Paste 2009 — R.J. Jewell, A.B. Fourie, S. Barrera and J. Wiertz (eds)
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https://papers.acg.uwa.edu.au/p/963_2_de Araujo/

Factorial Design 2^n in Bauxite Tailings Flocculation and Bingham Model for Rheological Characteristics

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Abstract

In the last years, the disposal of tailings in the form of pastes and/or high-density slurries has gained importance as it may present significant advantages in comparison to more traditional disposal techniques. The knowledge of physical chemical characteristics of the material to be disposed, as well as the interactions that result from the use of polymeric flocculants on solid/liquid separation can lead to the formation of pastes and/or high-density slurries with adequate conditions for handling and final disposal.

With the help of factorial design tool (2^2)*, with pH and flocculant dosage as independent variables, the effects of three different polyacrylamide flocculants was evaluated on the final per cent solids of a bauxite tailings flocculated material, over a pH range from 5 to 7 and different dosages of flocculants. These factors were analysed by fitting the experimental data to a polynomial model, which plots settling rates response in the form of contour maps.*

Regarding the final percentage of solids of the flocculated material, a cationic polymer presented the best results among the three flocculants tested. With a dosage of 130 g/t and pH 5, the final percentage of solids (by wt.) was 31.2% after one hour.

The rheological characteristics for different percentage of solids are determined with the help of the Bingham model, where the viscosity and yield stress of a bauxite tailing are available without a presence of flocculant.

According to the utilised model, the yield stress show a signification increase for to the slurry with 25–30 per cent of solid by weight, with a viscosity of between 8.2 and 13.0 cP and a yield stress between 3.0 and 6.8 Pa.

1 Introduction

Large-scale mining and mineral processing operations around the world inevitably generate an enormous amount of solid residue that must be disposed of economically and in an environmentally acceptable manner. Generally, bauxite tailings are in form of slurry with low percents of solid and solid-liquid operations are required for their final disposal.

The use of mineral pastes and/or high-density slurry appears as an interesting alternative. Two interdependent factors should be considered. First, it is essential that the slurry must be handled and transported by pipeline at a minimum energy expending. A second important factor is the physical and economical capacity to produce this paste and/or high-density slurry. This requires a good understanding of the behaviour of the slurry in the dewatering operation and the development of a suitable technology for producing slurries with high solids loadings (Boger and Nguyen, 1998).

1.1 Flocculation

Suspended fine particles are often resistant to flocculation due to repulsive forces resulting form electrical double layer interactions, solvation forces or the presence of protective coatings. The first step in a flocculation process is, therefore, destabilization of the suspension by eliminating these repulsive forces. Double-layer repulsion can be overcome by reducing particle surface charge—commonly through pH control—or by screening the charge through the addition of electrolytes, especially types containing multivalent counter ions. Polymers may also serve as destabilisation agents. Very low molecular weights polyelectrolytes, of opposite charge to the particles, can function more or less as counter ions. Polyelectrolytes of somewhat higher molecular weight can adsorb to form oppositely charged patches on particle surfaces. Such patches can interact with regions of bare surface on other particles—the so-called ‘charge-patch’ mechanism of flocculation. High molecular weight polymers, charged or uncharged, can provide a link between particles by ‘bridging’ over the double layers and become adsorbed on more than one particle simultaneously—so-called ‘bridging’ flocculation. Generally, the process is initiated by destabilisation of the suspension followed by floc formation and growth and is finally limited by floc degradation due to breakage. While the development of any individual floc must follow this sequence, in practice, all of these stages occur simultaneously in the same chemical and physical environment. Manipulation of the process variables, to control one stage, generally leads to changes in the other stages (Hogg, 2004).

Farinato et al. (2003) shows the sequence of events after addiction of flocculant in a suspension (Table 1). It is important to observe the dynamic character of this process. An efficient flocculation does not depend on the total recovery of the particle.

