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Research paper

Determining the size distribution-defined aspect ratio of rod-like particles

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ABSTRACT

Mineral particles are used in many industrial applications as fillers, in coatings, as ad- and absorbers or in catalysis. In these fields the particle size and shape may control the final performance and properties of the minerals. This work aims to develop a size distribution and surface area defined particle aspect ratio for rod-like particles, using a previously discussed improvement of the input parameters to the Hohenberger model. The tested aragonite particles were shown to have an aspect ratio of ~2 determined using laser scattering particle size data and surface area data, proven by image analysis. Palygorskite showed the limitation of the current model with respect to the surface area input parameter as measured by nitrogen adsorption due to its internal porosity. An aspect ratio of 21 of the fibrous material was calculated in contrast to the value of 7 found by image analysis. The calculation procedure can thus be recommended to approximate the aspect ratio of non-porous fibrous and rod-like particles in a fast, easy and reproducible way.

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1. Introduction

The properties and uses of particulate materials depend on the particle size and shape. Recently we published a method to determine the size distribution-defined particle aspect ratio for disc-like particles (Gantenbein et al., in press) using both the size and the specific surface area as input parameters of the Hohenberger model (Hohenberger, 2001). By measuring the specific surface area and the particle size distribution by several methods, it is possible to approximate a number-based aspect ratio, which can be directly compared with other methods for shape determination.

The particle size and shape are not only important for disc-like particles but also for rod-like and fibrous particles. These parameters, for example, control the rheological properties of dispersions (Baltar et al., 2009; Pabst et al., 2006; Yin et al., 2009). Properties of particulate materials in other applications, like catalysis, environmental control or drug delivery, may also be affected by the particle shape (Yang et al., 2010).

This study aimed to adapt the model (Gantenbein et al., in press) for rod-like and fibrous materials, and compared it with image analysis results and other methods based on various methods of particle sizing (Jennings and Parslow, 1988). The proposed model had the advantage of being based on readily available, reproducible and independent methods for particle characterisation. Sensitivity in respect to the physical and geometrical interpretation of the specific

surface area as measured by nitrogen adsorption was illustrated by comparing non-porous (aragonite) and porous (palygorskite) particles.

1.1. Aspect ratio (ρ)

1.1.1. Definition

Needle-like mineral particles can be considered geometrically to approximate idealised cylindrical rods. The aspect ratio, ρ , of a particle is defined as the ratio of its major dimension and minor dimension (Jennings and Parslow, 1988), which, in the case of rod length l and width w , can be expressed as

$$\rho = \frac{l}{w} \quad (1)$$

The surface area s of one such rod-like particle is given by

$$s = 2 \left(\frac{\pi \cdot w^2}{4} \right) + \pi \cdot w \cdot l \quad (2)$$

so that

$$\rho = \frac{s}{\pi \cdot w^2} - \frac{1}{2} \quad (3)$$

The specific surface area (ssa) ε for a single particle is defined as

$$\varepsilon = \frac{s}{m} \quad (4)$$

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where m is the mass of the particle having the surface area s . If the density of the material is δ , then

$$\varepsilon = \frac{s}{\left(\frac{\pi \cdot w^2 \cdot l}{4}\right) \delta} \quad (5)$$

which, upon rearranging, gives

$$s = \varepsilon \left(\frac{\pi \cdot w^2 \cdot l}{4}\right) \delta \quad (6)$$

Now, applying to Eq. (3) provides

$$\rho = \frac{\varepsilon \left(\frac{\pi \cdot w^2 \cdot l}{4}\right) \delta}{\pi \cdot w^2} - \frac{1}{2} \quad (7)$$

such that

$$\rho = \frac{\varepsilon \cdot \delta \cdot l - 2}{4} \quad (8)$$

With the knowledge of the specific surface area determined by the BET method (Brunauer et al., 1938), ε_{BET} , expressed in $\text{m}^2 \text{kg}^{-1}$, the aspect ratio can be written as

$$\rho = \frac{\varepsilon_{\text{BET}} \cdot \delta_{\text{M}} \cdot l - 2}{4} \quad (9)$$

ε_{BET} Specific surface area by nitrogen adsorption (BET) in $\text{m}^2 \text{kg}^{-1}$.

δ_{M} Mineral particulate density, in kg m^{-3} .

