة بنتائج الاسمنت الاعتيادي. تم عمل فحص بالأشعة السينية لمعرفة هيكل العجينة الاسمنتية وتوزيع الاطوار في العجينة بعد فحص الثبات بطريقة المحمم.

Introduction

The effective components in cement that can cause unsoundness are uncombined lime and MgO in the form of periclase. Their presence in the final product of Portland cement causes a delayed excessive expansion in cement-based materials. This expansion is due to the formation of $Ca(OH)_2$ and $Mg(OH)_2$ upon hydration of free CaO and MgO respectively. Nevertheless, the limits of MgO and free CaO that cause damage in cement-based materials are not yet distinct. A research conducted by Gonnerman et al. [1] concluded that about (1.4 - 2) % free CaO and about (4 - 5) % MgO is needed to cause any excessive expansion. Rehsi et al. [2] showed that the volume expansion of cement rises very sharply beyond 5% MgO. As reported by Lea [3] cement with free lime below about (2)% will pass the autoclave test when the total MgO content is in the range of (1-2)%. However, with high contents of MgO, the free CaO may need to be below (1) % to be sure of conformity. Chopra et al. [4] found that cement containing MgO below (3.5)% could be unsound in the autoclave test. These variations in the results are effected by several factors such as cement fineness, cooling conditions, C_3A content, alkalis, etc.

The third cement component, which draws the researchers attention, is the sulfates. Sulfates may cause concrete or mortar deterioration when exist 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. The effect of sulfates on concrete durability is associated with ettringite formed by chemical reaction between sulfate ions contained in gypsum and certain constituents in cement paste [3]. To avoid unsoundness, the value of the upper limits of SO_3 and MgO contents in cement are specified individually in the various national standards. No upper limit of free CaO content in cement is specified, however, the autoclave test is used as a control for the combined effect of MgO and free CaO. The effect of MgO content on the optimum SO_3 content in concrete was not considered. The autoclave test does not take into consideration the effect of SO_3 on its results. Because of the presence of sulfates in large content in most Iraqi sands and coarse aggregates, which have somehow similar effect on concrete as MgO, and because no increase in minimum surface area was effected in Iraqi cements, it was thought that a study is needed to ensure soundness of Iraqi cements. For these reasons, this study was conducted to investigate the combined effect of MgO and SO_3 contents in cement on the autoclave soundness test of cement paste.

Experimantal work

Materials used:

Cement:

Type I Ordinary Portland Cement (OPC) and Type V Sulfate Resistance Portland Cement (SRPC) were used in this study. They conformed to ASTM C150 / C150M - 15. Their physical characteristics and chemical analysis are listed in Tables 1and 2.

Gypsum and magnesia:

The gypsum was grinding to pass No.200 standard sieve, and added to the cement in different values to reach (2.6, 2.8, 3.2, 3.6, 4.0, 4.5, 5, 6, and 8)% as SO_3. Periclase was prepared by burning magnesium oxide up to 1400 ^{o}C 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. Their chemical compositions are shown in Table 3.

Testing:

Soundness test by autoclave method:

ASTM C151-09 was followed to carry out the autoclave soundness test. (25×25×285) mm prisms were used. The water to cement ratio of the paste was determined from the normal consistency test. For OPC it was in the range of (25-26)% and for SRPC it was in the range of (23.8-24.5)%.

XRD analysis:

The X- ray diffraction analysis was conducted to examine the microstructure and phase distribution of cement paste made from OPC after autoclave treatment with different MgO and SO_3 percentages.

Results and discussions

The results obtained from the autoclave test showed that an increase in SO_3 content at low MgO value (originally in cement) does not lead to a significant expansion in cement pastes when either OPC or SRPC were used as shown in Figure 1 and Table 4. In contrast, there is a tendency for decreasing expansion with increasing SO_3 content in cement even at high SO_3 content (4.5, 5, 6 and 8 % in OPC and 3.6, 4 % in SRPC). These results are in agreement with the results obtained by many researchers [5, 6]. A study by Abdul-Latif [7] showed that the autoclave expansion at first decreased as the SO_3 content increased, while at higher SO_3 contents there was an increase in expansion. He attributed the reduction in autoclave expansion to the formation of monosulfate phase. When the SO_3 is insufficient to allow C_3A and C_4AF to react completely to form ettringite, the hydration product of these components (i.e. C_4AH_{13}) reacts with ettringite under the autoclave test conditions. He suggested that such reaction leads to a decrease, rather than an increase, in solid volume. However, the results obtained in the present work contradict this interpretation, the decrease in expansion occurred even at high percentages of SO_3 as mentioned earlier.

