Pergamon

Cement and Concrete Research, Vol. 26, No. 9, pp. 1315-1324, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00129-9

INVESTIGATIONS ON HIGH SO_3 PORTLAND CLINKERS AND CEMENTS
II. PROPERTIES OF CEMENTS

H. Zhang and I. Odler
Technical University Clausthal, Clausthal-Zellerfeld, Germany

(Refereed)
(Received April 1, 1994; in final form July 15, 1996)

ABSTRACT

Six cements made from clinkers containing the phases C_3S, C_4A_{3s}, C_4AF and C_2S in different proportions and ground with different amounts of gypsum were studied with respect to their hydration kinetics as well as composition ans physico-mechanical properties of the hydrated material. Th3 obtained results were compared with those found in a reference ordinary portland cement.

Introduction

In the first paper of this series [1] we studied the synthesis of clinkers that contained simultaneously the phases C_3S and C_4A_{3s}, besides of C_4AF and C_2S, as well as the preparation of cements made from them. In the present paper we are reporting our data on the hydration and properties of these cements.

Experimental

The composition and synthesis of the clinkers included in this study was reported in the first paper of this series. To produce the experimental cements the clinkers were ground to a specific surface area of 300 m^2/g with amounts of gypsum yielding optimum strength. Altogether 7 experimental cements were prepared from 6 clinkers, selecting two gypsum additions for one of the clinkers. An additional cement, with a composition corresponding to an ordinary portland cement, was included in the study as well, to serve as a reference. The composition of the studied cements is given in Table 1.

The consistency of pastes prepared from the cements was determined in a way as follows: A plastic ring 50 mm in diameter and 25 mm high was placed on a glass plate and filled with the cement paste. After removing the ring the glass plate was lifted 10 mm and allowed to fall back 15 times. After that, the diameter of the paste on the plate was measured and the obtained value used as a parameter that expresses the flow properties of the material. The employed water/cement ratio was in all instances constant, i.e. 0.35.

The setting properties of the pastes were determined by the Vicat method. All measurements were done with the same water-cement ratio, i.e. 0.35.

The strength development of the cements was studied both on plain pastes with w/c = 0.35 and on ISO mortars with w/c = 0.50 and sand/cement = 3:1 (specimens 15 × 15 × 60 mm^3). After demolding the specimens were cured in humid air at 20 ± 2 °C until testing.

The expansion of the pastes was studied on paste specimens 10 × 10 × 60 mm^3 (w/c = 0.35). The length of the specimens was measured after different hydration times and compared with that found at the time of demolding, i.e. after one day. One series of specimens was cured permanently in water vapor saturated air (air curing). Another series was cured first three days in air and subsequently under water (water curing). All measurements were done at 20 ± 2 °C.

The liberation of the heat of hydration was determined by isothermic calorimetry on pastes with w/c = 0.70.

The progress of hydration was studied on samples in which the free water was removed by grinding the hardened paste in a porcelain mortar with excessive amounts of acetone, filtering the suspension and washing the material on the filter with additional acetone and ethyl ether and finally by drying the residue on air. In the material obtained this way the amount of combined water was determined as the loss on ignition at 1000 °C.

The amounts of nonreacted gypsum, free calcium hydroxide and formed ettringite were determined by differential thermal analysis.

The amount of nonreacted C_3S was determined by X-ray diffraction on samples preignited at 600 °C. The amounts of nonreacted C_4AF and C_4A_{3s} were also determined by X-ray diffraction, however, on samples that were first extracted with a methanolic salicylic acid solution, to dissolve and separate the present C_3S, C_2S phases C-S-H phases and calcium hydroxide.

