STUDIES OF CAPILLARY POROSITY OF CLINKER PHASES DURING HYDRATION

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Abstract

The capillary porosity of clinker phases, i.e. 3CaOSiO₂, β2CaOSiO₂, 3CaOAl₂O₃ and 4CaOAl₂O₃Fe₂O₃, at the early stages of hydration has been studied by the methods of Differential Scanning Calorimetry and nitrogen adsorption (BET).

It was established that pores of 3–70 nm were formed during the hydration of 3CaOSiO₂ and the maximum of their distribution was found at about 10 nm. The hydration of 2CaOSiO₂ is much slower and the porosity is one order of magnitude lower. During the hydration of 3CaOAl₂O₃ the content of crystalline hexagonal hydrates prevailed and the porosity was in the range 5–90 nm with the average pore diameter of about 16 nm. This average pore diameter was much smaller for thermoporosimetry and lay at about 7 nm. The hydrated 4CaOAl₂O₃Fe₂O₃ sample had the porosity in the range 3–90 nm with the maximum of the pores distribution at about 4 nm. There are some differences between the porosities measured by BET and thermoporosimetry. Principally thermoporosimetry gives no information about larger capillary pores in the range 30–50 nm.

Keywords: BET, clinker phases, C–S–H gel, porosity, surface area, thermoporosimetry

Introduction

A microstructure formation of the paste during hardening is the function of chemical reactions occurring between water and cement phases.

During this process the products of chemical reactions fill the volume previously occupied by water. These products are amorphous such as C–S–H gel and crystalline, such as calcium hydroxide, calcium aluminates and calcium sulpho-aluminates hydrates. The final microstructure of cement paste covers hydration products, unreacted cement relics and pores, partially or fully filled with water.

Physico-chemical properties of cement paste are to a considerable degree dependent on its porosity, namely on the content of capillary pores between 2 and 100 nm [1]. These capillary pores determine durability, permeability and frost resistance of concrete [2].

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There are several methods of determination of total porosity and pore-size distribution; the intrusion mercury porosimetry is the most frequently used [3]. The paper presents the results of porosity measurements of pure clinker phases during hydration.

**Experimental**

Two methods were used for porosity measurements of the samples: thermodesorptions with DSC apparatus and BET. Thermodesorptions is based on the utilization of Kelvin's equation and entropy of phase transformation [4, 5]; the effect of the superficial phase transformations on the entropy changes was included by Brm [6].

The BJH [7] method was used in case of BET for capillary calculation. This method is based on Cohen's [8] model.

In case of thermodesorptions the measurements were made in the interval +20–60°C at the cooling/heating rate of 0.5°C min⁻¹, the samples were in hermetic aluminium containers.

Before the BET measurements the samples were flushed with helium under pressure of about 10⁻¹ Pa. The measurements were performed with nitrogen, using the automatic ASAP 2000. For the investigation four samples of synthetic clinker phases were used: Ca₃[SiO₄]O, βCa₂[SiO₄], Ca₃[Al₂O₆] and Ca₄[Al₂Fe₂O₁₀]. The chemical composition of these phases is presented in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loss of ign.</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>free CaO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>0.15</td>
<td>26.14</td>
<td>73.17</td>
<td>0.72</td>
<td>0.1</td>
<td>0.7</td>
<td>100.28</td>
</tr>
<tr>
<td>C₃S</td>
<td>0.2</td>
<td>34.3</td>
<td>64.8</td>
<td>trace</td>
<td>trace</td>
<td>no</td>
<td>99.3</td>
</tr>
<tr>
<td>C₃A</td>
<td>0.33</td>
<td>0.42</td>
<td>61.73</td>
<td>37.61</td>
<td>0.08</td>
<td>trace</td>
<td>100.17</td>
</tr>
<tr>
<td>C₃AF</td>
<td>0.13</td>
<td>1</td>
<td>45.5</td>
<td>20.77</td>
<td>32.9</td>
<td>0.4</td>
<td>100.3</td>
</tr>
</tbody>
</table>

The pastes were prepared from these phases with w/c ratio equal 0.5 in case of silicates and w/c=1 for tricalcium aluminate and brownmillerite. The pastes were stored in the air of 100%RH and temperature 20±1°C for one and three days. The phase composition of hydrated samples were examined by X-ray diffraction and SEM.

**Results**

C₃S underwent rapid hydration and the samples were composed of well developed fibres of C–S–H and plates of Ca(OH)₂ (Fig. 1).

βCa₃S reacted very slowly with water and the SEM picture presented the unhydrated grains of belite and a small quantity of amorphous C–S–H gel. Tricalcium