The grinding-aids effect of moisture, triethanolamine (TEA) and ethylene glycol (EG) on grinding performance and product quality of calcite

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Abstract— *In this study, the effects of liquid additives such as water, triethanolamine (TEA) and ethylene glycol (EG) on the dry fine grinding of calcite were investigated by using a laboratory scale vertical stirred mill. The experiments were carried out by a batch operation, and the change in average particle size (D_{50}) and specific surface area (SSA) (m^2/g) and colour properties (L*, a*, b*, ΔE, WI) of product. The results show that the chemical additives and water promotes the fine grinding of calcite and that the maximum specific surface area of calcite (2.97 m^2/g) obtained with EG additives 0.5%. The average particle size at this point was 3.16 µm. The results also show that the lightness (L) values of the ground calcite products slightly increased from 97.62 to 98.53 with grinding aids (TEA) increased from 0% to 0.5%. The whiteness index (WI) value of the ground calcite products slightly increased from 97.41 to 98.25 with grinding aids (TEA).*

Keywords— Stirred mill, fine grinding, calcite, grinding aid, fineness, surface area, colour properties.

I. INTRODUCTION

Grinding is an important industrial operation that is used for the size reduction of materials, production of large surface area and/or liberation of valuable minerals from their matrices. In addition to mineral processing, it is widely used in the manufacture of cement, pigments, paints, ceramics and pharmaceuticals [1]. However, it is known that it is also one of the unit operation with the lowest energy efficiency [2]. The need for fine particles has increased in the field of preparing raw powders and high value added products in many industries such as mineral, ceramic, pigments, paint and pharmaceutical, therefore, the research in fine grinding has gained more importance. Stirred media mill has been used in recent years for grinding particles to micron and submicron sizes due to their easy operation, simpler construction, higher grinding rate and lower energy consumption compared with other fine grinding machines [3]. On the other hand, it is known that particle aggregation/agglomeration causes poor flowability of dry material to be ground in a mill. Also, grinding media and liner coating results in a poor dry grinding efficiency due to the cushioning effect [4]. Grinding aids (GAs) which can improve the efficiency of the grinding remarkably with a small amount addition should more positively be applied to the grinding operations, especially to dry ultrafine grinding with higher energy consumption [2]. Moreover, the penetration of GAs into a crack within a particle could promote propagation or the crack, resulting in easier breakage of the particle [3]. They are mostly organic compounds and commonly consist of glycols and amines. The high polarity in their chemical functioning of –OH, $-NH_2$, causes the tendency to resist the agglomeration [5].

In most of the studies on GAs, the effect of moisture [6] and grinding aids [7-11] have been discussed to get the fine powders in wet grinding method for calcite/limestone, but there are only a few reports in dry conditions for calcite/limestone [2,12,13]. Moreover, in these studies, product analyses consist of surface area, fineness, particle size distribution, crystalline structure and specific energy consumption. Neverthless, effects of GAs on colour properties of ground products were not found in the literature.

The purpose of this study was to investigate the effects of moisture and chemical additives such as triethanolamine (TEA) and ethylene glycol (EG) on grinding performance (fineness and surface area) and product quality (colour properties) during dry fine grinding as grinding aids of calcite using a laboratory stirred bead mill.

II. MATERIALS AND METHODS

2.1 Materials

Powder samples used in this study were calcite ($CaCO_3$) (D_{50}=0.23 mm) (Fig.1) from Microns Co. (Nigde, Turkey) and its density was 2700 kg/m^3. Chemical properties of sample are shown in Table 1.