Results

Consistency, Setting Time and Strength Development. The consistency of the pastes, their setting characteristics and the compressive strengths after 1, 3, 28 and 180 days are summa-

TABLE 1

Composition, Consistency, Setting Times and Strengths of Studied Cements

Cement		RC/3	C1/4	C2/4	C2/6	C3/4	C4/6	C5/6	C6/6
Clinker (target composition) [%]	C3S	70	70	70	70	70	70	60	40
	C2S	10	0	0	0	0	0	0	40
	C4AF	10	30	20	20	10	0	20	10
	C4A3s	0	0	10	10	20	30	20	10
	C3A	10	0	0	0	0	0	0	0
Gypsum [% SO3]		3	4	4	6	4	6	6	6
Consistency [cm] (w/c = 0.35)		12	12.5	12	9	12	10	9	11.5
Setting time [min.] (w/c=0.35)	beg.	265	320	240	95	125	70	70	120
	end	355	555	410	165	185	120	110	190
Compr. strength [MPa] (pastes, w/c=0.35)	1d	25.1	23.9	29.0	20.2	16.1	40.5	19.2	15.9
	3d	46.0	51.4	59.3	65.7	36.3	45.3	42.2	36.3
	28d	80.1	104.8	92.9	100.3	66.9	77.6	64.9	79.0
	180d	95.2	132.4	115.1	130.9	85.9	93.5	82.1	113.6
Compr. strength [MPa] (mortars, w/c=0.50)	1d	11.0	5.2	13.9	10.5	6.0	18.1	12.2	9.0
	3d	26.3	21.9	30.0	24.0	25.0	26.7	25.7	15.2
	28d	42.2	49.5	44.8	45.2	42.2	42.0	51.0	34.1

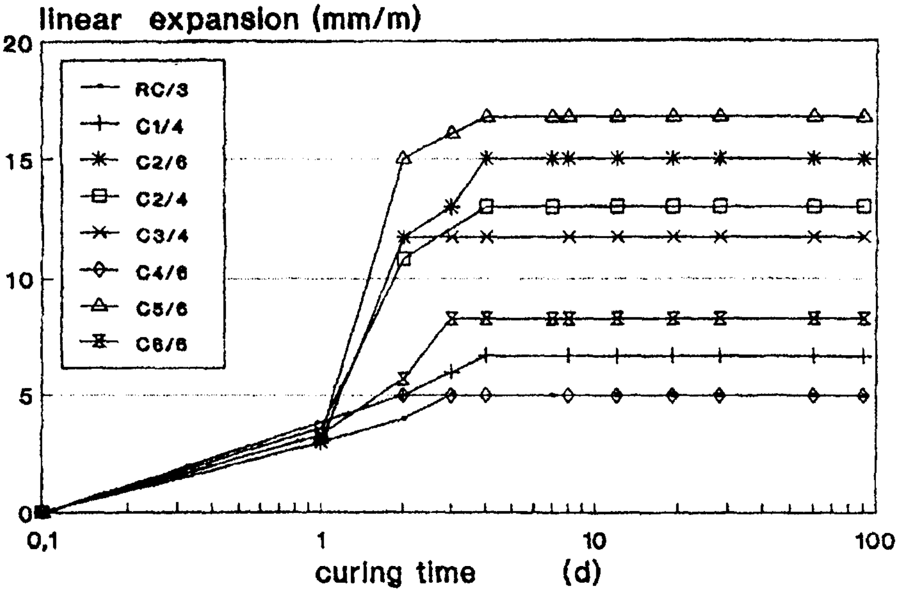

FIG. 1.
Linear expansion of cement pastes in humid air.

rized in Table 1. It appears that the flow properties of all the pastes were rather similar whereas their setting times varied distinctly. All cements that contained the phase C_4A_{3s} set faster than the control, ordinary portland cement. The longest setting time exhibited cement C1/4 that contained only the phases C_3S and C_4AF in its clinker.