Table 1 Events in flocculation process

Dispersion and transport	
Contact particle-polymer	
Adsorption	
Reconformation	
Contact particle-particle	
Destabilisation of particles	Flocculation
Aggregation particle-particle	
Aggregate structure and floc growth	
Settling and thickening	
Dewatering	

Flocculants based on the polyacrylamide family represent the largest class of these organic reagents employed for mineral slurries. The polyacrylamide molecule can be tailored to virtually every mineral processing solid-liquid separation condition. Substitution in the polyacrylamide chain of various cationic and anionic functional groups gives a spectrum of reagents that will effectively treat all slurry environments from monomineralic to multi-mineralic, low to high solids in suspension, low to high dissolved solids and low to high pH. Manipulation of molecular mass allows successful application to be made on all solid-liquid separation equipment—clarifiers, thickeners, filters of all types and centrifuges (Pearse, 2005).

Such particles are often small enough to be only slightly affected by gravity and, as a result, their interactions with each other large particles are controlled by a range of attractive and repulsive inter-particle forces. In the simplest cases, the net inter-particle force is governed by the sum of the attractive van der Waals and repulsive electrical double layer forces, as defined by so-called DLVO theory (Derjaguin and Landau, 1941; Vervey and Overbeek, 1948). In systems more complex, however, a number of other forces may further influence the interaction of colloidal particles. These include structural (hydration), hydrophobic, steric, and bridging and depletion forces. From a practical perspective, the magnitude and nature of the above inter-particle forces can be controlled by manipulation of a range of experimental parameters. These include (but are not limited to) the particle size, the solution pH, the nature and concentration of simple electrolyte ions, and addition of other soluble and/or surface-active species including surfactants, polymers and polyelectrolytes (Johnson et al., 2000).

The immersion of a solid into an aqueous solution produces a region of electrical inhomogeneity at the solid-solution interface. An excess (+ or -) charge apparently fixed at the solid surface is exactly balanced by a diffuse region of equal but opposite charge (termed counter ions) and is called the electrical double layer.

Since adsorption of polymers at mineral-water interfaces is controlled in many cases by electrical double layer, one must be concerned with the behaviour of ions that adsorb as counter ions to maintain electroneutrality.

Several different parameters that quantify the electrical double layer are useful in interpreting sedimentation behaviour, this includes factors such as the magnitude of the surface charge, the point of zero charge of the mineral, interfacial potentials, thickness of the electrical double layer, specific adsorption of polymers, and ion exchange phenomena.

For oxide minerals, hydrogen and hydroxyl ions have long been considered a potential determining, but today there remains a difference in opinion as to how pH controls the surface charge on oxides (Fuerstenau and Pradip, 2005). Since the oxide minerals form hydroxylated surface when in contact with water vapour, a hydroxylated should also be expected when the solid is in equilibrium with an aqueous solution. Adsorption/dissociation of H^+ from the surface hydroxyls can account for the surface charge on the oxide.

With regard to aqueous minerals processing, the single most important parameter that describes the electrical double layer of a mineral in water is the point of zero surface charge (PZC). The importance of the PZC is that the sign of the surface charge has a major effect on the adsorption of all other ions (and particularly those ions charged oppositely to the surface) because those ions function as the counter ions to maintain the electroneutrality. In contrast to the situation in which the potential-determining ions are special for each system, any ions present in solution can function as the counter ions (Fuerstenau and Pradip, 2005).

1.2 Factorial design

The optimisation of sedimentation process is a complex task and many process (independent) variables can affect sedimentation responses. Studies, which employ a 'one variable at a time' approach to sedimentation optimisation, can be highly inefficient, and sometimes misleading, since many process variables can often interact to influence a measured (dependent) variable or response. Often multiple interactions occur between independent variables, and identification of these interactions plays an important role in advancing our understanding of the chemistry of such systems in plant operations. Factorial experimental designs are efficient affords optimisation process conditions in a multivalent system. Box et al. (1978) present an excellent discussion on the theory of fractional–factorial designs (Sheridan et al., 2002).

For this factorial design, the regression equation with interactive terms can be written as Equation (1), and the main interaction coefficients are evaluated:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 \tag{1}$$

where: Y = response (final percentage by solid).

