Factors Affecting the Sulfate Expansion in Cement Systems

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The ettringite phase was obtained from the reaction of lime with aluminum sulfate solutions of stoichiometric and non stoichiometric sulfate concentrations at room temperature. In the sulfate-deficient solutions the gibbsite was added. The expansion of the ettringite–bearing solids and that of clinker mixed with these solids were measured in hydroxide and sulfate solutions. The expansion is higher in saturated lime solution than in alkali hydroxide and water. It increases with the sulfate content of the solids and with increasing the sulfate concentration of the curing media.
The expansion of mortars made of OPC and SRC heat treated at 85°C then stored in hydroxide and sulfate solutions at room temperature was investigated. Fineness and sulfate contents of the cements were varied. The expansion is mostly affected by fineness. The high Blaine mortars are strongly attacked by sulfate solutions. The rate of expansion of SRC mortars is faster than the OPC.

1. Introduction

The ettringite phase is the high sulfate form of the calcium sulfoaluminate hydrate. It exists indefinitely in a cement system at room temperature without initiating an expansion thread, but expands appreciably in alkali sulfate solutions [1-3]. The expansion phenomenon is also attributed to its ability to absorb water when present in the colloidal state, its gel nature increases in lime solution [4]. Its expansion is also interpreted by osmotic and crystallization pressures [5]. The formation of the ettringite phase from non stoichiometric sulfate media and its existence with sulfate amounts exceeding or less than that of the stoichiometry is reported [6-7] The DEF (ISA) phenomena was interpreted in terms of an instantaneous decomposition of the monosulfate hydrate to a sulfate-deficient ettringite upon wet storage of the heat treated cement systems without a sulfate supply from the CSH phases. The sulfate-deficient ettringite is suggested to be non expansive and gains expansive properties with the incorporation of more sulfates in its structure. This paper describes the expansion behavior of the ettringite prepared from stoichiometric and non stoichiometric sulfate solutions at room temperature. The expansion of the ettringite–bearing solids as well as that of clinker samples mixed with these solids is measured in hydroxide and sulfate solutions. Also the expansion of heat treated mortars made of ordinary Portland and sulfate

resisting Portland cements, with different fineness and sulfate doping, then stored in hydroxide and sulfate solutions at room temperature is studied.


2. Experimental

2.1. Materials

Reagent grade calcium hydroxide, hydrated aluminium sulfate and gibbsite were provided for the preparation of ettringite. Gypsum was used for doping the cements. The curing media for the different samples were water, solutions of chemically pure sodium hydroxide, potassium hydroxide, hydrated sodium sulfate and hydrated magnesium sulfate. Portland cement clinker (C), ordinary Portland cement (P) and sulfate resisting Portland cement (S) were supplied from National Cement Company (NCC), Cairo, Egypt, to prepare pastes and mortars. Their contents in the silicate phases estimated from Bogue equation, lied in the range of 49.96-52.70% for C_3S and 18.87-22.74% for C_2S. The amount of C_3A in the clinker (C) was 7.69%, in the ordinary Portland (P) 6.92% and in the sulfate resisting cements (S) 2.70%. The C_4AF and sulfate contents were 12.31, 11.98 and 15.82% and 1.68, 2.25 and 2.32 SO_3 % in the three samples respectively.

2.2. Sample preparation and expansion measurements

2.2.1. The ettringite

The preparation of the ettringite referred to its formation from the reaction of calcium hydroxide with aluminium sulfate in aqueous solution at room temperature according to Eq.(1). The mole ratio of SO_3/Al_2O_3= 3, CaO/SO_3= 2 and CaO/Al_2O_3 = 6.

$$6CaO + Al_2(SO_4)_3.8H_2O + H_2O \longrightarrow 6CaO.Al_2O_3.3SO_3.32H_2O \quad (1).$$
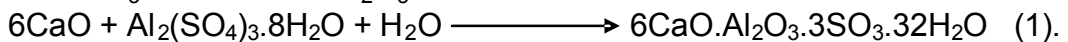
Details of the preparation of the ettringite from three different concentrations of the sulfate solutions are reported elsewhere (8-10). In a first series, it was aimed to prepare the ettringite phase with a stoichiometric amount of sulfate (3 moles), the goal of the second and the third series was to synthesize it from sulfate-deficient media (2 and 1 moles) while keeping the aluminum concentration constant. The preparation procedure included the addition of increasing concentrations of lime suspensions to the aluminum sulfate solutions. Gibbsite was added to the solutions of the second and the third series. The mole ratio of SO_3/Al_2O_3 was kept constant at 3, 2 and 1 in the three series. It was started with a mole ratio of CaO/SO_3=1, and ended to 2, 3, 6; with an end mole ratio of CaO/Al_2O_3 = 6 in all series. The mixtures were filtered off after two minutes mixing, the filtrates were analyzed and the solids were dried 1day at 50°C then identified by means of X-ray diffraction. Their morphology was characterized by means of Hitachi scanning electron microscope type S-3400N with EDAX attachment type. Their oxide composition and the free lime content were determined wet chemically.