The sensitivity of the autoclave test to the variations of SO_3 content increases with increasing MgO content as shown in Figure 2 and Table 5 for both OPC and SRPC. Lawrence [8] observed that MgO content has a significant effect on expansion due to ettringite formation. He suggested that the expansive hydration of MgO at elevated temperature or at room temperature might increase the sensitivity of cement to heat curing by acting as an initiator for subsequent ettringite recrystallizion pressure generation and expansion. This interpretation can also be applicable to the results of the autoclave test at high MgO content; however, it does not explain the reduction in the expansion resulting from increasing SO_3 content at low MgO percentages.

The XRD analysis was curried out to explain the autoclave test results. It can be observed from Figures 3 and 4 that there is no significant change in peaks state when increasing SO_3 content in cement except limited changes in C-S-H and CH peaks. The addition of MgO results in clearer and higher peaks for all phases as shown in Figures 5 and 6, specially the peaks of ettringite, C-S-H and $Ca(OH)_2$. The C-S-H gel may play a role in the expansion process. The conditions of the autoclave test may induce C-S-H gel to adsorb SO_4^{-2} ions, which causes the decrease or no more expansion in cement pastes. $Mg(OH)_2$ increases the basicity of the solution which leads to an increase in the rate of hydration. More ettringite can be formed and more $SO4^{-2}$ can be adsorbed in C-S-H gel that affects its structure and results in poor strength and then high expansion.

The effect of MgO on the autoclave expansion with constant SO3 content (2.41%) is recorded in Table 6 and shown in Figure 7 for OPC and SRPC. There is a considerable increase in autoclave expansion with increasing MgO content in cement. Beyond (3.11) % MgO in OPC and (2) % MgO in SRPC the expansion rises very sharply. This behaviour is in the line with the results reported by many researchers [1, 2, 4]. However, the percentages of MgO that exhibit such expansion are higher than that in the authors study. In the present work, the method of preparation of cement, which consists of MgO deliberately added, may be the reason for this difference in the value. The results obtained by Lea [3] showed that about (1.5-2) per cent MgO is existing in cement in glass form due to rapid cooling of the clinker, therefore, MgO in this case has no undesirable effect (unsoundness). He attributed this phenomenon to that rapid cooling produce smaller size of MgO grain. Small grains of periclase (crystalline MgO) hydrated more rapidly than larger ones and have less tendency to cause delayed expansion. The reactivity of MgO depends also on clinkering temperature, the reactivity of MgO drops sharply above 900 ^{o}C.

Gaze [9] showed that cement with added magnesia exhibited greater expansion than that produced from cement with periclase already present in cement clinker. The difference in expansion between the case of added MgO and that originally present in clinker may be ascribed to that in the former case the larger particle size is prevailing due to slow cooling, as well as more MgO will be expected to hydrate i.e. its presence out of the cement grains makes it highly exposed to water compared with that in the clinker. The latter MgO is intercrystallized with other compounds and some of MgO may remain unhydrated. Thus the expansion expected would be less than that when MgO is added to cement in periclase form, despite the fact that the reactivity of MgO added is lower as it was heated to about 1400oC.

SRPC is observed to be more sensitive to increase MgO content. The MgO percentage that exhibited sharp expansion in the autoclave test is less than that in OPC, although, C3A content in SRPC is less than that in OPC. Lea and Chopra [3, 4] reported that increasing C3A content results in increase the autoclave expansion. However, the value of C3A in their study is higher than that in the present work. More work is required to study the effect of chemical composition of cement, especially a wider range of C3A and C3S contents on the autoclave test results.

