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Selective flocculation of low grade iron ore slimes using different types of polymers

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A study on selective flocculation of low grade iron ore slimes employing carboxymethyl cellulose (CMC) and starch as flocculants and sodiumhexameta phosphate (SHMP) as dispersant has been carried out. The mineralogical studies reveal that the presence of hematite and goethite as major iron bearing phase. Quartz and kaolinite are found to be gangue minerals. The experiments carried out indicate that the Fe grade is enhanced from 58.24% to 65.32% Fe using starch as flocculant. A Fe grade of 63.44% is obtained using CMC as flocculant. Further, the efficacy of the studies was analysed using separation index, which indicate that the higher separation index was obtained with the tests employing starch.

Keywords: Beneficiation, CMC, Iron ore slimes, Selective flocculation, Starch

India is gifted with huge reserves of high grade hematite ores and one of the prominent producer in the world. As the high grade iron ores exhaustively mined necessitates the use of low grade ores, fines and slimes to meet the market demand. Also, generation of fines and slimes may contribute to loss of minerals to the extent of 30% of total value mineral during processing[1]. These slimes often discarded as waste into tailing ponds, having considerable amounts of iron content. Utilization of these low grade iron ore slimes is crucial for optimization and conservation the ore minerals. Therefore, in recent years, interest in recovery of value minerals from low grade ores, slimes and tailings have been increased by many folds worldwide. These activities are initiated not only to recover minerals but also to address various environmental issues associated with fine particle treatment. From the literature it may be observed that several technologies have been employed in this direction, which includes flotation[2,3], advance gravity separation[4], high intensity magnetic separation[5], etc. However, these processes are found to be ineffective in fine particle treatment due to decreased collision probability in flotation, decreased gravitational effect in gravity separation[6] and reduced drag force in magnetic separation etc. Therefore, it is in this regard selective flocculation of fines has gained importance in treating fine particles processing. Also, selective flocculation process also has advantage of being eco-friendly[7], economical[8-11] and addresses the environmental issues related to the treatment of fine particles.

From the literature it may also be observed that selectiveflocculation studies of iron ore has been carried out using dispersant in grinding circuit with starch as a flocculant. From the studies, it was noticed that dosing sequence of various reagents affects the effectiveness of flocculation[12]. Studies carried out on alumina rich Indian iron ore slimes indicated that amylopectin a constituent of starch is more selective towards flocculation of hematite particles[13]. Also, an earlier study carried out using polyacrylic acid indicated that polyacrylic acid selectively adsorbed on hematite particles rather than gangue particles present along with hematite such as quartz[14]. In another study carried out by Weissenborn et. al. optimization of selective flocculation of ultrafine iron ore using less than 10 µm containing kaolinite as a main gangue mineral reported[15]. From the studies, it was possible to upgrade iron ore fines containing 46% Fe to 56% Fe with a recovery of up to 75% using wheat starch as a flocculant. Studies carried out showed that hydrolysed polyacrylamide[16] facilitates better adsorption by chemical bonding having very little adsorption on quartz. Hence, the phenomena indicate hydrolysed polyacrylamide may be used for selective flocculation of hematite particles.

Therefore, it is in this direction a study on selective flocculation process has been envisaged with reference to Indian iron ore slimes. These studies were carried out using starch and carboxymethyl cellulose (CMC) as flocculants with sodium hexametaphosphate (SHMP) dispersant. The effectiveness of the studies were also analysed using separation efficiency technique.

Experimental Section

Material

The iron ore slime sample used in this study was obtained from Kiriburu region of Jharkhand State, India. The samples collected were air dried, thoroughly mixed and representative sample was drawn by coning and quartering method, subjected for chemical, characterization, mineralogical and beneficiation studies. The size analysis of the representative sample was carried out by dry sieving method in laboratory sieve shaker. The chemical analysis of the representative sample and different size fractions obtained from the size analysis were determined by wet chemical method. Method of characterization using X-ray diffraction, FE-SEM and FTIR was used to characterize the ore.

Flocculants

For selective flocculation studies, flocculants such as CMC (non-ionic) was obtained from Saiguru food and gum industries, Mumbai. It has dull white colour powder in appearance, *p*H of 2% solution in water was 7-9 and loss on drying was found to be less than 10%. Starch was procured from Central Drug House (P) Ltd., New Delhi. Starch has white colour free flowing powder in appearance, odourless, *p*H of a 2% solution @ 25°C was 5-7, loss on drying was 10% and molecular weight was about 80×10^6. SHMP was provided by Merck, India used in this study. Sodium hydroxide and hydrochloric acid are used to adjust the pH of the solution. All the chemicals used for the experiments are analytical grade.

