A new hypothesis of sulphate expansion*

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The hypothesis of sulphate expansion put forward by Chatterji and Jeffery has certain novel features, but is open to criticism on several counts. The main criticism relates to the assumption, on which the hypothesis is wholly dependent, that C_4AH_{13} exists in set C_3A or cement pastes under moist conditions and that this hydrate is soluble in capillary water. This is contrary to the conclusion of phase-equilibrium studies^(1,2) that the higher C_4AH_{19} hydrate is the only tetracalcium aluminate hydrate formed in contact with solution at 25°C and atmospheric pressure. However, the authors suggest that C_4AH_{13} is formed under the conditions of internal suction in the pore structure of set paste, or, alternatively, that the inter-layer water of C_4AH_{19} may be more labile in the small crystals formed in a paste. The little experimental evidence bearing on this problem of the precise state of hydration of C_4A hydrate in hardened pastes that is put forward by Chatterji and Jeffery is inconclusive. Thus the observations of Seligmann on C_4AH_{19} in Portland cement pastes which are quoted in the paper are not satisfactory, since although it is claimed that the initially formed C_4AH_{19} disappeared at longer times of hydration it is not indicated that C_4AH_{19} changed into C_4AH_{13} . It is possible that the C_4AH_{19} disappeared owing to reasons other than dehydration, for instance carbonation or transformation to C_3AH_6 . Similarly, the observation that a C_3AH_6 structure containing SiO_2 is formed in pastes of alite, C_3A and C_4AF , apparently by a "through-solution" reaction, does not provide evidence that C_4AH_{13} dissolves directly, since the work did not establish that this compound was ever present. It is quite possible, therefore, that C_4AH_{19} was present initially in the hardened paste and that it was this higher hydrate, not the $13H_2O$ hydrate, which was concerned in the transformation to the cubic structure. Indeed, C_4AH_{13} in the dry state shows little, if any, tendency to transform into stable C_3AH_6 at room temperature; even on heating it dehydrates without forming C_3AH_6 . On the other hand, under moist conditions, where rehydration to C_4AH_{19} may occur, transformation into C_3AH_6 takes place much more readily, and particularly so on heating above room temperature.

In an attempt to provide more direct experimental

evidence on the state of hydration of C_4A hydrate in set pastes, some experiments have recently been done in which X-ray examinations were made of various C_3A and cement pastes after different periods of hydration. For this purpose, the solids were mixed with water inside a manipulator box fitted with rubber gloves and containing CO_2 -free air at high humidity, and a portion of the paste was placed in a film frame specimen holder, as used in the X-ray focussing camera, and sealed each side with polythene self-adhesive tape. After taking an X-ray powder photograph immediately after preparation, the specimen holder containing the paste, and still sealed each side with polythene tape, was then stored in air over water inside a small desiccator containing soda lime to absorb any CO_2 present, and further X-ray examinations of the specimen were made at various periods up to 3 months. The results obtained with a C_3A - CaO - $CaSO_4 \cdot 2H_2O$ paste (water/solids ratio = 0.6, CaO/Al_2O_3 molar ratio = 3.47, $CaSO_4/Al_2O_3$ molar ratio = 0.16) showed that a little $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ was present after 3 h and after 1 day, together with unreacted C_3A , $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$; at 7 days the $CaSO_4 \cdot 2H_2O$ and $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ had disappeared and $C_3A \cdot CaSO_4 \cdot 12H_2O$ (or more probably a $C_3A \cdot CaSO_4 \cdot aq$ - $C_4A \cdot aq$ solid-solution phase) together with C_4AH_{19} were formed instead. There was little further change at times of hydration of up to 3 months. These results are similar to those obtained by Chatterji and Grudemo for a paste of identical composition, except that the presence of C_4AH_{19} was indicated, whereas Chatterji and Grudemo treated their paste samples with alcohol and ether before X-ray examination and consequently they observed the presence of C_4AH_{13} . The initial formation of $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ in this paste can be explained by the excess of sulphate with respect to the reacting C_3A during the early stages; as more and more C_3A hydrates the sulphate becomes used up, and at this point the $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ changes to $C_3A \cdot CaSO_4 \cdot 12H_2O$ (or solid solution) and C_4AH_{19} is also formed because of the low $CaSO_4/Al_2O_3$ molar ratio and the fact that the $C_3A \cdot CaSO_4 \cdot aq$ - $C_4A \cdot aq$ solid-solution series is formed only over a restricted range of compositions⁽³⁾. However, a different behaviour was observed in Portland cement paste (water/cement ratio = 0.4) in that there seemed to be no tendency for the $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, formed initially, to transform to $C_3A \cdot CaSO_4 \cdot 12H_2O$. Thus, X-ray examination of the paste specimen at 7 days and longer times up to 3 months

