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Cement and Concrete Research 36 (2006) 409 – 415

Cement and Concrete Research

Statistical analysis of impact-fracture characteristics and microstructure of industrial Portland cement clinkers

L.M. Tavares *, M.C. Cerqueira

Department of Metallurgical and Materials Engineering, Universidade Federal do Rio de Janeiro, COPPE/UFRJ, Cx. Postal 68505, CEP 21941-972, Rio de Janeiro, RJ, Brazil

Received 17 March 2005; accepted 22 September 2005

Abstract

Impact is the dominant breakage mode in most industrial grinding mills used in cement manufacture. The physical amenability of two industrial Portland cement clinkers to size reduction was determined through measurement of their fracture strengths under impact loading. It was found that the fracture strength of clinker is strongly dependent on size, which is consistent with the increasing expenditure of energy in fine grinding. Also, it was observed that the measured fracture strengths could be well described by either single or multiple Weibull distributions. The appearance of these distributions was consistent with the variability in the composition and microstructure of the clinker nodules, observed in a detailed examination under the microscope. Possible reasons for the appearance of these populations are given. It is concluded that the fracture strength of clinker is generally determined by porosity at coarser nodule sizes and by mineralogy and texture at finer sizes.

Keywords: Portland cement; Clinker; Microstructure; Petrography; Mechanical properties

1. Introduction

Size reduction is an important part of cement manufacture. In the preparation of the raw meal, materials such as limestone, marble, marl and silica-based materials such as shale, slate or granite are crushed and ground to fine sizes. These are then dried and burned in rotary kilns and the resulting cement nodules, called clinker, are ground along with gypsum to produce the marketable product.

Comminution operations consume as much as 40% of the overall energy in the cement-making process [1]. Size reduction of the cement nodules is typically carried out in modern plants in large two- or three-compartment tube mills, using balls as grinding media. Inside these mills, clinker nodules of up to a few centimeters in size are reduced to powders finer than 100 μm. While simplifying the size reduction circuit, these multi-compartment mills are notably inefficient in their use of energy.

Strength is a property that determines the physical amenability of cement clinker nodules to mechanical size reduction. The size-dependent strength of clinker is studied in the present work. Relationships between strength (and its variability) and microstructure and composition of clinker are analyzed. The appropriate quantification of the relevant mechanical properties of cement clinker and the establishment of their relationship to size reduction will allow, in the future, tailoring the milling conditions to the material being ground.

2. Experimental

In industrial comminution equipment, clinker nodules are ground through the application of compressive loading at moderate speeds. Loading under these conditions can be conveniently studied in the laboratory using a modified drop weight apparatus, called impact load cell. In this device, clinker nodules are subject to diametrical compression by placing each granule on the top of the rod and impacting them by a falling steel ball (Fig. 1). Loads are measured using solid-state strain gauges and are recorded as a function of time using a digital storage oscilloscope. The impact load cell was developed at the Utah Comminution Center [2] and has been used in studying

* Corresponding author. Tel.: +55 21 25628538.
E-mail address: tavares@ufrj.br (L.M. Tavares).

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doi:10.1016/j.cemconres.2005.09.012

