

The Sometimes Host of Destruction



SP-177

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Ettringite—The Sometimes Host of Destruction

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Bernard Erlin



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PREFACE

The papers presented in this volume were prepared for a session sponsored by Committee 201, Durability of Concrete, on delayed ettringite formation (DEF) at the ACI Convention in Seattle, Washington, on April 9, 1997. In line with the practice and requirements of the American Concrete Institute, peer review, followed by appropriate response and revision by authors, has been used.

Delayed ettringite formation, a form of internal sulfate attack, is a subject of considerable current interest and concern, as well as of controversy. In such an atmosphere, it is not surprising that conflicting data and interpretations were presented and, as a consequence, some of them cannot be corrected. The session organizers and editors of this volume feel that all interpretations and viewpoints will serve to stimulate thinking and additional research, and help in the process of developing a more sound scientific understanding of the DEF phenomena.

Readers are urged to evaluate critically both the investigative work and the reasoning presented. There is a large body of information on this subject in the scientific literature that should also be confronted and considered when using the presented data.

We greatly appreciate the participation of Udo Ludwig, (co-author of the first published paper on DEF) for his participation in the session and for his current paper. It is to him that we dedicate this volume of papers.

The editors would like to thank all the authors for their participation in the session, their technical contributions to the DEF mysticism, and the professional attitude during the review process, as well as the reviewers for their sincere and objective evaluation of the papers.

Bernard Erlin, Chairman and Editor
E. D. Hill, Co-Chairman
J. P. Skalny, Co-Chairman

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Present State of Investigation on Damaging Late Ettringite Formation (DLEF) in Mortars and Concretes

by D. Heinz, M. Kalde, U. Ludwig , and I. Ruediger

INTRODUCTION

Since the past 25 to 30 years, preferably heat treated precast concrete members ($> 70^{\circ}\text{C}$) manufactured with high early strength Portland Cements with higher sulphate contents, under adverse exposure conditions have sometimes exhibited structural damage in the form of map cracking and loss of strength. These damages are characterized as Damaging Late Ettringite Formation (DLEF) (1).

The cause for the increased occurrence of DLEF starting about 1970 is to our opinion the world wide increase of the permissible sulphate contents of the Portland-Cements (2-5).

It is important that 1 wt.-% SO_3 can form 5 wt.-% of ettringite or 7.7 wt.-% thaumasite.

In "German directions" a maximum heat treatment (HT) temperature of 80°C is specified for concrete exposed to dry environmental conditions. For concrete exposed to intermediate or permanent wet conditions, a maximum HT temperature of 60°C is specified. Though the standard does not provide clear directions, it is believed that cements containing pozzolanic admixtures can be subjected to more intensive HT (6).

DLEF is caused by a formation, destruction and a later renewed formation of ettringite occurring preferably after HT at $\geq 70^{\circ}\text{C}$ of pastes, mortars and concretes made with high strength Portland cements. - Very early start of HT showed no significant influence on DLEF. Late or repeated HT resulted in more severe or repeated damaging. - Humidities $\leq 95\%$ at 20°C resulted up to 780 d of storage in no DLEF. - After treatment with interim some FTC and/or cured at low temperatures provoked more early and severe destruction.

Keywords: fly ash; hydraulic cements; pozzolans; sulfates; tests; wetting and drying

The use of flat prisms $1 \times 4 \times 16 \text{ cm}^3$ instead of standard prisms $4 \times 4 \times 16 \text{ cm}^3$, increasing w/c-ratios and higher proportions of coarse standard sand provoked an earlier starting of DLEF. - Portland cements and those with alumina free admixtures with higher sulphate contents $\geq 3 \text{ wt.-%}$ at $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratios > 0.45 , higher fineness and higher early heat and strengths evaluation are susceptible to DLEF. Portland cements free of $\text{C}_3\text{A}^*)$, Portland limestone cements or limestone aggregate may reduce or prevent DLEF. - Portland cements with appropriate amounts of alumina-bearing latent hydraulic slags or pozzolans maintaining the $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratio below 0.45 exhibiting no DLEF.

EXPERIMENTAL

The experimental work was done according to DIN 1164 or EN 196-1, but with stainless steel gauge points. The exceptions were that the standard sand composition and the w/c-ratio were changed and the dimensions of the mortar prisms were reduced to $1 \times 4 \times 16 \text{ cm}^3$. HT was started at prestorage times $\leq 4 \text{ h}$ in the mould with a plastic foil cover, and at $\geq 1 \text{ d}$ demoulded in a water bath, at heating rates from 15 to 23 K/h. $T_{\text{max.}}$ was 20 to 100 °C, preferably 5 h/90 °C and 4 h/95 °C. - The cooling rate was generally about 20 K/h and was occasionally varied to 5K/h, 240 K/h and 360 K/h. In two cases HT was repeated up to four times.

Further curing was generally done in water of 20 °C, and occasionally at 10 and 2 °C, in humid air in a desiccator to hinder carbonation and with interim freeze-thaw-cycles. The evaluation was done by periodic measurements of the mass, length and resonant frequency. Additional measurements of bending-, compressive- and shear strength were also made. Examination of the porosity (by gas permeability, O_2 -diffusion, water saturation, mercury intrusion), of the paste, mortar and concrete structure and of the mineralogical composition was performed by scanning electron microscopy, micro analysis and x-ray diffraction (SEM, MA, XRD). - Forty commercial cements, 22 commercial cements with anhydrite additions ground to a high specific surface area (SSA) of $10.000 \text{ cm}^2/\text{g}$ in order to reach the max. SO_3 acc. to DIN 1164, and 28 laboratory cements made of technical clinker and admixtures were examined.

*) the usual shortening are utilized: C-CaO, M-MgO, A- Al_2O_3 , F- Fe_2O_3 , s- SO_3 , S- SiO_2 , c- CO_2 , H- H_2O

RESULTS AND DISCUSSION

Fundamentals of DLEF

The DLEF briefly is the formation of ettringite through the reaction of the calcium aluminatic ferritic phases and the soluble sulphates of the cements in the presence of water. This formation proceeds as long as the sulphate ions in the solution are enough to form and stabilize ettringite. Subsequently, instable monosulphate hydrate (C_3ACsH_{12}) and solid solutions of other mono-phases are formed with the parallel dissolution of the previously formed ettringite and the remaining aluminatic ferritic phases from the cements (7, 8, 9, 10). Parallel to the ettringite formation and dissolution, a major part of the sulphate ions are reversibly bound into the CSH-phases (11). - The stability of the previously formed ettringite is increased with higher SO_3/Al_2O_3 -ratios by mass (7, 10) of the cement and is decreased with increased fineness of the cement and increased temperature at the reaction (10). - Under moist conditions, at and below room temperature ettringite again becomes the stable phase and may cause DLEF (12, 13).

Safe HT-Temperature

The influences of the HT-temperature between 20 and 100 °C on the durability of mortars were examined twice. The duration of HT was calculated with the Saul-formula revised by Mironov and Ganin:

$$t_T = t_{20} \left(\frac{20 + 30}{T + 30} \right)^2$$

t_T = time interval with average concrete temperature in h

T = average concrete temperature at the time interval in °C

PC 55-III with 3.9 wt.-% SO_3 , $SO_3/Al_2O_3 = 0.69$ and $SSA = 5720$ cm^2/g was used. In the first case only at treatment temperatures ≥ 90 °C expansions of about 7 to 10 mm/m after 750 d were measured (14, 15). - In the second case mortars with the same cement showed expansion, loss in resonant frequency and increase of mass with HT at 75 to 100 °C during about 1000 days of water storage. DLEF started at HT of 100 °C after 14 days, at HT of 90 °C after 42 days, at HT of 85 °C after 70 days, at HT of 80 °C after 6 months and at HT of 75 °C after about 1 year. The max. expansion was about 10 mm/m with a 100 °C HT and the minimum was about 1 mm/m with a 75 °C HT (16, 17). However, it must be considered that higher expansions sometimes coincided with lower resonant frequencies and vice versa. This means, that there is less correlation between resonant frequencies and

expansion in mortars. - The XRD, directly after HT, showed with increasing treatment temperatures up to 60 °C decreasing intensities of the ettringite and increasing AFm-Phases. At 70 °C no ettringite could be identified and at 90 and 100 °C a strong intensity drop of the AFm-Phases was visible. - Three years of storage in water at 20 °C provokes strong DLEF, especially in mortars with HT at 80 °C. Mortars with HT at 60, 70 and 75 °C showed medium and those treated at 50 °C and the untreated ones showed low or no DLEF (16, 17). - Other experiments (18) performed with 70 °C HT mortar showed after 10 freeze-thaw-cycles (FTC) in water during the storage period. - This means, that the maximum **HT for Portland cements should be ≤ 70 °C**. This limitation corresponds with other data or opinions (19, 20). Nevertheless, in special cases, even at lower temperatures, mortar or concrete can exhibit DLEF (21).

Precuring period and intensities of heat treatment

Significant importance is given in the "German directions" (6) as well as in other references, for example Sylla (22) and Neck (23), to sufficient pre-storage of concretes. In case of HT of mortars in the standard steel molds **very early start of HT results in no significant influence on DLEF** in comparison with longer precuring (17, 24), however, it can physically damage the heat treated paste, mortar or concrete by air or steam pressure especially if the HT takes place at the stage of demolding. - Heat treatment after 1 year precuring or up to three times repeated HT resulted in a higher value of expansion and corresponding decrease of resonant frequencies. **Late and repeated HT provoked a direct decrease of resonant frequencies** but no significant weight or dimensional changes. This direct decrease of resonant frequencies can be attributed to the dissolution of the ettringite and formation of AFm-phases and/or a recrystallization of CSH due to HT. Further water curing leads to further decrease of resonant frequencies and increase of weight and expansions (13-15). At repeated HT, interim XRD and SEM plus MA examinations showed the formation of monophases in cracks and interfaces and the reformation of damaging pure Al-ettringite. **Excessive SO_4^{2-} due to the influence of HT again migrates into the surrounding cement paste and migrates back at lower temperatures to reform damaging At-phases together with the Am-phases** (13, 25).

After-Treatment

After-Treatment of the heat treated mortars, deviating from 20 °C water storage, at 2 and 10 °C in water or with interim 10 FTC at -25 and +20 °C results in an earlier appearance of measurable DLEF (13, 17, 26). The influence of interim FTC is confirmed by Shao et al. (27). In cases where

the after-curing was done at 20 °C in a water basin with interim 10 FTC (+20/-25 °C) in water the specimen are still surviving after a total period of 14 years. But all specimen restored after 160 days from 20 to 2 °C in a water basin are completely disintegrated between 4 and 5 years after curing. Unfortunately no XRD-examinations were done. But together with other experiences (28) it can be concluded that this disintegration at low temperature wet or water curing is in all probability due to a not expanding but structure loosening formation of thaumasite ($\text{CS}'\text{Cc}'\text{Cs}'\text{H}_{14.5}$).

With mortar prisms $1 \times 4 \times 16 \text{ cm}^3$ the after-treatment at 20 °C and a relative humidity greater than 95 % instead of water curing produces DLEF starting from 14 days to > 1 year delayed. After 120 days storage, from 20 °C/60 % r.h. to 100 % r.h., rearranged prisms showed increased weight, increased expansion and decreased resonant frequency. Storage at 20 °C and relative humidities $\leq 95 \%$ up to 780 d of storage period, did not result in any measurable DLEF. This is established by XRD examinations as no ettringite formation could be detected (13).

Differing mortar compositions and specimen size

Decreasing w/c-ratios of 0.7, 0.5, 0.45 and 0.4 resulted in delayed starting of the expansion between 90 and 180 d. After about 8 years the expansions of the mortar amounted to 11 - 12 mm/m. With w/c = 0.4 it proceeds up to 2 years slightly, up to nearly 8 years, increasingly reaching about 7 mm/m without completion of the reaction. The resonant frequencies decreased with increased w/c-ratios and showed further decrease with the starting of the DLEF (13, 17, 24).

Higher proportions of coarse standard sand 0.5 FS : 0.5 MS : 2.0 CS or 0.5 FS : 1.5 MS : 1.0 CS in the standard mortar with a lower w/c of 0.4 and 0.45 lead to an earlier starting of the DLEF. Higher proportions of fine standard sand 2.5 FS : 0.5 MS : 0 CS at a w/c = 0.7 or the entraining of 14 % air voids into the standard mortar resulted in no DLEF after curing in water at 20 °C for a period of about 8 years. Interim 10 FTC resulted in earlier starting of the DLEF. The earlier starting DLEF with increased amounts of coarse standard sand can be explained by the finding of Johansen et al (29). **The expansion occurs relatively evenly throughout the cement paste causing gaps between aggregates and cement paste whose width is proportional to the aggregates size.** Thus, the more coarse standard sand accelerates, and more fine standard sand retards the formation of DLEF. But the highest retardation is obtained with neat cement paste (30, 31). Own checking (32) of paste HT also resulted in a prolonged induction period before starting DLEF though the work was done with only $1 \times 4 \times 16 \text{ cm}^3$ flat cement paste prisms.

In order to accelerate the starting of DLEF, instead of $4 \times 4 \times 16 \text{ cm}^3$ sized DIN 1164/EN 196-1 standard prisms, $1 \times 4 \times 16 \text{ cm}^3$ flat prisms were used and lead to a reduction of the starting of DLEF from 6 month to 7 days (24, 33). The same reduction could have been derived from the results obtained by Heinz (13).

