

## Shear-flocculation of quartz

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(Received February 20, 1990; accepted after revision March 27, 1991)

### ABSTRACT

G. Bhaskar Raju, T.V. Subrahmanyam, Z. Sun and Willis Forsling, W., 1991. Shear-flocculation of quartz. *Int. J. Miner. Process.*, 32: 283-294.

The present work deals with the shear-flocculation of quartz in aqueous solutions of dodecylamine chloride. The variables studied include pH, concentration of the amine, size of the coarse particles, stirring speed and time. The zeta potentials were correlated with flocculation behaviour. It was observed that particle hydrophobicity and pH were most important since the dodecylamine chloride-flocculation reactions are pH- and concentration-dependent.

### INTRODUCTION

Particle hydrophobicity is a basic criterion for the separation of minerals in the flotation process and by shear-flocculation. The hydrophobic aggregates formed by shear-flocculation can be subjected directly to flotation. The collector coated particles, depending on the mineral-collector system under study, usually hold high surface potentials and hence higher energies are required to overcome the energy barrier between the similarly charged particles to effect shear-flocculation. The aggregates form by hydrophobic interaction, once the particles collide with each other. For non-sulphide minerals a hydrophobic reagent (usually a collector) is necessary. For example, in the case of scheelite the aggregates were found to form only in the presence of sodium oleate (Warren, 1975a,b). The removal of anatase impurity from kaolin-clay by using calcite as a coarse carrier mineral was explained to be due to the preferential adsorption of oleate on to calcite and anatase and not on kaolin-clay (Chia and Somasundaran, 1983). In the carrier flotation of wolframite, where collisions between particles take place at high shear rates, better recoveries obtained at pH 6-7 were explained to be due to a favourable reagent adsorption and lower electrostatic repulsion (Hu et al., 1988). In both shear-

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flocculation and carrier flotation, the aggregation mechanism, to a large extent, is governed by the particle hydrophobicity and the charge. A recent review covers the aspects related to shear-flocculation and carrier flotation in greater detail (Subrahmanyam and Forssberg, 1990).

The present work deals with the shear-flocculation of quartz and the variables investigated were pH, concentration of dodecylamine chloride (DDACl), size of the coarse particles, stirring speed and time.

#### EXPERIMENTAL: MATERIALS AND METHODS

##### *Preparation of quartz samples*

The silica sand sample obtained from Ahlsell, Stockholm, was dry ground in a steel rod mill and sieved to separate different size fractions. The fines were further subjected to microsieving to separate the  $-5 \mu\text{m}$  and the coarse size fractions  $-20+5$ ,  $-38+20$ ,  $-53+38$  and  $-75+53 \mu\text{m}$  were treated with dilute HCl to remove the impurities and then washed several times with deionized water to obtain a clean surface. The samples thus obtained were pure white in colour, and under microscope appeared like transparent glass crystals of angular to sub-angular shape. The  $-5 \mu\text{m}$  fraction was checked with a sedigraph to determine the size distribution of the particles and was found to be 65%  $-5 \mu\text{m}$  and 35%  $5-10 \mu\text{m}$ .

##### *Reagents*

The reagent used for the flocculation tests was dodecylamine chloride, and fresh solutions of desired concentrations were prepared in deionized water before the tests. Dilute HCl or NaOH was used to adjust the pH of solutions.

##### *Electrokinetic measurements*

The zeta potentials were measured with a Laser Zee Meter model 501. A known quantity of  $-5 \mu\text{m}$  quartz was added to deionized water or fresh prepared aqueous solution of dodecylamine chloride of desired concentration and dispersed in ultrasonic for 15 min after adjusting the pH. The pulp was injected into the cell of the zeta meter for measurements.

##### *Measurement of degree of aggregation*

The degree of aggregation was measured by the decrease in turbidity of suspension. A known quantity of fines was taken in an aqueous medium and dispersed in an ultrasonic bath after adjusting the pH. To this suspension coarse particles were added along with the solution of dodecylamine chloride.

of required concentration and pH. The suspension was later stirred in a baffled plexiglas container with a paddle type stirrer. The stirring speeds were varied from 500–1500 rpm. The turbidity of solutions was measured by a Hach Ratio XR Turbidimeter.