Conclusions

According to the results obtained in this study, from the autoclave test, the following can be concluded: -

1- The autoclave test is not sensitive to the variation in SO_3 content in cement at low MgO percentages; its sensitivity increases with increasing MgO content in cement.
2- The autoclave expansion increases with increasing MgO content in both OPC and SRPC. This expansion rises very sharply when the total MgO in cement (i.e. MgO originally present in cement plus MgO added to the cement) was increased beyond (3.11%) by weight of OPC and (2%) by weight of SRPC.
3- The results showed that SRPC more sensitive to increasing MgO and SO_3 content compared with OPC.
4- Finding an alternative for autoclave test to provide an indication about the delayed expansion caused by MgO, free lime and SO_3 in cement is recommended

References

1. *Gonnerman, H.F., Lerch, W. and Whiteside, T.M., 1953,"Investigations of The Hydration Expansion Characteristics of Portland Cements", Portland Cement Association, Research Department Bulletin 45, Chicago, pp.168.*
2. *Rehsi, S.S. and Majumdar, A.J., 1967,"The Use of Small Specimens for Measuring Autoclave Expansion of Cements", Magazine of Concrete Research, Vol.19, No.61, pp.243-246.*
3. *Lea, F.M., 1970,"The Chemical of Cement and Concrete", 3rd Edition, reprinted 1983, Edward Arnold LTD., London, pp.727.*
4. *Chopra, S.K., Narang, K.C., Ghosh, S.P. and Sharma, K.M., 1980,"Studies on Unsoundness of Clinker with Below 3.5 per cent MgO Content", 7th International Conference on Chemistry of Cement, Paris, Vol.3, Communications, VII-51-56.*

5. *Meissner, H.S., Cook, H.K., Gonnerman, H.F., Hansen, W.C., Mc Coy, W.J., Tremper, B. and Wilsnack, G.C., 1950,"The Optimum Gypsum Content of Portland Cement", ASTM Bulltin, pp.39-45.*
6. *Lerch, W., 1946,"The Influence of Gypsum on The Hydration and Properties of Portland Cement Pastes", ASTM Proceedings, Vol.46, pp.1252-1292.*
7. *Abdul-Latif, A.M., 2001,"Optimum Gypsum Content in Concrete and Cement Mortar", Ph.D. Thesis, University of Baghdad*
8. *Lawrence, C.D., 1995,"Mortar Expansions Due to Delayed Ettringite Formation: Effects of Curing Period and Temperature", CCR, Vol.25, No.4, pp.903-914.*
9. *Gaze, M.E. and Smith, M.A.,1977,"The Effect of Pre-Curing at 50 oC on Autoclave Expansion of High Magnesia Cements", CCR, Vol.7,No.6, pp.659-668.*

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 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 4 Autoclave test results for OPC and SRPC (MgO value originally in cement)

OPC (MgO =2.71%)									
SO_3 %	2.41	2.80	3.20	3.60	4.0	4.50	5.0	6.0	8.0
Autoclave expansion%	0.10	0.12	0.15	0.12	0.09	0.15	0.12	0.10	0.10
SRPC (MgO =1.58%)									
SO_3 %	2.41	2.8	3.2	3.6	4.0	-	-	-	-
Autoclave expansion%	0.04	0.03	0.03	0.01	-0.02	-	-	-	-

Table 5 Autoclave test results for OPC and SRPC (different MgO and SO_3 contents)

OPC (SO_3 = 2.41%)									
MgO %	2.71	2.91	3.11	3.21	3.50	4.00	-	-	-
Autoclave expansion%	0.1	0.14	0.2	0.6	2.24	**	-	-	-
SRPC (SO_3 = 2.41%)									
MgO%	1.58	2.00	2.02	2.04	2.08	2.10	2.20	2.30	2.50
Autoclave expansion%	0.04	0.17	1.56	1.84	2.28	2.8	3.7	**	**

