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ORIGINAL CONTRIBUTION

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Effect of sodium metasilicate on natural flotability of coal

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Abstract The effect of the quantity of sodium metasilicate and conditioning time in one set of experiments, and the effect of the solution concentration of sodium metasilicate, added at the same dosage and conditioning time to coal slurry, on flotability of a typical Indian coal in another set of experiments are studied. Two sets of 3^2 full factorial experiments are carried out to assess the effects of the aforementioned variables. The generated data are analyzed quantitatively and explained qualitatively. At 0.1% (w/v) solution concentration of solution added (0.02 g/kg) and 8 min conditioning time, sodium metasilicate acted as activator for kaolinite, whereas at 1.0% (w/v) solution concentration (0.2 g/kg), it acted as dispersant. The best observed condition of depressant is obtained at an added concentration of 10.0% (w/v, 0.2 g/kg) and 8 min conditioning time. The desired effect of the sodium metasilicate can be achieved by controlling its quantity, solution concentration added, and conditioning time.

Keywords Sodium metasilicate · Coal · Flotation · Activator · Dispersant · Depressant

Introduction

Sodium silicate is one of the most important modifiers in flotation. It is traditionally used as a dispersant, but it may also act as depressant and even as activator [1]. The soluble silicates hydrolyze extensively and interact with the mineral surface. The aqueous solution equilibria of soluble silicates have been studied [2, 3] and the species diagram has been constructed [4]. Iler (1979) [5] has dealt extensively with the chemistry of silica. The description of Lagas (1995) [6] on mineral dissolution and precipitation rates and that of Dove (1995) [7] on kinetic and thermodynamic study on silica reactivity gave important insight into the chemistry of silica solution. Water glass is widely used as a dispersant/depressant. Commercial water glass is available with ratios of SiO_2 to Na_2O ranging from 1.6 to 3.25. Dispersing/depressing ability of water glass in flotation systems can be improved by reacting polyvalent metal salts with sodium silicate. The depressing properties of different metal hydroxy silicate hydrosols in flotation had been reported by a number of investigators [8–13].

Coal is a mixture of carbon and ash forming mineral matter. It is usually negatively charged or, at most, neutral at pH values above 5.0 [14]. Aplan (1976) [14] has

discussed flotation of coal in detail with reference to reagents (collector, frother, and modifier), process variables (pulp density, conditioning, aeration and agitation, pH, temperature), and feed characteristics. The various modifiers used in coal flotation are listed and discussed. Sodium metasilicate is generally used to depress silicate gangue [14]. Flotation is the most efficient method in treating −0.5 mm coal, as coal is a low-value material and only frother and/or collector and/or sodium silicate are used as flotation reagent.

The authors have studied the effect of sodium metasilicate in the presence of collector and frother and found that the former acted as a dispersant [15]. Mercade's [9] work indicates that calcite flotation is very strongly depressed by water glass. The hydrolysis products of sodium silicate contain a number of monomeric, polymeric, and colloidal species. According to Gong et al. [3] the active species in silicate solution for the depression of flotation are polymeric silicate species and small colloidal particles.

The solubility of amorphous silica is 120 ppm/l, as SiO_2 [16] and the solution of even 0.1% (w/v) is above the solubility limit. As soon as sodium silicate solution above the solubility limit is added into the slurry, readjustment of the silicate species will start according to the existing conditions, but it may not reach equilibrium in the given conditioning time and the flotation may take place in dynamic equilibrium condition. Thus, the concentration of solution added to the slurry and duration of the conditioning time will control the silicate species present in the slurry. The different silicate species affect the flotability of mineral/coal differently. In the present work, the effect of the quantity of sodium metasilicate, the concentration of its solution added, and duration of conditioning time on flotability of coal is studied.

Experimental

Materials

Sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$), supplied by LOBA Chemie, USA, was used for the experiments. The sodium metasilicate solution was freshly prepared before experiments. Coking coal fines were collected from Bhelatand Coking Coal Washery in Jharkhand, India for this purpose. The sample was sieved at a 500-μm sieve for the purpose of the experiment. The complete size distribution and ash in different closed size fractions of the sample taken for the experiment is given elsewhere [15]. The sample on average contained 0.1% moisture, 19.6% volatile matter, 15.6% ash, and 64.7% fixed carbon. The coal possesses natural hydrophobicity, and 25.33% of combustible material can float without addition of any reagent [15]. The major ash forming minerals present are quartz, kaolinite, chloritoid, microcline, and anorthite [15].

