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Comparison of selective flocculation of low grade goethitic iron ore fines using natural and synthetic polymers and a graft copolymer

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Abstract: This study aims to beneficiate low grade goethitic iron ore fines using a selective flocculation process. Selective flocculation studies were conducted using different polymers such as starch amylopectin (AP), poly acrylic acid (PAA), and a graft copolymer (AP-g-PAA). The obtained results were analyzed; they indicate the enhancement of the iron ore grade from 58.49% to 67.52% using AP-g-PAA with a recovery of 95.08%. In addition, 64.45% Fe with a recovery of 88.79% was obtained using AP. Similarly, using PAA, the grade increased to 63.46% Fe with a recovery of 82.10%. The findings are also supported by characterizing concentrates using X-ray diffraction (XRD) and electron probe microanalysis (EPMA) techniques.

Keywords: low grade iron ore fines; selective flocculation; graft copolymer; amylopectin (AP); poly acrylic acid (PAA)

1. Introduction

High grade iron ores are being depleted worldwide at a rapid rate due to enhanced mining and mineral processing activities and the increased consumption of steel in different sectors. In recent years, it has been observed that the complex nature of the mineralogical association of iron ore can cause an increase in the degree of fineness of the minerals, leading to difficulties in beneficiating such iron ores. It is also observed in literature that many processes such as gravity concentration, magnetic separation, and froth flotation are widely used to beneficiate fine grained, low-grade ores [1–2]. However, these processes suffer from inherent disadvantages such as reduced efficiency in processing fine particles, enhanced slime content, decreased response to magnetic and gravity separation, and reduced floatability due to the slime coating [3–4].

The recovery of the valuable minerals is necessary in low grade ores that contain high amounts of iron minerals. Such ores are currently being dumped and are un-utilized prior to beneficiation and extraction processes; thus, exploring the possibility of developing alternate beneficiation techniques such as selective flocculation is imperative for the treatment of low grade iron ore fines/slimes/tailings. Consequently, such techniques have gained considerable attention in recent years.

Literatures report that selective flocculation can be conducted using various synthetic and natural polymers such as starch [5–8], poly acryl amide (PAM) [9–10], and poly acrylic acid (PAA) [11–12]. However, although these flocculants provide advantages, they also have inherent limitations. For example, synthetic flocculants are highly efficient, but they are not biodegradable and may cause serious environmental problems due to toxic monomer release [13]. Conversely, natural polymer-based flocculants are shear resistant, biodegradable, and eco-friendly; moreover, they are known as the "green flocculants of 21st century" [14], but they are less efficient than synthetic flocculants. Therefore, both polymer types are combined to obtain benefit from their respective advantages and to minimize their respective disadvantages; in addition, their combination is expected to improve their flocculant characteristics. In this study, therefore, a grafting process is used to determine effectiveness by grafting a synthetic polymer onto a natural polysaccharide

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backbone. This study aims to determine the effect of the use of a graft copolymer, starch amylopectin grafted with poly acrylic acid (AP-g-PAA), as a selective flocculant for low grade iron ore fines. Furthermore, the study aims to analyze and compare selective flocculation processes using the graft copolymer, starch amylopectin (AP), and poly acrylic acid (PAA).

2. Experimental

For the present study, low grade iron ore fine samples were collected from Gua mines in the Singh Bhum district, Jharkhand, India. Representative samples were subjected to chemical analysis and characterization studies. Results of chemical analysis showed 58.49wt% FeO, 5.44wt% SiO_2, 4.51wt% Al_2O_3, and 3.74wt% loss on ignition.

The reagent amylopectin (AP) was supplied by Fluka, Switzerland, and acrylic acid was obtained from E. Merck Germany. Potassium persulphate (KPS) was obtained from Qualigens, Mumbai, India; acetone and hydroquinone, sodium hexametaphosphate (SHMP), sodium hydroxide (NaOH), and hydrochloric acid were obtained from E. Merck, Ltd, Mumbai, India. All chemicals used in the study were of analytical grade.

2.1. X-ray diffraction (XRD) study

In determining the presence of various minerals present in the ore sample, XRD was conducted using Cu K_α radiation. Study results are provided in Fig. 1, wherein hematite and goethite are evidently the major iron phases along with alumina, quartz, and kaolinite as the major gangue minerals.