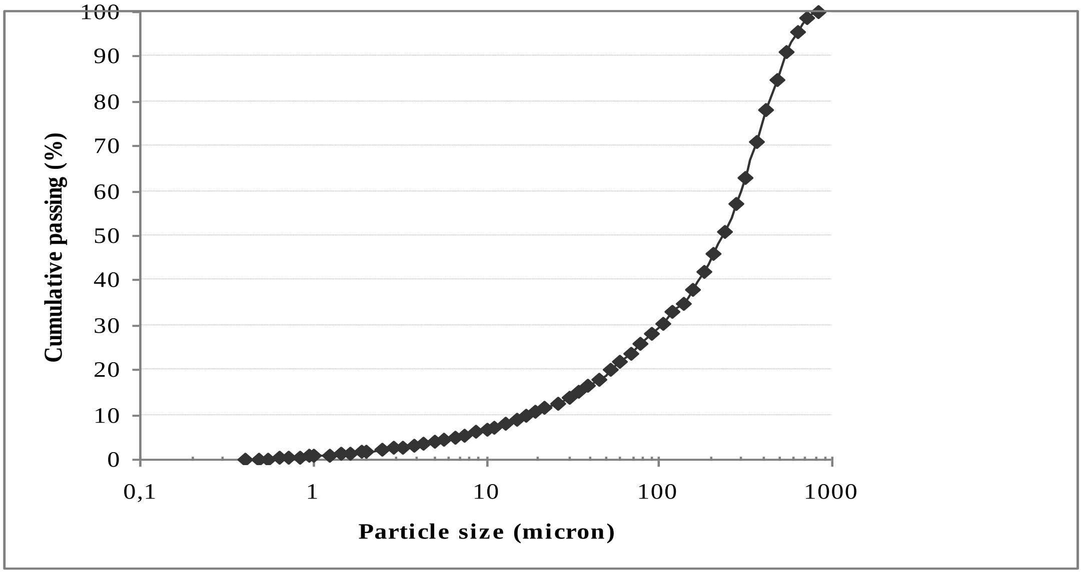

FIG. 1. THE PARTICLE SIZE DISTRIBUTION OF CALCITE

TABLE 1
CHEMICAL COMPOSITION OF THE SAMPELE (WT%)

$CaCO_3$	$MgCO_3$	Fe_2O_3	SiO_2	Al_2O_3	Total
99.5	0.2	0.01	0.01	0.02	99.74

The specific surface area (SSA) of the calcite sample before grinding was 0,23 m^2/g. The grinding media selected for the tests was 3.5-4.0 mm alumina (Al_2O_3) beads (Table 2). The physical properties of grinding media are presented in Table 3. Two kinds of liquid additives (TEA and EG) and distilled water were used as grinding aids, as shown in Table 3. TEA is kind of polar organic compound with amino, hydroxyl and other groups, which has a strong adsorption. EG as an organic compound is produced from ethylene, via the intermediate ethylene oxide. These additives were special grade reagents (Merck) and used without further purification. Summary of experimental conditions is also shown in Table 4.

TABLE 2
PHYSICAL PROPERTIES OF GRINDING MEDIA

Composition	Specific gravity (kg/m^3)	Hardness
Al_2O_3 (95%) +SiO_2 (5%)	3600	H_v 1200 kg/mm^2

TABLE 3
GRINDING AIDS USED

Additives	Density (kg/m^3)	Chemical Molecular formula	Molecular weight (g/mol)	Additive dosages (wt.%)
Triethanolamine (TEA)	1124.50	$N(CH_2CH_2OH)_3$	149.19	0.0625, 0.125, 0.25, 0.5, 1, 2
Ethylene glycol (EG)	1113.20	$HOCH_2CH_2OH$	62.07	0.0625, 0.125, 0.25, 0.5, 1, 2
Water	999.97	H_2O	18.01	0.0625, 0.125, 0.25, 0.5, 1, 2

TABLE 4
SUMMARY OF EXPERIMENTAL CONDITIONS

Item	Experimental conditions
Bead filling ratio	0.70
Sample filling ratio	0.07
Rotation speed of stirrer	600 rpm
Grinding time	15 min
Internal volume of grinding pot	750 ml
Temperature	Room temperature
Material of grinding media	Alumina
Grinding media size	3.5-4 mm
Powder sample (calcite)	
Density	2700 kg/m^3
Size range	-1 mm
Specific surface area	0.23 m^2/g

2.2 Methods

Grinding tests were carried out in a vertical type stirred media mill Standard-01 Model manufactured by Union Process (U.S.A.). The net volume of the milling chamber is 0.75 liter. In order to reduce the amount of wear from materials of the mill, the grinding chamber is made of ceramic (Al_2O_3). For cooling purposes, the grinding chamber is also equipped with a water jacket for cooling. The grinding experiment was carried out as a batch process in which samples were taken from the pot at a determined grinding time interval. After each test, all of the media and ground samples were removed from the mill, and the media were separated from the products by sieving.

A Wet Laser Diffraction Particle Sizer Malvern 2000 Ver. 2.00 with Hydro 2000 MU attachment (Malvern Co., Ltd., UK) was used for the particle size analysis of the feed and the ground products. A dispersant was applied during the preparation of the sample for sizing. Each test was repeated three times and the values reported are a mean average.