X_1 = factor referent to flocculant dosage.

X_2 = factor referent to pH.

b_0 , b_1, b_2 and b_3 = coefficients of regression.

The present study employ a factorial design (three level, two factors), to investigate the effect of chemical variables pH and flocculant dosage, for three different types of flocculant (cationic, anionic and non-ionic), in the final percentage of solid of bauxite tailings and help the understanding the influence of these two different factors in the flocculation process.

1.3 Rheology

The rheology of slurries comprehends the study of the flux of pulp behaviour, where usually the phases are formed for water and ore. One manner for rheological characterisation for these slurries consists in measurement of shear stress and shear rate, withdraw with a flux curve. In accordance with Barnes et al. (1989) and Ferreira et al. (2005) the study of deformation and material flux, that which involve elasticity phenomenon, plasticity and viscosity, constitute the principal objective of rheology.

Concentrated particulate slurries typically exhibit non-Newtonian flow behaviour because of the inter-particle forces that act in these physically and chemically complex systems. It is well known that a number of factors may influence the rheological behaviour of slurries. These include solid content, particle shape, particle size and the surface chemistry of the particles. Inter-particle forces, which arise from the solid–solution interfacial chemistry, increasingly dominate the interaction between neighbouring particles as the particle size of the slurry decreases. Thus, manipulating the chemistry of the particle surfaces may alter the rheological behaviour of the slurry. A description of the rheological behaviour of the slurry is important in order that the optimum conditions for hydraulic transport may be identified. For example, the energy required to pump slurry may be predicted from the yield stress and viscosity of the slurry. As pumping is an energy-intensive process, there is an obvious financial benefit to be gained if the energy requirements to transport particulate slurries can be reduced (Ralston et al., 2000).

The flow properties of a high-density slurries and/or paste for surface disposal must be engineered to ensure adequate distribution of the material after release from a discharge point. If the material has high solids content and thus a large resistance to flow, it will not spread and will stack directly below the discharge point. On the other hand, if the solids content is too low and the material is watery, it will flow far and will not form the desired stack. Drying will also take longer as the water content increases. Optimising the surface disposal requires understanding the slurry rheological properties and the relevant operational parameters, as well as understanding how these properties and parameters can be modified. This study focuses on measuring the governing rheological properties (yield stress and apparent viscosity) of high solids slurry, understanding your properties and relating the rheological parameters with a Bingham model in accordance to Equation (2) (Kwak et al., 2005):

$$\tau = \mu\,\gamma + \tau_0 \tag{2}$$

where: τ = shear stress.

μ = apparent viscosity.

γ = shear rate.

τ_0 = yield stress.

Fine particle slurry may be described as a colloidal system in which the solids are dispersed through the liquid. Electrostatic repulsive forces and van der Waals attractive forces dominate interactions between particles because of the high surface charge and the nature of the slurry rheology can be determined by the sum of these two forces. The net particle interactions can be strongly repulsive, where the particles remain dispersed, so that the fluid exhibits Newtonian characteristics. Alternatively, the net interaction between particles can be strongly attractive so that a floc structure is created. Flocs can form networks that cause the slurry to exhibit non-Newtonian characteristics. This structure can resist shear distortion giving the fluid a yield stress (Falcucci, 2007).

The rheological characteristics of fine particle slurries can be manipulated by altering the concentration of solids and by controlling the electrostatic repulsive forces between particles. The electrostatic repulsive forces can be increased or decreased by manipulating the pH and the ionic content in the suspending medium. Increasing the repulsive forces with the addition of a dispersing agent may break down the structure and reduce or eliminate non-Newtonian behavior. Conversely, by decreasing the repulsive forces and allowing the net interaction of particles to be dominated by attractive forces, the non-Newtonian behaviour can be increased (Litzenberger, 2003).