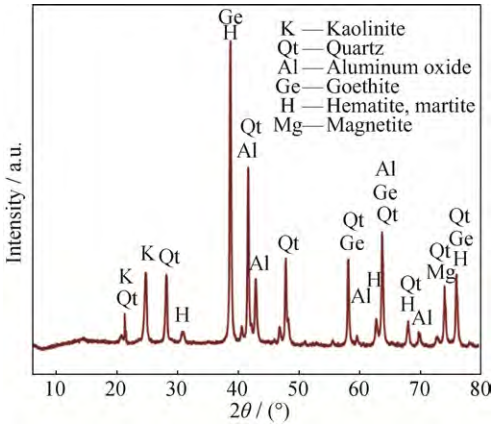

Fig. 1. XRD pattern of low grade iron ore fines.

2.2. Mineralogical studies

Mineralogical studies were conducted using a Leicamake ore microscope interfaced with QWIN image analysis software. Study results are given in Fig. 2, wherein hematite is seen to alter to martite with iron present in a colloform structure. From the micrograph, the presence of magnetite particles is observed to be in trace amounts, whereas iron-bearing minerals are mostly contaminated with kaolinite.

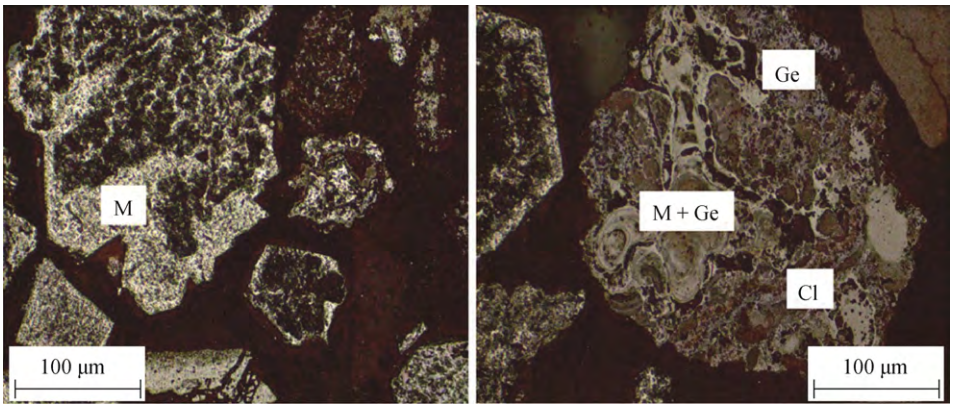

Fig. 2. Microscopic view of low grade iron ore fines. M—Martite; Ge—Goethite; Cl—Clay.

2.3. Zeta potential analysis

Samples were subjected to zeta potential analysis using a Zeta-meter 4.0 (U.S.) with a microprocessor unit to directly measure the average zeta potential and its standard deviation. Studies were conducted under different pH values to maintain constant electrolyte concentrations.

2.4. EPMA analysis

The feed sample and concentrate sample (obtained after selective flocculation) were subjected to EPMA analysis using a fifth generation electron probe micro analyzer SX V

(CAMECA, France).

2.5. Synthesis of graft copolymer (AP-g-PAA)

The graft copolymer of AP with PAA was synthesized in laboratory using a free radical polymerization technique in an inert atmosphere of nitrogen using potassium persulfate (KPS) as the initiator. For synthesis, the standard procedure described in literature was employed [15].

Furthermore, the optimization of the grafting process was determined with respect to the grafting efficiency, intrinsic viscosity (dL/g), and hydrodynamic radius (RH) (nm) [15].

Synthesized AP-g-PAA and starch AP were then subjected to analysis with a field emission scanning electron microscope (FE-SEM, Model-Supra 55, Carl Zeiss, Germany) to confirm the grafting process; the results are shown in Figs. 3(a) and 3(b). Fig. 3(a) shows that starch AP has a granular morphological structure, but the graft copolymer exhibits a fibrillar morphology (Fig. 3(b)) after the completion of the grafting process; this is attributed to the agglomeration of the PAA chains. This observation also indicates that the grafting process affects the morphological characteristics of AP.

AP-g-PAA 5 is used in the present study because it provides a high grafting efficiency of 86.57% owing to the grafting of PAA chains onto the backbone of AP. The graft copolymer has been reported to possess a high grafting efficiency (i.e., AP-g-PAA 5) with the maximum viscosity (47.27 dL/g).