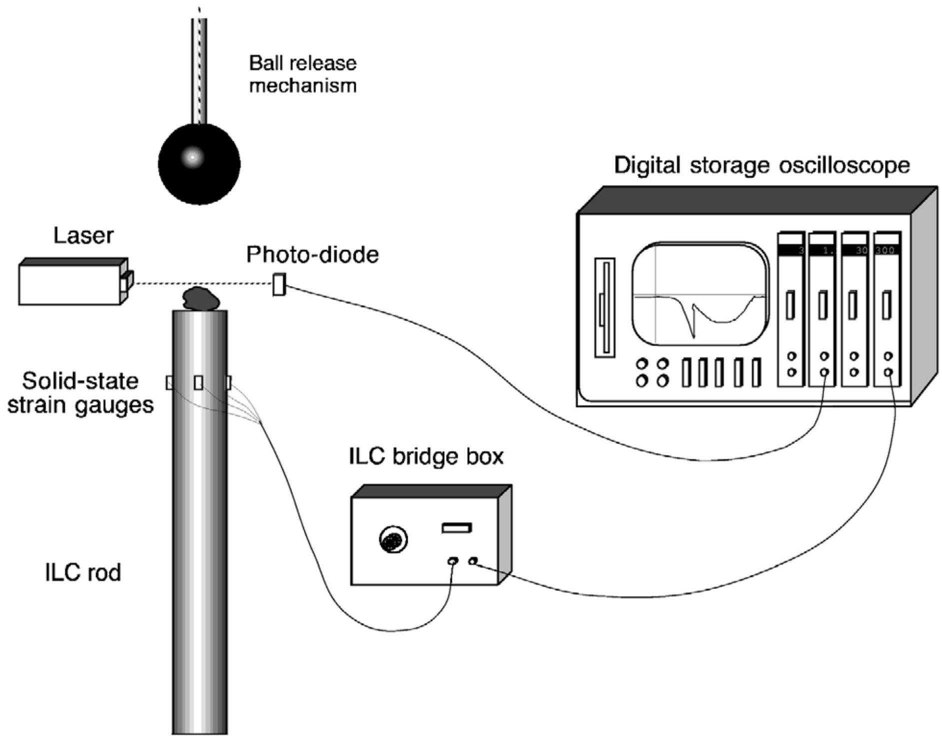

Fig. 1. Outline of the impact load cell (ILC).

the mechanical properties of a variety of geological materials [3]. Impact velocities used in the experiments ranged from 0.3 to 1.3 m/s and the number of particles tested of each narrow-sized sample was typically larger than 40. The precision of the device in measuring loads depends on the rod diameter used, being about 20 N for the 50 mm ILC (used, in the present work, for testing particles coarser than 8 mm), about 0.2 N in the 9 mm ILC (used for testing the size fraction 0.25–0.35 mm) and about 2 N in the 19 mm ILC (used in testing the remaining sizes). More detailed descriptions of the device and the experimental procedure can be found elsewhere [3].

Comminution behavior of the materials has also been characterized using the standard ball mill test to determine the Bond work index [4], which can be considered to have a precision of at least 1 kWh/t.

Samples of two Portland cement clinkers produced in industrial plants in Mexico were used in the present investigation. The samples were denoted clinkers A and B and were screened into narrow size fractions for testing in the impact load cell. Clinker particles tested ranged from a fraction of a millimeter to nearly 2 cm. Samples of both clinker types were placed in resin, ground, polished, etched and then examined under reflected light using an optical microscope.

3. Results and discussion

3.1. Microscopic examination

Simple visual inspection by naked eye showed that clinker A presented a black outer shell and a yellowish inside, while clinker B presented an overall dark gray coloration.

Examination of both clinkers on the microscope under reflected light indicated widely different microstructures, as

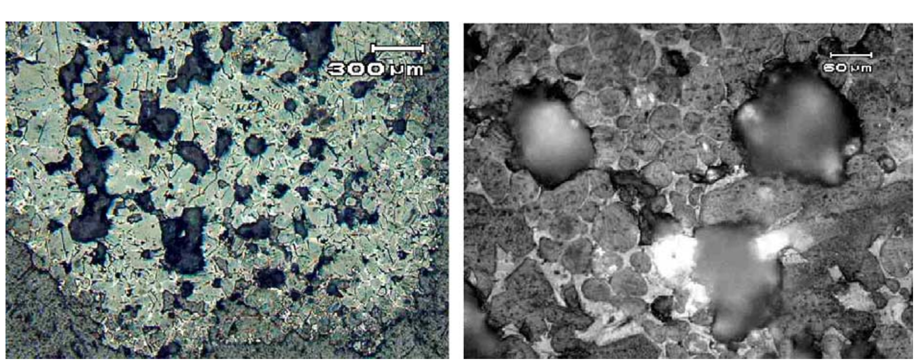

Fig. 2. Micrographs of clinker A inspected on reflected light at different levels of magnification (left: nodules of interconnected porosity; right: belite nests around isolated pores).

