Some aspects on selective dispersion of fine particles with special emphasis on Egyptian ground calcium carbonate

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Synopsis

A selective dispersion process is presented and the work carried out to find optimum process conditions to minimise the colouring material in ground calcium carbonate (GCC) is described. The feed material is the overflow product from a hydrocyclone which results from using a Denver Attritioning machine with semi-autogenous grinding for one hour and a 1:1 ore/water ratio. By using sodium silicate (SS), with pH 9 and pulp density 5%, the iron content (as colouring impurities) is decreased from 0.21% in the original concentrate to 0.12% in the final concentrate. The degree of whiteness reached is improved to 85% from 63% in the original material. However, by using hexametaphosphate (SHMP) at pH 10 at the same pulp density, the iron content decreased to about 0.073% and hence the whiteness degree increased to about 96% .

Introduction

Ground Calcium Carbonate (GCC) and several minerals such as kaolin, talc and titanium oxide are used for coating and filling processes ranging from automobile dashboard plastic to ultrapremium paper. But nowadays there is a world trend to use GCC instead of other minerals that were used in these processes. There are several reasons why consumption of GCC has increased greatly: the first reason is the rich resources and wide distribution of limestone. The second reason is the high degree of limestone whiteness that reaches a value of over 90%. The third reason is the relatively low cost . Moreover, highly efficient grinding equipment has been developed to produce GCC of various kinds with > 90% of superfine powder, which is a high quality for coating and filler grades. Moreover, the energy consumed in production per ton of such products has decreased from 250 Kwh/t to 120–170 kwh/t[1].

In the USA, the cheaper grades of calcium carbonate , where whiteness is not too important and fineness is limited to a top size of 40 μm, are supplied by Canadian sources[2]. The better grades for pigment and plastic uses have, however, up till now, been supplied by imports amounting to several millions of dollars per year.

Calcium carbonate specification varies widely for the same application due to individual company processes being slightly different. Many trade names are used, which further complicates any evaluation process. The properties that help to make calcium carbonate important as a pigment are whiteness, fine particle size (-10 μm), close particle size distribution, strong affinity for the binders used, good adhesion in highly loaded systems, and thus the ability to reduce shrinkage, and low cost in relation to the properties it contributes to the finished product[2].

The selective flocculation technique is one of the most significant advances in fine particle separation in recent years. This technology aims to recover the valuable mineral from ultrafine ore suspension[3]. It is achieved by selectively aggregating the mineral particles in question to such a size as to enable their effective separation from the suspension. However, selective flocculation is also applied in colloid tested fine particles for separating low density cholesterol particles from high density ones and in separation of treated paper from pulp[4].

Flocculation is widely used in solid/liquid separation unit operations. The flocculation of fine suspensions depends on a number of factors, which include type, molecular weight and ionization degree of the flocculant, mineralogical composition and particle size of solid particles, pH, and chemical composition of the solutions. The process also depends strongly on hydrodynamic conditions (Laskowski *et al.*, 2000[5]).

Although various flocculation mechanisms are possible, the most important, flocculation by bridging, is considered to be a consequence of the adsorption of the segments of the flocculant macromolecules onto the surfaces of more than one particle. While adsorption of the

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polymer is necessary for bridging flocculation to occur, it is important to realize that adsorption and flocculation are not separate, sequential processes, but occur simultaneously (Hogg.1999[6]).

Optimum flocculation occurs at flocculant dosages corresponding to a particle coverage that is significantly less than complete. Incomplete surface coverage ensures that there is sufficient unoccupied surface available on each particle for adsorption during collisions of segments of the flocculant chains attached to the particles (Hogg ,1993[7]).

In the flocculation process, the polymer may be applied either after destabilizing the suspension via coagulation, or without prior destabilization, (Kitchener, 1972[8]). This can be visualized as follows:

➤ Stable suspension → coagulation → flocculant addition → flocculation,

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This investigation aims to beneficiate the ultrafine ground calcium carbonate by selective dispersion process. Parameters that affect the dispersion process, such as pH of the pulp, dose of sodium silicate (SS), dose of sodium hexametaphosphate (SHMP), conditioning speed, conditioning time, and pulp density were studied. Finally, a tentative flow sheet was suggested to treat GCC.