Three samples E_3, E_2, and E_1, were chosen at the first appearance of the free lime in the solids, to study the expansion behavior of the ettringite-bearing solids and pastes prepared from clinker doped with these solids in different curing media at room temperature. The subscripts denote the number of SO_3/Al_2O_3 of the series. The expansion measurement for the ettringite–bearing solids E_3, E_2 and E_1, was performed according to a self designed method due to the difficulty of keeping the specimens well adhered. The white powders were well packed in a graduated, open end glass cylinder, 8mm in diameter and 150mm height. The top surface of the solids were wrapped with glue and dried at 50^oC for 24 hours. The zero reading was measured by means of a Precision Vernier Caliper, with a sensitivity of 0.05mm. The glass molds containing each of the E_3, E_2 and E_1 solids were immersed in separate solutions of the curing media at room temperature and kept in the vertical direction. The expansion was monitored at different time intervals starting from 2 minutes to 60 days. The curing media were distilled water, saturated calcium hydroxide solution, 0.1M sodium hydroxide-, 0.1M potassium hydroxide solutions and 0.01, 0.1 and 1M sodium sulfate solutions.

2.2.2. Pastes

Part of the as received Portland cement clinker (C_0) was intimately mixed with each of the three solids E_3, E_2 and E_1, to attain a total sulfate value of 5% SO_3. The clinker specimens doped with the ettringite-bearing solids were labeled as C_3, C_2 and C_1. The pastes were prepared by mixing the samples with a water/solid ratio of 0.3. They were casted in cylindrical shaped plastic molds, 20mm in diameter and 40mm height. The molds were covered with plastic bags, left 24 hours to harden then demolded. The zero reading was measured using a micrometer with a sensitivity of 0.01mm. The cylinders were cured in media analog to those of the E-series and for the same duration.

2.2.3 Heat treated mortars

Part of the as received cements (P and S) was doped with gypsum to increase the sulfate content from 2.32 and 2.52% to 4.30 and 4.74% SO_3 in the two cements respectively (11). The cement-gypsum powders were intimately mixed for 5 minutes in a porcelain ball mill, the resulting samples were labeled as (PS') and (SS'). A second part of the cements was milled 5 times, 15minutes each, to raise their fineness from 3218 and 3734 cm^2/g to 5170 and 5070 cm^2/g, the respective samples were denoted by (PB) and (SB). A third part was prepared to obtain cements with high sulfate content as well as high Blaine. This was achieved through further milling the (PS') and (SS') specimens up to a fineness of 5400 and 5100 cm^2/g, the respective samples were labeled as (PS'B) and (SS'B). Mortar bar prisms were made of the eight cements (P, PS', PB,

PS'B and S , SS', SB, SS'B). The cement/sand ratio used was 1:2 and the water/cement ratio 0.433. The prisms were cast in steel molds 1x1x11.25 inches with stainless steel gauge studs in their end faces in accordance with test method ASTM C 157 and ASTM 490 .Three bars were cast for each cement mix. The molds were precured one hour in air at room temperature. The surface of the molds was covered by a rubber sheet then immersed in a water bath attached to a Ni/Cr thermocouple at its bottom and a stirrer to insure temperature distribution and water circulation. Steel molds were put over the rubber covering the prisms to reduce leaching. The temperature of the bath was raised to 85 ºC with a heating rate of 20ºC/hr. The molds were kept 12 hours at 85 ºC then left to cool in the bath to room temperature with the same rate. After cooling they were demolded and the zero reading was measured according to the ASTM C490-93a by means of a length comparator device ASTM C157. The heat treated mortar prisms were immersed in the following curing media: tap water, saturated lime, 0.5M potassium hydroxide, 0.5M magnesium sulfate and 0.5M sodium sulfate solutions. The containers were well covered and stored in a closed chamber at room temperature. The length change of the bars was monitored at different time intervals from 1 day to 2-2.5 years.