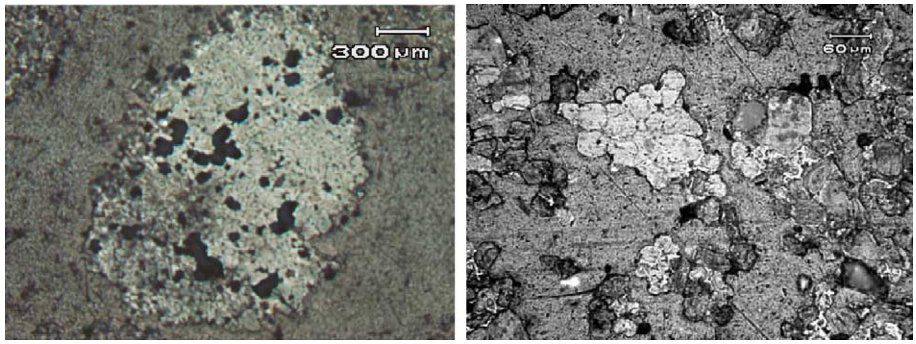

Fig. 3. Micrographs of clinker B inspected on reflected light at different levels of magnification (left: nodules of lower porosity; right: regions of isolated agglomerates of belite crystals, limited porosity).

shown in Figs. 2–5. It is possible to observe both at low and high magnification that clinker A is composed of two types of regions: one with intense grain corrosion with interconnected porosity and the other that consists of belite clusters and nests around isolated pores (Fig. 2). Belite clusters, especially when having a pore in the center, are often associated with the presence of coarse quartz particles in the raw meal [5]. The first type of region is more often encountered in coarser nodules (8.0–9.5 mm), which also shows a significant macroporosity, whereas the second type is more frequently found in smaller nodules (0.50–0.70 mm).

Clinker B mainly presents nodules with lower macroporosity, similar to the latter type of clinker A, but with only a very limited proportion of belites (Fig. 3). It is composed mainly by cracked alite grains that have irregular shape or by uncracked grains that have regular shape, immersed in a fibrous cryptocrystalline matrix (Fig. 3).

Clinker A is composed of a mixture of spheroid belite grains and corroded alite grains in a glassy matrix. In this latter, rounded striated belite grains appear isolated or as inclusions in alite, whereas belites with narrow polysynthetic twinning in two directions appear in abundance in rosette structures, around pores (nests) and as ellipsoidal clusters (Fig. 4). In all, corrosion zones are more frequently encountered in clinker A and, in these areas, interconnected porosity predominates, which is common in coarse nodules. In these regions, clusters of belite are common (Fig. 2).

In clinker B, corrosion zones are seldom found. In these corrosion zones isolated pores surrounded by zoned alites are common (Figs. 2 and 4). In regions where no grain corrosion occurs, pores are seldom found and alites present coarser grain sizes and intense microcracking, with nearly no belites found (Fig. 5).

3.2. Statistical analysis of fracture strengths

The strength of an irregularly shaped specimen – such as a clinker nodule – cannot be determined unambiguously. The importance of knowing the strength of cement clinker in its natural particulate state makes the use of approximate expressions worthwhile. Hiramatsu and Oka [6] observed that the state of stresses of an irregularly shaped specimen subject to diametrical compression is similar to that of a sphere and that its strength σ could be approximately given by

$$\sigma = \frac{2.8F}{\pi d^2} \tag{1}$$

where d is the specimen size and F is the fracture load (the load needed to create a cross crack). In the case of cement clinker nodules, such approximation is not particularly severe, given its natural spheroid shape.