Methods

Denver D-12 subaeration flotation machine with 1-l capacity cell was used for flotation studies. One hundred grams of coal sample was mixed with 500 ml of water and conditioned in the flotation cell for 2 min. Sodium metasilicate of predetermined quantity, at a particular solution concentration, was added and conditioned for the desired time according to design of experiments. In the first set (Table 1a), at quantity of 2 g/kg sodium metasilicate, it was necessary to add 200 ml of 0.1% (w/v) solution, which made up the total water content during conditioning to 700 ml. All the experiments were carried out at ambient (7.0 to 7.5) pH. Both the froth and the tailings were collected separately, dried, and analyzed for combustible material. Grade was calculated using the following formula.

$$\%\ Grade = \left(Combustible\ material / Total\ weight\ of\ material\right) \times 100$$

and recovery of combustible material was calculated as

$$\%\ \text{Recovery} = (\%\ \text{weight of product} \times \%\ \text{combustible material in the product}) / \%\ \text{combustible material in the feed}$$

Variables

In the first set of experiments, effect of quantity of sodium metasilicate and conditioning time was studied using 3^2 full factorial design. In the second set of 3^2 full factorial experiments, the solution concentration of the sodium

Table 1a 3^2 full factorial design for coal flotation (first set)

Variables	Level		
	1	2	3
Quantity of sodium metasilicate, g/kg (Q)	0.02	0.2	2.0
Conditioning time, min (T)	2	4	8

Coal, 100 g; concentration of sodium metasilicate solution added, 0.1% w/v

Table 1b 3^2 full factorial design for coal flotation (second set)

Variables	Level		
	1	2	3
Solution concentration of sodium metasilicate added, w/v (c)	0.1	1.0	10.0
Conditioning time, min (t)	2	4	8

Coal, 100 g; quantity of sodium metasilicate, 0.2 g/kg

metasilicate added at a fixed dosage of sodium metasilicate and conditioning time was studied. The variables studied and the corresponding levels are given in Tables 1a and 1b. The volume of slurry during conditioning of the first and second set of experiments are 700 and 500 ml, respectively. All the experiments were carried out under identical conditions except the variation of desired variable. All the studies are carried out at 1,500 rpm, 700-ml slurry, and ambient pH.

Results and discussion

Statistical analysis

Two sets of experiments were conducted according to 3^2 full factorial designs [17], and another two experiments were conducted for each set at level 2 (Tables 1a and 1b) to estimate error and standard deviation. The purpose of the first set was to study the effect of quantity of sodium metasilicate and time (Table 1a), and the purpose of the second set was to study the effect of solution concentration of sodium metasilicate added and time (Table 1b). The experimental data were fitted to regression equations with quadratic and interaction terms using MS Excel. Because the coefficients of developed equations cannot be compared as such, the coefficients were standardized according to the following formula [18]:

$$B_k = b_k\left(s_k/s_y\right)$$

Where B_k = standardized partial regression coefficient, b_k = partial regression coefficient, s_k = standard deviation of the variable, and s_y = standard deviation of the response. The standardized equations were subjected to Student's t test [17] to test the significance of the coefficients. It was found that all the terms of the equations, except the interaction term in both the recovery equations, were significant at the 95% confidence level. As the coefficients are correlated, both the recovery equations are computed again after omitting the interaction term. The test of significance is valid only when the equations satisfy the F test and fit the experimental data adequately. The developed regression equation and equation after standardization are given below:

(1) First set of experiment

$$Q_r = 29.24049 - 4.04012Q - 2.58T + 0.77161Q^2 + 0.18667T^2 \quad (1a)$$

The equation after standardization is

$$Q_r = 29.24049 - 1.2673\,Q - 2.25813\,T + 0.50795\,Q^2 + 1.69788\,T^2 \quad (1b)$$

R^2=0.973, F value=2.077

$$Q_g = 95.42232 + 4.430781\,Q - 0.75512T\,T + 0.1184\,QT - 2.19697\,Q^2 + 0.03153\,T^2 \quad (2a)$$

The equation after standardization is

$$Q_g = 95.42232 + 3.87028\,Q - 1.84044\,T + 0.58747\,QT - 4.02745\,Q^2 + 0.79857\,T^2 \quad (2b)$$

R^2=0.980, F value=0.945

Where Q_r and Q_g = recovery and grade of combustible material, respectively, Q = quantity of sodium metasilicate added, and T = conditioning time.

