Solid-liquid separation of ultrafine Calcium carbonate (CaCO_3) suspensions by using therm-compression filtration technology

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Abstract. The ultrafine CaCO_3 was usually produced by wet chemical synthesis technique currently. The solid-liquid separation techniques of mechanical filtration and two-stage thermal drying were needed to separate the ultrafine powder from the CaCO_3 slurry. A new technology of thermo-compression filtration was taken to dispose the ultrafine CaCO_3 suspensions for purpose of simplifying the traditional producing technique in this paper. The thermo-compression filtration not only combined the process of mechanical filtration and thermal drying on one single filter press, but also saved energy because of its non-phase-change thermo-compression drying characteristic. The external heat energy was used to offer assistant thermo-motive, but not to vaporize all of the moisture in the saturated cake. The experimental results indicated that the thermo-compression filtration was much more effective than mechanical filtration or thermal drying respectively. The moisture content of filter cake after thermo-compression drying was about 18.75%~21.89%, much lower than that after mechanical filtration, about 25.5%~28.5%. Furthermore, to keep a relative higher temperature of drying plates when mechanical filtration process was an available method to obtain the product with lower moisture content, but use a minimum working time.

1 Introduction

Ultrafine calcium carbonate (CaCO_3) is an important chemical product which is widely used in the fields of plastics, rubber, paper, paints, adhesive, sealant, oil ink, pharmaceutical, food, and so on[1-4]. Commercial production of ultrafine CaCO_3 powder uses a wet chemical precipitation technique. However, the technique causes considerable agglomeration of particles during synthesis, and requires the precise control of a number of operation parameters to obtain a better distribution of nanoparticles[5]. Another CaCO_3 nanoparticle synthesis method is through carbonation of lime solution in microemulsion systems. This method again requires the precise control of various operation parameters [6]. Both methods synthesized the CaCO_3 as slurry. The Solid-liquid separation process was needed to obtain the CaCO_3 powder.

Centrifugal or mechanical filtration dehydration methods were used currently to dehydrate the water of CaCO_3 slurry and the moisture content of the product which seen like paste was 55% ~ 65%. Then, two stages of thermal drying operations were taken separately. The first stage of thermal drying operation usually used the drying

machineries such as drying chamber, drying conveyor, disc dryer and vacuum rake dryer, et al. The moisture content of the product after this stage was about 20%. The second stage usually used the methods of rotating flash drying or air drying process to drying the product to the moisture content of 0.5%. Those two drying operations would take about 70% of energy consumption of the whole production process, especially the first stage.

A new thermo-compression filtration technology was used in this paper to instead the mechanical filtration and the first stage of drying. The filter cake would send to the second stage of thermal drying directly. This will simplify the manufacturing technique and economize the energy consumption.

2 Thermo-compression filtration technology

The thermo-compression filtration technology which had been used in some areas of coal preparation, ore concentrate, Ti-gypsum and so on[7-9] was also suitable for realizing the solid-liquid separation of ultrafine CaCO_3 suspensions. The thermo-compression filtration process

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consists of two stages. The first stage is mechanical filtration producing the saturated cake that is similar to the conventional mechanical pressing. The second stage is thermo-compression drying which starts after the formation of saturated cake in the filter chamber (Fig.1). Therefore, the entire process of mechanical filtration and thermo-compression drying can be achieved continuously on a single filter press [10,11]. In the second stage the heating medium was pumped into the drying plate (as shown in Fig.1). The saturated cake close to the drying

plate was heated, and the moisture in those parts of saturated cake was vaporized and expanded. Thus the moisture in another part of saturated cake which far away from the drying plate could be pushed out as liquid phase by the vapor pressure. That meant the heat energy was used to offer assistant thermo-motive but not to vaporize all of the moisture in the saturated cake. Therefore the thermo-compression filtration technology was much more energy conservation than traditional mechanical filtration and thermal drying.

