INFLUENCES OF SURPLUS SO$_3$ IN FBC ASH ON FORMATION OF BELITE-RICH SULFOALUMINATE CLINKER

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ABSTRACT:

When FBC fly ash, usually rich in SO$_3$, is used in high proportion in the raw mixtures for belite-rich sulfoaluminate clinker, the surplus SO$_3$ besides forming calcium sulfoaluminate (C$_4$A$_3\overline{S}$*) would affect the formation and hydration of the clinker. This study revealed that surplus SO$_3$ resulted in calcium silicosulfate (2C$_2$S·C$\overline{S}$) remaining in the clinker fired at temperatures below 1250°C and that the sintering temperature for the clinker should be within 1250°C to 1350°C. In order to acquire steady strength development of cement, the mole ratio of C$\overline{S}$ to C$_4$A$_3\overline{S}$ and C$_4$AF with clinker should be kept as low as possible and at most, no more than 1.3.

INTRODUCTION

In the past decades, with growing concerns about energy, conservation, environmental protection and economy, the maximum utilization of industrial wastes and by-products has been one of the major concerns of the cement industry [1-7].

As one of the main raw materials, fly ash has found its use in cement manufacture [1]. One factor impeding its wider application in cement process is its high SO$_3$ content, especially with ashes from FBC (fluidized bed combustor) processes. Since there is a limitation for SO$_3$ content in portland clinker, efforts were devoted to having fly ash applied in production of some special cement, such as belite-rich sulfoaluminate cement [2], since it could consume more SO$_3$ than portland cement clinker.

For a clinker composed of C$_2$S, C$_4$A$_3\overline{S}$* and C$_4$AF (referred to hereafter as SAF clinker), it is difficult to raise C$_4$A$_3\overline{S}$ to a high level because fly ash usually contains more SiO$_2$ than Al$_2$O$_3$, and other alumina-bearing materials may not be available or economical. If fly ash is adopted in large proportions in the raw mix, it would result in C$_2$S-rich SAF clinker which contains less C$_4$A$_3\overline{S}$ and C$_4$AF with a surplus of SO$_3$.

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*The cement chemistry notations are used in which C, S, A, F, $\overline{S}$, are CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O and SO$_3$, respectively.

In this study the influence of surplus SO_3 on the formation and hydration of SAF clinker was investigated. The rational mineral composition and firing temperature were also discussed for the clinker.

EXPERIMENTAL MATERIALS AND METHODS

In this study, a few industrial wastes were used to make a clinker similar to the commercial SAF cement clinker [3], but with different mineral combinations. One distinguishing feature was the prominent proportion of belite in the clinker. A study was carried out to examine the influences of surplus SO_3 on the phase composition of the SAF clinker and the suitable temperature range for firing the clinker.

The chemical analyses of the raw materials are shown in Table 1.

Table 1. Chemical Analysis of Raw Materials

Material	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	TiO_2	SO_3	L.O.I.
Lime Dust	5.19	56.0	3.79	0.75	0.44	0.13	7.81	0.21	7.81	37.30
FBC Ash	12.51	38.03	6.77	0.72	1.33	0.25	23.91	0.61	16.02	17.36
Fly Ash	25.90	1.73	16.10	0.75	2.19	0.24	48.40	1.31	0.61	1.90

The raw mixtures, prepared in different proportions according to the compositions in Table 2 were homogenized, granulated and dried. After firing at a given temperature in an electrical muffle furnace for 30 minutes, clinkers were taken out and cooled in air, then ground into cement. The paste specimens, molded in 1-inch cubes, were cured under water at 38°C to the testing ages.

X-Ray diffraction was used to examine the phase components and SEM to observe the mineral morphology of clinker. Compressive strength was measured at 3, 7 and 28 days.

RESULTS AND DISCUSSION

Composition and Strength

An increase in C_2S content while lowering the $C_4A_3\bar{S}$ and C_4AF in the clinker means that more SiO_2 is allowed and less Al_2O_3 is needed in the raw materials. This change favors utilization of low-grade raw materials and industrial by-products containing more SiO_2 than Al_2O_3, but it also leaves more surplus SO_3 in the clinker when the starting materials contain much SO_3. Sometimes surplus SO_3, in the form of anhydrite, is needed to increase the proportion in the clinker to even more than 20 percent [2].

Generally speaking, an appropriate surplus of SO_3 is advantageous for sulfoaluminate clinker. In order to ascertain if these surplus amounts of SO_3 have any effect on the formation and hydration of SAF clinker, a few clinkers were prepared which were within the following projected composition ranges:

$C_2S=44\sim50\%$, $C_4A_3\overline{S}$ $14\sim20\%$, $C_4AF=16\sim19\%$ and $C\overline{S}=12\sim18.5\%$

Table 2 gives the compressive strengths of SAF clinkers with different theoretical mineral combinations. It can be seen from the table that when the mole ratio $R=MSO_3/(MC_4A_3\overline{S}+MC_4AF)$ increased, the early strength before 7 days increased, but the 28 days strength decreased. It seemed that the R value of a clinker should not be over 1.3 in order to attain a steady development of strength.

The reason for the retrogression in the 28-days strength of clinker might be that too great a surplus caused a continuous formation of ettringite in the later stage of hydration.