Flocculation tests

Selective flocculation studies were carried out by using 1000 mL measuring cylinder. For this purpose, a desired amount of iron ore slimes having size below 75 micron size was mixed in 950 mL of water for required pulp density. Required amount of dispersant was added to the slurry and the mixing was done by perforated plunger. The *p*H of the slurry was adjusted by using dilute NaOH or HCl solution. After *p*H adjustment, the slurry was conditioned for sufficient period of time. Then the requisite amount of freshly prepared flocculant was added to the slurry. After addition of flocculant, mixing was done. After conditioning, the slurry was allowed to settle for definite time and the supernatant above 75% part of the cylinder was siphoned off. Four stages of cleaning of flocs were carried out by adding make-up water to the settled portion of previous stage. The flocculated and un-flocculated mass were collected separately, dried and subjected to analysis.

Results and Discussion

Characterization studies

The chemical analysis of the iron ore slimes is indicated that the sample contains 58.24% Fe and major impurities are 4.72% SiO_2, 3.47% Al_2O_3 and 5.18% loss on ignition (LOI). The particle size distribution of the sample is shown in Table 1. It has been observed that the particles below 212 microns size are 78.4% by weight. It is observed that the iron values in finer size fraction, i.e. below 150 microns are found to above 60% Fe. However, gangue minerals are preferentially accumulated in the coarser sizes.

Mineralogical studies

X-ray diffraction analysis

X-ray diffraction (XRD) analyses were conducted for phase identification of the minerals. For this purpose, Rigaku X-ray diffractometer (model Ultima IV) was used. The diffractogram (Fig. 1) shows a

Table 1 — Particle size distribution and chemical analysis of iron ore slimes sample

Size (µm)	Weight (%)	Fe%	SiO_2	Al_2O_3	LOI
+212	21.6	53.18	9.12	8.05	6.69
-212 +180	3.4	55	8.81	6.68	5.7
-180 +150	7.4	59.6	5.56	4.22	4.76
-150 +125	15.5	61.14	4.67	3.86	3.81
-125 +106	2.7	62.12	3.87	3.73	3.39
-106 +90	2.6	62.96	4.01	2.17	3.53
-90 +75	11.6	62.4	3.62	3.8	3.12
-75 +63	9.5	63.35	3.03	2.97	2.83
-63 +53	3.4	64.49	2.51	2.56	2.56
-53	22.3	63.79	2.99	2.92	2.76

typical X-ray diffraction pattern of the slimes. XRD analysis of the slimes sample revealed that the major iron bearing minerals are hematite (72.1%) followed by goethite (12.2%) and the other silicates gangue minerals are kaolinite (10.6%) and quartz (5.1%) in order of abundance.

FTIR analysis

Further, samples were analysed for vibrational spectra with Fourier transform infrared spectroscopy using Perkin Elmer instrument in the range 400-4000 cm^{-1}. FTIR test was performed on iron ore slime sample to find out the functional groups presents. The FTIR spectrum of iron ore slime is shown in Fig. 2. It is reported in the literature[17] that peaks around 410-415, 450-470, and 670-680 cm^{-1} shows the presence of hematite. The peak observed around 913.72 cm^{-1} indicates the presence of hematite. Most of bands such as 3667.47, 3447.24, 1033.58, 913.72, 538.81, 468.43 cm^{-1} shows the presence of kaolinite. From the spectrum, the Si-O stretching vibrations were observed at 538.81 and 468.43 cm^{-1} showing the presence of quartz. A band at 3437.24 and 3667.47 cm^{-1} indicate the possibility of hydroxyl linkage. The O-H bending bands of Fe-OH appear at 913 cm^{-1} while Fe-O stretching band appears at 513 cm^{-1}.