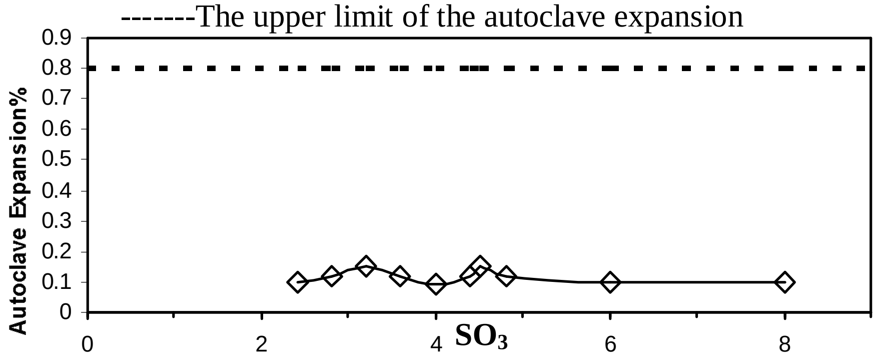
** Disintegrated

Table 6 Autoclave test results for OPC and SRPC with different MgO content

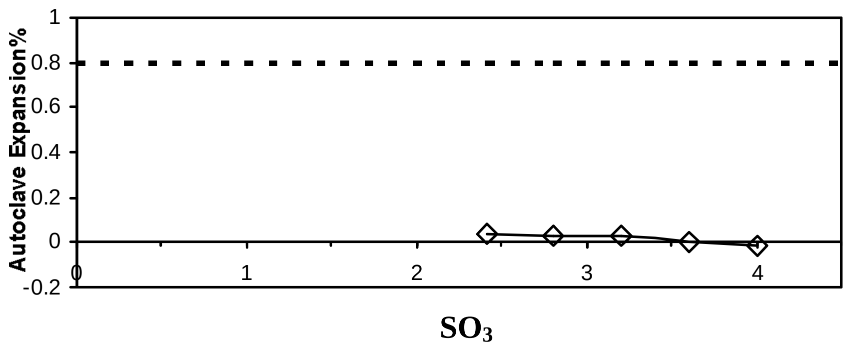
OPC (SO_3 = 2.41%)									
MgO %	2.71	2.91	3.11	3.21	3.50	4.00	-	-	-
Autoclave expansion%	0.1	0.14	0.2	0.6	2.24	**	-	-	-
SRPC (SO_3 = 2.41%)									
MgO%	1.58	2.00	2.02	2.04	2.08	2.10	2.20	2.30	2.50
Autoclave expansion%	0.04	0.17	1.56	1.84	2.28	2.8	3.7	**	**

** Disintegrated

-------The upper limit of the autoclave expansion



(a)

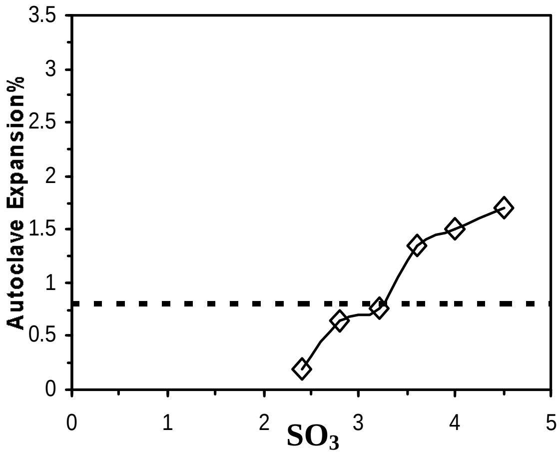


(b)

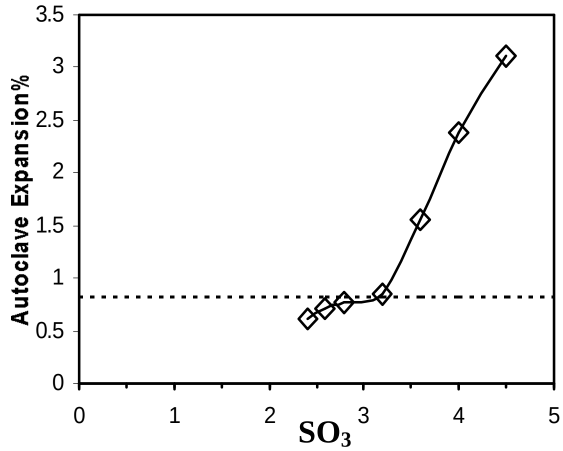
Figure 1 Autoclave expansion of cement paste versus SO_3 content in cement

a)MgO=2.71%(OPC) b)MgO=1.58% (SRPC)

