Pergamon

Cement and Concrete Research, Vol. 25, No. 4, pp. 809-818, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00071-2

FROST RESISTANCE OF CEMENT MORTARS WITH DIFFERENT LIME CONTENTS

Dr.- Ing. habil. Anette Müller
Hochschule für Architektur und Bauwesen Weimar - Universität
Coudraystraße 11 , D - 99421 Weimar

Dipl.- Chem. Christiane Fuhr
Deitermann GmbH
Lohstraße 61, D - 45711 Datteln

Prof. Dr. rer. nat. habil. Dietbert Knöfel
Universität - Gesamthochschule - Siegen
Labor für Bau- und Werkstoffchemie
Paul- Bonatz- Straße, D - 57076 Siegen

(Refereed)
(Received June 24, 1994; in final form March 10, 1995)

ABSTRACT

Tests for the frost resistance were made on laboratory cements containing different amounts of belite activated by rapid clinker cooling. If freezing begins after the hydration of the belite cements has nearly been completed these cements will offer better frost resistance than cements rich in alite. This is due to the lower portlandite content and the more dense microstructure of the cements containing a high amount of belite.

1. Introduction

The most important properties of the main clinker minerals which Portland cement is composed of are well- known. But their influence on frost resistance has not been fully explained yet. In 1971 BLAINE and ARNI [1] found by comprehensive tests on 199 ASTM Type Cements that the main clinker phases are of less importance for the frost resistance of mortars and concretes than the air content. Statistical calculations show that an increase in C_2S, K_2O and MgO content or an increased specific surface area are followed by a slight deterioration of the durability factor according to ASTM C 290.

New results of investigations on the influence of the C_3A content of cements on the frost resistance of mortars and concretes have recently been published by STARK and LUDWIG [2]. They found that an increase in the C_3A content leads to improved frost resistance but to a reduction in freeze- deicing salt resistance.

In connection with investigations on the durability of cements rich in belite [3,4] tests were also made for the frost resistance of these cements. The results are presented in this paper.

