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CORRELATION BETWEEN PORE STRUCTURE AND LOW-TEMPERATURE DILATATION OF HYDRATED CEMENT PASTES AND MORTARS

II. Effects of the water-cement ratio and the compacting conditions

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The pore structure and low-temperature dilatation behavior of traditional hydrated Portland cement paste compacted by different methods were investigated. The aim of the investigation was to demonstrate the influence of the water-cement ratio and the compacting conditions on the developing pore structure and the frost dilatation during the early stage of the hydration process. A low water-cement ratio and a high compacting pressure resulted in initially low porosity, but in coarser pore sizes. Vibration resulted in lower pore volumes as compared with those of cast cement pastes, but the pore size distributions were similar. In accordance with the pore size distribution, two frost dilatation effects were measured when macro- and mesopores also occurred in the hydrated cement pastes. In the samples compacted by high pressure, a single frost dilatation effect occurred in connection with the macropores present in the sample. The magnitude of the frost dilatation effect decreased with increasing curing time. The decrease is caused by a decrease in the volume of the pores and also by an increase in matrix strength.

Introduction

Some properties of hydrated cement pastes and mortars of different ages in the early stage of hydration were investigated to obtain information about the correlation of these properties and frost resistance.

The pore size distribution and the low-temperature dilatation in the saturated condition were the two properties compared, as porosity is one of the major factors controlling the mechanical properties and the resistance to frost action of cement pastes or mortars, while low-temperature

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dilatometry is an appropriate method for recording the change in size during frost attack.

In the first part of this paper, the influence of the cement type on the pore structure and low-temperature dilatation behavior of hydrated cement pastes was discussed. In the present paper, the effects of the water-cement ratio and the compacting conditions will be discussed.

Experimental

The experiments were carried out on traditional Portland cement pastes. The properties of the cement were reported earlier [1]. Cylindrical specimens were cast and compacted by vibrating and pressing of cement pastes mixed with water-cement ratios of 0.3 and 0.1, respectively (Table 1).

Table 1 Composition and compacting condition of Portland cement pastes

Sample No.	Water-to-cement ratio	Compacting condition
1.	0.1	pressing by 200 MPa
2.	0.1	pressing by 100 MPa
3.	0.3	vibrating
*4.	0.31	casting

*Its results published in the 1st part under the name of 'Portland Cement'

After demolding at the age of 1 day, 5×5×50 mm prism-shaped samples were cut for dilatation measurements. They were cured at room temperature in a water-saturated atmosphere until the measurements. The experiments were carried out at paste ages of 1, 2, 3, 7, 28 and 90 days. Prior to the experiments, the samples were vacuum-saturated and covered by a flexible film to avoid water loss during the measurement.

For porosity measurements, the samples were dried in vacuum at room temperature.

Porosity measurements were carried out with a MICROMERITICS 915 mercury penetration porosimeter, while low-temperature dilatation curves were measured on a NETZSCH ET 402 dilatometer, according to the method described earlier [1].

Results and discussion

Pore structure of hydrated cement pastes

Cumulative porosity curves of the hydrated cement pastes at different stages of hydration are presented in Figs 1–2.