The specific surface area is one of the basic properties of the powder and is generally represented by the total surface area of all particles contained in a unit mass of the powder. The specific surface area (SSA), derived from Lecoq et al. [14]:

$$SSA=6/[\rho_s*d(3,2)] \quad (1)$$

where ρ_s is the specific gravity of calcite (t/m^3) and $d(3,2)$ is the surface-volume diameter calculated from the Malvern Master Sizer according to:

$$d(3,2)=\frac{\sum x_k dk^3}{\sum x_k dk^2} \quad (2)$$

where, x_k is the number fraction of detected size d_k (number, %) and d_k is the mean size of detected class (micron).

An organization called Commission Internationale del'Eclairage (CIE) determined the standard values that are used worldwide to measure color. The values used by CIE are called L*, a*, and b*, and the color measurement method is called CIELAB. Symbol L* (Lightness) represents the difference between light ("pure white") (where L*=100) and dark ("black") (where L*= 0); a* (Redness-Greenness) represents the difference between green (−a*) and red (+a*); and b* (Yellowness-Blueness) represents the difference between yellow (+b*) and blue (−b*) [15]. The CIELAB values are calculated from the red green and blue filters of the colorimeters and are particularly suited to describing near white samples according to the following equations [16]:

$$L^* = 116\,(Y/Y^n)^{1/3} - 16 \quad (3)$$

$$a^* = 200[((X/X^n)^{1/3} - (Y/Y^n)^{1/3}] \quad (4)$$

$$b^* = 200[((Z/Z^n)^{1/3} - (Y/Y^n)^{1/3}] \quad (5)$$

where X, Y and Z are the tristimulus values for the samples arising from the colourimetric system and X^n, Y^n and Z^n are those of a surface colour chosen as the nominal white stimulus. Accordingly, the perfect colourless white has the values L*=100, a*=0 and b*=0 in theory.

Another useful parameter for describing white, which is given in the BS 3900 [17] is delta E (ΔE). The total color difference (ΔE) was calculated using the measurements and Equation 4, by using *L**, *a** and *b** values [18,19]. The color parameters (L*a*b*) of ground products were measured using a Datacolor Elrepho SF450X spectrophotometer in the study.

$$\Delta E = [(L_0 - L^*)^2 + (a_0 - a^*)^2 + (b_0 - b^*)^2]^{0,5} \quad (6)$$

where subscript "0" refers to the color reading of the control feed sample used as the reference, and a larger ΔE indicates greater color change from the reference sample. Delta E represents the magnitude of the difference in colour, but does not indicate the direction of the colour difference [15]. If this value is positive, this means that the product is lighter than the reference sample or vice versa. Table 5 shows total colour difference values (ΔE). If this value is positive, this means that the product is lighter than the reference sample or vice versa.

TABLE 5
TOTAL COLOR DIFFERENCE VALUES [22]

(ΔE)	0	1	2	3	4	5
Total color difference	no	very low	low	medium	high	very high

Moreover, a whiteness index (WI) has been described based on the distance of a color value from a nominal white point, represented in CIELAB color space as L*=100, a*=0 and b*=0. In spectral terms a white material is one whose reflectance across the visible wave length range is constant and high (i.e. close to 100% or reflectance factor of 1). Varying shades of gray to black have a constant reflectance with the perfect black having a reflectance of 0% [20].

$$WI = 100 - [(100 - L^*)^2 + a^{*2} + b^{*2}]^{0,5} \quad (7)$$

III. RESULTS AND DISCUSSION

3.1 Effect of liquid additives on fineness of product

The effects of grinding aids on grinding have been explained mainly by two kinds of mechanism. One is based upon the alteration of surface and mechanical properties of individual particles, such as reduction of surface energy and modification of surface hardness, and the other is the change in arrangement of particles and their flow in suspensions [7]. It can be seen from Table 6, the average particle size of ground products is decreased with the increase of additive dosage from 0.0625% to 0.5%. Beyond this dosage an increasing trend of particle size is observed. Results indicates the best addition of grinding aids were 0.5% of TEA and EG, and both of them decreased the average particle size (D_{50}) from 6.47 µm to 3.46 µm and 3.16 µm, respectively.