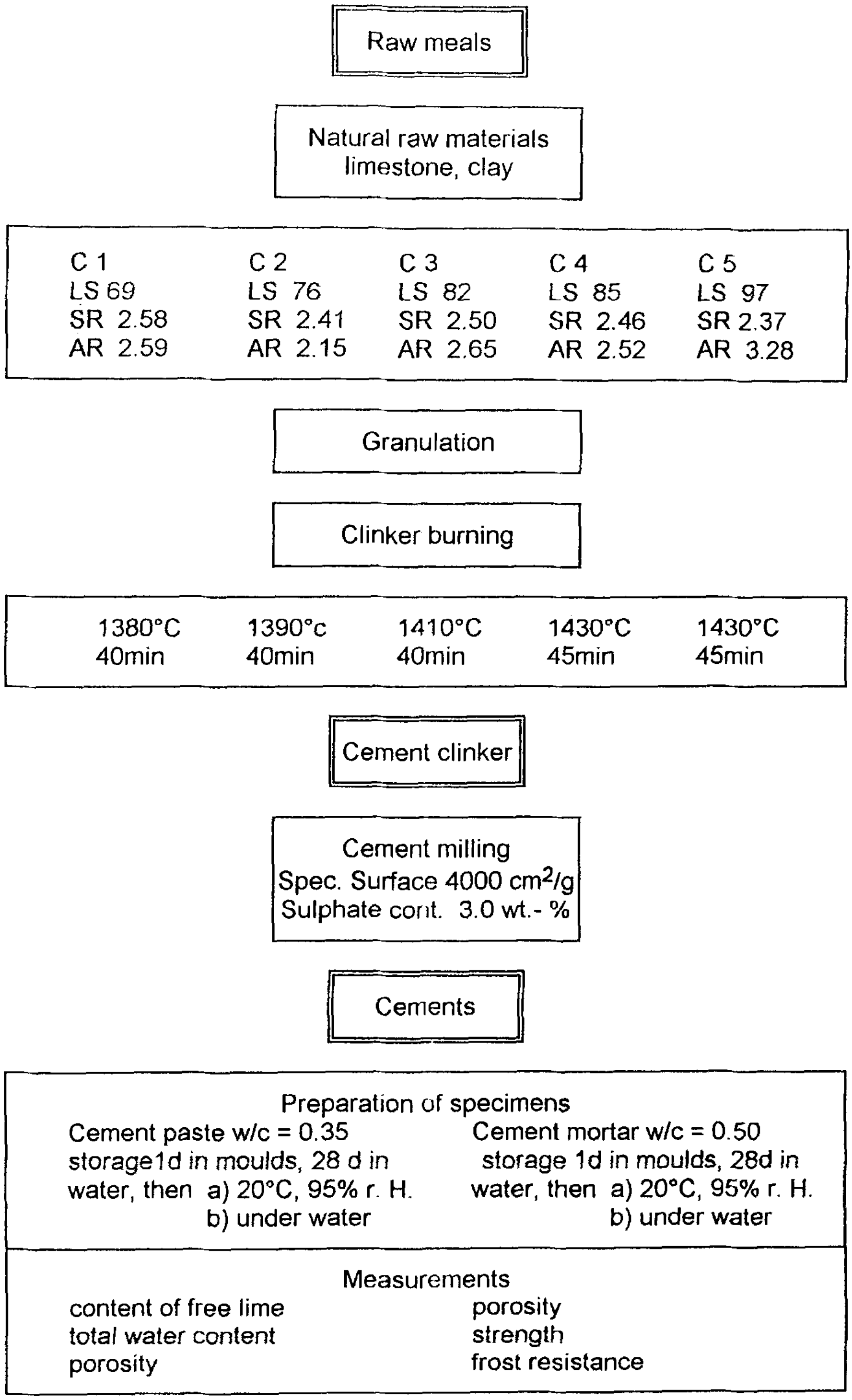


Figure 1: Test programme

2. Test Programme

Fig. 1 gives an overview of the test programme. The tests were made on 5 cements produced in the laboratory with belite contents between 25 and 70%. The aluminate and ferrite contents were nearly constant (Table 1).

The cements were made of technicalgrade raw meal components. The clinkers were burnt in an electrically heated laboratory furnace. The belite in the clinkers was activated by rapid cooling.The clinkers were ground in a ball mill, with natural gypsum added for the regulation of the setting process. The specific surface area of the cements was 4000 cm^2/g, their SO_3 content 3%.

TABLE 1: Phase composition of the laboratory cements [wt.- %]

	C 1	C 2	C 3	C 4	C 5
C_3S	0.0	0.0	14.4	21.9	43.2
C_2S	70.7	68.0	54.0	47.2	25.0
C_3A	10.5	12.5	13.2	12.8	13.9
C_4AF	8.1	9.4	7.5	7.8	6.0
CaO_{free}	0.30	0.40	0.60	0.63	2.31
CsH_2	5.5	5.5	5.6	5.6	5.5
rest	4.9	4.4	4.8	4.2	4.1

From these cements, pure cement paste and standard cement mortar according to German standard DIN EN 196 were produced, moulded into prisms of $4x4x16cm^3$ and stored under various conditions. The cement pastes were used for determinations of the phase composition, the rate of hydration, the porosity and the pore size distribution of the hydrated cements. Porosity and pore size distribution of the mortar prisms were also studied.

For the investigation of the relationship between frost resistance and belite content, mortar prisms were chosen which had either been stored in water for at least 135 days or in air at 95% r. h. for two years before they were exposed to freezing. The prisms were frozen in air but thawed in water. Depending on the equipment used, 2 or 3 cycles of freezing and thawing a day were carried out. The reduction in compressive strength after freezing was considered the criterion of frost resistance. The frost resistance was tested in three separate series of 100, 140 and 200 cycles of freezing and thawing.

