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Performance evaluation for selectivity of the flocculant on hematite in selective flocculation

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Abstract: Increased demand for iron ore necessitates the utilization of low-grade iron ore fines, slimes, and existing tailings. Selective flocculation can be an alternative physico-chemical process for utilizing these low-grade fines, slimes, and tailings. In selective flocculation, the most critical objective is the selection of proper reagents that will make floc of desired minerals. In present study, selective flocculation was applied to ultra-fine synthetic mixtures of hematite and kaolinite, and the Fe value was upgraded up to 65.78% with the reduction of Al_2O_3 and SiO_2 values to 2.65% and 3.66%, respectively. Here, degraded wheat starch was used as a flocculant.In this process, separation occurs on the basis of the selectivity of the flocculant. The selectivity of the flocculant can be quantified in terms of separation efficiency. Here, an attempt was also made to develop a correlation between separation efficiency and major operating parameters such as flocculent dose, pH value, and solid concentration to predict the separation performance.

Keywords: hematite; kaolinite; selective flocculation; modeling; iron ores; tailings

1. Introduction

A huge amount of tailings is generated from iron ore beneficiation plants in India, which contains a good amount of iron value in the form of hematite or magnetite phases. This iron value needed to be recovered. This would not only increase the overall process recovery but also increase natural resources utilization and minimize environmental pollution footprints of these processing plants. Iron industry requires high-grade hematite ore with the alumina and silica ratio less than 1 and the alumina content less than 2% [1]. Because of high-grade ore depletion and tailing disposal constraints, it is now becoming necessary to beneficiate low-grade slimes/tailings. Lots of researches were carried out in the past to beneficiate iron ores for reducing silica and alumina contents using conventional methods [1-5]. However, these conventional methods have limitations in handling ultra-fines particles. Selective flocculation is one of the alternative processes to beneficiate ultra-fine iron ore particles. Many investigations were carried out in the past to establish selective flocculation processes [6-14]. However, these processes are not successfully commercialized in the plant scale. The selectivity of the flocculant to desired minerals, which is a critical parameter, depends on the complex mineralogy of ores/tailings. Moreover, the situation gets more complex when ores from different locations/mines have wide change in mineralogy, making the feed highly heterogeneous. The higher the selectivity of the flocculant to desired minerals, the more efficient the separation of desired minerals from gangue would be. In addition to this, there is hardly any mathematical model that is available in open literatures for predicting separation performance in selective flocculation processes based on operating parameters.

The separation performance of selective flocculation processes can be judged by separation efficiency, which considers both the grade and recovery of the concentrate [6-7,15]. In present work, an attempt was made to study the selectivity of the flocculant to desired minerals in terms of separation efficiency. A synthetic mixture of hematite and kaolinite was used as a raw material and degraded

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wheat starch was used as a flocculant for the present study. In addition to this, few tests were conducted to see the applicability of wheat starch to natural iron ore slimes from Joda area, India. Furthermore, an empirical mathematical correlation was also developed to predict the separation efficiency which depends on major operating parameters including flocculant dose, pH value, solid concentration, etc., using dimensional analysis.

2. Materials and methods

2.1. Sample preparation

A high-grade iron ore sample rich in hematite mineral used in this study was from an iron ore processing plant of India. It was further grounded in a ball mill to reduce the particle size below 45 μm, and then, the ground sample was upgraded to 67.57% Fe by wet lnigh intensity magnetic separator. A Kaolinite sample used in this study was prepared by desliming the low-grade blue dust sample of below 45 μm fraction collected from Jabalpur area in Chattisgarh, India. This blue dust contains a good amount of free and ultra-fine kaolinite minerals, which was easily deslimed with a laboratory hydrocyclone. Chemical analysis of the prepared iron ore and kaolinite sample is given in Table 1 [14]. From X-ray diffraction (XRD) study, it was observed that hematite was the major phase present in the iron ore along with little amount of gibbsite and kaolinite. Similarly the XRD study of the kaolinite sample showed that kaolinite is the major phase present in the sample along with little amount of hematite and quartz phase. A detail XRD phase analysis was explained by Lopamudra *et al.* [14]. For natural iron ore slimes, samples were collected from Joda area, India. The slime contains an Fe value of 50.9% and size analysis shows more than 95% is less than 38 μm.

