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Wet grinding of CaCO₃ with a stirred media mill – Influence of obtained particle size distributions on pressure filtration properties

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Abstract

Chemical and process industries utilize stirred media mills for efficient fine grinding of solids. Stirred media mills, also referred to as stirred ball or stirred bead mills, generally have a good ability to produce fine particles with a relatively narrow particle size distribution. Wet grinding with vertical stirred ball mills is typically carried out for slurries containing particles smaller than 200 µm, such as industrial minerals and pigments. Filtration is an important unit operation, which is performed in order to reduce the water content of the slurry after grinding and concentration, and prior to drying and transportation. Pressure filters are used to obtain maximum dryness of the product. A number of properties of solids affect the filtration performance. The particle size and shape, the width of particle size distribution, and the net surface charge of the particles are among the factors having a significant influence on the filtration characteristics.

In this study, the dependency of the pressure filtration properties of wet ground calcium carbonate (GCC) slurries on the grinding result obtained by a stirred media mill is investigated. After grinding, subsequent filtration experiments were carried out with a laboratory-scale pressure filter. Average specific cake resistances, porosities of the filter cakes, and cake compressibility parameters were determined from the filtration data. The results showed clear correlations between the particle size data and the related filtration properties. Interesting observations were also made regarding the average porosity of the filter cakes and the uncertainty of the experiments.

Keywords: stirred media mill; ground calcium carbonate; operational conditions; pressure filtration; cake resistance; porosity

1. Introduction

The separation of mineral particles from a liquid in the industry is always affected by the upstream process conditions applied during the size reduction by the grinding circuit. One of the most important characteristics of ground solid material is the particle size distribution (PSD) of solids,

which depends on the material [1], and may have substantial influence on separation performance in cake filtration. In order to make filtration as easy as possible, the particles should ideally be as large as possible, perfectly spherical and of the same size [2]. Because of the given requirements for the mineral product, such as narrow size distribution of fillers and pigments [3], fine grinding is necessary in many cases, albeit excessive reduction of particle size should be avoided.

Fine and ultrafine wet grinding of minerals, pigments, coatings, pharmaceuticals and other materials using stirred media mills is increasing [4-6]. The size of these mills varies, from $< 1 \text{ dm}^3$ to several m^3 , depending on the application [7]. Unlike in the case of tumbling ball mills, grinding in stirred media mills is not limited by the critical rotational speed, because the mill wall is stationary and the grinding media are kept in rapid motion by an axial stirrer. This enables high energy intensity, which is beneficial when the primary aim is to obtain fine particles. Stirred media mills have the ability to produce even extremely fine powders [8,9] with narrow PSD. For the purpose of very fine grinding, stirred media mills are also energy efficient, compared with tumbling and vibrating ball mills [10].

The operational parameters of stirred media mills have a significant influence on the properties of the ground powder product. The most important properties of the product include particle size distribution [3], the shape of particles of different sizes [11], and surface properties and interactions that determine the stability of the slurry [9,11]. The grinding medium consists of balls or beads, typically made of steel, glass or ceramics. Spherical media have been shown to facilitate grinding, compared to non-spherical media [13]. In addition to factors related to equipment design (dimensions and geometry, etc.), the most important factors affecting the grinding results include, for instance, the stirring speed, ball diameter and density, charge ratio, and slurry density [14-16], and interactions between the variables [17]. More generally, the grinding result obtained in a certain time is closely related to the specific energy input of the mill [18,19], provided that the suspension is electrostatically stable and no particle agglomeration occurs [12].