3. Results

Hydration products and process of hydration

The calculated phase composition of the cements, taking into consideration not only the main clinker minerals but also the minor components and the gypsum are shown in Table 1. The lime content of cements C 1 and C 2 is very low. They contain no alite, and their belite content is about 70%. At least in cement C 1 part of the aluminate phase exists in the form of $C_{12}A_7$. The phase composition of the cements C 3 and C 4 is typical of Active Belite Cements [5]. Cement C 5 already represents the transition to the Ordinary Portland Cement.

Based on the stoichiometric relationships shown in Figure 2, an approximate calculation of the mineral composition of the cement pastes was made. The results in Fig. 3 show nearly the same contents of monosulphate and cubic hexahydrate for all cement pastes.

Hydration of the silicates and the free lime

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH$$
$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH$$
$$C + H \longrightarrow CH$$

$$m_{H2O} = 0.236C_3S + 0.209C_2S + 0.321C$$
$$m_{CSH} = 0.750C_3S + 0.994C_2S$$
$$m_{CH} = 0.487C_3S + 0.215C_2S + 1.321C$$

Hydration of the aluminate and ferrite phase

$$C_3A + CSH_2 + 10H \longrightarrow C_3A \cdot CS \cdot H_{12}$$
$$C_3A + 6H \longrightarrow C_3AH_6$$
$$C_4AF + 2CH + 10H \longrightarrow 2(C_3A_{0.5}F_{0.5}H_6)$$

$$m_{H2O} = 0.902SO_3 + 0.400C_3A + 0.370C_4AF$$
$$m_{monosul.} = 7.783SO_3$$
$$m_{hexahyd.} = 1.400C_3A - 4.729SO_3 + 1.6754C_4AF$$
$$m_{CH} = -0.305C_4AF$$

Figure 2: Stoichiometry of hydrate formation used for the calculations

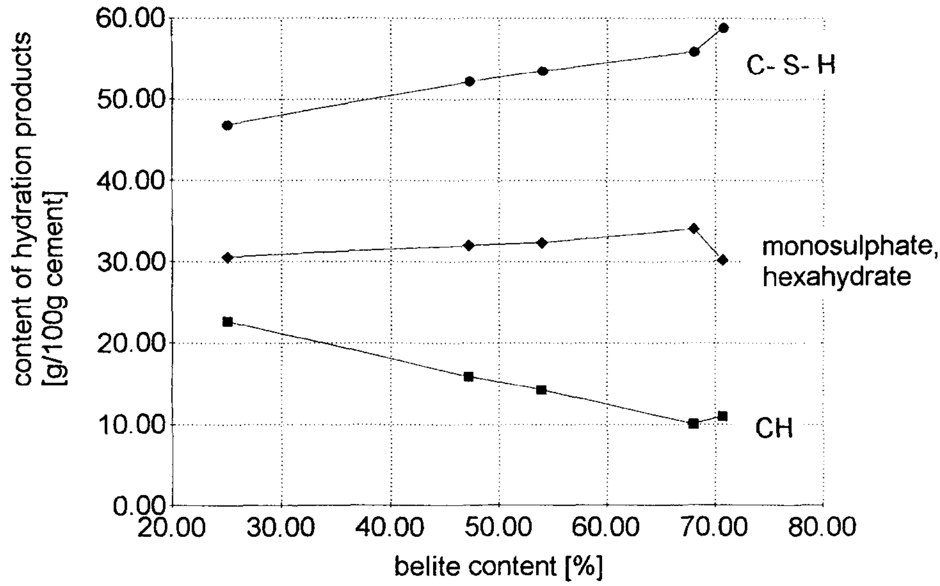


Figure 3: Calculated phase composition of the completely hydrated cements

The content of C- S- H- phases grows slightly when the belite content increases. The greatest differences occur in the portlandite content. In the pure belite cement C 2 only 12% Ca $(OH)_2$ are formed. In the cement C 5, on the other hand, which has nearly the composition of a Portland Cement, a portlandite content of 23% may be expected. The calculated decrease in the $Ca(OH)_2$ content is confirmed by measurements of the portlandite content by the FRANKE method (Fig. 4). The slight difference between the