(2) Second set of experiment

$$c_r = 27.60837 + 19.83971\,c - 2.85917\,t - 10.13\,c^2 + 0.19792\,t^2 \quad (3a)$$

The equation after standardization is

$$c_r = 27.60837 + 6.11542\,c - 2.4591\,t - 6.55306\,c^2 + 1.76901\,t^2 \quad (3b)$$

R^2=0.974, F value=1.943

$$c_g = 93.44184 + 2.69737c - 0.1296t - 0.02982ct - 1.02226c^2 + 0.01972t^2 \quad (4a)$$

The equation after standardization is

$$c_g = 93.44184 + 5.50511\,c - 0.73805\,t - 0.34564\,ct - 4.37854\,c^2 + 1.16718\,t^2 \quad (4b)$$

R^2=0.970, F value=0.251

Where c_r and c_g = recovery and grade of combustible material, respectively, c = solution concentration of sodium metasilicate added, and t = conditioning time.

All the equations showed high R^2 value (greater or equal to 0.97). From the F test [17], it was found that all the equations fit the experimental data adequately.

Qualitative analysis

First set (effect of quantity of sodium metasilicate)

Different volume of sodium metasilicate solution of 0.1% (w/v) was added to vary its quantity in the slurry at ambient pH.

With the increase in the quantity of sodium metasilicate and conditioning time, the recovery decreases (Fig. 1). The grade at low quantity (0.02 g/kg) of sodium metasilicate and conditioning time of 8 min is at nadir (Fig. 2). The recovery is also low compared to 2 min conditioning time. The solubility of amorphous silica is assumed to be 120 ppm as SiO_2 [16]. In 0.1% $Na_2SiO_3{\cdot}9H_2O$ solution, SiO_2 exceeds its solubility limit and it will be in polymeric or colloidal form. The quantity of silica will be within the solubility limit when 2 ml of this solution is added to the slurry and the water content is made up to 700 ml, and then, silica species will start depolymerization, dissolution, and will adsorb on silicate minerals (quartz, kaolinite, etc). During depolymerization and dissolution of SiO_2 as $Si(OH)_4$, an intermediate, positively charged species like $> Si(OH)_2^+$ [19] may be formed or it may combine with Na^+ and form positively charged species like >SiO–Na^+ [20], ≅$SO^-(H_2O)Na^+$, where ≅S = general symbol for surface functional group [21].

The positively charged species are likely to be attracted by negatively charged surfaces due to electrostatic force of attraction and adsorb on them. The species adsorbed on the carbon surface will decrease the hydrophobicity of the coal

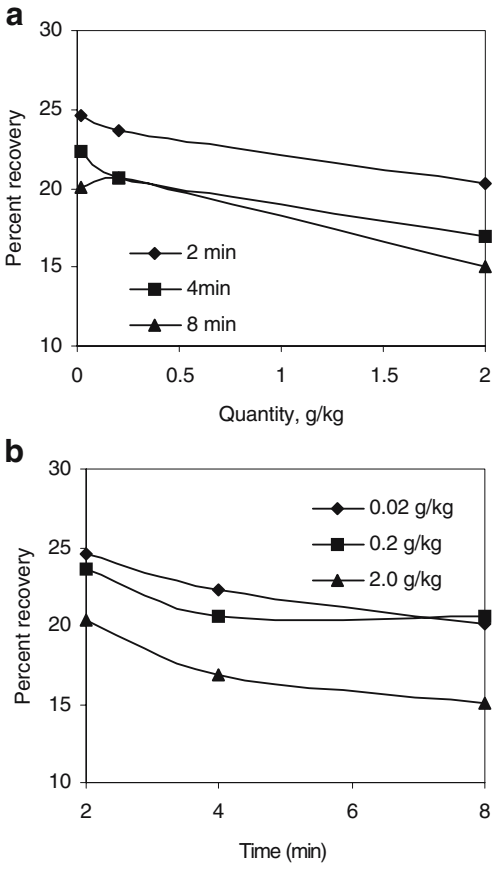

Fig. 1 Plots showing the quantity of sodium metasilicate vs recovery of combustible material (**a**) and conditioning time vs recovery of combustible material (**b**)

