

# EFFECT OF FLUXES AND MINERALIZERS IN CLINKERIZATION OF HIGH SULPHUR CEMENT RAW MIX

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Abstract:

This article describes the outcome of lab scale investigations carried out to produce low energy cement by burning an industrial ordinary portland white cement mix that contained high sulphate lime sludge as a source of CaCO<sub>3</sub>. The binding masses produced in furnace, after addition of fluorspar at burning temperature of 1300°C, exhibited excellent behavior in physical properties and mechanical performance.

## 1.0 Introduction

Utilisation of fluorspar for burning cement raw mix at temperatures lower than those common in production of conventional clinkers is widely supported in literature (1-5). White belitic portland cement with good physical, mechanical and whiteness properties was produced at 1300°C by adding (0.5 wt%) of MeSO<sub>4</sub> (Me= Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>) to a white cement mix (6). Odler and Hua Zhang (7) produced portland cement clinker in furnace at 1230°C temperature by burning raw meal that contained high SO<sub>3</sub> fluidized bed ash, limestone and fluorspar. Most of the SO<sub>3</sub> contained in this clinker was found in the form of C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> phase. The other phases identified in the clinker were C<sub>3</sub>S and C<sub>4</sub>AF. Wang Xinrong *et al* (8) synthesized low energy clinker by burning mixture of limestone, clay, gypsum and CaF<sub>2</sub> at 1300°C. The mineral phases identified in the clinker were alite, β-C<sub>2</sub>S, C<sub>4</sub>AF, C<sub>3</sub>A, C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> and CaSO<sub>4</sub>. M.T Blanco *et al* (9) produced a new low cost white cement clinker at 1350°C temperature using 2 wt% fluorspar and 5 wt% gypsum. The minerals present in this clinker were alite, β-C<sub>2</sub>S, CaO, 3(C<sub>2</sub>S).3(CaSO<sub>4</sub>).CaF<sub>2</sub>, C<sub>3</sub>A, C<sub>11</sub>A<sub>7</sub>CaF<sub>2</sub>, C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> and occasionally some CaSO<sub>4</sub>. Based on the research studies carried out by the above mentioned authors, we used fluorspar and high sulphur production mix to synthesize low heat clinker. The experimental work carried out in this study involved followings:

- Burnability studies of control and plant mix
- DTA studies of control and plant mix
- Mineral formation studies of low heat clinker
- Physical and mechanical properties of low heat and plant cement
- Hydration studies of low heat and plant cement

## 1.1 Material and Experimental Detail

The mineralizer fluorspar (88 % pure) was prepared to a residue of less than 5.0 wt% on 172 mesh. Plant raw mix containing high sulphate lime sludge (~4.84% SO<sub>3</sub>), flint clay and silica sand was obtained from a production plant. The chemical composition of both fluorspar and the plant mix is given in (Table 1). Control raw mix was prepared in laboratory mill by grinding pure limestone with flint clay and silica sand. The chemical composition of both the plant and control mixes was kept similar except the SO<sub>3</sub> contents which was 4.0 wt% in the plant mix and 0.2 wt% in the control mix.

(Table 1) Chemical and mineralogical composition (wt%) of fluorspar and plant mix