Materials and experimental procedures

Material

A sample of about 500 kg was kindly provided from Zaweit Sultan locality, a hard variety from El Minya province, Egypt. The sample was crushed in a 5x6 Denver Jaw Crusher. The feed of top size is about one inch which is fed to the attritioner followed by spiral classifier, and the overflow was fed to the 3 inch hydrocyclone, the overflow of which was the feed for selective dispersion tests. The chemical analysis of the bulk sample is shown in Table I.

Analytical grades of sodium hydroxide, sodium silicate and sodium hexametaphosphate from BDH chemicals, UK, were used.

Experimental procedures

In selective dispersion, sodium silicate and sodium hexametaphosphate were used in this study at laboratory scale. Pulp was prepared from a 5% suspension of GCC in water using an electrical stirrer at 2000 rpm for 60 min. conditioning time. The suspension was then transferred to a

Table I

Complete chemical analysis of the sample

Constitutents	%	
CaO	55.24	
SiO_2	1.06	
Al_2O_3	0.247	⎤
Fe_2O_3	0.234	⎦ → R_2O_3
Na_2O	0.111	
Cl	0.044	
SO_3	0.028	
P	0.024	
HFO_2	0.179	
SrO	0.028	
L.O.I.	42.94	

38 cm long and 4.7 cm diameter glass cylinder fitted with side outlets at 4cm and 11 cm levels from the bottom. This was shaken 10 times at 180° and, then left to settle for 3 min. The dispersed fraction was withdrawn through the side outlets, and collected together; the non-dispersed fractions were collected separately. The products were dried, weighed and chemically analysed. The degree of whiteness was measured by DR LANGE Whiteness Tester, Germany.
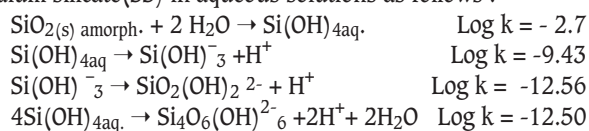
Results and discussion

The results of the quantitative complete chemical analysis of the bulk sample by X-ray flouresence are shown in Table I. It is obvious that the sample has CaO and CO_2 approaching that of the stoischiometric percentage in pure $CaCO_3$. The main impurities in the sample are SiO_2 and R_2O_3, both constitute ~1.5%. The source for colouring material is clayey bearing iron oxides. Therefore it is suggested that a selective dispersion process be applied to the hydrocyclone overflow product to minimize the impurities. The chemical analysis of this product is 0.2% Fe, 63.50 whiteness degree and 7.5 μm D_{97} size analysis.

Inorganic dispersants such as sodium silicate (SS), known commercially as water glass, and sodium hexametaphosphate phosphate salts (SHMP) were used in dispersion system. There are many parameters that affect the selective dispersion processes such as pH, type of dispersing agent, conditioning speed, conditioning time and pulp density.

Effect of the change in pH levels on selective dispersion

The tests were carried out at a constant dosage of sodium silicate (SS) (3.5kg/t), pulp density of 5%, conditioning speed of 8000 rpm, and conditioning time of 2 min. The results of changing the pH levels are shown in Figure 1. It is clear from these results that the iron content decreased from 0.18% Fe at pH 7.4 to 0.09% at pH 9 consequantly the degree of whiteness increased from ~ 64 to ~ 87 at the same pH levels mentioned before. At pH 10, the iron content in the concentrate increased and hence the degree of whiteness decreased to 69. This dispersion of ferrogineous clayey material takes place at a pH range from 7.4 to 9 and then it is flocculated at a pH above 9. This may be due to hydrolysis of sodium silicate (SS) in aqueous solutions as follows :

$$SiO_{2(s)\ amorph}. + 2\ H_2O \rightarrow Si(OH)_{4aq}. \qquad Log\ k = - 2.7$$
$$Si(OH)_{4aq} \rightarrow Si(OH)^-_3 + H^+ \qquad Log\ k = -9.43$$
$$Si(OH)^-_3 \rightarrow SiO_2(OH)_2{}^{2-} + H^+ \qquad Log\ k = -12.56$$
$$4Si(OH)_{4aq}. \rightarrow Si_4O_6(OH)^{2-}{}_6 + 2H^+ + 2H_2O \quad Log\ k = -12.50$$