3. Results
3.1. Characterization of the ettringite –bearing solids
The E_3 solid was obtained from the first series with a mole ratio SO_3/Al_2O_3 =3, at a lime addition of CaO/SO_3 =1.4 and CaO/Al_2O_3 =2.10 (9). Its free lime content was equal to 1.13 (%). Its composition is expressed by the empirical formula $C_2AS'_{1.5}$. The E_2 solid was obtained from the second series with a mole ratio SO_3/Al_2O_3 =2, at a lime addition of CaO/SO_3 =1.6 and CaO/Al_2O_3 =3.2. Its free lime content was equal to 1.37(%). Its composition is expressed by the empirical formula $C_{1.6}AS'_{1.0}$. The E_1 solid was obtained from the third series with a mole ratio SO_3/Al_2O_3 =1, at a lime addition of CaO/SO_3 =2.5 and CaO/Al_2O_3 =2.5. Its free lime content was equal to 0.43%. Its composition is expressed by the empirical formula $C_{1.5}AS'_{.0.44}$.

The X-ray diffractogram of Fig. (1) Illustrates that the E_3 solid is composed of well formed ettringite with hemihydrate as a second constituent. The phases present in the E_2 and E1 solids are quite similar and are represented by the E_2 patterns in Fig.(1).Gibbsite is seen to be the main phase composing the two solids and is present together with a weak amount of ettringite and hemihydrate. Weak gypsum patterns are observed only in the E_2 sample. The solids are denoted as ettringite-bearing because they are multiphase.
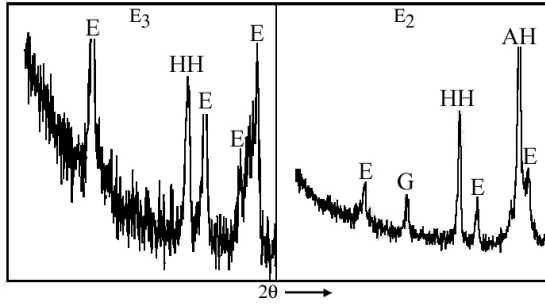
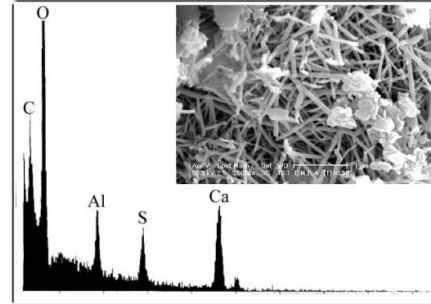Figure (1): The X-ray diffraction patterns of the E_3 and E_2 solids

Figure (2): Fiber like ettringite in the E_1 solid, deficient in sulfate

Needle shaped crystals were observed in the E_3 solid (9). Their EDAX attachment showed sulfur content fitting the stoichiometric formula of the ettringite. In the E_2 solid the ettringite appeared as needle few hundred nanometers in length embedded in a gel matrix. The ettringite detected in the E_1 solid was a fiber- like agglomerate with sulfur content less than the stoichiometric ratio of the ettringite (Fig. 2). The EDAX of the E_2 solid was similar to the E_1.

3.2. The expansion behavior
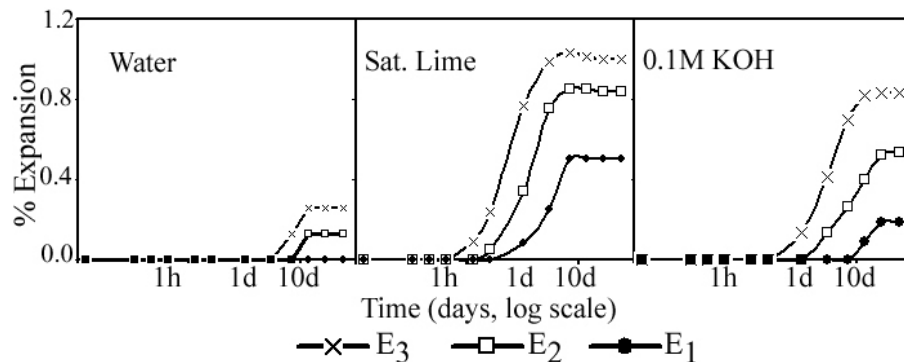3.2.1. The ettringite-bearing solids

Figure (3): The expansion behavior of the ettringite-bearing solids in water and hydroxide solutions

