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Grinding-aid effect on the colour properties (Ry, whiteness and yellowness) of calcite in stirred media milling

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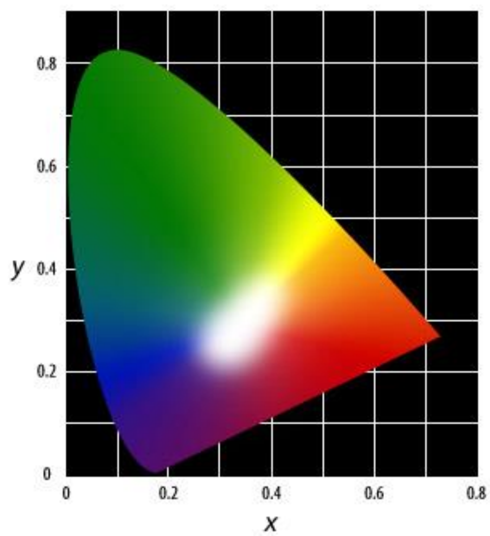
HIGHLIGHTS

- Dry fine grinding of calcite was performed in a batch type stirred media mill.
- The effects of grinding aids on fineness and color properties were investigated.
- Ethanol and methanol are noticeably effective with regard to colour properties.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the influence of some chemical additives such as methanol, ethanol, sodium oleat, chloroform and sodium hexametaphosphate (SHMP) on the dry fine grinding of calcite (X_{50}= 33 µm) using a stirred media mill. The experiments were carried out by a batch operation, and the change in colour properties (Ry, whiteness and yellowness) of calcite powder. The results showed that the chemical additives promote the fine grinding of calcite obtained with ethanol and methanol at a range of 0.5%. Ry and whiteness values of the ground calcite products very slightly increased from 94.10 and 87.04 to 94.76 and 87.75 respectively with grinding aid (ethanol) increased from 0% to 1%. Ry value was affected slightly adversely with sodium oleat, chloroform and hexametaphosphate indicating that the quality of colour of calcite deteriorates. It was also found that ΔRy increases with increasing amount of grinding aids from 0% to 0.5% for methanol and ethanol, indicating that the quality of colour of calcite heals.

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1. Introduction

It is known that 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 but it is also one of unit operations with the lowest energy efficiency [1]. The need for fine/ultrafine 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. On the other hand, stirred bead mills have 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 [2]. It is also known that particle aggregation/agglomeration causes poor flowability of dry material to be ground in a mill. Moreover, grinding media and liner coating result in a poor dry grinding efficiency due to the cushioning effect [3]. Grinding aid has been used successfully for decades in many industries such as mineral, cement, ceramics, pigments etc. It 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 [1]. Moreover, it can reduce the surface free energy of powder and prevent fine particles from closing each other. And they change the surface charge distribution by shielding or neutralizing the particles surface partial charge and prevent fracture surface from healing and promoting the cracks to extend easily [4]. When it is used a grinding aid, it must be selected an appropriate one that has no detrimental effect on downstream processing or the final product [5]. If it is actually used a grinding aid at the present technical level, it must be empirically determined the variety and quantity of the grinding aid based on experimental data [6]. In most of the studies on grinding aids, the effect of moisture [7] and grinding aids [8-12] 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 [5,13]. In these studies, product analyses consist of surface area, fineness, particle size distribution, crystalline structure and specific energy consumption. Neverthless, effects of grinding aids on colour properties of ground products were not found in the literature.

The main purpose of this study was to systematically investigate the effects on colour parameters (Ry, whiteness and yellowness) of some chemical additives such as methanol, ethanol, sodium oleat, chloroform and sodium hexametaphosphate on dry fine grinding of calcite powder using a laboratory scale stirred media mill.

2.Materials and Methods

2.1.Materials

Powder sample used in this study was calcite ($CaCO_3$) (X_{50}=33 μm) from Micron'S Co. (Nigde, Turkey) and its density was 2700 kg/m^3. Chemical properties of sample are shown in Table 1. The grinding media selected for the tests was 3.5-4.0 mm alumina (Al_2O_3) beads. Four kinds of additives were used as grinding aids, as shown in Table 2. These additives were special grade reagents (Merck and Sigma-Aldrich Corporation, St. Louis, MO, USA) and used without further purification. Summary of experimental conditions is also shown in Table 3.