Table 1. Chemical composition of the iron ore and kaolinite [14] %

Sample	Fe	Al_2O_3	SiO_2	LOI
Iron ore	67.57	2.04	0.88	0.96
Kaolinite	13.17	18.12	46.43	11.3

2.2. Reagents

Degraded wheat starch was used as a flocculating reagent for present study, which is selective to hematite phase in the iron ore. Selection of the flocculant for selective flocculation was done on the basis of some previous literature findings [7-9]. Analytical grade sodium silicate was used for a synthetic mixture and sodium hexa-metaphosphate was used for natural tailings, as a dispersant. A solution of the dispersant was prepared by adding 5% of sodium silicate in 1000 mL of water. Then, based on required amount, the dispersant dose was added to the feed slurry for maintaining a disperse phase. A solution of the flocculent was prepared according to the standard procedure given by Hanumantha Rao and Narasimhan [7], and the freshly prepared flocculent was used for the experiments [9]. Analytical grade sodium hydroxide and hydrochloric acid were used for pH adjustment.

3. Experiment

During all the selective flocculation experiments, feed samples were added in water in a graduated glass beaker of 1000 mL to prepare the desired solid concentration of slurry. Then, dispersants were added, and a proper pH value of the slurry was maintained. Proper mixing was done by the help of a mechanical stirrer, with the high shearing rate at 2000 r/min. Proper mixing would allow all the particles to remain in dispersed state for the effectiveness of the flocculent. Then, the required amount of the flocculant dose was added to form the floc of hematite particles. After the addition of flocculants, shearing rate was adjusted to slow shearing action of around 50 r/min. Then, the floc was allowed to settle at the bottom of the beaker, and supernatant liquid was separated out from the floc by decantation. Floc was collected as a concentrate, and supernatant liquid containing gangue particles was collected as tailings. After drying the collected samples, chemical analysis was done for both the flocculated sample and supernatant part.

3.1. Flocculation of single mineral

One of the critical steps in selective flocculation is the selection of a proper flocculant, which can make floc only with the desired mineral selectively. Some tests were conducted for evaluating the selectivity of degraded wheat starch to hematite and kaolinite individually by varying degraded wheat starch dose and keeping all other parameters such as dispersant dose, percent solid, and pH value constant. In Fig. 1, it was observed that the flocculant is selective to iron mineral only, because when increasing flocculant dose, the sediment yield of hematite increases more than 90%, whereas the sediment yield of kaolinite was less than 10%. Tests were conducted at pH 10.5, the solid concentration of 5%, and the dispersant dose of 4 g/kg. During all these single mineral tests, the pH value of 10.5 was maintained, because according to Ma and Bruckard [16], around this particular pH value, the flocculant is less

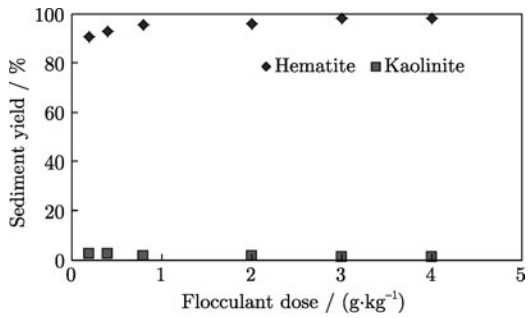

Fig. 1. Effect of flocculant dose on sediment yield at pH 10.5.

selective to kaolinite mineral.

3.2. Selective flocculation for synthetic mixtures

A synthetic mixture of hematite and kaolinite mixed in 70:30 ratio was subjected to selective flocculation process. A schematic flow diagram of the selective flocculation process is shown in Fig. 2. Chemical analysis of the synthetic mixture was carried out, which showed that the synthetic mixture contains 47.06% Fe, 13.76% SiO_2, and 10.1% Al_2O_3. Experimental runs were conducted by varying the flocculant dose from 0.2 to 4 g/kg by keeping the pH value around 10.5 and the dispersant dose at 4 g/kg. Experiments were conducted around the pH value of 10.5, because based on Ma and Bruckard investigation [16], the flocculant is less selective to kaolinite around this pH value. From experimental results, it was observed that, around 65.78% grade was achieved with 80.71% recovery at 0.8 g/kg of flocculant dose, 4 g/kg of dispersant dose, and pH 10.5. It was also observed that the Al_2O_3 content reduces from 10.1% to 2.65% and the SiO_2 content reduced from 13.76% to 3.66%. The result of the above typical experimental run is given in Table 2.