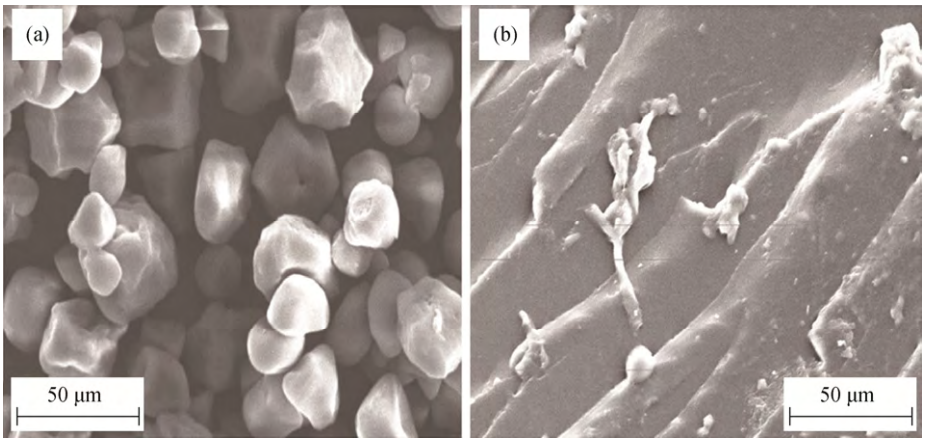

Fig. 3. Scanning electron micrographs of (a) amylopectin (AP) and (b) graft copolymer (AP-g-PAA 5).

2.6. Selective flocculation studies

Flocculation studies were conducted using standard settling tests, and the effects of different parameters such as pH value, pulp density, and flocculant dosage were investigated.

All experiments were conducted using a 1000 mL graduated cylinder. A specific amount of solid was mixed with water to maintain the necessary pulp density, and the slurry was thoroughly mixed using a perforated plunger for approximately 2–3 min. The pH value of the slurry was adjusted using dilute HCl or NaOH, and the required amount of flocculant and dispersant dosage were then added. The slurry was thoroughly agitated by inverting the cylinder 10–12 times [12]. After mixing the particles, the slurry was allowed to stand undisturbed for 3–5 min and particles were allowed to settle; 75wt% of the slime was then siphoned out after determining the mud-line height (interface between settled pulp and clear water). Both the flocculated (concentrates) and non-flocculated fractions (tailings) were collected separately, and both products were dried in an oven at a temperature of approximately 100°C, weighed, and then subjected to chemical analysis.

3. Results and discussion

Initial tests were conducted prior to selective flocculation studies using a pulp density of 6wt%–10wt% to determine the settling rate and the effect of pH value on the settling rate. For this purpose, the experimental method described by Talmage and Fitch [16] was used. Results are presented in Fig. 4, wherein maximum settling rate of 1.02 cm/s was obtained at a 6wt% pulp density and pH value of 12. However, to provide selective flocculation and allow the particles to be suspended, a constant pH value of 10 and a pulp density of 6wt% were maintained in the experiments. These results were substantiated by determining the settling rate with different flocculant dosages; these are provided in Fig. 5, wherein as compared to the other flocculants, the graft copolymer can be seen to provide a better settling rate throughout the studied range. A maximum settling rate of 1.58 cm/s was obtained at a high dosage (3.0 mg/g) of AP-g-PAA. Similarly, settling

rates of 1.37 and 1.19 cm/s were obtained at the same dosages (3.0 mg/g) with AP and PAA, respectively.

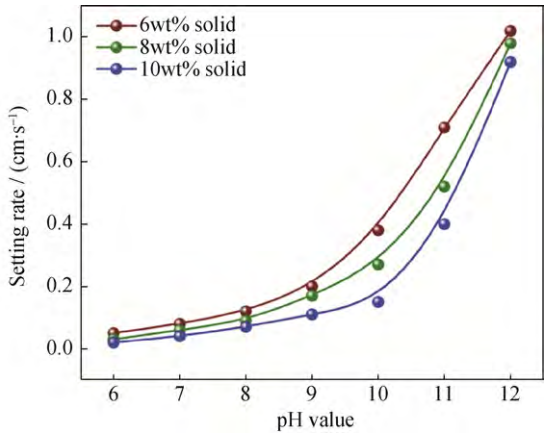

Fig. 4. Effect of pH value on settling rate at various pulp densities with 0.5 mg/g of SHMP.

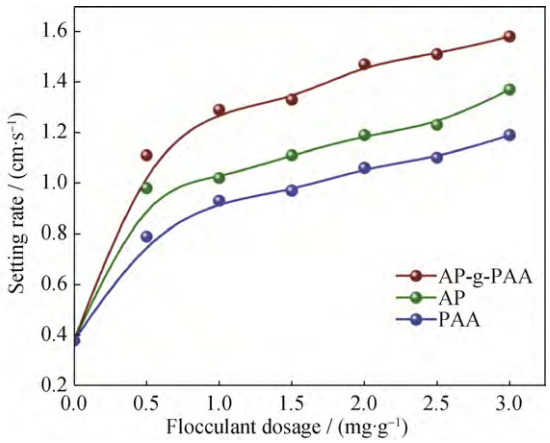

Fig. 5. Effect of flocculant on settling rate at various dosages with 0.5 mg/g of SHMP.