Flocculation studies

After completion of characterisation of feed sample, the sample was subjected for settling characteristics and effect of *p*H on settling rate of iron ore slimes. The results of the study are depicted in Fig. 3. From the results it may be seen that increase in *p*H increases the settling rate and maximum settling rate of 1.1 cm/sec

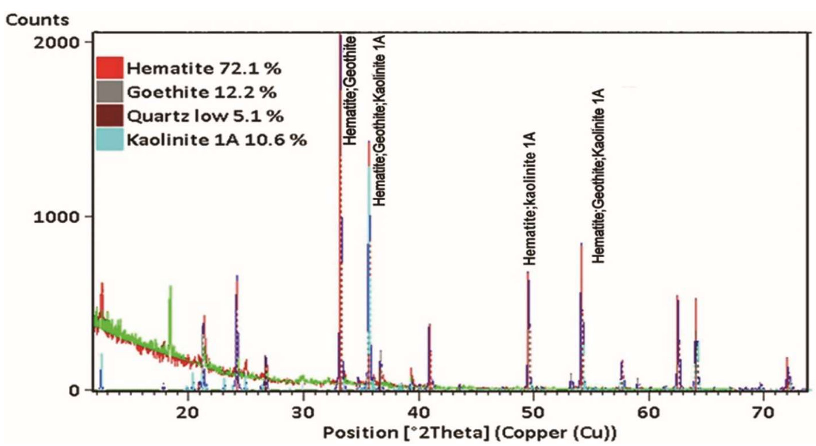

Fig. 1 — X-ray diffraction pattern of iron ore slimes

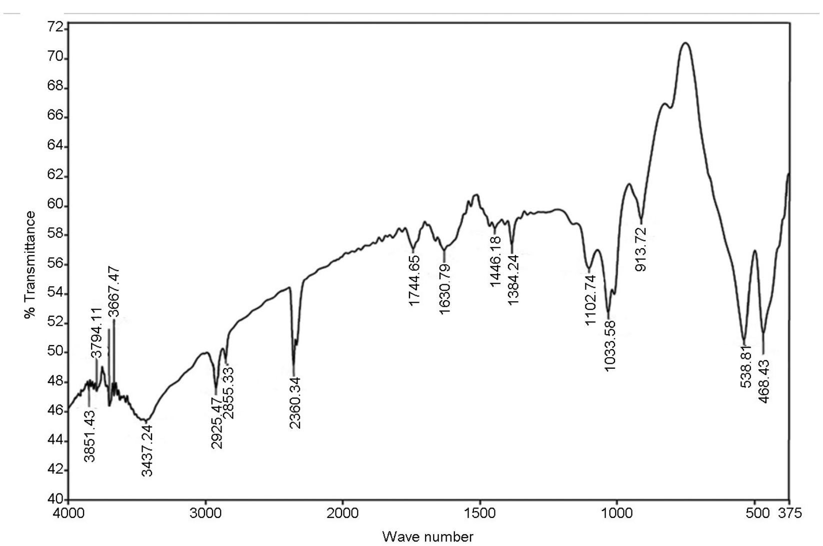

Fig. 2 — FTIR spectra of iron ore slimes

was obtained at *p*H 12 and as pulp density increase the settling rate decreases and the maximum settling rate obtained at a pulp density of 1% by weight. However, in order to initiate selective flocculation process all tests were carried out at *p*H 10, at which particles were found to be in transition state. Therefore, for all flocculation experiments a constant pulp density of 1% and *p*H of 10 was maintained. Further, the selective flocculation studies were carried out using different flocculants i.e. carboxymethyl cellulose and starch. The results of experiments are given below.

Initially the studies were carried out with different flocculant dosage of carboxymethyl cellulose. The results of the tests are depicted in the Fig. 4 and Fig. 5 for grade and recovery of the concentrate respectively. From the figures it may be seen that the grade of iron ore slimes increases with increase in concentration of CMC flocculant to a maximum value of 61.6% with a recovery of about 97.52% using 0.21 mg/g of CMC. However, it has been observed that beyond 0.21 mg/g of CMC the grade of iron was found to be decreasing with increase in recovery, which may be attributed to the settling of gangue particles present in the slimes.

In order to know the effect of starch some studies were carried out with different concentration of starch. The results of the tests are given in Fig. 4 and Fig. 5 for the grade and recovery respectively. From the figures, it may be seen that a similar trend has been observed as in case of CMC. From the results it was also observed that a maximum of 62.68% Fe with a recovery of 95.78% could be obtained using 0.15 mg/g of starch flocculant. From the studies here, it may be noted that the experiments carried out with starch showed higher grade of iron compared to CMC used in the studies. This may be attributed to the starch flocculant selectively adsorb onto the hematite particles up to 0.15 mg/g flocculant dosage. Beyond this dose starch flocculant adsorb onto the gangue minerals present in the slimes and makes polymer bridges with the hematite particles.