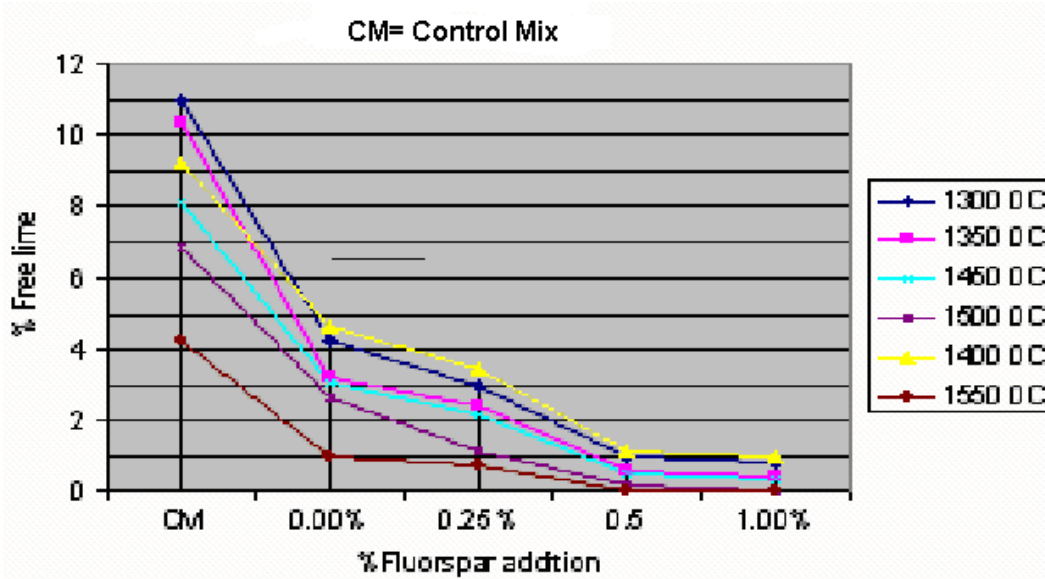
Composition (wt%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	F <sub>2</sub>	LOI
Fluorspar	4.80	0.80	0.50	44.5	0.90	39.5	8.86
Plant raw mix	15.5	3.04	0.34	43.3	2.09	-	34.0
Mineral identified in fluorspar are calcite, quartz, calcium fluoride and probably cesium fluoride							

The nodules of control and plant mixes containing different proportions of fluorspar were made by using tap water. After drying in heating oven, these were fired in platinum dishes within an electric furnace of high precision, at a heating rate of 10°C/min and were retained at final temperatures for 30 minutes. The clinkers thus formed were allowed to cool initially within the furnace and were then rapidly quenched in air. The level of uncombined lime in the synthesized clinkers was determined by hot ethylene Glycol extraction method as BS 4550 part 2 (10). The clinker formation process was evaluated for industrial and control mix through XRD and /or DTA/TG studies. Physical, mechanical, whiteness and other hydration studies of low heat cement made in laboratory furnace were evaluated vis -a-vis ordinary portland white cement obtained from the production plant.

## 1.2 Free Lime Combinability Studies

The amount of free lime left after clinkering a cement raw mix is an indication of the progress of clinkering reaction and therefore, the relative burnability. Free lime combinability results of control mix (CM), plant mix

(PM) and mineralized plant mix (PM1,PM2) burnt at different temperatures under a defined heating regime are illustrated in (Fig. 1). Free lime data depicted in (Fig 1) shows that control mix (LM) does not burn completely at 1550°C. This is evident from 4.20 wt% free lime contents that remain unreacted after burning the mix at 1550°C. On the contrary, plant mix, containing 4.0 wt% SO<sub>3</sub>, is burnt almost to the same level of free lime (4.26 wt%) at temperatures as low as 1300°C. It is apparent from the results that burnability of cement mix improves if sulphates are present in the mix.



(Fig 1) Burnability of raw mixes

These results confirm earlier studies (11) where SO<sub>3</sub> in high silica ratio mix, reduced the free lime below 1400°C. It is observed during the study that when plant mixes are burnt at 1400°C, a sudden increase in free lime contents of the clinkers is noticed. The anomalous behavior of increasing free lime is due to dissociation of C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> which takes place above 1300°C. H.M.Cheong *et al* (12) in their studies report that C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> is stable up to 1300°C and thereafter it starts decomposing giving rise to free lime. As the burning temperature exceeds 1450°C, the released free lime reacts with C<sub>2</sub>S to form more C<sub>3</sub>S. It is pertinent to mention here that lowest combinability temperature at industrial plant for 1.0 wt% free lime is 1550°C. The order of reactivity for the studied raw mixes in terms of free lime combinability is found in the following descending order:

Mineralized plant mix > Plant mix > Control mix

### 1.3 DTA Studies

Thermal behavior of control mix (CM), plant mix (PM) and plant mix containing 0.25 wt% and 0.5wt% fluorspar (PM1,PM2) was evaluated in terms of calcination and other transformation reactions by using Simultaneous Thermal Analyzer (STA-409). The instrumental conditions used during this study are given in (Table 2).