-------The upper limit of the autoclave expansion



(a)



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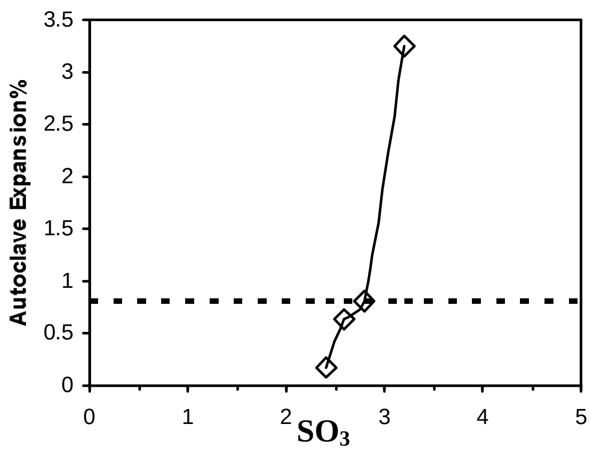


(c)

Figure 2 Autoclave expansion versus SO_3 content in cement
a) OPC(MgO=3.11%) b) OPC(MgO=3.21%) c) SRPC(MgO=2%)

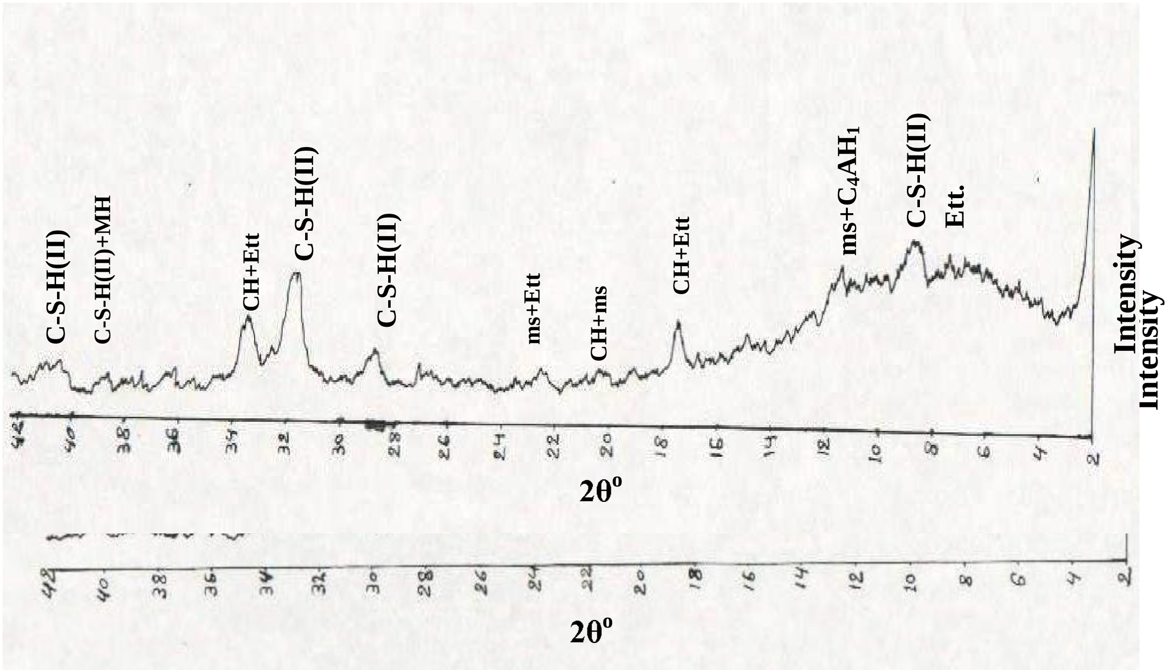


Figure 3 XRD patterns of cement paste after autoclaving
(SO_3= 2.41% and MgO=2.71%)

