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INVESTIGATIONS ON HIGH SO_3 PORTLAND CLINKERS AND CEMENTS
I. CLINKER SYNTHESIS AND CEMENT PREPARATION

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ABSTRACT

Portland clinkers containing side by side the phases C_3S, and C_4A_{3s} and optionally also C_4AF and C_2S, ay be produced by burning pertinent raw meals with added small amounts of CaF_2 to temperatures 1250-1300°C. Such clinkers exhibit a significantly improved grindability as compared to ordinary portland cement clinker. The Sterength development of cements made from these clinkers depends greatly on the amount of added gypsum and at optimum gypsum additions is similar to that of ordinary portland cement.

Introduction

In this series of papers we are reporting our data on the synthesis and structure of high SO_3 portland clinkers and on the properties of cements produced from them. Unlike in similar so called "sulfobelitic" cements, developed in the past, our clinkers do contain the phase tricalcium silicate ($3CaO.SiO_2$; abbr. C_3S) side by side with calcium aluminate sulfate ($4CaO.3Al_2O_3.SO_3$; abbr. C_4A_{3s}), the phase in which the bulk of the present SO_3 is incorporated. Other phases may include the ferrite phase ($4CaO.Al_2O_3.Fe_2O_3$; abbr. C_4AF) and dicalcium silicate ($2CaO.SiO_2$; abbr. C2S). The production of clinkers of this type appeared desirable, as sulfobelitic cements, though having acceptable 1 day and 1 year strengths, exhibit a poor strength development between 1 and 28 days.

The possibility to produce these "sulfoalitic" clinkers appeared uncertain initially, as in the published literature an incopatibility of the phases C_3S and C_4A_{3s} was suggested [1]. Moreover, the ranges of thermal stability and the optimum temperatures for the synthesis of both phases differ significantly: Whereas C_4A_{3s} is easily formed at around 1250°C and decomposes above 1300°C a temperature of at least 1350°C is required to synthesize C_3S with an acceptable rate. As to the formation of C_3S in the presence of sulfates it has been reported that the latter ions, if present in the raw meal in greater amounts, tend to reduce the amount of formed tricalcium silicate and along with it to increase the amount of residual free lime [2-9].

In our work we studied the possibility to overcome the outlined difficulties by adding mineralizers/fluxes to the raw meal, out of which CaF_2 was found to be most effective. The

TABLE 1
Targeted and Actual Composition of the Raw Meals Studied

Raw meal		R	1	2	3	4	5	6
Targeted clinker potential phase composition (%)	C3S	70	70	70	70	70	60	40
	C2S	10	-	-	-	-	-	40
	C3A	10	-	-	-	-	-	-
	C4AF	10	30	20	10	-	20	10
	C4A3s	-	-	10	20	30	20	10
Theoretical oxidic composition of raw meal (g)	CaO	68.92	65.42	64.48	63.53	62.60	60.78	63.80
	SiO2	21.91	18.41	18.41	18.41	18.41	15.78	24.48
	Al2O3	5.88	6.30	9.22	12.15	15.06	14.24	7.12
	Fe2O3	3.29	9.87	6.58	3.29	-	6.58	3.29
	SO3	-	-	1.31	2.62	3.93	2.62	1.31
Actual composition of raw meal (g)	CaO (as CaCO3)	68.92	65.09	59.49	56.85	56.67	56.13	59.76
	SiO2	21.91	18.31	17.75	17.63	17.86	15.37	23.84
	Al2O3	5.88	6.27	8.89	11.64	14.61	13.87	6.93
	Fe2O3	3.29	9.82	6.35	3.15	-	6.41	3.20
	CaSO4	-	-	6.56	9.77	9.89	7.44	5.78
	(=SO3)	-	-	(3.86)	(5.76)	(5.84)	(4.39)	(3.41)
	CaF2	-	0.50	0.96	0.96	0.97	0.78	0.49
Burning temp. (°C)		1450	1350	1250	1230	1300	1250	1250

results reported in this paper were obtained on raw meals, clinkers and cements produced from pure chemicals in the absence of minor constituents.

In studies related to this subject Blanco-Varela and coworkers [10] studied the system $CaO-SiO_2-Al_2O_3-Fe_2O_3-CaSO_4-CaF_2$ and produced clinkers with exeptionally high alite + belite contents at 1300°C. They also produced low iron "white" clinkers by burning the raw meal at a reduced temperature with added $CaSO_4$ and CaF_2 [11-12] and they reported the formation of fluorellastidite ($3C_2S.3CaSO_4.CaF_2$) as the main SO3 bearing phase.