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indicated the presence of unhydrated cement together with $\text{Ca}(\text{OH})_2$, $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ and “ $\alpha\text{-C}_4\text{AH}_{13}$ ”. The latter compound is a tetracalcium aluminate hydrate containing CO_2 ⁽²⁾, and it was probably formed in the cement paste owing to the presence of a small amount of carbonate in the original cement sample. It is possible that the formation of this carbonate compound may have some connexion with the persistence of $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ in the cement paste. Owing to preferential reaction with sulphate and carbonate, and possibly also incomplete hydration, tetracalcium aluminate hydrate was not formed in the cement paste. However, in a similar paste made from ground clinker which contained very little sulphate or carbonate, the presence of a little C_4AH_{19} was observed at times of hydration of from 7 days up to 3 months. Similarly, the formation of C_4AH_{19} rather than C_4AH_{13} in moist pastes was also observed in a C_3A - CaO paste (water/solids ratio = 0.6, $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio = 3.95) at times of hydration of up to 3 months, though here some transformation into stable C_3AH_6 also occurred.

The thickness of the various 10×15 mm paste specimens used in the above experiments was rather variable, from 0.2 to 0.6 mm. It may be argued that these thin paste specimens did not develop or maintain the normal pore structure of a massive specimen, and that C_4AH_{19} rather than C_4AH_{13} was formed for this reason. Additional experiments were therefore done with discs of hardened paste several mm thick, which were stored in CO_2 -free air over water. After 3 months the discs were crushed in a mortar and samples prepared for X-ray examination, these operations being carried out inside the manipulator box at high humidity in order to prevent any decomposition of the samples by dehydration or carbonation. The results of the X-ray examination were found to be very similar to those obtained with the thin paste specimens prepared in the film frame specimen holder, and in particular it was established that in every case where the C_4A hydrate was formed this compound was present as C_4AH_{19} and not as C_4AH_{13} . On the basis of the above results, it seems that in agreement with phase-equilibrium studies it must be concluded that when C_4A hydrate is formed during the paste hydration of cement compounds it is the $19\text{H}_2\text{O}$ hydrate which is present under moist conditions and not the lower $13\text{H}_2\text{O}$ hydrate. Both dehydration and carbonation can occur under the conditions of preparation used by Chatterji and Grudemo, and by Chatterji and Jeffery, and any C_4AH_{19} originally present would certainly be decomposed before X-ray examination. It is not surprising, therefore, that C_4AH_{19} was not found in these paste hydration studies, and that the results also indicated appreciable contamination with carbonate and the formation of the carbonate compounds “ $\alpha\text{-C}_4\text{AH}_{13}$ ” and $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 12\text{H}_2\text{O}$.

