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Mechanical strength of highly porous ceramics

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This paper reports on the mechanical strength of highly porous ceramics in terms of the Weibull and Duxbury-Leath distributions. More than 1000 side-crushing strength tests on silica-catalyst carriers of various particle sizes have been performed in series. Within a series, preparation conditions were kept constant. Analysis of the fluctuations of the failure pressure around its expectation value proves that the length dependence of the mechanical strength is well described by both distributions. Focusing upon the failure pressure dependence, the $\mu=1$ Duxbury-Leath distribution appears to be the more appropriate.

Extensive studies have been done on the mechanical breakdown of spring networks.[1] Attention has been focused on the question whether the Duxbury-Leath[2] distribution

$$F_V=1-\exp\left[-cV\exp\left(\frac{-k}{\sigma^\mu}\right)\right] \tag{1}$$

is more appropriate than the Weibull[3] distribution

$$F_V=1-\exp(-cV\sigma^m) \tag{2}$$

to describe the mechanical strength. We use the standard notations cumulative failure F_V, volume V, failure pressure σ, Duxbury-Leath constant k, and Weibull modulus m. The μ is a screening constant and c is a fit constant in both distributions. So far no comparison has been made between the two failure distributions for highly porous materials. We performed experiments on cylindrical silica extrudates (pore volume up to 80 vol%, median pore diameter less than 100 nm). More than 1000 particles (length between 2 and 20 mm, diameter between 1 and 3 mm) were broken. In this Rapid Communication we will focus on the shape of the failure distribution. More details on the manufacturing conditions, together with the results of extensive microstructural analysis (mercury porosimetry, nitrogen adsorption, scanning electron microscopy, and transmission electron microscopy) and the influence of the microstructural changes on the mechanical strength will be reported in another paper.

High mechanical strength of highly porous ceramic particles is of crucial importance for the petrochemical industry, where such materials are used as catalyst carriers. The mechanical strength of the catalyst particles has been determined by a side-crushing strength (SCS) test. In this SCS test a particle is slowly compressed at a constant strain rate. The pressure σ, at which a cylindrical particle of length L and diameter D fails, is given by[4]

$$\sigma=\frac{2F}{\pi LD} \tag{3}$$

where F is the maximum force on the particle during the SCS test. Equation (3) is an approximation of the tensile stress perpendicular to the direction of deformation. In our experiments most extrudates broke into two half cylinders axially, which suggests that this tensile stress initiated the fracture. In fact, the significantly lower strength of the diametrically broken particles can be explained by the smaller volume that is deformed during the test. This is confirmed experimentally since these particles show a smaller contact area in the SCS apparatus owing to their curved shape. Therefore, we only analyzed the strength data of extrudates that had broken along the length axis. A typical force-strain curve is presented in Fig. 1. The small dips are caused by local fracture that

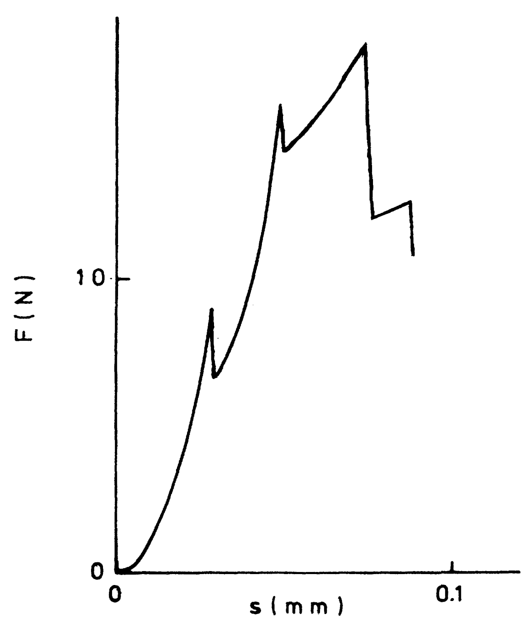

FIG. 1. A typical force-strain curve as measured in a side-crushing strength test.

does not lead to global failure. The SCS test ends when the total force on the particle reaches a value lower than 60% of the maximum experienced during the test.

In Fig. 2(a) the cumulative failure distribution is depicted normalized to a constant volume of 25 mm^3 for four series of samples prepared under different conditions. Results of the mercury porosimetry[5] measurements are listed in Table I. The normalization is necessary since the length of the test specimen varies within a series. The cumulative failure distribution can be analyzed, if

$$y = \ln\left[\frac{-\ln(1-F_V)}{V}\right] \tag{4}$$

is presented as a function of $\ln\sigma$ and $\sigma^{-\mu}$, for the Weibull and Duxbury-Leath distributions, respectively. For the Weibull distribution we have sorted the experimental data on the basis of increasing $V\sigma^m$, which affects the order F_V and minimizes the standard deviation in the analyzing plot. It does not affect the direction of the curve, i.e., the Weibull modulus m. In the Duxbury-Leath analysis we applied the identical method with $V\exp(-k\sigma^{-\mu})$. Note that in the Duxbury-Leath distribution [Eq. (1)] only values between 0 and $1-\exp(-cV)$ are generated. From our analysis we learned that $\exp(-cV)$ is very small. We can therefore apply the order

$$F_V = \frac{i-\frac{1}{2}}{N} \tag{5}$$

as we did in the Weibull analysis. If the failure distribution follows one of the theoretical distributions exactly then a straight line will show up in the corresponding figure.

