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THE DISTRIBUTION OF SULFUR IN PRESENT-DAY CLINKERS OF VARIABLE SULFUR CONTENT

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ABSTRACT

This study focuses on the identification of sulfur-containing phases present in portland cement clinkers from North American cement plants. The clinkers were studied using X-ray fluorescence, X-ray diffraction, and selective dissolution extraction techniques. The samples contained sulfate levels from a few hundredths of a percent to about 2.5%. The samples were found to contain alkali sulfates, alkali/calcium sulfates, and some sulfate substituted in the silicate phases. In no case was anhydrite (β-$CaSO_4$)found. The study concludes that under ambient curing conditions, the sulfur-containing phases present in present-day commercial clinkers are unlikely to cause any internal sulfate attack that might lead to expansive stress and cracking. *Copyright © Elsevier Science Ltd*

Introduction

There has been a significant surge of interest in the question of how sulfur is distributed in present day portland cement clinker. This note addresses research in progress into the results of tests on 33 North American and European clinker samples from all significant kiln types (long wet, long dry, preheater, and precalciner). Although the SO_3 contents of these clinkers vary from 0.03 to 2.65% by mass, there is by design a disproportionate population of high (>1.5%) SO_3 clinkers, since it is these that have aroused the greatest interest, and therefore were specifically requested for this program.

Clinker samples were sampled, crushed to pass a 200 mesh (74 µm) sieve, examined using powder X-ray diffraction (XRD) methods, and then analyzed for elemental composition using X-ray fluorescence (XRF). They were subsequently subjected to extraction using salicylic acid in methanol (SAMX) to extract the calcium silicate phases and the free lime, and concentrate the calcium aluminates, aluminoferrites, and sulfate phases [Takeshima, 1958]. (Analytical procedures are given in Appendix A). These residues were then also analyzed by XRD and XRF.

The parent clinkers were also extracted using the KOH/sugar extraction method, which is known to remove all phases except the calcium silicates, free lime, and periclase [Gutteridge, 1979]. These calcium silicate-rich residues were then also subjected to XRF and XRD characterization.

Data relative to a selection of eight of the clinker samples will be presented here. These span the range of chemical and mineralogical compositions noted in the entire suite of 33 samples.

Results and Discussion

The sulfate in modern North American clinkers may be distributed in the following mineralogical forms:

- Arcanite (K_2SO_4)
- Aphthitalite (a solid solution series, nominally $3K_2SO_4 \cdot Na_2SO_4$)
- Calcium Langbeinite (usually designated $2CaSO_4 \cdot K_2SO_4$)
- Sulfate substituted in silicates (probably chiefly in belite)

The arcanite, aphthitalite, and calcium langbeinite are readily identified using XRD. The sulfate incorporated in belite (and alite) appears in the analysis of the KOH/sugar solution residues, from material balance calculations subtracting the sulfate in the SAMX residues from the total clinker sulfate, and from the appearance of γ-$CaSO_4$ ("soluble anhydrite", JCPDS number 2-0131) in the SAMX residues. No anhydrite (β-$CaSO_4$) was found in any clinkers, either in the whole clinkers or in the SAMX residues. (XRD detection limits for the presence of anhydrite are estimated at 0.5% on the whole clinker and on the SAMX residue. The latter is equivalent to about 0.1% on a whole clinker basis.)

Anhydrite is unstable at cement kiln burning zone temperatures. Dreizler et al [1985] were unable to find evidence for its presence even in clinkers rich in sulfate but of low alkali content. Hanic et al [1985] have provided useful information on its decomposition in the range of 1170-1450°C, that shows that the calcium oxide generated by decomposition can form an eutectic melt with calcium sulfate. This effect inhibits the ability of lime to deter the decomposition; hence anhydrite decomposes very readily at cement kiln clinkering temperatures. The removal of CaO by reaction with C_2S or by dissolution in the clinker melt would tend to further accelerate the decomposition. Pliego-Cuervo and Glasser [1979] show a decomposition pressure at about 7.6 mm Hg at 1200°C, and indicate further that anhydrite is not stable in the presence of C_3A, but only in the presence of $C_4A_3\bar{S}$. Further insight into this issue is provided by Demoulian et al [1981]. The authors refer to two different kinds of alite—one with smooth borders, and the other with corroded edges. They interpret the former, for clinkers with excess or equivalent alkali, as resulting from the slow vaporization of K_2SO_4, and condensation of the same. The vaporization is slow and does not disturb the cohesion, which in fact is aided when it condenses again. By contrast, in high sulfur environments, the compounds present are the Klein ternary, $C_4A_3\bar{S}$, and anhydrite ($CaSO_4$). Both of these compounds decompose rapidly at temperatures above 1300°C, and rapidly perturb the internal structure and the surface of the grains of clinker. Therefore, although anhydrite may be present in clinker manufactured with mineralizers that permit alite formation at reduced temperatures, one would not anticipate finding anhydrite in clinker samples produced in kilns operated at temperatures above 1400°C, and certainly not above 1450°C.