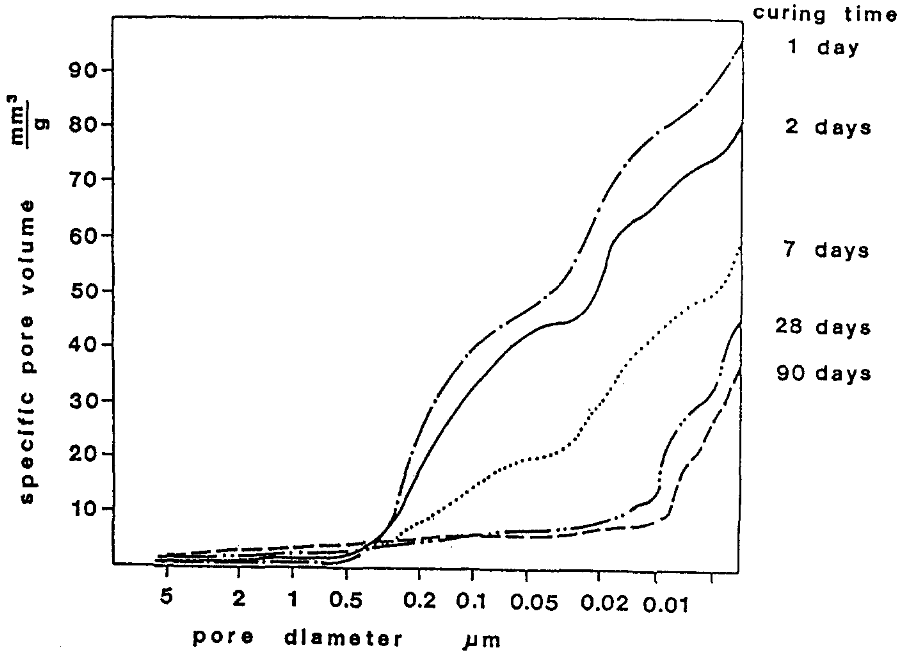

Fig. 1 Cumulative porosity curves of hydrated Portland cement pastes compacted by pressing with 200 MPa

The median pore size and specific pore volume of the characteristic pore size ranges are given in Table 2 to demonstrate the pore size and pore volume changes during hydration.

The range of the micropores is shown separately, because the range of mercury porosimetry covers only a part of the range of the micropores, and therefore the specific pore volume measured does not involve the volume of all micropores.

The pore size distributions of hydrated cement pastes compacted by vibration can be discussed on the basis of Parcevaux's pore size ranges [2]. All the proposed pore types (e.g. surface, macro-, meso- and micropores) can be distinguished in the curves (Fig. 1). In the course of the hydration process, the specific pore volume decreased with increasing curing time,

Table 2 Porosity data of hydrated Portland cement pastes

Sample	Curing time, day	Specific pore volume in the 0.005–177 μm pore diameter range, $cm^3 \cdot g^{-1}$	Specific pore volume in the micropores in the 0.005–0.0036 μm pore diameter range, $cm^3 \cdot g^{-1}$	Median pore diameters of the characteristic pore ranges, μm			Specific pore volume of the characteristic pore ranges, $cm^3 \cdot g^{-1}$		
				surface pores	macro-pores	meso-pores	surface pores	macro-pores	meso-pores
1.	1	0.0426	0.0131		0.440			0.0426	
	2	0.0375	–		0.300			0.0375	
	7	0.0250	0.0170		0.180			0.0250	
	28	0.0112	0.0160		0.100			0.0112	
	90	0.0110	0.0093			0.006			0.0110
2.	1	0.0620	0.0170		1.75			0.0620	
	2	0.0600	0.0155		0.710			0.0600	
	7	0.0510	0.0210		0.470			0.0510	
	28	0.0245	0.0350		0.0170			0.0245	
	90	0.0150	0.0102			0.008			0.0150
3.	1	0.0858	0.011		0.200	0.020		0.0450	0.036
	2	0.0633	0.017		0.150	0.020		0.0400	0.017
	7	0.0520	0.008		0.150	0.015		0.0170	0.026
	28	0.0315	0.014		0.065	0.009		0.0100	0.020
	90	0.0300	–		0.059	0.008		0.0050	0.014
4.	1	0.1040	0.0031	8.0	0.12			0.1040	
	2	0.0940	0.0041		0.170	0.015	0.010	0.049	0.033
	3	0.0900	0.0021		0.170	0.012		0.054	0.031
	7	0.0720	0.0068		0.170	0.013		0.038	0.028
	28	0.0616	0.0056		0.130	0.013		0.024	0.031
	90	0.0390	0.0052			0.013			0.030

mainly due to the decrease in the number of macropores, but there were slight decreases in the number and median pore size as well. The changes in pore structure were similar to those for cast cement paste [1].