#### Scanning electron micrographs

Scanning electron micrographs were taken on selected samples of flocculated quartz with a CAMSCAN microscope. A dilute suspension of the flocculated quartz sample was prepared in acetone solution. The aggregates were evaporated onto a carbon stub while the suspension was under magnetic stirring.

#### RESULTS

##### Electrokinetic studies on quartz

The effect of pH on the zeta potentials of quartz in the absence and presence of DDACl is shown in Fig. 1. The i.e.p. (isoelectric point) of quartz in the absence of amine is observed at pH 1.8 and is in agreement with earlier studies (Fuerstenau and Fuerstenau, 1982). With increasing pH the negative potential increases. For a DDACl concentration of  $9.02 \times 10^{-5} M$ , positive potentials are observed in the acid range upto pH 3.2 beyond which charge reversal occurs and to negative and once again the particles attain a positive charge at pH 9.6. The change in zeta potential from positive to negative at pH 10.7 was reported to be the iep of the dodecylamine precipitate (Laskowski,

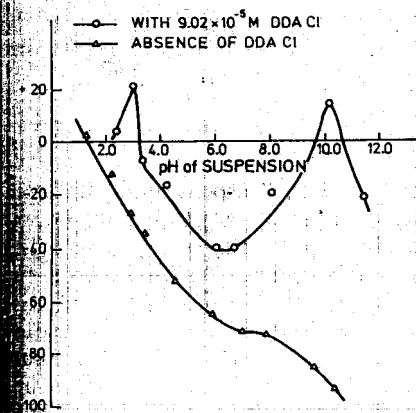


Fig. 1. Zeta potentials of quartz as a function of pH.

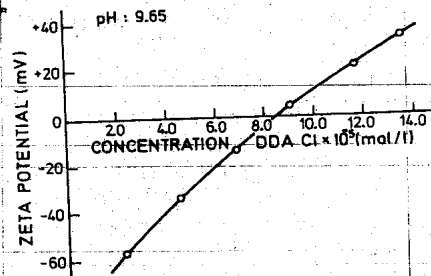


Fig. 2. Zeta potentials of quartz as a function of DDACl concentration.

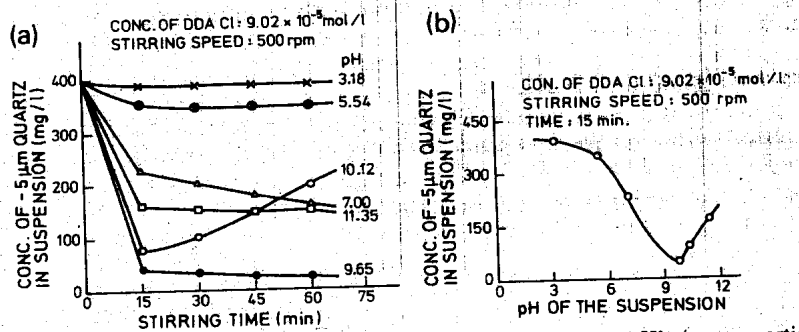


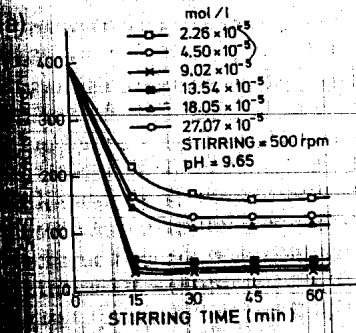
Fig. 3. (a) Turbidity of solution as a function of time for different pH's (coarse particle size  $-38+20 \mu\text{m}$ ); (b) Turbidity of solution as a function of pH.

1988). Figure 2 shows the effect of DDACl concentration on the zeta potential of quartz. For concentrations below  $8.5 \times 10^{-5} M$  the surface holds negative potentials.