Further, all the experiments carried out were analysed to assess the effectiveness of the flocculation by calculating separation efficiency. The separation efficiency can be calculated as given in equation no. (1).

$$\%S.E = = \frac{100*X*t*(c-f)}{f*(t-f)} \quad ...(1)$$

where, c is grade of the concentrate, f is the feed grade of the ore, t is the theoretical maximum grade in the concentrate possible, X is the yield of the concentrate. From the Fig. 6, it may be seen that the separation efficiency of the process increased with the increase of concentration of the CMC flocculant with the maximum value of 31.66% by using 0.21 mg/g of the CMC. Whereas for starch the maximum value of separation efficiency was 40.39% by using 0.15 mg/g of starch. However, it may be seen that beyond 0.21 mg/g of the CMC and 0.15 mg/g of the starch, it was found to be decreasing with increase in flocculant dosage which may be attributed to surface heterogeneity of the particles, the flocculants adsorb on

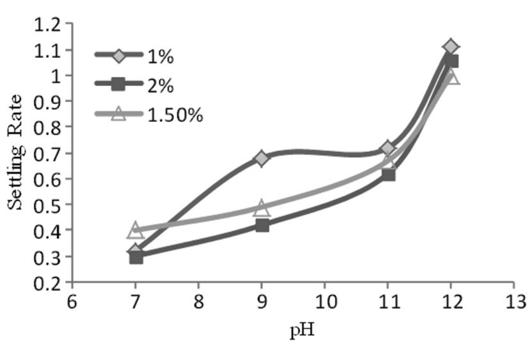

Fig. 3 — Effect of *p*H on settling rate at various pulp densities

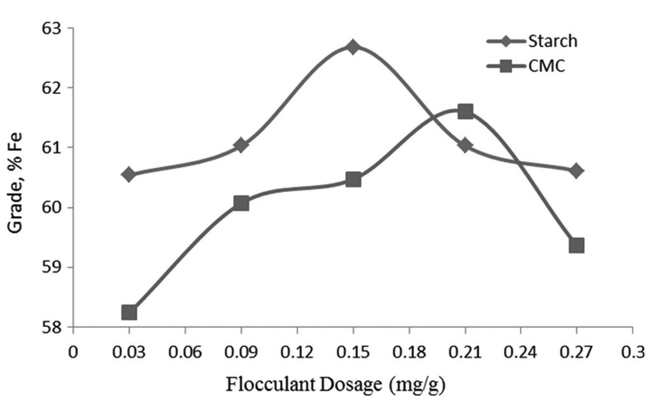

Fig. 4 — Grade of iron as a function of flocculant dosage of CMC and starch

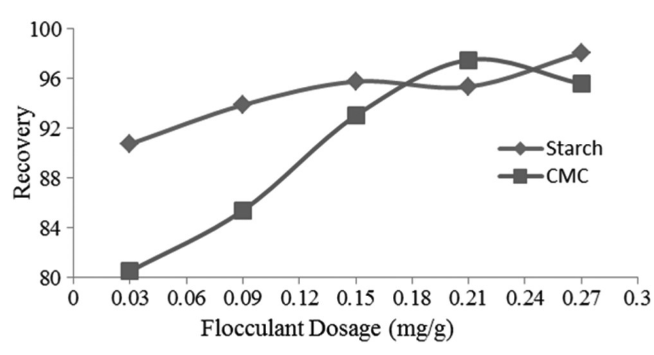

Fig. 5 — Recovery of iron as a function of flocculant dosage of starch and CMC

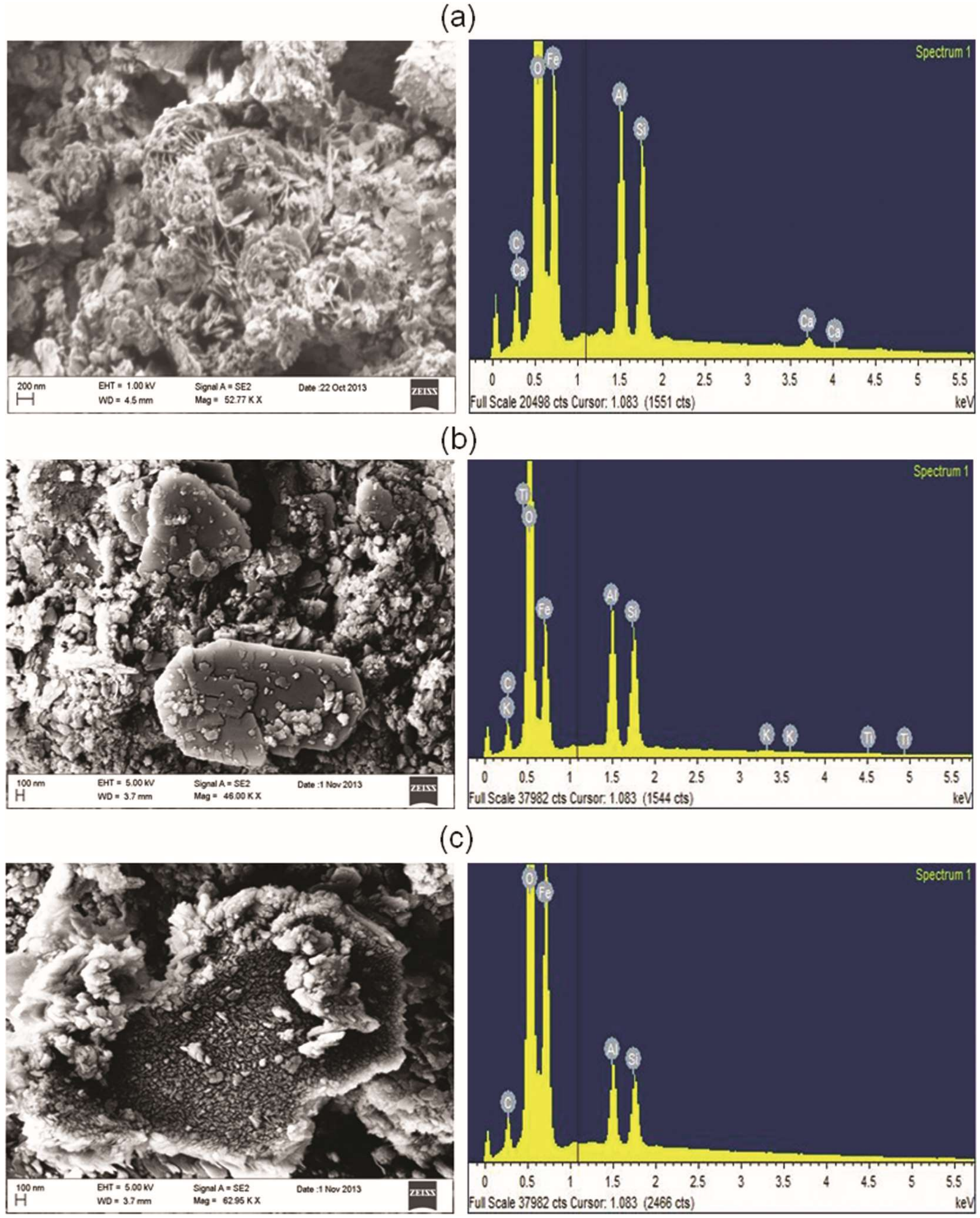