The concentration pH domains for these species are given in the above equations. Alkaline conditions are seen to promote the formation of polyanions. Further, for all sodium silicate solutions, when the concentration of $Si(OH)_{4aq}$ is less than about 5×10^{-3} mole/ litre, colloidal silica is not stable[9]. The effect of sodium silicate in alkaline conditions beyond the point of zero charge, (PZC) of calcite 8–10 and of hematite 3–4 may be due to the complexity of its dissociation process, which produces a number of ionic and colloidal species. The predominant mechanism of silicate adsorption to the negative surfaces of the pulp may be through the unavoidable release of Ca^{2+} cations, which anchored the silicate to the solid surface, as the following equation shows:
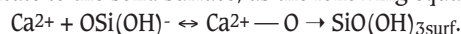
$$Ca^{2+} + OSi(OH)^- \leftrightarrow Ca^{2+} - O \rightarrow SiO(OH)_{3surf}.$$

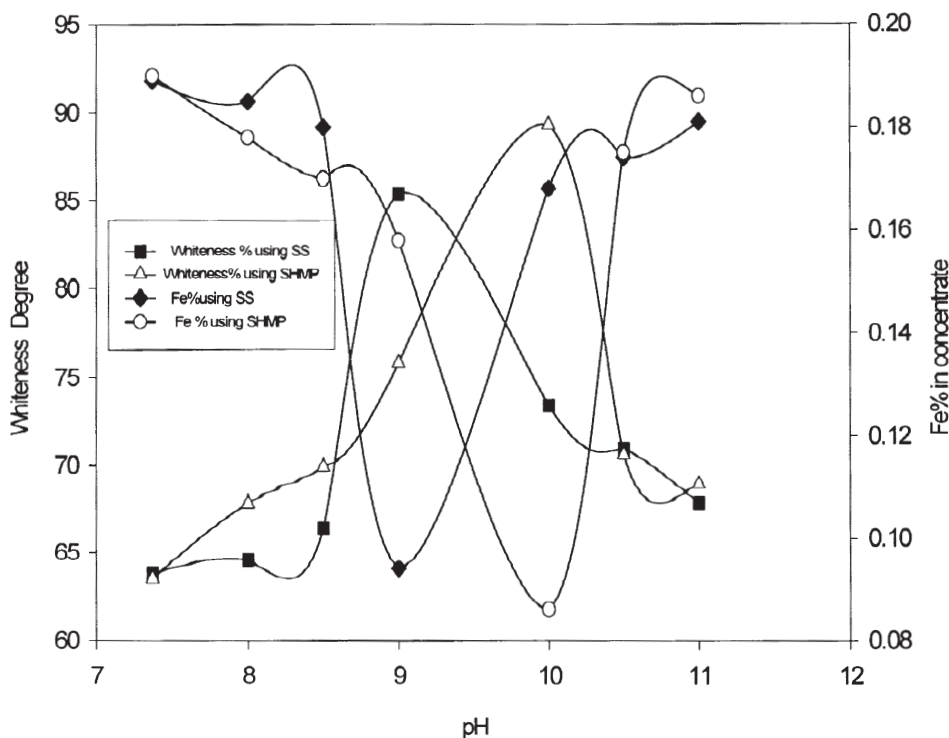# Some aspects on selective dispersion of fine particles

Figure 1—Effect of pH on the selective dispersion of impurities in GCC

The flocculation of impurities above pH 9 may be due to the presence of a higher concentration of inoraganic cations such as Na+, which cause coagulation of clayey ferruginous fraction with the GCC and hence lead to a lower degree of whiteness. Therefore, the optimum pH for selective dispersion of ferruginous clayey fraction is pH 9.

However, the change in pH levels in the presence of a constant dose of sodium hexametaphosphate (4kg/t) on the selective dispersion of impurities is clear from the results in Figure 1. The increase in pH levels affected the selective dispersion of the impurities of ferruginous clayey material, dispersion increased by increasing the pH up to pH 10, where the iron content decreased and the degree of whiteness increased to more than 90. However, if the pH level increased beyond pH 10, the dispersion of impurities decreased. This may be due to the increase of inorganic cations created by pH adjustment reagents (i.e. NaOH) and because the cations of Na+ result from the hydrolysis of sodium hexametaphosphate (SHMP), as is clear from the configuration[4] shown in Figure 2.