Cake filtration is an important unit operation in a large number of different applications in minerals processing and chemical industries. Filtration is typically performed after grinding and enrichment operations. The objective of filtration is to remove excess liquid from the slurry to improve the overall economy of the process, e.g. by minimizing the amount of water that is to be evaporated in the final drying stage. When there is a need to produce as dry a cake as possible, pressure filters rather than vacuum filters are likely to be applied. Depending on the product requirements, cake washing, squeezing and desaturation of the cake by the use of pressurized gas can also be performed in many pressure filters. The operational conditions in the filtration stage are selected on the basis of the properties of the slurry, i.e., a high pressure difference is often helpful for relatively incompressible mineral cakes, while super-compressible materials are more readily filtered by using low pressures. Various particle sizes are used to characterize the PSD of the solids in the slurry to be filtered. For a monomodal distribution with a relatively regular shape, particle sizes of the undersize distribution, such as D_{10} , D_{25} , D_{50} , D_{75} , and D_{90} , are typically used to describe the distribution numerically. Additionally, the description of particle size can be done using the mean diameter of surface area distribution ($D[3,2]$), which is also called the Sauter mean diameter [20], and the mean determined from the volume-based distribution ($D[4,3]$) [21]. In theory, the Sauter mean diameter is also related to the filtration theory, for instance by the Kozeny-Carman equation. The prediction of filtration properties on the basis of the properties of the slurry is difficult, due to the numerous affecting factors and the interactions between them. Regarding the properties of

solids, the most important parameters include PSD [22-25], shape [26,27] rigidity/deformability [28], and electrostatic stability [29,30], especially when small particles are present [2]. Recently, cake filtration has been studied to improve the understanding of the behavior of filter cakes during filtration and compression [31] and changes in cake porosity [32].

The aim of this study is to investigate the effect of fine grinding with a stirred media mill on the average specific cake resistances and other filtration properties of ground calcium carbonate (GCC) slurries in a pressure filter. GCC was ground under different conditions to produce slurries with various size distributions of the solids, to be able to associate the grinding results with the pressure filtration properties. The topic has not been widely discussed in the literature, in spite of its importance for the minerals and pigment industries. Laboratory-scale equipment was used in both the grinding and filtration stages to minimize the variance resulting from the experimental procedure.

2. Theory and Calculations

At a glance, particle size distributions look relatively simple, but the complexity in the particle size measurement techniques and related calculations may cause misunderstandings when the results are finally interpreted. The particle characterization methods applied in this study are therefore described thoroughly. The filtration equations used for the calculation of the average specific cake resistance, cake porosity, and approximation of the cake compressibility are also introduced.

2.1. Particle characterization

Several different techniques have been developed for the measurement of particle size distributions. These techniques include for instance sieving, measurement of settling velocity of particles, laser diffraction, and direct image analysis. Because the number of small particles in mineral powders, including GCC, is much higher than the number of large particles, a number-based distribution cannot be used to describe the particle system properly. In this case, volumetric PSD is more applicable.

The diameters of D_{10} , D_{50} and D_{90} practically mean that 10 %, 50 % and 90 % of the particles in the sample are smaller than these particle diameters. Considering a volumetric PSD instead of number distribution, D_{10} , D_{50} and D_{90} represent particle diameters that divide the total volume of particles into similar volumetric classes as described above for the number distribution.

By converting the volumetric distribution to surface area distribution, the so-called surface mean diameter $D[3,2]$, or Sauter mean diameter, is obtained. The definition of the Sauter mean diameter is given in Eq. (1) [33].

$$D[3,2] = \frac{\sum_{i=1}^n D_i^3 v_i}{\sum_{i=1}^n D_i^2 v_i} \quad (1)$$

where D is the diameter of a particle (m) and v_i is the number of particles in the size fraction. The Sauter mean diameter is inversely proportional to the volume-based specific surface area, which is defined by Eq. (3) below.

The volume mean diameter $D[4,3]$ is calculated from the volumetric PSD according to Eq. (2) [33].

$$D[4,3] = \frac{\sum_{i=1}^n D_i^4 v_i}{\sum_{i=1}^n D_i^3 v_i} \quad (2)$$

The different particle sizes concerned in this study are illustrated graphically in Fig. 1. The example presented in Fig. 1 shows the measured representative particle sizes for the original GCC sample. As regards filtration, the presence of small particles in the slurry is typically the main cause for high cake resistances. It can therefore be assumed that the D_{10} and $D[3,2]$ particle sizes may correlate best with the filtration characteristics. In the Results and discussion section of this paper, the different particle sizes presented in Fig. 1 are called representative particle sizes, to make a difference between them and the characteristic particle size, which is sometimes used in filtration studies and can be solved from the Kozeny-Carman equation (see Eq. 8 below).

