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Distribution of sulfate between phases in Portland cement clinkers

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Abstract

Sulfate can occur in Portland cement clinkers as alkali sulfates, potassium calcium sulfate (calcium langbeinite), anhydrite, and as a substituent in the major phases, especially alite and belite. Data for the contents in alite and belite are reviewed and relations to bulk clinker composition are discussed. Evidence on sulfate distribution from extraction procedures is similarly considered. A procedure for predicting sulfate distribution from bulk composition is described and tested and potential sources of error in such calculations are discussed. The evidence does not support suggestions that, in concrete made with present-day cements and not subjected to an elevated temperature, damage through delayed ettringite formation can occur for reasons connected with the SO_3 present in the clinker. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Durability; Delayed ettringite formation; Clinker; Sulfate; Anhydrite

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1. Introduction

Considerable interest has been shown in the past few years in mechanisms of damage to concrete associated with internal or external sulfate attack, and, largely for this reason, a number of new studies on the sulfate in Portland cement clinkers have been reported. In this paper, the evidence on the distribution of sulfate between phases is critically reviewed and gaps in our understanding that call for further research noted. It has been suggested that normally cured concrete can be damaged by delayed ettringite formation arising from either excessive contents of SO_3 in the clinker, or the presence of such SO_3 in phases from which it is only slowly released. This hypothesis is examined in the light of evidence on the distribution and properties of the sulfate in clinkers.

2. Sulfate-containing phases in Portland cement clinker

Table 1 lists the phases known to contain sulfate that occur in Portland cement clinkers, with an indication of the rate at which the sulfate is released in each case. Because most raw materials contain more K_2O than Na_2O, and for other reasons, thenardite is a rare constituent, as also is anhydrite. The latter is chemically and structurally identical with natural anhydrite, which is often present in the added calcium sulfate, either as an adventitious impurity or a deliberate addition made to combine proper control of setting with optimisation of early strength. Until recently, there were few published data on the rate at which clinker anhydrite reacts, but an X-ray diffraction (XRD) study [1] of pastes of clinkers containing it showed that it is consumed within 24 hours. Another study [2] showed that in slurries with C_3A, Ca-langbeinite, and $Ca(OH)_2$, anhydrite that had been fired at 1400°C reacts at about the same rate as natural anhydrite, but when burned at 600°C reacted much more quickly.

3. Concentrations of sulfate in the major clinker phases

X-ray microanalyses show that sulfate can occur in the alite, belite, and ferrite, though the amounts present in the ferrite are small enough to be ignored. In Fig. 1, recent data for SO_3 concentrations in alite and belite are plotted against that in the clinker [1,3–5]. Except where otherwise stated, all quantities in this paper are given in mass percent. Most of the clinkers with up to 2% SO_3 were works clinkers, and most of those with more were laboratory or pilot plant clinkers. For clinkers with up to 3% SO_3, the concentrations are below 0.5% in the alite and rarely exceed 2.0% in the belite. SO_3 contents as high as 3% are extremely rare in production

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Table 1
Phases in which sulfate can occur in Portland cement clinkers

Phase	Rate of reaction in cement paste
Alkali sulfates	
K_2SO_4 (arcanite)	Very high
$3K_2SO_4 \bullet Na_2SO_4$ (aphthitalite)	Very high
Na_2SO_4 (thenardite)	Very high
$K_2SO_4 \bullet 2CaSO_4$ (calcium langbeinite)	Very high
$CaSO_4$ (anhydrite)	Similar to that of anhydrite added before grinding
Major clinker phases, as a substituent	That of the phase in which it is present

clinkers, but may occur in small, unrepresentative samples, which will normally be highly diluted by blending prior to grinding.

The correlations between the concentrations of SO_3 in the alite or belite and that in the clinker are low. This is almost certainly due in part to experimental errors, which are discussed later. However, the total SO_3 content of the clinker is probably not the only factor affecting the concentrations in the silicate phases. Regression equations have been suggested [4], but appear to be successful only when applied to a limited range of data.