(Table 2) Instrumental conditions for DTA and TG

Parameters	Reference
Atmosphere	Air
Reference crucible	Al <sub>2</sub> O <sub>3</sub>
Sample	Al <sub>2</sub> O <sub>3</sub>
DTA Range	50.0 Uv
TG Range	100 mg
Heating Rate	10 °C/min

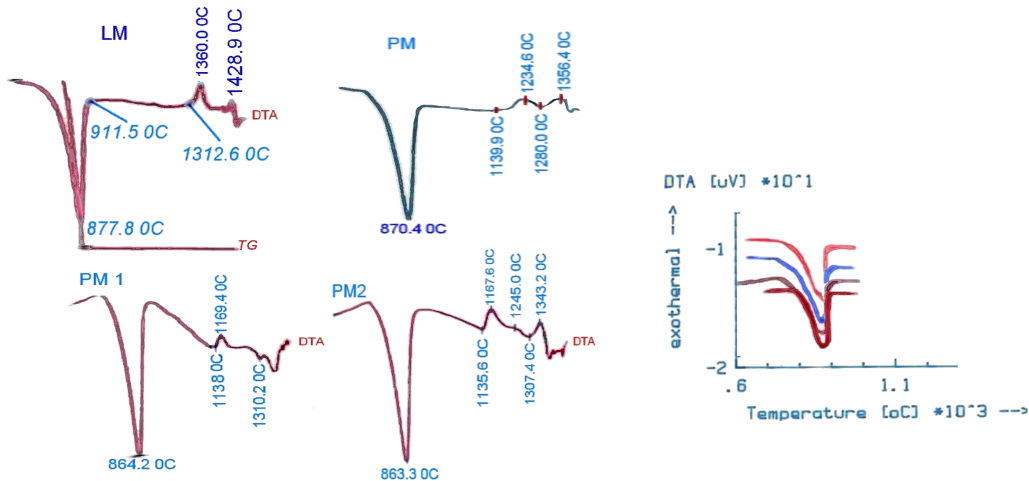
The temperature range of different reactions occurring during the burning of control and other plant mixes is identified through DTA curves and mentioned in (Table 3).

(Table-3) Differential Thermal Analysis of Experimental Compositions

Composition	Temperature (°C)			
	CaCO <sub>3</sub> Decomposition	Melt Formation		C <sub>3</sub> S Formation
		Initial	Final	
CM	877.8	1312	1400	1360/1482
PM	870.4	1200	1280	1234/1356
PM1	864.2	1128.2	1310	1169.4
PM2	863.6	1128	1307	1167.6/1343

The thermograms of mixes CM, PM, PM1 and PM2 show endothermic effects between 700°C to 900°C as a result of calcination reaction. It is clear from DTA curve PM1, (Fig. 2) that calcination of plant mix begins at lower temperature than control mix (CM). Addition of fluorspar to the plant mix helps further reduce the calcination temperature. These observations support the earlier studies (13,14) where it was found that CaSO<sub>4</sub> had some catalytic effect on the decomposition of CaCO<sub>3</sub>. Soon after the termination of calcination reaction, an endothermic descent of base line between 1035°C and 1312°C corresponds to the on-set of melt formation in control mix. Then follows a strong exothermic peak representing the formation of C<sub>3</sub>S with peak maximum at 1363°C. In plant mix, melt formation is shifted towards lower temperature and the