In most practical cases of naturally occurring materials, sediments, single particle precipitates and mechanically ground minerals, particle size distributions can be reasonably approximated statistically by using the log-normal distribution (Randall, 1989). If a log-normal distribution of rod lengths is considered, then l has to be expressed according to the model number occurrence probability of that rod length in order to obtain an aspect ratio representing the most commonly occurring particles. The most commonly occurring rod length is given by the mode value,

$$\bar{l}_N = l_{N50} \cdot e^{-\ln^2 \left(\frac{l_{N84.13}}{l_{N50}}\right)} \quad (10)$$

Combining Eq. (9) with Eq. (10) leads to Eq. (11).

$$\rho = \frac{\varepsilon_{\text{BET}} \cdot l_{N50} \cdot e^{-\ln^2 \left(\frac{l_{N84}}{l_{N50}}\right)} \cdot \delta_{\text{M}} - 2}{4} \quad (11)$$

Eq. (11) is different to the one proposed earlier (Gantenbein et al., in press), and the difference accounts for the change of geometry from a circular disc (the limit of an oblate spheroid) to a cylindrical rod (the limit of a prolate spheroid). Of course, it would also be possible to apply a geometrical transform between the equation presented for discs (Gantenbein et al., in press; Hohenberger, 2001) and that presented here for rods. The resulting aspect ratio would undergo a conversion between that of a thin disc to that of an extremely thick disc, with an inverted definition of the aspect ratio, i.e. it would represent the inverse of the aspect ratio defined for disc geometry. However, we pointed out before (Gantenbein et al., in press) that the value expressed by a particle size measurement device is related to an equivalent spherical diameter (esd). The model for rods in Eq. (11)

Table 1

Formulae to calculate the rod length l based on the esd (d_s , d_a , d_v and d_T) response from the corresponding particle sizing method.

Method	$esd_{N50}(\rho)$
Sedimentation (Stokes law)	$d_s = \frac{l}{\rho} \sqrt{\frac{3}{2} \ln \rho}$
Laser light scattering/projected area (Fraunhofer)	$d_a = l \sqrt{\frac{1}{\rho} + \frac{1}{2\rho^2}}$
Laser light scattering/particle volume (Mie-theory)	$d_v = l \sqrt[3]{\frac{3}{2\rho^2}}$
Photon correlation spectroscopy/translational diffusion	$d_T = \frac{l}{\ln(2\rho)}$

requires the rod length, whereas that for discs requires the disc diameter. Therefore, the size parameter needs also to be re-defined. A proposed answer to this is given by Jennings and Parslow (1988) and Jennings (1993). They offer, for the three measurement methods; sedimentation, time averaged laser light scattering (SLLS) and dynamic light scattering, in the form of photon correlation spectroscopy; a mathematical conversion from esd for each method into the rod length l (Table 1). A theoretical discussion of the different particle size methods was reported earlier (Gantenbein et al., in press).

Since all the relationships in Table 1 are linear in l , the exponent ratio can adopt each esd parameter without modification. The relation between esd and rod length, $l_{N50}(esd_{N50}(\rho))$, (Table 1) gives

$$\rho = \frac{\varepsilon_{\text{BET}} \cdot l_{N50}(esd_{N50}(\rho)) \cdot e^{-\ln^2 \left(\frac{esd_{N84}}{esd_{N50}}\right)} \cdot \delta_{\text{M}} - 2}{4} \quad (12)$$

where, Eq. (12) can be solved by iteration until convergence of ρ is achieved.

1.2. Other methods and model to determine aspect ratios

To compare the results found by the presented model, the Jennings–Parslow solution (Jennings and Parslow, 1988) for rods as the limit of prolate spheroids (Eq. (13)) was considered. The solution is based on the connection between the diameter measured by the sedimentation technique d_s and the projected area diameter d_a of the prolate spheroid.

$$\frac{d_s}{d_a} = \sqrt{\frac{2 \cdot \rho \cdot \ln(\rho + \sqrt{\rho^2 - 1})}{\sqrt{\rho^2 - 1} + \rho^2 \cdot \tan^{-1}(\sqrt{\rho^2 - 1})}} \quad (13)$$

Image analysis from micrographs was also used to achieve a number-based aspect ratio distribution for rod-like minerals as proposed by Pabst et al. (2007).

