Powder Technology 246 (2013) 504–510

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Effect of drying method on the specific surface area of hydrated lime: A statistical approach

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ARTICLE INFO

Article history:
Received 9 January 2013
Received in revised form 29 April 2013
Accepted 5 June 2013
Available online 14 June 2013

Keywords:
Drying
Specific surface area
X-ray powder diffraction
$Ca(OH)_2$
Lime putty

ABSTRACT

Lime putty is a traditional binder, experiencing a new advent in the preservation of historical buildings. Recently it was shown that lime putty microstructure evolves with ageing time, generally resulting in a continuous quality improvement, but possibly also passing a minima/maxima. Hence, periodical quality checks during ageing are needed to optimize quality and avoid excessive storage. The specific surface area (SSA) of lime putty is a potentially valuable parameter for quality control as it influences the workability and setting of lime mortars. Gas adsorption and the Brunauer–Emmet–Teller (BET) theory is a popular method for its determination, requiring a dry powder. Generally, freeze-drying is used for powder preparation as this method is assumed to diminish particle aggregation. However, no systematic investigation of the effect of powder preparation method on BET SSA has previously been reported. In addition, reproducibility evaluations of such methods are also lacking. This work was aimed to fulfil these gaps, using both calcitic and dolomitic lime putties. Freeze-drying was compared to heat-induced drying (105 °C) under air as well as at low pressure. In addition, sample microstructure was evaluated using X-ray Powder Diffraction data and Rietveld refinements as well as Electron Microscopy techniques (SEM, TEM). It was statistically proven that freeze-drying, compared to the other dehydration methods, resulted in a 20–35% higher BET SSA for calcitic lime putties consisting mainly of nanoparticles. Instead, BET SSA of a dolomitic lime putty containing micrometre-sized hexagonal platelet crystals was not influenced by drying method. No statistically significant difference in phase composition was found between the samples dried by the different methods, excluding carbonation of the hydroxides as influencing factor. Finally, high reproducibility of BET specific surface area was obtained regardless of drying method which is an important characteristic of a standard test method for quality control.

1. Introduction

Lime putty is a traditional binder used in mortars and plasters, obtained by hydration of calcined limestone or dolomite in an excess of water. The resulting product appears as a creamy liquid. The system is rather simple from a compositional point of view, consisting of an aqueous dispersion of calcium/magnesium hydroxide (i.e. portlandite/brucite) particles. Due to incomplete calcination of limestone and/or reaction with carbon dioxide, a small amount of carbonates may also be present. After being replaced by Portland cement in the second half of the nineteenth century, lime putty has in the recent years been reconsidered as a binder for repair of historic buildings [1]. The binding capacity depends on carbonation of hydrated lime particles, resulting in the formation of interlocking calcium carbonate crystals [2]. The overall reaction mechanism includes dissolution of hydrated lime and CO_2 in water retained in the porous structure, followed by precipitation of calcium carbonate [3,4]. Previous studies indicate that the binding capacity of magnesium hydroxide (brucite) present in dolomitic limes is due to the formation of calcite via de so-called dedolomitization reaction of the previously formed dolomite [5].

The size and shape of the portlandite particles, and consequently the specific surface area (SSA) of the hydrated lime, determine the workability of the mortar in the fresh state [6,7] as well as carbonation and quality of the hardened building material [8]. Workability is basically related to water retention and viscosity of lime putty which both depend on microstructure. Generally speaking, smaller crystals and hence larger SSA increase water retention [6] and viscosity (for equal mass fraction) [9]. Carbonation of lime mortars was shown to depend on the SSA of the hydrated lime particles [3,10,8], as expected for a surface reaction. For example, van Balen studied the carbonation kinetics of hydrated lime and found that the

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http://dx.doi.org/10.1016/j.powtec.2013.06.009

carbonation rate increased with increasing BET specific surface [3]. This result was also in concert with Swenson and Sereda, who found that hydrated lime compacts with higher surface area manifested a higher degree of carbonation [10]. In summary, the quality of lime putty generally increases with increasing SSA.

It is known since a long time that prolonged storage (i.e. ageing) of lime putty in excess of water has a beneficial effect on quality. In fact, the producers generally age the lime putty before putting it on the market and the time of storage is given as a sort of quality indicator. Recently, this empirical knowledge has been explained by the microstructure evolution during ageing in terms of crystal size and shape [6,11–14]. Generally, ageing leads to an increased SSA due to a reduction in overall crystal size and a change of the crystal morphology from prismatic to platelike [6,11–14]. However, Ruiz-Agudo and Rodriguez-Navarro also showed that the microstructural evolution with time depends on the type of quicklime used and does not always result in positive effects on the performance of the lime putty [13]. Hence, these results imply that there could be an optimum ageing time and periodical quality checks during storage could therefore have important economical advantages such as improved quality and unnecessary long ageing times. In addition, a possibility exist that a best-before date should be provided by the producers who wish to give quality guarantees. Considering the close relationship between the technological properties of lime putty and its microstructure, SSA could be a valuable parameter for quality ranking.