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.) which was reported in our previous study [14]. Sympatec HELOS (H0983) laser diffraction analyser (Sympatec GmbH, Clausthal-Zellerfeld, Germany) was used for the analysis of the feed and the ground products. Each test was repeated three times and the values reported are a mean average. The colour parameters (Ry, whiteness and yellowness) of ground products were measured using a Datacolour Elrepho SF450X spectrophotometer in the study.

CIE considered the tristimulus values for red, green, and blue to be undesirable for creating a standardized colour model. Instead, they used a mathematical formula to convert the RGB data to a system that uses only positive integers as values. The reformulated tristimulus values were indicated as XYZ (Fig.1). These values do not directly correspond to red, green, and blue, but are approximately so. The curve for the Y tristimulus value is equal to the curve that indicates the human eye's response to the total power of a light source. For this reason the value Y is called the luminance factor and the XYZ values have been normalized so that Y always has a value of 100.

Tristimulus value Y (*ISO 5631- Y-value C/2°*) in the CIEXYZ-system of a layer of material of such a

Table 1. Chemical composition of the calcite sample (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

Table 2. Physical properties and addition amount of grinding aids used

Additives	Density (g/cm^3)	Chemical formula	Molecular weight (g/mol)	Additive dosage (wt%)
Methanol	0,792	CH_3OH	32,0	0.25, 0.5, 1, 2
Ethanol	0,789	C_2H_5OH	46,1	0.25, 0.5, 1, 2
Sodium oleate	0,900	$C_{18}H_{33}NaO_2$	304,4	0.25, 0.5, 1, 2
Cloroform	1,49	$CHCl_3$	119,4	0.25, 0.5, 1, 2
Sodium hexametaphosphate (SHMP)	2,48	$Na_6P_6O_{18}$	611,7	0.25, 0.5, 1, 2

Table 3.Summary of experimental conditions

Item	Experimental conditions
Bead filling ratio	0.70
Sample quantity	40 g
Sample filling ratio	0.05
Rotation speed of stirrer	600 rpm
Grinding time	10 min
Internal volume of grinding pot	750 ml
Temperature	Room temperature
Material of grinding media	Alumina
Grinding media size	3.5-4 mm

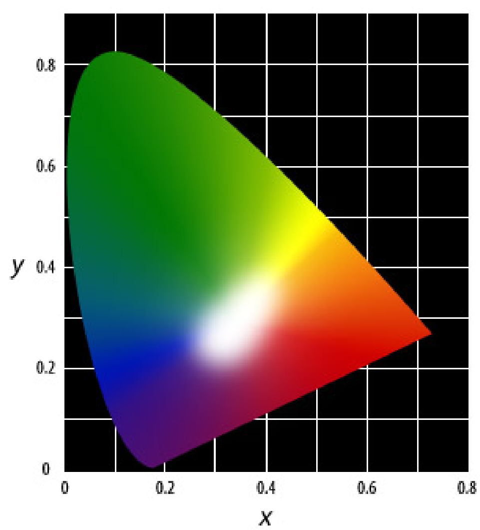

Fig. 1. The tristumulus values XYZ [15]

thickness that there is no change in Y when the thickness is increased. The illumination is here CIE illuminant C [16].

3. Results and Discussion

3.1. Effect of additive on the fineness (X_{50}) of calcite

The effect of grinding aid on fine grinding performance has 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 [6]. Table 4 shows the summary of experimental results on product size (X_{50}, X_{97}). The result with (0.25-2%) and without (0%) an additive are shown in this table. The use of grinding aid in the mill indicated enough beneficial effect on product particle size. The observed beneficial effect is due to the adsorption of grinding aid on fine calcite particles by influencing the mass transport. It can be seen from Table 5, the median diameters (X_{50}) of ground products are decreased with the increase of additive dosage from 0.25% to 1% for methanol, ethanol and sodium oleat. But, all X_{50} values are increased with chloroform and sodium hexametaphosphate. Especially, the obvious function of methanol and ethanol was both of increasing the content of fine powder and decreasing of average particle size (X_{50}). The results indicate that the best addition of grinding aids were 0.5% of ethanol and methanol, and both of them decrease the average particle size from 33.02 to 2.71 and 2.79 µm (Fig 2).