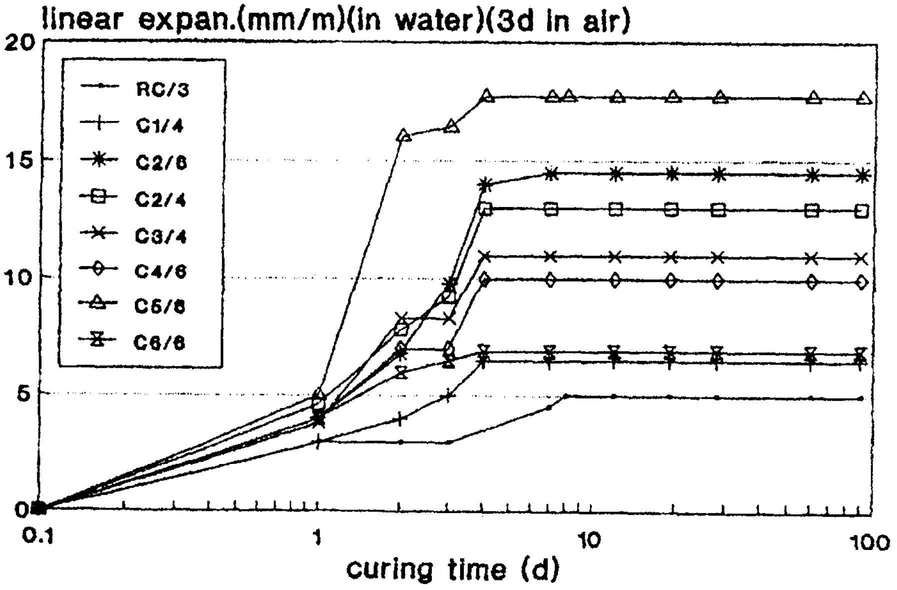

FIG. 2.
Linear expansion of cement pastes in water.

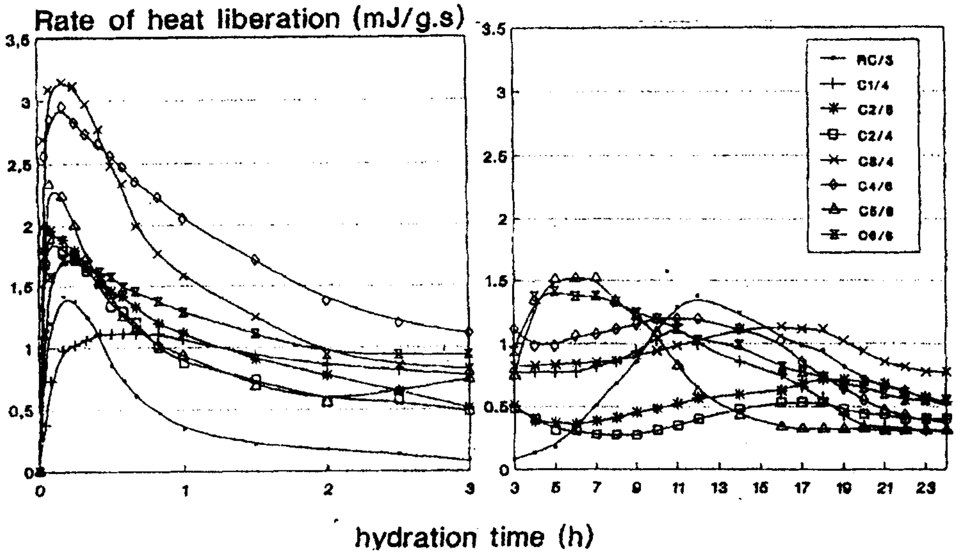

FIG. 3.
Hydration heat liberation of the studied cements.

The strength development of the experimental cements varied depending on their composition, but generally was not too different from that of the control ordinary portland cement. The exceptionally high one day strength of cement C4/6 may be attributed to its high C_4A_3s content.

