GRAVIMETRIC, VOLUMETRIC AND CALORIMETRIC STUDIES OF THE SURFACE STRUCTURE OF PORTLAND CEMENT

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Abstract

Dry cement powder and hardened cement paste were characterised by means of laser granulometry and volumetric measurement of the nitrogen adsorption isotherm at 77 K. Water sorption isotherms at ambient temperature were measured stepwise by means of a gravimetric apparatus. The isotherms show a very large hysteresis loop, reaching down to zero relative pressure, which reflects swelling of the cement gel. Thermoporometric measurements reveal that swelling of that gel consists in water take up within the continuously growing structure; no stable pore structure could be observed.

Keywords: calorimetry, cement, gravimetry, sorption, surface, thermoporometry, volumetry, water adsorption

Introduction

Cement consists mainly of CaO, SiO_2 and Al_2O_3. A variety of standardised types is on the market. Its composition, however, varies with origin, because the powder is burned of natural calcareous clay or of the individual natural components by addition of natural and artificial aggregates. By addition of water cement paste is formed which dries in air to give a crumbly material: cement glue or CSH-gel (CaO, SiO_2, H_2O). CSH-gel hardens with time and results in cement stone. The original powder of typical commercial cements (Dyckerhoff, Mainz-Amöneburg) and its CSH-gels are objects of our study.

Cement characterisation

Besides results of imaging microscopic methods, density, particle size distribution, specific surface area, pore volume and pore size distribution are useful parameters and functions to characterise the micro- and nanostructure of cement [1]. The particle size distribution was determined with a laser granulometer [2]. From this the outer specific surface area can be derived by using a spherical model for the particles. The

area obtained from the resistance *vs.* gas flow (Blaine test [3]) yields a similar value for the outer surface area and therefore we can abstain from that measurement. The nitrogen adsorption isotherm at 77 K can be measured by means of a vacuum microbalance or volumetrically. We used the more common volumetric method. From the isotherm pore volume, pore size distribution and the specific surface area (which includes the inner pore surface) was derived.

Table 1 Instrumentation

Instrument/ method	Manufacturer	Type	Results
Laser granulometer	Sympatec	HELOS VECTRA	particle size distribution specific surface area
Volumetric adsorption	CE Instruments	SORPTOMATIC 1990	nitrogen adsorption isotherm at 77 K, specific surface area [6], pore size distribution [7]
Mercury porosimetry	CE Instruments	PASCAL 140/440	pore size distribution [8] specific surface area
Differential scanning calorimeter	Mettler-Toledo	DSC 821	thermoporometry [9, 10] pore size distribution
gravimetric apparatus with Cahn balance	surface measurement Systems	DVS1	water adsorption isotherm at 298 K, specific surface area pore size distribution sorption kinetics

The results of surface area and pore structure analysis in comparison to previous measurements [4] are summarised in Table 2. The nitrogen isotherms of all samples correspond to type II of the IUPAC classification [5] (Fig. 1).
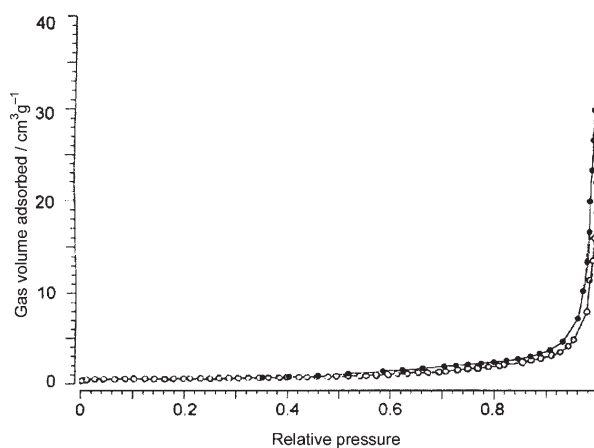

Fig. 1 Nitrogen sorption isotherm at 77 K on hydrated Iron Portland cement normal