2. Materials and methods

2.1. The minerals

2.1.1. Aragonite

The sample of aragonite (Fig. 1), a precipitated calcium carbonate, was used here as an example of needle-like particles. It had a specific surface area of $14 \text{ m}^2 \text{g}^{-1}$. X-ray diffraction (XRD) showed the minerals present in the sample to be aragonite (predominant), calcite and quartz. Semi-quantitative analysis by XRD showed an aragonite content of 70% and 25% calcite.

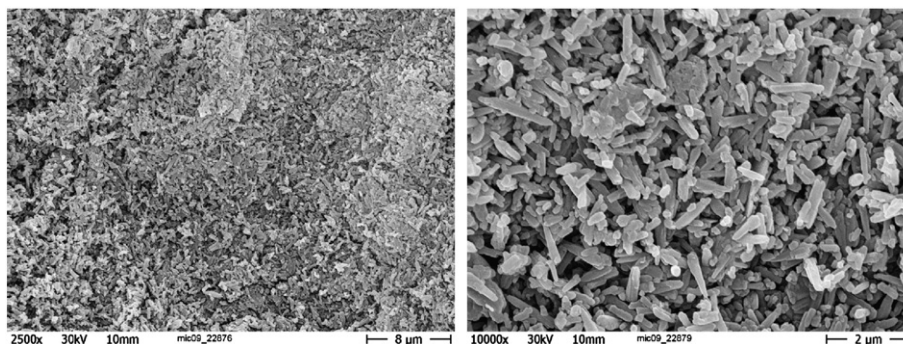


Fig. 1. SEM picture of the aragonite particles.

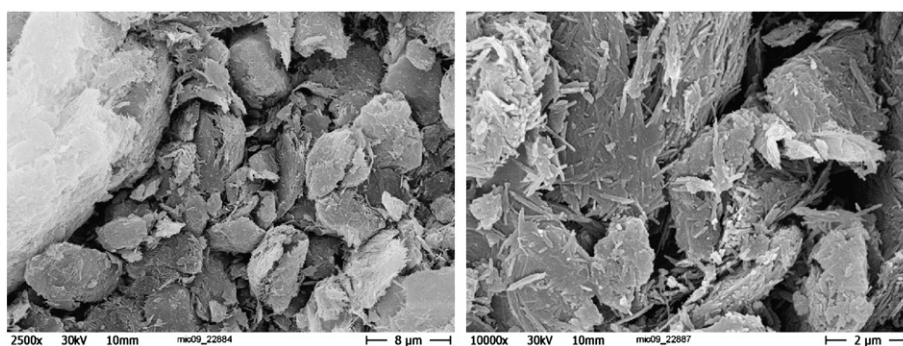


Fig. 2. SEM picture of palygorskite. In dry state the needles aggregate.

2.1.2. Palygorskite

The sample of palygorskite (Fig. 2) was obtained from BASF,¹ available as Attagel® 50. It had a specific surface area of $175 \text{ m}^2 \text{ g}^{-1}$. XRD analysis indicated the minerals palygorskite (75%), quartz (10%), montmorillonite (9%), calcite (4%) and brookite (2%).

2.2. The methods

A general overview of the theoretical and experimental aspects of particle size measurements was given by Allen (1997). Schoelkopf et al. (2008) and Gantenbein et al. (in press) gave a more detailed description about particle size measurement, specific surface area, density and XRD.

For sedimentation particle size measurements, the Sedigraph® 5120 from Micromeritics² was used. Static laser light scattering (SLLS) particle size data were recorded on the Malvern³ Mastersizer 2000. Dynamic laser light scattering measurements were performed using the Malvern³ Zetasizer Nano ZS.

2.2.1. Image analysis

Samples of 5 mg dried mineral were dispersed in 5 cm^3 ethanol by means of an ultrasonic bath. The dispersion was diluted in a ratio of 1:40 with ethanol. The samples were prepared for microscopy as follows.

Aragonite: one drop of the above described dispersion was put on a membrane filter with a pore size of $0.1 \mu\text{m}$. The membrane was fixed on the microscope sample holder and coated with carbon. The sample was studied with the Zeiss-Gemini⁴ DSM982 electron microscope

applying 5 kV acceleration voltage using an Everhart Thornley detector. Image acquisition was made by the Voyager Software from Noran⁵ Instruments having a pixel size of 22 nm .