In Fig. 2, the concentrations in the alite are plotted against those in the belite in the same clinker. The concentration in the belite is typically between four and five times that in the alite. This is approximately the same as the ratio of alite to belite in many present-day clinkers, and the amounts of SO_3 present in alite and in belite are thus often comparable.

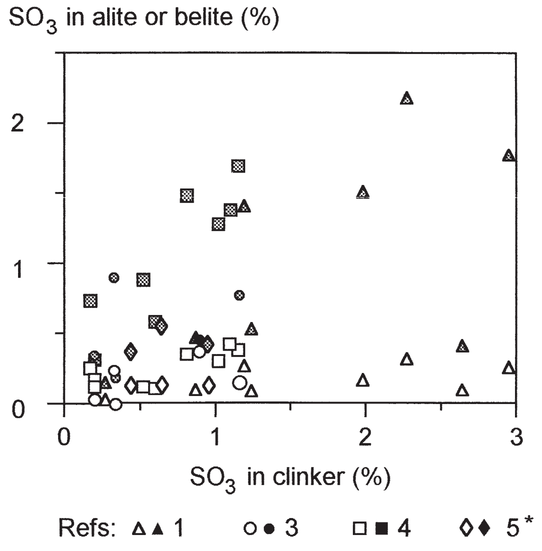

Fig. 1. SO_3 concentrations in the alite and belite of some Portland cement clinkers. Open symbols, alite; filled symbols, belite. *Recalculated from atomic ratios in original paper.

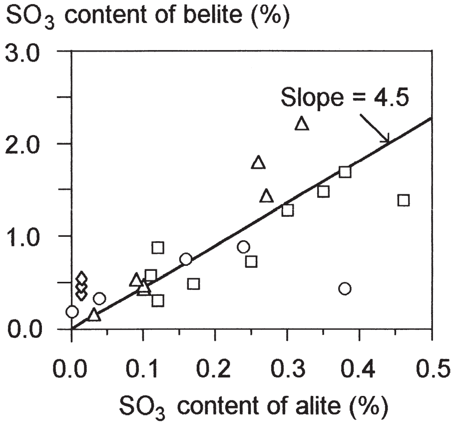

Fig. 2. SO_3 contents of belite and alite in the same clinker. Symbols as in Fig. 1.

4. Chemical extraction methods

Another experimental approach is that of chemical extraction methods. Fig. 3 shows the contents of SO_3 that are *not* extracted by various procedures [6–9]. With the exception of the 10-min water extraction (ASTM C-114), all these procedures give results in very broad mutual agreement. All appear, to varying degrees of approximation, to measure the content of sulfate present in the silicate phases, though they cannot distinguish that in alite from that in belite.

The KOSH (potassium hydroxide and sucrose) extraction dissolves the aluminate, ferrite, and sulfate phases, leaving mainly the alite and belite. As such, it should be a reliable procedure for determining the content of SO_3 in the silicate phases. Sulfate not dissolved in a 1.5–2.5-min treatment with water is also mostly that present in the alite and belite, but almost certainly includes some of the anhydrite.

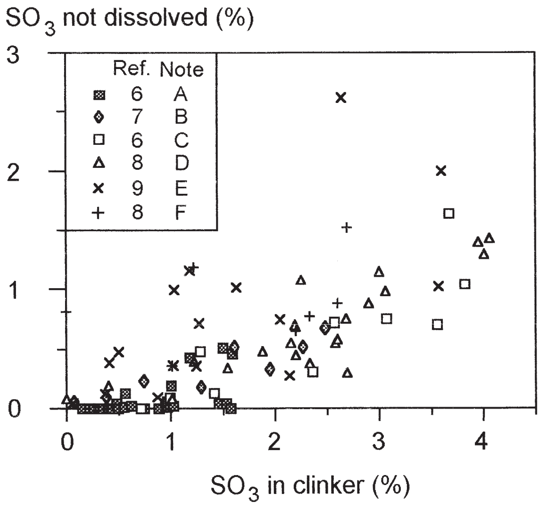

Fig. 3. Clinker SO_3 remaining undissolved after various extraction procedures, plotted against total clinker SO_3. Notes: A, B, works clinkers; C–F, lab clinkers; A, C, 1.5–2.5-min water extraction; B, 30-min KOSH extraction; D, 30-min Na_2CO_3 extraction; E, F, 10-min water extraction.