TABLE 6.
SUMMARY OF RESULTS ON EACH EXPERIMENTAL CONDITION

Additive dosage, %		Particle size, µm			SSA m^2/g
		D_{10}	D_{50}	D_{97}	
Feed		18.21	230.68	662.67	0.23
No additive		0.96	6.47	53.03	2.18
Water	0.0625%	0.97	7.46	88.19	2.09
	0.125%	0.93	6.28	33.95	2.26
	0.25%	0.88	4.93	31.74	2.49
	0.5%	0.87	5.73	39.19	2.42
	1%	3.53	99.07	744.92	0.71
	2%	3.33	62.70	593.93	0.74
Triethanolamine (TEA)	0.0625%	0.89	4.28	20.48	2.58
	0.125%	0.87	4.01	19.50	2.71
	0.25%	0.86	3.93	16.10	2.73
	0.5%	0.86	3.46	14.39	2.85
	1%	0.90	3.84	17.43	2.66
	2%	1.41	22.23	571.72	1.33
Ethylene glycol (EG)	0.0625%	0.83	3.65	20.87	2.85
	0.125%	0.94	3.90	20.59	2.57
	0.25%	0.89	3.35	16.82	2.80
	0.5%	0.84	3.16	16.67	2.97
	1%	1.17	10.76	251.42	1.71
	2%	1.41	25.39	577.31	1.32

3.2 Effect of liquid additives on specific surface area of product

Grinding aids can reduce the surface free energy of power and prevent fine particles from closing each other. And they change the surface charge by shielding or neutralizing the particles surface partial charge and prevent facture surface healing and promoting the cracks to extend easily [21]. Fig. 2 shows the relationship between amount of additive and specific surface area (SSA) in our experimental results.

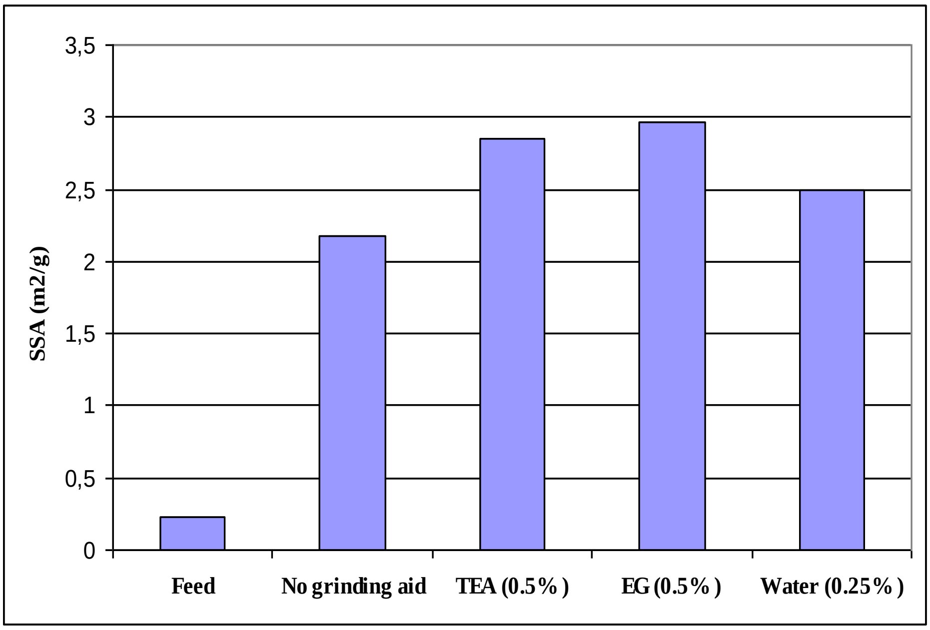

FIG. 2. RELATIONSHIP BETWEEN TYPE OF ADDITIVE AND SPECIFIC SURFACE AREA

The surface area of ground products is increased with the increase of additive dosage from 0% to 0.5% by weight of the solids. Beyond this dosage a decreasing trend of SSA is observed (Table 6). The decrease in the surface area is called as "negative grinding" and attributed to reagglomeration of the fine particles [12]. The surface area at the addition amount of 0.5% of EG was about 0.35 times as large as the area without an additive, and about 9 times larger than that before grinding. The results with TEA additive showed also a similar tendency to those with EG additive.