Palygorskite: the membrane filter (pore size $0.1 \mu\text{m}$) was coated with carbon. One drop of the palygorskite dispersion was put on the coated membrane, which was fixed on the microscope sample holder. The analysis was made on the Zeiss² Ultra 55 with 1 kV acceleration voltage and an EsB-detector, also from Zeiss. Image acquisition was made again using the Voyager Software, having a pixel size of 7.4 nm .

For both samples, image analysis was performed with the digital imaging system of the Voyager software. The software calculates the aspect ratio according to Eq. (1). In the case of aragonite, 1600 particles, and in the case of palygorskite, 270 particles were automatically analysed, resulting in a number aspect ratio distribution.

Micrographs and binary images are shown in Fig. 3.

3. Results and discussion

The specific surface area of aragonite was $14 \text{ m}^2 \text{ g}^{-1}$ and the density was 2750 kg m^{-3} . The surface area of palygorskite was found to be $175 \text{ m}^2 \text{ g}^{-1}$ having a density of 2310 kg m^{-3} . For the investigated model it is crucial to apply the outer surface area of the dispersed particles, as exemplified in the case of aragonite. Minerals like palygorskite, having a porous structure (Bergaya et al., 2006; Helmy et al., 2007; Yang et al., 2010) display an inner surface area, thus not representing the external surface s of the representative cylinder (see section 2.1.1). Fig. 4 shows the nitrogen adsorption and desorption isotherms of palygorskite, giving a total pore volume of $0.35 \text{ cm}^3 \text{ g}^{-1}$ (Barret et al., 1951).

⁵ Noran Instruments Inc., 2551 West Beltline Highway, Middleton, WI, United States.

¹ BASF Corporation, 100 Campus Drive, Florham Park, NJ 07932, United States.

² Micromeritics NV/SA, Eugene Plaskyalaan 140, 1030 Brussels, Belgium.

³ Malvern Instruments Ltd., Enigma Business Park, Grovewood Road, Malvern, Worcestershire WR14 1XZ, United Kingdom.

⁴ Carl Zeiss NTS GmbH, Carl-Zeiss-Str. 56, 73447 Oberkochen, Germany.