The amount of sulfate incorporated in the calcium silicate phase is self-limiting, as a practical matter. This fact results from the inhibiting effect of calcium sulfate on the reaction of belite and lime to form alite. Work done by Gutt and Smith [1968], Odler and Abdul-Maula [1982], and Christensen and Johansen [1980] indicates that calcium sulfate (especially in the presence of alumina) strongly impedes the conversion of belite to alite. As a practical matter, the resulting high free lime would cause the kiln operator to increase the burning temperature, causing increased volatilization of the stoichiometric excess of sulfur over alkali. The solubility of calcium sulfate in belite is cited by Gutt and Smith [1968] as 1.1 mole% at 1200°C and 1.7 mole% at 1000°C. Gartner and Tang [1987] also point out that magnesia reduces the solubility of SO_3 in the belite. These findings are in agreement with the earlier work by Gutt and Smith [1968]. Since magnesia seems to favor exsolution of the sulfate from the belite, the inhibition of its conversion to alite is more readily overcome.

Experimental Section

A cross-section of the results of the investigation of the 33 clinkers are offered, including the following clinker types:

1. A clinker very low in both alkali and sulfur contents (long wet kiln)
2. A clinker with moderately high alkali level, but low SO_3 content (long wet kiln)
3. A clinker with moderate levels of both alkali and sulfate (preheater kiln)
4. A clinker with moderately high levels of both alkali and sulfate (long wet kiln)
5. A clinker with low alkali content, but high SO_3 (precalciner kiln with bypass)
6. A clinker with high alkali and even higher sulfate (long dry kiln)
7. A mineralized clinker, with moderate alkali and high sulfate, and fluoride (precalciner kiln)
8. A very high sulfate clinker (preheater kiln with bypass)

The chemical analytical results on these clinkers are shown in Table 1.

The nominal compound composition can be calculated making a number of assumptions, similar to those made by Pollitt and Brown [1968], Newkirk [1951], and Skalny and Klemm [1981]:

1. Potassium and sulfur have a very high mutual affinity. Potassium sulfate will form readily. It will tend to combine first with sodium sulfate to form aphthitalite, assuming availability.

TABLE 1

Chemical Analysis of Selected Clinkers

Clinker No.	1	2	3	4	5	6	7	8
SiO_2, %	21.1	22.53	23.18	21.68	21.4	21.18	20.37	22.31
Al_2O_3, %	5.15	5.66	2.66	5.15	4.35	5.89	5.40	4.80
Fe_2O_3, %	3.86	2.84	4.21	2.37	3.67	2.56	3.15	3.26
CaO, %	67.7	63.68	65.61	66.17	66.27	64.25	66.74	63.76
MgO, %	1.23	3.28	2.631	1.68	1.139	1.97	0.85	1.00
SO_3, %	0.07	0.38	0.74	1.29	1.61	2.27	1.95	2.48
Na_2O, %	0.11	0.36	0.14	0.16	0.20	0.38	0.28	0.29
K_2O, %	0.18	0.93	0.61	1.24	0.45	0.96	0.56	0.92
Others, %	0.71	0.48	0.29	0.60	0.59	0.73	0.70	0.66
Total	100.11	100.14	100.07	100.33	99.70	100.13	100	99.49
Na_2O eq., %	0.22	0.97	0.54	0.97	0.49	1.01	0.65	0.90

2. Assuming there is excess sulfate present, the potassium sulfate will then associate with calcium sulfate to form calcium langbeinite.
3. Any residual potassium sulfate will then remain as arcanite. The alkali/calcium sulfate melt is immiscible with the clinker liquid.
4. Sodium sulfate in excess of that required for aphthitalite will not remain in the sulfate melt phase. It will either become incorporated in the silicates or, without some or all of the sulfate, in the aluminates (as prismatic aluminate).
5. Sodium and potassium in excess will be incorporated in the silicates and/or aluminates.
6. Sulfate in excess of all the above requirements will be present as anhydrite.