Table 2. Compressive Strength of Clinker

#	Potential Composition of Clinker				R	BET Area (M^2/g)	W/S	Compressive Strength (MPa)		
	C_2S	$C_4A_3\overline{S}$	C_4AF	$C\overline{S}$				3d	7d	28d
1	47.0	18.5	17.5	12.0	1.33	0.76	0.33	46.2	46.5	45.6 (98.1)
2	49.5	14.3	18.1	14.4	1.73	0.78	0.34	43.8	57.3	52.3 (91.2)
3	44.0	17.6	16.5	16.5	1.93	0.76	0.33	49.7	54.1	37.3 (68.9)
4	43.5	17.2	16.3	18.5	2.20	0.76	0.33	59.2	59.4	31.7 (53.3)
0	OPC					0.92	0.33	49.70	51.05	60.47

*The values in brackets are the 28-day strength in percentage in relation to 7-day strengths

Influence of SO_3 on Phase Formation

As stated before, when fly ash from FBC is used in large proportion in a raw mix, it would provide more SO_3 in the clinker than is needed for the formation of $C_4A_3\overline{S}$. Surplus SO_3 present is favorable to the formation of C_4A_3S. However, it was found that when both SiO_2 and SO_3 were high in the raw mix, it was easy to form $2C_2S \cdot C\overline{S}$. In theory $2C_2S.C\overline{S}$ will decompose into C_2S and $C\overline{S}$ at 1300°C [4], but in the current experiments, this compound still remained in the clinker fired under 1300°C, and only disappeared before reaching 1350°C (Fig. 1).

Firing Temperature

For SAF clinker, all the three main compounds C_2S, $C_4A_3\overline{S}$, and C_4AF can be formed at 1200°C. However, clinker sintering needs not only the appropriate temperature, but experiencing enough time in the kiln. When too much $2C_2S \cdot C\overline{S}$ appears during clinkering, it is necessary to heat to a high temperature to make this compound decompose. The reaction kinetics appear to require a longer time or higher temperature to reach the desired equilibrium phase assemblage.
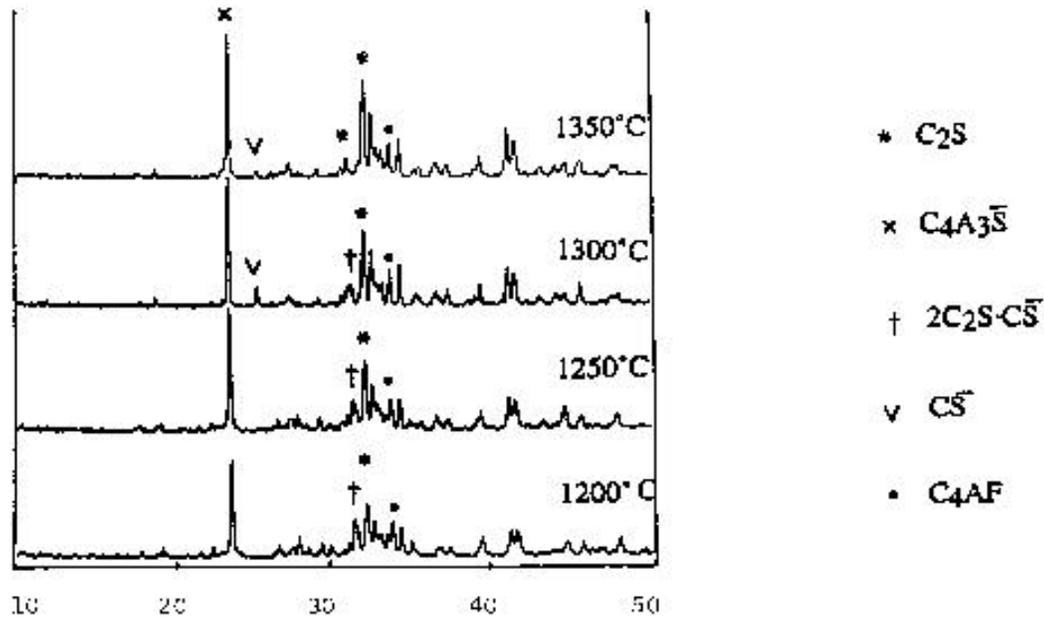
Fig. 1. XRD diagrams of clinker #6 fired under different temperatures.

As apparent from Fig. 1, the amount of $2C_2S\cdot C\bar{S}$ remaining decreased with the temperature rise. In fact, below 1250°C, $C\bar{S}$ in clinker was hardly detected by XRD when almost all of the sulfate was in the form of $2C_2S\cdot C\bar{S}$. By 1300°C there was substantial release of $C\bar{S}$. With increase in the firing temperature, both $C_2\bar{S}$ and $C_4A_3\bar{S}$ crystals formed at 1300°C, increased in amount and were larger and better developed than those formed at 1200°C. Since $C_4A_3\bar{S}$ would decompose at temperatures above 1400°C [4], limits for the firing temperature for SAF clinker should be within 1250-1350°C.

CONCLUSIONS

The results of the current study have shown that:

1. Surplus SO_3 results in $2C_2S\cdot C\bar{S}$ remaining in SAF clinker at temperatures up to 1300°C with short firing times. Excess $C\bar{S}$ may also compromise the strength development of cement by forming ettringite at a later period of hydration.

2. The surplus SO_3 proportion in SAF clinker should be kept at a low level. At most, the mole ratio $SO_3/(MC_4A_3S + MC_4AF)$ within the clinker should not be over 1.3.

3. In order to reduce the remaining $2C_2S\cdot C\bar{S}$ in SAF clinker, the recommended firing temperature for high belite clinker is between 1250-1350°C.

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