Each molecule of SHMP released 6 cations of Na+ on hydrolysis. The unavoidable cations (Ca2+) released from GCC anchored the hexametaphosphate to the negative centres at pH levels higher than ZPC of the impurities and increased their selective dispersion up to pH 10, at which point the GCC contains a lower percent of iron (0.085%) and higher degree of whiteness. Therefore, the optimum pH in the case of SHMP is pH 10. From Figure 1, it is clear that SHMP is more effective for dispersing the impurities, where the degree of whiteness reached more than 90, in spite of its higher dose (i.e. 4kg/t), which may be one of the drawbacks of its usage in this beneficiation process.

Effect of conditioning speed on the selective dispersion of impurities

The conditioning speed was changed from 1 000 rpm to 9

500 rpm at constant values of other parameters i.e. dispersing agents doses (3.5kg/t SS and 4kg/t SHMP) and a 2 min. conditioning time, and at optimum pH levels (i.e. 9 for SS and 10 for SHMP). The results of this parameter are shown in Figure 3 from which it is clear that the increase in conditioning speed increased the selective dispersion of impurities up to 2 700rpm, where the iron content decreased from ~ 0.2% Fe to ~ 0.082% Fe in case of SHMP dispersing agent and to ~ 0.12% from Fe in the case of SS. On increasing the conditioning speed above 2 700 rpm, the iron percentage is increased and consquently the degree of whiteness decreases to nearly its original value. This unselectivity of dispersion due to the increase of conditioning speed may be attributed to destroying of the flocculates. These findings were also encountered by Laskowski *et al.*[5] (2000).

Therefore, the optimum conditioning speed may be about 2 700 rpm for both reagents SS and SHMP.

Effect of conditioning time on the selective dispersion of impurities

The change in conditioning time at fixed optimum values of the other parameters affects the selective dispersion of the impurities. The results of increasing conditioning time are shown in Figure 4, from which it is clear that the selectivity of dispersion increased by increasing the conditioning time up to 7 min. in the case of SHMP and up to 2 min. in the case of SS. The improvement in the selective dispersion minimized the iron content in the GCC concentrate, and hence improved the degree of whiteness, which reached 97% in the case of SHMP and >85% in the case of SS at 7 and 2 min., respectively. Beyond these two conditioning time values, the iron content increased in GCC concentrate and the degree of whiteness decreased simultaneously.
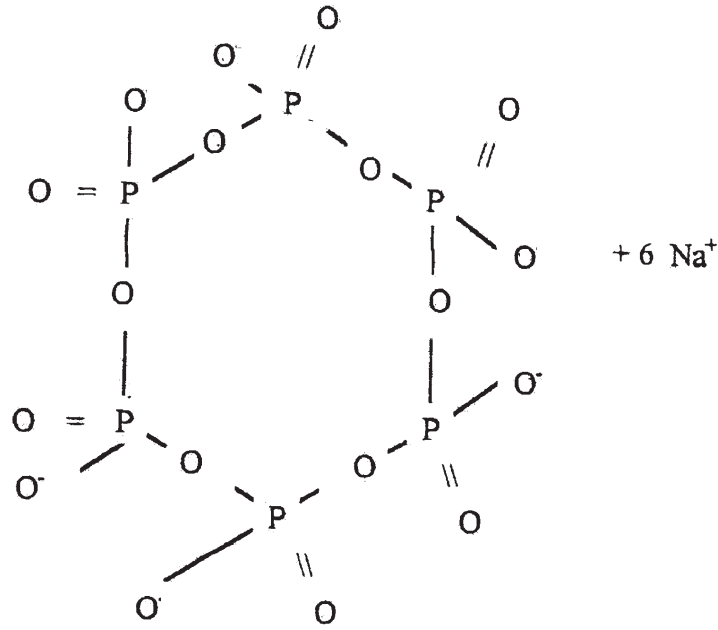
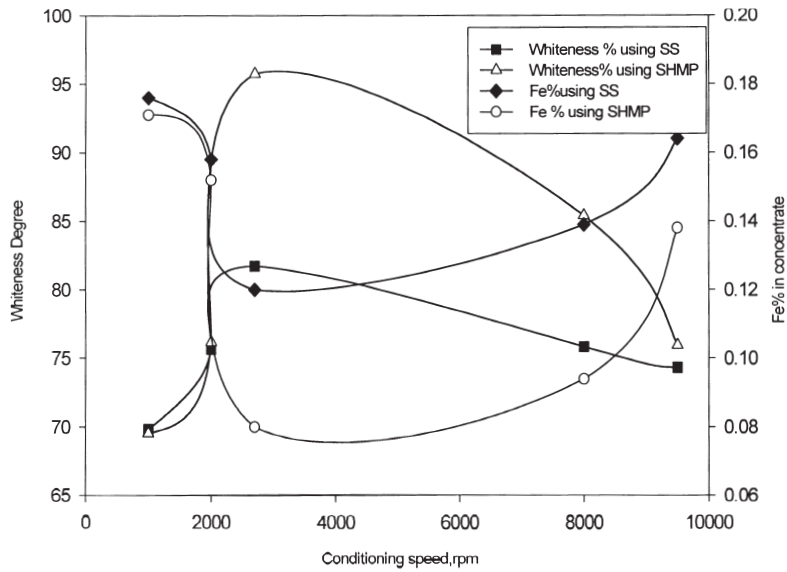# Some aspects on selective dispersion of fine particles