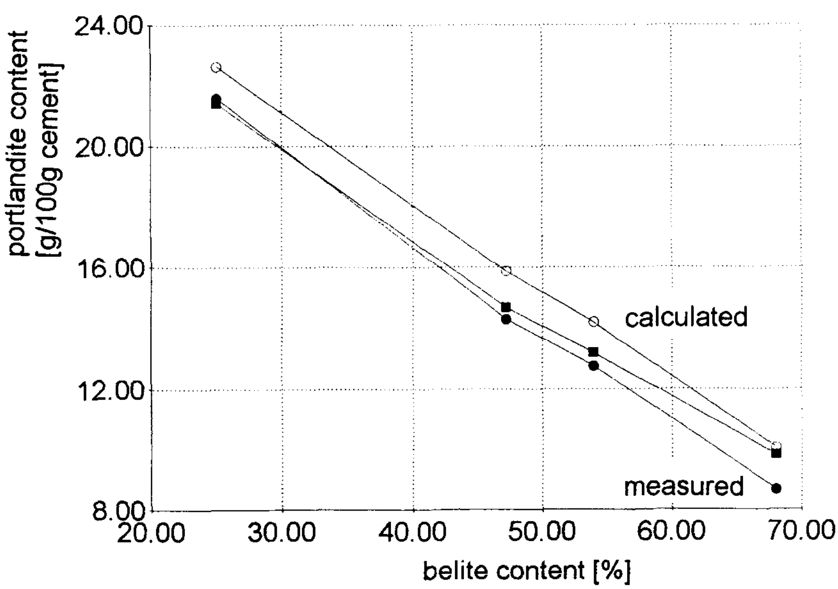


Figure 4: Calculated and measured portlandite content versus belite content

calculated and the measured $Ca(OH)_2$ contents may be due to inaccuracies of calculation, the carbonation during preparation of the samples and the dissolution of $Ca(OH)_2$ during storage in water.

In Fig. 5 the progress in hydration of the cements C 2 and C 5, on the basis of the amount of portlandite formed, and the degree of hydration calculated from it are compared. Differences exist only until the 90th day of hydration. After 135 days no increase in the amount of portlandite may be observed in both the belite cement and the cement with the composition of a Portland Cement. The process of hydration has been completed.