In an attempt to eliminate the danger of precipitating ettringite or other sulfate-containing phases during extraction with water, Jøns [8] devised the Na_2CO_3 method, which he believed would precipitate carbonate phases in preference to sulfoaluminates. The results it gives are broadly similar to those obtained using KOSH reagent or the 1.5–2.5-min water extraction, but Klemm and Miller [10] found that it gave systematically higher results for unextracted SO_3 than the KOSH method. They considered that it may not have totally eliminated the formation of ettringite or syngenite.

Extraction with water for 10 min often gives much higher results for unextracted SO_3 than the other methods; in some cases, no sulfate at all is dissolved. Osbæck [11] found that the quantities of alkali extracted from some clinkers were lower if gypsum was present, and Struble [12] showed that, with some clinkers, more alkali was extracted in 10 min than in 1 min or 5 s, which gave similar results to each other. Both investigators attributed the effects to the reaction of alkali-substituted C_3A. One might expect this to form ettringite, and Struble [12] confirmed that XRD patterns for the residue from one clinker included weak peaks of this phase. Ten-minute extraction with water thus does not provide valid information on the distribution of sulfate between clinker phases.

5. Comparison of results from X-ray microanalyses and extraction methods

By multiplying the concentration of SO_3 in the alite by that of alite in the clinker, the amount of SO_3 present in alite can be obtained. Thus, for a clinker containing 65% of alite and having a very high SO_3 content (e.g., 3%), the maximum probable amount of SO_3 present in alite is 0.65×0.5, or 0.33%. For the same clinker, assuming a belite content of 15%, the maximum probable amount of SO_3 present in belite is 0.15×3.0, or 0.45%. The total value for the silicate phases, about 0.8%, is probably about the most that is likely to be found in any works clinker. For a clinker containing 3% of SO_3, the extraction data in Fig. 3 suggest that the amount of SO_3 present in the silicate phases is in the region of 0.9%. Taking into account the probable errors and approximations in both methods, this agrees well with the result obtained by X-ray microanalysis. In a study of 33 North American plant clinkers containing up to 3.0% of SO_3, Miller and Tang [7] found the largest amount of SO_3 present in the silicate phases to be 0.68%.

6. Estimation of quantitative sulfate distribution from the bulk chemical analysis

Attempts to calculate the quantitative distribution of sulfate between phases from bulk composition in Portland cement clinkers have developed out of corresponding calculations relating to alkalis. In 1952, Newkirk [13] made the important observation that the alkalis combined preferentially with sulfate, but he did not recognise the possible formation of calcium langbeinite, and he incorrectly assumed that in clinkers containing more sulfate than was needed to balance the alkalis, the latter would be present entirely as sulfates. In a subsequent study of 30 works clinkers and 11 laboratory clinkers, Pollitt and Brown [6] used a water extraction procedure to determine what they called water-soluble K_2O, Na_2O, and SO_3. The procedure, which was not described in their paper, entailed drawing water through the sample on a filter, with a contact time of between 1.5 and 2.5 min [14]. Their results for unextracted SO_3 have already been given in Fig. 3. It is important to recognise that the term “water soluble” relates only to the method used and does not imply that any of the alkalis or sulfate do not react in a cement paste.