The prevention of DLEF is achieved by the exchange of the standard sand by crushed limestone of the same grain size distribution with raised w/c-ratio of 0.5 to 0.6 in order to get a sufficient flow of the otherwise standard mortar. The PC 55-IV with 3.73 wt.-% SO_3 , 0.48 wt.-% Na_2O_e , 0.82 wt.-% MgO and a SSA of $5230 \text{ cm}^2/\text{g}$ was used. The maximum HT was $80^\circ\text{C}/9 \text{ h}$. After a period of 12.2 years a max. expansion of 1.1 mm/m and no reduction in resonant frequency was measured. Interim FTC exerted no higher values that could be contributed to DLEF (18, 34, 24). Scrivener and Lewis (34) measured 1.3 mm/m expansion that is still continuing measured under similar conditions but higher HT intensity of $12 \text{ h}/90^\circ\text{C}$, after about 3 years water curing at 20°C .

Cement type and quality

In the first research program due to an incident a high intensity HT $1 \text{ day}/80^\circ\text{C}$ and $6 \text{ h}/100^\circ\text{C}$, was used with two high strength PC 55 A and B with $\text{SO}_3/\text{Al}_2\text{O}_3 = 0.75$ and 0.70 . The expansion and the decrease of resonant frequency started after about 1 and 2 months of 20°C -water curing. The ultimate expansions are about 6 and 13 mm/m. - The substitution of 8 wt.-% of both cements by finely ground limestone resulted in only a small or no reduction of the expansion (15). - **The exchange of PC 55 B by PC 45 HSR (higher sulphate resistance) at constant SO_3 of 4.0 wt.-%** showed an expansion of 1.5 mm/m, after very intensive HT and a 20°C water curing of about 19 years. The same values were measured for the untreated mortars with PC 55 B or PC 45 HSR respectively. **From this it was concluded that HT with PC-HSR (with little or no C_3A) mortars is harmless (15).** - However, later experiments with standard mortars after $4 \text{ h}/95^\circ\text{C}$ HT with one type 55 and four type 45 C_3A -free cements in delivery state and with the max. SO_3 of 4.0 and 3.5 wt.-% acc. to DIN 1164 showed in four from 10 cases expansions > 3 to 7.6 mm/m after about 6 years of 20°C curing (24). The PC 55 HSR is in addition to a low Na_2O_{eq} of 0.46 wt.-%, also has a low A/F-ratio of 0.49. Thus, the chemistry and the fineness of the HSR cement may influence its HT-stability.

In earlier experimental work (15, 16) cements with 30 wt.-% of fly ash or Bavarian trass or with 50 wt.-% of ground gbfs, and subjected to very intensive HT with the same SO_3 -content as in the PC 55 B of 4.0 wt.-% showed no damage after now about 19 years of subsequent 20°C water storage. Repeated experiments with gbfs and fly ash in amounts of 10, 20 and

30 wt.-% replacement of PC 55-III or IV without SO_3 adjustment (20, 34) or with industrial EPZ/CEM II/B-S and HOZ/CEM III A to C (24) showed after HT at 90 and 95 °C that 10 wt.-% PC-replacement are not enough to hinder DLEF. In one case the EPZ with the limit SO_3 -content of 3.5 wt.-% exhibits > 9 mm/m. **The HOZ behave in every case safe (24).**

The same was done with silicious fly ash as replacement of PC 55 (20, 34). The exchange of 10 wt.-% PC 55 was unsufficient and resulted in an expansion of 7.7 mm/m. **The exchange of 20 wt.-% of PC 55 by fly ash and the fly ash cements with and without additional anhydrite brought safe HT.**

Moreover Portland cements blended with appropriate amounts of alumina-bearing latent hydraulic slags or pozzolans showed in contrary to plain Portland cements only low or no loss in strength, after intensive HT.

The exchange of 5 and 10 wt.-% of the PC 55-IV by silica fume (34) resulted in a reduction of the mortar expansion from 13.6 mm/m to 11.5 mm/m and 6.7 mm/m, respectively, after 5 h/90 °C HT and subsequent water storage at 20 °C.

Finally the industrial PKZ/CEM II/A-L (24) in delivery state and with additional finely ground anhydrite to reach the limitation of the standard created no DLEF at 4 h/95 °C HT and after 7 years of 20 °C water curing. The explanation of the save HT with PKZ-mortars can be given by the stabilisation of the early formed ettringite in the presence of sufficient CaCO_3 according to Ghorab's (14) results at the experimental work in the neat system $\text{C}_3\text{A}-\text{CaCO}_3-\text{CaSO}_4-\text{Ca}(\text{OH})_2-\text{H}_2\text{O}$ at 80 °C.

Experimental work with the PC 55-III (17, 20) showed that excess sulphate contents by anhydrite additions of 6.3 and 8.6 wt.-% leads to a direct starting of expansion after 5 h/90 °C HT of the mortar. **By XRD even direct after HT the presence of ettringite is established. From this it is quite clear that the otherwise observed decomposition of ettringite during a 90 °C HT is not caused by a thermal instability.** Moreover initially formed ettringite reacts with free aluminate to form monophases. Parallel sulphate and aluminate ions get increasingly bound in the CSH. **Increased SO_3 -contents increasingly stabilize the ettringite and further sulphate is present in the pore solution (36) to form directly after HT ettringite connected with DLEF.** - With the SO_3 -content of the delivered cement the DLEF starts later after about 6 month with a max. expansion of 11.5 mm/m. - By the addition of finely ground clinker of the same plant and with the same SSA to the PC 55-III the total SO_3 -contents were reduced to 3.5, 3.0, 2.5 and 2.0 wt.-%. The DLEF after HT with the corresponding mortars started again later after about

365 and 500 days and resulted in decreased max. expansions of 10.5 and finally 3.8 mm/m, respectively with the cements containing 3.5 and 3.0 wt.-% SO_3 . With cements with 2.5 and 2.0 wt.-% SO_3 the expansion amounts after about 14 years to 0.9 mm/m. That means **the sulphate content of the Portland cements save at HT should be < 3 wt.-%.**

At the evaluation of the potential formation of DLEF in mortars and concretes the ratio of soluble SO_3 and active Al_2O_3 would be of special interest (20, 34). The soluble SO_3 is preferably the added sulphate and the soluble sulphates of the clinker (37). The sulphates incorporated in the less reactive belite as solid solutions are considered to be predominantly insoluble. The alumina in C_3A is active. The alumina in the $\text{C}_2(\text{A}, \text{F})$ solid solution becomes, with increasing iron oxide content, less active. The alumina in pozzolans (fly ash, trass, calcined clays etc.) and in blast furnace slags also is only active to a smaller extent depending on its surface area and chemical stability. So far, these influences on reactivity of the SO_3 and Al_2O_3 could not be considered. Therefore the ratio of total SO_3 and Al_2O_3 were used: $\text{SO}_3/\text{Al}_2\text{O}_3$.

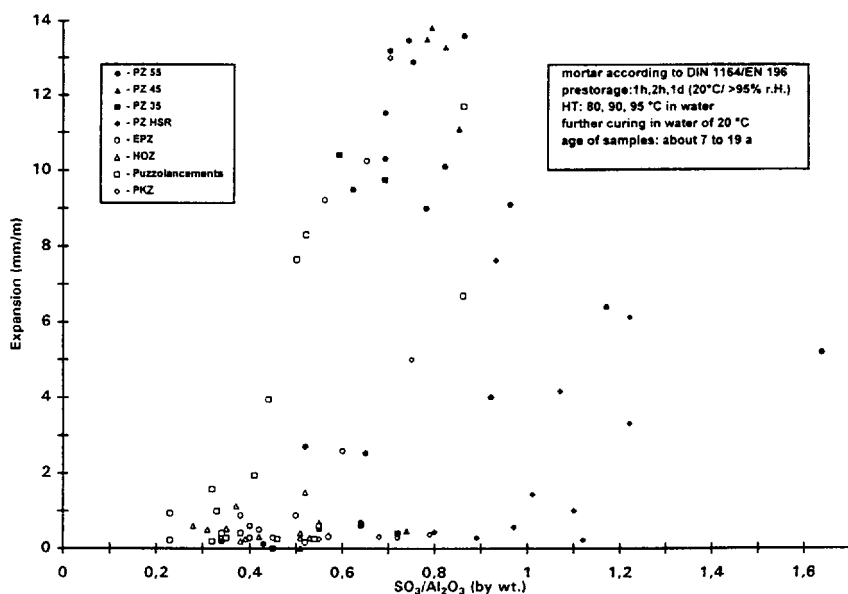


Fig. Max. expansions of 90 HT different cement mortars in dependence of the $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratio by mass

In the figure the max. expansions of 90 different heat treated cement mortars were registered against the $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratio. The mortars with PC 55 showed decreased at ratios < 0.5, at > 0.5 to 1.0 maximum and at > 1.0 again

decreased expansions. The PC 45 and 35, only with high surface areas and/or higher $\text{Na}_2\text{O}_e \geq 1.0$ wt.-%, showed high pessimum expansions. The HSR-Portland-cements exhibit none to medium expansions at ratios > 0.8 . The EPZ gave higher expansions at slag contents of only 10 wt.-%. The HOZ resulted in expansion of 1.5 mm/m after about 19 years water curing. Cements with low pozzolan contents of 10 to 15 wt.-% or with a high $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratio of 0.85 (with alumina-free silica fume) reached higher expansions ≥ 4 mm/m. The PKZ produced, by mixing 92 wt.-% PC 55 A or B with 8 wt.-% finely ground limestone, exhibited higher expansions > 5 mm/m. The other heat treated PKZ-mortars are safe after HT of 4 h/95 °C and about 7 year 20 °C water curing.

CONCLUSION

Plain or blended Portland cements may exhibit renewed and/or damaging late ettringite formation (DLEF) either with or without heat treatment (HT).

With increasing HT, particularly ≥ 70 °C, the primary ettringite formation and its subsequent reduction or dissolution is finished quite early and completed. This may give an early and high potential for DLEF.

Very early starting HT results in no significant influence on DLEF. After-treatment of the heat treated mortars, deviating from the normal 20 °C water curing to 2 and 10 °C in water or interim FTC, results in an earlier appearance of DLEF and may result subsequently to an entire disintegration in all probability due to thaumasite formation. - Due to the high water demand the DLEF is starting from the surface of a cement paste, mortar or concrete. Therefore test specimen should be as narrow as possible.

The chemical characteristics of Portland cements and those with alumina-free admixtures like silica fume susceptible of DLEF are higher sulphate contents ≥ 3 wt.-% and $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratios > 0.45 . Higher $\text{Na}_2\text{O}_e > 1.0$ wt.-% contribute to DLEF by increasing the early rate of hydration. - The physical features are higher surface areas, water demands, early heats of hydration and high early strengths. - Portland cements free of C_3A or those with ground limestone admixtures are less susceptible to DLEF. - Increased HT with plain Portland cement results in significantly decreased final strength.

Portland cements blended with appropriate amounts of alumina-bearing latent hydraulic slags (blast furnace slag) or puzzolans (silicious fly ash, trass, calcined clays) must keep the $\text{SO}_3/\text{Al}_2\text{O}_3$ -ratio < 0.45 to exhibit no DLEF. These cements showed after intensive HT an increase of the early strengths and only very low or no losses in final strengths.

LITERATURE

- (1) Day, R. L.: „The Effect of Secondary Ettringite Formation on the Durability of Concrete: A Literature Analysis“, Portland Cement Association 1992
- (2) DIN 1164 „Portlandzement, Eisenportlandzement, Hochofenzement“, Ausgabe 12.58
- (3) DIN 1164 „Portland-, Eisenportland-, Hochofen- und Traßzement; Begriffe, Bestandteile, Anforderungen, Lieferung“, Ausgabe 6.70
- (4) DIN 1164-2 „Zement - Teil 2 - Übereinstimmungsnachweis“, Ausgabe 11.96
- (5) prEN 197-1 „Cement-composition, specification and conformity criteria - Part 1: Common cements“ Draft 9.96
- (6) Richtlinie zur Wärmebehandlung von Beton, 9.1989, Beuth Verlag, Berlin-Köln, Vertriebs-Nr. 65013
- (7) Jäger, P.: „Untersuchungen der Hydratation von Tricalciumaluminat, Dicalciumferrit und Calciumaluminatferriten mit Calciumhydroxid und Calciumsulfaten“, Diss. RWTH Aachen 1966 mit Schwiete, H. E. und Ludwig, U.: Zement-Kalk-Gips 17 (1964), S. 229 - 236
- (8) Ludwig, U.: „50 Jahre Institut für Gesteinshüttenkunde - 26 Jahre Lehre und Forschung auf dem Gebiet der Bindemittel“, Tonind.-Ztg., 102 (1978), S. 358 - 369
- (9) Ghorab, H. Y.: „Thermische und chemische Stabilität der Calciumaluminatsulfathydrate“, Diss. RWTH Aachen 1979; mit Ludwig, U.: „Modellversuche zur Klärung von Schadensursachen an wärmebehandelten Betonfertigteilen, Teil 1: Zur Stabilität von Monophasen und Ettringiten“, TIZ 105 (1981), Heft 9, S. 634 - 640
- (10) Mori, H.; Minegishi, K.: „Effect of the Temperature on the Early Hydration of the System $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 2\text{H}_2\text{O}\cdot\text{Ca}(\text{OH})_2\cdot\text{H}_2\text{O}$ “, 5. Int. Symp. Chem. Cem. Tokio 1968, Vol. 2, S. 349 - 361
- (11) Odler, I.: „Interaction between gypsum and the C-S-H phase formed in C_3S hydration“, 7th International Congress on the Chemistry of Cement, Vol. IV, Paris 1980, S. 493 - 495
- (12) Mcedlov-Petrosjan, O. P.: „Thermodynamik der Silikate“, VEB-Verlag für Bauwesen, 2. Aufl. Berlin 1966, S. 251 ff.
- (13) Heinz, D.: „Schädigende Bildung ettringitähnlicher Phasen in wärmebehandelten Mörteln und Betonen“, Diss. RWTH Aachen, 1986

