# 2. ALKALIES IN CEMENT AND CEMENT MANUFACTURE

# ALKALI COMPOUND FORMATION OF COMMERCIAL PORTLAND CEMENT CLINKERS

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ABSTRACT

The effect of kiln atmosphere in the burning zone on the formation of alkali compounds was studied. It was concluded that the double salt $K_3N\bar{S}_4$ was produced under reduced kiln conditions while $C_2KS_3$ tended to be formed under oxidizing conditions.

The data I wish to present to this conference was based upon x-ray diffraction studies of alkali sulfate compound formations of some commercial clinkers. The effect of reduced clinkers have been the subject of various investigations in the past (1,2), and also much has been published on the alkali sulfate compounds (3,4) in cement clinkers. This study seems to indicate that the atmosphere in the burning zone can have as much influence on the alkali sulfate compound formation as does the chemical composition. These conclusions are tentative and could be modified as additional information is obtained from the ionic concentration of the liquid phase studies currently underway. The effect of these alkali compounds on early hydration is also being investigated.

This study was prompted by two relatively recent events which occurred in the cement industry of the United States.

1. The sudden fuel shortage made it necessary for plants which had previously burned natural gas and/or oil to switch to less expensive coal containing higher sulfur.

2. Increasing field complaints because of variable water demand, variable setting times, and incompatability with some admixtures were registered.

I will report on only six of over one hundred commercial clinker composites which were analyzed. The clinkers discussed in this paper were produced in commercial kilns to which various amounts of dust were returned. The criteria for selection were based on two factors:

1. The amount of alkalies and sulfates in the clinker.

2. The estimated oxygen deficiency in the burning zone during the production of these clinkers.

The chemical analyses of these clinkers (Table 1) exhibit a general range of alkalies and sulfur which could be expected during various production periods. Naturally, when the clinker

alkali and sulfur reach the upper control limits, adjustments to kiln parameters are made to lower them to acceptable limits.

The primary method of alkali sulfate compound determination was by x-ray diffraction studies of the maleic acid residues(5). Figure 1 shows the XRD scans of these clinkers and the Cu 2-theta location of the compounds. Atomic absorption analysis of the maleic acid filtrate is also tabulated (Table 2). This analysis relates the chemical composition of the alite-belite phases plus the free lime content. Except for Clinker "D" one finds that the chemical composition of the silicate phases remains rather constant, and the greatest differences between these clinkers are found in the diffraction studies of the maleic acid residue. Table 3 relates the salient differences of the compound products and an estimation of the burning zone atmosphere.

It becomes apparent that the compound formations are contingent upon not only the amount of alkali and sulfur but also upon the burning atmosphere. Clinker "A", which has the lowest alkali sulfur content of this series, appears to have formed only two alkali compounds: arcanite ($K\bar{S}$) and the alkali substituted $C_3A$ [$(N,K)C_8A_3$]. One could assume that $K\bar{S}$ is formed until the sulfur is exhausted then the remaining alkali is consumed in the formation of $(N,K)C_8A_3$. The alkali preference for sulfur appears to be substantiated by Clinker "B" and "C" which differ from "A" only by increasing amounts of alkali and sulfur. In the "B" and "C" clinkers there is the formation of calcium langbeinite ($KC_2\bar{S}_3$) and aphthitalite ($K_3N\bar{S}_4$) in preference to $(N,K)C_8A_3$ of Clinker "A"; thereby leaving $C_3A$ as the only alumina compound.

Clinker "D" represents the product of an experimental burn which inadvertently was conducted under severe reducing conditions, while Clinker "E" was collected a few hours earlier. Only the kiln atmosphere was different. It is interesting to note that $K_3N\bar{S}_4$ appears to be the only alkali compound present in the severly reduced clinker while under less reduced conditions the clinker gave strong diffraction patterns for both $KC_2\bar{S}_3$ and $(N,K)C_8A_3$. This would seem to indicate that $K_3N\bar{S}_4$