Fig. 6 — FESEM-EDS characteristics of (a) iron ore slimes (before flocculation), (b) flocculated iron with CMC and (c) flocculated iron with starch

the gangue minerals and co-flocculate with the hematite particles to form flocs, causing loss in selectivity of the process.

After completion of the above studies, tests were carried to know the effect of dispersant on selective flocculation of iron ore slimes. To accomplish this, studies were carried out using SHMP as dispersant. Dispersants are used to achieve the goal of separation so that the undesired minerals remain in dispersed state. The tests were carried out to the effect of dispersant on settled weight% of iron ore slimes. It was found that SHMP was more effective at 0.5 kg/ton of SHMP for slurry stabilization. Washing of flocs was carried out in order to enhance the grade of iron ore slimes with the help of SHMP. A four stage cleaning technique was employed during the studies and the results are given in Table 2. From the table it may be seen that there is an increase in grade 65.32% using 0.15 mg/g of starch after four stage cleaning with a corresponding recovery of 62.08%. Similarly, there

Table 2 — Effect of washing

No. of Washing	Grade (%) Fe)		Recovery (%)		Separation Efficiency (%)	
	*Starch	*CMC	Starch	CMC	Starch	CMC
1	62.96	61.95	78.81	80.95	35.17	28.85
2	63.46	62.37	67.29	69.50	32.95	27.39
3	64.24	62.87	64.50	66.60	35.86	29.20
4	65.32	63.44	62.08	63.72	40.05	31.09