- (14) Ghorab, H. Y.; Heinz, D.; Ludwig, U.; Meskendahl, T.; Wolter, A.: „On the Stability of Calcium Aluminate Sulphate Hydrates in Pure Systems and in Cements“, VII. Int. Congr. Chem. Cem., Vol. IV, Paris 1980, S. 496 - 503
- (15) Heinz, D.; Ludwig, U.; Nasr, R.: „Modellversuch zur Klärung von Schadensursachen an wärmebehandelten Betonfertigteilen, Teil II: Wärmebehandlung von Mörteln und späte Ettringitbildung“, TIZ 106, Heft 3 (1982), S. 178 - 183
- (16) Heinz, D.; Ludwig, U.: „Ettringitbildung in Mörteln und Betonen - kein Problem mehr?“, 8. ibausil, Weimar 1982, Tagungsbericht Bd. 1, S. 34 - 39
- (17) Heinz, D.; Ludwig, U.: „Mechanism of Secondary Ettringite Formation in Mortars and Concretes Subjected to Heat-Treatment; Concrete Durability“, Katherine and Bryant Mather, Int. Conf. 27. April - 1. Mai 1987, American Concrete Institute, Detroit, Vol. 2, S. 2059 - 2071
- (18) Redjai-Razavi, H.: „Einfluß der Vorlagerung auf die Schadensentwicklung wärmebehandelter Mörtel und Feststellung potentieller Gefährdung durch Wärmebehandlung“, Dipl.-Arb. 1990, RWTH Aachen
- (19) Lawrence, C. D.: „Mortar Expansions due to Delayed Ettringite Formation, Effects of curing period and temperature“, Cem. Conc. Res. Vol. 25, No. 4, 1995, S. 903 - 914
- (20) Kelham, St.: „Effects of cements composition and hydration temperatures on volume stability of mortar“, Proc. 10th Int. Cong. Chem. Cement, Gothenburg, June 1997, Vol. 4 Performance and durability, 4 IV 060-8 pp
- (21) Stark, J.; Bollmann, K.: „Ettringite formation - A Durability Problem of Concrete Pavements“, Proc. 10th Int. Cong. Chem. Cement, Gothenburg, June 1997, Vol. 4 Performance and durability, 4 IV 062-8 pp
- (22) Sylla, H.-M.: „Reaktionen im Zementstein durch Wärmebehandlung“, beton 38 (1988), S. 449 - 454
- (23) Neck, U.: „Auswirkungen der Wärmebehandlung auf Festigkeit und Dauerhaftigkeit von Beton“, beton 38 (1988) S. 488 - 493
- (24) Ludwig, U.: „Probleme der Ettringitrückbildung bei wärmebehandelten Mörteln und Betonen“, 11. ibausil, Weimar, 6.-10. Mai 1991, Band 1 Beton- und Bauelementproduktion - Bindebaustoffe, S. 164 - 177

- (25) Heinz, D.; Ludwig, U.: „Mechanism of Subsequent Ettringite Formation in Mortars and Concretes After Heat-Treatment“, 8th Int. Cong. on the Chemistry of Cement, 22.-27. September 1986, Rio de Janeiro, Brasilien, Vol. V., S. 189 - 194
- (26) Heinz, D.; Ludwig, U.: „Einflüsse auf die Schadreaktionen in wärmebehandelten Betonen“, Baustoffe 85, Bauverlag Wiesbaden und Berlin, S. 105 - 110
- (27) Shao, Y.; Lynsdale, C. J.; Lawrence, C. D.; Sharp, J. H.: „Deterioration of Heat Cured Mortars due to the Combined Effect of Delayed Ettringite Formation and Freeze/Thaw Cycles“, prepared for publication in Cement & Concrete Research, 1997
- (28) Mehr, S.: „Entwicklung von sulfatbeständigen Mörteln auf Zement-Hüttensand-Puzzolan-Basis“, Diss. RWTH Aachen, 1986; mit Ludwig, U.: „Destruction of Historical Buildings by the Formation of Ettringite or Thaumasite“, 8th Int. Cong. on the Chemistry of Cement, 22.-27. September 1986, Rio de Janeiro, Brasilien, Vol. V, S. 181 - 188
- (29) Johansen, V.; Thaulow, V.; Idorn, G.: „Dehnungsreaktionen in Mörtel und Beton“, ZKG 47 (1994), S. 150 - 155
- (30) Odler, I.; Chen, Y.: „Effect of cement composition on the expansion of heat cured cement pastes“, Cement & Concrete Res., Vol 25 (1995), S. 853 - 862
- (31) Yang, R.; Lawrence, C. D.; Sharp, H. J.: „Delayed Ettringite Formation in 4-year old cement pastes“, Cement & Concrete Res., Vol. 26 (1996), S. 1649 - 1659
- (32) Abdou, L.: „Quantitative Bestimmung von Ettringitrückbildung an wärmebehandelten Zementpasten“, Studienarbeit RWTH Aachen, 1997
- (33) Winkler, K.: „Einfluß der späten Ettringitbildung auf die Schadensbildung an wärmebehandelten Mörteln“, Studienarbeit RWTH Aachen, 1991
- (34) Heinz, D.; Ludwig, U.; Rüdiger, I.: „Nachträgliche Ettringitbildung an wärmebehandelten Mörteln und Betonen“, Betonwerk und Fertigteil-Technik, Heft 11/89, S. 56 - 61
- (35) Scrivener, K.; Lewis, M.: „A Microstructural and Microanalytical Study of Heat Cured Mortars and Delayed Ettringite Formation“, Proc. 10th Int. Cong. Chem. Cem. Gothenburg, June 1997, Vol. 4, p. 4 IV 061 and Lewis, M., PhD-Thesis, University of London

- (36) Herr, R.; Wieker, W.; Winkler, A.: „On the Chemical Equilibria of Hydroxide and Sulphate Ion Concentrations in the Pore Solution of Thermal Treated Cement“, Proc. of the 5th National Conf. on Mechanics and Technology of Composite Materials, Varna/Bulgarien, 29. September - 1. Oktober 1988, S. 550 - 555
- (37) Klemm, W. A.; Miller, F. M.: „Plausibility of Delayed Ettringite Formation as a Distress Mechanism - Considerations at Ambient and Elevated Temperatures“, Proc. 10th Int. Cong. Chem. Cem. Gothenburg, June 1997, Vol. E, p. 4 IV 059 10 pp

SP 177-2

Solubility of Sulfates in High SO₃ Clinkers

by V. Michaud and R. Suderman

Synopsis: Changes in the cement manufacturing process such as the use of higher sulfur fuels have tended to raise clinker sulfate levels and SO₃/alkali ratios. As a consequence, interground gypsum additions to cement have dropped because more sulfate is available from the clinker. Also, these clinker sulfates tend to be available as double sulfate salts; calcium langbeinite instead of potassium sulfate.

What is the impact of clinkers with high SO₃ level on concrete performance; mainly on its workability and durability ? The aim of this study is to provide some answers to this question.

Cements made from either high SO₃ clinker or low SO₃ clinker and gypsum or hemihydrate, but with a given chemical composition, have been simulated by pure phase materials and hydrated up to one hour. Calcium langbeinite is rapidly dissolved. Because of its dissolution rate and ability to form "blocking ettringite", high calcium langbeinite clinkers should provide improved rheological properties. Moreover, cements made with clinkers containing significant quantities of calcium langbeinite should have a similar workability and durability to a cement made with a low sulfate clinker to which larger quantities of gypsum have been added.

The dissolution rate of anhydrite potentially existing in very high SO₃/alkali clinker has also been simulated. Experiments indicate that it dissolves and reacts quite quickly so that it should not provide any durability problem if present in cement and concrete.

Keywords: anhydrite; calcium; clinker; durability; rheology; workability

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INTRODUCTION

Changes in the cement manufacturing process such as the use of higher sulfur fuels, reduced dust wasting and lower SO_x emissions have tended to raise clinker sulfate levels and SO₃/alkali ratios. As a consequence, interground gypsum additions to cement have dropped because more sulfate is available from the clinker. Also, these clinker sulfates tend to be available as double sulfate salts; calcium langbeinite (2CaSO₄·K₂SO₄) instead of potassium sulfate (K₂SO₄).

Sulfate ions play an important role in the early hydration reactions and on concrete rheology. When water is first added to cement; calcium, sulfate and aluminate and hydroxide ions become solubilized. If the sulfates are rapidly soluble, ettringite is formed at the surface of the C₃A and, for a period of time, block further aluminate hydration. This is termed "blocking ettringite". If the sulfate is less readily soluble, ettringite is formed in the solution away from the surface of the C₃A particle. These ettringite crystals adversely affect the concrete rheology if present in sufficient quantities (high water demand and slump loss).

In a hydrating cement system there are several sources of sulfate ions; namely gypsum, hemihydrate, anhydrite as well as the clinker sulfates which are mainly alkali sulfate and calcium langbeinite. By providing different quantities of calcium and sulfate ions into the solution they will contribute differently to ettringite formation. Hemihydrate and clinker sulfates are rapidly soluble and contribute most to the formation of "blocking ettringite".

It is known that calcium langbeinite is rapidly soluble but this rate has not been determined in relation to the early hydration reactions. In clinkers with high sulfate contents that require little or no interground gypsum addition, can the calcium langbeinite dissolve rapidly enough and provide sufficient calcium and sulfate ions to form "blocking ettringite" and slow the reaction of further C₃A ?

It has been suggested¹ that insoluble anhydrite or "dead-burned" anhydrite can be present in high sulfate clinkers. This might be the case in laboratory clinkers² but up to now it has never been detected in industrial clinkers³.

This study will examine the dissolution rates of calcium langbeinite and anhydrite potentially existing in clinker.

EXPERIMENTAL CONDITIONS

The dissolution rate of calcium langbeinite and its ability to block C₃A hydration has been studied using pure clinker phase materials; C₃A, Ca(OH)₂ and calcium langbeinite (2CaSO₄.K₂SO₄). The calcium hydroxide represents the clinker free lime which provides a source of calcium and hydroxide ions in the short term, soon after water is added.

Two mixtures were prepared composed of 0.185 moles/liter of C₃A, 0.675 moles/liter of Ca(OH)₂ and either 0.223 or 0.357 moles/liter of calcium langbeinite. This represents clinker with the compositions shown in Table 1 hydrated with a water/solids ratio to 0.35 at 23°C.

Table 1
 Equivalent Clinker Composition (%)

Mixture	K ₂ O	SO ₃
1	.74	2.10
2	1.18	3.36

At selected time intervals after water addition, the liquid and solid phases were separated by filtering and washed with acetone and ether. The solid phase was examined by XRD. The solution concentrations were measured by atomic absorption for calcium and potassium, by turbidimeter for sulfate and by titration with 0.05N HCl solution in the presence of helianthine indicator for the hydroxide ions.

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A second set of experiments was done to compare the efficiency of either potassium sulfate and gypsum or hemihydrate in blocking C_3A hydration with calcium langbeinite. The same relative quantities of K_2O , SO_3 and free lime were maintained. The gypsum used was an industrial grade product with 97% purity. The hemihydrate was prepared by heating the gypsum at $100^\circ C$ for 14 hours.

A third set of experiments looked at the dissolution rate of anhydrite. Mixtures containing C_3A (0.88 moles/liter), $Ca(OH)_2$ (1.01 moles/liter), calcium langbeinite (0.223 moles/liter), and either anhydrite or gypsum for comparison (0.335 moles/liter) were stirred at $23^\circ C$ for various times between 2 hours and 16 days. These quantities correspond to a clinker or cement which contains 0.74 % K_2O , 2.81 % SO_3 and 3.12 % Al_2O_3 , hydrated at a water / solids ratio equal to 0.35.

In order to make the anhydrite similar to that which could hypothetically be present in industrial clinker, it was produced from gypsum burned at $1400^\circ C$ for 2 hours. For comparison, anhydrite has also been synthesized from gypsum burned at $500^\circ C$.

RESULTS AND DISCUSSION

Dissolution Rate of Calcium Langbeinite

The changes in the solution concentrations with time are shown in figure 1.

These results, confirmed by the XRD analysis of the residual solid phases, show that the calcium langbeinite dissolves very rapidly. It is mostly dissolved after 5 seconds and totally after 20 seconds. Its dissolution liberates a very high quantity of calcium, potassium and sulfate ions into the solution which becomes supersaturated. Gypsum begins to precipitate as soon as 10 seconds after the water is added and its quantity increases up to 30 seconds. With the higher amount of calcium langbeinite, equivalent to a clinker with 3.36% SO_3 , syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) is also precipitated after 30 seconds and its amount increases up to 1 hour.

The calcium and sulfate ions also react with aluminates from the C_3A to form ettringite. This latter phase can be detected by XRD after 3 minutes of hydration. At 1 hour of hydration only a very minor amount of the C_3A had reacted.