Results

Burning Experiments. The clinkers to be studied were prepared from pure chemicals, i.e. $CaCO_3$, SiO_2 (quartz), Al_2O_3, Fe_2O_3, $CaSO_4$ and CaF_2, that contained no more than 0.1 per cent of foreign ions. Table 1. shows the targeted potential phase composition of the clinkers to be produced and the corresponding raw meal oxidic composition. Included in the study were six experimental raw meals, designed Nr. 1 to 6, whose composition corresponded to clinkers with variable contents of the phases C_3S, C_4A_{3s}, C_4AF and C_2S. A seventh raw meal, designated "R", served as a reference and its composition corresponded to a clinker with the phases C_3S, C_2S, C_3A and C_4AF in proportions as common in ordinary portland cement.

In preliminary burnability studies raw meals corresponding to the "theoretical" composition as shown in Table 1. were studied. 0.5 per cent of CaF_2 was added to the raw meals 1-6, whereas the reference raw meal "R" was burnt in the absence of any mineralizer. About 50 g of pellets 50 mm in diameter and 10 mm high, prepared from the raw meals by compaction, were placed in a Pt-dish and burnt in an electric furnace in air to different temperatures, with a heating rate of 10°C/min. After reaching the maximum temperature the material was removed

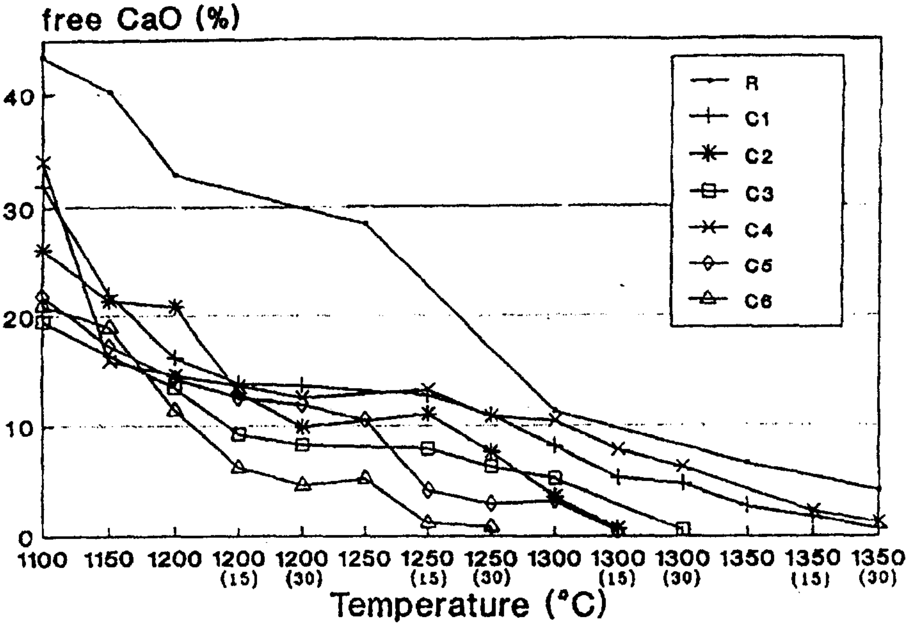

FIG. 1.

Free lime content of raw meals as function of burning temperature and burning time at maximum temperature.

from the furnace either immediately, or after 15 or 30 min. and cooled in air. To assess the degree to which the clinker formation process had been completed the free lime content was determined in the burnt products by the Franke extraction method. Figure 1. shows the free lime content of the produced clinkers as function of maximum burning temperature. It appears that at any maximum burning temperature employed the free lime content of all studied experimental raw meals No. 1-6 was below that of the reference raw meal "R", indicating a better burnability of the former ones.

Based on these preliminary results clinker samples needed for a systematic study were prepared subsequently. The "actual" composition of the raw meals used in the production of such clinkers is also shown in Table 1. Here the SO_3 content was increased above the theoretical value, to compensate for the SO_3 losses expected to take place in the course of burning. The production of all clinkers was done in batches of 300 g. The material was heated at a heating rate of 10°C/min. and kept at the maximum burning temperature, indicated in Table 1., for 30 min. prior to cooling in air.