2 Methodology

2.1 Materials and procedures

The samples utilised in the experimental procedures are the bauxite tailings from a plant in Minas Gerais State, Brazil. Mineralogical identification by X-ray diffraction revealed that the tailings are formed chiefly by the minerals Kaolinite, Gibbsite and Quartz, with small amounts of Goethite, Anatase and Hematite.

The particle size distribution follows a Rosin-Rammler equation (Equation (3)). It revealed that 100% of the particles were finer then 212.0 µm and 50% finer than 9.0 µm.

$$Y = 100.e\text{-}(d/4.82)\ (\text{-}0.62) \tag{3}$$

The Point of Zero Charge (PZC), determined for the Mular and Roberts's procedure (Mular and Roberts, 1966) occurred at pH 6.2.

Three different high molecular weight flocculants with different active principles are utilised, one type by factorial plan, with one cationic, one anionic and one non-ionic. A concentrate polymer solution of 0.1% weight/volume was prepared and the stock solution was used within one day of preparation.

The sedimentation experiments followed the classical methodology (Fitch, 1966), in a 1000 mL graduate cylinder, and followed the operation conditions in the plant with the slurry prepared with the 10% of solid by weight. The slurry was mixed by moving a plunger up and down three times after the flocculant addition and the measurements of final per cent of solid were made one hour from the beginning of the experiment.

2.2 Factorial design

The sedimentation experiments were carried out according the two-factor (2^2), three-level conditions, with a corner and a centre of a square. According to the basic principles of the design of experiments, two experiments were carried out at the base level to estimate error and the standard deviation. A full factorial study of these two levels would have required four experiments with two more experiments in base level, totalising six experiments per type of flocculant. Three replicate factorial experiments were also conducted in order to quantify the reproducibility. The variables studied were pH and the flocculant dosage and the response were the final percentage of solid for the flocculated material.

For the three types of flocculants, the pH levels are 5 to the lower level, 6 to the base level and 7 to the higher level. To the dosages, for the cationic flocculant, the levels are 90, 110 and 130 g/t for the lower, base and higher levels respectively. For the anionic flocculant, the dosages are 70, 90 and 110 g/t and for the non-ionic flocculant, the dosage levels are 60, 90 and 120 g/t.

2.3 Rheology

The yield stress and apparent viscosity are determined with a rheometer Haake — RS1 equipped with a spindle type concentric cylinder, for different percentage of solids, were the different flux curves (with the shear stress and shear rate) are modelled in accordance with a Bingham fluid (Equation (2)) and the yield stress is fitted as a function of final percentage of solids.

3 Results and discussion

3.1 Flocculation

The experimental data were analysed statistically and the effect of the variables were quantified and interpreted. The relationship between the flocculation dosage and pH was established and a contour map was constructed. Modelled results are valid within the intervals for the full factorial design utilised for any type of flocculant.

3.1.1 Cationic flocculant

The experimental results are modelled in accordance with the regression exposed above, with the adjusted by least square model and its final form, for cationic flocculant, is presented in Equation (4).

$$Y = 28.9 + 2.4\,X1 - 3.9\,X2 + 3.6\,X1X2 \qquad (4)$$

The best response is observed for pH 5 and 130 g/t for the flocculant dosage with a final percentage of solid of 31.2% after one hour. Figure 1 shows the contour map for the model in accordance with the modelled equation.