particles. The species adsorbed on silicate minerals will polymerize with them, extending the OH group outwards. The silicate minerals may polymerize the silica species adjacent to it uncovering the carbon surface again. The adsorbed $> Si(OH)_2^+$ on carbon surface will form $Si(OH)_4$ in due course of time. The latter species bears no charge and is not known to adsorb on hydrophobic surfaces [5]. At low concentration of solution and starvation quantity of silica, soluble monomeric silica species will predominate, and polymeric form, which is a more effective depressant, cannot be formed. The hydrophilicity of silicate minerals adsorbed with a monomeric silica species with the OH group extending outwards will possibly be lower than the original silicate minerals. It is known that hydroxides are less hydrophilic than silicates [22]. So high-grade coal particles may be covered by silica species containing Na^+ ion and depress, whereas comparatively low-grade coal particles uncover the carbon surface by subsequent polymerization by adjacent silicate minerals and float. The decrease in both grade and recovery at 0.02 g/kg of sodium metasilicate and 8 min time is attributed to this. From 0.02 to 0.2 g/kg sodium metasilicate and at 2 and 4 min

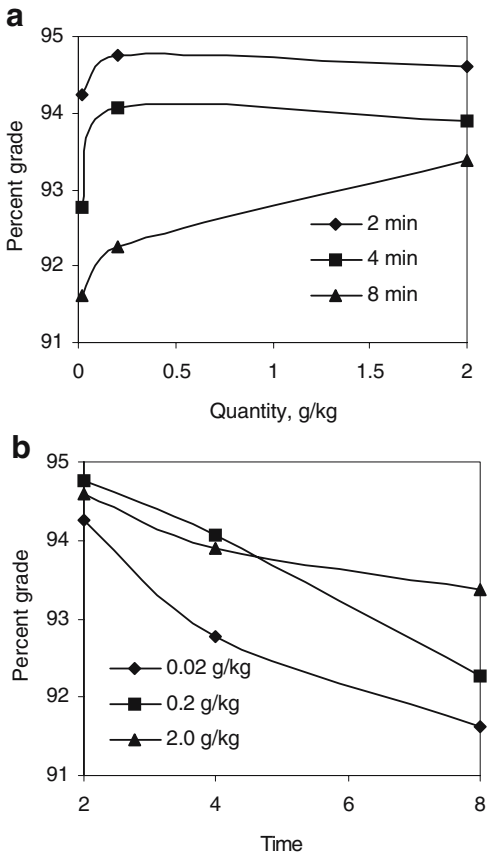

Fig. 2 Plots showing the quantity of sodium metasilicate vs grade of combustible material (**a**) and conditioning time vs grade of combustible material (**b**)

conditioning time, there is a rapid increase in grade after, causing it to remain more or less the same. But there is a continuous increase in grade from 0.02 to 2.0 g/kg at 8 min conditioning time. The positive interaction of quantity of sodium metasilicate and conditioning time on grade (Eq. 2) is due to this increase in grade. In Fig. 3, the X-ray diffraction pattern of float at 2 and 8 min time, with 0.02 g/kg of sodium metasilicate, are compared. The peak intensity count of kaolinite (108) and quartz (412) at 2 min is lower than the corresponding counts of kaolinite (388) and quartz (480) at 8 min. The difference in peak intensity counts of the above minerals, especially kaolinite, gives an indication of activation. All the peaks in the X-ray diffraction pattern of 8 min could not be identified with certainty. The change in d-spacing due to adsorption of monomeric silica cannot be ruled out. The low recovery and grade at 8 min time indicate that there is depression of some high-grade coal particles.