If it is accepted that C_4AH_{19} is present in hardened

C_3A and cement pastes under CO_2 -free moist conditions, then the hypothesis of sulphate expansion put forward by Chatterji and Jeffery is untenable, since conversion of C_4AH_{19} into $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ should theoretically result in a decrease in solid volume, the respective molar volumes of C_4AH_{19} and $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ being 371 cm^3 and 313 cm^3 . When CO_2 is present, “ $\alpha\text{-C}_4\text{AH}_{13}$ ” or $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 12\text{H}_2\text{O}$ may be formed in place of C_4AH_{19} and in this case it is indicated⁽³⁾ that these carbonate compounds react with sulphate in solution to form $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ rather than $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$. An alternative explanation must therefore be sought to explain the observation of Chatterji and Grudemo that vials in which pastes containing C_3A and gypsum were stored became cracked. As indicated by Lea⁽⁴⁾, cement pastes sealed in glass tubes with excess water also eventually expand enough to crack the glass, and it was suggested that the reason was that the hardened paste was not able to accommodate itself to the localized growth of hydrated solid around the cement grains. It seems possible therefore that the expansion observed by Chatterji and Grudemo is not directly connected with the formation of $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$, but rather with the continued hydration of the C_3A in the paste and the formation of C_4AH_{19} . The fact that expansion was not observed in C_3A - $\text{Ca}(\text{OH})_2$ pastes may be connected with the formation of C_3AH_6 in this case, and it would be interesting to observe the expansion tendency of this paste at lower temperatures so as to avoid the formation of C_3AH_6 . The additional observation by Chatterji and Grudemo that expansion occurred only in the presence of excess lime seems to fit in with the theory of Lafuma⁽⁵⁾ that “solid-state” reactions resulting in expansion occur at high lime concentrations owing to the very low solubility of C_4A hydrate under these conditions. On the other hand, at low lime concentrations there is more alumina in solution and the hydration reactions can take place by a “through-solution” mechanism, and under this condition expansion is not considered to occur. It may also be noted that alkali (NaOH or KOH) not only decreases the lime solubility but, more important, it increases the amount of alumina in solution so that it is possible for “through-solution” reactions to occur in the presence of alkali even with excess lime as well. This effect may possibly explain the observations made in the paper on the effect of NaOH on sulphate expansion.

Another unacceptable feature of the paper is that an attempt is made to explain the sulphate expansion of concrete made with different cements simply on the basis of a single reaction which is believed to occur in a C_3A paste admixed with gypsum before setting. In paste experiments with a gypsum admixture the phenomena are more closely allied to those which occur in the setting of cement, or in the hydration of so-called expanding cements, than to those taking place when an external source of sulphate in solution

comes into contact with a hardened cement paste. In the latter case the action of sulphate is much more complex, physical factors such as the permeability of the specimen and the formation of protective surface films being involved together with the possibility of different chemical reactions occurring with sulphates of different metals.⁽⁶⁾ The section of the paper dealing with sulphate expansion of different cements seems to consist for the most part of speculation, particularly the discussion relating to aluminous cement. Chatterji and Jeffery assume that C_4A hydrate is formed in hydrated aluminous cement, but this is extremely unlikely as insufficient lime is available. As discussed by Jones and Roberts, the reported conversion of C_2AH_8 into C_4AH_{13} in the dry state has not been confirmed.⁽²⁾ The experiments by Brocard which are referred to in the paper as further supporting evidence for the formation of C_4A hydrate from C_2AH_8 were hydrolysis experiments, and the results are open to some doubt because it is apparent that appreciable carbonation occurred. Furthermore, in numerous studies made on hydrated aluminous cements the formation of C_4A hydrate as a hydration product has never been observed.⁽⁷⁾ The resistance of hydrated aluminous cement to sulphate attack is therefore not connected in any way with C_4A hydrate. There also does not appear to be any evidence that the sulphate resistance is connected with a mechanism of protective surface layers arising from orientation of hexagonal plates as suggested by Chatterji and Jeffery. Indeed, if it is formed at all, the hexagonal plate compound C_2AH_8 is only a minor constituent of hydrated aluminous cement under ordinary conditions, the main hydration products being poorly crystalline CAH_{10} and alumina gel. It seems more likely therefore that the resistance shown by high alumina cement to sulphate solutions may be attributed to the absence of free lime and possibly to the formation of protective surface films of hydrated alumina. The conclusion of Chatterji and Jeffery that the formation of $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ gives rise to second order expansive forces with at most a minor increase in disruptive expansion is also very much open to question. The work done on "expanding cements" has clearly shown that the formation of $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ can result in intensive expansion and in certain cases it can cause disruption of a set cement structure.⁽⁸⁾ Moreover, this work also indicates that the formation of $C_3A \cdot CaSO_4 \cdot 12H_2O$ does not lead to expansion. It seems probable that the formation of $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ is still an important factor involved in the expansion and disruption of mortars and concretes attacked by sulphate solutions.

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Bogue⁽⁹⁾ and Lea⁽¹⁰⁾ have discussed the large volume changes that can take place when calcium aluminate-calcium hydroxide phases in cement pastes form calcium sulphotoaluminates and calcium sulphate hydrates. Lea has emphasized more the volume change associated with the conversion of calcium hydroxide into sulphate. More recently Hansen has stated that expansion due to the formation of sulphotoaluminates is not compatible with the "through-solution" theory.^(11,12) He believes that when C_3A chemisorbs calcium sulphate and water to form the calcium sulphotoaluminates or the hydrated tetracalcium aluminate the crystals expand several hundred per cent through a solid-state reaction mechanism. In short, the mechanism of sulphate expansion is not altogether clear. The hypothesis put forward by Chatterji and Jeffery, therefore, is a definite advancement in this field. However, some points need further clarification and confirmation.