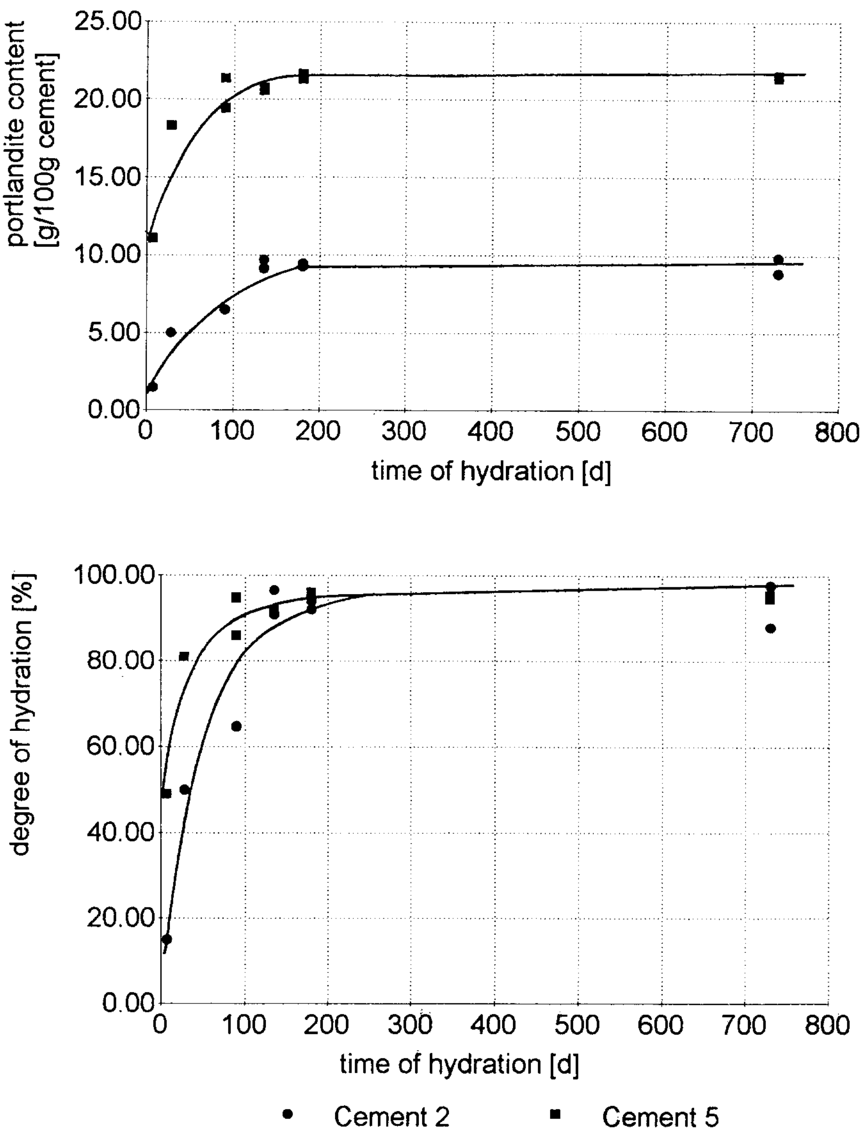


Figure 5: Progress in hydration of the cement C 2 and the cement C 5
5a: Portlandite content versus hydration time
5b: Degree of hydration versus hydration time

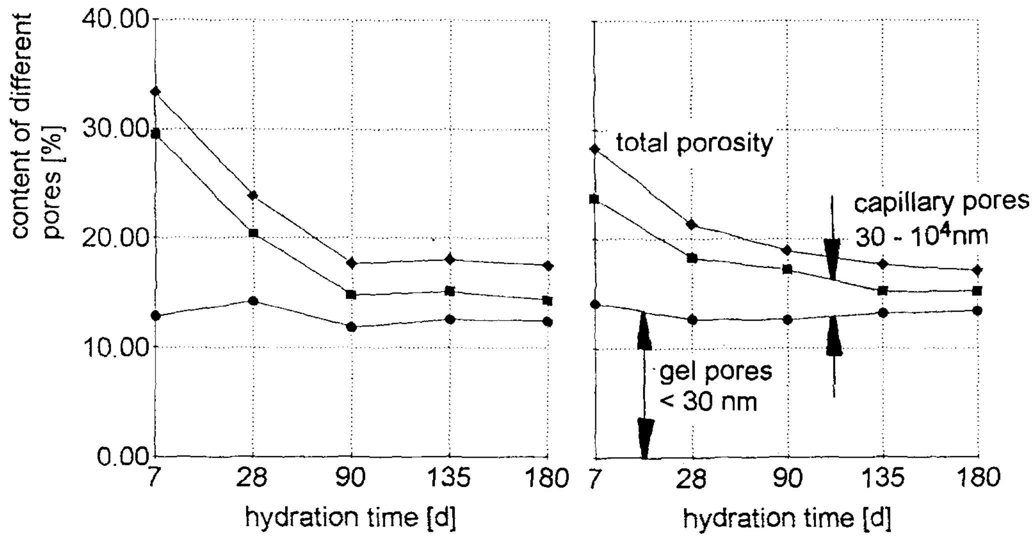


Figure 6: *Total porosity and proportions of different kinds of pores of the cement paste C 2 (left) and the cement paste C 5 (right) versus hydration time*