With these assumptions, the compound composition of the eight clinkers would be as shown in Table 2. It follows from these assumptions that four of the clinkers should contain natural anhydrite.

The compositions of the residues from extraction with salicylic acid in methanol appear in Table 3. These results indicate the expected enrichment of sulfur and alkali in the residues.

TABLE 2

Calculated Compound Composition and Burnability Moduli Clinkers

Calculated Compound Composition and Burnability Moduli of Clinkers

Clinker No.	1	2	3	4	5	6	7	8
C_3S	74.79	44.32	65.98	64.52	71.89	55.72	76.07	51.48
C_2S	4.07	31.16	16.69	13.47	7.12	18.69	1.03	25.14
C_3A	7.10	10.19	0	9.65	5.32	11.27	8.97	7.19
C_4AF	11.75	8.64	12.81	7.20	11.16	7.79	9.59	9.93
LSF	100.38	89.32	92.70	97.28	98.51	95.08	101.96	91.03
Silica Ratio	2.34	2.65	3.38	2.88	2.67	2.51	2.38	2.77
A/F Ratio	1.33	1.99	0.63	2.18	1.19	2.30	1.71	1.47
Total K_2SO_4	0.16	0.83	1.12	2.28	0.82	1.77	1.04	1.71
Total Na_2SO_4	0.00	0.00	0.23	0.24	0.45	0.88	0.64	0.67
Total $CaSO_4$	0.00	0.00	0.17	0.18	1.70	1.64	1.89	2.24
Calc. Compounds								
Aphthitalite	0.00	0.00	0.88	1.11	0.65	1.39	0.81	1.34
Remaining K_2SO_4	0.16	0.83	0.43	1.41	0.31	0.68	0.40	0.65
$2CaSO_4 \cdot K_2SO_4$	0.00	0.00	0.28	0.30	0.81	1.73	1.01	1.67
Arcanite	0.16	0.83	0.32	1.29	0.00	0.00	0.00	0.00
Thenardite	0.00	0.00	0.04	0.01	0.31	0.58	0.47	0.38
Anhydrite	0.00	0.00	0.00	0.00	1.21	0.58	1.27	1.22
Na_2O-clinker phases	0.11	0.36	0.04	0.05	0.00	0.00	0.00	0.00
K_2O-clinker phases	0.09	0.48	0.00	0.00	0.00	0.00	0.00	0.00
SO_3(total)	0.07	0.38	0.74	1.29	1.63	2.27	1.95	2.48
K_2O(total)	0.18	0.93	0.61	1.24	0.45	0.96	0.56	0.92
Na_2O(total)	0.11	0.36	0.14	0.16	0.20	0.38	0.28	0.29

TABLE 3

Chemical Analysis-SAMX Residues

Clinker No.	1	2	3	4	5	6	7	8
% Residue	19.1	21.7	14.7	17.8	17.2	22.8	19.7	18.9
SiO_2, %	4.02	4.36	3.59	3.39	2.47	3.53	2.81	2.62
Al_2O_3, %	23.27	23.96	14.27	23.32	18.76	22.06	20.79	18.37
Fe_2O_3, %	17.75	10.88	24.41	11.08	17.83	9.76	13.84	13.89
CaO, %	49.79	45.80	42.18	47.49	46.15	46.53	47.05	45.53
MgO, %	3.06	10.65	8.85	4.24	2.66	4.95	1.68	2.33
SO_3, %	0.15	1.09	3.19	4.84	7.48	8.33	8.79	10.65
Na_2O, %	0.36	1.20	0.45	0.67	0.73	1.29	1.04	1.16
K_2O, %	0.44	2.65	2.86	5.51	2.14	3.73	2.77	4.32
TiO_2, %	0.90	0.68	0.46	0.75	0.72	0.74	0.57	0.36
P_2O_5, %	0.05	0.03	0.02	0.05	0.10	0.11	0.09	0.16
Mn_2O_3, %	0.05	0.13	0.21	0.09	0.11	0.54	0.11	0.37
SrO, %	0.08	0.02	0.03	0.06	0.17	0.07	0.20	0.18
Total	99.92	101.43	100.50	101.48	99.32	101.63	99.74	99.92

