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Reliable specific surface area measurements on anhydrous cements

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ABSTRACT

The specific surface area (SSA) of anhydrous cement has a direct impact on its reactivity and on the properties of fresh and hardened concrete. However, measuring this physical parameter is non-trivial.
The choice of the degassing conditions (temperature, pressure and time) is essential for reliable SSA measurements by nitrogen adsorption because of the dehydration of the gypsum it contains. Such dehydration involves a significant increase of the SSA_{BET}, whereas Blaine test is poorly sensitive to the hydration state and structural modification of the calcium sulfate carrier. Because of this, SSA_{BET} values may be more variable than Blaine fineness. More consistent SSA_{BET} results could be obtained by degassing anhydrous cement samples at 40 °C under N_2 flow for 16 h, as at these conditions the cement composition is preserved.

1. Introduction

The specific surface area (SSA) of cement is broadly recognized to impact its reactivity as well as physical and mechanical properties of fresh and hardened concrete, such as rheology [1], hydration kinetics [2,3] and strength development [4]. Because of this, SSA is commonly included as quality control measurement in cement production, in addition to the particle size distribution [5,6] and the phase composition [7]. The SSA also fundamentally affects the interaction between cement and superplasticizers. However, the quantification of such effects is non-trivial because SSA measurements on fresh [1] and hydrated cement paste are delicate [8–10] due to the possible dehydration of hydrated phases. The fact that such problems are also highly relevant for anhydrous cement is barely documented.

There are three major methods to measure the specific surface area of anhydrous cement, Blaine air permeability, laser diffraction (calculating SSA from the particle size distribution) and gas adsorption. The cement industry largely relies on Blaine measurements, often arguing that results are more consistent than nitrogen adsorption measurements, which additionally are more time consuming. In contrast, academics tend to prefer nitrogen adsorption measurements because of their more fundamental basis and mostly look down onto Blaine measurements because of their semi-empirical nature.

The Blaine test [11] is based on measuring the resistance encountered by air passing through a well-packed but still porous powder bed under a given air pressure gradient. In its most common use, both the pressure gradient and the flow rate of air vary during the test. This greatly simplifies the measurement, but prevents the use of basic equations (Kozeny–Carman equation) for the flow of air through a bed of packed particles [12–14]. The main contribution of R.L. Blaine was to propose semi-empirical equations to overcome this problem [11], involving a calibration procedure now defined in ASTM C204-11 [15]. Nevertheless, this semi-empirical procedure can compromise the reliability of results and their comparison between laboratories.

Laser diffraction (LD) is the most common technique to determine the particle size distribution of powders, from which the SSA can be calculated assuming a specific shape (most often spherical). Because of the irregular shape of cement particles [16–18], their real size will be smaller than the one determined by LD and consequently, the SSA will be underestimated [19]. In addition, it is necessary to know the refractive index of the measured powder in the dispersive media. In the case of Portland cement, this value has been measured but it needs to be determined for cements containing supplementary cementitious materials [20].

The nitrogen adsorption method is based on quantifying the volume of nitrogen molecules needed to cover the sample surface. The SSA is calculated using the BET (Brunauer–Emmett–Teller) model [21]. In contrast with the two methods described above, nitrogen adsorption does not postulate the particle shape or include semi-empirical equations, which is why it is considered more reliable.

In contrast to Blaine and LD tests, samples measured by nitrogen adsorption must be degassed before the measurement. This is required to remove physisorbed molecules so that the adsorptive gas may interact directly with the sample along its small cavities. Degassing is normally performed by heating the samples, by purging them with an inert gas (N_2) or by applying a vacuum. While extremely important, degassing conditions are not always reported in the literature, in particular for anhydrous cements.

Although relatively high degassing temperatures do not affect the clinker phases of anhydrous cement, it is known that gypsum

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($CaSO_4 \cdot 2H_2O$) is thermodynamically stable at temperatures lower than 42 °C and at relative humidity higher than 50% [22,23]. At higher temperature or lower relative humidity it partially or totally dehydrates [24] to hemihydrate or anhydrite, which has a direct effect on its SSA [25,26]. Therefore, the degassing conditions should be carefully chosen to prevent gypsum dehydration from compromising SSA measurements of cement.

In the present work, we detail the impact of gypsum dehydration on SSA measurement performed either by nitrogen adsorption or by Blaine air permeability. It is shown that normal degassing conditions are inadequate for cement, which explains why industry experiences a higher variability of BET versus Blaine measurements. Finally, we propose a degassing procedure that leads to reliable SSA of measurements of anhydrous cements by nitrogen adsorption.

2. Materials and methods

2.1. Materials

A commercial cement CEM I 52.5 R and a clinker supplied by Holcim (Switzerland) were used in the present work. The clinker was milled in the Vibratory Disk Mill (Retsch) for 45 s at 700 rpm and, afterwards, in the planetary mill (Pulverisette 5) for 4 min at 400 rpm to reach a similar particle size distribution to the commercial cement. The ground clinker was homogenized in Turbula for 2 h. The gypsum (Acros Organics, 98%, extra pure) was sieved under 20 μm in order to reach a similar PSD as the clinker. A model cement was produced by mixing the clinker and 5% of sieved gypsum (by mass of clinker) in a Turbula for 16 h. In commercial cements, where clinker and gypsum are ground together, PSD of gypsum could be smaller than that of clinker due to its lower hardness.