Fig. 1. Visualization of the different particle sizes used to describe the particle size distributions.

The specific surface area per unit volume S_v can be readily calculated for spherical particles using the Sauter mean diameter of particles [33]:

$$S_v = \frac{6}{D[3,2]} \quad (3)$$

The specific surface area relative to the mass of particles, referred to as S_w ($\text{m}^2 \text{kg}^{-1}$), can be calculated using Eq. (4) if the density of solids ρ_s (kg m^{-3}) is known.

$$S_w = \frac{S_v}{\rho_s} \quad (4)$$

2.2. Filtration equations

The calculation of the average specific cake resistance is performed with filtration equations that utilize Darcy's law. The flow through a filter cake and filter cloth can be calculated from [34]

$$Q = \frac{\Delta p A}{\alpha \mu w + \mu R_m} \quad (5)$$

where Q is the volumetric flow rate ($\text{m}^3 \text{s}^{-1}$), Δp is the pressure difference (Pa), A is the filtration area (m^2), α is the specific cake resistance (m kg^{-1}), μ is the viscosity of the liquid (Pa s), w is the weight of the cake per unit area (kg m^{-2}), and R_m is the resistance of the filter medium (m^{-1}).

In order to determine the average specific cake resistance from experimental data, Eq. (5) is converted to its reciprocal form:

$$\frac{dt}{dV} = \alpha_{av} \mu c \frac{V}{A^2 \Delta p} + \frac{\mu R_m}{A \Delta p} \quad (6)$$

where t is time (s), V is the volume of the filtrate (m^3), α_{av} is the average specific cake resistance (m kg^{-1}), and c is the filtration concentration (kg m^{-3}), i.e. the mass of dry solids in cake divided by the volume of the filtrate. After integration from the starting point of constant pressure filtration, Eq. (6) finally becomes

$$\frac{t}{V} = \frac{\alpha_{av} \mu c}{2 A^2 \Delta p} V + \frac{\mu R_m}{A \Delta p} \quad (7)$$

The average specific cake resistance α_{av} is calculated for each cake from Eq. (7), utilizing the filtrate accumulation data recorded during each filtration experiment.

The average specific cake resistance in the filtration of incompressible cakes is theoretically related to the Sauter mean diameter of particles and the porosity of the filter cake by the Kozeny-Carman equation:

$$\alpha_{av} = \frac{180 (1 - \varepsilon)}{\rho_s (D[3,2])^2 \varepsilon^3} \quad (8)$$

where ε is the porosity, i.e. the void ratio, of the filter cake (-). The porosity of the filter cake increases with the distance from the filter medium [35]. Eq. (8) should not be used for compressible cakes [34]. When the local porosity cannot be measured, the average porosity of the whole cake can be calculated from Eq. (9).

$$\varepsilon_{av} = \frac{V_v}{V_c} \quad (9)$$

where V_v is the void volume (m^3) and V_c is the total volume of the cake (m^3).

The compressibility index of the filter cake n (-) can be approximated on the basis of the correlation (Eq. (10)), presented in the literature for instance by Ripperger et al [36].

$$\alpha_{av} = \alpha_0 \left(\frac{p_s}{p_0} \right)^n \quad (10)$$

where α_0 is the average specific cake resistance (m kg^{-1}) at unit applied pressure p_0 (Pa). It is usually assumed that the solid compressive stress p_s equals the applied pressure difference Δp during the cake compaction stage.

3. Materials and methods

The batches of slurry for the experiments were prepared by dispersing ground calcium carbonate (GCC, Nordkalk Oy, Finland) in water. The mass and solids content of the slurry were 2.5 kg and 20.0 w-%, respectively, in all experiments. The density of solids was $2,700 \text{ kg m}^{-3}$, according to the product description obtained from the manufacturer of the GCC. Prior to the grinding experiments, the GCC slurry was analyzed for particle size and filtered with the pressure filter described below, to obtain necessary data about the initial properties of the slurry. The particle size distributions (PSD) of the initial and milled samples were measured by using a Malvern Mastersizer 3000 laser diffraction particle size analyzer. The slurry samples were dispersed in water to obtain a solids concentration of 0.1 g dm^{-3} . Two parallel sub-samples were measured five times, without ultrasonication, using a stirrer speed of 3000 rpm. Fig. 2 presents the volumetric PSD of the original, non-milled solids. In the case of this sample, the relative standard deviations for D_{10} , D_{50} and D_{90} were 1.4, 0.7 and 0.6 %, respectively.