According to Chatterji and Jeffery the formation of ettringite from monosulphate is a "through-solution" reaction and may give rise only to second order expansive forces. This is a very important observation and requires confirmation as several references in the literature speak of the formation of ettringite in the powder form by a solid-state reaction mechanism. In fact, expansions in many expansive cements are believed to be due to the formation of ettringite in the hard phase.⁽¹³⁾ Chopra and Rai had also reached a similar conclusion while working with pastes of cement, kaolin, lime and gypsum and using d.t.a. and X-ray techniques.⁽¹⁴⁾ While reporting new developments in self-stressed concrete, Mikhailov discusses the conditions of the conversion of monosulphate into the high sulphate form, the process of recrystallization being accompanied by large expansions and rupture which cannot be considered to have resulted from second order forces.⁽¹⁵⁾ In other words formation of ettringite in powder form through solid-state reactions and crystallization of monosulphate to the high form with accompanying large expansions must either be confirmed or disproved in order that expansions arising from the conversion of C_4A .aq. to monosulphate may be placed in their right perspective.

The discussion on the sulphate expansion of slag cements and supersulphated cement is of special interest to us as the work mentioned in the paper relates to the use of Indian slag. Sulphate resistance of slag-based cements is of particular importance because of the doubtful performance of high alumina cement in the tropics. Chopra and Patwardhan had concluded from sulphate susceptibility tests that Portland blast-furnace cements (slag 30-45 parts) were relatively non-resistant to sulphate attack but may show greater resistance than ordinary Portland cement.⁽¹⁵⁾ But subsequent tests on the expansion of mortar bars in 5% Na_2SO_4 solution showed the latter deduction to be

wrong. The performance of cement containing even 45 parts slag was no better than that of ordinary Portland cement even though the expansion due to the formation of either sulphaaluminate or CaSO_4 in the slag cement was expected to be less. Continued hydration of slag and a smaller degree of "accommodative processes" could be the explanation but it requires further study as the strength development characteristics of the cement appear to be an important factor in sulphate resistance. In other words, sulphate expansion alone may not give a true picture of sulphate resistance, the mechanism being probably more complex.

Chopra and Kishan Lal have also studied the sulphate activation of the Indian slag.⁽¹⁶⁾ A study of the expansion of mortar bars prepared with two laboratory made super-sulphated cements in 5% Na_2SO_4 solution was begun more than 3 years ago. The maximum expansion after $3\frac{1}{2}$ years is 0.052%, while the companion specimens in water show negligible expansion. The surfaces of some of the bars in sulphate solution have corroded slightly at corners. The loss of strength in sulphate solution ranges from 8 to 25% for the two cements. The d.t.a. curves of the two cements after $3\frac{1}{2}$ years storage either in water or in sulphate solution show a similar pattern, the only difference being that the magnitude of the ettringite peak is greater in specimens stored in sulphate solution. In none of the hydrated samples was the presence of monosulphate or calcium aluminate hydrate or calcium hydroxide detected.

At this stage it is difficult to say whether expansions will continue owing to the formation of further quantities of ettringite and, if so, what type of disruptive forces would result, or whether the specimens will disintegrate without any appreciable expansions as opined by some. Nevertheless the nature of the slag glass and composition of the super-sulphated cement appear to be important factors because some of the super-sulphated cements have shown very good performance in actual structures.

Reply by the authors

Introduction

As the basic points raised by Dr Roberts and Mr Chopra are similar in nature, the two contributions will be taken together. Only those points which seem to us relevant and not covered by the original paper will be dealt with. It should be kept in mind that our hypothesis was on sulphate expansion of different types of cement, not on sulphate resistance as measured by strength tests, which may well involve other complicating factors.