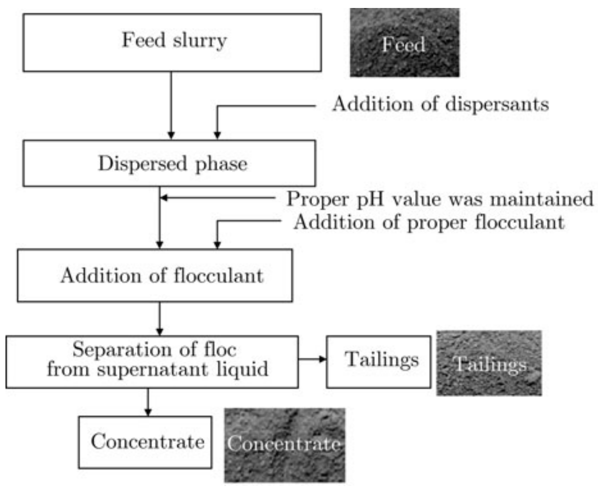

Fig. 2. Schematic diagram of selective flocculation process.

Table 2. Selective flocculation results by using synthetic mixtures (70:30 ratio)

Sample	Fe / %	Al_2O_3 / %	SiO_2 / %
Concentrate	65.78	2.65	3.66
Tailings	22.13	16.59	22.35
Feed	47.06	10.10	13.76

Fig. 3 shows the effect of flocculant dose on the grade and recovery of the concentrate obtained after selective flocculation. In Fig. 3, it is observed that with an initial increase of flocculant dose, the grade increases up to 65.78% and with a further increase of flocculant dose the grade start to decrease slightly. When increasing the flocculant dose the floc of only hematite particles starts forming but with a further increase of flocculant dose, the floc with gangue minerals also starts forming because of the bridging mechanism of floc formation [9].

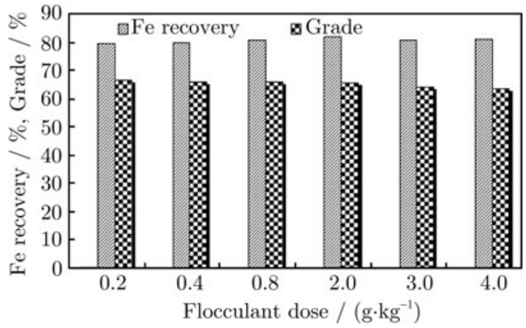

Fig. 3. Effect of flocculant dose on the grade and recovery at pH 10.5 and a dispersant dose of 4 g/kg.

Selective flocculation performance can be judged in terms of separation efficiency, which takes into account both grade and recovery [6-7,15]. The separation efficiency can be calculated as given below [17-18]:

$$\mathrm{SE} = R_{\mathrm{m}} - R_{\mathrm{g}} = \frac{100Ym(c-f)}{(m-f)f} \tag{1}$$

where R_{m} is the percentage recovery of valuable mineral, R_{g} is the percentage recovery of gangue into the concentrate, Y is the yield of the concentrate, m is the percentage metal content of pure valuable mineral, c is the metal content in the concentrate, and f is the metal content in feed.

The result of the selective flocculation process was also analyzed by X-ray diffraction. X-ray diffraction patterns from a typical experiment (pH 10.5, dispersant dose 4 g/kg, and flocculant dose 0.8 g/kg) are shown in Fig. 4. This experiment was performed with the synthetic mixture of 70:30 ratio. In Fig. 4, it was observed that the feed contains major peaks of both hematite and kaolinite. The concentrate shows major intense peaks of hematite along with some small peaks of kaolinite. Similarly, the tailing shows major intense peaks of kaolinite with small peaks of hematite. This indicates the flocculant is selective to hematite phase.

3.3. Adsorption mechanism by FTIR study

Fourier transform infrared (FTIR) spectroscopy test was carried out for both the feed sample and concentrate after flocculant addition. The result is shown in Fig. 5. In Fig. 5(a), it was observed that the broad peak at 3183.1 cm^{-1} shifts to 3222 cm^{-1}, in concentrate, which corresponds to the presence of –OH band and hydrogen bonded interaction [19]. Similarly, in Fig. 5(b), it was observed that, peak shifting from 1008.2 cm^{-1} to 1011 cm^{-1} corresponds to the presence of Fe–O stretching and C–O stretching [20]. Shifting of the peak reveals adsorption of flocculants on the feed sample. The peak at 916 cm^{-1} corresponds to Al–OH bending [21] and the peak at 3696 cm^{-1}