In Fig. 4, Pollitt and Brown’s results for the molar fraction of total alkali that is dissolved under the conditions used are plotted against the molar ratio of SO_3 to alkali. For ratios up to about 0.5, the points lie close to a straight line with a slope of unity. This almost certainly implies that all the SO_3 is present in alkali sulfates. At higher ratios, the points lie below this line, indicating that some of the SO_3 is present in other phases. These could include any or all of alite, belite, calcium langbeinite, and anhydrite.

Fig. 5 gives similar data for K_2O and Na_2O separately. At any given value of the SO_3/alkali ratio, the fraction of the K_2O that is rapidly water soluble is close to twice that of the Na_2O. At a ratio of 1.0, about 90% of the K_2O, but only some 45% of the Na_2O, is rapidly water soluble. At higher ratios, the values tend to decrease with increasing SO_3/alkali ratio. Possible explanations of this effect are discussed later.

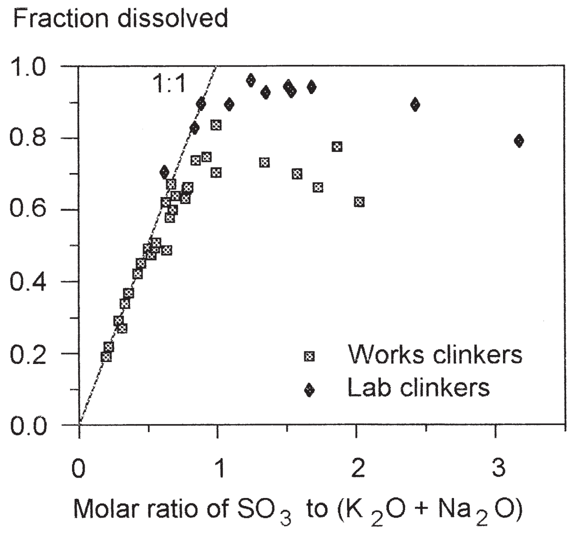

Fig. 4. Fraction of the total alkali dissolved in a 1.5–2.5-min extraction with water (data from [6]).

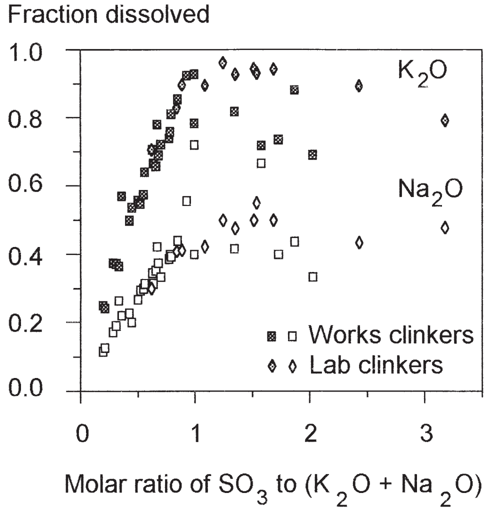

Fig. 5. Fractions of the K_2O (filled symbols) and Na_2O (open symbols) dissolved in a 1.5–2.5-min extraction with water (data from [6]).

7. Calculation of the distribution of sulfate between phases

Previous attempts to calculate the quantitative distribution of sulfate between clinker phases from the bulk composition have been only partly successful [7,8,15,16]. The more extensive data now available permit a new approach.

1. Estimate the amounts of SO_3 that are balanced by K_2O and by Na_2O, using smoothed curves drawn through the data in Fig. 5.
2. Estimate the amounts of SO_3 present in alite and belite. Given the existing data, it is probably best in most cases to use smoothed curves drawn through the data in Fig. 3 to obtain the total quantity in the two phases. The partition of this between alite and belite is not needed in the subsequent stages, but if required it could be made using reference data from X-ray microanalyses and estimates of the alite and belite contents from XRD, microscopy, or a modified Bogue calculation [15]. Failing this, an arbitrary division such as a 60:40 split between belite and alite would rarely be grossly inaccurate. In some cases, due to shortcomings in the procedure or inconsistencies in the reference data, the estimated amount of SO_3 present in the silicates plus that balanced by K_2O and Na_2O can exceed the total available. This is probably best treated by scaling the amounts to this total. Rarely, another complication arises if the estimated amounts of rapidly soluble K_2O and Na_2O exceed that of SO_3 not present in sulfate phases. Several explanations have been suggested, of which the most likely is probably carbonate substitution in the arcanite [17].
3. Deduct the amounts of SO_3 balanced by K_2O and Na_2O and those present in alite and belite from the total amount in the clinker. The SO_3 that remains is that balanced by CaO, in calcium langbeinite or anhydrite or both.