Figure (3) illustrates that the expansion curves of the ettringite-bearing solids follow a sigmoid shape with the following sequence: the E_1 curves are lowest, those of the E_2 lay in the middle and the E_3 curves are highest. The expansion of the solids is relatively low in water and is markedly higher in lime solution where an ultimate value of 1% is attained by E_3 after 1d curing. In alkali hydroxide solutions, represented by KOH solution, the expansion is slower than in lime solution with lower values. It is

strongly promoted by sodium sulfate solutions and values of 0.2,1 and 2%; 1, 2 and 4% and 2, 4 and 8% are measured after 60 d for the E_1, E_2 and E_3 solids in 0.01, 0.1 and 1M solutions respectively. Fig.(4) illustrates the expansion curves of the three solids in 1M solution.
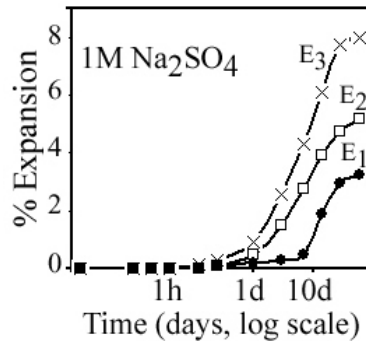

Figure (4): The expansion behavior of the ettringite-bearing solids in 1M sodium sulfate solutions

3.2.2. Pastes

The expansion curves of the pastes prepared from clinker doped with the ettringite-bearing solids follow the same sequence of the E- series i.e. the sample C_1 exhibits the lowest expansion, sample C_2 lays in the middle and C_3 undergoes the highest expansion. The expansion of the reference sample C_0 is insignificant in all media.
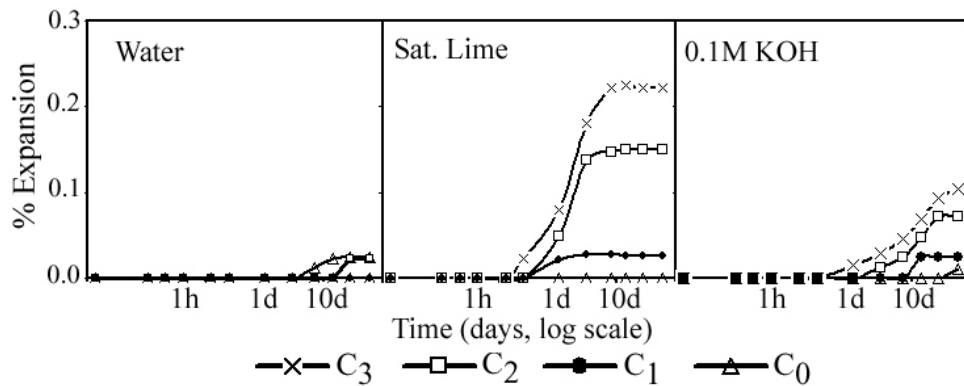

Figure (5): The expansion behavior of the ettringite- bearing pastes in water and hydroxide solutions

Fig.(5) illustrates the expansion behavior of the pastes in water and hydroxide solutions. The length change of the pastes in water is negligible. That in lime solution is noticeably higher than in water and in alkali hydroxide solutions. The ultimate values exhibited by the C_3 specimens after 60d in lime and alkali hydroxide solutions are 0.222 and 0.104%

respectively. They all show a sigmoid shape. In sodium sulfate solutions, however, the expansion increases significantly and the values increase with increasing the sulfate ion concentration of the solutions. The C_1, C_2 and C_3 specimens expand by 0.038, 0.121, 0.124% and 0.05, 0.22 and 0.334% after 60d in 0.01 and 0.1M sodium sulfate solutions. In 1M solution the increase in length was as high as 0.723, 1.9 and 2.19% after 60d, 28d and 7 d for the C_1, C_2 and C_3 samples respectively. The curves followed a sharp steep rise after 1d. Longer exposure leads to the deterioration of the C_2 and C_3 samples.