Localized growth theory

If we assume with Lea⁽¹⁷⁾ that the expansion is due to lack of accommodation of the localized growth of the hydrated solids around the cement grains, then the density data of anhydrous and hydrated cement compounds show that all pastes of cement compounds and their mixtures, irrespective of the presence or absence of gypsum, should expand. But, in our experiments with pastes of alite and alite + C_3A , the plastic vials remained intact; whereas the paste containing alite + $\text{C}_3\text{A} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ expanded sufficiently to crack the vials. This difference in expansive force between the two types of paste showed that something different was happening in the paste containing gypsum. From the localized growth theory it is difficult to explain both the above observations. From our hypothesis, on the other hand, we can explain both our observations and the observations of Lea on the cracking of glass vials containing cement paste.⁽¹⁷⁾ The expansion in the latter case would be due to the formation of monosulphate corresponding to the amount of gypsum added to the Portland cements.

Mechanism of ettringite formation and its relation to sulphate expansion

It must be remembered that the often-quoted theory of Lafuma⁽⁵⁾ has no direct experimental evidence. In our recent study⁽¹⁸⁾ on the early hydration of heat-treated cements, we found that C_4AH_x plates were formed with annealed cements by 4 min, together with ettringite crystals. The eroded appearance of the C_4AH_x plates and the nature of the ettringite crystals indicated a "through-solution" mechanism of ettringite formation even in the presence of saturated lime solution. Lafuma's theory would require that ettringite should grow by solid-state reaction in these circumstances. Further evidence for the non-applicability of Lafuma's theory is provided by the work of Heller⁽¹⁹⁾ discussed below.

Mikhailov⁽⁸⁾ claimed, on the basis of optical microscope observations, that monosulphate changes over to ettringite. In our X-ray study we could not find any evidence for the change of monosulphate to ettringite, at least up to 2 years, in paste conditions. We believe that the X-ray evidence is more reliable than that of the optical microscope and this belief is strengthened by a number of anomalies in Mikhailov's results, e.g. the alleged presence of C_5AH_x .

The effect of continued hydration of C_3A

Dr Roberts has suggested that expansion of pastes containing C_3A may be due to C_4AH_{19} formation from continued hydration of C_3A and that the failure to observe expansion in $\text{C}_3\text{A} + \text{Ca}(\text{OH})_2$ pastes may be connected with the formation of C_3AH_6 . In this connexion we would like to report the results of some

experiments for another research programme which unfortunately did not call for X-ray control. In that project the hydration of C_3A and $C_3A + Ca(OH)_2$ pastes was carried out at low temperature (about $4^\circ C$). It was observed (at least up to one month) that the pastes shrank somewhat and became loose in the vials. Since, according to Dr Roberts, C_4AH_{19} should have formed in both cases, expansion should also have occurred in both cases. In fact, neither expanded and it therefore seems that expansion cannot be due to the formation of C_4AH_{19} .

Hydration state of C_4AH_x and monosulphate in pastes

We have carried out some experimental work, similar to that of Dr Roberts, to prove or disprove the existence of C_4AH_{13} in moist pastes. In these experiments, 5 g of finely ground clinker were intimately mixed with 1 g of C_3A . The mixture was then formed into small pellets under pressure, burnt at $1,400^\circ C$ for several hours, and then quenched in water. The dried pellets were ground to pass a 200 mesh B.S. sieve and the powder was divided into two parts: one part was used as it was; to the other part, 0.1 g of finely ground gypsum was added for each 1.9 g of powder. Both parts were then treated in the following way.

The powder was mixed with boiled and cooled (about $8^\circ C$) distilled water (water/cement ratio 0.6) for 2 min and the paste was separated into several vials. The vials were in their turn stored under lime suspension to prevent carbonation. After different times of hydration (7 days to 1 month) the contents of the vials were ground and samples were made for X-ray examination. The whole operation of grinding the paste and making samples was done inside a "glove box" through which nitrogen at 85 or 100% R.H. was continuously passed. The X-ray sample was sealed between adhesive tape and a piece of X-ray film base, which acted as the sample carrier. The X-ray patterns were taken by a Guinier camera. During X-ray exposure, the film cassette and the sample were covered by a sealed plastic dome and nitrogen at 85 or 100% R.H. was continuously passed through the dome. Another part of the sample was ground under acetone, washed with ether, and finally dried in air. X-ray patterns of the dried samples were also taken.