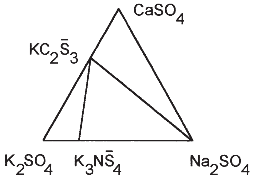

Fig. 6. Suggested phase assemblages in the system K_2SO_4-Na_2SO_4-$CaSO_4$ as found in Portland cement clinkers at ordinary temperatures.

4. Determine which combination of sulfate phases occurs and the amount of each phase. Fig. 6 shows what appear to be the most probable phase assemblages of sulfate phases as found in clinkers at ordinary temperatures. The relative quantities of SO_3 balanced by K_2O, Na_2O, and CaO are represented by a point in this triangle, and both these and the absolute quantities are known. By solving the appropriate simultaneous equations one may determine which sulfate phases are present and the amount of each. The Appendix outlines a procedure based on the above principles.

8. Tests of the calculation of distribution of sulfate phases

In Table 2 the qualitative distributions calculated by the procedure outlined in the Appendix are tested against observed data for some laboratory and works clinkers. The observed data were not quantitative. It was assumed that phases present in amounts below 0.3% would not have been detected. The laboratory clinkers covered a wide range of SO_3 contents (0.06–4.65%), but were atypical with regard to alkali contents. The works clinkers were modern ones obtained from a number of North American plants and included ones produced in long wet, long dry, preheater, and precalciner kilns. The level of agreement between observed and calculated phase distributions is similar to that for the laboratory clinkers. The most common discrepancy with the works clinkers was that arcanite was often found where it was not predicted. The calculations indicated that detectable amounts of anhydrite would not be expected in any of the works clinkers, which agrees with the experimental finding. This contrasts with the results of calculations by Miller and Tang [7], which indicated that anhydrite would be expected to form in several of these clinkers. The calculation was also tested against data for eight clinkers from Herfort et al. [1]; the agreement was excellent. Two other clinkers that contained $C_5S_2\bar{S}$, $C_4A_3\bar{S}$ or C_2AS were excluded.

9. Sources of error in the calculation of sulfate distribution and requirements for further research

Discrepancies between calculated and observed distributions of SO_3 between phases might arise for a number of reasons, of which the following will be considered.

Table 2
Predicted and observed distributions of sulfate phases

	24 lab clinkers* [9]					33 works clinkers† [10]				
Column reference	1	2	3	4	5	1	2	3	4	5
Arcanite	7	12	5	0	79	14	12‡	0	7	79
Aphthitalite	2	22	0	0	100	19	7	3	4	79
Thenardite	0	19	5	0	79	0	33	0	0	100
Ca-langbeinite	8	14	2	0	92	15	12	5	1	82
Anhydrite	5	15	3	1	83	0	33	0	0	100

* Of these clinkers, 13 contained K_2O, 4 contained Na_2O, 3 contained both and 4 were alkali-free. The SO_3 contents were 0.06–4.65%; $SO_3/(K_2O + Na_2O)$ molar ratio 0.35–2.91.

† SO_3 contents 0.03–3.00%; $SO_3/(K_2O + Na_2O)$ molar ratio 0.06–2.54.

‡ Includes two for which a trace was found.

Key to columns:

1. Number of clinkers for which calculated content was $\geqslant$0.3% and the phase was detected.
2. Number of clinkers for which calculated content was $<$0.3% and the phase was not detected.
3. Number of clinkers for which calculated content was $\geqslant$0.3% but the phase was not detected.
4. Number of clinkers for which calculated content was $<$0.3% but the phase was detected.
5. Percentage of cases for which the prediction was correct.