Table 2 Volume median diameter, specific surface area and volume adsorbed

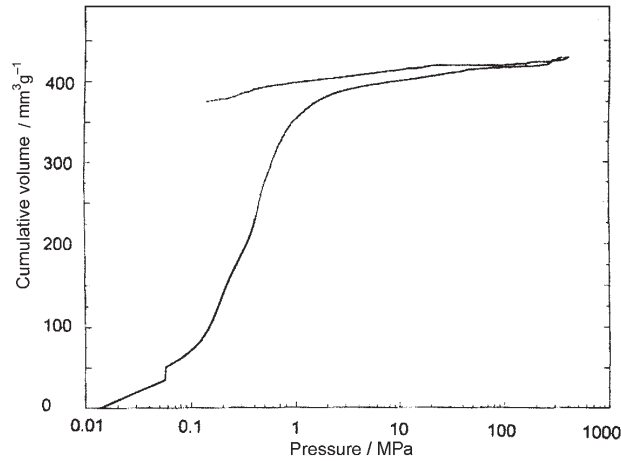| Sample	Treatment	Median/ µm	S_{grain}/	S_{BET2}/	S_{BET3e}/	V_G/	V_{Hg}/	V_{H_2O}/
				$\mathrm{m^2\,g^{-1}}$			$\mathrm{mm^3\,g^{-1}}$	
White		13.6	0.47	1.42	0.36	8.88		
	hydrated	11.4		3.55		26.33	481	>70
Portland double		7.9	0.48	1.07	0.36	6.81		
	hydrated	15.8		1.09		8.54		
Portland triple		12.1	0.67	1.54	0.53	12.81		
	hydrated			3.80		27.85		
				2.36	2.33	19.33		
Iron Portland normal			0.39	0.37	0.30	2.90		
	hydrated			2.76		21.97	431	>100
				1.81	2.17	21.01		
Aquadur			0.45	1.22	0.36	7.27		
	hydrated			2.20		13.11		

Fig. 2 Mercury intrusion with HG-porosimetry on hydrated Iron Portland cement normal

The long and small hysteresis loop can hardly be attributed to a mesoporous structure within the particles but to interparticulate voids. The maximum adsorbed amount of nitrogen at relative pressure $p/p_0 = 0.99$ indicates the total specific volume V_G (Gurwitsch volume) of that pore system. S_{grain} denotes the surface area calculated from laser granulometry. S_{BET2} and S_{BET3} were calculated from the nitrogen isotherm at 77 K using the two-parameter equation of Brunauer, Emmett and Teller and the three-parameter equation, respectively. On account of roughness and irregular shape of the particles S_{BET} is always larger than S_{grain} calculated from the particle size distri-
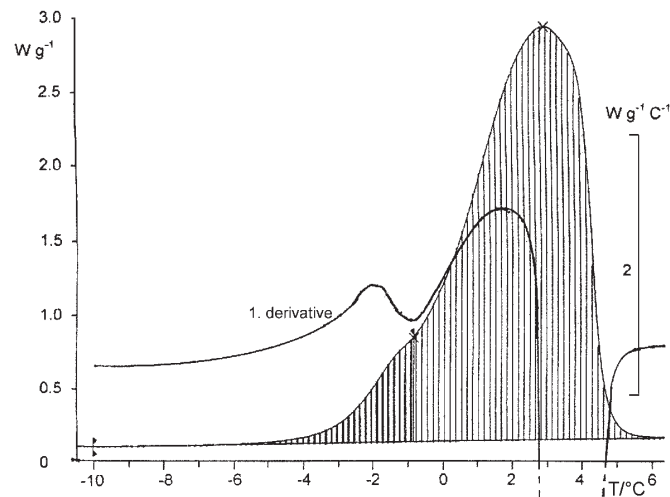

Fig. 3 Thermoporometric curve on hydrated Iron Portland cement normal

bution. After hydration of the cement, the specific surface area and the pore volume increased. Mercury porosimetry exhibits a broad pore spectrum with maximum at about 2 μm (Fig. 2). Peculiarities in the curves need more detailed investigations.