SAMPLES WITHOUT GYPSUM

The X-ray patterns of the undried samples (both 85 and 100% R.H.) containing no gypsum showed a diffuse line at about $10.7 \text{ \AA}$ and a band at 8.0 to $8.3 \text{ \AA}$, together with lines of anhydrous clinker and $Ca(OH)_2$. On the other hand, the X-ray patterns of the dried samples showed lines at about 10.7 and $7.9 \text{ \AA}$ in addition to those of anhydrous clinker and $Ca(OH)_2$, but there were no lines at 7.6 or $8.2 \text{ \AA}$. The presence of the $10.7 \text{ \AA}$ line in both moist and dried samples

showed that C_2AH_8 was present in both. This may explain, at least partly, the inference of Dr Roberts that C_4AH_{19} (basal spacing $10.6 \text{ \AA}$) had formed in moist cement pastes. The band at 8.0 to $8.3 \text{ \AA}$ in the moist samples, which was replaced by the $7.9 \text{ \AA}$ line on drying, can be explained on the basis of alternating layers of C_4AH_{13} and C_4AH_{19} with a large preponderance of the former.

SAMPLES WITH GYPSUM

In the X-ray pattern of the moist sample, the $10.3 \text{ \AA}$ line (corresponding to the higher hydration state of monosulphate) and the $8.9 \text{ \AA}$ line of the lower hydrate were both present. The $8.9 \text{ \AA}$ line was stronger, indicating that the sample contained more of the lower hydrate. While this does not prove that the lower hydration state of C_4AH_{19} is produced under similar circumstances, it shows the possibility of at least the metastable existence of a lower hydration state and the evidence is confirmed both by Dr Roberts⁽¹⁾, who found an $8.9 \text{ \AA}$ line (corresponding to dried monosulphate) in moist specimens of the pure material, and by our own work with pure monosulphate. Our material was prepared by shaking an appropriate mixture of C_3A and gypsum in a large excess of water. The X-ray examination of the moist solid was carried out in an atmosphere of 100% R.H. and the solid was tested for free moisture after the X-ray exposure. The X-ray diagram of the moist solid showed both 10.3 and $8.9 \text{ \AA}$ lines. Another part of the moist solid was treated with acetone and ether; in the dried solid only the $8.9 \text{ \AA}$ line was present.

When all the evidence is considered it seems probable that C_4AH_{13} forms in the paste hydration of cements.

Corroboratory evidence

The following additional corroboratory evidence for our hypothesis has also been obtained since the original paper was written. We found⁽²⁰⁾ that in sulphate-resisting Portland cement a monosulphate type of compound does not form in any quantity. This finding was based on the evidence of hydration data up to 3 months only. Recently we have taken X-ray patterns of the same sulphate-resisting cement after 2 years' hydration and found that ettringite was the only sulphate-bearing compound in that sample although significant amounts of anhydrous aluminoferrite compound were left unreacted.

Dr Heller⁽¹⁹⁾ has recently studied the formation of ettringite in ordinary and sulphate-resisting cement pastes exposed to sulphate solution. She found that, although the amounts of ettringite formed were similar in both cases, the expansion characteristics of the two types of cement were quite different. These data are difficult to explain on the basis of Lafuma's theory

because excess Ca(OH)_2 was present in both types of cement paste. Dr Heller's data point to the fact that the formation of ettringite is not directly connected with the sulphate expansion of cements, as we have already suggested.

Slag cements

In the Bogue sulphate-susceptibility test, the reactivities of the aluminate and aluminoferrite compounds were empirically related to the sulphate resistance of Portland cements. This test method cannot be used for Portland blastfurnace cements without it first being shown that this empirical relation holds good for such cements. The use of this test in the absence of proof of its applicability⁽¹⁵⁾ cannot produce significant results.

Super-sulphated cements

In the original paper we commented that "It would be interesting to compare the performance of sulphate-resisting Portland cement with that of super-sulphated cement over long periods of exposure to sulphate solutions". The recent work of Burke⁽²¹⁾ has shown that the performance of sulphate-resisting Portland cement is better than that of super-sulphated cement over long periods. Although there was no X-ray or electron-optical investigation of the variation of composition with time, the strength test results provide some support for our hypothesis.

Conclusion

We would reiterate that we have only put forward a hypothesis to try to organize many apparently contradictory findings on sulphate expansion and that much more corroboration will be needed before it can be taken as an established theory. However, the further evidence produced since the original paper seems sufficiently encouraging to warrant more investigation.

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