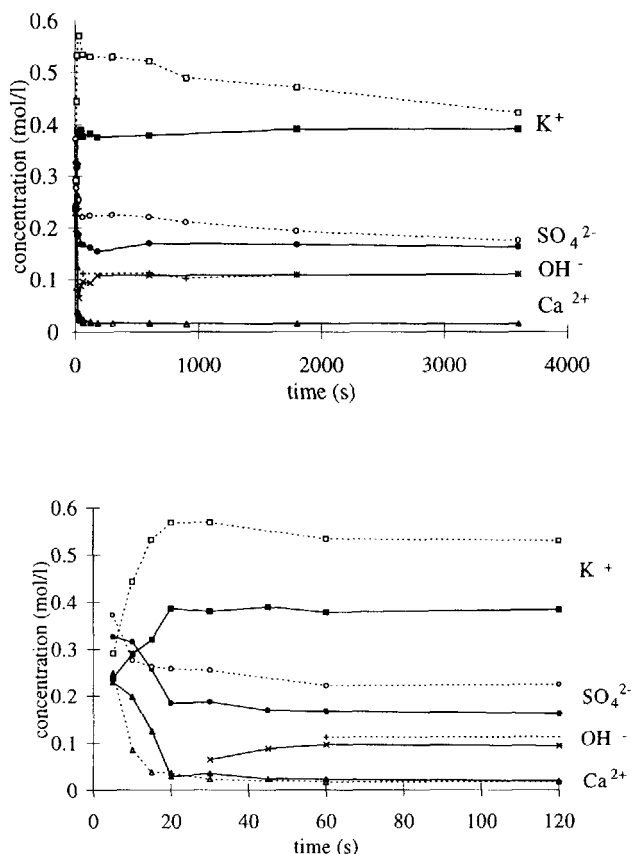


Fig. 1

Evolution of the ions in solution for mixtures of calcium langbeinite, C_3A and $\text{Ca}(\text{OH})_2$. The dotted lines represent an equivalent clinker SO_3 of 2.1% and the solid lines a clinker SO_3 of 3.36%.

The almost instantaneous dissolution of calcium langbeinite coupled with the small amount of C_3A that had reacted after 1 hour indicates that the calcium langbeinite can form a "blocking ettringite" layer around the C_3A . This in turn should slow its hydration and provide a favorable rheology to concrete.

It is well known that syngenite formation should be avoided as it contributes to false set. This study has indicated that syngenite will begin to precipitate if the concentration of potassium in

the pore solution is higher than 0.39 moles per liter. In a hydrating cement system with a w/c ratio of 0.5%, this corresponds to an available K_2O content of 0.93%.

Efficiency of calcium langbeinite in comparison with alkali sulfates, gypsum and hemihydrate to form "blocking ettringite".

To compare the ability of calcium langbeinite to form a "blocking ettringite" layer around the C_3A with other sources of sulfate, the same experiments were performed using blends of potassium sulfate and gypsum or potassium sulfate and hemihydrate instead of calcium langbeinite.

The changes in the solution concentrations for the mixture containing potassium sulfate and gypsum are compared with the ones containing calcium langbeinite and are shown in figure 2.

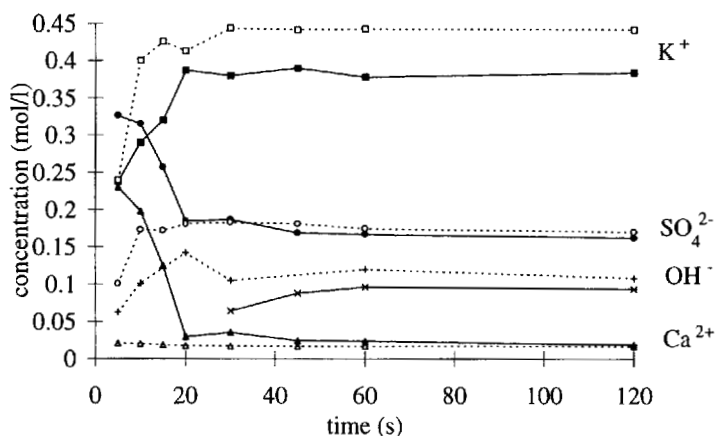


Fig. 2

Comparison of the evolution of the ions in solution for mixtures containing initially either calcium langbeinite or potassium sulfate and gypsum. C_3A and $Ca(OH)_2$ are also present in the initial mixtures. The dotted lines represent the mixture with potassium sulfate and gypsum, the solid lines represent the one with calcium langbeinite. The initial sulfate quantity in both cases is equivalent to a clinker with 2.1% SO_3 .

At 5 seconds, the sulfate ion concentration of the calcium langbeinite mixture is much higher than the potassium sulfate and gypsum mixture; 0.33 moles/liter versus 0.10 moles/liter. Therefore, the calcium langbeinite is at least as efficient as potassium sulfate and gypsum in slowing the C_3A hydration.

The mixtures have a similar behavior after 20 seconds of hydration. They contain the same solid phases; gypsum, calcium hydroxide and ettringite after 3 minutes. The ionic concentrations are virtually identical and they are regulated by the solid phases in equilibrium with the solution. The only difference is the potassium ion concentration; a consequence of the stoichiometry of the calcium langbeinite which has a $K_2SO_4/CaSO_4$ ratio slightly less than 0.5.

The changes in the solution concentrations for the mixture containing potassium sulfate and hemihydrate are compared with the ones containing calcium langbeinite and are shown in figure 3.

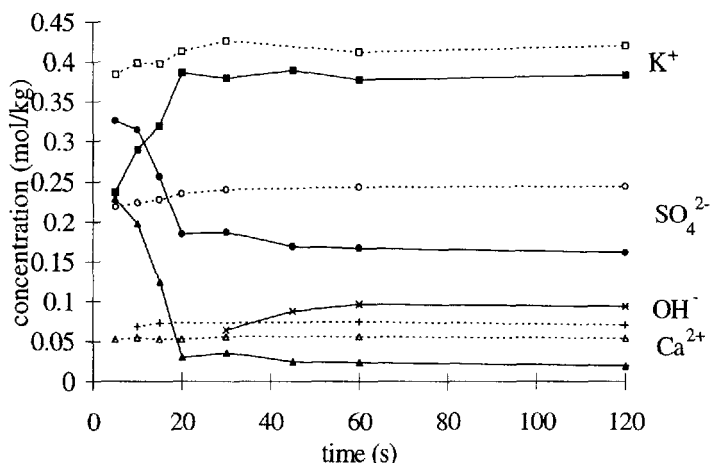


Fig. 3

Comparison of the evolution of the ions in solution for mixtures containing initially either calcium langbeinite or potassium sulfate and hemihydrate. C_3A and $Ca(OH)_2$ are also present in the initial mixtures. The dotted lines represent the mixture with potassium sulfate and hemihydrate, the solid lines represent the one with calcium langbeinite. The initial sulfate quantity in both cases is equivalent to a clinker with 2.1% SO_3 .

For the first few seconds, the mixture containing calcium langbeinite exhibits higher calcium and sulfate ion concentrations than the mixture of potassium sulfate and hemihydrate. However, after 15-20 seconds, the reverse is true and the hemihydrate mixture has higher sulfate ion concentrations. The quantity of hemihydrate remains constant for the first 5 minutes, then it decreases until it is not detectable after 10 minutes. At the same time, after 5 minutes, gypsum begins to precipitate and this process continues up to 30 minutes.

As long as hemihydrate is present, the calcium and sulfate ion concentrations are determined by its solubility. As soon as all the hemihydrate has reacted, the sulfate and calcium ion concentrations begin to decrease and the hydroxide ion concentration increases. Ettringite is detected by XRD after 3 minutes of hydration. Figure 4 shows the same mixtures as Figure 3 on a longer time scale.

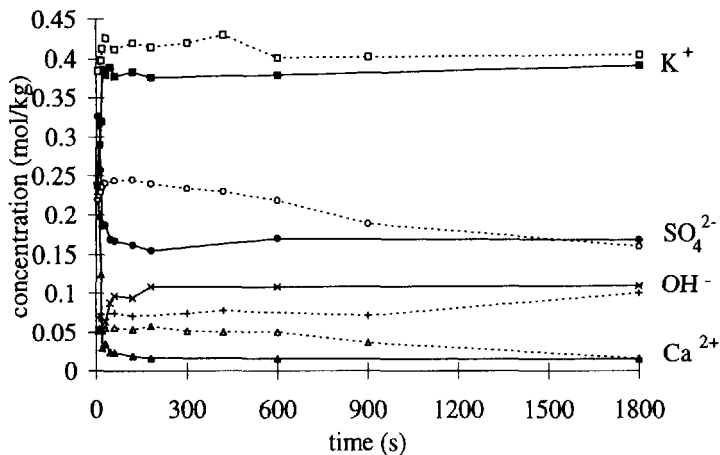


Fig. 4

Same mixtures as in Figure 3 with a longer time scale.

After 30 minutes of hydration the 2 mixtures have identical behaviors. The solid phases are composed of gypsum, calcium hydroxide and ettringite. A small amount of syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) can also be detected in the hemihydrate mixture. The solution is in equilibrium with the solid phases.

From these results it is difficult to determine if the calcium langbeinite is as effective in slowing C_3A hydration as potassium sulfate and hemihydrate. For the first few seconds calcium langbeinite provides the solution with more sulfate ions; however, after 20 seconds the situation reverses.

The Dissolution Rate of Anhydrite

The object of this phase of the study is to examine the dissolution rate of "dead-burned" anhydrite and compare it with other forms of anhydrite and gypsum.

To do this, mixtures containing C_3A , $Ca(OH)_2$ and calcium langbeinite with either gypsum or 1400°C anhydrite or 500°C anhydrite or natural anhydrite were hydrated for up to 16 days at 23°C. Since anhydrite could only be found in clinker in conjunction with calcium langbeinite, the mixtures used here contain both. The results are shown in Figure 5.

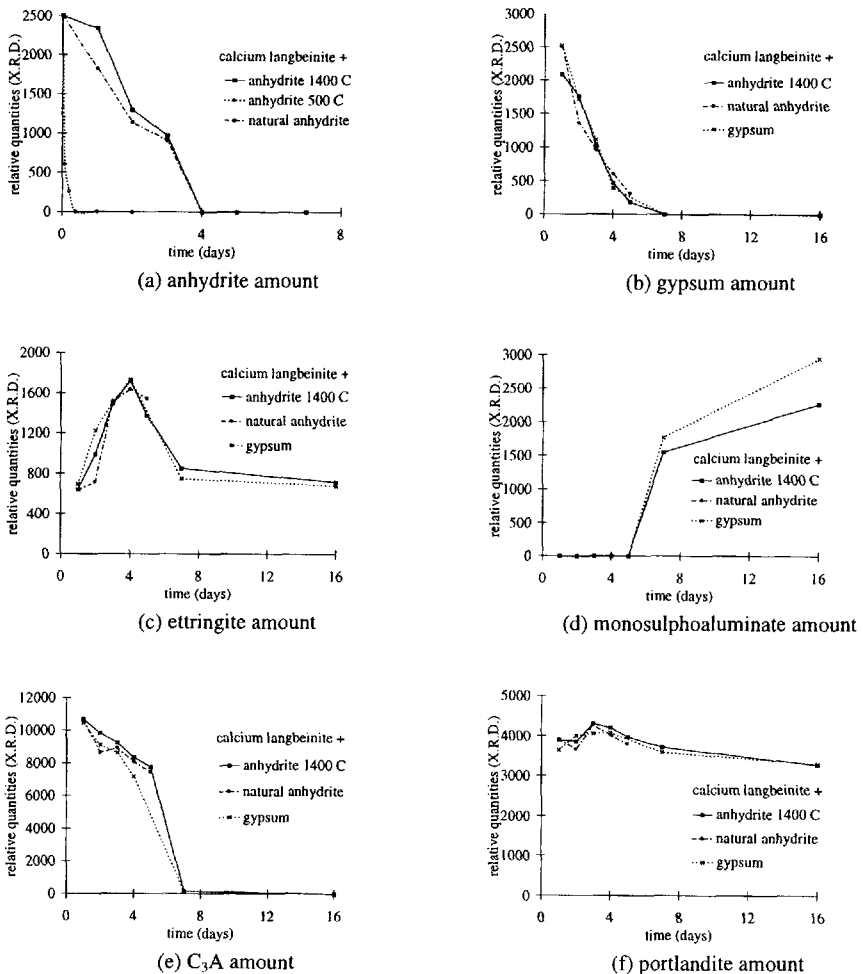


Fig. 5

Influence of anhydrite on the hydration of pure clinker phases. The mixtures are initially composed of 0.223 moles per liter of calcium langbeinite, 0.875 moles per liter of C_3A , 1.0135 moles per liter of $Ca(OH)_2$ and 0.335 moles per liter of various anhydrite forms or gypsum.

Figure 5 (a) indicates that the 1400°C anhydrite dissolves at the same rate as natural anhydrite. It has totally reacted at 4 days; that is to say before the total dissolution of the C_3A . The 500°C anhydrite dissolves much faster.

Figure 5 (b) indicates that regardless of the starting form of sulfate, gypsum is present from the start of hydration. It is precipitated from calcium langbeinite within a few minutes of the start of hydration.

Figure 5 (c) indicates that the C_3A is converted to ettringite while significant quantities of gypsum are present. After 4-5 days, when the anhydrite is gone and the gypsum amount is negligible, the amount of ettringite begins to deplete as the remaining calcium and aluminate reacts with ettringite to form monosulfoaluminate.