3.2.3. Heat treated mortars

Figure (6) illustrates the expansion behavior of the heat treated mortars bar prisms in potassium hydroxide, magnesium and sodium sulfate solutions at room temperature for 2-2.5 years on semilogarithmic scale of time.
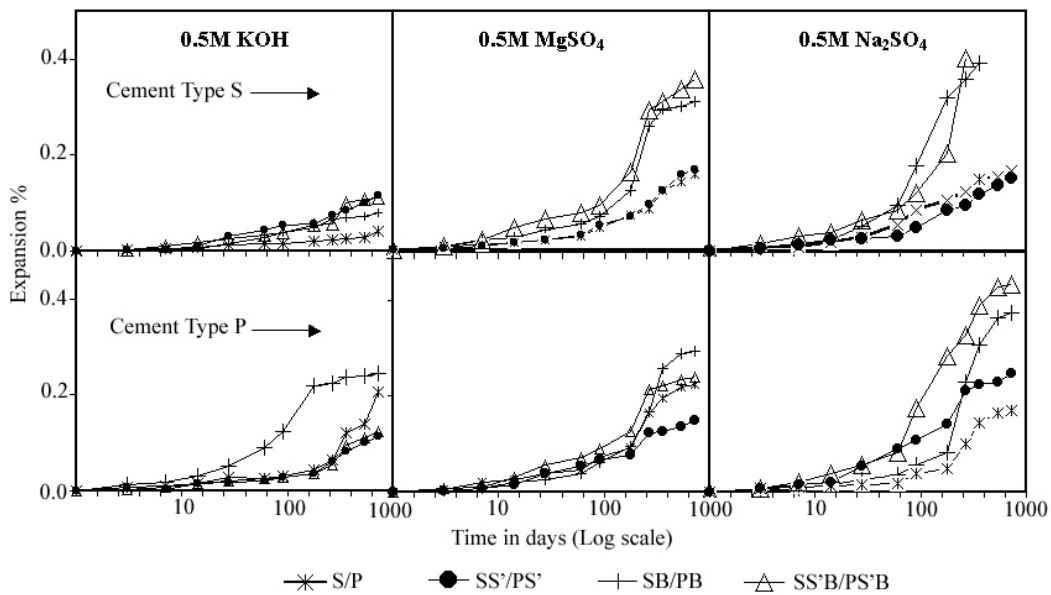

Figure (6): The expansion behavior of the heat treated mortars in potassium hydroxide and sulfate solutions.

All the heat treated mortars were sound upon storage in water at room temperature, the maximum value monitored after 2.5years was ~0.05%. Lime solution had a stronger influence on the length change of the mortars, the highest expansion value measured after 2 years was 0.1%; the shape of the curves, however, predicted a further increase in length with time. Figure (6) shows that, in KOH solution, the high Blaine ordinary Portland cement mortar (PB) expands rapidly at 28d and reaches a value of 0.25% at ~100d. This expansion is, however, reduced with sulfate doping in the sample PS'B and this curve matches with those of the

mortars made from the sulfate-doped ordinary Portland cement (PS') and the as received cement (P). They undergo a steep rise after 3 months curing. The sulfate resisting mortars are less influenced by alkali hydroxide solution, the expansion values are low and the curves tend to a sigmoid shape. After 2 years immersion in magnesium and sodium sulfate solutions, the expansion of the mortars made of the as received ordinary Portland cement (P) is ~0.22%. Those prepared from the sulfate-doped cements (PS', SS') also from the as received sulfate resisting cement (S) expand with low value of ~ 0.15% throughout the immersion duration. However, the heat treated mortars prepared from the cements with high Blaine (PB, SB) and high sulfate-high Blaine (PS'B,SS'B) are susceptible to attack by sulfate solutions. The expansion rate of the sulfate resisting mortars is faster than that of ordinary Portland and the effect of sodium sulfate is stronger than the magnesium sulfate. In magnesium sulfate solution, the mortars made of the cements with high Blaine (PB, SB) expand with values of 0.29 and 0.31% after 2 years. Gypsum doping reduces the expansion of the ordinary Portland cement mortars (PS'B) to 0.23% but that of the sulfate resisting samples (SS'B) rises to 0.35%. In sodium sulfate solution the expansion values attained after 1 and 1.5 years by the high Blaine and the high sulfate-high Blaine mortars are 0.37, 0.42 and 0.4% for the PB, PS'B, SB-SS'B respectively and all samples deteriorate, the rate of deterioration is faster in the sulfate resisting mortars.