Strengths were measured for both clinker types in the impact load cell as a function of nodule size. Attempts to fit the data using several statistical distributions showed that, in

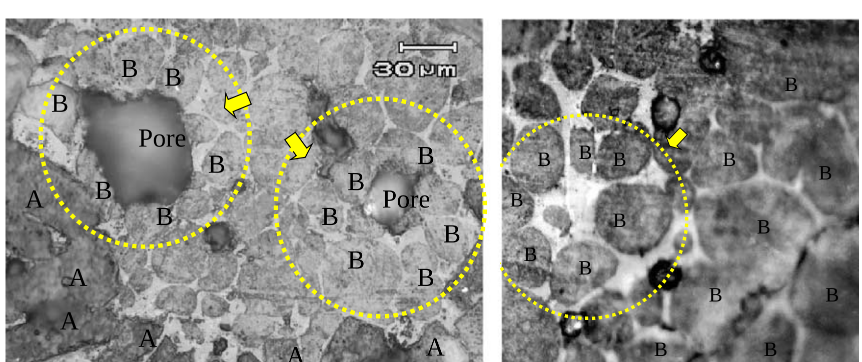

Fig. 4. Micrographs of clinkers A inspected on reflected light at high magnification (left: belite (B) nests and alite grains (A); right: belite rosette structure).

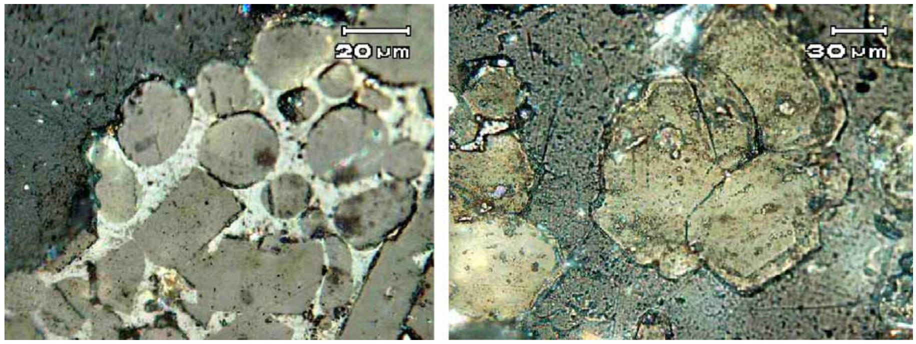

Fig. 5. Micrographs of clinkers B inspected on reflected light at high magnification (left: alite and belite grains of regular shape without corrosion or striation; right: cracked alite grain with irregular shape).

general, the Weibull distribution was the one with the fewest parameters that produced the best fit. The Weibull distribution is given by [7]

$$P(\sigma) = 1 - \exp[-(\sigma/\sigma_0)^m] \quad (2)$$

where m is the Weibull modulus and σ_0 is the characteristic strength.

Fracture strength data of nodules of cement clinkers A and B are plotted in Weibull coordinates in Figs. 6 and 7, respectively. While data from clinker B appropriately fits into a straight line (Eq. (2)), the lack of fit of data from clinker A suggests the presence of multiple populations [8]. The appearance of these multiple populations of fracture strengths of clinker A is analyzed in light of evidences from microscopic examinations, given that nodules of this clinker were either of massive structure or highly porous (Section 3.1). Indeed, these different populations were not only characterized by different strengths, but also by widely different mechanical responses, as shown in the load–displacement profiles in Fig. 8. The fracture strengths of a material composed of a mixture of two mutually exclusive populations [8] can be described by

$$P(\sigma) = \pi P_1(\sigma) + (1-\pi)P_2(\sigma) \quad (3)$$

where π is the fraction of the sample having distribution of type 1. Considering that each population can be described by the Weibull distribution, then substituting (2) in (3) it gives

$$P(\sigma) = 1 - \pi\exp[-(\sigma/\sigma_1)^{m_1}] - (1-\pi)\exp[-(\sigma/\sigma_2)^{m_2}] \quad (4)$$

where σ_1, σ_2, m_1 and m_2 are parameters of the distribution.