These studies have been conducted in the absence of calcium silicates. Even if C-S-H were present, these equilibria should not be modified. A thermodynamic calculation by using the method of Pizer⁴ has shown that C-S-H is in equilibrium with ettringite, gypsum, syngenite and portlandite and its presence does not affect the solution concentrations.

CONCLUSION

Calcium langbeinite, one of the sulfate forms found in clinkers with a high SO_3 /alkali ratio, is rapidly soluble. Cements made with clinkers containing significant quantities of calcium langbeinite should have a similar performance to a cement made with a low sulfate clinker to which larger quantities of gypsum have been added. In fact, because of its dissolution rate and ability to form "blocking ettringite", high calcium langbeinite clinkers should provide improved rheological properties.

As for anhydrite, this study has shown that even material that is burned at 1400°C for 2 hours is totally dissolved in a hydrating system within 4 days. This relatively rapid dissolution rate should not adversely affect the durability of concrete. In fact the solubility rate is comparable to natural anhydrite, a material that has been widely used in cement for decades to reduce false setting tendencies.

REFERENCES

1. Mielenz, R.C., Marusin, S.L., Hime, W.G., Jugovic, Z.T., "Investigation of Prestressed Concrete Railway Tie Distress", Concrete International, pp. 62-68 (dec. 1995)
2. Pollitt, H.W.W. and Brown, A.W., "The distribution of Alkalis in Portland Cement Clinker", 5th Intl. Symp. on Cem. Chem., Tokyo, I-126, pp. 322-333 (1968).
3. Miller, F.M. and Tang, F.J., "The Distribution of Sulfur in Present-Day Clinkers of Variable Sulfur Content", Cement and Concrete Research, 26, 12, pp. 1821-1829 (1996)
4. Pitzer, K.S., and Mayorga, G., "Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes With One or Both Ions Univalent", The Journal of Physical Chemistry. 77, pp. 2300-2308 (1973).

SP 177-3

Influence of Cement Composition on Volume Stability of Mortar

by S. Kelham

Synopsis: The volume stabilities of mortars have been monitored for periods up to 5 years. In addition to controls maintained at 20°C, prisms were subjected to high temperature curing regimes, typically 12 hours at 70, 80 or 90°C. Curing temperature was found to be the dominant factor in determining whether significant (>0.1%) expansion took place during subsequent water storage at 20°C. Most of the mortars expanded after curing at 90°C but very few at 80°C and none at 70°C.

Analysis of the results for mortars cured at 90°C indicated that expansion increased with cement fineness and levels of alkali, C_3A , C_3S and MgO and showed a maximum at a cement SO_3 content of ~4%. The pessimum SO_3 content increased with cement alkali content. The incorporation of ground limestone accelerated expansion but did not affect the ultimate value. Cement replacement levels of 30% or 40% with siliceous fly ash and 30% or 50% with ground granulated blastfurnace slag appeared to prevent expansion. A sample of Type K cement gave only moderate expansion. The mortars that expanded after curing at 80°C had high alkali levels, through the incorporation of KOH or K_2SO_4 in the mixing water.

At 20°C no long-term expansions were observed, despite the inclusion of cements with total SO_3 levels up to 5.6% and clinker SO_3 levels up to 2.6%. The Type K cement expanded by ~0.05% within the first 7 days and was then stable. Cements based on a high C_3A clinker gave early expansions (~56 days) which increased as the cement SO_3 content increased and as the specific surface area decreased, although all expansions were <0.1%.

Keywords: alkali; clinker; curing; fly ash; mortars; prisms

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INTRODUCTION

The volume stability of heat-treated mortars and concretes has been studied widely in recent years. Expansion during subsequent moist storage is often observed. This expansion has been associated with the observation of ettringite filling voids and cracks, particularly around aggregate particles (1, 2, 3). The paste/aggregate interface appears to be important, since the nature of the aggregate affects expansions, but expansions have also been reported in paste samples (4). A full explanation of the expansion process is not yet available.

The published data indicate a critical early age temperature of $\sim 70^{\circ}\text{C}$ below which no expansions are observed (5, 6). Higher temperatures may lead to subsequent expansion but some cements do not expand even after prolonged initial curing at 100°C (7). It has recently been suggested that certain clinkers may lead to expansion through a similar process in the absence of high temperatures during or after hydration (8, 9). The present study is an attempt to clarify the influences of temperature and cement composition and fineness on volume stability. The cements were laboratory prepared to allow controlled variations of the factors believed to be important. Some of the data have been analysed previously (6) and an expression derived to predict expansion from cement chemistry and fineness data. Knowledge of the factors that determine the relative susceptibility of cements will assist in the development of models of the expansion process.

MATERIALS

Seven portland cement clinkers were used to produce the cements. The chemical analyses of the clinkers are given in Table 1 together with phase compositions obtained from Bogue calculations. Clinker A was high in C_3A , clinker B high in K_2O , clinker C high in MgO and low in Na_2O eq. and clinker D low in SO_3 . Clinker E was low in C_3A and suitable for producing sulfate-resisting cement to BS 4027 or ASTM C 150 Type V. Clinker F had moderate levels of all parameters and clinker G was a mineralised active clinker produced at the same works as clinker F. Although the Bogue calculation for clinker G assumed that all the sulfate was present as CaSO_4 , much of it will be present as calcium langbeinite. This clinker contained $\sim 0.2\%$ fluorine. Three sources of added SO_3 were used: a natural gypsum, a natural anhydrite and a flue gas desulfurisation (FGD) gypsum. The natural anhydrite was

used blended with a small proportion of natural gypsum, giving 20% of the SO_3 present as the dihydrate. Limestone was used in some grinds. The limestone met the requirements in ENV 197-1 for the production of portland limestone cements.

The cements prepared with clinkers A to E were ground in a 450 mm diameter laboratory ball mill. The grinding was carried out cold and the cements then heat treated at 105°C for four hours to produce a similar degree of gypsum dehydration to that found in production cements. Specific surface area (SSA) targets were 350 and $450\text{ m}^2/\text{kg}$, plus some at $250\text{ m}^2/\text{kg}$ with clinker A. Cement sulfate targets were 4 and 5% SO_3 , plus some at 3% with anhydrite. The limestone was used at 5% and 15% levels in grinds with clinker A and natural gypsum. These grinds were designed to give a similar clinker fineness to that in the equivalent grind without limestone, as indicated by the $45\mu\text{m}$ residue. A number of blends containing fly ash or ground granulated blastfurnace slag were also tested.

The cements prepared from clinkers F and G were ground in a pilot scale closed circuit ball mill equipped with a high efficiency separator. Target SO_3 contents were 3.5% and target surface areas 400 and $550\text{ m}^2/\text{kg}$. Tests were also carried out on a sample of a commercial Type K cement.

METHODS

Mortars (3:1:0.5 sand:cement:water by weight) were prepared as described in EN 196-1. The standard silica sand used was German 'Normensand' supplied in pre-weighed bags. $16 \times 16 \times 160\text{ mm}$ prisms were cast with stainless steel studs in their end faces. Up to four moulds, each containing three prisms, were used for each mortar mix. The prisms were cast in a single layer and compacted with 60 jolts. After striking off excess mortar, a top-plate in each prism compartment provided essentially sealed curing conditions. Each mould was further sealed in a polyethylene bag together with a water-soaked cloth to ensure 100% relative humidity during curing.

Samples were either maintained at 20°C or subjected to a heat treatment regime. Curing at 70°C and 80°C was carried out in environmental cabinets. After a 20°C pre-cure for 4 hours the temperature was increased by $20^\circ\text{C}/\text{hour}$ up to the required maximum temperature, which was maintained for 12 hours. Cooling was also at $20^\circ\text{C}/\text{hour}$. Curing at 90°C was carried out in an accelerated curing tank with the moulds held $\sim 50\text{ mm}$ above the surface of the water. After the 4 hour pre-cure at 20°C the water was heated to 95°C in 1 hour and maintained at this temperature for 12 hours. Calibration with sand filled moulds showed that this gave a sample temperature of 90°C . Unforced cooling to 20°C took ~ 6 hours.

All prisms were demoulded at 24 hours and subsequently stored in water at 20°C . Lengths and weights were measured at regular intervals. Data for 5 years of water storage are available for the grinds containing clinkers A to E and for 3.5 years for the grinds containing clinkers F and G. All cements were tested with 20° , 70° and 80°C curing and most also at 90°C . Some additional mortars were prepared with K_2SO_4 or KOH dissolved in the mixing water to raise the SO_3 and/or Na_2O eq. levels.

RESULTS

Control prisms

Length changes of prisms maintained at 20°C were always <0.1%. The data for cements based on clinker D are plotted in Fig. 1. The data for the other cements are similar, including the Type K cement. Expansion takes place during the first 28 to 56 days and the prisms are then stable within the accuracy of the present tests.

The expansions of prisms cured at 20°C are plotted against cement SO₃ content in Fig. 2. The plotted values are the means of the data for ages greater than 600 days in order to reduce the scatter. The lines in the plot connect data points for cements which were ground from the same clinker and sulfate source to the same target SSA and thus differ only in SO₃ content. It can be seen that generally the expansion increased as the sulfate content increased. Cements based on clinker C expanded more than the others at the same sulfate content which may be due to the high MgO content. Fig. 3 shows the same data plotted against SSA. The lines connect data points for cements with the same clinker, sulfate source and target sulfate content. Clearly expansion decreased as the SSA increased. In both plots vertical lines connect results for repeated measurements and indicate the reproducibility of the method.

Heat-treated mortars

The mortars cured at 70° and 80°C normally gave no significant expansion while most mortars cured at 90°C expanded by ~1% between 56 and 200 days. A typical set of curves is shown in Fig. 4. The only mortars to expand after curing at 80°C were those containing added K₂SO₄ or KOH. No expansions were observed with cements containing the sulfate-resisting clinker (E). Where initial rapid expansion took place, continued water storage gave further slow expansion but, in order to analyse the effect of various parameters on the expansion, plots such as Fig. 4 have been used to estimate a value for the ultimate long term expansion for each set of prisms. Expansions were associated with increases in weight, 1% expansion corresponding to ~1.5% weight increase.

Fig. 5 shows the dependence of the ultimate expansion on the cement SSA for mortars cured at 90°C in the same format as Figs. 2 and 3. It can be seen that in all cases where expansion took place an increase in surface area gave an increase in expansion. The results for cements based on clinker E are not included. The cements with low expansions at ~450 m²/kg were based on clinkers B and D and had SO₃ contents >5%.

In Fig. 6 the dependence on cement sulfate content is plotted. The expansions pass through a maximum at sulfate contents near 4%. Only clinker C gave expansion at 3% SO₃. The results for cements based on clinker E are not included. The cements that gave low expansions at ~4% SO₃ were ~350 m²/kg grinds based on clinker D. The vertical lines on the plot again indicate results from repeated tests.

Tables 2, 3 and 4 give expansion data for the laboratory prepared cements at selected ages. Data for the mortars prepared with added alkali are in Table 5 and data for the fly ash and ggbs blends are in Table 6. Data at 3.5 and 5 years are for single prisms while earlier data are mean values for sets of three prisms. This leads to small apparent changes between 1 and 3.5 years, but no significant changes normally took place during this period.

There was no indication of dependence of expansion on the sulfate source. Excluding the very low C_3A cement, clinker source also appeared to have little influence on the expansions. The grinds containing 5% or 15% gave similar ultimate expansions to the equivalent cements without limestone, although the expansion occurred earlier as the limestone content increased. The blends containing fly ash or ggbs showed no expansions although the cements used gave large expansions.

The Type K expansive cement expanded by a moderate amount ($\sim 0.3\%$) after curing at 90°C . The data are plotted in Fig. 7.

Effect of added alkali

The tests with added K_2SO_4 were carried out on cements prepared from clinkers A, B and C with target SO_3 contents of 4% (Table 5). The quantity of K_2SO_4 used was calculated to give the same sulfate content in the mortar as in that containing the equivalent cement with a target sulfate content of 5%. This allowed a comparison to be made of the effects of adding SO_3 as $CaSO_4$ and K_2SO_4 . Control and 70°C prisms were cast only for the cement prepared from clinker A and the added alkali had no effect on the expansion of these prisms. After curing at 80°C all the mortars with added K_2SO_4 gave significant expansions of $\sim 0.5\%$ while after curing at 90°C the expansions were very large, $\sim 2\%$. Increasing cement sulfate from 4% to 5% by increasing the $CaSO_4$ added during grinding thus led to a lower expansion after curing at 90°C (Fig. 6) while adding the same quantity of sulfate as K_2SO_4 dissolved in the mixing water led to much higher expansions. One mortar was prepared with ground gypsum blended with a cement to give a total sulfate content equal to that of the higher sulfate grind (Table 6). The effect of the additional gypsum was identical whether it was interground or ground separately and blended.

KOH was added to mortars prepared with a grind containing clinker C, with a target sulfate content of 4%, to give effective Na_2O eq. levels of $\sim 0.4\%$, 0.6% , 0.8% and 1.2% . As with the K_2SO_4 , the KOH was dissolved in the mixing water. The expansion data are plotted in Fig. 8. The alkali level had no effect on the expansion after curing at 20°C or 70°C but the high alkali mortar expanded after curing at 80°C . Curing at 90°C gave large expansions with all the mortars and the expansion increased as the alkali content increased.