9.1. Errors in the sample or reference data or how the data are used

Pollitt and Brown's [6] observation that the SO_3 in clinkers of low sulfate-to-alkali ratio is present entirely in alkali sulfates conflicts with the X-ray microanalyses, which show small amounts to be present in the silicate phases. Either or both could be in error. On the one hand, the concentrations in the alite and belite at low clinker SO_3 contents are barely outside the limits of detection by X-ray microanalysis. Although the results are conventionally expressed as concentrations of SO_3, what are measured are those of sulfur; an SO_3 content of 0.5% represents a sulfur content of only 0.2%. No adequate study of the errors in determining low SO_3 contents in clinker phases by X-ray microanalysis has been reported, and one is badly needed.

On the other hand, there could be inherent errors in any of the extraction methods. As already noted, 10-min extraction with water often gives meaningless results due to the formation of ettringite or other hydration products containing sulfate. With extraction periods up to 2.5 min, this error appears to be eliminated, but the tendency for the fractions of the alkalis to decrease with increasing SO_3/alkali ratios above approximately 1 needs to be explained. It is not obvious why increases in this ratio should *decrease* the amount of alkali dissolved. One possibility is that the dissolution of alkali sulfates and calcium langbeinite is incomplete if relatively large amounts of these phases are present. Small quantities of alkali sulfates can be encapsulated in alite or belite, but this effect is said to be unusual in high sulfate clinkers [1]. In a study similar to that of Pollitt and Brown [6], Osbæck [11] did not observe a decrease at high SO_3/alkali ratios, but he used a 10-min extraction, and his results could have been influenced by reaction of C_3A. The fractions of Na_2O and K_2O extracted were systematically higher than those of Pollitt and Brown [6]. There could, however, be a real decrease in the contents of these phases due to increased competition for sulfate from the silicate phases. Further investigation of all the extraction methods is needed. This should include examination of the effects of variables such as particle-size distribution and the duration and other conditions of extraction.

In some investigations, including those providing the observed data in Table 2, the sulfate phases were concentrated using extraction with salicylic acid plus methanol reagent to remove the silicate phases. The assemblage of sulfate phases could possibly change during the extraction. There is no positive reason for supposing that this happens, but, equally, no tests of the hypothesis appear to have been reported, and these are needed. Sulfate present in the silicate phases has been found to occur as γ-calcium sulfate (so-called "soluble anhydrite") in the residues from this extraction [7,9,10].

A weakness of the existing data is that no comprehensive study on a single set of clinkers, using all the available methods, has been carried out. This limits the confidence with which the results can be interpreted.

9.2. Ionic substitutions and the attainment of equilibrium

The procedure that has been described for calculating the distribution of SO_3 between phases implicitly assumes that, although the sulfate liquid probably crystallises independently of the silicate liquid [18], equilibrium exists during its solidification and subsequent cooling to ambient temperature. These assumptions are not necessarily correct. At ordinary temperatures, the equilibrium compositions of the sulfate phases are close to those given in Table 1, but at higher temperatures, substantial regions of solid solution exist. K_2SO_4 can accommodate Na^+ [19], Ca^{2+} [17,20], and $CO_3{}^{2-}$ [17]. Also, at higher temperatures aphthitalite can have higher Na/K ratios than in the conventional formula [19]. If such solid solutions persist after cooling, this might account for the formation of arcanite in cases where aphthitalite would be expected. For arcanite and calcium langbeinite, the most extensive solid solutions exist in high temperature polymorphs [17], and these could possibly persist to ambient temperature.