3.3 Effect of liquid additives on colour properties of product

As it is known, whiteness is an important specification of micronized mineral filler products, and it is important for marketing purposes that whiteness be high (≥95%). The *L**, *a**, and *b** values of feed and ground calcite products are given in Figure 3, 4 and 5. Notably, the *L** values of the ground calcite products slightly increased from 97.62 to 98.53 as grinding aids (TEA) increased from 0% to 0.5%. Lightness (L*) is affected very slightly positively in all additives (Table 7).

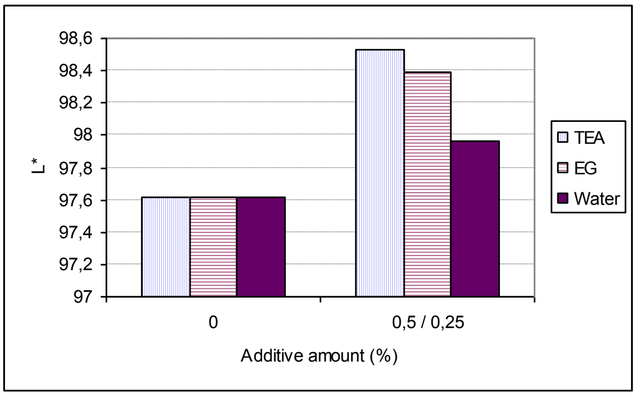

FIG. 3. L* VALUES OBTAINED WITH DIFFERENT AMOUNT OF VARIOUS GRINDING AID

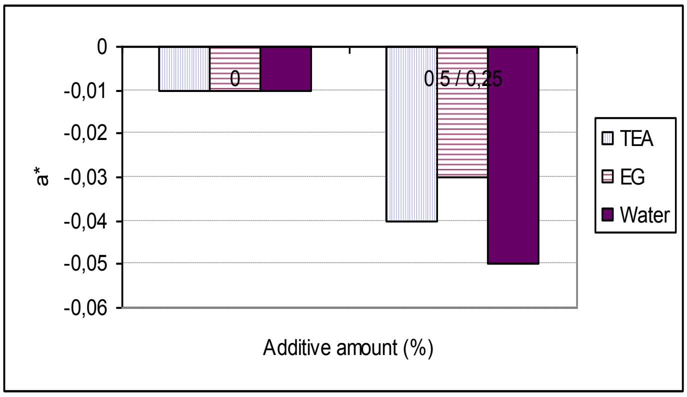

FIG. 4. A* VALUES OBTAINED WITH DIFFERENT AMOUNT OF VARIOUS GRINDING AID

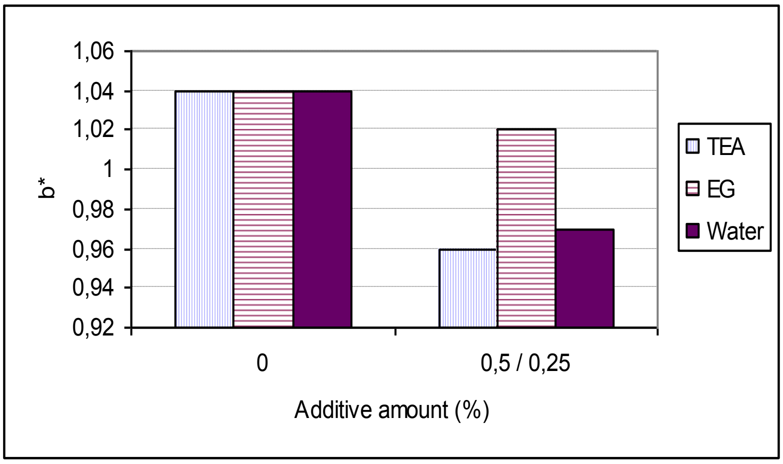

FIG. 5. B* VALUES OBTAINED WITH DIFFERENT AMOUNT OF VARIOUS GRINDING AID

TABLE 7
SUMMARY OF RESULTS ON EACH EXPERIMENTAL CONDITIONS

Grinding aids	Additive dosage, %	L*	a*	b*	ΔE*	WI
Feed material		94.53	0.32	2.98	0.00	93.77
Without grinding-aids	0	97.62	-0.01	1.04	3.67	97.41
Water	0.25	97.96	-0.05	0.97	3.99	97.71
Triethanolamine (TEA)	0.5	98.53	-0.04	0.96	4.49	98.25
Ethylene glycol (EG)	0.5	98.39	-0.03	1.02	4.34	98.10