Figure 2

Figure 3—Effect of conditioning speed on the selective dispersion of impurities
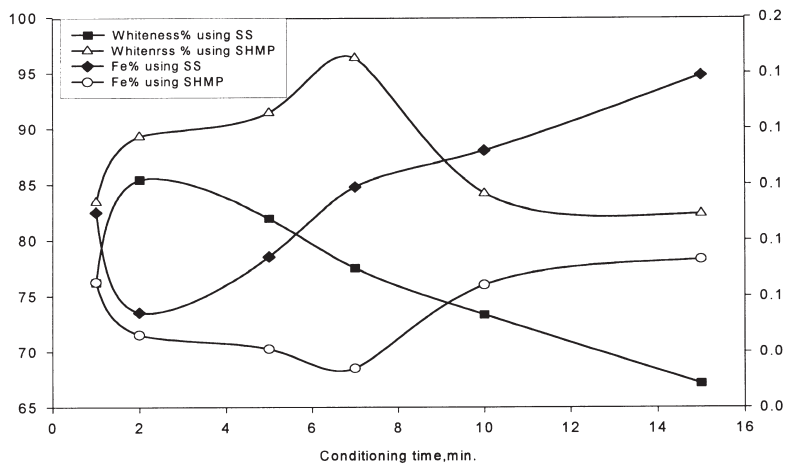

Figure 4—Effect of conditioning time on the selective dispersion of impurities

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However, the improvement in dispersion selectivity may be due to adsorption activation by released calcium cations, which anchored the dispersing agents on the solid surface of negative impurities up to a certain time. On a prolonged conditioning time more Ca²⁺ were released and this may lead to coagulation of dispersed particles of impurities, since long peroid of conditioning caused more Ca²⁺ released, and it is well known that the increase in inorganic electrolytes causes coagulation of dispersed impurities. Also, prolonged conditioning time may cause desorption of the dispersing agent from the surface of the impurities and minimize dispersing selectivity of the dispersing agents. Therefore, the optimum conditioning times are 2 min and 7 min for SS and SHMP, respectively.

Effect of pulp density on the selective dispersion of impurities

At the fixed optimum values of other parameters, the change in pulp density was studied. The results of change in pulp density are shown in Figure 5, from which it is obvious that the increase in pulp density up to 5% improved the selective dispersion of the impurities and yielded a GCC concentrate of minimium iron content and a higher degree of whiteness. Although a further increase in pulp density decreases the selective dispersion of the impurities, increases the iron content in GCC concentrate sharply, and lowers the degree of whiteness, also sharply in the case of SHMP and to the same extent in the case of SS. This effect of increasing the pulp density may be due to the increase of entrainment of impurities in the GCC concentrate or may be due to the increase in the unavoidable release of bivalent cations (i.e. Ca²⁺ cations), which increases the probability of coagulation.