Fig. 2. Volumetric particle size distribution of the original ground calcium carbonate (GCC) sample.

The slurries were then ground with a laboratory-scale stirred media mill, using 3 kg of stainless steel beads of three different diameters (1, 2, and 3 mm), three grinding times (5, 10, and 15 min), and three grinding speeds (300, 500, and 700 rpm). The inner diameter and the height of the stirred media mill were 152 mm and 300 mm, respectively. Within the mill, stirring was performed by a pin stirrer with the rotational diameter of 120 mm. The pins were located on opposite sides of the stirrer shaft, in total 6 pairs of pins attached crosswise on the shaft, with a gap of 28 mm between these pairs of pins. The diameter of each cylindrical pin was 12 mm. Fig. 3 illustrates the dimensions of the mill and the stirrer.

Fig. 3. Dimensions of the pin stirrer and the stirred media mill in millimeters.

The experiments were carried out according to a three-level full-factorial experimental design with five repetitions for the center point, as shown in Table 1. The order of the experiments was randomized to minimize the time-dependent variations on the results [37]. Three grinding variables were considered at three different levels, which were chosen on the basis of previous experience, and this resulted in a total of 31 grinding experiments. In addition to these 31 experiments, the same experimental and analytical procedures were carried out for the original GCC sample (Test 0 in Table 1).

An in-depth discussion about the effect of grinding variables on the obtained grinding result is out of the scope of this paper, and the results presented in Table 1 are discussed by concentrating on the dependency of the filtration properties on the grinding results. Probably the most unclear points presented in Table 1 that must be explained in closer detail are the grinding speed, which is expressed as the rotational frequency (rpm) and the tip speed of the stirrer pins (ms^{-1}); and definitions of the particle sizes $D[3,2]$ and $D[4,3]$, as well as the specific surface area of the particles (S_w), which are explained in Section 2.

Table 1. Grinding parameters and results. Test 0 indicates the original sample. The center point of the experimental plan was repeated five times (Tests 1, 5, 8, 16, and 23). The definition of particle sizes is given in Section 2. S_w means specific surface area.

Test	Bead size (mm)	Grinding time (min)	Grinding speed / Tip speed (rpm / ms ⁻¹)	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	D[3,2] (μm)	D[4,3] (μm)	S_w (m ² kg ⁻¹)
0	-	-	-	4.02	28.6	83.4	9.29	36.9	645.6
1*	2	10	500 / 3.14	1.38	6.2	25.7	3.54	11.1	1694
2	3	15	300 / 1.88	1.43	6.89	21.8	3.69	10.4	1627
3	3	5	300 / 1.88	2.39	15.9	53.0	6.09	23.2	985.6
4	3	15	700 / 4.40	1.14	4.70	13.8	2.89	7.10	2076
5*	2	10	500 / 3.14	1.33	6.01	23.1	3.45	10.6	1740
6	1	15	300 / 1.88	1.59	10.0	51.1	4.35	19.7	1380
7	3	5	700 / 4.40	1.38	6.38	19.5	3.54	9.50	1695
8*	2	10	500 / 3.14	1.23	5.29	18.7	3.16	9.01	1900
9	1	15	700 / 4.40	0.95	3.13	11.1	2.23	6.76	2689
10	1	5	300 / 1.88	2.57	21.8	80.4	6.85	32.9	876
11	1	5	700 / 4.40	1.55	9.01	61.3	4.21	22.0	1425
12	3	10	500 / 3.14	1.33	5.94	17.8	3.4	8.82	1765
13	1	10	500 / 3.14	1.41	8.27	63.6	3.91	21.9	1535
14	2	5	500 / 3.14	1.72	9.93	43.3	4.52	17.7	1329
15	2	10	700 / 4.40	0.92	3.24	8.59	2.20	5.02	2725
16*	2	10	500 / 3.14	1.23	5.85	23.2	3.27	10.6	1833
17	2	10	300 / 1.88	1.72	10.4	45.1	4.58	18.3	1310
18	2	15	500 / 3.14	1.04	4.24	13.4	2.66	7.01	2259
19	2	5	300 / 1.88	2.21	16.0	60.2	5.81	24.7	1033
20	3	10	300 / 1.88	1.80	10.2	32.3	4.65	14.8	1291
21	1	10	300 / 1.88	1.86	13.3	55.9	5.05	22.3	1189
22	1	5	500 / 3.14	2.09	18.6	80.4	5.78	31.2	1038
23*	2	10	500 / 3.14	1.27	5.76	22.2	3.30	9.81	1817
24	2	5	700 / 4.40	1.25	5.76	19.6	3.27	9.49	1834
25	2	15	300 / 1.88	1.43	7.71	36.4	3.86	14.4	1553
26	3	15	500 / 3.14	1.14	4.81	14.0	2.92	7.13	2057
27	3	10	700 / 4.40	1.07	4.35	12.7	2.71	6.46	2213
28	2	15	700 / 4.40	0.878	2.7	6.68	1.96	4.19	3054
29	3	5	500 / 3.14	1.7	8.91	27.9	4.36	13.3	1375
30	1	10	700 / 4.40	1.05	4.19	23	2.7	10.5	2224
31	1	15	500 / 3.14	1.19	5.46	42.4	3.18	15.1	1887