Clinker Composition. To establish the phase composition of the produced clinkers, first the free lime content was determined by the Franke extraction method. The amount of C_3S (in clinkers Nr. 6 and "R" the amount of C_3S+C_2S) was determined by substracting the amount of free lime from the total amount dissolved in a methanolic salicylic acid solution (salicylic acid soluble fraction SASF). The residual fraction (salicylic acid extraction residue SAER) corresponded

TABLE 2
Composition of Clinkers

Clinker		R	1	2	3	4	5	6
Whole clinker (%)	CaO	68.9	64.7	62.5	61.1	61.0	58.9	62.3
	SiO2	21.9	18.3	17.8	17.7	18.2	15.5	23.8
	Al2O3	5.88	6.76	8.92	11.7	15.3	14.1	6.92
	Fe2O3	3.29	9.82	6.32	3.26	0.03	6.72	3.23
	SO3	-	-	3.81	5.68	5.10	4.36	3.38
	CaF2	-	0.32	0.59	0.53	0.52	0.47	0.32
Fraction soluble in salicylic acid [SASF] (%)	C3S(+C2S)	80.9	69.5	67.4	66.7	68.7	57.5	75.6
	CaO free	0.15	0.23	0.24	0.53	0.51	0.22	0.88
	CaO	72.5	71.3	71.1	70.4	71.3	69.6	66.6
	SiO2	25.3	25.2	25.7	25.2	25.7	25.5	30.2
	Al2O3	1.22	1.89	1.87	2.84	2.46	2.53	1.64
	Fe2O3	1.01	1.25	0.00	0.95	0.01	1.89	0.00
	SO3	-	-	0.68	0.24	0.00	0.00	1.32
	CaF2	-	0.32	0.68	0.47	0.58	0.45	0.21
Salicylic acid extraction residue [SAER] (%)	C3A	9.5	-	-	-	-	-	-
	C4AF	9.5	30.3	17.6	9.6	-	15.5	7.3
	C4A3s	-	-	14.8	23.2	30.8	26.8	16.2
	CaO	53.8	49.6	45.9	42.2	38.0	44.1	48.4
	SiO2	7.58	2.54	2.69	2.32	0.78	1.73	3.10
	Al2O3	25.7	18.0	22.6	30.0	44.2	30.0	24.1
	Fe2O3	12.8	29.5	18.6	8.00	0.00	13.4	13.7
	SO3	-	-	9.69	16.8	16.6	10.3	10.1
	CaF2	-	0.33	0.41	0.67	0.39	0.50	0.69

to the amount of C_4A_{3s} and/or C_4AF in clinkers Nr. 1-6 and to the amount of C_3A+C_4AF in clinker "R". The mutual ratio of the phases C_4A_{3s} and C_4AF in the residues of clinkers Nr. 2,3,5 and 6 was determined by X-ray diffraction. The amounts of C_3A and C_4AF in clinker "R" were determined by extracting the residue with a 3% sucrose solution in water, by which the phase C_3A became dissolved. The oxidic composition of the whole clinkers and the SAERs was determined directly by chemical analysis, whereas that of SASFs was calculated from the composition of the whole clinker and the SAER and the amount dissolved in salicylic acid.

Table 2 summarizes the composition of the clinkers found this way. It appears that the actual phase composition of the clinkers was not too different from the targeted one. The amount of the phase C_3S was somewhat lower than expected in all clinkers except clinker "R". The amount of the phase C_4A_{3s} was consistently higher and that of C_4AF lower than intended. This was due to a lesser evaporation of SO_3 in the course of burning than anticipated, leading to a somewhat higher SO_3 content in the produced clinker. The free lime content was in all clinkers low, i.e. below one per cent. As to the distribution of SO_3 it appears that most of it was confined in the salicylic acid extraction residue, whereas the amount of SO_3 incorporated into C_3S was small.

Clinker Grindability. The grindability of the produced clinkers was studied by grinding 25 g of the material, precrushed to a size 1-2 mm, in a small laboratory swing mill and by determining the specific surface area (Blaine) as function of grinding time. The results are summarized in Figure 2. There existed great differences between the grindabilities of the individual clinkers. Generally, the grindability of those clinkers that contained the phase C_4A_{3s} was better than that of the reference clinker "R" or the one that contained only C_3S and C_4AF (clinker Nr. 1).