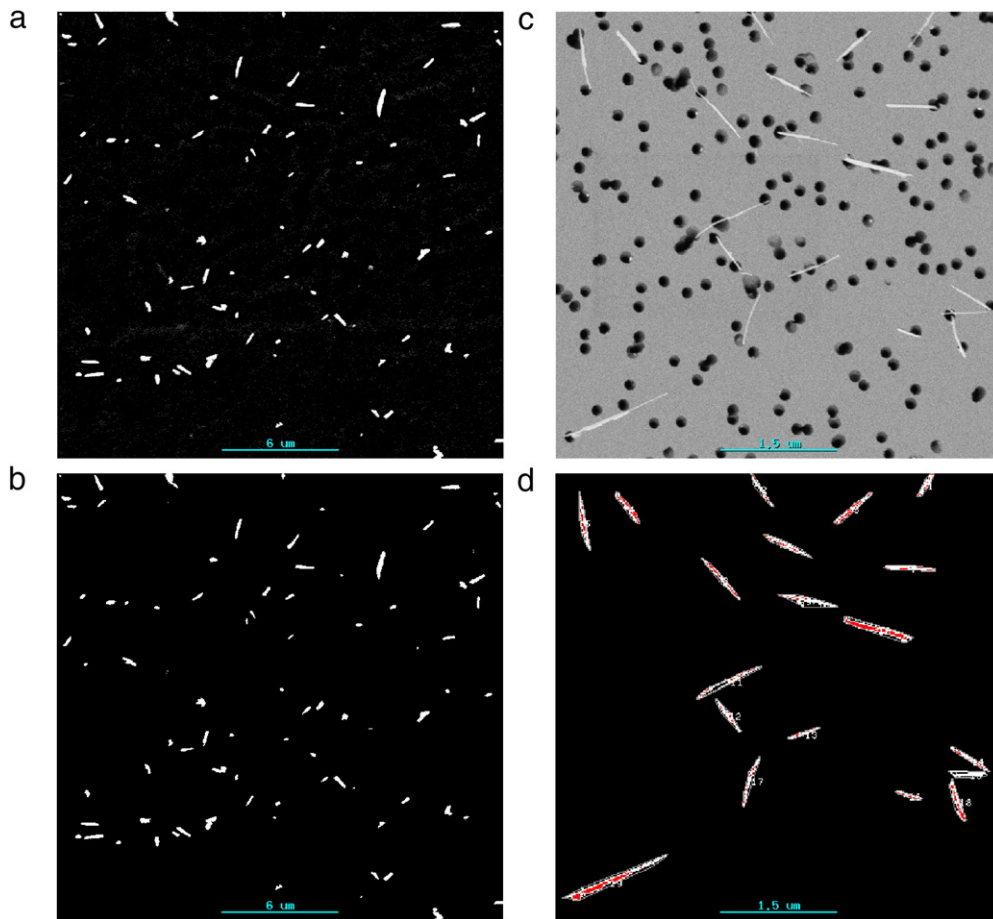


Fig. 3. a) SEM micrograph with very high contrast of aragonite used for image analysis. Image width corresponds to 22.9 μm . b) Binary image of the SEM micrograph for aragonite used for image analysis. Image width corresponds to 22.9 μm . c) SEM micrograph of palygorskite used for image analysis. Image width corresponds to 5.7 μm . d) Binary image of palygorskite used for image analysis. Image width corresponds to 5.7 μm .

The number-based particle size distributions for the aragonite, derived from the various measurement techniques, are presented in Fig. 5. The distribution data deviate only slightly from the log-normal behaviour. The fitted log-normal distribution is based on d_{N50} and d_{N84} or d_{N16} , and all fits had an $r^2 > 0.99$. A small deviation from a log-normal distribution was observed especially in the coarse region, suggesting either a slight aggregation or the presence of oversize material passing through the refining process. d_{N50} and d_{N84} or d_{N16} values, relevant for the aspect ratio calculation, are summarised in Table 2.

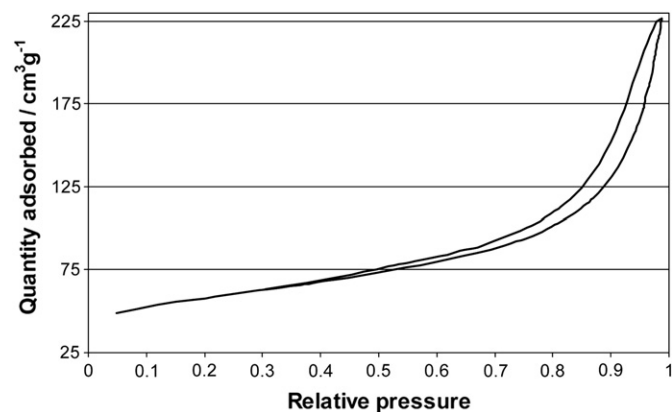


Fig. 4. Nitrogen adsorption and desorption isotherm on palygorskite.

The calculated aspect ratios are presented in Table 3. To generate a ranking, the aspect ratios were compared with the value from the image analysis (Fig. 6). The image analysis showed a median aspect ratio of 2.1 and a mode value of 1.8.

Laser scattering methods gave results best comparable with the data from image analysis, whereas sedimentation results deviated significantly from the image analysis result. This can be mainly related to the inappropriate transformation of the mass-based sedimentation result into the number-based distribution. The transform used to

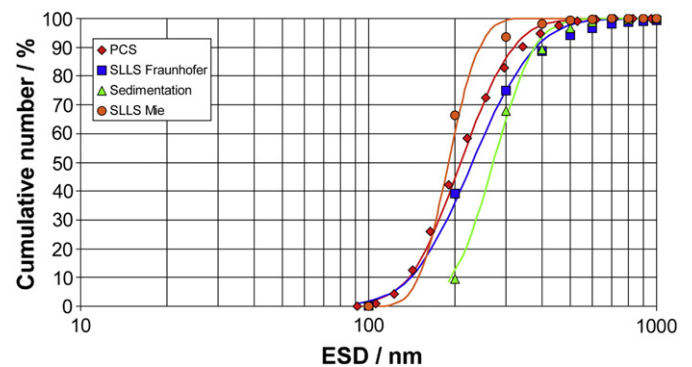


Fig. 5. Particle size distribution measured by photon correlation spectroscopy (PCS), static laser light scattering (SLLS) (Fraunhofer and Mie optics) and sedimentation of aragonite. The corresponding lines are based on a cumulative log-normal distribution calculated by the d_{N50} , d_{N84} or d_{N16} giving an $r^2 > 0.99$.