The Duxbury-Leath analysis [Fig. 2(c)] for $\mu=1$ is nearly straight for all series. The Duxbury-Leath analysis (Fig. 3) for higher μ and the Weibull analysis [Fig. 2(b)] are curved. This indicates that the Duxbury-Leath distri-

TABLE I. Results of mercury porosimetry measurements.

	Porosity vol %	Median pore diam nm	Average length mm	Average diam mm
Series 1	71	44.4	9.2	2.50
Series 2	73	21.6	7.6	2.55
Series 3	74	20.1	5.8	1.26
Series 4	79	28.7	5.8	1.32

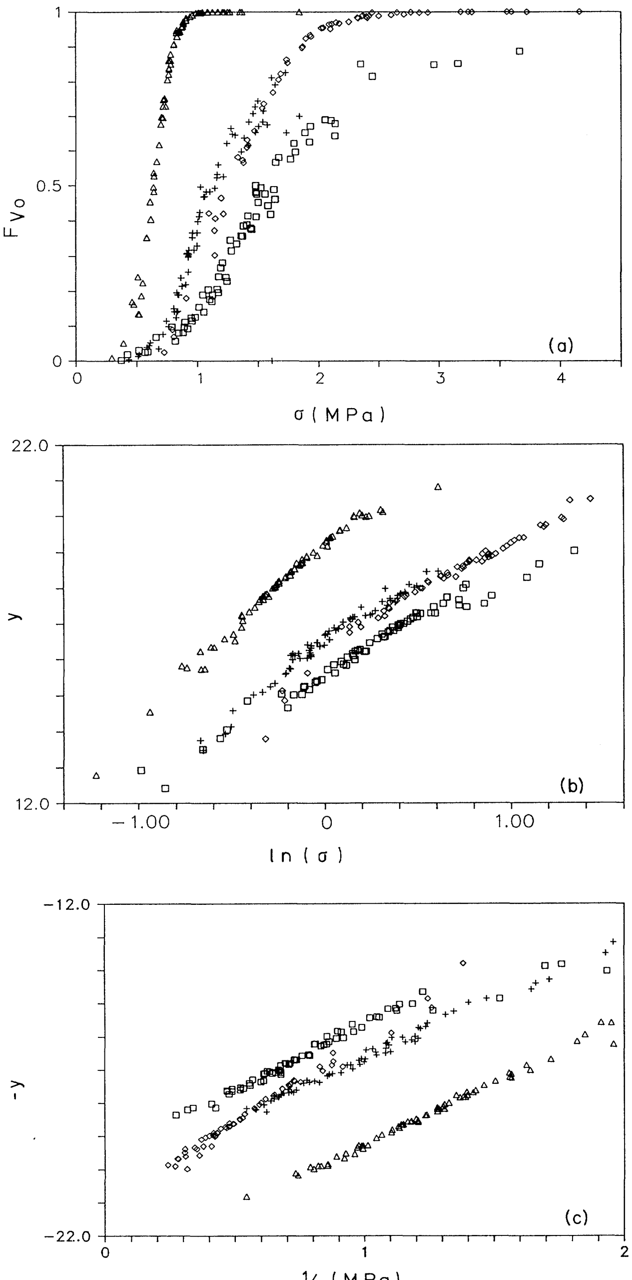

FIG. 2. Experimental data from side-crushing strength tests. (a) Cumulative failure distribution normalized to a constant volume of 25 mm^3; (b) Weibull analysis; (c) Duxbury-Leath analysis for $\mu=1$: □, series 1; +, series 2; ◇, series 3; △, series 4.

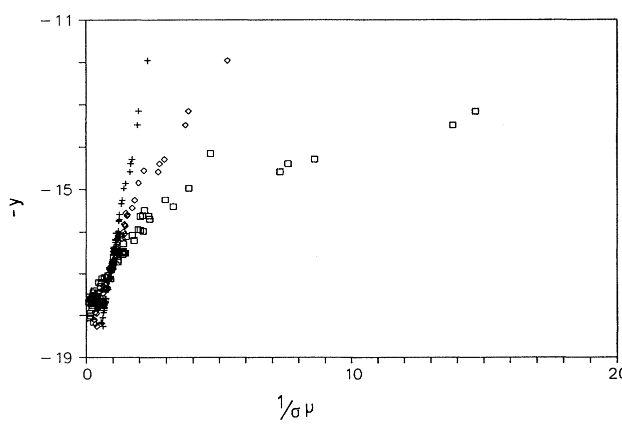

FIG. 3. Duxbury-Leath analysis for higher μ (series 2): +, $\mu=1$; ◇, $\mu=2$; □, $\mu=4$.