DISCUSSION

Control prisms

The expansion data for the mortars cured at 20°C are consistent with data obtained by Hobbs (10) who also observed increasing expansion with increasing cement SO₃ content and decreasing fineness. The precision of the present data is not sufficient to make a detailed analysis worthwhile (see Figs. 2 and 3) but expansions appear to be higher for cements containing clinkers A and C, which have high C₃A and MgO contents respectively. The results obtained with high sulfate cements, ~5%, with these clinkers were similar to those obtained with the Type K expansive cement, ~0.05%. The expansions for the Type K cement are smaller than those obtained using the ASTM C806 procedure because only expansion after demoulding at 24 hours is measured by the method used in this investigation.

It has recently been suggested that cements with high clinker sulfate contents, particularly when linked with low alkali contents, may give long term expansions due to 'late' ettringite formation (8, 9). It is proposed that the clinker sulfate may be unavailable during early hydration, either because it is in an insoluble form or is incorporated in the clinker minerals. Clinker sulfate is normally present as alkali sulfates and calcium langbeinite (K₂SO₄·2CaSO₄) and is readily soluble. As the sulfate/alkali ratio increases the proportion of potassium present as calcium langbeinite increases. An estimate of the maximum SO₃ that can be incorporated in these readily soluble phases in a clinker can be calculated by assuming that all sodium in the clinker is present as Na₂SO₄ and all potassium as calcium langbeinite. If the sulfate content of the clinker is greater than this value, the 'excess' sulfate (= total minus readily soluble) would be expected to occur as CaSO₄ or in solid solution in the main clinker phases, particularly C₂S (11). Applying this method to the clinker analyses in Table 1 gives excess SO₃ contents of 0.4% in clinker C and 1.6% in clinker G. Only alkali sulfates and calcium langbeinite would be expected in the other clinkers. Despite this excess SO₃ the cements based on these clinkers behaved in the same way as all the other cements, with no signs of continuing or late expansions when cured and stored at 20°C.

Heat-treated mortars

The curing temperature is clearly the dominant factor in determining whether large mortar expansions are observed. Expansions after curing at 70°C are the same as those obtained at 20°C. Curing at 80°C, for high alkali mortars only, or 90°C for most of the mortars, led to large expansions. These results are in agreement with other published data (1, 7), where no large expansions were observed with curing temperatures below some critical value, typically ~80°C, unless other expansion mechanisms were also present, such as ASR (12, 13). In the case of heat-treated pastes long delays have been observed before significant expansion takes place (4) but the critical temperature appears to be the same as for mortars.

The evidence from laboratory investigations thus indicates that a temperature

above $\sim 70^{\circ}\text{C}$ is necessary for subsequent expansion due to DEF. The reports of expansions not associated with high temperatures during curing have all involved investigations of field concretes. Analysis of crack patterns and the distribution and form of ettringite may be argued to be consistent with cracks having developed through the late formation of ettringite but in such field cases the large number of unknown factors makes definite identification of the cause of damage very difficult. It is generally accepted that ettringite will be deposited in cracks caused through some other mechanism but the extent to which the growth of such crystals can contribute to crack growth and damage to the concrete is still not clear (3, 9).

The expansion data for mortars cured at 90°C containing the laboratory prepared cements (Tables 2, 3, 4 and 5) have been analysed previously (6). The expression

$$\text{Risk}(90^{\circ}\text{C}) = 0.00474 \cdot \text{SSA} + 0.0768 \cdot \text{MgO} + 0.217 \cdot \text{C}_3\text{A} + 0.0942 \cdot \text{C}_3\text{S} + 1.267 \cdot \text{Na}_2\text{O eq.} - 0.737 \cdot \text{ABS}[\text{SO}_3 - 3.7 - 1.02 \cdot \text{Na}_2\text{O eq.}] - 10.1$$

IF Risk > 0 THEN Expansion = Risk ELSE Expansion = 0

was found to give good agreement with the data, as shown in Fig. 9. The factors involving SSA, SO_3 and $\text{Na}_2\text{O eq.}$ are consistent with the data presented in Figs 6, 7 and 8 and Table 5. The model is generally consistent with the published data (1, 7, 14, 15). The factors SSA, C_3S and $\text{Na}_2\text{O eq.}$ suggest that the rate of early silicate hydration is important. Brown and Bothe, (16), have shown that ettringite stability is reduced by the presence of C-S-H and Lewis et al., (17), have demonstrated that subsequent expansion is correlated with the quantities of sulfur and aluminium within the C-S-H immediately after heat treatment. Early strength is strongly linked to C_3S hydration (18), and Kelham, (6), noted a correlation between cement early strength and expansion of heat-treated mortars.

The data for blends containing fly ash or ggbs (Table 6) agree with the data from Heinz et al., (1). Even when cured at 90°C no damaging expansions were observed for blends containing 30% or more of fly ash or ggbs with portland cements which expanded by $\sim 1\%$ when used alone. In one mortar the ggbs was pre-blended with ground fgd gypsum to increase the SO_3 content to the same value as in the portland cement. No significant expansion was observed, indicating that the good performance of the blends is not simply due to dilution of the sulfate content.

CONCLUSIONS

1. The dominant factor in determining expansions was the curing temperature. Curing at temperatures below 80°C did not produce damaging expansions for any of the portland cements tested.
2. The expansions observed in mortars maintained at 20°C were within the normal range for portland cements. They increased with increases in cement SO_3 , C_3A and MgO contents and decreased with increasing cement fineness (SSA).
3. Cements prepared from clinkers containing sulfate in the form of CaSO_4

(anhydrite) and/or included in the silicate phases showed no abnormal expansions.

4. For mortars cured at 90°C expansions increased with increases in
 - Cement fineness (SSA)
 - Alkali (Na₂O eq.) content
 - C₃A and C₃S (Bogue) contents and
 - MgO content,
 and showed a maximum at a cement SO₃ of ~4%, increasing with cement alkali content.
5. The presence of interground limestone accelerated expansions but did not influence the final expansion or the critical temperature.
6. Mortars containing blends of fly ash (30% or 40%) or ggbs (30% or 50%) with cements that gave large expansions when used alone, did not expand after curing at 90°C.
7. A Type K cement gave very similar behaviour to the portland cements.

REFERENCES

1. Heinz, D., Ludwig, U. and Rüdiger, I., "Delayed Ettringite Formation in Heat Treated Mortars and Concretes", *BFT (Conc. Precasting Plant and Technology)*, Vol. 55, No. 11, 1989, pp. 56-61.
2. Lawrence, C.D., Dalziel, J.A. and Hobbs, D.W., "Sulfate Attack Arising from Delayed Ettringite Formation", *Interim Technical Note 12*, British Cement Association, 1990, 43 pp.
3. Johansen, V., Thaulow, N. and Skalny, J., "Internal Reactions Causing Cracking of Concrete", *BFT (Conc. Precasting Plant and Technology)*, Vol. 61, No. 11, 1995, pp. 56-68.
4. Yang, R., Lawrence, C.D. and Sharp, J.H., "Delayed Ettringite Formation in 4-year old Cement Pastes", *Cem. Conc. Res.*, Vol. 26, No. 11, 1996, pp. 1649-1659.
5. Heinz, D. and Ludwig, U., "Mechanism of Secondary Ettringite Formation in Mortars and Concretes Subjected to Heat Treatment", In *'Concrete Durability. Katherine and Bryant Mather Int. Conf.'*, SP-100. Vol. 2, edited by J.M. Scanlon. American Concrete Institute, Detroit, 1987, pp. 2059-2071.
6. Kelham, S., "The Effect of Cement Composition and Fineness on Expansion Associated with Delayed Ettringite Formation", *Cem. Conc. Comp.*, Vol. 18, No. 3, 1996, pp. 171-179.
7. Lawrence, C. D., "Mortar Expansions due to Delayed Ettringite Formation. Effects of curing period and temperature", *Cem. Conc. Res.*, Vol. 25, No. 4, 1995, pp. 903-914.

8. Hime, W.G., "Clinker Sulfate: A Cause of Distress and a Need for Specification", *Proc. Int. Conf. Concrete in the Service of Mankind, Concrete for Environmental Enhancement and Protection*, Dundee, UK, 24-26 June, 1996, pp. 387-395.
9. Diamond, S., "Delayed Ettringite Formation - Processes and Problems", *Cem. Conc. Comp.*, Vol. 18, No. 3, 1996, pp. 205-215.
10. Hobbs, D.W., "Expansion and Shrinkage of Oversulphated Portland Cements", *Cem. Conc. Res.*, Vol. 8, No. 2, 1978, pp. 211-222.
11. Taylor, H.F.W., *Cement Chemistry*, Academic Press Ltd., London, 1990.
12. Shayan, A. and Ivanusec, I., "An Experimental Clarification of the Association of Delayed Ettringite Formation with Alkali-Aggregate Reaction", *Cem. Conc. Comp.*, Vol. 18, No. 3, 1996, pp. 161-170.
13. Diamond, S. and Ong, S., "Combined Effects of Alkali Silica Reaction and Secondary Ettringite Deposition in Steam Cured Mortars", In *Cement Technology*, edited by E.M. Gartner and H. Uchikawa, Ceramic Transactions, Vol. 40, Amer. Ceram. Soc., Westerville, OH., 1994, pp. 79-90.
14. Hempel, G., Böhmer, A. and Otte, M., "Investigations of the Influence of Material-technological Parameters on the Durability of Heat Treated Concretes", *BFT (Conc. Precasting Plant and Technology)*, Vol. 58, No. 5, 1992, pp. 75-79.
15. Odler, I. and Chen, Y., "Effect of Cement Composition on the Expansion of Heat-cured Cement Pastes", *Cem. Conc. Res.*, Vol. 25, No. 4, 1995, pp.853-862.
16. Brown, P.W. and Bothe, J.V., "The Stability of Ettringite", *Adv. Cem. Res.*, Vol. 5, 1993, pp. 47-63.
17. Lewis, M.C., Scrivener, K.L. and Kelham, S. "Heat Curing and Delayed Ettringite Formation", *Microstructure of Cement Based Systems*, MRS Symp. Proc., Vol. 370, 1995, pp. 67-76.
18. Kelham, S. and Moir, G.K., "The Effect of Cement C_3S Level on Concrete Properties", *Proc. 9th Int. Congr. on the Chemistry of Cement*, New Delhi, Vol. V, 1992, pp.3-8.



TABLE 1—CLINKER ANALYSES (PERCENT BY WEIGHT).

Clinker	A	B	C	D	E	F	G
SiO ₂	20.7	21.6	19.8	22.4	21.4	21.9	22.6
Al ₂ O ₃	6.0	5.2	5.2	5.1	3.5	4.9	2.2
Fe ₂ O ₃	2.4	3.2	3.0	2.4	5.1	3.2	0.8
CaO	66.8	66.3	66.2	67.5	66.0	67.0	70.0
MgO	0.7	1.0	2.5	0.6	2.0	0.7	0.6
SO ₃	1.5	1.0	1.6	0.3	0.4	0.5	2.6
LOI †	0.4	0.2	0.2	0.3	0.3	0.5	0.3
K ₂ O	0.59	0.83	0.48	0.48	0.51	0.49	0.31
Na ₂ O	0.22	0.17	0.06	0.26	0.14	0.25	0.22
Na ₂ O eq	0.61	0.72	0.38	0.58	0.48	0.57	0.42
Free Lime	1.5	0.4	1.8	0.4	2.0	1.0	1.2
C ₃ S	64.8	64.6	72.5	65.2	67.1	64.8	85.0
C ₂ S	10.5	13.2	2.1	15	10.8	14.0	0.7
C ₃ A	11.8	8.4	8.7	9.5	0.6	7.6	4.5
C ₄ AF	7.3	9.7	9.1	7.3	15.5	9.7	2.4

† Loss on ignition

TABLE 2—EXPANSION DATA FOR CEMENTS PREPARED FROM CLINKER AT SELECTED AGES (PERCENT) (D = DAYS, Y = YEARS).