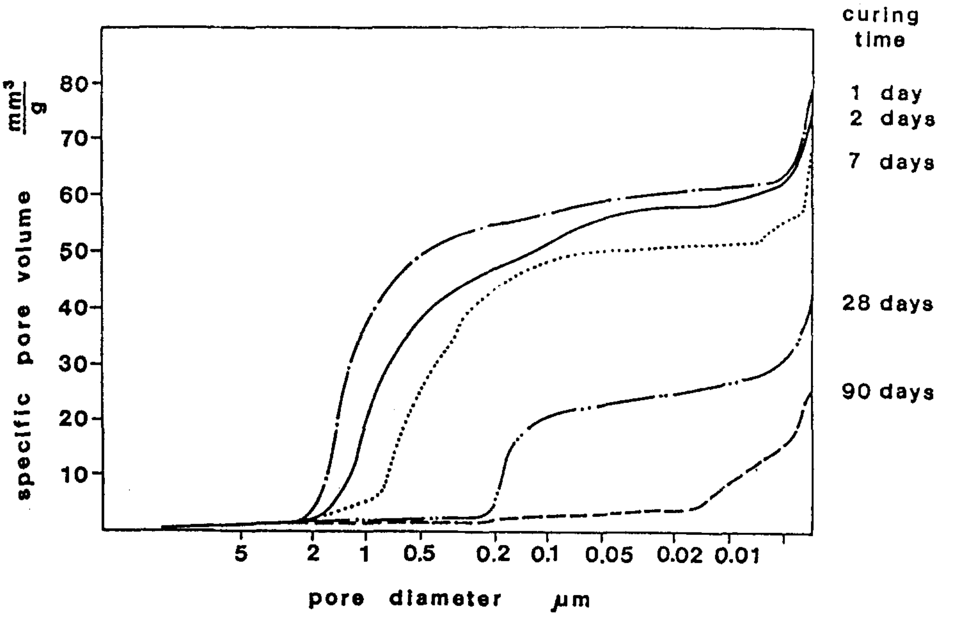

Fig. 2 Cumulative porosity curves of hydrated Portland cement pastes compacted by vibration

Less characteristic pore size ranges were found in the pastes compacted by high-pressure pressing (Fig. 2). No appreciable pore volume was measured in the mesopore range at any stage of hydration. Due to the low water-cement ratio and the high compacting pressure, the total pore volumes are extremely low even in the very early stage of hydration. For the same reason, however, the hydration process is limited, and thus the hydrates may not perfectly fill the space surrounded by cement grains.

Low-temperature dilatation of water-saturated hydrated cement pastes

The low-temperature dilatation curves of the samples at different stages of hydration are shown in Figs 3–4.

Two distinct expansion effects can be seen in the cooling curves of specimens in which both macro- and mesopores have considerable volumes, when a comparison is made of the pore size distribution and the low-temperature dilatation behavior of the samples. At higher temperatures (about –17°C), freezing of the water saturating the macropores occurs, while freezing of the water saturating the mesopores takes place at about –40°C.

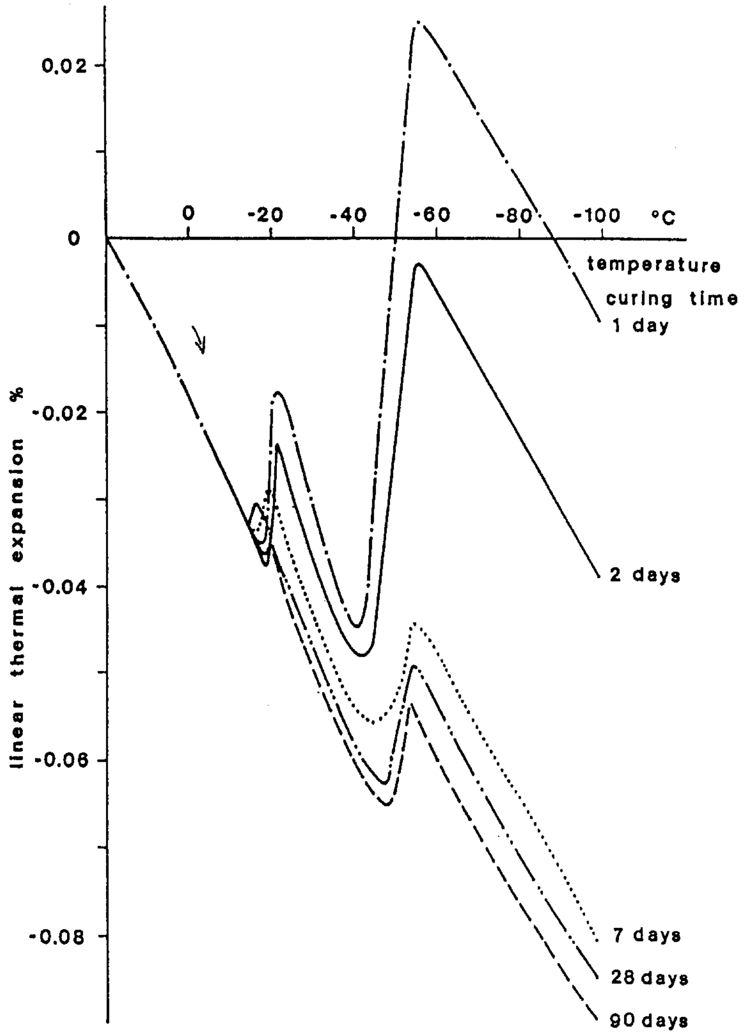

Fig. 3 Low temperature dilatation curves of hydrated Portland cement pastes compacted by pressing with 200 MPa