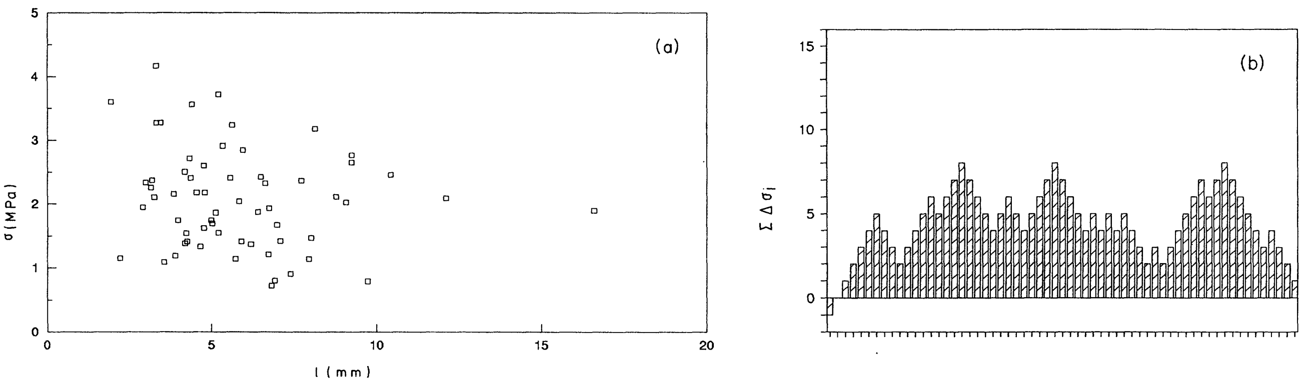

FIG. 4. Analysis of the fluctuations of the failure pressure for series 3: (a) Length dependence of the measured failure pressure; (b) cumulative Boolean deviation of the Duxbury-Leath expectation value. Particles are sorted on the basis of length. We used Duxbury-Leath constant $k = 5.0$ and $\ln c = 21$ [see Fig. 2(c)].

bution for $\mu = 1$ is the more appropriate for describing the mechanical strength of these highly porous particles.

Here, mechanical strength is presented as a statistical value. The actual strength of a single particle will fluctuate around an expectation value. The experimental data can be analyzed in more detail by investigating these fluctuations. For the Weibull distribution the expectation value, defined as the pressure at which half the particles have been broken, is

$$\sigma_W^{\text{expt}} = \left[\frac{\ln 2}{cV} \right]^{1/m} . \tag{6}$$

The expectation value for the Duxbury-Leath distribution is

$$\sigma_{\text{DL}}^{\text{expt}} = \left[\frac{k}{\ln c + \ln V - \ln \ln 2} \right]^{1/\mu} . \tag{7}$$

The Weibull modulus m, the Duxbury-Leath constant k, and the intercepts c are obtained from all SCS tests within one series of experiments. We can use these expectation values to validate the method used for producing Fig. 2(a), but, moreover, it proves that the size effect in the experiments is described well by Eqs. (1) and (2). In Fig. 4(a) the measured failure pressure is depicted as a function of the length of that extrudate. More detailed information can be obtained from Fig. 4(b). Here the cumulative Boolean deviation from the expectation value is presented. The other series and analysis of the Weibull expectation value (6) give similar figures. Since the deviation from zero is small in relation to the number of experiments (namely 71), we can conclude that the length effect (1-3) is well understood.

In conclusion, analysis of the fluctuations around the expectation values of the mechanical strength of highly porous silica extrudates proves that the length dependence is well described by both Weibull and Duxbury-Leath distributions. Focusing upon the failure pressure dependence, the $\mu = 1$ Duxbury-Leath distribution appears to be the most appropriate. We are interested in how the distribution of the failure pressure depends on the microstructure. In the future, we shall try to link the Duxbury-Leath constant k and the intercept c with the micro structural features.

[1]See, for instance, Muhammad Sahimi and Joe D. Goddard, Phys. Rev. B **33**, 7848 (1986); Paul D. Beale and David J. Srolovitz, *ibid.* **37**, 5500 (1988).
[2]P. M. Duxbury and P. T. Leath, J. Phys. A **20**, L411 (1987).
[3]W. Weibull, Ingeniörsvetenskapsakad., Hand. **151**, 1 (1939).
[4]S. P. Timoshenko and J.N. Goodier, *Theory of Elasticity* (McGraw-Hill, Singapore, 1982); P. J. F. Wright, Mag. Concr. Res. **7**, 87 (1955).
[5]See, for instance, J. R. Anderson and K. C. Pratt, *Characterization and Testing of Catalysts* (Academic, Sydney, 1985).