3.1. Zeta potential studies

To support the above findings, zeta potential studies were conducted in both the absence and presence of the flocculants, and the zeta-potential was analyzed as a function of pH value as well as flocculant and dosage. Study results are provided in Figs. 6(a) and 6(b). Fig. 6(a) shows the variations of the zeta-potential value from +38 to −37.96 mV throughout the pH value range (zeta-potential at natural pH value of 6.07 was found to be +20 mV). Herein, it may be observed that the point of zero charge occurs at approximately pH value of 6.5, indicating that all minerals present in the ore tend to flocculate at this pH value. However, with an enhanced pH value of over 7, particles remain in suspension owing to the higher negative zeta-potential, which occurs because the particles remain in a dispersed state as primary particles without forming aggregates. Therefore, to enable selective flocculation on a desired mineral, it is necessary for the particle to be maintained in suspension to enable reagent and particle interaction [17]. A pH value of 10 was thus maintained in all selective flocculant tests.

Fig. 6(b) shows results of studies conducted to determine the effect of different flocculant dosages on the zeta-potential, where it can be observed that a lower zeta-potential (−17.62 mV) can be obtained using the graft copolymer (AP-g-PAA) at a concentration of 0.5 mg/g. It can also be seen that an increase in the AP-g-PAA dosage results in a decrease in the zeta-potential value; this observation can be ascribed to the better adsorption of flocculant onto the surface of the particles, thereby indicating better selectivity. Furthermore, the tests conducted using starch AP and PAA indicate that maximum magnitudes of zeta-potentials of −24.22 and −33.31 mV can be obtained using concentrations of 2.0 mg/g of starch AP and 3.0 mg/g of PAA, respectively. It is thus determined that a graft copolymer with a low zeta-potential magnitude can be obtained by using the minimum dosage of the polymer.

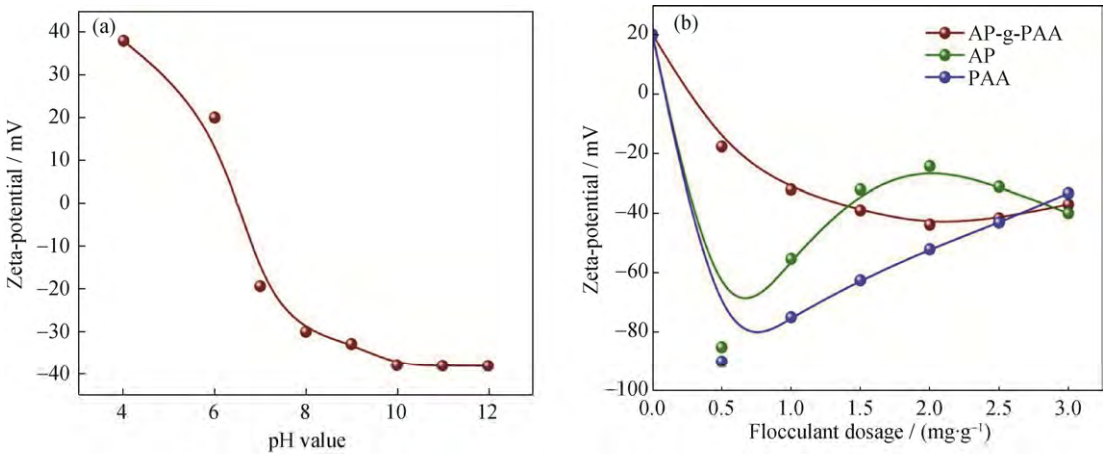

Fig. 6. Effects of pH value (a) and flocculant dosage (b) on zeta-potential.