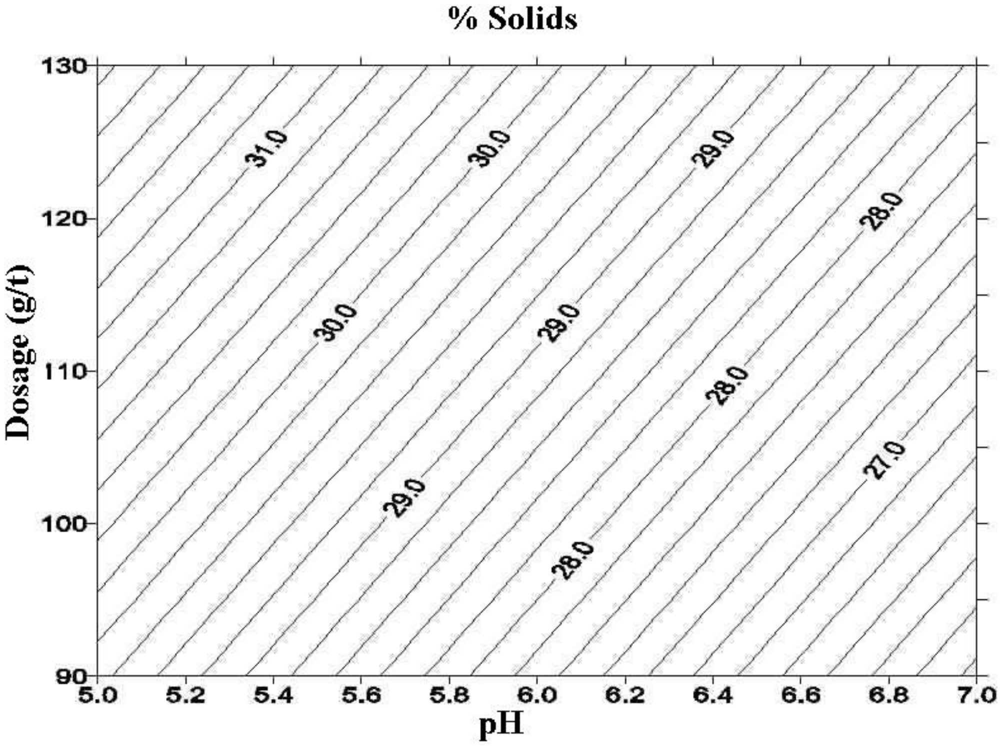

Figure 1 Response contours for cationic flocculant (% solids)

The correlation between the model and the experimental results are used to check the models ability to predict the response accurately and the standard deviation factor adjusted by linear fit model is $r^2 = 0.95$.

In accordance with the modelled equation, for the cationic flocculant, the pH represent the most influent factor in this sedimentation process, followed by the interactions between pH and flocculant dosage and with a third most influent factor the flocculant dosage.

3.1.2 Anionic flocculant

Over again, the experimental results are modelled in accordance to Equation (1) and the final form of the equation, for the anionic flocculant, is presented in Equation (5).

$$Y = 21.6 + 1.8\ X1 + 3.8\ X2 - 0.1\ X1X2 \qquad (5)$$

The best response is observed for the pH 7 and 110 g/t for the flocculant dosage with a final percentage of solid of 24.4%. The Figure 2 shows the contour map for the model in accordance with the modelled equation.

The correlation factor between the model and the experimental results adjusted by linear fit model is $r^2 = 0.88$.