Clinker sulfate	Added sulfate	SO ₃ %	SSA m ² /kg	20°C			70°C			80°C			90°C				
				56d	1y	3.5y	5y	56d	1y	5y	56d	1y	5y	56d	1y	3.5y	5y
A	A	3.0	448	0.002	0.007	0.012	0.009	0.020	0.025	0.029	-0.005	-0.002	-0.001	0.001	0.009	0.025	0.011
A	A	4.3	248	0.017	0.020	0.018	0.018	0.011	0.028	0.009	0.016	0.021	0.014	0.070	0.148	0.164	0.164
A	A	4.3	352	0.022	0.011	0.001	0.007	0.011	0.028	0.009	0.010	0.030	0.027	0.178	0.779	0.826	0.833
A	A	4.3	456	0.010	0.012	0.011	0.014	0.006	0.004	-0.010	0.035	0.014	0.007	0.041	0.897	0.917	0.929
A	A	5.1	355	0.045	0.045	0.036	0.041	0.011	0.028	0.021	0.012	0.030	0.028	0.395	0.705	0.750	0.759
A	A	5.1	451	0.014	0.009	0.008	0.012	0.010	0.009	0.018	0.042	0.028	0.026	0.376	0.695	0.658	0.666
"	"	"	"					-0.001	0.008	0.013	0.002	0.009	0.019				
A	A	5.5	248	0.043	0.050	0.059	0.063	0.025	0.034	0.034	0.036	0.038	0.051				
A	F	4.2	352	-0.011	-0.011	-0.006	-0.006	0.017	-0.013	-0.011	-0.005	-0.009	-0.010	0.296	0.680	0.702	0.706
A	F	4.2	449	0.006	0.010	0.015	0.016	0.001	0.004	0.009	0.009	0.010	0.024	0.100	0.797	0.876	0.886
A	F	5.1	355	0.009	0.012	0.017	0.019	0.008	0.010	0.013	0.013	0.012	0.015	0.028	0.029	0.034	0.031
A	F	5.1	444	0.025	0.024	0.031	0.033	0.019	0.022	0.021	0.022	0.024	0.029	0.311	0.671	0.701	0.707
A	G	4.0	252	-0.001	0.013	0.005	0.010	-0.006	0.012	0.012	0.016	0.025	0.025				
A	G	3.9	356	0.016	0.014	0.005	0.009	0.015	0.005	0.016	0.006	0.013	0.019				
A	G	3.9	449	0.000	0.020	-0.003	0.000	-0.004	0.017	-0.007	0.016	0.041	0.046	0.023	0.651	0.689	0.699
A	G	4.9	248	0.030	0.046	0.034	0.039	0.013	0.025	0.017	0.020	0.033	0.031				
A	G	4.8	355	0.031	0.017	0.026	0.029	0.025	0.014	0.016	0.025	0.035	0.027				
A	G	4.8	462	0.016	0.035	0.016	0.022	0.008	0.025	0.011	0.023	0.033	0.013				
A15	G	3.8	456	0.006	0.015	0.011	0.016	0.006	0.014	0.017	0.003	0.031	0.022				
A15	G	3.8	596	0.009	0.015	0.001	0.004	0.015	0.022	0.004	0.024	0.020	0.013	0.170	0.848	0.899	0.901
A15	G	4.6	515	0.029	0.037	0.029	0.035	0.013	0.020	0.021	0.010	0.049	0.025				
A15	G	4.6	612	0.028	0.041	0.018	0.021	0.038	0.053	0.021	0.021	0.017	0.029	0.017	0.015	0.009	0.013
A5	G	3.8	382	0.012	0.029	0.027	0.035	-0.006	0.005	0.007	0.005	0.042	0.016				
A5	G	3.8	497	0.013	0.025	0.016	0.026	0.010	0.027	0.024	0.003	0.022	0.013	0.060	1.025	1.011	1.017
A5	G	4.7	383	0.013	0.028	0.025	0.031	0.013	0.027	0.026	0.014	0.044	0.023				
A5	G	4.7	485	0.006	0.020	0.017	0.036	0.006	0.023	0.016	0.013	0.042	0.026				

A5, A15 - 5, 15% limestone replacement of clinker.

A5, A15 - 5, 15% limestone replacement of clinker.

Added sulfate

A - Natural anhydrite

F - Flue gas desulfurisation gypsum

G - Natural gypsum

TABLE 3—EXPANSION DATA FOR CEMENTS PREPARED FROM CLINKER S, B, AND C AT SELECTED AGES (PERCENT)
(D = DAYS, Y = YEARS).

Clinker	Added sulfate	SO ₃ %	SSA m ² /kg	20°C				70°C				80°C				90°C			
				56d	1y	3.5y	5y	56d	1y	5y	5y	56d	1y	5y	5y	56d	1y	3.5y	5y
B	A	3.0	456	0.001	0.005	0.011	0.005	-0.014	0.014	-0.001	-0.001	0.000	0.004	0.006	0.006	0.001	0.006	0.016	0.006
B	A	4.2	362	-0.011	0.007	0.006	0.010	0.013	0.027	0.014	-0.001	-0.005	0.011	0.001	0.001	0.022	0.696	0.777	0.784
B	A	4.2	462	0.000	0.018	0.012	0.017	0.000	0.025	0.011	0.000	-0.004	0.023	0.014	0.001	0.031	0.206	0.258	0.268
B	A	5.2	365	0.006	0.029	0.018	0.019	-0.003	0.017	0.014	0.000	-0.002	0.020	0.024	0.006	0.054	0.403	0.481	0.495
B	A	5.2	470	0.018	0.033	0.024	0.026	0.000	0.004	0.028	0.000	0.001	0.007	0.014	0.001	0.020	0.338	0.381	0.359
"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
B	F	4.1	362	0.011	0.004	0.007	0.009	-0.031	-0.032	-0.022	-0.022	-0.024	-0.029	-0.027	-0.027	-0.022	0.436	0.537	0.551
B	F	4.1	454	-0.040	-0.037	-0.038	-0.036	-0.015	-0.015	-0.004	-0.004	-0.012	-0.015	-0.011	-0.011	-0.012	-0.008	-0.008	-0.011
B	F	5.1	352	-0.003	-0.010	-0.006	-0.001	-0.028	0.005	-0.031	-0.031	-0.022	-0.021	-0.018	-0.018	-0.013	-0.013	-0.008	-0.006
B	F	5.1	457	-0.020	-0.018	-0.009	-0.009	-0.013	0.004	0.000	0.000	-0.012	0.015	0.013	0.013	0.009	0.052	0.140	0.146
B	G	3.9	357	-0.010	-0.005	-0.012	-0.006	-0.024	0.001	0.000	0.000	-0.011	0.002	0.006	0.006	0.007	0.435	0.574	0.571
B	G	4.8	361	-0.020	-0.007	-0.008	-0.021	-0.001	0.016	0.005	0.005	-0.014	0.018	0.006	0.006	0.007	0.435	0.574	0.571
B	G	4.9	459	-0.007	0.008	-0.001	0.016	-0.028	-0.009	-0.008	-0.008	-0.006	0.019	0.013	0.013	0.007	0.435	0.574	0.571
C	A	3.0	451	0.010	0.016	0.029	0.021	0.038	0.036	0.021	0.021	0.031	0.048	0.030	0.030	0.052	0.735	0.716	0.723
C	A	4.3	364	0.036	0.035	0.043	0.044	0.022	0.047	0.024	0.024	0.009	0.047	0.030	0.030	0.046	0.110	0.200	0.206
C	A	4.2	457	0.028	0.059	0.036	0.037	0.041	0.065	0.056	0.056	0.036	0.063	0.060	0.060	0.033	0.182	0.265	0.272
C	A	5.0	369	0.072	0.077	0.061	0.066	0.042	0.076	0.050	0.050	0.021	0.068	0.045	0.045	0.046	0.110	0.200	0.206
C	A	5.3	464	0.040	0.059	0.051	0.055	0.015	0.019	0.029	0.029	0.031	0.040	0.024	0.024	0.033	0.182	0.265	0.272
"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
C	G	4.0	352	0.028	0.032	0.034	0.037	0.018	0.031	0.030	0.030	0.020	0.033	0.034	0.034	0.092	1.077	1.074	1.079
C	G	4.2	453	0.018	0.026	0.021	0.019	0.032	0.037	0.016	0.016	0.021	0.034	0.030	0.030	0.092	1.077	1.074	1.079
C	G	5.1	356	0.045	0.056	0.056	0.062	0.040	0.056	0.049	0.049	0.024	0.051	0.047	0.047	0.092	1.077	1.074	1.079
C	G	5.3	459	0.055	0.057	0.056	0.061	0.025	0.045	0.030	0.030	0.028	0.054	0.034	0.034	0.092	1.077	1.074	1.079

Added sulfate

A - Natural anhydrite

F - Flue gas desulfurisation gypsum

G - Natural gypsum

TABLE 4—EXPANSION DATA FOR CEMENTS PREPARED FROM CLINKERS D, E, F, AND G AT SELECTED AGES (PERCENT)
(D = DAYS, Y = YEARS).

Clinker	Added sulfate	SO ₃ %	SSA m ² /kg	20°C				70°C			80°C			90°C			
				56d	1y	3.5y	5y	56d	1y	5y	56d	1y	5y	56d	1y	3.5y	5y
D	A	3.0	451	0.001	0.005	0.006	0.000				0.002	0.002	0.006	-0.005	-0.004	0.007	0.003
D	A	4.1	347	0.048	0.038	0.031	0.031	0.037	0.020	0.036	0.046	0.021	0.029	0.034	0.044	0.052	0.054
"	"	"	"					0.022	0.025	0.004	0.030	0.026	0.013	0.060	0.096	0.079	0.084
D	A	4.1	452	0.016	0.011	0.018	0.009	0.013	0.011	0.010	0.018	0.017	0.015	0.039	0.677	0.714	0.723
D	A	4.6	354	0.035	0.025	0.021	0.020	0.030	0.015	0.009	0.042	0.027	0.024	0.040	0.027	0.024	0.021
D	A	4.6	448	0.050	0.010	0.022	0.016	0.038	0.005	0.010	0.047	0.012	0.009	0.084	0.551	0.517	0.522
"	"	"	"					0.018	0.009	0.013	0.025	0.012	0.019	0.049	0.609	0.573	0.586
D	A	5.6	350	0.070	0.060	0.056	0.056	0.047	0.035	0.025	0.056	0.046	0.025	0.056	0.042	0.036	0.034
D	A	5.6	450	0.064	0.033	0.035	0.034	0.053	0.020	0.021	0.059	0.030	0.036	0.054	0.035	0.043	0.044
D	G	4.1	358	0.037	0.046	0.024	0.028	0.019	0.027	0.019	0.033	0.042	0.026	0.039	0.036	0.026	0.027
D	G	4.1	451	0.029	0.027	0.009	0.009	0.023	0.024	0.008	0.030	0.017	0.009	0.035	0.372	0.394	0.401
D	G	5.1	367	0.054	0.062	0.046	0.046	0.039	0.053	0.027	0.036	0.042	0.028	0.040	0.056	0.028	0.024
D	G	5.1	462	0.034	0.030	0.030	0.031	0.014	0.012	0.018	0.018	0.017	0.019	0.029	0.021	0.024	0.024
E	A	4.1	363	0.004	0.006	0.009	0.008	-0.007	-0.009	-0.004	-0.002	-0.004	-0.001	-0.012	-0.015	-0.011	-0.012
E	A	4.1	468	0.014	0.019	0.011	0.009	-0.001	0.000	0.009	-0.008	-0.009	-0.005	-0.006	-0.006	-0.005	-0.005
E	A	5.1	362	0.003	0.009	0.010	0.011	-0.002	0.019	0.004	-0.002	0.001	0.004	0.000	0.002	-0.006	-0.005
E	A	5.1	467	0.012	0.018	0.028	0.026	-0.003	0.000	0.005	-0.001	-0.003	-0.008	0.002	0.000	-0.004	-0.003
E	G	4.1	359	0.030	0.044	0.039	0.039	0.024	0.032	0.029	0.025	0.029	0.029	0.020	0.021	0.030	0.029
E	G	4.1	464	-0.018	-0.020	-0.021	-0.023	-0.017	-0.014	-0.024	-0.017	-0.016	-0.016	-0.019	-0.025	-0.026	-0.027
E	G	5.1	367	0.032	0.049	0.051	0.059	0.015	0.029	0.029	0.016	0.026	0.028	0.016	0.026	0.026	0.023
E	G	5.1	470	0.015	0.018	0.021	0.021	-0.008	-0.008	0.001	-0.008	-0.005	-0.004	-0.012	-0.012	-0.008	-0.008
F	G	3.5	400	0.005	0.009	0.012		0.005	0.008		0.009	0.012		0.015	0.029	0.043	
F	G	3.6	547	0.007	0.010	0.011		0.010	0.011		0.010	0.012		0.014	0.056	0.236	
G	G	3.5	400	0.008	0.011	0.013		0.004	0.005		0.007	0.008		0.054	0.927	1.065	
G	G	3.5	542	0.002	0.003	-0.017		0.012	0.013		0.014	0.015		0.093	1.294	1.291	

Added sulfate

A - Natural anhydrite

F - Flue gas desulfurisation gypsum

G - Natural gypsum

TABLE 5—EXPANSION DATA FOR MORTARS WITH ADDED ALKALI AT SELECTED AGES (PERCENT) (D = DAYS, Y = YEARS).

Clinker	Added sulfate	SO ₃ %	SSA m ² /kg	Added alkali [% by weight]	20°C			70°C			80°C			90°C		
					56d	1y	3.5y	56d	1y	3.5y	56d	1y	3.5y	56d	1y	3.5y
A	A	4.3	456	0.8% SO ₃ as K ₂ SO ₄	0.010	0.019	0.018	0.006	0.006	0.018	0.230	0.456	0.513	0.615	1.940	1.991
A	A	5.1	451	0.6% eqNa ₂ O as KOH	0.011	0.011	0.014	0.008	0.011	0.012	0.103	0.321	0.359	0.704	1.909	1.916
B	A	4.2	462	1.0% SO ₃ as K ₂ SO ₄							0.070	0.315	0.358	0.237	1.604	1.563
C	A	4.2	457	0.2% eqNa ₂ O as KOH	0.020	0.012	0.021	0.018	0.002	0.009	0.016	0.011	0.039	0.119	0.865	0.885
"	"	"	"	0.4% eqNa ₂ O as KOH	0.031	0.022	0.029	0.018	0.010	0.016	0.018	0.020	0.025	0.144	1.370	1.247
"	"	"	"	0.8% eqNa ₂ O as KOH	0.034	0.023	0.033	0.026	0.015	0.021	0.037	0.145	0.174	0.243	1.257	1.260
"	"	"	"	1.1% SO ₃ as K ₂ SO ₄							0.012	0.252	0.325	0.428	1.568	1.605
C	A	5.3	464	0.8% eqNa ₂ O as KOH	0.041	0.051	0.055	0.034	0.073	0.084	0.034	0.103	0.131	0.255	1.160	1.15

TABLE 6—EXPANSION DATA FOR BLENDS AT SELECTED AGES (PERCENT) (D = DAYS, Y = YEARS).