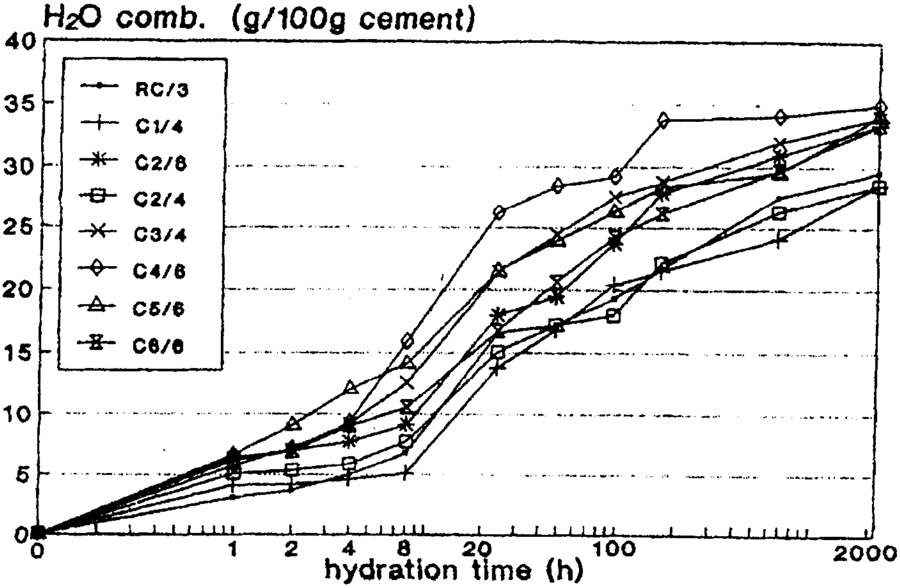

FIG. 4.
Combined water as function of hydration time.

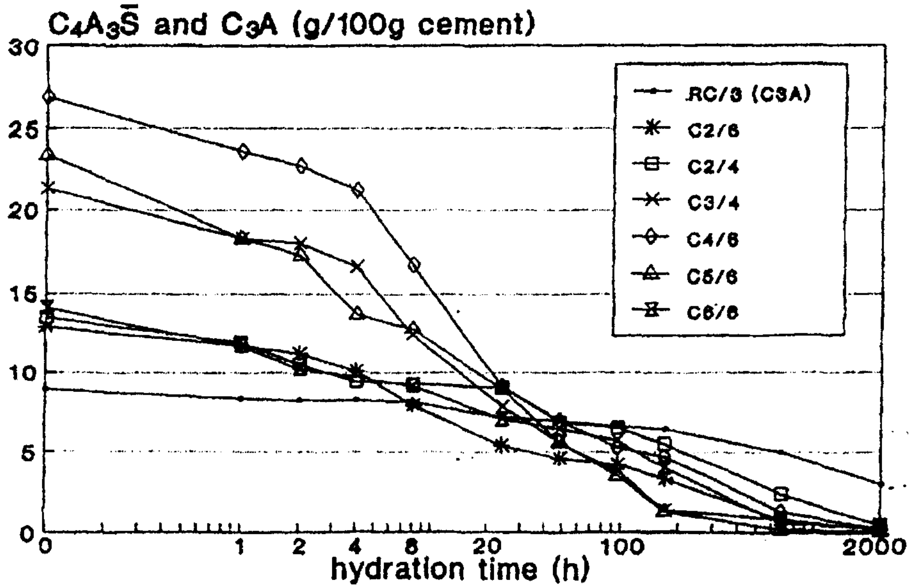

FIG. 5.
C_4A_{3s} and C_3A contents as function of hydration time.

Expansion. The expansion data are summarized in Figures 1 and 2. All results represent the average values found in two independent experiments, each of them performed with three test specimens. In all cements, regadless of composition or curing conditions, the expansion

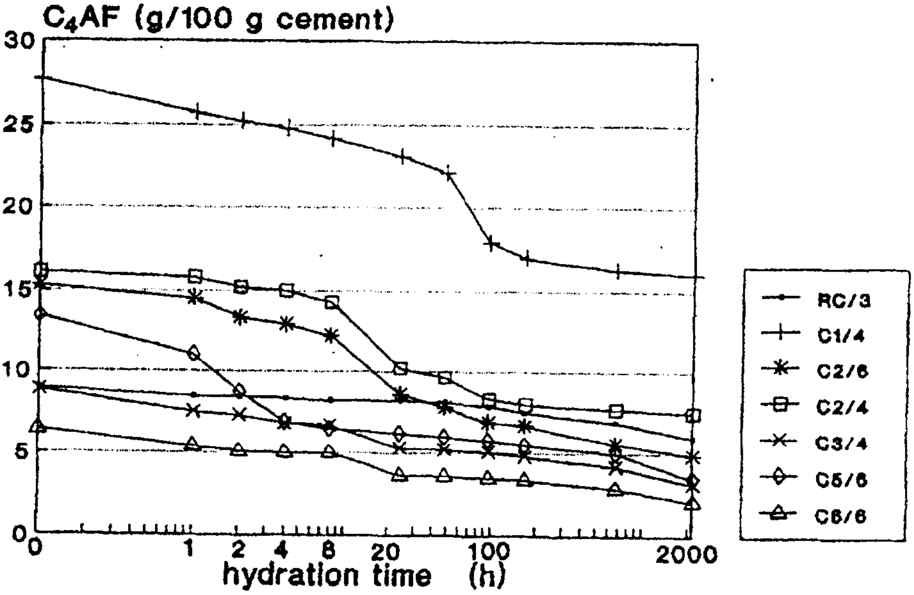

FIG. 6.
C_4AF content as function og hydration time.