Thermoporometry and water adsorption

Thermoporometric measurements using the hydrated samples show a peak of two samples only near the upper detection limit at –1°C, corresponding to a pore width >100 nm. Since the most part of this peak is covered by the broadened bulk water peak, its evaluation does not seem to be useful (Fig. 3). It can be concluded that, within the mesopore range by swelling of the gel, the space available for water is continuously extended without development of a stable pore system.
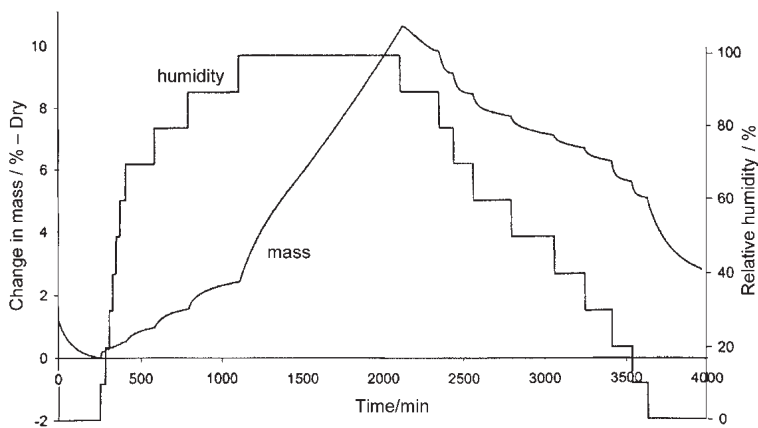

Fig. 4 Stepwise measurement of water adsorption and desorption at 25°C on hydrated Iron Portland cement normal
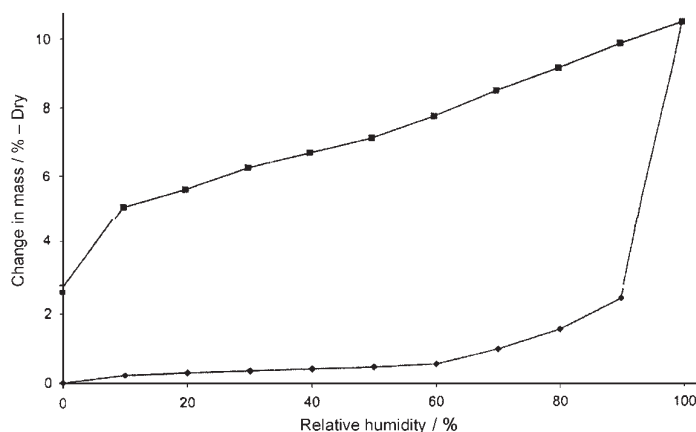

Fig. 5 Water sorption isotherm at 25°C on hydrated Iron Portland cement normal

The water vapour adsorption slowly proceeds so that equilibrium could not be established in reasonable time (Fig. 4). In a subsequent work we will treat our curves by an extrapolation method [11]. The isotherms exhibit a very large hysteresis loop, reaching down to zero relative pressure (Fig. 5). The long time needed for water exchange is in accordance with practical experience and allows the investigation of water and other constituents required as well as of the time needed for the process of setting.

Conclusions

1. The most important graphs and parameters characterising the surface structure of cement and hardened cement paste are density, particle size distribution and specific surface area. Because the outer surface of the particles can be derived from the particle size distribution, we consider the Blaine test to be unnecessary. Scattering results suggest a representative sampling by use of a sample divider.

2. Thermoporometry revealed that swelling of CSH-gel is a continuous process, during which no stable pore structure is established. Regarding published work, thermoporometry may be useful to characterise cement stone after an extended hardening process [12–14].

3. Water sorption isotherms are important means to clear processes occurring in the hardening process of cement [15]. Since the measurements are time consuming and equilibrium values are uncertain, extrapolation methods and the analysis of the kinetic curves would be useful.

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