Porosity

Porosity is an important parameter used for describing the system of hydrated cement and water. Distinctions between the types of pores may be made according to origin and size. Gel pores give information on the progress in hydration. The movements of liquids in the capillary pores have a decisive influence on the durability. If the total porosity and the proportions of gel and capillary pores in the cement paste C 2 are compared with those of C 5 (Fig. 6), clear differences are only to be found at the beginning of the hydration. In the

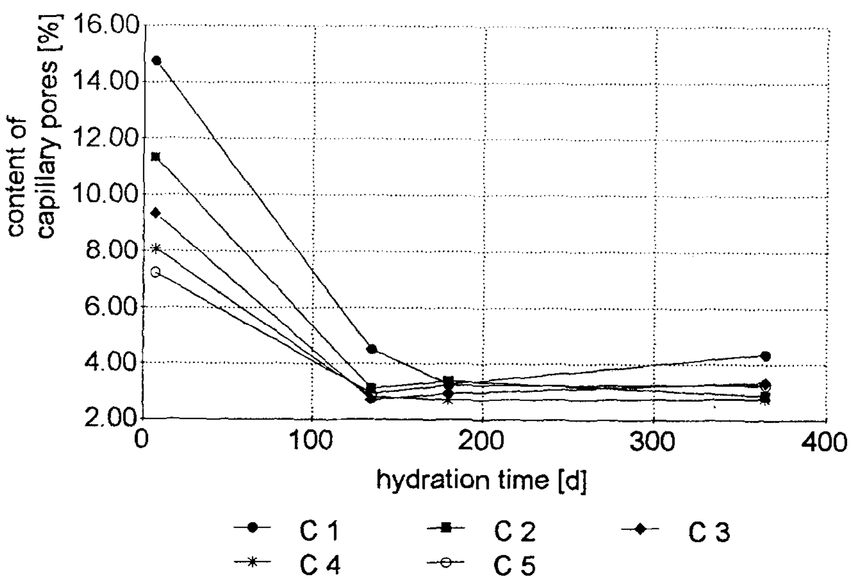
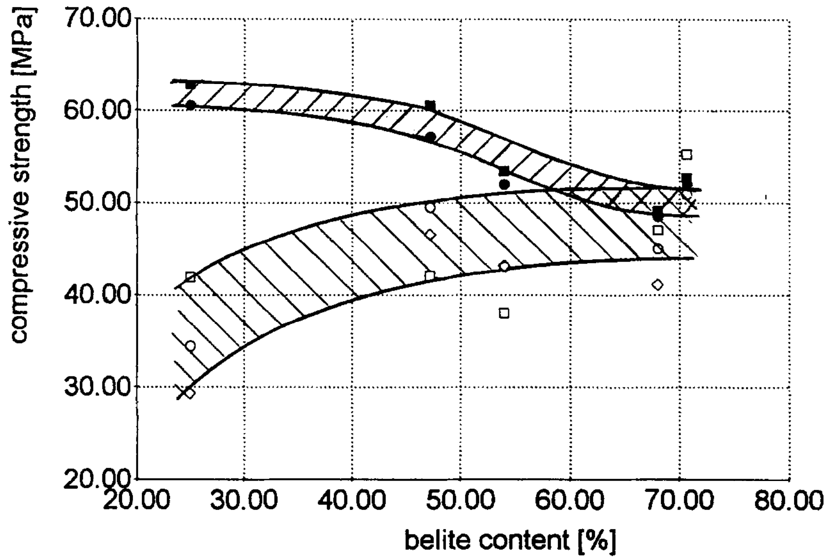


Figure 7: *Content of capillary pores of the mortars C 1 to C 5 at different hydration times*



Filled circles and squares: Strength before freezing
Open squares: Strength after 100 freezing and thawing cycles
Open rhombs: Strength after 140 freezing and thawing cycles
Open circles: Strength after 200 freezing and thawing cycles

Figure 8: Compressive strength before and after different number of freezing and thawing cycles versus belite content