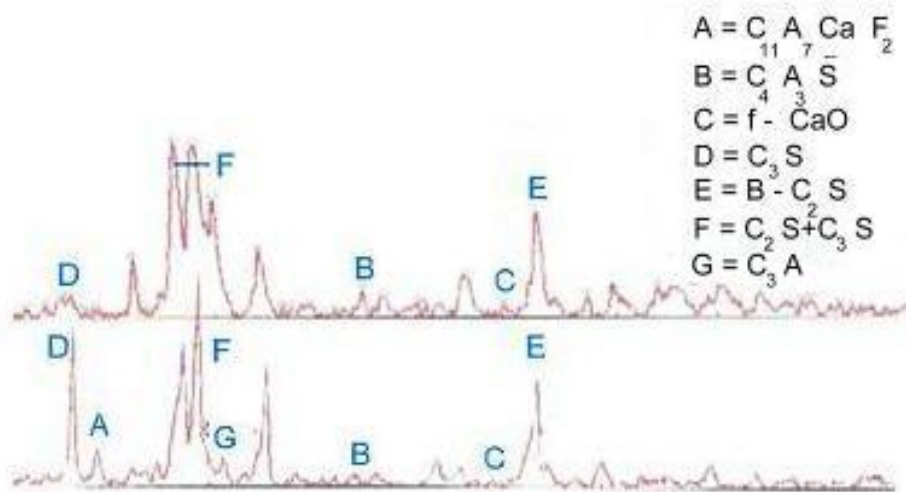
corresponding endothermic peak appears at 1140°C. The reduction of 172°C temperature in initial melt formation of plant mix is due to CaSO<sub>4</sub>. The previous studies (15) confirmed CaSO<sub>4</sub> as an effective flux which lowered initial melt formation temperature of raw mix by over 100°C. The initial melt formation in mineralized plant mix (PM2) is completed at 1135°C. Soon after this, a strong exotherm appears at 1168°C and denotes the formation of C<sub>3</sub>S. Addition of fluorspar to the plant mix results in the formation of low temperature fluosulphatic melt which allows SiO<sub>4</sub><sup>4-</sup>, Ca<sup>2+</sup> ions to diffuse through it and increase the rate of formation of alite at 1168°C. During this study, it is revealed that complete clinkerization of high SO<sub>3</sub> plant mix is possible in presence of fluorspar at temperatures as low as 1300°C. When clinkering temperature of the plant mix is increased beyond 1300°C, dissociation of C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> and C<sub>11</sub>A<sub>7</sub>CAF<sub>2</sub> takes place. The free lime released in dissociation of C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> and C<sub>11</sub>A<sub>7</sub>CAF<sub>2</sub> reacts with C<sub>2</sub>S to form additional amount of C<sub>3</sub>S minerals.



(Fig 2) DTA of raw mixes

#### 1.4 XRD Studies

The mineralogical composition of low heat clinker burnt with and without fluorspar is given at (Fig. 3). X-ray diffractogram of non-mineralized clinker burnt in laboratory furnace at 1300°C shows β-C<sub>2</sub>S as the main mineral phase. Other phases detected through XRD in the clinker are C<sub>3</sub>S, C<sub>2</sub>S + C<sub>3</sub>S, CaO, C<sub>4</sub>A<sub>3</sub>S<sup>-</sup>. The clinker burnt in the presence of 0.5 wt% fluorspar at 1300°C, results in the formation of C<sub>3</sub>S as the main mineral along with other minerals like β-C<sub>2</sub>S, C<sub>2</sub>S+C<sub>3</sub>S, C<sub>4</sub>A<sub>3</sub>S<sup>-</sup>, C<sub>11</sub>A<sub>7</sub>CaF<sub>2</sub>, CaO, C<sub>3</sub>A. In this case C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> is formed to a lesser extent and the peak intensity of C<sub>4</sub>A<sub>3</sub>S<sup>-</sup> phase is reduced in X-ray diffractogram (Fig. 3) due to the primary and advantageous formation of C<sub>11</sub>A<sub>7</sub>CaF<sub>2</sub>.



(Fig 3) XRD studies of clinker made from plant mix-A and plant mix-C

### 1.5 Mechanical and physical properties of low heat cement

The performance of plant and low heat cement is evaluated in terms of mechanical, physical and other hydration properties. The low heat mineralized clinker prepared in laboratory furnace was interground with 2% gypsum to a blain value of 380 m<sup>2</sup>/kg. The 3, 7 and 28 days compressive strength of 25.4mm mortar cubes for both cements is reported in (Table 3). The compressive strength of low heat cement tested in laboratory, at all ages, is higher than the compressive strength of normal plant cement. The high strength shown by low heat cement is the result of activated alite minerals due to mineralizing action of fluorspar. Further rise in early strength of the mortar cubes is due to newly formed  $C_{11}A_7CaF_2$  and  $C_4A_3S^-$  minerals which possess high early hydration characteristics. It is also evident from (Table-3) that rate of strength gain between 3 and 7 days is higher in low heat cement than conventional plant cement. This is explained on the basis of  $C_4A_3S^-$  and  $C_{11}A_7CaF_2$  minerals, which at early ages hydrates more rapidly than  $C_3A$ .