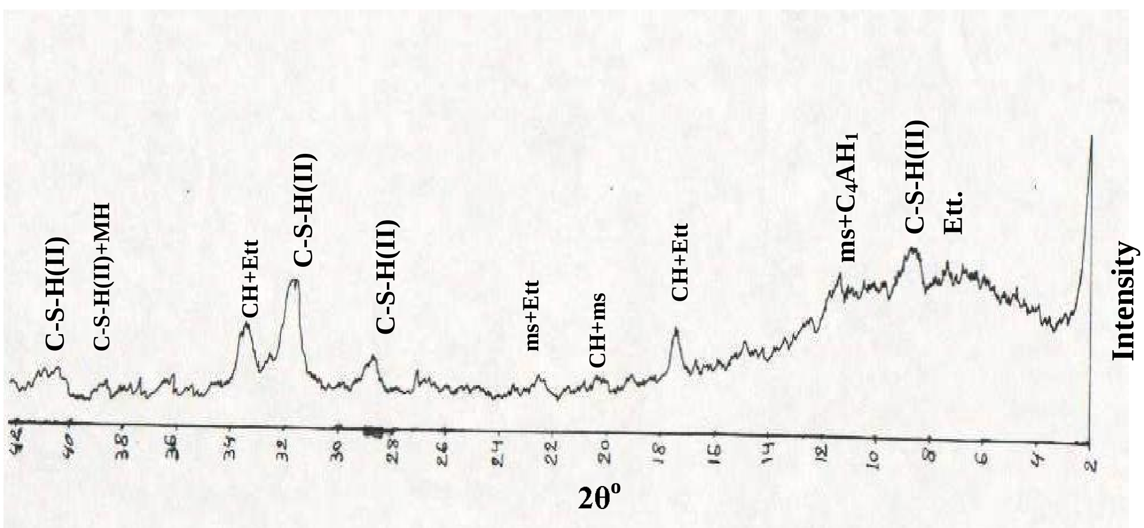


Figure 4 XRD patterns of cement paste after autoclaving (SO_3=4.5% and MgO=2.71%)

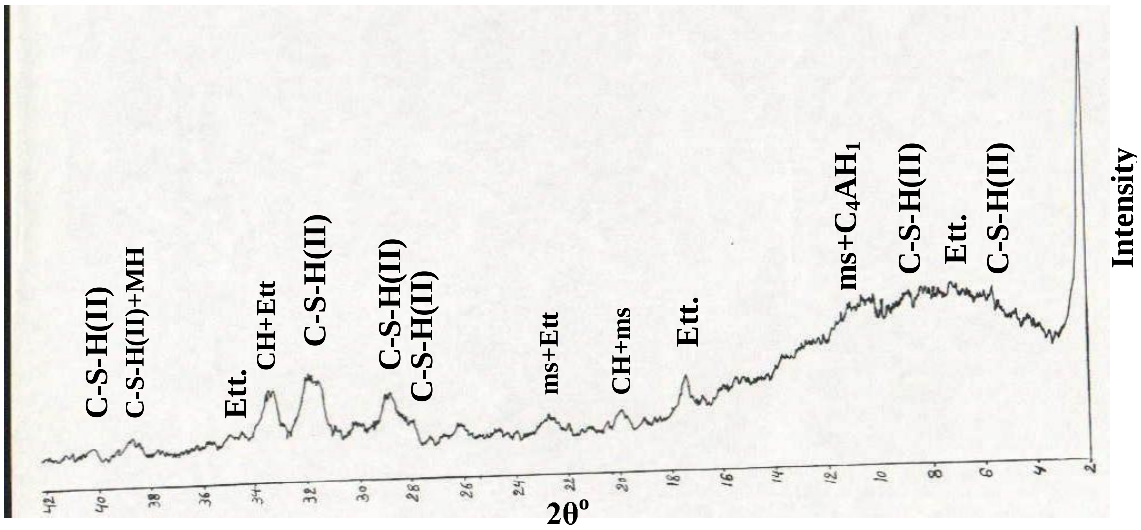


Figure 5 XRD patterns of cement paste after autoclaving (SO_3=2.41% and MgO=3.11%)