Arceo and Glasser [17] suggested that observations that some clinkers contain CO_2 could perhaps be explained by carbonate substitution in arcanite. As noted earlier, this could also account for observations that some clinkers contain more water-soluble alkali than is needed to balance the SO_3 that is not present in silicate phases. In the writer's experience, the arcanite in works clinkers normally contains significant quantities of sodium and calcium and its sulfate content is sometimes insufficient to balance the cations, while aphthitalite sometimes has a Na/K ratio greater than 1:3, and may also contain calcium.

Pliego-Cuervo and Glasser [18] found that C_3A and anhydrite did not coexist stably in the CaO-Al_2O_3-K_2SO_4-$CaSO_4$ system. On the basis of this and other evidence, Miller and Tang [7] and Klemm and Miller [10] concluded that anhydrite was unlikely to form in normal Portland cement clinkers burned at the usual temperatures unless they were high in sulfate and very low in alkali. Calculations using the procedure described in this paper suggest that for high alkali clinkers anhydrite is unlikely to form unless the total clinker SO_3 content is well above 2.5%. For low alkali clinkers (equivalent Na_2O 0.4%) it could form at SO_3 contents as low as 1.5%, especially if the ratio of K_2O to Na_2O is low.

10. Can the amount or phase distribution of clinker SO_3 cause distress in concrete not subjected to elevated temperatures?

During the past few years, it has been suggested [21–23] that cracking in field concretes cured at ordinary temperature can be caused by delayed formation of ettringite, and that this in turn is due either to too high a total content of SO_3 in the cement, too much of it being in the clinker, or the presence in the clinker of significant amounts in phases from which it is only slowly released. It was suggested that these phases were anhydrite and the silicates. Hime [22] concluded from experience to date that damage due to delayed ettringite formation in nonsteam cured concrete might be prevented by limiting clinker sulfate content to 1%, or that distress might be minimised or prevented with high sulfur clinkers through air entrainment or use only under low moisture conditions. No data on the relevant clinkers or cements, as opposed to field concretes made using them, appear to have been reported in support of these views.

The evidence presented here does not support the view that anhydrite can be a cause of distress. It does not react slowly. For the same reason, alite can be ruled out. Belite, however, reacts relatively slowly, and the possibility of damage arising from its sulfate content needs to be examined.

The X-ray microanalyses and extraction data both show that, except perhaps in clinkers unusually high in belite, the amount of SO_3 present in this phase is unlikely to exceed half a percent. Possibly half of the belite will have reacted in 28 days. This leaves, at the most, around 0.3% to be released later. It is difficult to believe that the amount of ettringite formed from this quantity of SO_3, or from the additional small amount that might be present in encapsulated alkali sulfate, could cause damage.

Recent work on doped belites [24,25] supports earlier conclusions that sulfur and aluminium enter the structure as substituents for silicon and that charge balance is maintained by substituting $2Al^{3+} + S^{6+}$ for $3Si^{4+}$. One would not expect the Al/S ratio in a clinker belite to be exactly 2, because there are other substitutions. X-ray microanalyses [1,3–5] show that it is nearly always more than 2, even in individual analyses. It never approximates the value in ettringite, which is 0.67. When the belite reacts, the Al and sulfate are released together. If they enter a sulfoaluminate phase, this should be monosulfate and not ettringite [7].

Finally, we must consider the effect of high contents of total clinker SO_3. The amounts that can occur in the alite and belite are limited by the ability of these phases to accommodate it. Any excess of SO_3 above what can be contained in these phases, or in alkali sulfates and calcium langbeinite, will be present in anhydrite. Assuming that the amount of added gypsum is such that the total cement SO_3 is acceptable, there is no reason to suppose that this would impair durability. In practice, clinker SO_3 contents are limited by the fact that SO_3 tends to decrease alite contents [26–28]. Klemm and Miller [10] noted that the resulting increases in free lime content would cause the kiln operator to raise the temperature, which would increase the volatilisation of SO_3. The present results provide no basis for a limit of 1% on clinker SO_3. Hime [22] quoted a statement by the writer [29] that "for ratios above 1.0, appreciable fractions of the SO_3 are not water soluble" and correctly noted that these were, in reality, slowly soluble, but this statement related to the conditions of the extraction method used and not to a Portland cement paste.