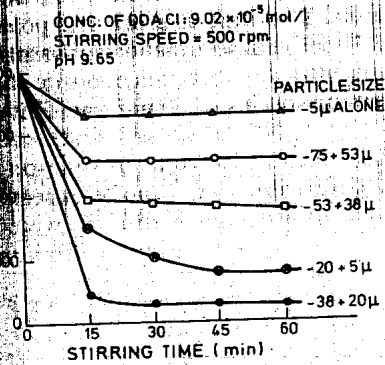
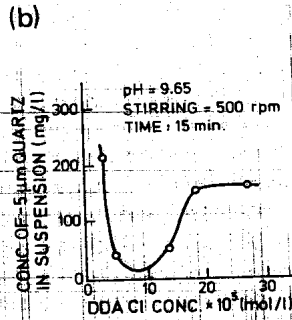
#### Shear-flocculation of quartz

The concentration of  $-5 \mu\text{m}$  quartz particles in suspension for different pH's as a function of stirring time is shown in Fig. 3a. At pH 3.18 the flocculation was found to be negligible. Figure 3b was plotted by taking the turbidity values for 15 min stirring from Fig. 3a and the general trend in both the figures is that the flocculation reaches a maximum at pH 9.6. A further increase of pH rises the turbidity. Figure 4a shows the effect of DDACl concentration on flocculation for different stirring times. The maximum- and minimum flocculation correspond to concentrations of  $2.26 \times 10^{-5} M$  and  $9.02 \times 10^{-5} M$ , respectively and is in conformity with the data plotted in Fig. 4b for 15 min stirring. The effect of particle size on the concentration of fines in sus-

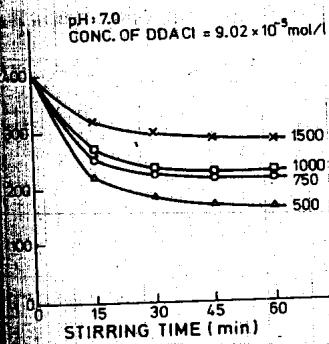
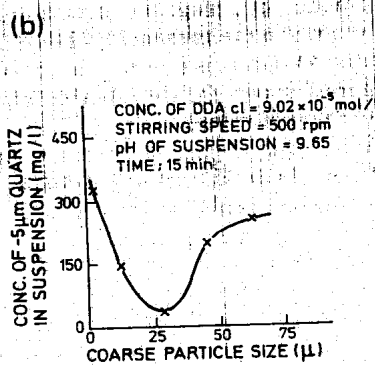
3. SHEAR-FLOCCULATION OF QUARTZ



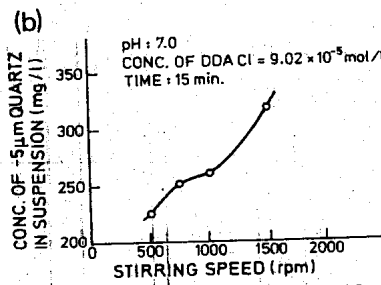
(a) Effect of DDACl concentration on shear-flocculation (coarse size:  $-38+20 \mu\text{m}$ ); turbidity as a function of DDACl concentration.



(a) Effect of particle size on shear-flocculation. (b) Turbidity as a function of coarse particle size.



(a) Effect of stirring speed on flocculation (coarse particle size:  $-38+20 \mu\text{m}$ ). (b) Turbidity as a function of stirring speed.



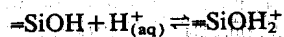
pension is shown in Fig. 5a. While there is a general decreasing trend in the concentration of fines for different coarse particle sizes, that for  $-38 + 20 \mu\text{m}$  shows the lowest turbidity, i.e. maximum flocculation. Figure 5b shows the flocculation behaviour as a function of coarse particle size. The effect of stirring speed on flocculation is shown in Fig. 6a. The tests were carried out at pH 7 and the turbidity was found to be lower for a stirring speed of 500 rpm. The data of Fig. 6b for 15 min stirring shows that the concentration of fines in suspension increases for stirring speeds higher than 500 rpm.

## DISCUSSION

### Interactions of quartz-DDACI

The charge on the particle may vary in accordance with the chemical environment - pH, reagent concentration, etc. The changes in the zeta potential of quartz in the presence of DDACI (Fig. 1) suggest that the adsorption of amine on quartz is physical i.e. involving attraction between opposite charges. Figure 7 shows the distribution of various species of quartz and DDACI at different pH values.