Table 1 shows a summary of the Weibull distribution parameters estimated by least-squares for the various sizes of clinker, while Table 2 summarizes the fitting deviations (sum of squares of the differences between the fitted values obtained from Eq. (2) or (4) and the calculated percentiles from the data, divided by the number of degrees of freedom — the number of data points minus one) in respect to each distribution. Values of

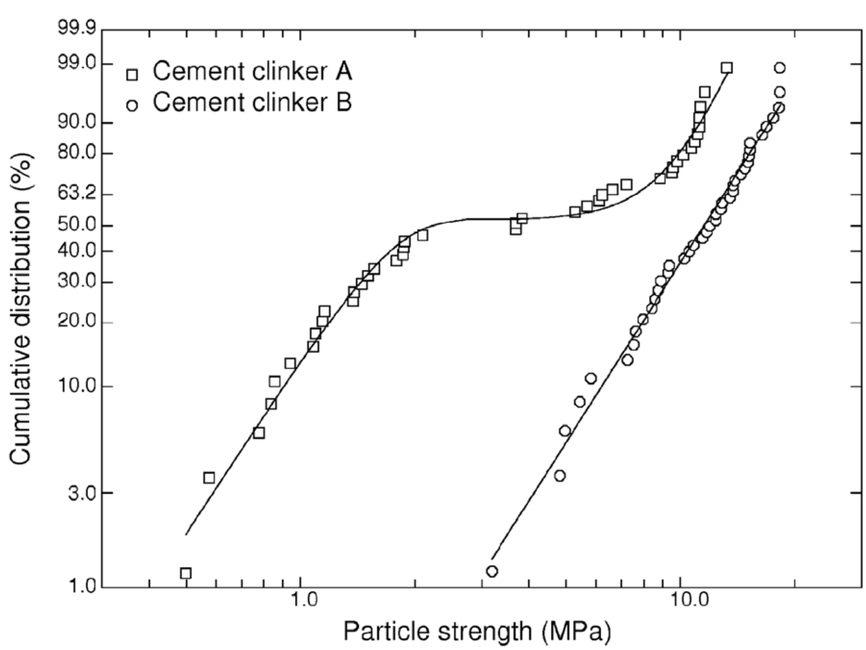

Fig. 6. Strength distributions of 8.0–9.5 mm nodules of cement clinker.

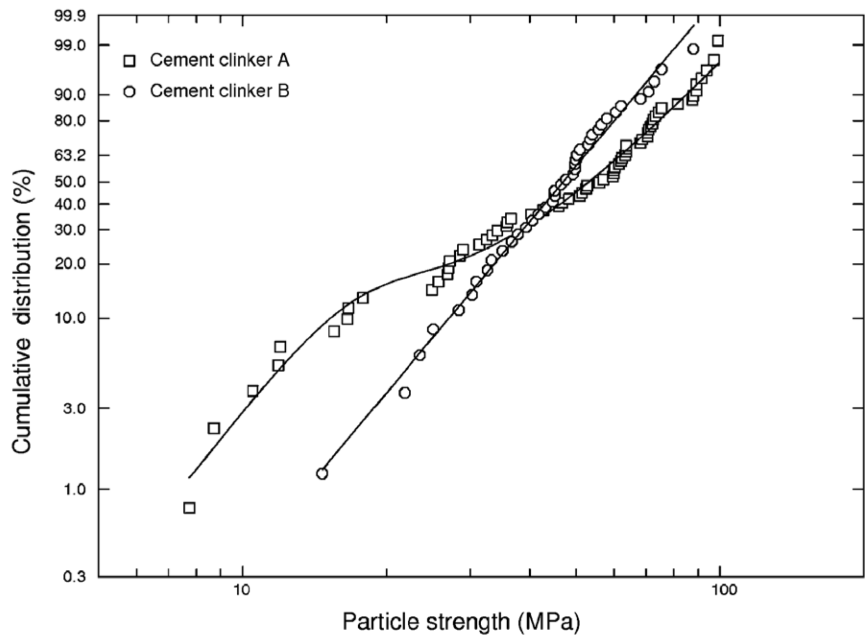

Fig. 7. Strength distributions of 0.5–0.7 mm nodules of cement clinker.

fitting deviations obtained from fitting data of the different clinkers and particle sizes analyzed did not vary significantly, which demonstrates the validity of the expressions used.