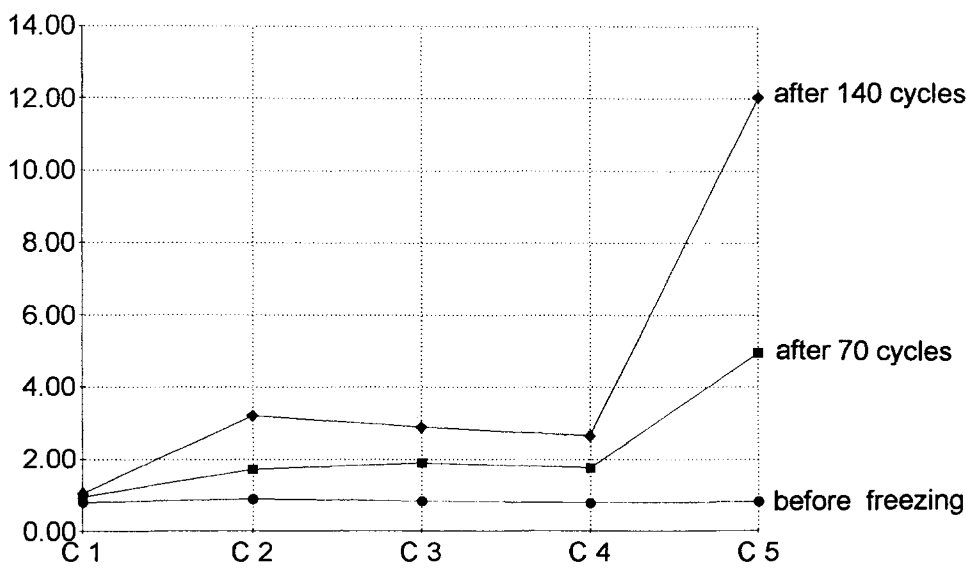
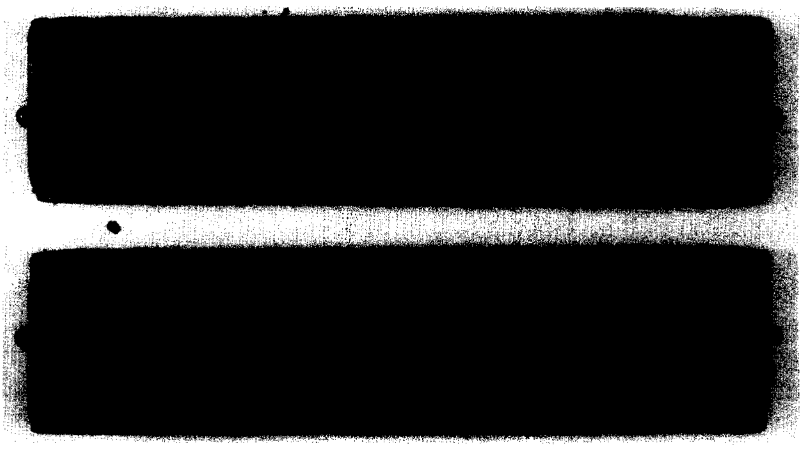


Figure 9: Increase of length of the mortar prisms C 1 and C 5 versus number of freezing and thawing cycles

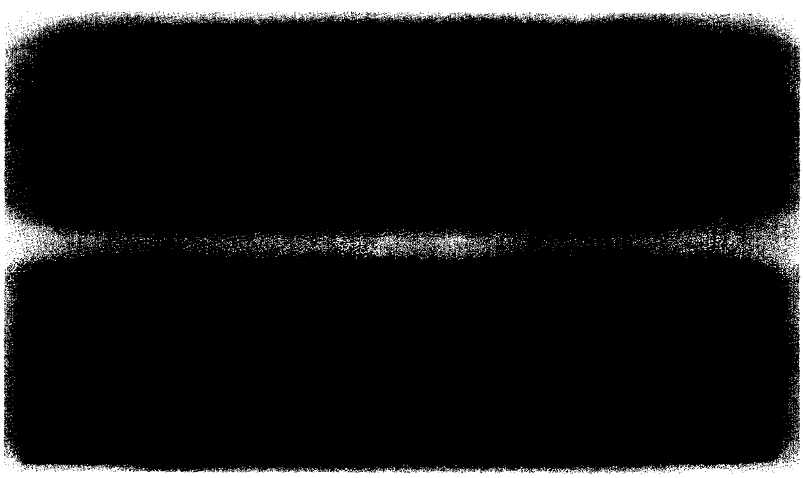
course of hydration the differences in total porosity, gel and capillary porosity will almost disappear. The result is that already after 90 days the mortars made of the cements C 2 to C 5 have nearly the same capillary porosity. Only the mortar made of cement C 1 has a slightly higher capillary porosity, even after a hydration time of one year (Fig. 7).