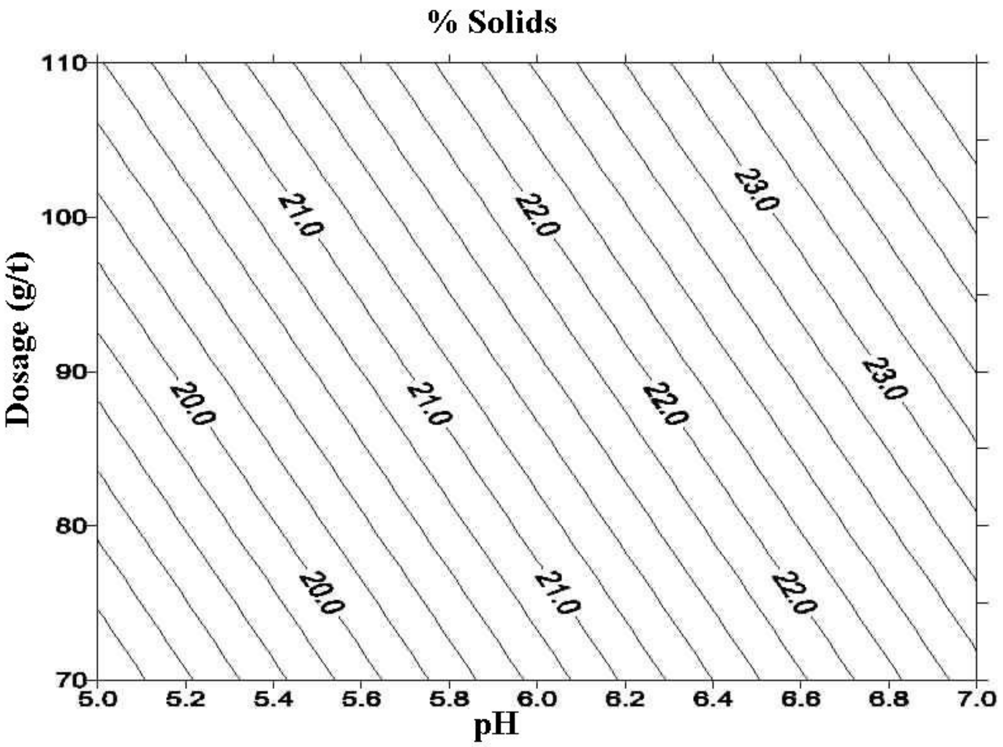

Figure 2 Response contours for anionic flocculant (% solids)

In accordance with the Equation (5) the pH represent the most influent factor in this sedimentation process, followed by the flocculant dosage and with a third most influent factor the interaction between the both independent variables.

3.1.3 Non-ionic flocculant

The experimental results, for this flocculant are modelled in accordance to Equation (1) and the coefficients of regression and the final form of the equation is presented in the Equation (6).

$$Y = 24.2 + 5.9\ X1 + 5.0\ X2 - 6.8\ X1X2 \quad (6)$$

The best response is observed for the pH 7 and 120 g/t for the flocculant dosage with a final percentage of solid of 28.0%. Figure 3 shows the contour map for the model in accordance with the modelled equation.

In accordance with the Equation (6), the interaction between the both independent variables represents the most influent factor in this sedimentation process, followed by the flocculant dosage and with a third most influent factor the pH.