(Table 3) Compressive strength of low heat cement and Plant cement

Cement Type	Compressive strength (N/mm <sup>2</sup> )			Strength gain (%) between 3 and 7 Days
	3 Days	7 Days	28 Days	
Low heat cement	12.56	17.05	23.24	35.75
Plant cement	9.40	11.34	19.83	20.6

## 1.6 Physical properties of low heat and plant cements

### 1.6.1 Time of set

The time of set data, soundness values and whiteness indices for both cements are compared at (Table 4). We have noted that when low heat clinker is ground with out gypsum, it shows rapid set behavior. Setting time of low heat cement is brought close to the setting time of the normal plant cement by adding 2.0 wt% gypsum to the low heat clinker. The test results regarding the soundness of low heat cement confirm that it can easily pass the lechatelier expansion test. The most peculiar features of low heat cement found in this study are quick setting, rapid hardening and high compressive strength. While grinding plant and low heat clinkers in laboratory to a certain fineness value, we have noticed that low heat clinker is softer in grinding than plant clinker.

### 1.6.2 Whiteness index

The whiteness index of low heat cement is comparable to plant cement despite the fact that blain value of former is low. In the presence of low temperature fluosulphatic melt,  $C_3S$  and  $C_2S$  form at the same time. With the result, the low heat clinker has totally different build up of minor coloring elements than high temperature plant clinker and gives low heat cement better whiteness characteristics.

(Table 4) Physical properties of low heat and plant cement

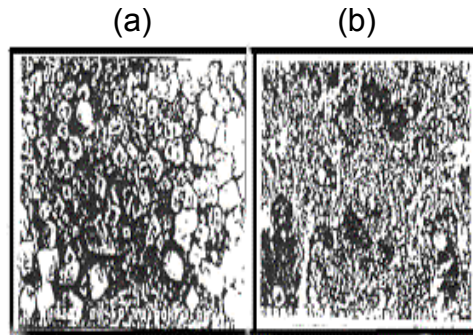
Cement Type	Gypsum added (%)	Setting Time (Min)		Expansion (Lechatelier) (mm)		Blain $m^2/kg$	Whiteness Index
		Initial	Final	Actual	Standard		
Low heat cement	2%	181	240	4.8	10.0	380	85
Plant cement	4%	160	220	2.0	10.0	440	86

## 1.7 Hydration studies

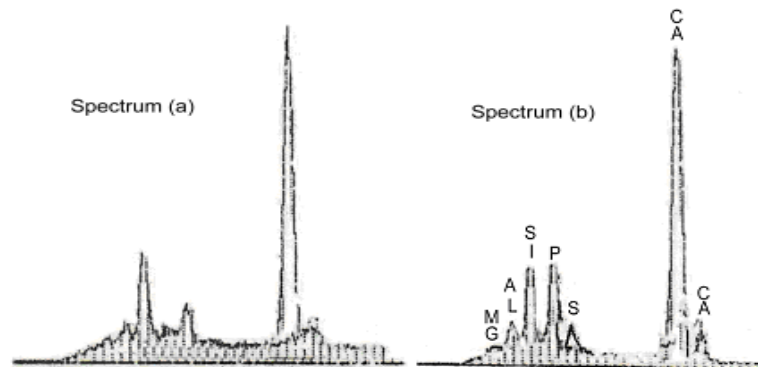
### 1.7.1 SEM/EDXA

Hydration behavior of low heat cement is studied vis-a-vis plant cement by SEM/EDXA. Majority of crystals shown in by micrograph (a), (Fig 4) are recognized as monosulphoaluminate while the crystals shown in micrograph (b) are ettringite. The EDXA spectrum (a) has low sulphur to

alumina ratio than spectrum (b) and therefore former is confirmed as monosulphoaluminate while the latter as Ettringite.



(Fig 4) SEM micrographs of plant cement and low heat cement pastes



(Fig 5) EDXA spectrum of paste of plant cement and low heat cement

The stable hydration products of ettringite crystals are known to fill the inner vacant spaces of hydrated paste, thereby decreasing the porosity of the paste, and thus results in the high early strength properties of low heat cement. In case of plant cement, monosulphoaluminate crystals grow in the form of thin plates with characteristic edge to face contact having some vacant spaces. This may be the reason of comparatively low early strength of plant cement.

## Conclusions

- Our experiments confirm that it is possible to produce low heat cement by utilizing high sulphur lime sludge with fluorspar as mineralizing agent.
- Quick setting, rapid hardening and high strength white cement can be produced at 1300°C burning temperature.



- Lime sludge produced as waste product in the manufacture of fertilizer can economically be utilized to produce low heat cement. This way considerable savings in terms of high quality limestone, reduction in pollutant emissions and fuel are possible.
- The low heat white clinker produced was soft to grind. There fore, power economy in grinding operation is anticipated.

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