As particle size decreases, the fraction of porous particles (type 2) in cement clinker A (equal to $1-\pi$) decreases, vanishing completely below 0.5 mm. Values of the Weibull modulus (m), which denotes the variability in fracture strengths, were found to be generally comparable for nodules of clinker A of massive structure and of clinker B. The limited variations of the Weibull modulus with nodule size are not likely to be statistically significant, since no distinct trend was found.

3.3. Size effects on clinker strength

Data from Table 1, plotted in Fig. 9, illustrate the effect of size on particle strength, with the two component populations of clinker A denoted by A1 and A2. All data show a marked increase in the strength of cement clinker with a reduction in size. This increase in strength with a reduction in size is generally attributed to the disappearance of defects in the material, such as cracks, pores and grain boundaries, as it becomes finer.

The strength of clinker at coarse sizes is controlled by its most severe discontinuities at that scale, which is typically large-scale porosity. On the other hand, at fine sizes, strength becomes dominated by texture and composition of the mineral grains, as well as by characteristics of the interstitial phase [5,9,10]. Fig. 9 shows that, at coarse sizes, both populations of clinker A presented lower strength than clinker B. This is attributed to the generally large porosity of nodules of clinker A, particularly of type 1 (Fig. 2), in comparison to clinker B (Fig. 3). At fine sizes, the opposite behavior was observed, with particles of type 1 in clinker A presenting higher strength than nodules of clinker B, while the population of nodules of type 2 of clinker A vanished completely.

These effects at different scales result in the crossover observed in the fracture strengths of clinkers A1 and B (Fig. 9). Indeed, the higher strength of clinker A in comparison to clinker B at fine sizes is consistent with both measurement of

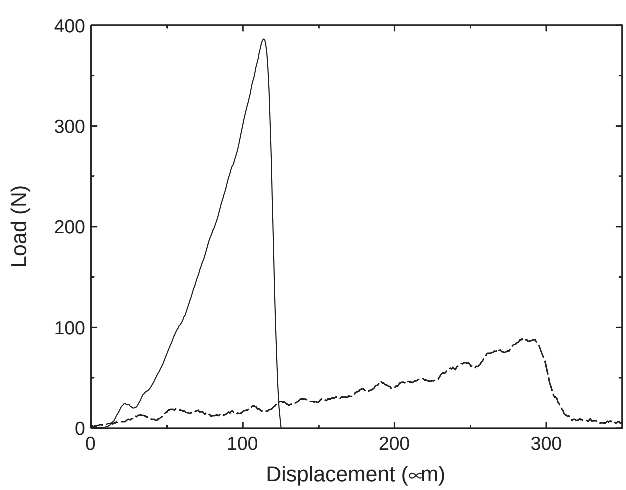

Fig. 8. Typical load–displacement profiles for 4.0–4.75 mm nodules of cement clinker A showing the different behavior of massive (solid line) and porous structures (dashed line).

Table 1
Summary of parameters of the Weibull distributions of strengths

Size (mm)	Clinker A					Clinker B	
	σ_1 (MPa)	m_1	σ_2 (MPa)	m_2	π	σ_0 (MPa)	m
13.3–18.0	5.5	2.86	0.70	2.55	0.395	–	–
8.00–9.52	10.2	4.61	1.52	2.99	0.476	13.0	3.04
4.00–4.75	14.0	2.87	2.23	3.99	0.639	20.6	3.37
2.00–2.80	19.0	2.62	1.44	3.24	0.805	24.1	3.88
1.18–1.40	37.8	3.80	5.93	2.07	0.845	32.6	3.88
0.50–0.70	65.4	2.93	15.2	3.85	0.863	52.2	3.42
0.25–0.35	97.7	3.63	–	–	1.000	72.2	2.87

Table 2
Fitting deviations of the Weibull distributions of fracture strengths and statistical comparison of the measured distributions

Size (mm)	Mean sum of squares of residuals ($\times 10^{-3}$)		Assessment[a]
	Clinker A	Clinker B	
13.3–18.0	1.73	–	Comparison not possible
8.00–9.52	0.93	0.64	Different
4.00–4.75	0.18	0.53	Different
2.00–2.80	0.31	0.77	Marginally different
1.18–1.40	0.25	0.55	Identical
0.50–0.70	0.78	0.55	Marginally equal
0.25–0.35	0.52	1.34	Marginally different

Tests conducted at a significance level of 0.05.
[a] Different: three tests rejected the null hypothesis (H_0); marginally different: two tests rejected H_0; marginally equal: one test rejected H_0; identical: no test rejected H_0.