11. Conclusions

1. Evidence on the distribution of sulfate between phases in Portland cement clinkers is critically reviewed. Sources of error in calculations of the qualitative and quantitative distribution from bulk composition are discussed, and requirements for further research outlined. A general need is for comprehensive studies on a single suite of clinkers of widely varying compositions by all the relevant techniques.
2. The evidence on clinkers does not support the hypothesis that in present-day cements either the total content of SO_3 in the clinker, or its distribution between phases, is a likely source of damage from delayed ettringite formation in concrete that has not been subjected to an elevated temperature.

Appendix

The stages in the procedure must all be carried out in the sequence given. Unless otherwise stated, all quantities are expressed in moles per 100 g of clinker.

Symbols

K, N, and S are the K_2O, Na_2O, and SO_3 contents of the clinker, respectively; $R = S/(K + N)$. SK and SN are the amounts of SO_3 balanced by K_2O and Na_2O, respectively. S followed by a three-letter combination denotes the amount of SO_3 present in the phase(s) indicated by the letters: SIL = silicates; ARC = arcanite ($K\overline{S}$); APH = aphthitalite ($K_3N\overline{S}_4$); THE = thenardite ($N\overline{S}$); CAL = Ca-langbeinite

($KC_2\overline{S}_3$); ANH = anhydrite ($C\overline{S}$); SUL = total for all sulfate phases. The values of SK, SN, and SSIL can change during the calculation. The amount of SO_3 balanced by CaO is not used explicitly; it is equal to (SSUL − SK − SN).

Procedure

1. Calculate R.
2. Estimate SK and SN.
   If $R < 1.0$, $SK = (0.00132 + 1.03339R + 0.37635R^2 - 0.51114R^3) \times K$; $SN = (0.00184 + 0.53016R + 0.16336R^2 - 0.24486R^3) \times N$. If $R \geqslant 1.0$, $SK = 0.9K$ and $SN = 0.45SN$.
3. Estimate SSIL:
   If $S < 6.245 \times 10-3$ (0.5% by mass), $SSIL = 0$. If $6.245 \times 10^{-3} \leqslant S < 49.96 \times 10^{-3}$ (4% by mass), $SSIL = 0.35(S - 6.245 \times 10^{-3})$. If $S \geqslant 49.96 \times 10^{-3}$, $SSIL = 15.30 \times 10^{-3}$ (1.225% by mass).
4. Test whether $SK + SN + SSIL > S$. If it is, scale them to a total equal to S.
5. Calculate SSUL, equal to $S - SSIL$. Test whether $SSUL < SK + SN$. If it is, decrease SK by the excess, which is possibly balanced by CO_2 in arcanite.
6. Test whether $SSUL > 3SK + SN$. If it is, the sulfate phases are thenardite, Ca-langbeinite, and anhydrite; $STHE = SN$, $SCAL = 3SK$, and $SANH = SSUL - SCAL - STHE$.
7. If $SSUL \leqslant 3SK + SN$, test whether $SSUL > 3SK - 5SN$. If it is, the sulfate phases are Ca-langbeinite, aphthitalite, and thenardite;
   $SCAL = -3SK/2 + 3SSUL/2 - 3SN/2$;
   $SAPH = 2SK - 2SSUL/3 + 2SN/3$;
   $STHE = SK/2 + SSUL/6 + 5SN/6$.
8. If $SSUL \leqslant 3SK - 5SN$, the sulfate phases are aphthitalite, Ca-langbeinite, and arcanite;
   $SAPH = 4SN$; $SCAL = 3(SSUL - SK - SN)/2$; $SARC = SSUL - SAPH - SCAL$.
9. From the amounts of SO_3 in each of the sulfate phases, calculate the mass percentage of each phase in the clinker. The distributions of K_2O and Na_2O between the phases are also readily calculated.

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