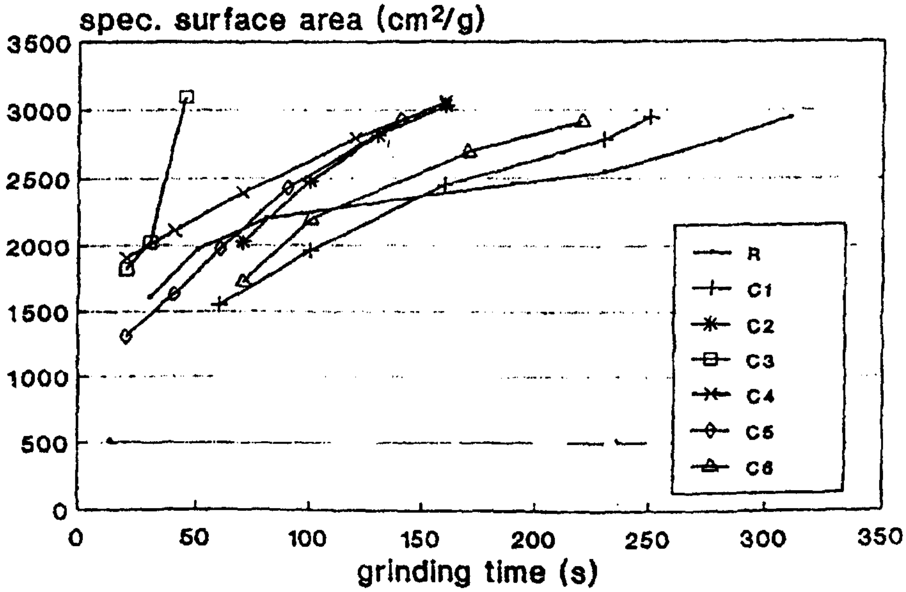

FIG. 2.
Grindability of experimental clinkers.

Optimum Gypsum. To determine the "optimum gypsum" content for cements to be produced, each experimental clinker was ground with five different amounts of gypsum, corresponding to between 2 and 10 per cent of SO_3, to a specific surface area of 300 ± 10 m^2/kg (Blaine). The strength development of cements produced this way was determined on test specimens $15x15x60mm^3$ made out of plain pastes prepared with w/c = 0.35 and cured in humid air at 20°C.

The obtained compressive strength values are summarized in Figures 3a-f. Here each result indicates the average value determined on three parallel specimens. It appears that for each clinker a gypsum addition existed, at which a maximum strength was attained. This "optimum gypsum" value varied in some clinkers for different hydration times. Generally the "optimum gypsum" value in experimental clinkers Nr. 1-6 was higher than it is common in ordinary portland cements.

The results obtained on cements produced from experimental clinkers Nr. 1-6 are to be compared with the strength values found in a cement produced from the reference clinker "R" with amounts of added gypsum corresponding to 3 per cent SO_3. Here the found values were as follows: 1d: 25.1 MPa; 3d: 46.0 MPa; 28d: 80.1 MPa and 180d: 95.2 MPa.

Discussion

Our experiments proved the possibility to produce portland clinkers that contain simultaneously the phases C_3S and $C_4A_3\bar{s}$. The synthesis of such clinkers became possible only by reducing the burning temperature to about 1250-1300°C, instead of about 1450°C commonly employed in the production of odinary portland clinkers, and by adding to the raw meal CaF_2 that stabilizes