The qualitative X-ray diffraction results obtained for these residues, given in Table 4, demonstrate that as the sulfur level increases, the likelihood of arcanite being present in significant quantities decreases, and calcium langbeinite and aphthitalite increase. At the very highest levels of sulfur, soluble anhydrite (γ-$CaSO_4$) appears. We suspect that this calcium sulfate is extracted from the silicate phases by the methanolic salicylic acid, as earlier reported by Tang and Gartner [1984]. It is, however, significant, that in no case has natural anhydrite, β-$CaSO_4$, been detected in the extraction residues, even though material balance calculations indicate that there should be residual anhydrite in samples 5, 7 and 8, and also a small amount in sample 6. The total SO_3 in the residues in general agrees quite well with the water-soluble SO_3 as determined on the KOH-sugar extract, then normalized to

TABLE 4

X-Ray Diffraction Results-SAMX Residues

Clinker No.	1	2	3	4	5	6	7	8
XRD Compounds								
Arcanite	-	present	present	present	-	-	-	present
Aphthitalite	-	-	present	present	present	present	present	present
Calcium Langb.	-	-	present	present	present	present	present	present
Sol. Anhydrite	-	-	-	-	present	present	present	present
Anhydrite	-	-	-	-	-	-	-	-
SO_3(total)	0.15	1.09	3.19	4.84	7.48	8.33	8.79	10.65
H_2O sol. SO_3 [1]	0.11	1.20	3.55	5.96	6.29	7.60	7.80	9.35

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[1] The water-soluble SO_3 is determined on the filtrate from the KOH/sugar extraction. The filtrate is acidified, and the sulfate determined gravimetrically as $BaSO_4$-see Appendix A.

TABLE 5

Chemical Analysis-KOH/Sugar Residues

Clinker No.	1	2	3	4	5	6	7	8
SiO_2, %	25.10	27.59	26.76	25.18	25.00	26.24	24.5	27.08
Al_2O_3, %	1.09	1.02	0.64	1.30	1.41	1.53	1.73	1.66
Fe_2O_3, %	0.87	0.78	1.11	0.67	1.15	0.72	0.77	1.12
CaO, %	71.07	67.30	69.08	70.08	69.85	68.56	70.8	68.22
MgO, %	0.93	3.62	2.68	1.50	0.87	2.19	0.67	0.75
SO_3, %	0.07	0.12	0.27	0.22	0.62	0.67	0.41	0.83
Na_2O, %	0.12	0.24	0.19	0.15	0.16	0.20	0.05	0.20
K_2O, %	0.08	0.34	0.16	0.13	0.04	0.06	0.03	0.10
Others, %	0.19	0.21	0.08	0.17	0.20	0.21	0.19	0.14
P_2O_5, %	0.38	0.12	0.04	0.30	0.15	0.19	0.32	0.23
Mn_2O_3, %	0.01	0.03	0.02	0.17	0.02	0.09	0.02	0.06
SrO, %	0.07	0.03	0.04	0.06	0.14	0.06	0.13	0.18
Total	99.98	101.40	101.08	99.93	99.61	100.73	99.6	100.58

its equivalent concentration in the residue. In the cases of the high-sulfur clinkers (5-8), the water soluble SO_3 is slightly less than the total in the residues, due probably to the sulfate extracted from the silicate phases of these clinkers. In the absence of detected γ-$CaSO_4$, the water-soluble sulfate is greater than or equal to the sulfate content in the residue.

The potassium hydroxide-sugar extracts were also analyzed for chemical composition, with results as given in Table 5.

The SO_3 content of the silicates as a whole ranges to 0.83%, for a clinker with 2.5% total SO_3. As a rule, it is in the range of 0.1–0.65%, which translates to less than 0.7% SO_3 in the clinker as a whole. The comparison of the sulfates determined in the silicate phases, and calculated for the silicate phases from the analyses of the salicylic acid extraction residues, appears in Table 6, and demonstrates that the sulfur is all accounted for in all the high sulfur clinkers.