4. Discussion

The ettringite-bearing E_3, E_2 and E_1 solids are composed of ettringite, calcium sulfate phases and an appreciable amount of gibbsite (in E_2 and E_1). In the E_3 solid, the sulfate concentration fits the stoichiometric value of the ettringite and in the E_2 and E_1 samples it is lower. Part of the sulfate, however, resides in the calcium sulfate phases. The dimensions of the ettringite crystallites embedded in the matrix vary from few microns to nanometer and their morphology change from needle to fiber-like particles parallel to the decrease of the sulfate ion concentration in the structure. The ettringite –bearing solids expand in all curing media with magnitude depending on the type of ions. The expansion values increase with increasing the sulfate concentration in the solids and that of the curing media. The ettringite being the phase responsible for the expansion in the solids is least influenced by water as the effect of hydroxyl ions is weak. The expansion is more significant in lime and alkali hydroxide solutions due to the enhancement of the aggressive action of the hydroxyl ions by potassium and calcium ions. Because of the strong electropositive character of potassium, the hydroxyl ions become freer to move than in lime solution. However, as the expansion values are higher in lime solution, another factor appears to affect the system, namely that of the incorporation of the calcium ion in the ettringite structure. This observation

suggests flexibility in the motion of the calcium ions in the ettringite column and predicts a longitudinal elongation. Further research is needed in this field.

In sulfate solution the expansion scale of the ettringite-bearing solids is around ten times higher than that occurring in the hydroxide solutions. The sulfate ions enter the channels of the ettringite structure and are quite delocalized. They interact with the surface of more than one column to balance the charge and to cause the column to bind into crystal [12].Their incorporation predicts a pressure in the x-direction of the columns. The columns need a negative charge for their balance which can be satisfied with anions such as sulfate, carbonate or others, the number of sulfates ions may therefore be less or more than the stoichiometric amount of the ettringite. In this work it is found that lowering the sulfate concentration of the solids depresses the rate of attack as well as the expansion values. The expansion curves of the solids with different sulfate concentration and different types of ettringite remain parallel and do not meet which observation deserves to be noted. This is possibly interpreted in terms of the difference in the morphology of the ettringite, the finer the crystallites the slower tendency to expansion and the lower the ultimate expansion values. The existence of gibbsite in the sample plays a dominant role in reducing the expansion.

The clinker specimens doped with the ettringite-bearing solids are equal in their sulfate content (5% SO_3). They show the same sequence of expansion as in the E-series which indicates their dependence on the type of phase composing the doping solids. The expansion rate of the clinker is reduced by solids composed of sulfate-deficient ettringite and gibbsite, the higher the deficiency of the solid in sulfate the lower the expansion values. In the C–series the expansion scale is much lower than that of the E-series but leads to the deterioration of the C_3 and C_2 samples in 1M sodium sulfate solution at values of ~2.0%. In this solution the rate of attack is tremendous and the curves change their shape from sigmoid to a steep rise, the curves, however remaining parallel and do not match.

The sulfate content of the heat treated mortars was also raised to ~ 5% SO_3 but with gypsum doping. In this series, the ettringite phase exists as a consequence of the hydration reactions in cement and its amount depends on the available aluminum. Gypsum doping leads to the formation of ettringite as long as aluminate is provided, further supply of sulfate remains as gypsum in the solids. Heat treatment of the mortars at 85°C leads to decomposition of the ettringite to the low sulfate form, followed by its reformation upon wet storage at room temperature. It also

causes gaps and voids in the pastes (13) which amount increases with fineness and with the increase of the colloidal phases due to the coagulation effect. Heat treatment promotes the precipitation of portlandite as well, similar and parallel to the effect of alkali hydroxides. In the present work the mortars are sound in water and neither the sulfate doping nor fineness had a negative influence on their expansion. In other words, the expansion due to ISA/ DEF (internal sulfate attack or delayed ettringite formation) does not occur in spite of the availability of sulfate and of space. The low alkali content in the cements (Na_2Oe= 0.417 and 0.35% for cement P and S) and their content in the ferrite phase (12 and 15% in cements P and S) are responsible for the observed soundness in water. The expansion is ,however, more significant in lime solution due to the space available for the precipitation of portlandite supplied from the curing medium, the higher the fineness the more space is available for crystallization. Calcium ions, however, might cause a longitudinal elongation of the ettringite. This factor is seen to play a minor role as the expansion of the sulfate-doped samples (PS') is insignificant. A more effective crystallization of portlandite occurs as a result of curing in potassium hydroxide solution. The penetration of the alkali hydroxide into the pores of the hardened mortars leads to the precipitation of portlandite resulting from the hydration of the paste and cause the decalcination of the calcium silicate phases with a strength weakening. Gypsum contributes further to the precipitation of portlandite as a result of its interaction with the alkali hydroxide and the formation of alkali sulfate. It may also reduce the expansion through filling the pores. The solubility of ettringite decreases in alkali hydroxide solution and does not play a dominant role in the expansion.