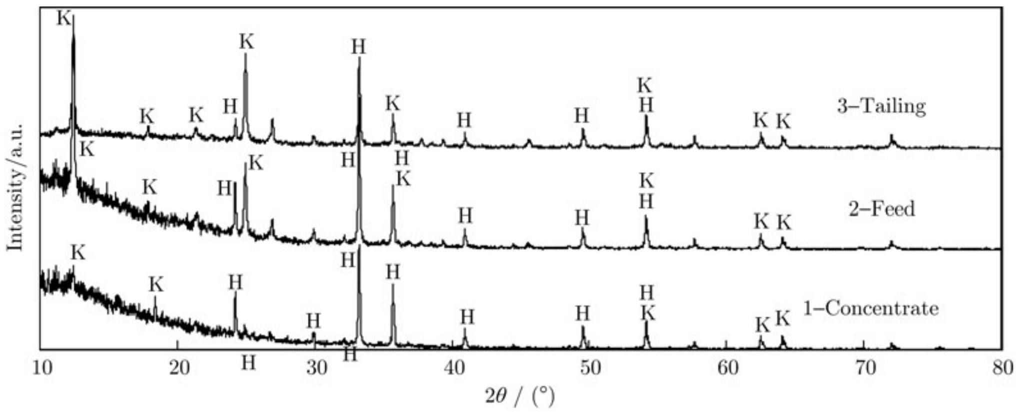

Fig. 4. X-ray diffraction patterns of the iron ore (H is hematite, and K is kaolinite).

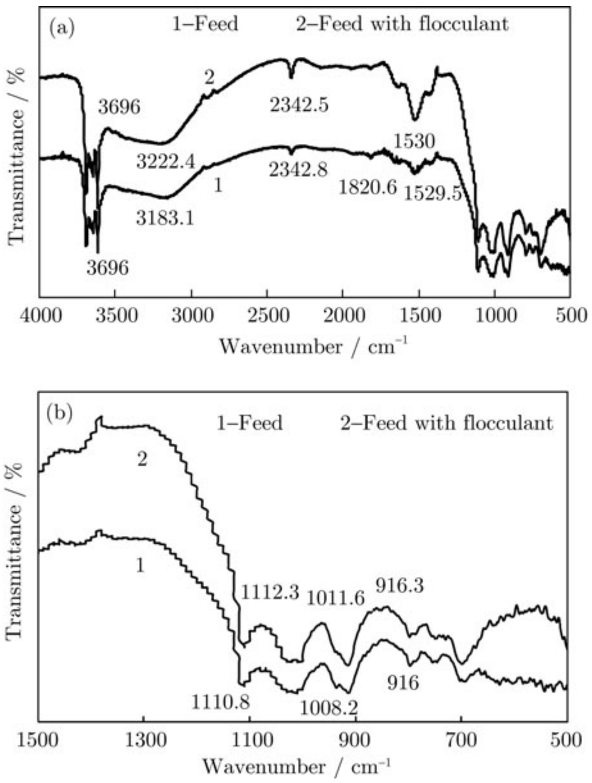

Fig. 5. FTIR spectra of the feed sample and the feed with the flocculant: (a) 4000 to 500 cm^{-1}; (b) 1500 to 500 cm^{-1}.

corresponds to Si–OH [22]. The peaks at 916 cm^{-1} and 3696 cm^{-1} represent kaolinite phase [22] in the feed, and it is observed that these peaks did not shift significantly after flocculant addition, indicating that the flocculant is not selective to kaolinite phase but to hematite phase.

3.4. Selective flocculation for natural iron ore slimes

Natural iron ore slimes from Joda area, India, were subjected to the selective flocculation. The procedure followed for selective flocculation was the same as that mentioned in the Fig. 2. Chemical analysis of the slimes shows that it contains an Fe value of 50.9%. Few preliminary tests were conducted just to see the applicability of wheat starch to the actual iron ore slimes as it was for the synthetic mixture. These tests were performed at 12% solid concentration. The results of tests are given in Table 3. It is observed from the results that the Fe value can be upgraded to 64.09% from the feed value of 50.9%. This indicates that wheat starch can be successfully used as a flocculant for actual iron ore slimes from Joda area, India.