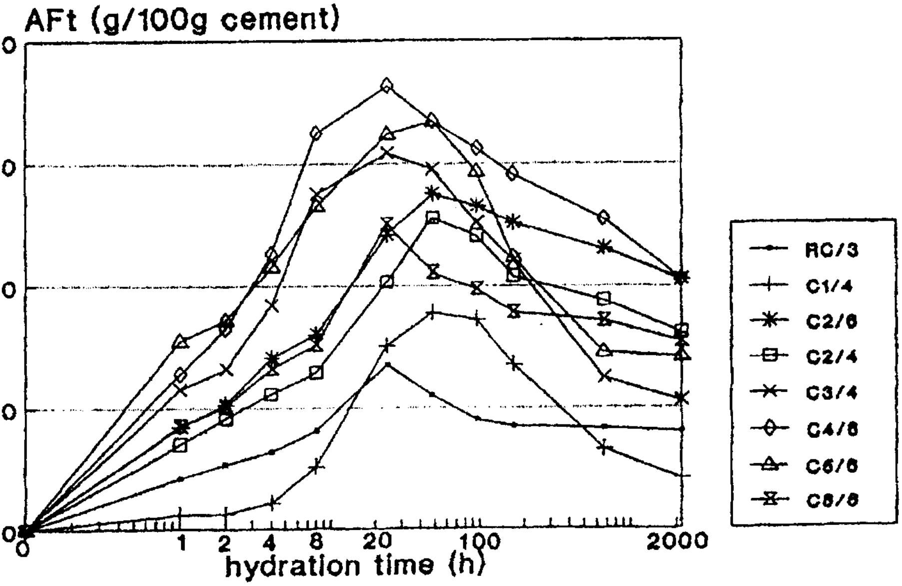

FIG. 7.
Gypsum content as function of hydration time.

process was completed within a few days. The extent of expansion was similar in samples cured just in humid air and those placed under water after three days of air curing. Out of the studied cements, the lowest expansion values were found in the control cement RC/3 and

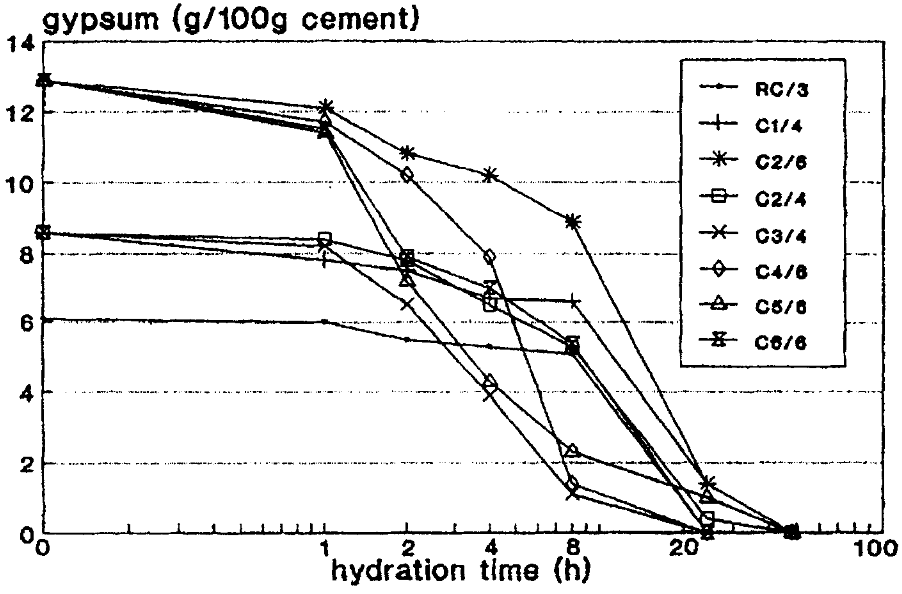

FIG. 8.
AFt (ettringite) content as function od hydration time.