Magnesium sulfate reacts with calcium hydroxide of the paste forming brucite and gypsum. Under these conditions, the pH is lowered, the ettringite phase is not stable and the CSH phase decomposes to replace the lime reacted. The coagulation of the ferrite phase through heating contributes to the total space offered and the increased porosity enhances the penetration of the sulfate salt. This might interpret the faster rate of expansion of the high Blaine sulfate resisting mortars compared to that of ordinary Portland. The dramatic increase in the expansion of the heat treated high Blaine mortars in sodium sulfate solution, the rate of deterioration in the sulfate resisting mortars being faster, suggests the predominant role of gaps and voids irrespective of the aluminate concentration and the corresponding ettringite formation. Sulfate doping for cement with moderate fineness has no or little effect as seen in the results of (PS') and (SS') samples relative to those of the as received cements (P) and (C). Sulfate doping decelerates the expansion rate of the high Blaine ordinary Portland (PB) in magnesium sulfate solutions but has

no effect on the high Blaine sulfate resisting mortars (SB). All high Blaine samples, however, deteriorate in sodium sulfate solution.

To summarize, the expansion behavior of heat treated ordinary Portland and sulfate resisting cements is attributed to several factors. It is determined by the type and content of the anhydrous components and the nature of the respective hydration products. In cement with moderate fineness, the calcium silicate phases are the first responsible for the supply of portlandite and controls the behavior towards the attack by alkali hydroxide and magnesium sulfate. In these two media the ettringite does not play a role because of its instability in magnesium sulfate solution and its increased solubility in alkali hydroxide solution. C_3A provides the aluminate necessary for the ettringite formation but its presence up to 6% has no effect on the expansion of the heat treated mortars with moderate fineness in the different curing media. Excess gypsum may act as filler and even reduces the effect of Blaine in the heat treated ordinary Portland cement mortars but not in the sulfate resisting. Increased fineness is the most important factor leading to a damaging expansion in sulfate solutions, the sodium sulfate being the most aggressive. This is due to the space and voids created through heating and enhanced by the coagulation of ferric hydroxide gel offering space for the ettringite precipitation and expansion as well as of the crystallization of gypsum. In these systems the salts crystallizing in the gaps and voids are the following: 1) portlandite supplied from lime as curing media, from its crystallization by alkali hydroxides as well as from the dissolution of gypsum in alkali hydroxide solution. 2)brucite, gypsum and a possible hydrated magnesium sulfate crystals which form as a result of attack by magnesium sulfate solution 3)ettringite, gypsum and a possible hydrated sodium sulfate crystals which form as a result of attack by sodium sulfate solution.

5. Conclusion
- The sulfate concentration of the ettringite is variable. The thickness of ettringite crystallites is reduced due to the lowering of the sulfate content in the structure. A sulfate deficient ettringite may appear in a fiber-like morphology.
- The expansion behavior of the ettringite –bearing solids increases with increasing the sulfate in its structure a well as that of the curing medium. The expansion in lime is more significant than in alkali hydroxide solutions.
- The expansion behavior of the clinker–doped with the ettringite -bearing solids is similar to that of the pure phase but appears with a lower scale. The samples deteriorate in 1M sodium sulfate solution.

- The expansion behavior of heat treated mortars of moderate fineness with C_3A content $\leq$ 6% doped with gypsum does not alter the behavior of the as received cement. Increased fineness accelerates the expansion of the heat treated mortars and leads to their deterioration in sulfate solutions. The rate of damage is faster in the heat treated sulfate resisting mortars. Gypsum doping decelerates the rate of sulfate attack of the heat treated mortars made of high Blaine ordinary Portland.

6. References

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