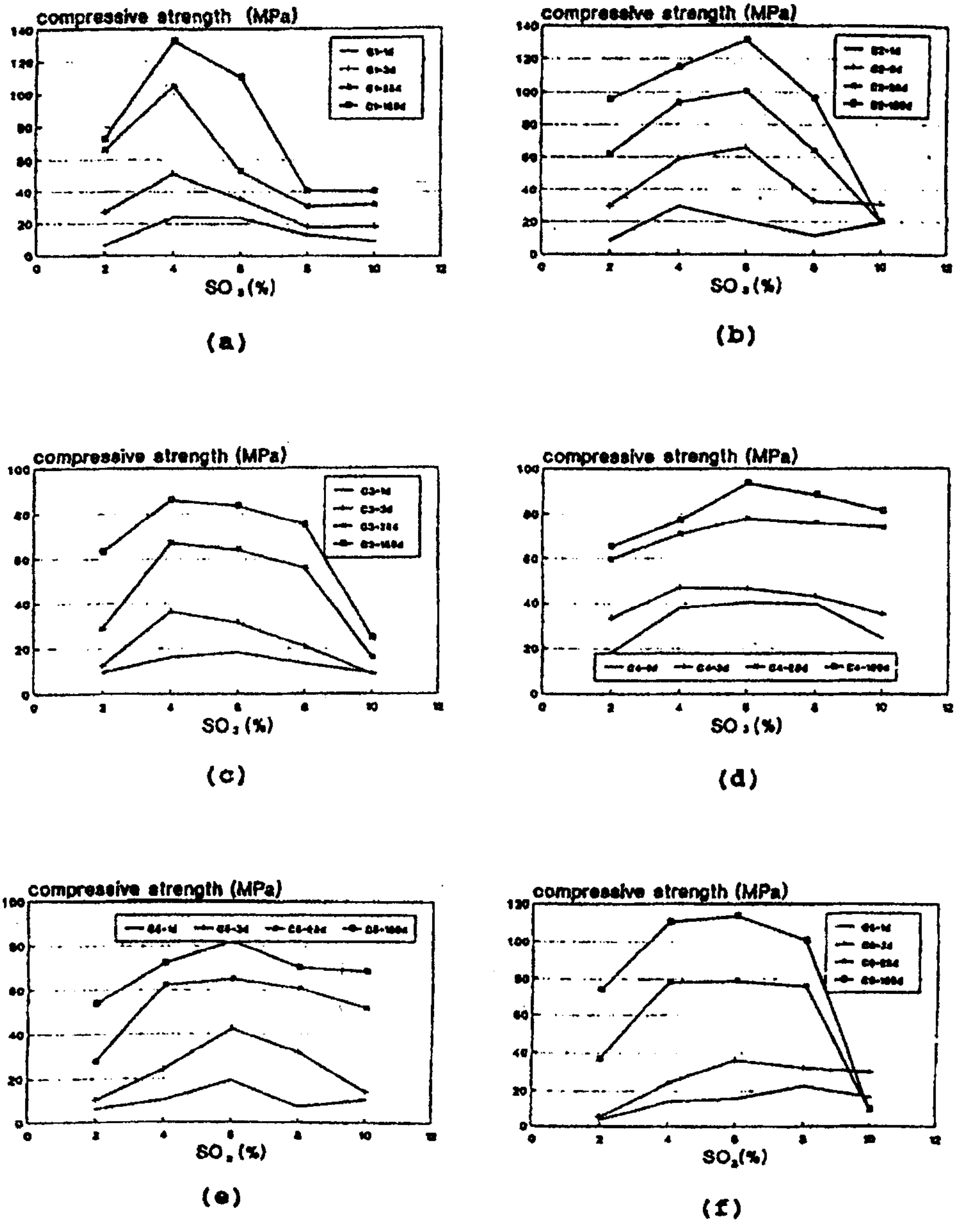

FIG. 3 a-f.

Compressive strength development of cements made from clinkers Nr. 1-6 with different amounts of added gypsum (in % of SO_3).

both phases and accelerates their formation. The formation of clinkers of this type may be facilitated by the simultaneous presence of Fe_2O_3 in the raw meal, leading to the formation of C_4AF as a third phase. Also present in the clinker may be the phase C_2S at a lime saturation factor below 100%, and even the phase C_3A, if an imbalance between the amounts of Al_2O_3, SO_3 and Fe_2O_3 in the raw meal exists. At "optimum" gypsum additions the strength development of the prepared experimental cements was not too different from that of the reference "ordinary" portland cement produced simultaneously.

Clinker of this type have the potential to be produced with a distinctly reduced energy consumption, as compared to ordinary portland cement clinkers with the same lime saturation factor. One reason for it is the lower burning temperature required; this way the heat losses occuring in the burning process may be reduced. Another reason is the lower heat of fusion, that is mainly due to the lower $CaCO_3$ content of the raw meal. This difference is brought about by a lower CaO content in the phases C_4A_{3s} and C_4AF that represent a significant fraction of these clinkers, as well as by the fact, that a part of the total amount of CaO is introduced in form of $CaSO_4$ and CaF_2, rather than in form of $CaCO_3$.

In addition to energy savings, the reduced consumption of fossile fuels and the lower calcium carbonate content of the raw meal may result also in a distinctly reduced CO_2 emission in the course of clinker burning. This, as well as a reduced NOx emission, due to the lower burning temperature, are factors important for enviromental reasons.

The significantly improved grindability of the produced experimental clinkers appears to be mainly due to a reduced amount of liquid phase formed in the burning process, and consequently to a higher porosity of the produced clinker.

Conclusions

SO_3-rich portland clinkers that contain simultaneously the phases C_3S and C_4A_{3s}, and optionally also C_4AF and C_2S, may be produced by burning pertinent raw meals with added small amounts of CaF_2 to temperatures of about 1250-1300°C.

Clinker of this type prepared in the laboratory exhibited an exeptionally good grindability, apparently due to their high porosity.

To obtain cements with optimum strength development the clinkers have to be interground with amounts of gypsum higher than common in ordinary portland cement.

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