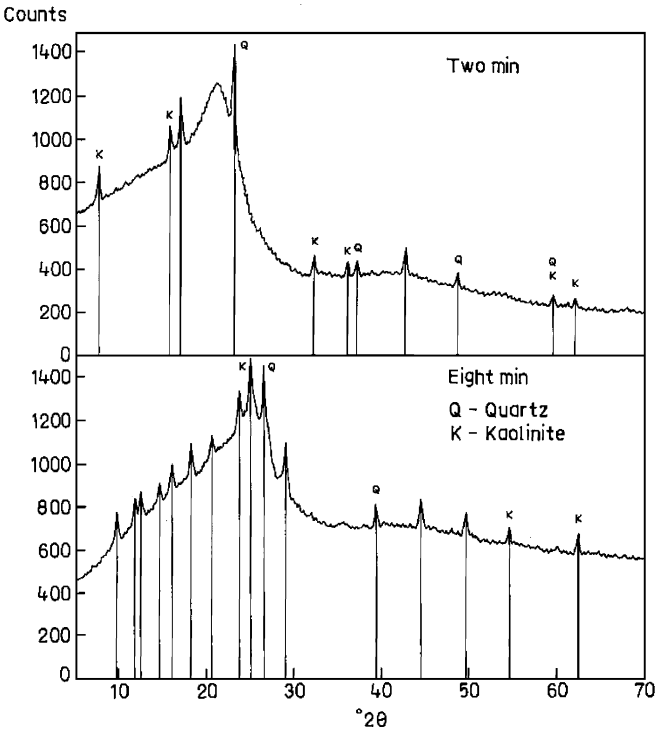

Fig. 3 X-ray diffraction pattern of float at 2 and 8 min time, quantity of sodium metasilicate 0.02g/kg and concentration of sodium metasilicate solution added 0.1% (w/v)

Second set (effect of solution concentration of sodium metasilicate added)

The sodium metasilicate solution of different concentrations was prepared and added to the slurry of neutral pH. The quantity of 0.2 g/kg was maintained for all experiments.

The recovery is minimum at 0.1% (w/v) sodium metasilicate solution. The recovery is maximum at 1.0% solution and it again decreases at 10.0% solution (Fig. 4a). The recovery decreases with the increase in conditioning time (Fig. 4b). An important observation is that the recovery is always higher at 1.0% solution concentration of sodium metasilicate added, in comparison to 0.1 and 10.0% solution concentration (Fig. 4a). The low recovery and grade at 0.1% sodium metasilicate solution is explained in "First set (effect of quantity of sodium metasilicate)." In 10.0% sodium metasilicate solution, the silica will be in the colloidal form with negative surface charge. After the addition of solution into the slurry, depolymerization of colloidal form will start and these will combine with silicate minerals by hydrogen bond and depress them selectively; thus, there is an increase in grade and a decrease in recovery (Fig. 5). The decrease in recovery with the increase in time indicates that some time is needed for depolymerization and selective attachment with the silicate minerals. The maximum recovery with moderate grade was obtained at 1.0% solution of sodium metasilicate added and 2 min time. It is possible that at this solution

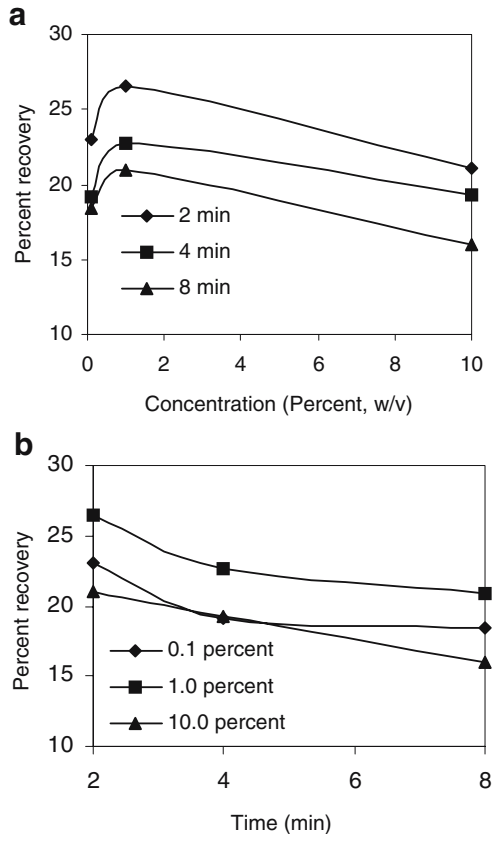

Fig. 4 Plots showing the concentration of sodium metasilicate solution added to the coal slurry vs recovery of combustible material (**a**) and conditioning time vs recovery of combustible material (**b**)