Table 2
Measured d_{N50} and d_{N84} for aragonite particles.

Method	Aragonite	
PCS	d_{N50}/nm	210
	d_{N84}/nm	290
SLLS/Fraunhofer	d_{N50}/nm	240
	d_{N84}/nm	360
SLLS/Mie	d_{N50}/nm	190
	d_{N16}/nm	160
Sedimentation	d_{N50}/nm	270
	d_{N84}/nm	350

convert from the mass to the number distribution assumed a spherical particle and a size-invariant aspect ratio. The effect of a varying aspect ratio over the size distribution has the strongest effect for sedimentation-based data because rod-like particles tend to settle faster than the equivalent spheres. This is especially important when considering coarse particles with high aspect ratios, which exceed the Brownian domain for random orientation, in contrast to fine particles with low aspect ratios, as is often the case due to the breakage of rod-like particles. It is also interesting to see that the Jennings and Parslow solution (Jennings and Parslow, 1988) could not be solved for number-based results from the sedimentation method, as the left side of Eq. (13) resulted in a value of $d_s/d_a > 1$. Also, this can be related to the effect of the size-variant aspect ratio. As a result, the aspect ratio obtained by the Jennings and Parslow method was calculated directly via the mass/volume distribution data. Interestingly, the results found for the model of Jennings and Parslow (1988), and calculated on the basis of the mass (and volume) distribution, provided a similar aspect ratio to that of the models considering sedimentation number distribution based data, i.e. the equivalent spherical assumption ignores the preferential sedimentation velocity of larger rods.

With the obtained aspect ratio the apparent particle dimensions, rod length, l , and rod width, w , were calculated for aragonite using the following procedure:

- Calculated the aspect ratio with Eq. (12).
- Calculated the mode value similar to Eq. (10) using esd instead of l .
- Insertion of the mode value and the calculated aspect ratio, ρ , using the appropriate equation from Table 1 to calculate the rod length, l .
- Calculated the rod width by dividing the rod length, l , by the aspect ratio, ρ .

The result of this procedure is shown in Table 4. The laser scattering techniques provided very similar values for the length (240–280 nm) and width (~130 nm). The sedimentation technique gave a width of 120 nm and a length of 2.5 μm .

Table 3
Calculated aspect ratios, determined by the different particle sizes and specific surface area measurements, compared with calculated values based on the model of Jennings and Parslow (1988) and those measured by image analysis.

Rank	Model	Method	ρ	Comment
1	Gantenbein et al.	SLLS/Mie	1.8	Minimum that can be determined
2		SLLS/Fraunhofer	1.9	Minimum that can be determined
3		PCS	2.2	Very sensitive to small changes in particle size data
4		Sedimentation	21.0	Inappropriate transformation from mass to number distribution
	Jennings and Parslow Eq. (13)	Sedigraph®/SLLS Fraunhofer Image analysis	21.0 ^a 1.8	Only applicable with volume/mass distribution data Given as the mode value

^a Volume based.

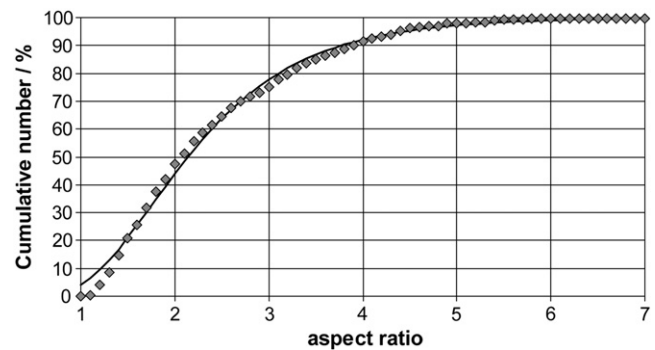


Fig. 6. Cumulative aspect ratio distribution based on the image analysis. The line corresponds to a fitted log-normal distribution with ρ_{N50} of 2.14 and ρ_{N84} of 3.33.