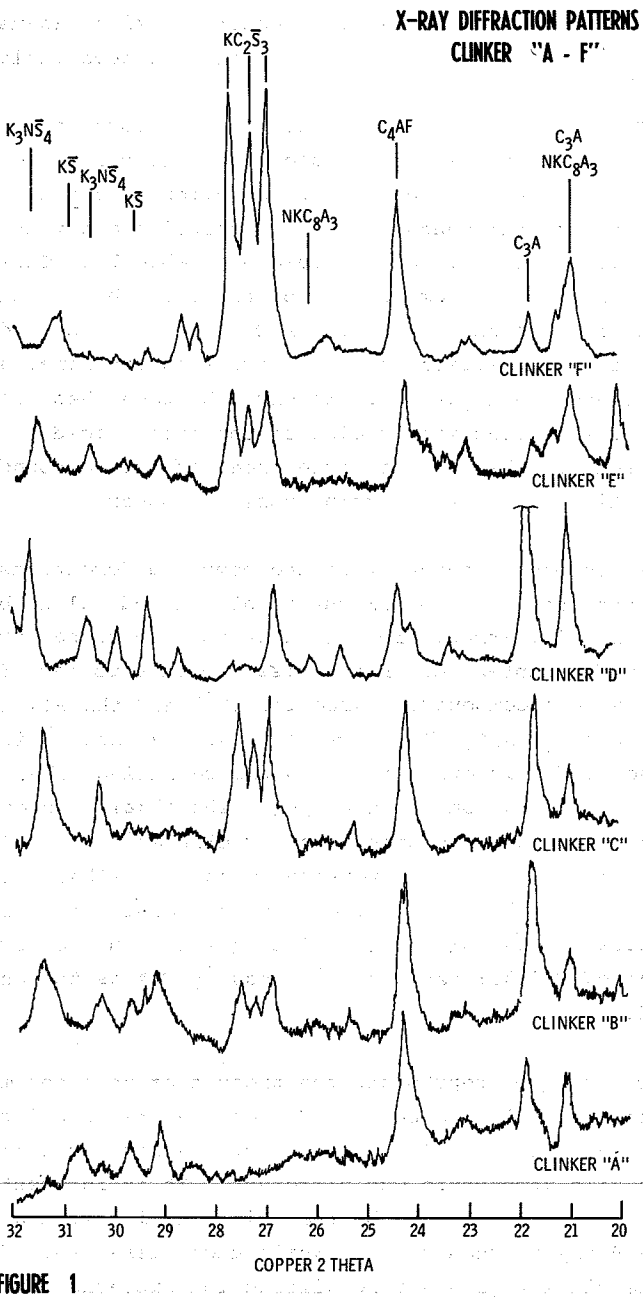
X-RAY DIFFRACTION PATTERNS
CLINKER "A - F"
$KC_2\bar{S}_3$
$K_3N\bar{S}_4$
$K\bar{S}$
$K_3N\bar{S}_4$
$K\bar{S}$
$NKC_8A_3$
$C_4AF$
$C_3A$
$C_3A$
$NKC_8A_3$
CLINKER "F"
CLINKER "E"
CLINKER "D"
CLINKER "C"
CLINKER "B"
CLINKER "A"
32
31
30
29
28
27
26
25
24
23
22
21
20
COPPER 2 THETA

FIGURE 1

is a preferential compound when produced in a reduced kiln atmosphere.

Clinker "F" would again seem to support the hypothesis that kiln atmosphere can dictate minor compound formation. This clinker was the product of another experimental burn in which every effort was made to maintain an oxidizing flame. The major alkali compounds of this clinker appear to be the same as Clinker "E": $(N,K)C_8A_3$ and $KC_2\bar{S}_3$. As mentioned earlier, these samples were selected from many that have been analyzed. These particular clinkers were selected to illustrate a relatively high degree of purity of the alkali sulfur compounds. We have diffraction patterns on which we have identified the presence of $K_{.67}N_{1.33}\bar{S}_2$*. We have also observed peak shifts for the above compound which indicate that a considerable range of the solid solution series of $K_xN_y\bar{S}_z$ (where $x + y = z$) compounds may be possible constituents of portland cement clinker.

Evaluations of the maleic acid filtrate analysis of these clinkers (Table 3) indicate that only minor portions of the alkalies and sulfur are found in the silicate phases. This gives additional support to the x-ray diffraction studies which place the majority of these elements in alkali sulfate and/or alkali aluminate compounds.

In summary these data would seem to suggest:

1. The preferential compound formation for alkalies in cement clinker is in some combination with the sulfur. When the sulfur has been depleted the alkalies appear to form $(N,K)C_8A_3$ as the next most preferential compound.

2. The burning zone atmosphere seems to dictate which alkali sulfate compound is formed. $KC_2\bar{S}_3$ tends to be produced in an oxidized flame while the excess

*JCPDS Pattern 20-926

alkalies form $(N,K)C_8A_3$. $K_3N\bar{S}_4$ appears to be formed during periods of reduced burning conditions and any excess alkalies going into the silicate phases.