Mineralogical composition of the used materials (see Table 1) was determined by Rietveld analysis of the X-ray diffraction (XRD) patterns and expressed in values normalized to 100% of crystalline phases (details given further in this section).

Characteristic particle diameters (volume based) of cement, clinker and gypsum are reported in Table 2 and were measured by laser diffraction (Mastersizer, Malvern Instruments) after dispersion in isopropanol.

2.2. Methods and techniques

The BET surface area measurements were carried out using a BET multi-point nitrogen physisorption apparatus (Micromeritics Tristar II 3020). The nitrogen adsorption was measured from an eleven-points isotherm in a relative pressure P/P_0 range of 0.05 to 0.30 at 77.3 K. The SSA measurements were repeated three times for each sample. The samples were degassed in an external degassing station (VacPrep 061 from Micromeritics) in the range of temperature between 40 and 150 °C, under vacuum (2.67 Pa) and N_2 flow (with a flux of about $3 \cdot 10^{-3}$ m^3/h) for 16 h. For the SSA measurements of the anhydrous commercial cement, longer degassing processes (24 and 48 h) were also considered.

Table 1
Mineralogical composition of Portland cement, clinker and gypsum determined by Rietveld analysis of the XRD patterns.

	Cement % (w/w)	Clinker % (w/w)	Gypsum % (w/w)
C_3S	66.3	72.6	–
C_2S	6.7	8.6	–
C_3A	5.9	5.9	–
C_4AF	10.8	12.9	–
Quartz	0.4	–	–
Calcite	3.9	–	–
Gypsum	4.3	–	93.5
Hemihydrate	1.7	–	5.9
Anhydrite II	–	–	0.6

Table 2
Characteristic particle diameters of the powders determined by laser diffraction.

	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
Cement	1.12	8.47	26.80
Clinker	0.66	6.95	29.19
Gypsum	3.19	8.99	22.40
Model cement	0.78	7.82	25.59

The temperature of the degassing station was calibrated by measurements in and out of the sample chamber. For the first case, a sensor Sensirion SHT21 was inserted into the glass tubes under N_2 flow and both temperature and relative humidity were measured over time. In the second case, a mercury thermometer with a precision of 0.05 °C was installed in the degassing station between the glass tube and the heating mantle. As shown in Fig. 1, a linear correlation exists between set temperature and measured temperature. The difference between the set temperature and the effective one is confirmed both by the sensor and the thermometer. At all temperatures, the relative humidity measured in the glass tubes under N_2 flow approached zero.

The Blaine surface area of the above-mentioned samples was measured according to ASTM C204-11 standard [15]. The density of each sample was measured by the pycnometer Micromeritics AccuPyc II 1340 using helium as inert gas.

X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were used to determine the mineralogical composition of the powders after the degassing and the SSA measurements. The XRD patterns were obtained using a Bruker AXS D8 ADVANCE diffractometer with CoKα ($\lambda = 1.7902$ Å) radiation. The qualitative analysis of powders was conducted using the DiFFPlus EVA software. AutoQuan software was used for Rietveld analyses. The TGA analyses were performed using the TGA/SDTA 851^e (Mettler Toledo). About 40 mg of dry sample was heated in an open crucible from 25 to 1000 °C using a heating rate of 10 °C/min under pure N_2 flow of 50 mL/min. Gypsum samples were studied by Scanning Electron Microscopy (SEM) by using a FEI Quanta 200 3D microscope (FEI, North America NanoPort, Hillsboro, OR, USA). Backscattered-electron (BSE) images were taken in low vacuum mode.

3. Results

In this section we initially show how the degassing conditions affect the SSA of anhydrous cement measured by N_2 adsorption. We then show the impact of gypsum transformations on the SSA

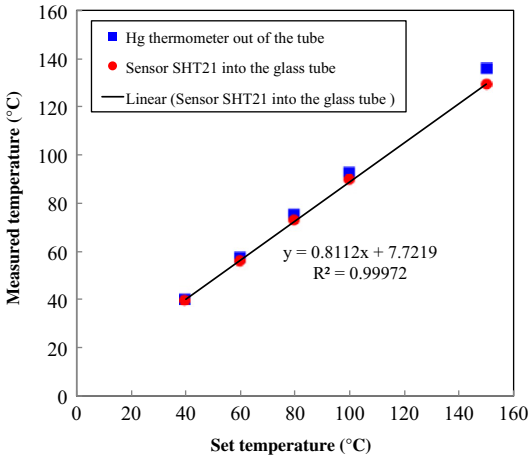

Fig. 1. Linear calibration of the degassing station VacPrep 061 between 40 °C and 150 °C.