When quartz particles are in equilibrium with the aqueous solution three different hydroxylated sites  $-\text{SiOH}_2^+$ ,  $-\text{SiOH}$  and  $-\text{SiO}^-$  can be expected depending on the pH. At very high  $\text{H}^+$  concentration, the hydroxyl covered surface can adsorb an extra proton to form a substituted surface hydronium  $-\text{SiOH}_2^+$ :



and at low  $\text{H}^+$  concentrations the negative site  $\text{SiO}^-$  is favoured by releasing a proton to the solution ( $\text{pK} = 6.8$ ; Schindler, 1981):

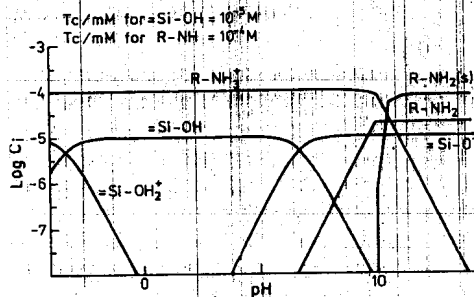


Fig. 7. Species diagram as a function of pH.

Changes in the zeta potentials of quartz are related to the hydroxylation of quartz surface at different pH values and the interaction of amine species. The positive potentials noticed at  $\text{pH} \leq 3.2$  (Fig. 1) can be attributed to the surface complexation of  $R\text{-NH}_3^+$  on to the neutral  $-\text{SiOH}$ :



The shift in the zeta potential to less negative values in the presence of DDACI is uniform in the range of  $\text{pH} 3.2\text{--}6.0$ .  $\text{pH} 6.0\text{--}9.6$  appears to be favourable for charge neutralization between  $\text{SiO}^-$  and  $R\text{-NH}_3^+$  and is dominated by an electrostatic interaction:



The positive potential observed above a collector concentration of  $8.5 \times 10^{-5}$  M is expected to be due to a further adsorption of  $R\text{-NH}_3^+$  and amine precipitation on the quartz surface (Fig. 2).

The reactions of amines in aqueous solutions are given by:



From the log concentration-pH diagram for  $1 \times 10^{-4}$  M dodecylamine, the critical pH for the precipitation of  $R\text{-NH}_2(s)$  species was shown to be 10.2 (Herstenau, 1982).

#### Dependence of aggregation on particle hydrophobicity and charge:

In the shear-flocculation tests the lowest turbidity, i.e. maximum flocculation, observed at  $\text{pH} 9.6$  (Fig. 3a) corresponds to the point of zero charge of

Table 1. Contact angles on quartz (data taken from Kellogg and Vasquez-Rosas, 1945)

DDACI conc.	pH	Contact angle ( $^\circ$ )	Comments
	6.0	0	
	10.0-10.5	~30	
	5.8	58	
	9.3	80	
	9.0-11.0	80	
	10.0-10.5	85	monolayer coverage
	> 12.0	0	amine molecule precipitation and neutral molecule alone cannot adsorb
	6.0	40	submonolayer coverage

quartz in aqueous solution of DDACl (Fig. 1). This situation is explained by eq. 4 and the reasons for maximum flocculation are: (1) less electrostatic repulsion, and (2) favourable collector adsorption.

The reactions of aqueous solutions of DDACl are pH and concentration dependent. Since hydrophobicity is a critical factor for aggregation of particles the results of the present work are also analysed by the data of Kellogg and Vásquez-Rosas (1945) on the contact angles of quartz with DDACl (Table 1). The higher the contact angle the more hydrophobic is the particle surface. In the pH range 9–11 the contact angle observed was  $80^\circ$  for an amine concentration of  $10^{-5}$  M. A contact angle of  $58^\circ$  at pH 5.8 indicates partial coverage of the amine. Even at a high concentration of  $10^{-3}$  M the surface of the particle attains only a submonolayer at pH 6. Higher contact angles ( $80^\circ$ – $85^\circ$ ; pH 9–11) for concentrations of  $10^{-5}$ – $10^{-4}$  M are attributed to the partial hydrolysis of the amine.