4. Development of mathematical correlations

Selective flocculation is a physicochemical solid-solid separation process, which depends on many operating parameters including flocculant dose, dispersant dose, pH value, percent solid, etc. Separation efficiency (SE) is a tool to judge the performance of the selective flocculation process. Separation efficiency (SE) of minerals in the selective flocculation process mostly depends on the operating parameters such as flocculant dose (FD), pH value of slurry, and solid concentration of slurry (SC). Dimensional analysis method was adopted for development of empirical mathematical correlations [23-24]. For development of these correlations, separation efficiency was

Table 3. Results of selective flocculation tests on actual iron ore slimes

Experimental run No.	Experimental condition	Grade, Fe content / %	Fe recovery / %
1	FD = 312.5 g/t, DD = 625 g/t, pH 7	62.39	53.99
2	FD = 187.5 g/t, DD = 750 g/t, pH 7	63.56	40.65
3	FD = 312.5 g/t, DD = 750 g/t, pH 9	64.09	33.69

Note: DD is the dispersant dose; FD is the flocculant dose.

normalized with feed grade of mixture used for selective flocculation, and this was considered to be the dependant variable. Different experimental runs were performed for generation of data to be used for model development by varying flocculant dose from 0.2 to 8 g/kg, solid concentrations from 0.03wt% to 0.1wt%, and pH value from 6.5 to 12.35. All these experiments for development of mathematic correlations were performed with the synthetic mixture of hematite and kaolinite with 60:40 ratio. The mathematical correlations so developed using dimensional analysis method are given in Eq. (2) for the pH value below and equal to 10.5 and Eq. (3) for the pH value above 10.5.

$$\left(\frac{\mathrm{SE}}{\text{Feed grade}}\right)=1.7864\,(\mathrm{FD})^{-0.0117}\,(\mathrm{SC})^{0.124}\left(\frac{\mathrm{pH}}{\mathrm{pH_{iep}}}\right)^{0.6201} \tag{2}$$

$$\left(\frac{\mathrm{SE}}{\text{Feed grade}}\right)=2.1524\,(\mathrm{FD})^{-0.01131}\,(\mathrm{SC})^{0.12}\left(\frac{\mathrm{pH}}{\mathrm{pH_{iep}}}\right)^{-0.0479} \tag{3}$$

where SE is the separation efficiency, FD is the flocculant dose, SC is the solid concentration, and $\mathrm{pH_{iep}}$ is the isoelectric point of pure hematite, which is taken to be 8 [10].

5. Results and discussion

Several tests were conducted by varying flocculant dose, pH value, solid concentration, and feed grade. All experiments for studying the effect of different parameters on separation efficiency were done with synthetic mixture of hematite and kaolinite with 60:40 ratio. The variation of separation efficiency with different operating parameters of selective flocculation (i.e., solid concentration, flocculent dose, and pH value of the slurry) is shown in Fig. 6. It was observed in Fig. 6(a) that as SC in slurry increases SE increases, because when solid concentration increases, particle-particle collision also increases, which gives a higher coagulation.

In Fig. 6(b), it was observed that with an initial increase of flocculant dose (FD), the flocculant starts forming floc by acting only on desired hematite minerals but after reaching the critical point, with a further increase of FD, the flocculant starts acting on kaolinite mineral also in addition to hematite, and kaolinite particles get entrapped in the floc matrix, so SE decreases.

In Fig. 6(c), it was observed that SE increases initially up to the critical pH value and with a further increase of pH value, SE decreases. Around pH 10.5, the flocculant is less selective to kaolinite, and for which, more separation occurs, so the separation efficiency was higher. It indicates that flocculation of hematite mineral is better, near to above its isoelectric point. As the isoelectric point of kaolinite is in the acidic range, the interference of kaolinite particles in flocculation process around pH 10.5 is less.