Clinker	Added sulfate	SO ₃ %	SSA m ² /kg	Blend details [% by weight]	20°C			70°C			80°C			90°C		
					56d	1y	3.5y	56d	1y	3.5y	56d	1y	3.5y	56d	1y	3.5y
A	F	4.2	352	0.9% SO ₃ as ground gypsum	0.015	0.011	0.018							0.034	0.037	0.032
A	G	3.9	449	50% ggbs	0.005	0.009	0.023				0.000	0.007	0.013	-0.004	0.000	0.009
A	G	3.9	449	30% fly ash	0.005	0.004	0.014				0.004	0.006	0.002	0.009	0.004	0.010
A	A	4.3	456	50% ggbs	0.013	0.019								0.009	0.015	
A	A	4.3	456	50% (ggbs + 4.3% SO ₃)	0.012	0.017	0.022	0.006	0.010	0.015	0.009	0.013	0.018	-0.002	0.004	0.021
G	G	3.5	400	30% ggbs	0.003	0.010	0.012	0.000	0.005	0.004	0.003	0.007	0.006	0.001	0.006	0.010
G	G	3.5	542	30% fly ash	0.005	0.006	0.006	0.004	0.005	0.006	0.008	0.010	0.011	0.015	0.019	0.027
G	G	3.5	542	40% fly ash	0.002	0.008	0.011	0.002	0.005	0.007	0.005	0.008	0.011	0.005	0.009	0.016

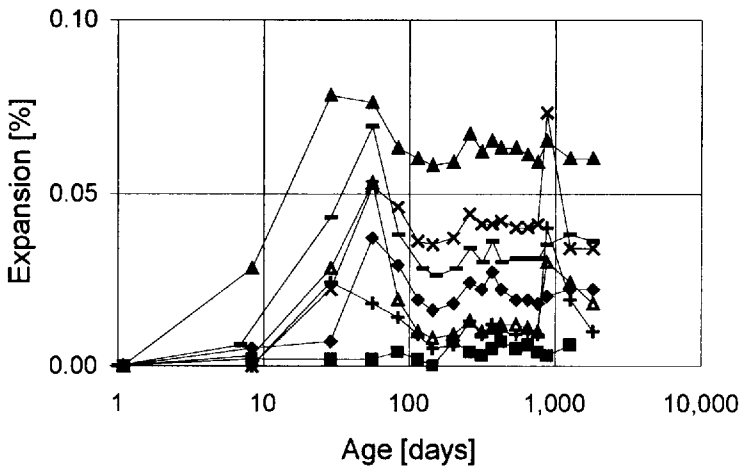


Fig. 1—Expansion for mortars cured at 20 C (Clinker D cements).

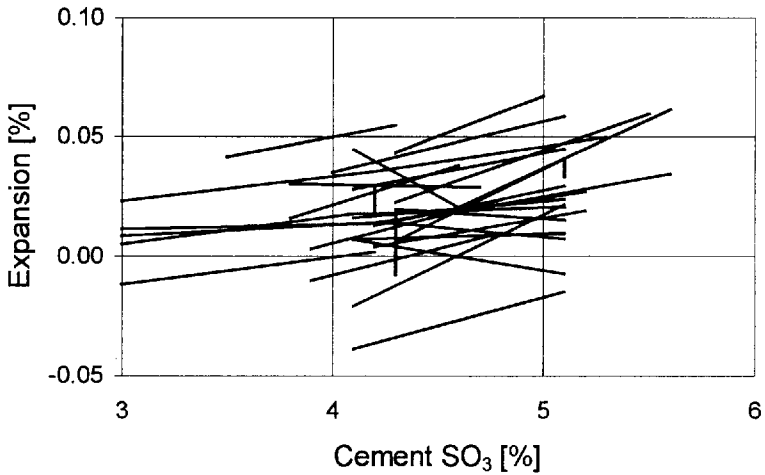


Fig. 2—Effect of cement SO_3 content on expansion after curing at 20 C.

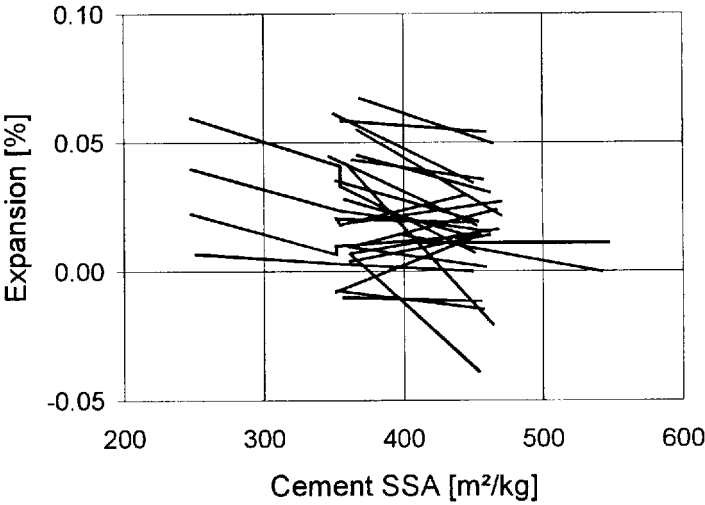


Fig. 3—Effect of cement SSA on expansion after curing at 20 C.

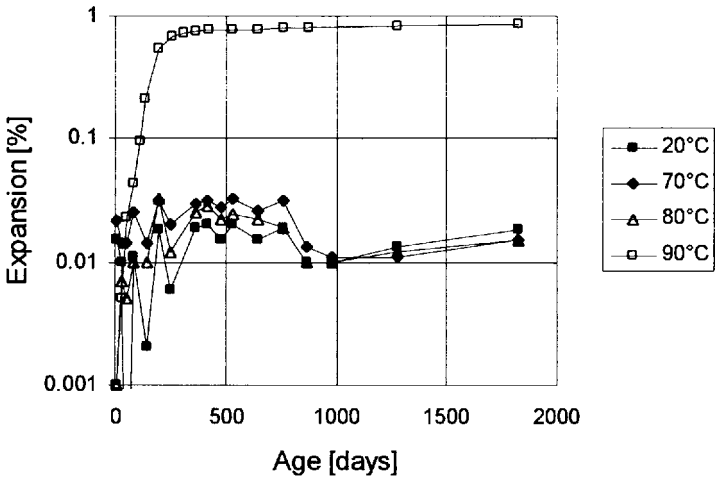


Fig. 4—Typical data for mortars cured at different temperatures.

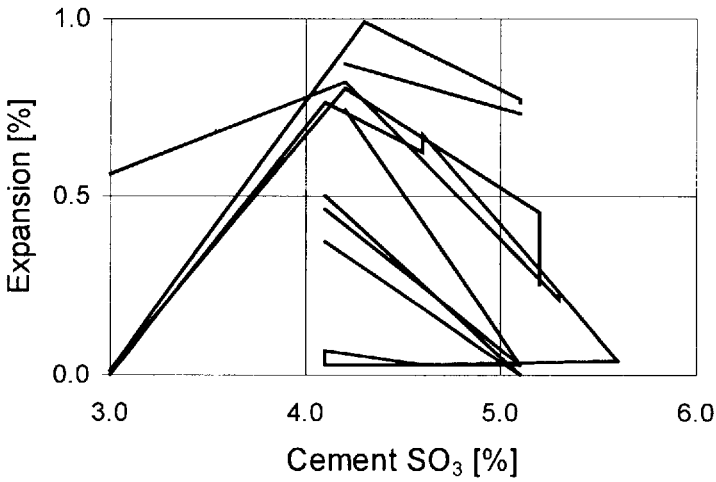


Fig. 5—Effect of cement SO_3 content of expansion after curing at 90 C.

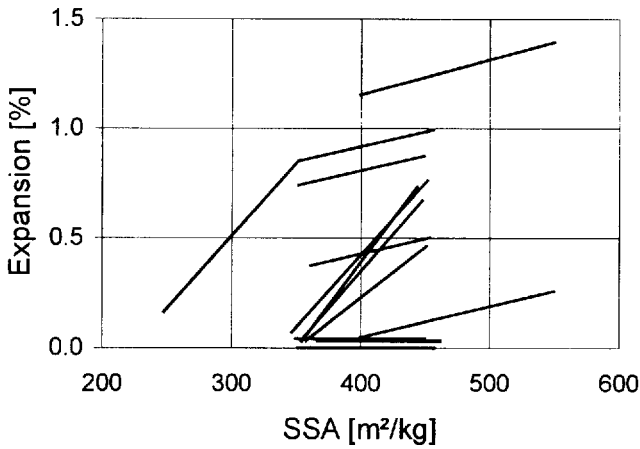


Fig. 6—Effect of cement SSA on expansion after curing at 90 C.

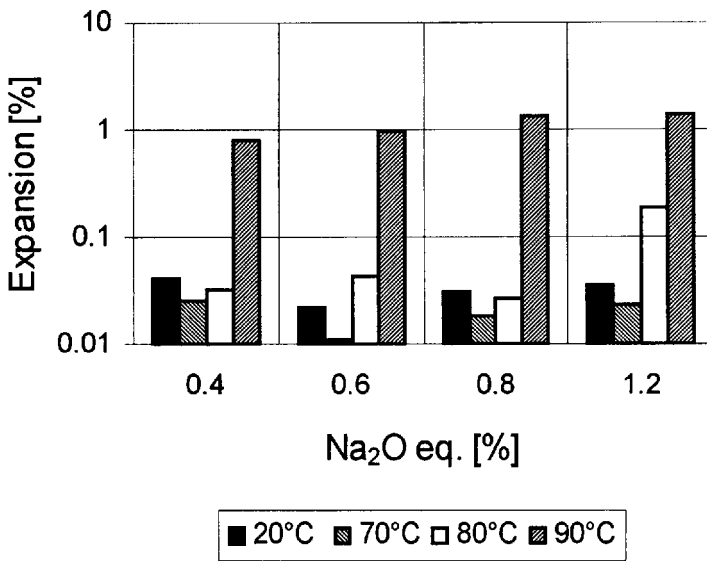


Fig. 7—Effect of KOH addition on expansions after curing at various temperatures.

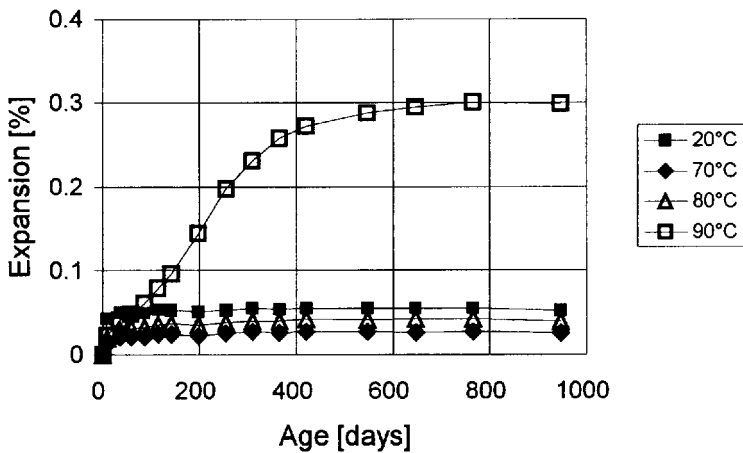


Fig. 8—Expansion of Type K cement.

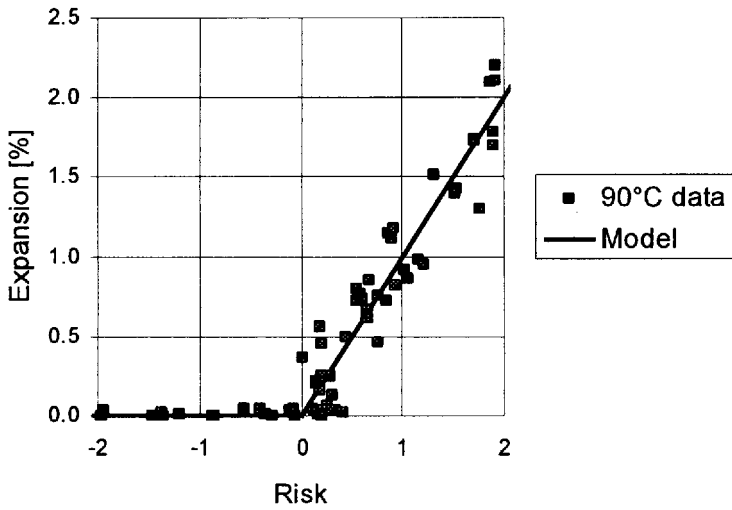


Fig. 9—Comparison of calculated risk and measured expansions (data from Tables 2, 3, 4, and 5).

SP 177-4

Heat Curing and Late Formation of Ettringite

by V. Johansen and N. Thaulow

Abstract: Paste, mortar, and concrete cured at temperatures above certain limits may exhibit expansion and cracking during subsequent exposure to varying moist conditions. This phenomenon originally became known as delayed ettringite formation, DEF. DEF results in a typical microstructure which is demonstrated with examples from field samples and laboratory-made samples. The microstructure is compared with examples of internal sulfate attack in laboratory samples. These typical features include gaps around the aggregate where the paste shows an almost perfect replica of the individual aggregate surfaces. Expansion of the paste on a scale which is homogeneous relative to the aggregate would lead to such features. The chemistry in DEF is similar to that of sulfate attack. A mechanism involving hydrates of aluminates and possible unhydrated cement clinker particles is discussed.

Keywords: curing; ettringite; expansion; models; sulfate attack