Table 5 also shows that the silicate phases contain variable amounts of alumina, and that there is some correlation between alumina and sulfur contents, as shown in Fig. 1. In addition, all silicate phases contain more alumina than sulfur, on a molar basis. Thus, the calcium, sulfur and alumina will be released together as the silicate phases hydrate, and the hydration product should be not ettringite, but monosulfate.

TABLE 6

Clinker Sulfur Distribution-Determined and Calculated

Clinker Number	1	2	3	4	5	6	7	8
Total clinker sulfate	0.07	0.38	0.74	1.29	1.61	2.27	1.95	2.48
Tot. SO_3 in silicates	0.055	0.097	0.232	0.181	0.517	0.517	0.331	0.676
Tot. SO_3 in SAMX-calc.	0.017	0.286	0.512	1.112	1.114	1.757	1.619	1.802
Tot. SO_3 in SAMX-anal.	0.028	0.237	0.468	0.861	1.284	1.895	1.735	2.015

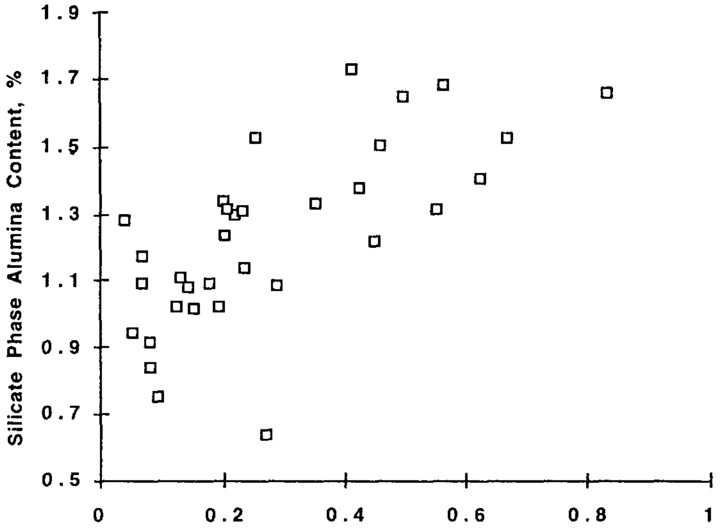

FIG. 1.
Relationship between alumina and SO_3 content in KOH/sugar residues.

Closing Remarks

A study of a large suite of North American and European clinkers has revealed that the sulfur compounds contained in these samples are unlikely to cause any difficulties with slowly available sulfate, and that even in the few cases where there was more than a negligible amount of such sulfate dissolved in the silicate phases, the resulting hydration product should be monosulfate, and not ettringite. In no case was anhydrite detected in the clinkers, even with SO_3 contents greater than 2.5%.

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Appendix A

Selective Dissolution Techniques for Cement and Clinker

Salicylic Acid-Methanol Extraction (modification of Takeshima[1958])

This dissolution technique selectively removes alite, belite ,and free lime from cement and clinker leaving a residue consisting of the aluminates ($3CaO.Al_2O_3$, alkali aluminate), ferrite, periclase (MgO), and alkali sulfates.

20 g sample of ground clinker (–200 mesh) or cement is dissolved in 1000 mL 12% salicylic acid methanolic solution and stirred for 1 hour. Next, the solution is filtered and the residue collected on the filter paper is weighed, recorded and stored for for further analyses by x-ray diffraction and by x-ray fluorescence.

KOH Sugar Extraction (modification of Gutteridge [1979])

This extraction allows for removal of the aluminates, ferrite, and alkali sulfates from cement and clinker leaving a residue of alite, belite, free lime and periclase.

5 g sample of ground clinker (~200 mesh) or cement is weighed and then dissolved in 150 mL hot 13% KOH/13% sucrose solution and stirred for approximately 5 minutes. The solution is then filtered and the residue is collected on a Whatman GF/A glass fiber filter and stored for further analysis by x-ray fluorescence. The filtrate is also recovered and stored for future use in determining soluble clinker or cement SO_3.

Soluble SO3

The filtrate (~200 mL) collected from the KOH/Sugar extraction is acidified with 30 mL of 36% HCl solution and then treated with 30 mL 5% $BaCl_2$ solution and stirred allowing all BaSO4 to precipitate. Next , the solution is filtered and the $BaSO_4$ precipitate collected on a previously tared Whatman GF/F glass fiber filter and weighed. From the weight obtained, the amount of soluble SO_3 by weight of cement or clinker is reported.