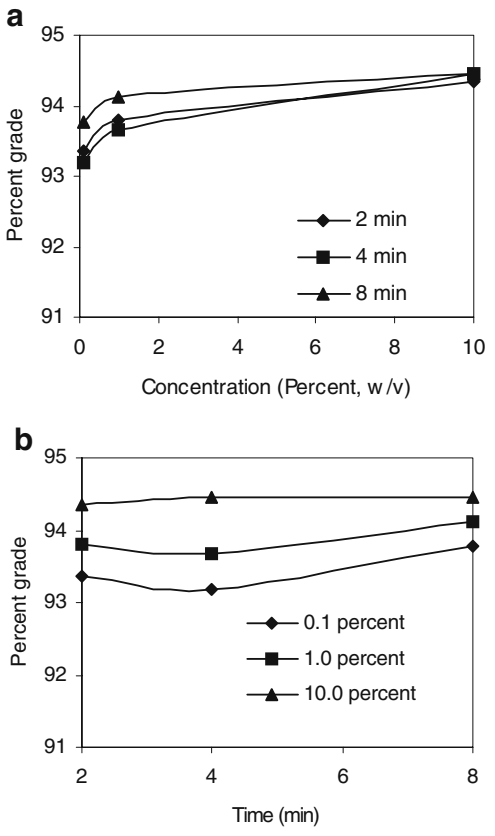

Fig. 5 Plots showing the concentration of sodium metasilicate solution added to the coal slurry vs grade of combustible material (**a**) and conditioning time vs grade of combustible material (**b**)

concentration added, first dispersion occurred after adsorption, and after depolymerization of adsorbed silica species to some extent and/or sufficient adsorption on silicate minerals beyond 2 min time, depression started. The positive interaction of solution concentration of sodium metasilicate added and time on grade (Eq. 4) is due to depolymerization of silica species to some extent and absorption on silicate minerals with the increase in time.

Conditions for activation, dispersion, and depression

The silica will be in the colloidal form above its solubility limit. The silica is above the solubility limit in 0.1% (w/v) solution concentration of sodium metasilicate and the colloidal particles are not observed by the naked eye, but at 10.0% (w/v) solution concentration, the colloidal particles are clearly visible. This indicates that the size of colloidal particles is smaller at 0.1% (w/v) solution concentration and bigger at 10.0% (w/v) solution concentration. At 0.1% (w/v) solution concentration added at a constant dosage of sodium metasilicate (0.02 g/kg) and 8 min conditioning time, activation of kaolinite is observed. The amorphous silica in solution can be dissolved by bringing out the insoluble limit by dilution [16]. With the addition of sodium metasilicate solution into slurry, the insoluble limit will go down and the depolymerization of colloidal silica will start, and dissolution will take place with the increase in time. The small colloidal particles are good depressants but the monomeric silica weakly adsorb on mineral surface and is not a good depressant [3]. In the present study, sodium metasilicate acted as activator for kaolinite. The possible interaction is discussed "First set (effect of quantity of sodium metasilicate)."

At 1.0% (w/v) solution concentration added at a dosage of 0.2 g/kg and 2 min conditioning time, sodium metasilicate acts as a dispersant, and with the increase in conditioning time it acts as depressant. The surface of colloidal silica is negatively charged [16]. These negatively charged particles are likely to disperse negatively charged slimes of kaolinite and quartz from negatively charged coal surface. But beyond the conditioning time of 2 min, depression is observed, possibly due to some degree of depolymerization of colloidal silica particles. At 10.0% (w/v) solution concentration added at a fixed dosage (0.2 g/kg) and 8 min conditioning time, the depressing action of sodium metasilicate is greater,

compared to other observed conditions. The high molecular weight polymers of silica are good depressants, but not the large colloidal particles [3]. With the increase in conditioning time, some degree of depolymerization of colloidal silica takes place and may act as good depressant.

Conclusions

Sodium metasilicate acts as an activator for silicate minerals (quartz, kaolinite) (Fig. 5) at 0.02 g/kg dosage of 0.1% (w/v) solution concentration and at 8 min conditioning time. The maximum recovery obtained at 0.2 g/kg at 1.0%(w/v) solution concentration and 2 min of conditioning time is an indication of dispersion. Sodium metasilicate solution added at 0.2g/kg of 10.0% (w/v) concentration acts as a more effective depressant. The positive interaction of quantity of sodium metasilicate and conditioning time (Eq. 2) is indicative of progressive polymerization of silica species, uncovering the carbon surface and selective depression of silicate minerals. In any flotation operation, the dosage of sodium silicate used would be such that it will not exceed the solubility limit of silica in the slurry. So the desired effect can be achieved by controlling the solution concentration of sodium metasilicate added and residence time.

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