TABLE 1

Clinkers Chemical Analysis (%)

| CLINKER | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| $SiO_2$ | 21.60 | 21.20 | 21.30 | 21.34 | 21.25 | 21.80 |
| $Al_2O_3$ | 5.95 | 5.80 | 5.85 | 6.21 | 6.05 | 4.40 |
| Total Fe as $Fe_2O_3$ | 2.60 | 2.70 | 2.65 | 2.38 | 2.51 | 3.00 |
| FeO | 0.05 | 0.15 | 0.05 | 0.93 | 0.15 | 0.01 |
| CaO | 65.80 | 64.50 | 63.30 | 63.52 | 63.42 | 61.92 |
| MgO | 3.00 | 2.90 | 2.85 | 2.43 | 2.46 | 4.44 |
| $P_2O_5$ | 0.10 | 0.01 | 0.01 | 0.28 | 0.13 | 0.11 |
| $TiO_2$ | 0.25 | 0.20 | 0.25 | 0.26 | 0.26 | 0.20 |
| $Na_2O$ | 0.25 | 0.25 | 0.25 | 0.44 | 0.48 | 0.23 |
| $K_2O$ | 0.55 | 0.95 | 1.10 | 0.82 | 1.41 | 1.11 |
| $SO_3$ | 0.40 | 1.80 | 2.50 | 1.56 | 1.01 | 2.90 |
| Sulfide Sulfur as $SO_3$ | 0 | 0 | 0 | 0.62 | 0.05 | 0 |
| LOI | 0.15 | 0.20 | 0.30 | 0.55 wt.gain | 0.09 | 0.41 |
| Free CaO | 0.40 | 0.40 | 0.80 | 1.21 | 0.80 | 0.30 |
| | | | Bogue Potential Compounds | | | |
| $C_3S$ | 58.88 | 53.50 | 45.59 | 46.83 | 49.57 | 44.28 |
| $C_2S$ | 17.51 | 20.42 | 26.67 | 25.85 | 23.53 | 29.10 |
| $C_3A$ | 11.37 | 10.80 | 11.02 | 12.43 | 11.79 | 6.58 |
| $C_4AF$ | 7.91 | 8.22 | 8.06 | 7.24 | 7.64 | 9.13 |

TABLE 2

Maleic Acid Filtrate Analysis (%)

| Clinker | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| $SiO_2$ | 20.77 | 20.55 | 20.54 | 21.12 | 22.09 | 21.74 |
| $Al_2O_3$ | 0.94 | 1.30 | 1.00 | 0.86 | 0.80 | 1.45 |
| $Fe_2O_3$ | 0.52 | 0.62 | 0.72 | 0.53 | 0.58 | 0.59 |
| CaO | 55.05 | 53.93 | 52.78 | 53.28 | 54.42 | 53.95 |
| MgO | 1.29 | 1.09 | 0.94 | 0.82 | 0.96 | 1.17 |
| $SO_3$ | 0.05 | 0.06 | 0.07 | 0.13 | 0.11 | 0.15 |
| $Na_2O$ | 0.09 | 0.10 | 0.10 | 0.14 | 0.15 | 0.11 |
| $K_2O$ | 0.21 | 0.26 | 0.20 | 0.33 | 0.21 | 0.16 |

TABLE 3

Compound Intensities vs Kiln Atmosphere

| Clinker | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| | | | Alkali Sulfur Analysis | | | |
| $SO_3$ | 0.40 | 1.80 | 2.50 | 0.94 | 0.96 | 2.98 |
| $K_2O$ | 0.55 | 0.95 | 1.10 | 0.82 | 1.41 | 1.11 |
| $Na_2O$ | 0.25 | 0.25 | 0.25 | 0.44 | 0.48 | 0.23 |

| | Kiln Atmosphere | | | | | |
|---|---|---|---|---|---|---|
| | Slight Reduced | Reduced | Reduced | Extreme Reduced | Slight Reduced | Oxidixed |
| $KC_2\bar{S}_3$ | O | W | S | W | S | VS |
| $K_3N\bar{S}_4$ | O | M | S | VS | W | O |
| $K\bar{S}$ | W | O | W | W | W | W |
| $(N,K)\,C_8A_3$ | M | W | W | O | S | VS |
| $C_3A$ | M | S | S | VS | W | W |

O = None Detected
W = Weak Intensity
M = Medium Intensity
S = Strong Intensity
VS = Very StrongIntensity

## References


1. Y. Susukava and T. Sasaki, Influence of Reducing Atmosphere on the Constitution of Clinker, 4th Int. Symp. Chem. Cem., Paper II-S3, Washington, 1960.

2. E. Woermann, Decomposition of Alite in Technical Portland Cement Clinker. 4th Inst. Symp. Chem. Cem., Paper II-S8, Washington, 1960.

3. M. Amafusi and A. Tsumagari, Formation of Double Salt in Cement Burning, 5th Int. Symp. Chem. Cem., Paper I-82, Tokyo, 1968.

4. H. Pollitt and A. Brown, The Distribution of Alkalis in Portland Cement Clinker, 5th Int. Symp. Chem. Cem. Paper I-126, Tokyo, 1968.

5. J. Mander, L. Adams and E. Larkin, A Method for the Determination of Some Minor Compounds in Portland Cement and Clinker by X-Ray Diffraction, Cement and Concrete Research, Vol. 4 No. 4, pp 533.