*The center point of the experimental plan (five repetitions)

After grinding (within 24 hours), the total volume of the slurry was recovered from the mill and placed in a mixing vessel ($V = 3 \text{ dm}^3$, propeller with baffles used), from which the samples for the PSD measurements were taken. The PSD of the solids was measured and the slurries were filtered with a Nutsche-type pressure filter under the pressures of 200, 400, and 600 kPa.

The filter utilized in this study was a laboratory-scale pressure filter with a chamber volume of 350 cm^3 . The filter was operated by using a constant mass of slurry, 0.25 kg, for each experiment. The pressure difference for the filtration was obtained from compressed nitrogen. Prior to each test, the pressure was set to the selected filtration pressure, and the slurry sample, taken from a properly stirred tank, was poured into the filter. After closing the inlet valve, filtration was started by opening the gas valve. A cellulosic disc (T1000, Pall Corporation, Germany) with a thickness of 3.6 mm was used as the filter medium, and each experiment was performed with a fresh filter medium to keep the initial resistance of the filter medium practically constant. The effective filtration area was 18.9 cm^2 , and all the experiments were carried out at room temperature 22°C .

The accumulation of filtrate during the experiments and the exact pressure in the filter chamber were recorded. Utilizing the recorded data together with the measured cake dimensions, mass, and moisture content, it was possible to calculate the average specific resistance and the approximate average porosity of each cake. The approximate cake compressibility indices were determined on the basis of experiments performed with the same slurry under different pressures. Because the aim of this study was to clarify the effect of the grinding result on the pressure filtration properties, the effects caused by each grinding variable are not discussed. In the future, a more detailed analysis of the interactions between the grinding variables and filtration characteristics will be performed by utilizing regression models.

4. Results and Discussion

4.1. General evaluation of the results

The results show that the obtained particle size after grinding correlated clearly with α_{av} . The average specific cake resistances were compared with the Sauter mean diameter, i.e. $D[3,2]$ and with other statistical particle sizes, such as the median and the $D[4,3]$ particle size.

Fig. 4 shows the correlation between the average specific cake resistances and the particle sizes D_{10} , D_{50} , and D_{90} of the solids in the filtered slurries. Power-type trend lines have been added to Fig. 4 to make the trends clearer to observe. It can be roughly generalized that, irrespective of the representative particle size, the average specific cake resistance was slightly increased with the applied filtration pressure. The correlation between the D_{10} particle size and α_{av} was very clear, as illustrated in Fig. 4(a), which shows that when the D_{10} particle size is smaller than one micron, α_{av} increases at an extreme rate, indicating that especially the presence of submicron particles have a significant influence on the level of how difficult the filtration actually was. In the case of Fig. 4(b), where exactly the same cake resistances as in Fig. 4(a) are presented as a function of the D_{50} particle size, the correlation is still clear, but the data starts to diverge slightly more. The largest representative particle size D_{90} , shown in Fig. 4(c), does not have such a clear effect on α_{av} , which

can be associated to two explaining factors. First, the high D_{90} particle size does not exclude the possibility that very fine particles exist and dominate the separation process, and second, the number of large particles in the analyzed sample is much lower than that of small particles, which makes the sampling error and plain randomness in the analysis of large particles more emphasized.