The developed empirical mathematical correlations of

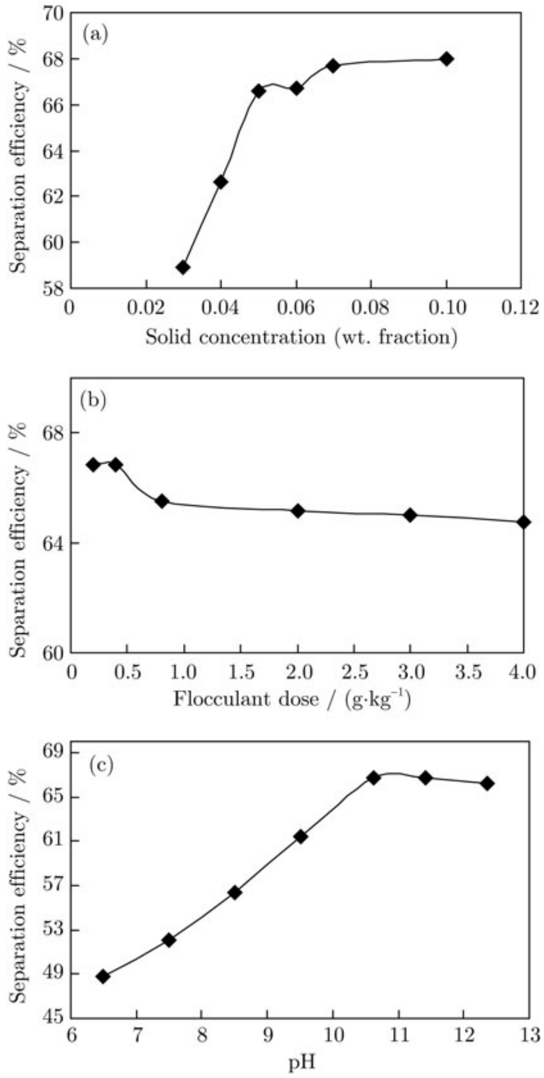

Fig. 6. Variations of separation efficiency with solid concentration (a), flocculant dose (b), and pH value (c).

separation efficiency given in Eqs. (2) and (3) indicate that with the increase of solid concentration there is an increase in separation efficiency, and with an increase of flocculent dose there is a decrease in separation efficiency. On the other hand, the separation efficiency increases with an increase of pH value up to 10.5 and decreases with an further increase in pH value. It was also observed that the separation efficiency has higher dependency on solid concentration and pH value in comparison with flocculent dose. The calculated $\frac{\mathrm{SE}}{\text{Feed grade}}$ from the empirical mathematical correlations was compared with the experimental $\frac{\mathrm{SE}}{\text{Feed grade}}$ and is shown in Fig. 7. It shows that calculated values from the empirical model have good agreement with the experimental ones. The empirical model was validated with a maximum error of 11.86%.

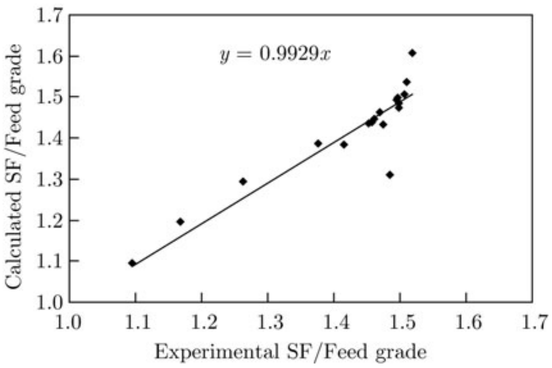

Fig. 7. Comparison between calculated SE/Feed grade from the empirical model and experimental SE/Feed grade.

6. Conclusion

A selective flocculation study was carried out on a synthetic mixture of hematite and kaolinite fines at different operating parameters. Empirical mathematical correlations were developed using dimensional analysis approach for determining the separation efficiency of minerals separation in selective flocculation. Separation efficiency can be calculated based on operating parameters like flocculent dose, solid concentration, and pH value. These mathematical correlations may be used to optimize the selective flocculation process for recovery of iron values from fines, slimes, and tailings in which desired minerals are associated with a lot of gangue minerals with very complex mineralogy.

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References

[1] D.S. Rao, T.V. Vijaya Kumar, S. Subba Rao, S. Prabhakar, and G.B. Raju, Mineralogy and geochemistry of a low grade iron ore sample from bellary-hospet sector, India and their implications on beneficiation, *J. Miner. Mater. Charact. Eng.*, 8(2009), No. 2, p. 115.

[2] R. Singh, R. Rath, B. Nayak, and K. Bhattacharya, Development of process for beneficiation of low-grade iron ore samples from Orissa, India, [in] *Proceedings of XXV International Mineral Processing Congress (IMPC) 2010*, Brisbane, Australia, 2010, p. 1235.

[3] B. Das, S. Prakash, B.K. Mohapatra, S.K. Bhoumik, and K.S. Narasimha, Beneficiation of iron ore slimes using hydrocyclone, *Miner. Metall. Process.*, 9(1992), No. 2, p. 101.