The value of *a** decreased significantly when the grinding aid increased to 0.5%, while *b**, the second most important color value after *L**, slightly decreased from 1.04 to 0.96, revealing increased yellowness. The total color difference was calculated for all grinding aids. Similar trends are observed for ΔE, which increases with increasing amount of grinding aids from 0% to 0.5% for TEA, indicating that the quality of colour of calcite heals (Fig. 6). The results are reported in Figure 6, which shows that ΔE increases with increasing grinding aid, apparently reaching a maximum at 4.49. With values >4, as it can be seen from Table 5, there is a high-very high color difference between the feed and micronized calcite products, which is considered to be a natural result of the grinding process and the effect of chemical additives. Fig. 7 indicates that an increase in chemical dosage for TEA increased the WI values of products from 97.41 to 98.25.

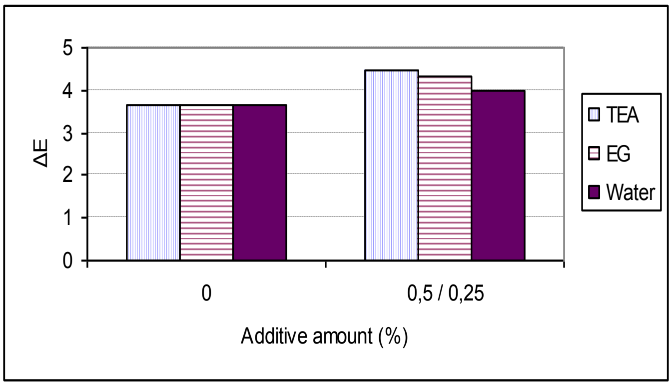

FIG.6. ΔE VALUES OBTAINED WITH DIFFERENT AMOUNT OF VARIOUS GRINDING AID

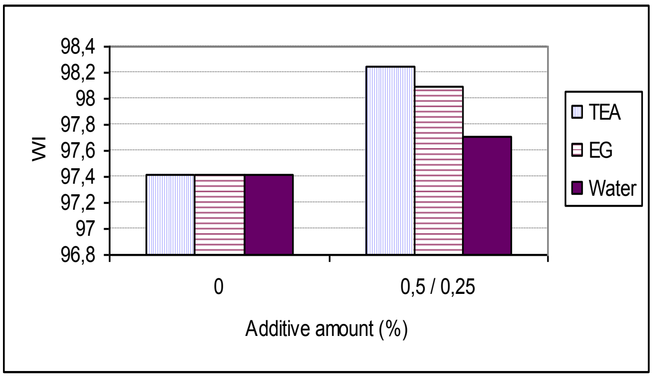

FIG.7. WI VALUES OBTAINED WITH DIFFERENT AMOUNT OF VARIOUS GRINDING AID

IV. CONCLUSION

Experimental studies on grinding performance using calcite in a stirred bead mill have been carried out. The effects of grinding aid on the particle size and size distribution (PSD) and surface area (SSA) area were examined. The followings were found out:

1. The median diameter (D_{50}) at the TEA and EG amount of 0.5% was about 0.35 times as small as the particle size without an additive, and about 9 times smaller than that before grinding.
2. The use of 0.5% weight of grinding aid in the mill indicated enough beneficial effect on product size, surface area and colour.
3. The lightness (L) values of the ground calcite products slightly increased from 97.62 to 98.53 and 98.39 with grinding aids TEA and EG, respectively.
4. The total colour difference (ΔE) increases with increasing grinding aid, apparently reaching a maximum at 4.49 for TEA at a rate of 0.5%. This means that there is a high colour difference between the feed and micronized calcite products with grinding aid, which is considered to be a natural result of the grinding process and depends on the chemical additive type.
5. The whiteness index (WI) value of the ground calcite products which is one of the colour properties slightly increased from 97.41 to 98.25 with grinding aids (TEA) at a rate of 0.5%.

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NOMENCLATURE

D_{10}	10% feed/product particle size
D_{50}	average particle size
D_{90}	90% feed/product particle size
SSA	specific surface area (m^2/g)
TEA	triethanolamine
EG	ethylene glycol

L* lightness of calcite
a* redness-greenness of calcite
b* yellowness-blueness of calcite
ΔE the total colour difference
WI whiteness index

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