From Fig. 3a it is observed that at pH 10.12 (pH region of amine precipitation) a fluctuation in solution turbidity, i.e. a decrease for the first 15 min with a subsequent increase for further period of stirring suggests both flocculation and dispersion of aggregates. Around the pH region of amine precipitation physical adsorption of the precipitate on the surface of quartz may impart enough hydrophobicity and consequently favour flocculation. But prolonged agitation may peel off the amine precipitate from the surface and thereby lead to floc redispersion. At pH 10.12 the particles hold positive charges  $\sim 15$  mV (Fig. 1). Figure 3b shows a higher concentration of fines in suspension beyond pH 10 – i.e. a lower flocculation when compared to the amount flocculated at pH 9.6. However, negligible flocculation at pH 3.18 (Fig. 3a) is due to lack of enough hydrophobicity and the potential at the referred pH, as observed from Fig. 1, is +22 mV. On the other hand, even though the particle is hydrophobic enough (Table 1: contact angle  $80^\circ$  at pH 9–11), the flocculation is only minimum (Fig. 4a) for a DDACl concentration of  $2.26 \times 10^{-5}$  M and the corresponding zeta potential is  $-58$  mV (Fig. 2). In this case hydrophobicity is not the factor for minimum flocculation but the surface charge is responsible for the observed behaviour. When the particles hold high potentials it becomes necessary to apply higher stirring speed to overcome the energy barrier. The same argument holds good for the decrease in flocculation at higher amine concentrations. As seen from Fig. 2 the positive potentials increase for amine concentrations above  $8.5 \times 10^{-5}$  M and the reasons are clear for the trend observed in Fig. 4b.

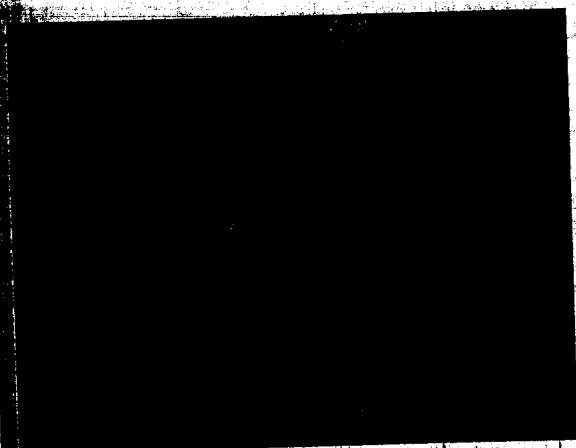
#### *Effect of particle size and stirring speed:*

The size of the coarse particle is an important factor in shear-flocculation since it influences the collision mechanism. Samygin et al. (1968) found that the adhesion rate of fines to coarse particles to be  $10^3$ – $10^4$  as high as the rate



of cohesion between the fines. Such effect was attributed to different mechanisms at work, i.e. diffusion for collisions between fines and inertia for collisions between fine and coarse particles.

Figure 5a shows the concentration of fines in suspension for different coarse particle sizes. With  $-5 \mu\text{m}$  alone no appreciable change was observed in solution turbidity. For  $-20+5$  and  $-38+20 \mu\text{m}$  particles the flocculation increases with size. A further increase in the coarse size ( $-53+38$  and  $-75+53 \mu\text{m}$ ) results in higher concentrations of fines in suspension. In principle, the flocculation should be more when the size of the coarse particle is increased for the reason that more surface is available to fines. However the aggregation in this case seems to be opposed by attrition, i.e. a process of re-dispersion of fines due to collisions between slime covered coarse particles. Earlier workers (Dianzou et al., 1988) observed breakage of aggregates due to attrition and shear forces generated in the liquid when the coarse particle size exceeded the microscale of turbulence. The effect of carrier size (coarse particle) on the recovery of  $-5 \mu\text{m}$  wolframite was investigated by Hu et al. (1988). With increasing carrier size the fraction of  $-5 \mu\text{m}$  adhering to coarse particles increased but when the carrier size was greater than the microscale of turbulence the adhesion of fines was found to decrease. Samygin et al. (1968), point out that as the difference between the sizes of coarse and fines increases the latter may flow past the former instead of colliding. Whether it is low collisions between fines and coarse (when the coarse size is beyond the optimum) or attrition that leads to a lower flocculation is open to question. The



Aggregate of fines ( $-75+53$  and  $-5 \mu\text{m}$  mixture; conc. DDACl  $9.02 \times 10^{-3} M$ ; stirring speed 500 rpm; pH 9.6).