In the case of pastes compacted by pressing, in accordance with the pore size distribution, only one expansion effects occurred, which shows the freezing of the water saturating the macropores. Even at the age of 90 days, when the virtual median diameter of the pores is in the range of mesopores, the frost dilatation effect remains at –15°C.

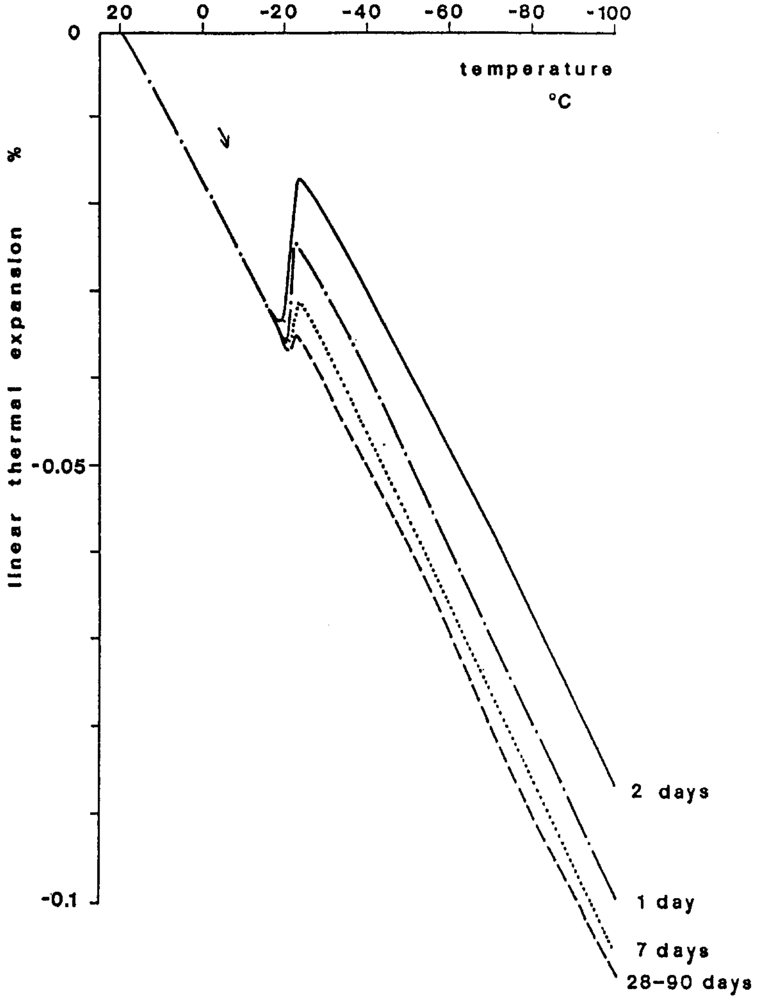

Fig. 4 Low temperature dilatation curves of hydrated Portland cement pastes compacted by vibration

The temperatures of the expansion effects measured are in agreement with the DTA results of Dorner and Setzer [3], but the values are lower than the real freezing points, because the temperature is measured in the surroundings of and not inside the sample.

The 'frost dilatation', a measure of the expansion effect, is the distance between the minimum and the maximum in the dilatation curve. The frost dilatation results are detailed in Table 3.