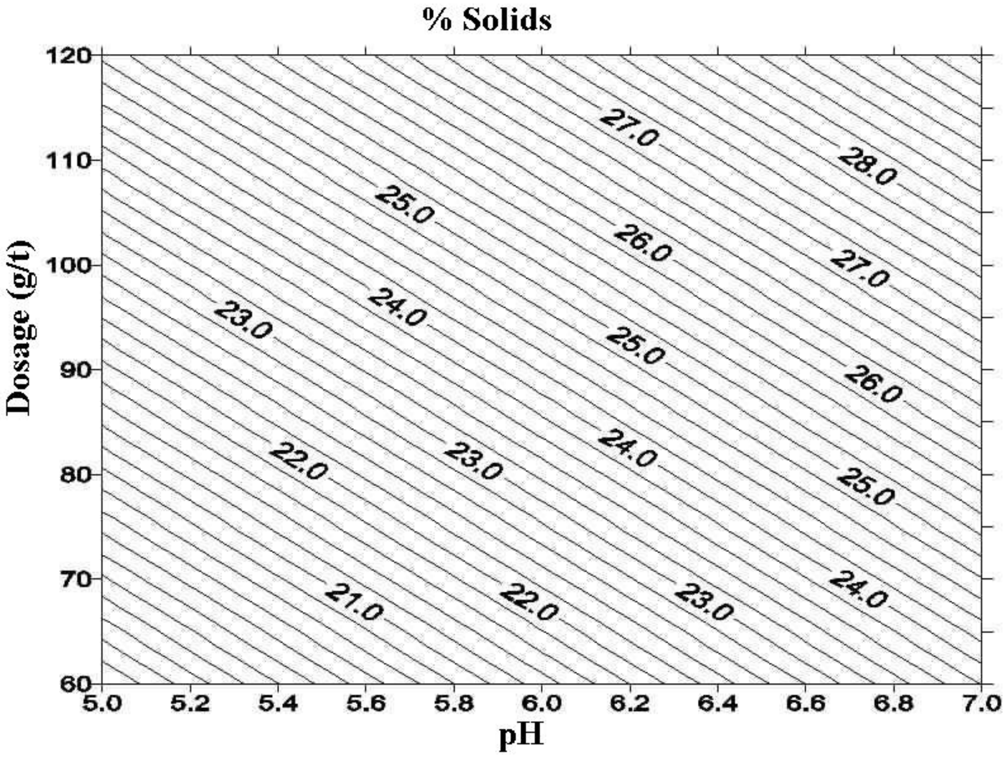

Figure 3 Response contours for non-ionic flocculant (% solids)

The correlation factor between the model and the experimental results, utilised to check the models ability to predict the response accurately, show a good correlation with an $r^2 = 0.98$.

3.2 Rheology

In accordance with the Bingham model, presented in Equation (2), the yield stress and apparent viscosity were determined for the sample without a presence of flocculant. Table 2 presents the results. All measurements of yield stress and apparent viscosity were made in duplicate to evaluate the reproducibility of the analysis and to minimise errors. A significant increase of yield stress takes place between 25–30% per cent of solids, where the slurry change its rheological characteristic.

Table 2 Bingham fluid model

Cw	Yield Stress (τ_0)	Apparent Viscosity (μ)	Yield Stress (τ_0)	Apparent Viscosity (μ)
%	(Pa)	(Pa . s)	(Pa)	(Pa . s)
10.0	0.40	0.00299	0.40	0.00183
15.0	0.70	0.00299	0.71	0.00300
20.0	1.37	0.00493	1.40	0.00496
25.0	2.97	0.00812	2.97	0.00817
30.0	6.82	0.01296	6.84	0.01322
32.0	8.13	0.01442	8.24	0.01452
34.0	10.43	0.01754	10.68	0.01725
36.0	14.00	0.02095	13.87	0.02150
38.0	19.14	0.02440	19.52	0.02514
40.0	22.65	0.02666	24.13	0.02766
42.0	33.51	0.03368	31.87	0.03364

4 Conclusions

Among the three types of flocculant the highest percentage of solid was reached by the use of the cationic flocculant, for the highest dosages utilised in the factorial design experiment, with a final percentage of solid of 31.2% for the dosage of the 130 g/t and pH 7. For the anionic flocculant, the best result is 24.4% with a dosage of 110 g/t and pH 7, and for the non-ionic flocculant, the best result is 28.0% with a dosage of 120 g/t and pH 7.

The results, modelled in accordance to regression, for prediction of final percentage of solid for the three types of flocculants showed good correlation for prediction of results. The best correlation factor is presented for the non-ionic flocculant, for this flocculant the correlation factor is $r^2 = 0.98$, for the cationic flocculant the correlation factor r^2 is 0.95 and for the anionic is 0.88.

For the flocculants with the charged active principles (anionic and cationic), the most important factor is the pH and for the non-ionic flocculant, the most important factor is the interaction between the two independent variables.

From the point of view of superficial charge, it is possible to observe the existence of relationship between the superficial charge of particles and the active principles of flocculants (positive, negative and uncharged). The best results were observed when the flocculants and the particles had the same signal of charge. These interactions are possible due to van der Waals forces with a minimal influence of electrostatic interactions. When the particles are charged positively, below of PZC, the best results were encountered with the cationic flocculant and, on the other hand, when the particles were negatively charged, above of PZC, the best results were displayed by the anionic flocculant. For the non-ionic flocculant, the best took place for values close to the PZC (pH 6) and above, where the particles are negatively charged.

For the rheological parameters, determined with the Bingham model, the yield stress show an abrupt and significant increase for to the slurry with 25–30 per cent of solids by weight, with apparent viscosity ranging from 8.2 to 13.0 cP and yield stress within the range from 3.0 to 6.8 Pa.

Acknowledgements

Support from CNPq and FAPEMIG (National Research Council of Brazil and Minas Gerais State Foundation for Research and Development, respectively) is gratefully acknowledged by the authors.

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