However, the pulp density improved the selective dispersion up to 5%, and above it, the selective dispersion is compelety minimized . Sworska *et al.*[5] studied the effect of bivalent cations, and found that it could increase the floccu-lation and minimize the selective dispersion.

Effect of dose of dispersing agents

The change in the dose of dispersing agents was investigated at fixed optimum values of the other parameters. The results of the change in the dosage are shown in Figure 6. It is clear from the results that the increase in the dosage of SS, as well as SHMP increases the selective dispersion up to 3.5 kg/t and 4 kg/t, respectively. As a result of the improvement in selective dispersion, the iron content was decreased in GCC concentrate sharply from about 0.18% Fe to 0.08% and 0.11% Fe in the case of SHMP and SS, respectively. Also, the degree of whiteness increased sharply by increasing the dosage, which reached more than 95 in the case of SHMP and more than 85 in the case of SS. However, both concen-trates of GCC may be suitable to match the application as filler or coating in the paper industry, plastic, paint and rubber due to the excellent degree of whiteness and iron content. The increase of both reagents, dosages up to a value of 3.5 kg/t and 4 kg/t of SS and SHMP, respectively, the anions of silicate and hexametaphosphate can be adsorbed, often physically at the positive edges of GCC surface or through the activation by the released Ca²⁺ cations, which anchored the negative centres on the surface and the negative anions of the dispersing agents, leading to a corresponding reduction in the possiblility of the edge-to-face flocculation process. Such adsorption is expected to be increased either at higher dosages of both dispersing agents, leading to an excessive increase in the negative charge of the impurities and the GCC minerals, and increased selective dispersion[10].

Conclusions

➤ To improve the degree of whiteness of GCC and minimize the colouring material, the selective dispersion process of beneficiation was adapted using sodium silicate SS and sodium hexametaphosphate SHMP as dispersing agents.
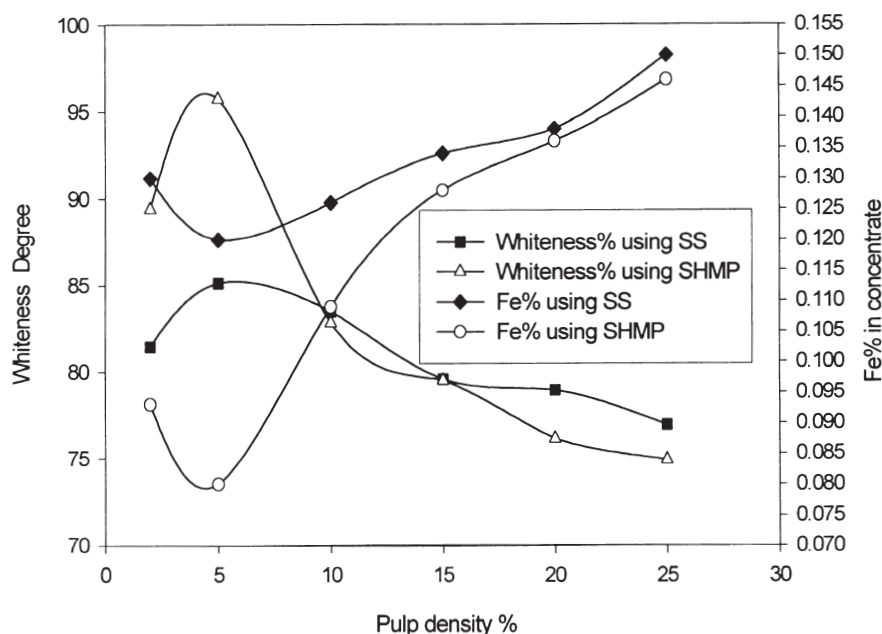