Frost resistance

For evaluating the frost resistance, the compressive strengths measured in reference prisms prior to freezing are compared to the compressive strength of mortar prisms after freezing (Fig. 8). All three test series led to the same result: If the belite content is



Mortar prism C 1



Mortar prism C 5

Figure 10 and 11: Mortar prisms C 1 and C 5 after 140 freezing and thawing cycles increased, the loss in compressive strength due to the frost attack will be reduced. The cement without alite shows almost no reduction in compressive strength at all.

The frost attack causes a disturbance of the microstructure of the mortar prisms which is indicated by an increase in length of the prisms after freezing compared to the original state prior to freezing. For cement C 5, this increase in length is much greater than for the other cements (Fig. 9) which results from a more serious disturbance of the microstructure.
Correspondingly, the mortar prisms made of cement C 1 seem to be in a much better state after freezing than the prisms made of cement C 5 (Fig. 10 - 11). Cement C 1 is almost undamaged, cement C 5 shows heavy scaling and cracks.

4. Conclusions

As could be shown by calculations and measurements, the composition of the hydrated cement paste which develops from the Active Belite Cements with graded belite contents is similar to that which develops from the cement which is comparable with a Portland Cement. Significant differences are only found in the amount of portlandite formed during hydration which is twice as high in the Portland Cement as in the Belite Cements.

The rate of hydration of the cements rich in belite is - despite of their activation by rapid cooling - slightly lower than that of the alite rich cement. This cement is completely hydrated after 90 days' storage in water whereas the cement which contains only active belite as silicate phase requires 135 days for complete hydration.
With the same degree of hydration and strength the cements rich in belite have a higher frost resistance. This observation cannot be explained by differences in capillary porosity or the pore size distribution of the Belite Cement and of the Portland Cement mortars. All tested mortars are very similar in capillary pores content and the size of these pores. Besides, all mortars have nearly the same water content at the beginning of the freezing and thawing cycles and none contains air voids.
The main reason for the better frost resistance of the Belite Cement mortars could be the lower portlandite content of the hydrated Belite Cements, as found by measurements and calculations. Because of the relativly high solubility of portlandite, the disturbance of microstucture by the dissolution of portlandite during the freezing and thawing cycles should be smaller in the Belite Cement mortars than in the Portland Cement mortar. As a consequence of the disturbance of microstucture, an increase of porosity can be assumed, which results in the decrease of strength and the increase of length. Under frost attack this effect is intensified by the increased solubility of portlandite resulting from the lower temperature.

References

[1] R. L. Blaine, H. T. Arnie, Freezing and Thawing Durability of Concrete. Part 5, U. S. Dep. of Commerce. Nat. Bur. Stand., Washington 1971.
[2] J. Stark, H.- M. Ludwig, Intern. Workshop on the Resistance of Concrete to Scaling due to Freezing in the Presence of Deicing Salt, Vol. I, p. 95 - 107, Quebec Sept. 1993.
[3] C. Fuhr, A. Müller, D. Knöfel, 9th International Congress on the Chemistry of Cement, Vol. V, p. 26 - 31, New Delhi, 1992.
[4] C. Fuhr, A. Müller, D. Knöfel, Bauzentralblatt, 33, p. 21 - 23, (1993).
[5] J. Stark et. al., Il Cemento, 84, p. 239 - 250, (1987).