Bond work index and evidence from microscopy. The values of Bond work index were measured as 20.9 kWh/t for clinker A and 15.4 kWh/t for clinker B. Further, the large proportion of belite crystals and their heterogeneous distributions in nests and clusters found in clinker A is generally found to decrease grindability of clinker, specially when the belite crystals are tightly packed, with little interstitial phase [5]. On the other hand, the large proportion of coarse alite crystals and the fact that they often appear microcracked explains its improved grindability and lower work index.

Non-parametric statistical hypotheses tests have been used to associate a statistical significance to the comparison of the distributions, where the null (H_0) hypothesis of equality of the distributions has been tested against the alternate (H_1) hypothesis that the data measured were drawn from different populations [11]. Table 2 shows that difference in strengths of clinker A in comparison to clinker B at finer sizes is significant, with clinker A being marginally stronger at these sizes. At coarser sizes, the opposite behavior is observed, with clinker A being significantly weaker than clinker B.

The information on the effect of scale on strength of clinker nodules is of great practical relevance to industrial size reduction. Higher mechanical resistance at coarse sizes requires, for example, the use of balls of larger diameter in a ball mill, which are very expensive. Higher resistance at fine sizes, usually results in higher energy consumption in size reduction, given the comparatively greater stresses (and energies) required to fracture particles as their size decreases.

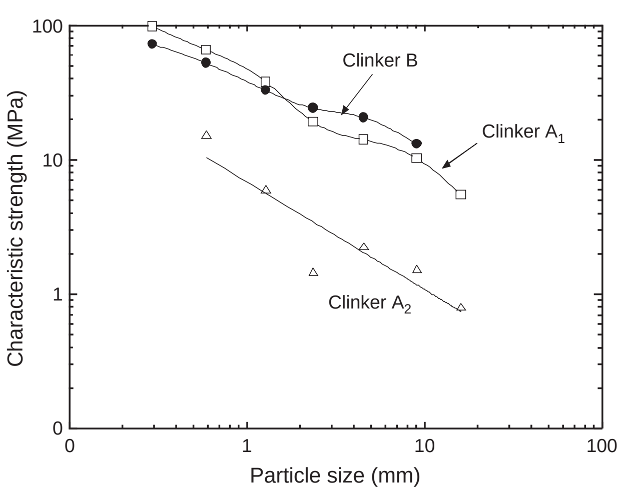

Fig. 9. Variation of clinker strength with particle size for the clinker studied.

4. Conclusions

The Weibull distribution appropriately fitted measurements of fracture strengths of clinker nodules subject to impact loading. For one type of clinker, which presented nodules of uniform composition and structure, a single distribution fitted the data. For the other clinker type, two distributions representing two mutually exclusive populations were required to fit the data. Nodules of lower porosity and higher strength and stiffness, possibly produced during the normal nodulization process, characterized one of the populations. The other was characterized by nodules of higher porosity and lower strength and stiffness and free of interstitial material, possibly produced in a later stage of intense sintering of finer nodules in the kiln mass.

The strength of clinker increased with a reduction in particle size and was influenced by porosity at coarse sizes and by microstructure and mineralogy at fine sizes. A correlation was found between the strength of clinker nodules at fine sizes and the Bond work index.

Acknowledgements

The authors would like to thank Professor R.P. King for his suggestions and guidance during the initial part of this work. The financial support from FAPERJ and the Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil is also greatly acknowledged. The authors also thank the assistance of Mrs. Vládia G. Souza in the analyses on the optical microscope.

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