Table 3 Frost dilatation effects of hydrated Portland cement pastes

<table>
<tr><th>Sample</th><th>Curing time,</th><th colspan="2">Frost dilatation effect,</th></tr>
<tr><th></th><th></th><th>at –15°C</th><th>at –40°C</th></tr>
<tr><th>No.</th><th>day</th><th>%</th><th>%</th></tr>
<tr><td>1.</td><td>1</td><td>0.007</td><td></td></tr>
<tr><td></td><td>2</td><td>0.025</td><td></td></tr>
<tr><td></td><td>7</td><td>0.009</td><td></td></tr>
<tr><td></td><td>28</td><td>0.004</td><td></td></tr>
<tr><td></td><td>90</td><td>0.002</td><td></td></tr>
<tr><td>2.</td><td>1</td><td>0.032</td><td></td></tr>
<tr><td></td><td>2</td><td>0.050</td><td></td></tr>
<tr><td></td><td>7</td><td>0.020</td><td></td></tr>
<tr><td></td><td>28</td><td>0.006</td><td></td></tr>
<tr><td></td><td>90</td><td>0.002</td><td></td></tr>
<tr><td>3.</td><td>1</td><td>0.018</td><td>0.083</td></tr>
<tr><td></td><td>2</td><td>0.022</td><td>0.040</td></tr>
<tr><td></td><td>7</td><td>0.008</td><td>0.008</td></tr>
<tr><td></td><td>28</td><td>0.003</td><td>0.010</td></tr>
<tr><td></td><td>90</td><td>0.004</td><td>0.013</td></tr>
<tr><td>4.</td><td>1</td><td colspan="2">0.1786</td></tr>
<tr><td></td><td>2</td><td>0.0456</td><td>0.0553</td></tr>
<tr><td></td><td>3</td><td>0.0407</td><td>0.0386</td></tr>
<tr><td></td><td>7</td><td>0.0473</td><td>0.0416</td></tr>
<tr><td></td><td>28</td><td>0.0037</td><td>0.0</td></tr>
<tr><td></td><td>90</td><td>0.0035</td><td>0.0110</td></tr>
</table>

From a comparison of the specific pore volume and frost dilatation values, it can be concluded that there is not a linear relationship between the two sets of data. The measure of expansion is influenced by the pore volume, i.e. by the volume of saturating water, and by the strength of the matrix material enclosing the pores. It must be emphasized that the extent of the expansion is one magnitude less than the theoretical value derived from the 9.02 % volume expansion of the freezing water saturating the pore types in question.

The effect of the strength of the solid matrix can be observed in the case of samples cured for 2 days. Although the pore volume is less than at the age of one day, the frost dilatation effect is higher, indicating a decrease in strength.

Conclusion

Hydrated cement pastes compacted only by casting or by vibrating have polydisperse pore structures. The porosity can be divided into four pore size ranges. The pore structures of pastes mixed with low water-cement ratios and compacted by high pressure can be characterized by only three pore size ranges.

The water which saturates the mesopores does not freeze under natural conditions, and thus a polydisperse pore size distribution is preferable, as regards the frost resistance at an early age, to the pore structure of samples compacted by high pressure.

In the course of the hydration, the size and the volume of the macropores decreases, and thus the risk of frost action likewise decreases.

References

1 Zs. E. Wagner, J. Thermal. Anal., 37 (1991) 1053.
2 P. Parcevaux, Cement Concr. Res., 14 (1984) 419.
3 H. W. Dorner and M. Setzer, Cement Concr. Res., 10 (1980) 403.

Zusammenfassung — Es wurde die Porenstruktur und das Tieftemperaturdilatationsverhalten von herkömmlichem, hydratiertem, durch verschiedene Methoden verdichtetem Portland-Zementleim untersucht. Das Ziel der Untersuchung bestand im Nachweis des Einflusses des Wasser-Zement-Verhältnisses und der Verdichtungsbedingungen auf die entstehende Porenstruktur und die Frostdilatation in der frühen Periode des Hydratationsprozesses. Ein niedriges Wasser-Zement-Verhältnis und ein hoher Verdichtungsdruck liefert eine geringe Porösität, aber größere Porenmaße. Vibration liefert im Vergleich zu gegossenem Zementleim ein geringeres Porenvolumen, aber die Beiträge zur Porengröße waren ähnlich. In Übereinstimmung mit dem Porengrößeeinfluß wurden zwei Frostdilatationseffekte gemessen, wenn sowohl Makro- als auch Mesoporen in den hydratierten Zementleimen vorkamen. In denjenigen Proben, die unter Hochdruck verdichtet wurden, tritt in Verbindung mit der Gegenwart von Makroporen in der Probe ein einfacher Frostdilatationseffekt auf. Die Höhe des Frostdilatationseffektes sinkt mit steigender Aushärtungszeit. Dieses Sinken wird durch eine Abnahme des Volumens der Poren verursacht und ebenfalls durch ein Ansteigen der Matrixfestigkeit.