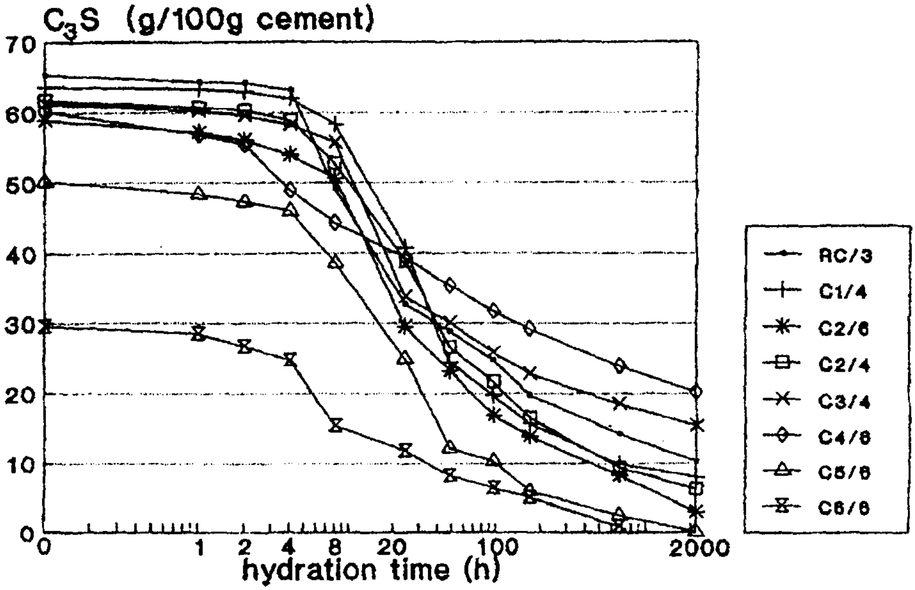

FIG. 9.
C_3S content as function of hydration time.

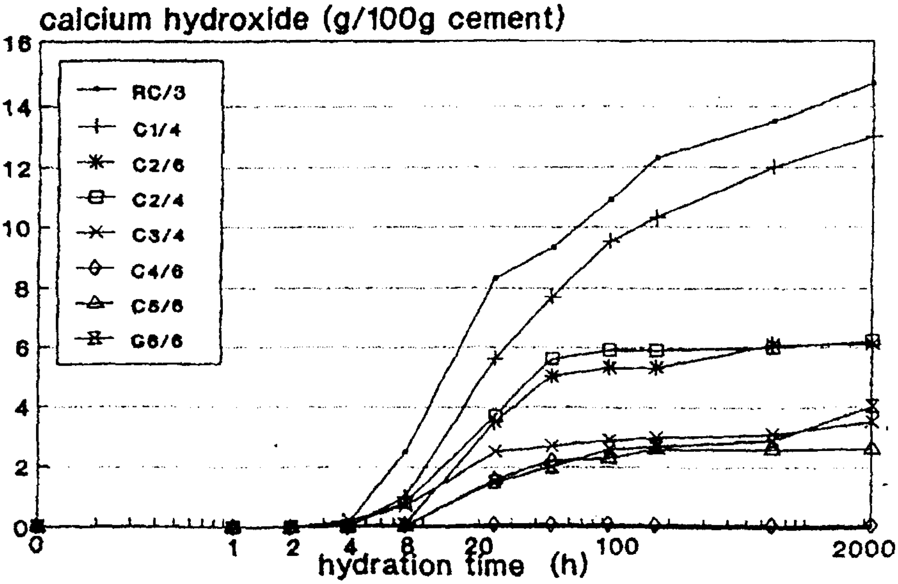

FIG. 10.
$Ca(OH)_2$ content as function of hydration time.

cement C1/4 with no C_4A_3s, whereas the expansion was higher in all cements containing the phase C_4A_3s. At equal clinker composition the expansion became higher with increased gypsum addition as may be seen from the comparison of cements C2/4 and C2/6. In one of the cements, i.e. C4/6, with the highest C_4A_3s content and no C_4AF, a distinct expansion was noticeable already within the first 24 hours after setting, i.e. prior to demolding. This may explain the rather low observed expansion of the paste after demolding, shown in the figures.