Gas adsorption and the theory of Brunauer, Emmet and Teller (BET) are established methods for the determination of SSA of solids in general [15]. However, as the measurement is performed on dry samples, the obtained results might not reflect the SSA of the primary particles in the lime putty as drying may induce particle aggregation with a consequent reduction in SSA [16]. This drying-induced particle aggregation may depend on the method of drying as suggested by Rodriguez-Navarro et al. [16]. The authors claimed that particle aggregation was more pronounced in oven-dried putties compared to freeze-dried putties, a phenomenon which has a negative effect on the BET SSA. More specifically, SSA of freeze-dried lime putty was about 22% larger than the one measured for heat-dried lime putty. Hence, the sample preparation for BET measurements might be important to obtain results which give a more accurate picture of the SSA of the particles in suspension.

A factor other than particle aggregation which could influence the BET specific surface is change in microstructure due to carbonation during preparation and storage of the powders [17,18]. Previous works have shown that the SSA of both hardened Portland cement [17,18] and lime paste [18] decreased when the hydrated phases (portlandite and calcium silicate hydrate C–S–H) carbonated. Hence, post-drying carbonation of powders could possibly bias the practical use of BET SSA for quality control in this system [18].

An appropriate technique to estimate the extent of carbonation of portlandite is X-ray powder diffraction (XRPD) and Rietveld refinements [19]. This approach is extensively used for quantitative phase analyses in solid state science in general but not to a great extent for hydrated limes. In this field, the mineralogy is most often approximated using thermal analyses [e.g. 20,21]. Although this has shown to be a valid method for hydrated limes, XRPD and Rietveld refinements have the advantage of giving a direct quantification of each phase (even amorphous), with high accuracy [19].

In the present work, the effect of sample preparation on the BET SSA of four different lime putties was investigated. The method of freeze-drying was compared to drying under air as well as at low pressure (105 °C). Data were evaluated using statistical analyses. The obtained results will aid to define a reproducible sample preparation strategy for SSA analyses which can eventually be used for quality control and ranking of lime putty.

2. Experimental

Four lime putties, from now on coded with the capital letters A–D, were investigated in this work. Sample A is a dolomitic lime putty whereas samples B–D are calcitic lime putties. The origin and ageing time of each lime putty are reported in Table 1. Following careful homogenization, 12 aliquots of ca 20 g each were extracted from each lime putty. Following extraction, three sample sets of three specimens each were dried using the following methods: 1) Dried under air for 24 h in an electrical furnace holding a temperature of 105 °C; 2) Dried at low-pressure conditions (P < 200 mBar) at 105 °C for 24 h using a vacuum furnace (ISCO, f.a.v.s., Bologna, Italy); 3) Freeze-dried for ca 48 h at −55 °C and 10^{-2} Torr using a Lyovac GT2 (Leybold, Germany). The specimens were coded in the following way: A capital letter which serves to distinguish between the four different lime putties, followed by two subsequent numbers which refer to the drying method (1 = air-drying, 2 = drying at low pressure (<200 mBar), 3 = freeze-drying), and the replicate number, respectively. All samples, regardless of drying method, were sealed in plastic containers and kept in a dessicator to avoid alteration of the phase composition prior to analyses [22].

The BET specific surface area (BET SSA) of each specimen was determined using a Gemini 2360 (Micromeritics), using adsorption of Nitrogen (high purity grade). About 1 g of powder was placed in the BET sample holder and conditioned at 120 °C under N_2 flux for ca. 2 h. Following conditioning, the precise weight (±0.0001 g) of the sample to be analysed was determined using an analytical balance.

The particle size and shape of each lime putty were investigated by electron microscopy techniques. Powders obtained by drying each lime putty at 105 °C were investigated by Scanning Electron Microscopy (SEM, Philips XL-40) equipped with an energy dispersive X-ray spectrometer. The dry powders were placed on carbon adhesive discs attached on aluminium stubs and subsequently coated with a thin (10 nm) layer of gold. Transmission electron microscopy (TEM) analyses were performed using a Jeol JEM 2010 instrument working at 200 kV. Samples for these analyses were prepared as follows: About 50 mg of each lime putty was dispersed in ca. 20 mL of propanol. The resulting suspensions were subjected to ultrasonic treatment for about 30 min. A Cu grid used as sample holder was passed through the dilute sol and dried under in UV radiation for ca. 5 min. Following drying, the samples were immediately mounted in the instrument.

Quantitative phase analyses of the crystalline fraction of the lime putty A, dried using the various techniques, were performed using XRPD data and Rietveld refinements. The samples for XRPD data collection were prepared as follows: Each powder was grinded in an agata mortar and mounted in an aluminium sample holder using a side-loading technique to minimize preferred orientation effects [23]. Following loading, the samples were immediately analysed using a θ/θ diffractometer (PANalytical, CuKα radiation), equipped with a real time multiple strip (RTMS) detector. The use of this detector in place of a conventional gas proportional detector drastically reduced the data acquisition time without compromising the quality of the data [24]. Divergence and anti-scattering slits of 0.125° and 0.25°, respectively, as well as a soller slit of 0.04 rad were mounted in the pathway of the incoming beam. A Ni filter and an antiscatter blade

Table 1
Geographic origin and ageing time of the lime putties under investigation.

Lime putty	Geographic origin	Approximate ageing time
A	Cuneo province, Italy	1 year
B	Brindisi province, Italy	2 weeks
C	Brindisi province, Italy	2 weeks
D	Brindisi province, Italy	4 years