Fig. 4. Relationships between (a) D_{10} , (b) D_{50} and (c) D_{90} particle sizes and the corresponding average specific cake resistances.

Further, when the same average specific cake resistances as above are plotted as a function of the Sauter mean diameter (Fig. 5(a)), the graphs look again quite consistent. As can be observed by comparing Figs. 4(a) and 5(a), the $D[3,2]$ particle size is roughly the double, of that of D_{10} . However, the volume average mean diameter $D[4,3]$, presented in Fig. 5(b), does not correlate so smoothly with α_{av} . As above with the D_{90} particle size, the data points that are most divergent from the corresponding trend lines, diverge relatively consistently at all filtration pressures. This

observation supports the assumption that factors related to the slurry, sampling and analyses may be the main contributors to the scattered data.

The average specific cake resistances and the weight-based specific surface areas of the solids are presented in Fig. 5(c). As described above in Section 2.1., the specific surface areas were calculated using the Sauter mean diameter and the solid density. It can be observed in Fig. 5(c) that there is a relatively clear correlation between the specific surface area S_w and α_{av} . Additionally, the effect of particle shape on the specific surface area is significant. High specific surface area resulting from the particle shape is therefore a typical reason for high average specific cake resistances in pressure filtration.

Fig. 5. Dependence of the average specific cake resistance on particle sizes (a) $D[3,2]$, (b) $D[4,3]$, and (c) the weight-based specific surface area S_w .

The void fraction of the filter cake is called porosity (Eq. (9)). The porosity of a packed bed, such as a filter cake, depends on a couple of important factors, including particle size distribution, particle shape, and the arrangement of particles within the porous matrix. In theory, the porosity of cakes consisting of incompressible spherical particles with a monosize PSD but different sizes is constant. It has been shown in previous studies that porosity may be strongly reduced when only binary [38,39] or ternary [40] mixtures are considered. Binary and ternary mixtures stand for mixtures consisting of only two or three different particle (sphere) diameters. However, in practical filtration applications it is clear that the mechanism of cake formation is affected by the particle size, which affects the resistance of the cake, influences the settling rate of the particles, and has an impact on the deposition of the particles in the cake [2]. In the case of the present study, it is unclear whether the particle shape was dependent on the particle size. The particle shape has been reported to depend on the grinding method [41] and for instance the grinding time [42], so it is probable that there has been some correlation between the particle size and shape in this study also.

Another factor to be considered here is the filtration pressure, which has an influence on the particle arrangement during the cake formation and compression stages. Typically, filter cakes are more or less compressible, which in practice means that an increase in the filtration pressure causes reduction in cake porosity. In a special case, when all particles are spherical, of the same diameter, non-compressible, and in a stable point contact with each other, the porosity is not affected by the particle size or pressure. The dependency of the average porosity ϵ_{av} of the GCC filter cakes on the particle sizes D_{10} , $D[3,2]$ and $D[4,3]$ is illustrated in Fig. 6(a-i). The filtration pressure can be seen to have some effect on the porosity of the cakes when the pressure is increased from 200 to 400 kPa, but the difference between porosities obtained at 400 and 600 kPa is practically negligible.

On the basis of Fig. 6(a-i), it is easy to conclude that the porosity of the filter cakes can be related to D_{10} , $D[3,2]$ and $D[4,3]$ particle sizes. The correlation is slightly negative, which means that at least one of the above-mentioned factors, namely particle size distribution, particle shape, or the arrangement of particles in pressure filtration has changed when GCC has been ground in the stirred media mill. Based on the data presented in Fig. 6(a-i), it is apparent that the porosity can be more consistently related to particle size when a low filtration pressure is used. Scattering of the data takes place especially when the highest filtration pressure of 600 kPa is used. This observation could basically be due to the faster cake formation and possibly also to increased but more or less random channeling of the flow through large pores. The importance of investigating the relationship between cake porosity and PSD when predicting cake permeability (and resistance) has been emphasized previously by Sorrentino and Anlauf [22-24] and Sorrentino [43].