*Starch dose = 0.15mg/g and CMC dose = 0.21 mg/g

is an increase in grade 63.44% using 0.21 mg/g of CMC after four stage cleaning with a corresponding recovery of 63.72%. The analysis of separation efficiency (Table 2) shows a maximum efficiency of 40.05 for starch and 31.09 for CMC which may be attributed to removal of entrapped gangue minerals from the flocs formed. It was observed that the grade of iron ore slimes was improved by 4.17% after washing in case of starch, but in case of CMC grade was improved by 2.98% after washing. The starch contains amylose and amylopectin, amylose having linear chain whereas amylopectin having branched chain. Due to the presence of amylopectin the flocs formed are robust and shear stable. The CMC is linear chain polymer and the flocs formed are not so robust and shear stable as compared to starch.

FE-SEM analysis

FE-SEM analysis was carried out to know the behaviour of flocculation studies. FE-SEM Supra 55 (Carl Zeiss, Germany) was used for this purpose. Fig. 6(a) shows the microphotograph of iron ore slimes before flocculation. The microphotograph indicates that the presence of hematite in the form of microplaty structure. From the EDS analysis shows variable percentage of alumina and silica also present in the iron ore slimes. Fig. 6(b) and Fig. 6(c) shows the microphotograph of flocculated iron ore slimes with CMC and starch respectively. FESEM-EDS observation shows that starch is highly selectively adsorbs onto the surface of hematite (Fig. 6c). However, Fig. 6(b) indicates that the adsorption of CMC onto the surface of hematite particles is less as compared to starch.

Conclusion

The iron ore slimes is low grade and contains 58.24%Fe with 4.72%SiO_2 and 3.47%Al_2O_3. The mineralogical characterization studies indicate the presence of hematite and goethite as major minerals and quartz and kaolinite as minor minerals. The effect of settling rate as a function of *p*H shown an increase in the settling rate with an increase in *p*H. The initial flocculation experiments without addition of dispersant indicate a concentrate of 62.68%Fe with a recovery of 95.78% was achieved by using starch as flocculant. The effect of cleaning of flocs by addition of dispersant improves the selective flocculation process. A maximum improvement of 58.24 to 65.32% Fe with a recovery of 62.08% was achieved with the addition of 0.15 mg/g of starch and 0.5 Kg/ton of SHMP after four stages of cleaning. Starch shows good results as compared with CMC. From the FESEM analysis, it may be said that starch is better than CMC.

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References

1 Mandre N R &Panigrahi D, *Int J Miner Process*, 50 (1997) 117.
2 Batisteli G M B & Peres A E C, *Miner Eng*, 21 (2008) 873.
3 Quast K B, *Mineral Eng*, 13 (2000) 1361.
4 Roy S, *The Open Mineral Processing Journal*, 2 (2009) 17.
5 Dworzanowski M, *J SAIMM*, 112 (2012) 197.
6 Das B, Prakash S, Das S K & Reddy P S R, *J Miner Mater Charact Eng*, 7 (2007) 27.
7 Sarkar A K, Mandre N R, Panda A B & Pal S, *Carbohydr Polym*, 95 (2013) 753.
8 Panda L, Biswal S K & Tathavadkar V, *J Miner Mater CharactEng*, 23 (2010) 842.
9 Panda L, Banerjee P K, Biswal S K, Venugopal R & Mandre N R, *Int J Minerals Metall Mater*, 20 (2013) 1123.
10 Haselhuhn H J, Carlson J J & Kawatra S K, *Int J Miner Process*, 102 (2012) 99.
11 Rocha L, Caneado R Z L & Peres A E C, *Int J Miner Process*, 42 (1994) 191.
12 Ma M, *Chem Eng Sci*, 73 (2012) 51.
13 Pradip & Rai B, *In Proceedings of the International conference on Beneficiation of Fines and its Technology*, (ICBenefit-2007), edited by A K Mukherjee & D Bhattacharjee, Tata Steel and Indian Institute of Mineral Engineers, Jamshedpur, (2009) 123.
14 Drzymala J & Fuerstenau D W, *Int J Miner Process*, 8 (1981) 265.
15 Weissenborn P K, Warren L J & Dunn J G, *Int J Miner Process*, 42 (1994) 191.
16 Jin R, Hu w, & Hou X, *Colloids Surf*, 26 (1987) 317.
17 Prakash S, Das B &Venugopal R, *J Sci Ind Res*, 58 (1999) 436.