3.2. Effect of additive on the colour properties of calcite

Table 6 shows the summary of results on colour properties of product. Notably, the Ry and whiteness values of the ground calcite products very slightly increased from 94.10 and 87.04 (Run2) to 94.76 and 87.75 (Run9) respectively as grinding aids (ethanol) increased from 0% to 1%. This means that these two additives have even partially positive effect to the colour properties of calcite. Ry is affected slightly adversely with sodium oleat, chloroform and sodium hexametaphosphate indicating that the quality of

Table 4. Summary of experimental conditions

Grinding aid	Run no	Additive dosage, wt% of sample
Feed material	1	
No grinding-aid	2	0
Methanol	3	0.25
	4	0.5
	5	1
	6	2
Ethanol	7	0.25
	8	0.5
	9	1
	10	2
Sodium oleat	11	0.25
	12	0.5
	13	1
	14	2
Chloroform	15	0.25
	16	0.5
	17	1
	18	2
Sodium hexametaphosphate	19	0.25
	20	0.5
	21	1
	22	2

Table 5. Particle size of the feed sample and products

Run no	X_{50}/X_{97} (μm)
1	33.02/139.11
2	3.50/42.67
3	3.10/30.49
4	2.71/28.62
5	3.22/25.93
6	6.82/104.36
7	3.09/29.76
8	2.79/24.12
9	3.30/28.26
10	5.68/122.54
11	4.27/25.20
12	4.78/30.38
13	3.91/25.97
14	4.18/43.41
15	3.57/70.87
16	3.92/70.68
17	4.04/70.52
18	3.63/70.97
19	3.30/57.31
20	3.62/69.82
21	4.04/70.41
22	3.27/68.64

colour of calcite deteriorates. The maximum value of Ry was measured in Run8 (94.62) and Run9 (94.76).

Table 7 shows the colour difference values (ΔRy). If this value is positive, this means that the product is lighter than the reference sample or vice versa. The total colour difference was calculated for grinding aids of 0.25, 0.50, 1, and 2%. Similar trends are observed for ΔRy, which increases with increasing amount of grinding aids from 0% to 0.5% for methanol (Run4) and ethanol (Run8), indicating that the quality of colour of calcite heals (Fig 3). The results with alcohols additives indicated that both two alcohols (methanol and ethanol) were effective as grinding aid and that the ΔRy increased positively with an increase in the addition amount of alcohol from 0% to 0.5% at the same grinding time. This is because it has also been obtained best fineness for this two alcohol as mentioned in section 3.1. It is obvious that the fineness of calcite is increased with grinding and the whiteness is also increased from 83.09 to 87.04 without grinding aid. This whiteness value is reaching up to 87.87 for 0.5% ethanol aid (Table 6). Consequently, ΔRy increases with increasing amount of grinding aids from 0% to 0.5% for methanol and ethanol, indicating that the quality of colour of calcite heals.

Table 6. Colour properties (Ry, whiteness and yellowness) of the feed sample and products

Run no	Ry	Whiteness	Yellowness
1	86.88	83.09	6.08
2	94.10	87.04	3.02
3	93.75	86.70	3.00
4	94.53	87.71	2.91
5	94.03	87.25	2.90
6	88.70	86.73	3.42
7	92.67	85.52	3.06
8	94.62	87.87	2.89
9	94.76	87.75	3.01
10	90.79	81.02	4.24
11	93.78	86.78	3.02
12	93.36	86.39	2.99
13	93.48	85.37	3.47
14	92.49	83.59	3.79
15	92.52	83.14	4.05
16	91.82	82.14	4.18
17	92.36	82.98	4.05
18	92.03	82.48	4.14
19	93.60	86.19	3.28
20	92.35	82.57	4.24
21	92.37	82.96	4.08
22	92.41	83.04	4.05