[4] S. Roy and A. Das, Characterization and processing of low-grade iron ore slime from the Jilling area of India, *Miner. Process. Extr. Metall. Rev.*, 29(2008), No. 3, p. 213.

[5] U. Srivastav, and S.K. Kawatra, Strategies for processing low-grade iron ore minerals, *Miner. Process. Extract. Metall. Rev.*, 30(2009), No. 4, p. 361.

[6] Y.A. Attia, Development of a selective flocculation process for a complex copper ore, *Int. J. Miner. Process.*, 4(1977), No. 3, p. 209.

[7] K. Hanumantha Rao and K.S. Narasimhan, Selective flocculation applied to Barsuan iron ore tailings, *Int. J. Miner. Process.*, 14(1985), No. 1, p. 67.

[8] S.A. Ravishankar, Pradip, and N.K. Khosla, Selective flocculation of iron oxide from its synthetic mixtures with clays: a comparison of polyacrylic acid and starch polymers, *Int. J. Miner. Process.*, 43(1995), No. 3-4, p. 235.

[9] P.K. Weissenborn, L.J. Warren, and J.G. Dunn, Optimisation of selective flocculation of ultrafine iron ore, *Int. J. Miner. Process.*, 42(1994), No. 3-4, p. 191.

[10] J. Drzymala and D.W. Fuerstenau, Selective flocculation of hematite in the hematite-quartz-ferric ion-polyacrylic acid system: Part 1. Activation and deactivation of quartz, *Int. J. Miner. Process.*, 8(1981), No. 3, p. 265.

[11] J.P. Friend, and J.A. Kitchener, Some physico-chemical aspects of the separation of finely-divided minerals by selective flocculation, *Chem. Eng. Sci.*, 28(1973), No. 4, p. 1071.

[12] G.C. Sresty and P. Somasundaran, Selective flocculation of synthetic mineral mixtures using modified polymers, *Int. J. Miner. Process.*, 6(1980), No. 4, p. 303.

[13] N.R. Mandre, and D. Panigrahi, Studies on selective flocculation of complex sulphides using cellulose xanthate, *Int. J. Miner. Process.*, 50(1997), No. 3, p. 177.

[14] Lopamudra Panda, S.K. Biswal, and Vilas Tathavadkar, Beneficiation of synthetic iron ore kaolinite mixture using selective flocculation, *J. Miner. Mater. Charact. Eng.*, 9(2010), No. 11, p. 973.

[15] B.K. Mishra and A. Tripathy, A preliminary study of particle separation in spiral concentrators using DEM, *Int. J. Miner. Process.*, 94(2010), No. 3-4, p. 192.

[16] X. Ma, and W.J. Bruckard, The effect of pH and ionic strength on starch-kaolinite interactions, *Int. J. Miner. Process.*, 94(2010), No. 3-4, p. 111.

[17] N.F. Schulz, Separation efficiency, *Trans. SME-AIME*, 247(1970), p. 56.

[18] B.A. Wills, *Mineral Processing Technology: An Introduction to the Practical Aspects of the Treatment and Mineral Recovery*, 6th ed., Butterworth-Heinemann, 1997, p. 19.

[19] S. Pavlovic and P.R.G. Brandao, Adsorption of starch, amylose, amylopectin and glucose monomer and their effect on the flotation of hematite and quartz, *Miner. Eng.*, 16(2003), No. 11, p. 1117.

[20] S. Subramanian and K.A. Natrajan, Some studies on the adsorption behaviour of an oxidised starch onto haematite, *Miner. Eng.*, 1(1988), No. 3, p. 241.

[21] J. Madejová, FTIR techniques in clay mineral studies, *Vib.*

Spectrosc., 31(2003), No. 1, p.1.

[22] D.O. Hummel, *Atlas of Plastics Additives Analysis by Spectrometric Methods*, Springer-Verlag, 2002, p. 46.

[23] G. Delaplace, R.K. Thakur, L. Bouvier, C. André, and C. Torrez, Dimensional analysis for planetary mixer: mixing time and Reynolds numbers, *Chem. Eng. Sci.*, 62(2007), No. 5, p.1442.

[24] A. Tripathy, A.K. Sahu, S.K. Biswal, and B.K. Mishra, A model for expansion ratio in liquid-solid fluidized beds, *Particuology*, 2013, Accepted in Press, DOI: 10.1016/j.partic.2012.11.006