Fig. 6. Measured cake porosities obtained for slurries with different D_{10} , $D[3,2]$ and $D[4,3]$ particle sizes at filtration pressures of 200, 400, and 600 kPa.

The third reason for the decreasing average porosity with increasing representative particle size observed in Fig. 6 is the width of the particle size distribution. In order to see whether the width of the distribution might have an influence on the average porosity in this case, subtraction $D[4,3] - D[3,2]$ was done and the results are presented in Fig. 7a. Previously, among others, Karbstein et al. [44] have used the span, i.e. the ratio $(D_{90}-D_{10})/D_{50}$ to describe the width of PSD. The span is presented in Fig. 7b for comparison. It can be observed that the difference $D[4,3] - D[3,2]$ correlates clearer with the average porosity. The most probable reason for this is that the D_{90} particle size is only a moderate measure of the large end of the distribution, while the $D[4,3]$ size, which in this study was larger than D_{50} but smaller than D_{90} , is less affected by experimental error and random error. In the case of this study, the D_{90} particle size was, on average, 20 times larger than the D_{10} particle size, which overemphasized the dependence of the span value (Fig. 7b) on D_{90} . Additionally, there is a good reason why the absolute width of the distribution should not be used here: the largest particles determine the width of the distribution, and the resolution in the coarse end of the distribution is inappropriately rough for reasonable comparisons.

It is relatively clear to see in Fig. 7 that the width of the particle size distribution has actually a significant influence on the porosity of the filter cake. A narrow size distribution seems to cause larger porosity than a wide distribution, which applies independent of the filtration pressure. The cake porosities obtained in this study comply with the porosities of various CaCO_3 cakes reported in the previous literature [32].

Fig. 7. Effect of the width of particle size distribution on the average porosity of filter cakes, using two definitions for the width: (a) the difference $D[4,3] - D[3,2]$ and (b) the span $(D_{90} - D_{10}) / D_{50}$.

In cake filtration, it is typical that an increase in the average specific cake resistance is caused by a filter cake with a decreased porosity. Fig. 8 presents the relationship between the measured average porosity ϵ_{av} and α_{av} . It can be easily concluded from Fig. 8 that the correlation between ϵ_{av} and α_{av} is negligible, and the results scatter quite randomly. This is an interesting result, because both ϵ_{av} and α_{av} were shown above to be clearly dependent on the grinding result. One apparent characteristic that may explain this scattering is again the width of the PSD (Fig. 7). Because of the different grinding conditions applied, the shape of the particles may also have been different between the experiments. Furthermore, other effects which were not investigated in this study, such as settling of particles during filtration, could have influenced on the cake porosity. Investigation of the local cake properties could help to explain the results presented in Fig. 8.

Fig. 8. Dependence of the average specific cake resistance on the average porosity of filter cakes.

Neither the particle size nor the width of the PSD had an influence on the compressibility index n in the pressure filtration stage. According to its definition (Eq. 10), n equals zero for incompressible materials, when α_{av} does not increase with the applied pressure, and can exceed 1 when the filtered material is super-compressible. The n values ranged from 0.11 to 0.43, and 80 % of the n values were between 0.15 and 0.30, so it can be generally concluded that the compressibilities of the GCC cakes were low.

4.2. Evaluation of repeatability

The uncertainty resulting from the experiments themselves can be associated with the two process stages, grinding with the stirred media mill and filtration with the pressure filter. The total error generated in the grinding stage was evaluated by comparison of five repetitions performed for the center point of the experimental plan. The variation of the different representative particle sizes obtained by repeating the same experiment is presented in Table 2.