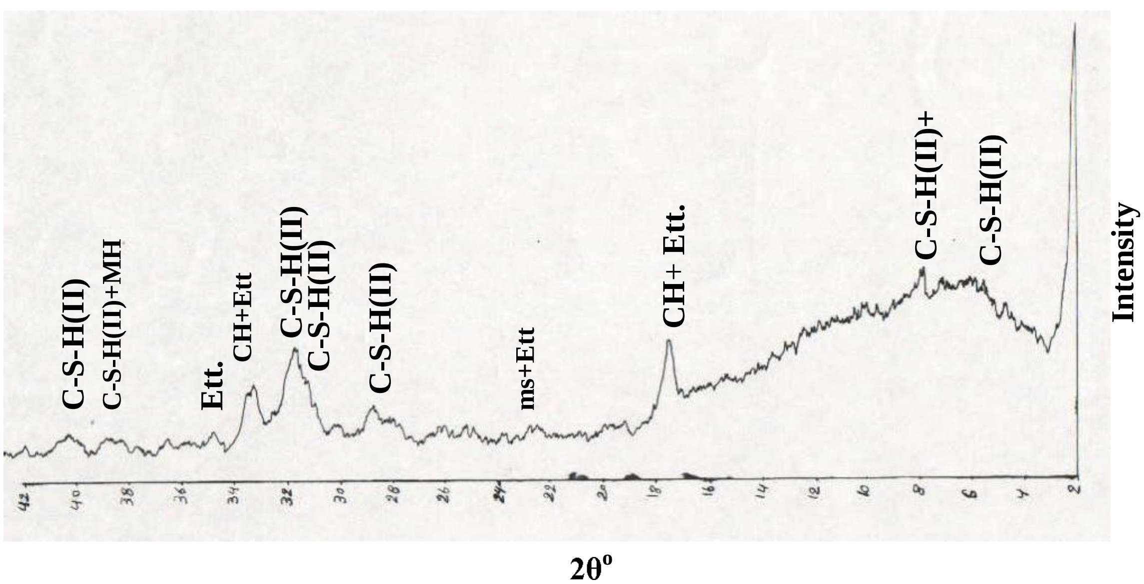
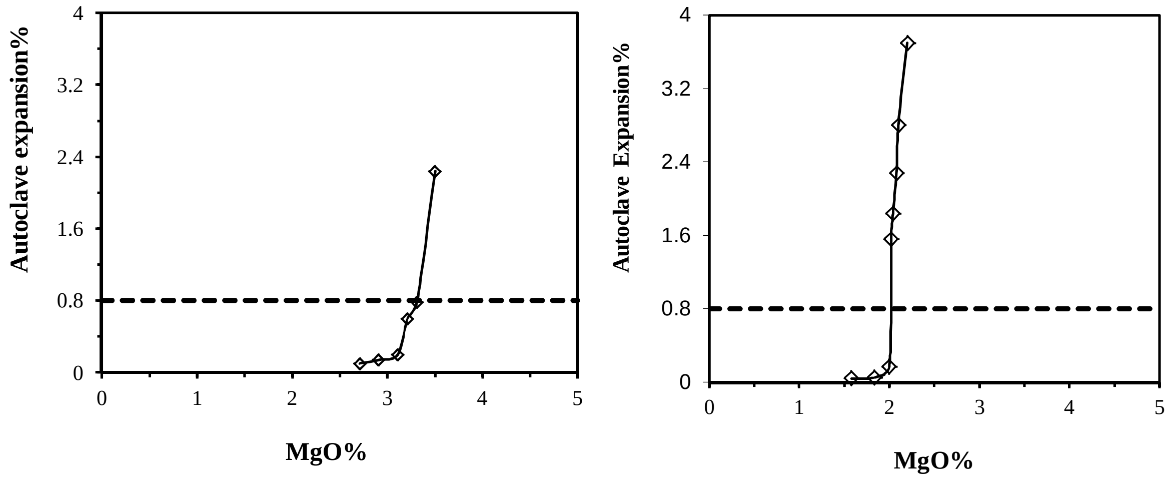


Figure 6 XRD patterns of cement paste after autoclaving (SO_3=4.5% and MgO=3.11%)

-------The upper limit of the autoclave expansion



(a) (b)

Figure 7 Autoclave expansion versus MgO content in cement (SO_3 =2.41%) a) OPC b) SRPC