Table 7. ISO-5631 Ry-value of the products after milling with grinding aid

Run no	Ry	ΔRy Before and after milling with grinding aid (%)
3	93.75	-0.35
4	94.53	0.43
5	94.03	-0.07
6	88.70	-5.40
7	92.67	-1.43
8	94.62	0.52
9	94.76	0.66
10	90.79	-3.31
11	93.78	-0.32
12	93.36	-0.74
13	93.48	-0.62
14	92.49	-1.61
15	92.52	-1.58
16	91.82	-2.28
17	92.36	-1.74
18	92.03	-2.07
19	93.60	-0.5
20	92.35	-1.75
21	92.37	-1.73
22	92.41	-1.69

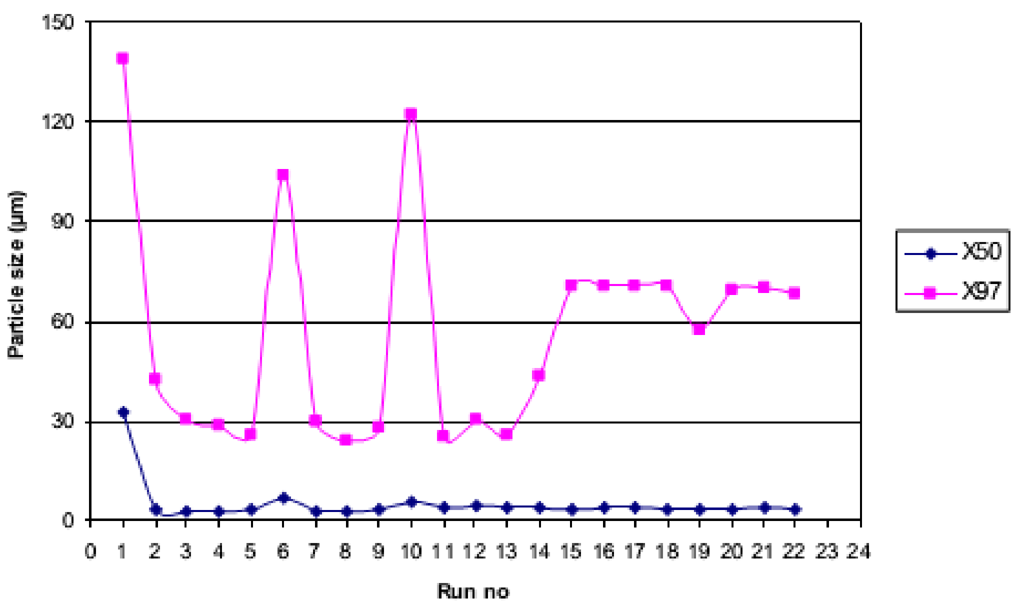

Fig. 2. Particle size (X_{50} and X_{97}) of the feed sample and products

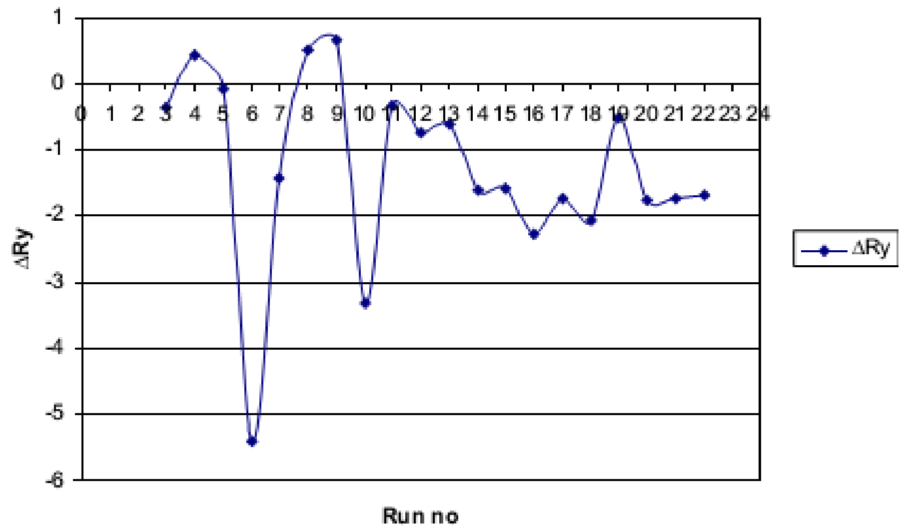

Fig. 3. ΔRy-value of the products before and after milling with grinding aid

4.Conclusions

The effects of grinding aid on the fineness (X_{50}) and some colour properties such as Ry, whiteness and yellowness were examined. The followings were found out:

1. The median diameter (X_{50}) at the methanol and ethanol addition amount of 0.5% was about 0.3 and 0.25 times as small as the particle size without an additive, and about 12.5 and 13 times smaller than that before grinding, respectively.
2. Ry and whiteness values of the ground calcite products very slightly increased from 94.10 and 87.04 to 94.76 and 87.75 respectively as grinding aids (ethanol) increased from 0% to 1%.
3. Ry value is affected slightly adversely with sodium oleat, chloroform and sodium hexametaphosphate indicating that the quality of colour of calcite deteriorates.
4. ΔRy increases with increasing amount of grinding aids from 0% to 0.5% for methanol and ethanol, indicating that the quality of colour of calcite heals.
5. As a result, ethanol and methanol used as grinding aid are noticeably effective as grinding aids with regard to colour properties of calcite.

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References

[1] M. Hasegawa, M. Kimata, M. Yaguchi, Effect of behavior of liquid additive molecules in dry ultrafine grinding of limestone, KONA Powder Part. J. 24 (2006) 213-221.

[2] H. Choi, W. Lee, S. Kim, Effect of grinding aids on the kinetics of fine grinding energy consumed of calcite powders by a stirred ball mill, Adv. Powder Technol. 20 (2009) 350-354.

[3] Y. Wang and E. Forssberg, Dispersant in stirred ball mill grinding, KONA Powder Parti. J. 13 (1995) 67-77.

[4] J. Zhao, D. Wang, X. Wang, S. Liao, H. Lin, Effect of grinding aids on the particles characteristics of cement and analysis of action mechanism, Adv. Mater. Res. 936 (2014) 1404-1408.

[5] M. Hasegawa, M. Kimata, M. Shimane, T. Shoji, M. Tsuruta, The effect of liquid additives on dry ultrafine grinding of quartz, Powder Technol. 114 (2001) 145-151.

[6] D. W. Fuerstenau, Grinding aids, KONA Powder Part. J. 13 (1995) 5-18.

[7] A. H. Shinohara, K. Sugiyama, E. F. Kasai Saito, Y. Waseda, Effects of moisture on grinding of natural calcite by a tumbling ball mill, Adv. Powder Technol. 4(4) (1993) 311-319.

[8] J. Zheng, P. Harris, P. Somasundaran, The effect of additive on stirred media milling of limestone, Powder Technol. 91 (1997) 173-179.

[9] R. R. Klimpel, The selection of wet grinding chemical additives based on slurry rheology control, Powder Technol. 105 (1999) 430-435.

[10] R. Greenwood, N. Rowson, S. Kingman, G. Brown, A new method for determining the optimum dispersant concentration in aqueous grinding, Powder Technol. 123 (2012) 199-207.

[11] H. K. Choi, W. S. Choi, Ultra fine grinding mechanism of inorganic powders in a stirred ball mill-The effect of grinding aids-, Korean J. Chem. Eng. 20(3) (2003) 554-559.
[12] H. Choi, W. Lee, D. U. Kim, S. Kumar, S. S. Kim, H. S. Chung, J. H. Kim, Y. C. Ahn, Effect of grinding aids on the grinding energy consumed during grinding of calcite in a stirred ball mill, Miner. Eng. 23 (2010) 54-57.
[13] O. Y. Toraman, Effect of chemical additive on stirred bead milling of calcite powder, Powder Technol. 221 (2012) 189-191.
[14] O. Y. Toraman, D. Katırcıoglu, A Study on the Effect of Process Parameters in Stirred Ball Mill, Advanced Powder Technol. 22(1) (2011) 26-30.
[15] Technical guides colour models CIEXYZ (http://dba.med.sc.edu/price/irf/Adobe_tg/models/ciexyz.html
[16] Scandinavian Pulp, Paper and Board Testing Committee (SCAN-P 89:03), Preparation of tablets for the measurement of ISO brightness, Y-value and colour (C/2°), 4 p. SE-114 86 Stockholm, Sweden, 2003.