Heat of Hydration. The hydration heat evolution of the studied cements is shown in Figure 3. All cements exhibited a short-lasting initial heat evolution maximum within the first few minutes after mixing, which was probably due mainly to the formation of the AFt-phase and in a lesser extent to C_3S hydration. The intensity of this maximum varied greatly. It was lowest in the reference ordinary portland cement and in cement C1/4 that did not contain the phase C_4A_3s. It was highest in cements C3/4 and C3/6 in which the amount of this phase was high. A second maximum, belived to be mainly due to the hydration of the present C_3S phase, developed within a few hours; its intensity varied also distinctly in different cements.

Combined Water. Figure 4 shows the combined water content in the studied cements as function of hydration time. It appears that this value was generally higher in cements containing C_4A_3s than in those, in which this phase was absent. The highest combined water value was found in cement C4/6 with highest C_4A_3s content.

Progress of C_4A_3s and C_4AF Hydration. Figure 5 shows the amount of C_4A_3s in the studied pastes. In all of them this phase became almost completely hydrated within about 28 days. In addition to C_4A_3s, the figure shows also the amount od C_3A found in the reference cement paste. The hydration of this phase progressed distinctly more slowly and about half of it was still present in nonhydrated form after 28 days.

Figure 6 shows the amount of C_4AF in the studied pastes. In the reference cement RC/3 this phase hydrated rather slowly and about 80 per cent of it was still present in nonhydrated form after 28 days. The hydration of C_4AF in the experimental cements was significantly faster, however, even here significant fractions of this phase remained nonreacted after 28 days.

Consumption of Gypsum and AFt Formation. Figure 7 shows the amount of free gypsum in the studied cements. In all of them this constituent became completely consumed within about 28 days.

The amount of ettringite (AFt-phase) in the studied pastes is shown in Figure 8. In all cements the amount of this phase increased up to a maximum and declined afterwards. This maximum was found consistently between about 24 and 48 hours after mixing. In pastes made from cements containing C_4A_3s the amount of formed ettringite was higher than in the reference cement RC/3 or cemennt C1/4 with no C_4A_3s.

C_3S Hydration and Calcium Hydroxide Formation. Finally, Figures 9 and 10 show the amount of nonreacted C_3S and formed calcium hydroxide in the studied cement pastes. Expectedly, a significant hydration of C_3S got under way only after an induction period of several hours. The overall progress of hydration was similar in different cements except C4/6 that contained, besides C_3S, only C_4A_3s. Here the hydration was slowed down distinctly.

Free calcium hydroxide became detectable only several hours after mixing, in line with the existence of a dormant period in the hydration of C_3S. The amount of formed calcium hydroxide varied greatly in different cements and declined to near zero values with increasing C_4A_{3s} content., as distict amounts of this phase, together with gypsum, had been consumed in the formation of ettringite from C_4A_{3s}.

Discussion

Our results, confined to laboratory made model cements so far, revealed the existence of both similarities and differences between cements that contain in their clinkers - besides C_3S, C_4AF and C_2S - the phase C_4A_{3s} and ordinary portland cement containing the phase C3A instead. These differences are mainly due to the formation of larger amounts of the AFt (ettringite) phase in the hydration of the former cements and to a parallel reduction of the amount of free calcium hydroxide. The shortening of the setting time and the increased initial hydration heat liberation are the consequences of a high reactivity of the present C_4A_{3s} phase and thus of a faster Aft formation.

As to the strength properties, the obtained results indicate the possibility to control the strength development to a significant degree by varying the mutual ratio of the clinker phases present. Generally, the early strength development appears to be increased with increasing C_4A_{3s} and C_3S contents, whereas the presence of C_4AF and C_2S appears to affect favorably the final strength.

Most critical for a possible use of SO_3-rich portland cements appears to be the expansion associated with the formation of increased amounts of the AFt phase in their hydration. Data available thus far suggest that these cements tend to expand somewhat more than ordinary portland cement. Nevertheless, the extent of such expansion does not seem to exceed acceptable limits. Moreover, the expansion may be controlled by adjusting the phase composition of the clinker and by controlling the amount of added calcium sulfate.