The particle size distribution of palygorskite could only be recorded by PCS (Fig. 7) due to the nano dimension of the particles. The curve was slightly bimodal with some coarse material between 100 and 300 nm. We tried to deagglomerate by ultrasonic treatment, but without success. We, therefore, decided to use d_{N50} (60 nm) and d_{N16} (47 nm) to describe the log-normal distribution of the data, where the fit was clearly more representative.

Based on the particle size data, the aspect ratio was calculated to be 21, giving for the rod length 210 nm and width 10 nm. These dimensions corresponded with other data published (Stoylov and Petkanchin, 1972), but the image analysis revealed an aspect ratio of 7. Other authors described that the particle length of palygorskite can vary from 10 nm up to 5 μm , and its width and thickness from 5 to 30 nm (Bergaya et al., 2006; Helmy et al., 2007). This difference between the image analysis and the presented method is caused by two factors. First of all, the image analysis showed aggregated palygorskite needles, thus underestimating the aspect ratio. Initially, the palygorskite was dispersed by following the instructions of the supplier. This procedure yielded the formation of some aggregates (Fig. 7). They formed at the drying front of the palygorskite dispersion droplets when dried on the microscope sample holder. Ethanol was selected to try to minimise this phenomenon, but was no more effective than water alone. Secondly, and most importantly, palygorskite is a highly porous mineral. The determined surface area was clearly too high with respect to the geometrically representative solid rod, and consequently the calculated aspect ratio was overestimated. This showed the limits of the presented model, which requires that the specific surface area be determined only by the external surface of the particles.

4. Conclusions

This publication evaluated a model of the particle size and specific surface area determined aspect ratio, developed previously for platy particles (Gantenbein et al., in press; Hohenberger, 2001), for application to rod-like particles. A review of the work of Jennings and Parslow (1988) explained the use of formulae that allow transformation from the equivalent spherical diameter into the rod length l as a function of the aspect ratio ρ . The newly and more fully

Table 4
Rod dimensions for the rod-like particles: rod length l and rod width w for the aragonite.

Method	l/nm	w/nm
PCS	280	130
SLLS/Fraunhofer	240	130
SLLS/Mie	240	130
Sedimentation	2480	120

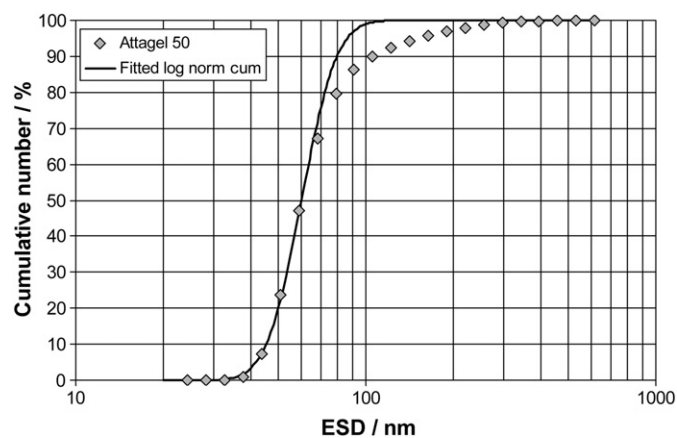


Fig. 7. Particle size distribution measured by photon correlation spectroscopy for the rod-like palygorskite particles, Attagel 50. The fitted log-normal distribution is based on d_{N50} and d_{N16} .

defined method for the determination of the aspect ratio related to the particle size and surface area for rod-like materials was tested for aragonite and for palygorskite particles adopting different particle size measurement methods. All laser scattering-based methods produced results comparable to those of image analysis. The investigated aragonite particles returned an aspect ratio of 1.8. The aragonite length l was determined to be between 240 and 280 nm with a rod width w of about 130 nm. Sedimentation particle size data indicated a too high aspect ratio of 21. The reason is related partly to the transformation of particle size from the mass distribution to the number distribution, data assuming a size-invariant aspect ratio. Nevertheless, the sedimentation-based aspect ratio gave a comparable rod width, w , of 120 nm.

Applying the model for porous minerals, like palygorskite, illustrated the drawback of using the surface area determination by nitrogen adsorption. It is only possible to receive a correct aspect ratio

if the geometrically appropriate outer surface only is used, and not the total surface area including internal pores.

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