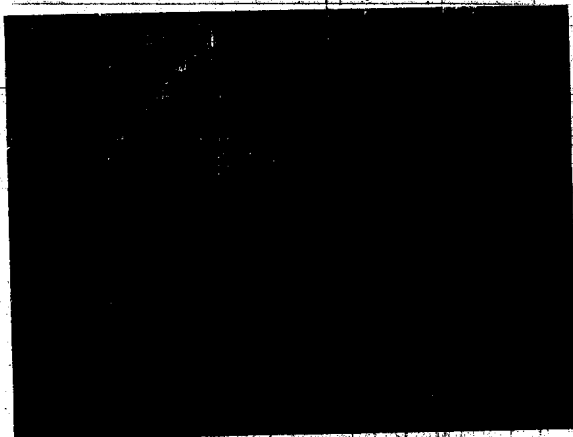


Fig. 9. Aggregate of coarse-fine particles ( $-53+38$  and  $-5 \mu\text{m}$  mixture; conc. DDACl  $9.02 \times 10^{-5} M$ ; stirring speed 500 rpm; pH 9.6).

scanning electron micrographs (Figs. 8 and 9) are shown for two experimental conditions. When a  $-75+53$  and  $-5 \mu\text{m}$  mixture was subjected to shear-flocculation the aggregates formed mainly between fines (Fig. 8) and the aggregates of coarse-fine were sparse. Figure 9 shows a coarse-fine aggregate formed after stirring a mixture of  $-53+38$  and  $-5 \mu\text{m}$  particles. Three types of aggregates, i.e. fine-fine, fine-coarse and coarse-coarse, can be expected to form when a mixture of coarse and fine hydrophobic particles is subjected to stirring.

In another set of experiments the stirring speed was varied from 500 to 1500 rpm and the pH was maintained at 7.0 (Fig. 6a). As the stirring speed increases the amount flocculated decreases. The reasons for such a trend will be apparent when the factors, i.e. degree of hydrophobicity and charge, are considered. The electrokinetic behaviour of quartz (Fig. 1) shows that a highly negatively charged surface ( $\sim -75$  mV at pH 7.0) in aqueous solution shifts to a less negative potential ( $-40$  mV at pH 7.0) as a result of the reagent adsorption. Further, Table 1 shows that for a collector concentration  $10^{-5} M$  the contact angle increases from  $58^\circ$  at pH 5.8 to  $80^\circ$  at pH 9.0. From the data it can be concluded that at pH 7.0 the surface should only be partly hydrophobic. If it is assumed that the particles are sufficiently hydrophobic and holding potentials of the order of  $-40$  mV then with increasing speed of stirring the flocculation should increase. The fact that the solution turbidity increases with stirring speed (Figs. 6a and b) suggests that the particles are not hydrophobic enough and the possibility of floc redispersion at higher stirring speeds is also not ruled out. It must be pointed out that the agitation speeds vary from system to system: 1500 rpm in scheelite-sodium oleate (Warren

1975); galena-xanthate (Subrahmanyam et al., 1990a,b); 400–1200 rpm in hematite-sodium dodecyl sulfonate (Fuerstenau et al., 1988) and even impeller speeds as low as 225 rpm were used by Samygin et al. (1968). Two phenomena, (1) lower flocculation and (2) floc redispersion, need to be recognized in shear-flocculation. Several reasons like high similar potentials between particles, lack of enough hydrophobicity, a large difference between the sizes of fine and coarse particles, insufficient stirring speed, etc. may result in a lower flocculation. Whereas floc redispersion occurs mainly because of the factors such as attrition, breakage of flocs due to a high stirring speed, removal of the adsorbed reagent (physical adsorption?) from the particle surface and consequently detachment of the adhered particles at higher speeds of stirring, etc.

#### CONCLUSIONS

(1) From the results of the study on shear-flocculation of quartz in aqueous solutions of dodecylamine chloride (DDACl) it has been shown that the hydrophobicity of the particle and charge influence the aggregation mechanism. At the point of zero charge the repulsive forces between the particles are minimum and the particles are hydrophobic enough to aggregate even at low stirring speeds.

(2) The electrokinetic behaviour of quartz in aqueous and DDACl solutions indicates that the mechanism of adsorption is physical. The reactions of aqueous solutions of DDACl are pH and concentration dependent; the hydrophobicity of quartz and consequently the charge on the particle are governed by those reactions. The flocculation was found to be maximum for the conditions: pH 9.6; DDACl concentration  $9.02 \times 10^{-5} M$ ; stirring speed 500 rpm and the size of the coarse particle  $-38 + 20 \mu m$ .

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