As to the durability and corrosion ressistance it may be expected that hardened pastes made from High SO_3 portland cements will behave not too differently from those made from ordinary portland cement, as in both of them the C-S-H phase is the predominant constituent. Nevertheless, some differences will exist between both systems: The significantly lower content of calcium hydroxide, the constituent with highest water solubility, will make high SO_3 cement pastes more resistant against water or weak acids. The higher amount of combined water per unit of hydrated cement will result in a lower porosity of the high SO_3 cement paste at an equal water-cement ratio and degree of hydration. This, in course, may contribute to a reduced permeability and thus improved corrosion resistance of such hydrated materials. On the other hand it must be expected that high SO_3 portland cements will be even less suitable than ordinary portland cement for heat curing applications in which the temperature in the course of hydration exceeds about 70 °C, due to a delayed ettringite formation and possible concrete damage associated with it. It has been namely observed that at elevated temperatures monosulfate (AFm-phase), rather than ettringite (AFt-phase), is formed as the primary product of hydration, that converts into the latter one only in the course of subsequnt curing at ambient temperature. This conversion may be associated with an excessive expansion resulting in crack formation [2-5]. There exists also some uncertainty about a possible degradation of the present AFt-phase by CO_2 of the air and about the effect of such reaction on cement paste integrity.

The overall heat of hydration of high SO_3 portland cements may vary greatly and may be well controlled by the phase composition of the clinker. By increasing C_2S and C_4AF contents at the expense of C_3S and C_4A_{3s} it appears possible to reduce the heat evolution significantly, if desired.

In related studies Kasselouri and co-workers [6] studied the kinetics of the hydration of a sulfobelitic cement that contained dicalcium silicate, rather than tricalcium silicate, as its sole calcium silicate phase. Just as in our experiments, they reported a complete hydration of C_4A_{3s} within the first 7 days, yet a formation of ettringite continued up to 90 days. The ferrite phase became almost completely hydrated within 6 hours, contrary to our own observations. Also, unlike in our experiments, the cement expanded less than odinary portland cement, which the authors attributed attributed to a calcium hydroxide deficiency in the liqid phase. Similar to our results the cement exhibited a faster setting, but its strength development was rather sluggish, apparently due to the absence of tricalcium silicate.

Finally, it has to be stressed that all data on high SO_3 portland clinkers and cements reported within this paper were obtained under laboratory conditions and on samples made from pure chemicals. Data obtained with starting materials that may be considered for large-scale production of these cements will be published at a later time.

Conclusions

Cements made by grinding clinkers that contain the phases C_3S and C_4A_{3s}, and optionally also C_4AF and C_2S, with amounts of calcium sulfate higher than usual in portland cements, exhibit properties that are similar but not identical with those of ordinary portland cement. Their setting time is generally shorter, whereas the strength development may vary and may be controlled by variations of clinker composition. All produced high SO_3 portland cements exhibited a distinct but variable expansion whose extent may be controlled by the composition of clinker and the amount of added gypsum. High SO_3 portland cements may be considered possible alternatives to conventional portland cements in many applications, which may be produced with a distinctly reduced consumption of both thermal energy and electric power for cement grinding.

References

1. I. Odler and H. Zhang, Cem. Concr. Res
2. H. Y. Ghorab, D. Heinz, U. Ludwig, T. Meskendahl and A. Wolter, in 7th International Congress on the Chemistry of Cement (Paris 1980), Vol. 4, pp. 496-503.
3. D. Heinz and U. Ludwig, in 8th International Congress on the Chemistry of Cement (Rio de Janeiro 1986), Vol. 5, pp. 189-194.
4. I. Odler and Y. Chen, Cem. Concr. Res. 25, 853 (1995)
5. Yan Fu and J. J. Beaudoin, Cem. Concr. Res. 26, 979 (1996)
6. V. Kasselouri, P. Tsakiridis, Ch. Malami, B. Georgali and C. Alexandrirou, Cem. Concr. Res. 25, 1726 (1995)