As shown in Table 2, the quantity of total experimental uncertainty generated in the grinding stage is dependent on the representative particle size that is investigated. Generally, the variability, which in this case is expressed as standard deviation and relative standard deviation (RSD), increases with the particle size and is therefore clearly highest for the D_{90} particle size. The level of the obtained standard deviations is very typical for experimental work with industrial minerals and pigments.

Table 2. Evaluation of the repeatability of the grinding experiments regarding particle size.

Test #	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	D[3,2] (μm)	D[4,3] (μm)
1	1.38	6.2	25.7	3.54	11.1
5	1.33	6.01	23.1	3.45	10.6
8	1.23	5.29	18.7	3.16	9.01
16	1.23	5.85	23.2	3.27	10.6
23	1.27	5.76	22.2	3.30	9.81
<i>Key statistical numbers</i>					
Average (μm)	1.29	5.82	22.6	3.34	10.2
Standard dev. (μm)	0.07	0.34	2.53	0.15	0.82
RSD (%)	5.10	5.86	11.20	4.51	8.03

When also the experimental uncertainty caused by the filtration stage is taken into account, the relative error becomes larger. Table 3 presents the average specific cake resistances for the repeated experiments and the key statistical numbers for each of them. On the basis of Table 3, it is difficult to say whether the repeatability is dependent on the applied filtration pressure. Comparison between Tables 2 and 3 reveals the same effect that can also be observed in Figs. 4 and 5: small changes in the particle size distribution have a direct influence on α_{av} when the slurry is filtered. A similar observation has been made earlier in the case of bioslurry filtration [43]. In large-scale industrial filters, variation of the PSD is often observed as unexpected variation of the filtration capacity, even though the process parameters are kept constant.

Table 3. Evaluation of the overall repeatability of the experiments including grinding and filtration for the center point of the experimental plan.

Test #	$\alpha_{av} \cdot 10^{11} \text{ (m kg}^{-1}\text{)}$		
	α_{av} (2 bar)	α_{av} (4 bar)	α_{av} (6 bar)
1	1.17	1.28	1.46
5	1.31	1.59	1.52
8	1.53	1.75	1.90
16	1.40	1.58	1.74
23	1.44	1.70	1.83
<i>Key statistical numbers</i>			
Average $\alpha_{av} \cdot 10^{11} \text{ (m kg}^{-1}\text{)}$	1.37	1.58	1.69
Standard dev. $\cdot 10^{10} \text{ (m kg}^{-1}\text{)}$	1.38	1.821	1.94
RSD (%)	10.08	11.53	11.47

The accumulation of error during the experiments can be seen by comparing the relative standard deviations presented in Table 2 (grinding) and Table 3 (grinding and subsequent filtration). Further, in order to get an impression of the uncertainty related to the filtration stage, and perhaps also

homogeneity of the GCC, three filtration experiments for the original GCC were performed at the pressure of 400 kPa, and two experiments were carried out at 600 kPa. The results imply that the repeatability of the filtration experiments was good. The relative standard deviation (RSD) was only 2.5 % for the three-point test series. It does not make sense to calculate the standard deviation for the two tests performed at 600 kPa, but it can be stated that the repeatability seems good also in this case, because the average of the two α_{av} values was $1.856 \cdot 10^{11} \text{ (m kg}^{-1}) \pm 0.85 \text{ \%}$.

5. Conclusions

The dependence of the pressure filtration properties of ground calcium carbonate slurries on the grinding results obtained by a stirred media mill was investigated in the study. The results showed that the average specific cake resistance α_{av} correlated relatively well with small representative particle sizes, such as D_{10} and $D[3,2]$. A small representative particle size indicated a high α_{av} . However, α_{av} could not be associated with the average porosity of the filter cakes, although the porosity was also observed to be dependent on the particle size distribution of solids. The average porosity of the cakes decreased with the increasing width of particle size distribution, which in turn became narrower when the particles were ground to higher fineness. Finer particles formed more porous cakes, which can be partially explained by the particle size distributions, as well as particle shape. The finer particles were also more difficult to filter, resulting in slow cake formation, which probably increased the porosity of the cakes. More generally, the results of this study illustrated very clearly that excessive grinding of particles has a strong negative effect on filterability, even though the changes in the size distributions did not seem to be very dramatic.

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