(A) Mechanical filtration stage (B) Thermo-compression drying stage
 a – Suspension b – Filtrate c – Compressed air d – Heating medium
 e – Filter cake 1 – Recessed filter plate 2 – Drying plate
 3 – Squeezing membrane 4 – Filter medium

Figure 1. Schematic Diagram Showing the Operating Principle of the Thermo-compression Filtration System[7]

Fig. 2 shows the state of the capillary water during the thermo-compression drying process. When the thermo-compression drying process started, the capillary water close to the drying plates was heated and changed from liquid to steam, and then the volume of the steam expanded. The capillary water far away from the drying plates permeated the filter medium and was removed when the saturated vapor pressure (P_s) was higher than the sum of capillary pressure (p) and ambient pressure (P_0) shown by Eq.1 [12]:

$$P_s \geq P_0 + p \geq P_0 + 2\sigma \cos \theta / r \quad (1)$$

where, P_s , P_0 , p , and r are the saturated vapor pressure (MPa), the ambient pressure (MPa), the capillary pressure (MPa) and the capillary radius (m) respectively. The capillary pressure (p) and the contact angle (θ) of water depended on the characteristics of the material and the temperature. The filter chamber will be evacuated to reduce P_0 then P_s will decrease as well.

Actually the capillary is not straight but curving and irregularity which will influence its characteristic of heat and mass transfer such as the capillary pressure (p) and the contact angle (θ). Therefore, the tortuosity conception of porous medium was introduced and the thermo-compression filtration kinetics equation was established by combining the Clapeyron-Clausius thermodynamic equation and the material characteristics, as shown by Eq.2.

$$V_m = \frac{d_p^2 \varepsilon^3}{43(1-\varepsilon)^2 \mu L} \cdot \frac{R}{V'' - V'} \ln T + C \quad (2)$$

Figure 2. Capillary Water in the Saturated Cakes

where, V_m , ε , d_p , L , V'' , V' , R and T are the average flow velocity in the bent capillary(m/s), porosity of porous medium, granular average effective diameter (m), straight line of both ends of the capillary (thickness of filter cake, m), specific volume of steam (m^3/kg), specific volume of liquid (m^3/kg), latent heat of vaporization (kJ/kg) and the absolute temperature (K). Thus, the thermo-compression solid-liquid separation efficiency has direct relationship with the porosity (ε), granular average effective diameter (d_p), thickness of filter cake (L) and thermo-compression drying temperature (T). When the thickness of filter cake (L) is certainly, the finer the material granularity, the smaller the porosity (ε) is, and the average flow velocity in the bent capillary (V_m) is lower then. The thermo-compression solid-liquid separation efficiency only can be increased by enhancing the thermo-compression drying temperature (T) to enlarge the saturated vapor pressure (P_s).

3 Experimental

3.1 Sample treatment and analysis

The sample ultrafine CaCO_3 was produced by Shanghai HuiJing sub-nanometer new material Co., LTD. The ultrafine Calcium carbonate (CaCO_3) suspensions with the concentration of 200g/L were prepared. The dispersing agent of sodium dodecyl benzene sulfonate (SDBS) with the content of 0.5~0.8% of CaCO_3 's quality was added in the CaCO_3 suspensions to increase its stability.

3.2 Experimental method and instrument

Fig. 3 shows the entity laboratory equipment of this system. There were two recessed filter plates with membrane on the surface and one drying plate with snakelike heating pipe that composed to a filter unit. Only one unit was used in this paper to take the experiment. The CaCO_3 suspensions were prepared first and then were pumped into the filter chamber by reciprocating diaphragm pump and the filter cake formed gradually. This process was called mechanical filtration. The reciprocating diaphragm pump was not only to transport the material but also proffered the filtration pressure on 0.8MPa. Then the saturated steam of 150°C which produced by the steam generator was pumped into the drying plate to heating the filter cake. This process was called thermo-compression drying. Those two processes together were called thermo-compression filtration.

There were three experimental methods were taken in this paper as following:

Masked as TC-a: The CaCO_3 suspensions were pumped into the filter chamber by reciprocating diaphragm pump. After 80 minutes later the pump stopped, and the filter cake was sampled to test the moisture content, then the thermo-compression drying process started and lasted 30 minutes.

Masked as TC-b: The experimental processes were the same as TC-a, but the mechanical filtration process lasted 25 minutes and the thermo-compression drying process lasted 30 minutes.

Masked as TC-c: The drying plate was kept the temperature of 70~80 °C in the mechanical filtration process and the thermo-compression drying process started after 15 minutes when the mechanical filtration process was started. The mechanical filtration process lasted 30 minutes and the thermo-compression drying process lasted 25 minutes. That meant there were 15 minutes working together time of mechanical filtration and thermo-compression and the whole process lasted 40 minutes.