Figure 5—Effect of pulp density on the selective dispersin of impurities in GCC

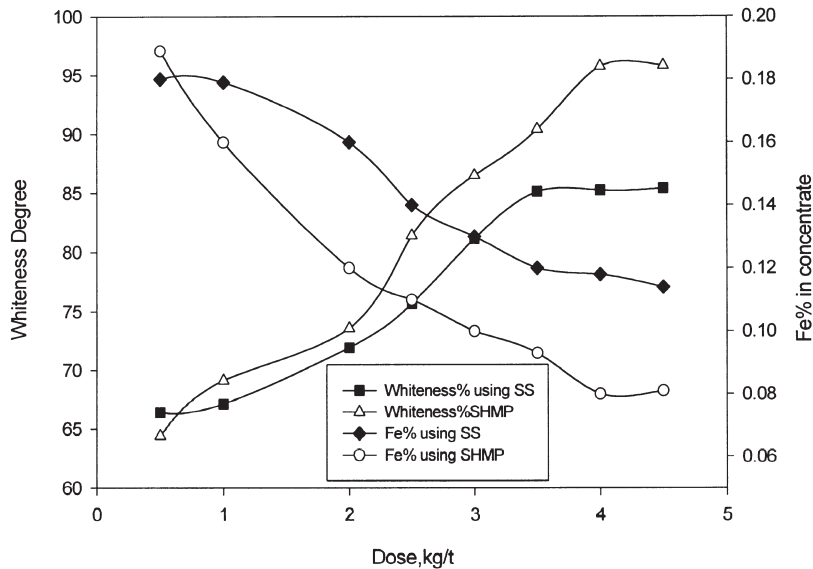# Some aspects on selective dispersion of fine particles

Figure 6—Effect of dose of dispersing agents

➤ The different parameters that may affect the selective dispersion were investigated a single variable at a time. The optimum values of these parameters at fixed constant values of the others are: pH 10 for SHMP and pH 9 for SS. The conditioning speed is 2700 rpm, the conditioning times are 2 min. for SS and 7 min. for SHMP. The dosages are 3.5 kg/t for SS and 4 kg/t for SHMP.

➤ The beneficiated GCC is characterized by its degree of whiteness and Fe%. Its degree of whiteness is > 95 and Fe% < 0.08% in the case of SHMP. In the case of SS is about 85 degree of whiteness and about 0.1% Fe. This concentrate of GCC has a higher degree of whiteness, minimum iron content of D50 is 3.7µm, and D97 ~ 7µm, which may be used as filler and coating material in paint, plastic, rubber and paper.

➤ The price of such a category of product from the categories, price tables shown by Brain Coope (11) (1997) US$125–160/S.t.FOB.

➤ The recovery of the concentrate in the case of SHMP treatment is 73.50% and that for SS is 90.22%.

➤ A suggested tentative flowsheet is shown in Figure 7.

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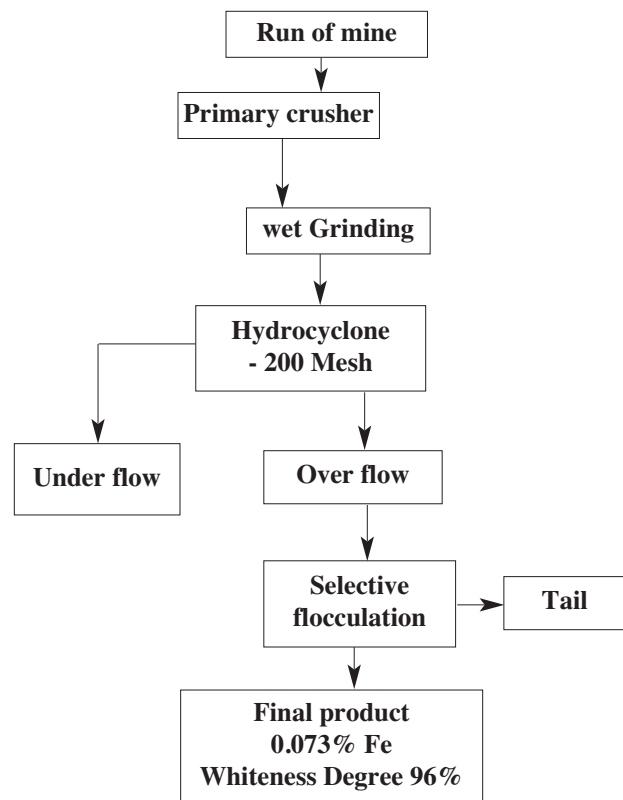7. HOGG, R., BRUNNAUAL, P., and SUHARYONO, H. Chemical and physical

Figure 7—Grinding, classification and flocculation flow sheet to treat Egyptian calcium carbonate sample

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