Figure 3. Laboratory equipment of the thermo-compression filtration system

3.3 Analysis method

The moisture content of the filter cake was measured by Rapid Moisture Analyzer (Mettler Toledo HR83). The particle size distribution of the powders of raw material and

filter cake were analyzed using particle size distribution analyzer (PSDA, Malvern Zetasizer Nano). 0.5% SDBS was added to improve the dispersion of CaCO_3 in distilled water and a total of 90 seconds of ultrasounds were applied to each sample before being analyzed by the PSDA. The scanning electron microscope (SEM) micrographs of raw material and filter cake were obtained using Hitachi S-4800 microscope.

4 Results and discussion

The experimental results of those three different experimental methods were shown in Table 1. It was found that the moisture content of filter cake after thermo-compression drying, about 18.75%~21.89%, was much lower than that after mechanical filtration, about 25.54%~28.49%. TC-a took more long time than TC-b, but the solid content of filter cakes that they obtained were basically the same, and the moisture content of filter cake (TC-a) was just a little lower than TC-b. So the TC-a experimental method could receive a relatively better thermo-compression drying effectiveness, but the economical efficiency was lower than TC-b according to contrast the working time. The dehydrating amounts of those two thermo-compression drying processes were 0.154kg and 0.156kg, separately. That water was removed as liquid phase but not gaseous phase. That meant a large number of energy which was used to evaporate the water was saved and just a fraction of the energy was worked to heat the water close to the drying plates. If we take no account of that fraction energy, the thermo-compression drying processes had the level of energy-efficient as 252.8kJ/kg(dry basis) of TC-a and 266.1kJ/kg(dry basis) of TC-b. The level of energy-efficient was calculated on the basis of the heat of evaporation of 100°C water as 2258.77kJ/kg.

The TC-c method was much similar to the industrial processes as a semi-batch processing. The moisture content of filter cake (TC-c) was lower than TC-b, and the solid content of filter cake that TC-c obtained was much more than TC-a and TC-b, although TC-c's working time was the least. That meant to keep a relatively higher temperature of drying plates when mechanical filtration process was beneficial to feed because high feeding temperature could reduce the viscosity of suspensions. Thus the TC-c method was a most efficient method. The moisture content of the filter cake was lower than 20%, and the product could send to the second stage of thermal drying directly to remove the remainder moisture.

Fig. 4 shows the SEM images of raw material and filter cake. Fig.5 shows the particles size distribution of raw material and filter cake. It was found that the CaCO_3 powder of raw material and filter cake had the similar morphology by SEM images, but their particle size had some difference. The particle size distribution of raw material was wide than filter cake, and there was a little more fine particles of raw material than filter cake. That meant the process of thermo-compression filtration would

make the CaCO_3 powder had a bit of aggregation but it will not make great effect.

Table 1. experimental results of different experimental method

Experimental method	TC-a	TC-b	TC-c
Mechanical filtration time(min)	80	25	25
Thermal-compression drying time(min)	30	30	25
Total time (min)	110	55	40
Moisture content of filter cake (A)(%)	25.54	28.49	—
Moisture content of filtercake (B)(%)	18.75	21.89	19.87
Quality of filter cake(kg)	1.694	1.695	1.970
Solid content of filter cake(kg)	1.376	1.324	1.579
Dehydrating amount of thermo-compression drying (kg)	0.154	0.156	—
Level of energy-efficient (kJ/kg(dry basis))	252.8	266.1	—

Notice: Moisture content of filter cake (A) indicated the filter cake after mechanical filtration, and (B) indicated the filter cake after thermo-compression drying.

Raw material

Filter cake

Figure 4. SEM images of raw material and filter cake

Figure 5. Particle size distribution of raw material and filter cake

5 Conclusion

The thermo-compression filtration technology was proved to be highly energy efficient and high in performance because of its non-phase- change thermo-compression drying process. Under the effect of external heat energy, the remaining moisture of the saturated cakes after mechanical filtration was removed by means of the thrust force produced by the vaporization of capillary water inside the cakes. The ultrafine CaCO_3 suspensions could be separated into clear water and dry CaCO_3 powder with moisture content lower than 20% using this technology. The products then would send to the second stage of thermal drying directly which will simplify the manufacturing technique and economize the energy consumption. The technology was also suitable to other fine powder slurry such as graphene primary product which was under experiment at present.

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