3.2. Grade and recovery

Study results were analyzed to determine the grade and recovery. In this respect, the supernatant obtained during the selective flocculation process was discarded, and the settled solid was selected for chemical analysis. These studies were conducted using different flocculant dosages at different pH values and at a constant pulp density of 6wt% and dispersant (sodium hexametaphosphate) dosage of 0.5 mg/g (to facilitate dispersion of particles). Results in Figs. 7(a) and 7(b) indicate that the feed grade enhanced from 58.49% to 67.52% can be obtained using 0.5 mg/g of the graft copolymer (AP-g-PAA) with a recovery of 95.08%. This result shows that with an increase in the flocculant dosage of AP-g-PAA, the grade of the iron ore tends to decrease. This phenomenon may be attributed to flocculation of gangue particles and mineral particle at an enhanced flocculant dosage. This phenomenon was also observed in the case of the flocculant AP beyond a flocculant dosage of 2.0 mg/g. However, the grade of the iron ore gradually increases in the case of PAA with an increase in the flocculant dosage from 0.5 to 3.0 mg/g. Results show that using more than 0.5 mg/g of AP-g-PAA polymer enhances the agglomeration of all the particles, leading to a loss in the selective flocculation process. From the results, it may also be noted that maximum grades of 64.45% and 63.46% Fe can be obtained using concentrations of 2.0 mg/g of starch AP and 3.0 mg/g of PAA, respectively. These tests therefore indicate that a better grade and recovery can be obtained at a lower dosage with a graft copolymer than starch AP and PAA. This observation may be due to the higher intrinsic viscosity and high molecular weight (10^5–10^6 g/mol).

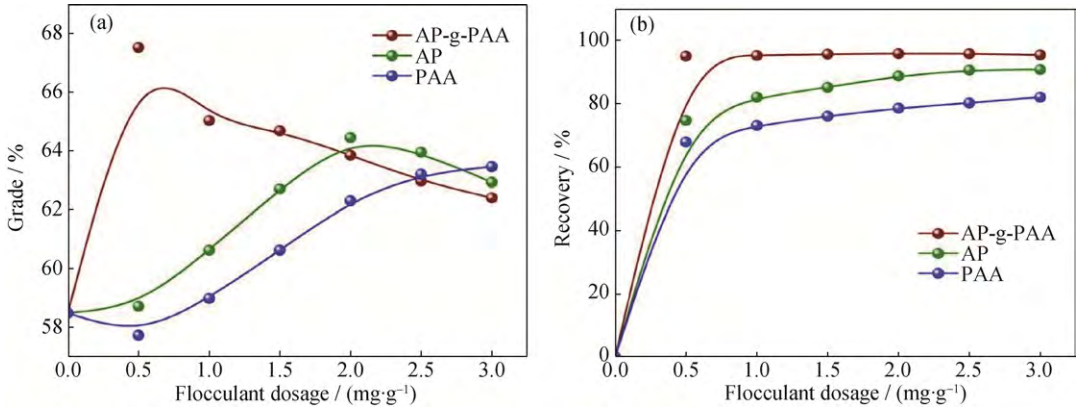

Fig. 7. Effect of flocculant dosage on grade (a) and recovery (b).

3.3. X-ray diffraction (XRD) of concentrate

To support the above findings, XRD analyses were conducted on the obtained concentrates to determine the various present mineral phases. Samples providing maximum grades and recoveries were used in XRD studies to ascertain the various phases present in concentrates. Results of XRD studies are presented in Fig. 8. The figures show distinct sharp peaks for hematite and goethite in the concentrate obtained using the graft copolymer AP-g-PAA (0.5 mg/g). However, the results obtained using starch AP (2.0 mg/g) as the flocculant indicates the presence of quartz along with iron minerals. Similarly, the diffractogram obtained using PAA (3.0 mg/g) as a flocculant indicate that the concentrate comprising alumina, quartz, kaolinite, and iron minerals; thus, the graft copolymer evidently yields better flocculation results than the other flocculants.

3.4. EPMA analysis

In addition to the above tests, the concentrate and tailing samples obtained from studies using AP-g-PAA (0.5 mg/g) were subjected to analysis with an electron probe micro analyzer. Results are provided in Fig. 9, wherein a superior flocculated mass containing a high amount of iron was observed to be obtained from tests using the graft copolymer. Similarly, the tailing obtained shows unflocculated gangue particles; this was further proved using elemental analysis. Results are provided in Table 1, which show that the

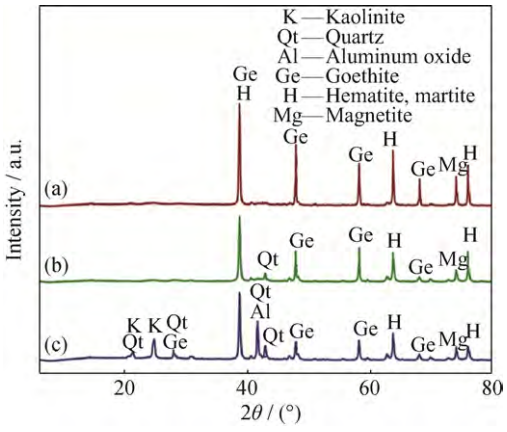

Fig. 8. XRD patterns of concentrates obtained using different flocculants: (a) graft copolymer (AP-g-PAA); (b) amylopectin (AP); (c) poly acrylic acid (PAA).

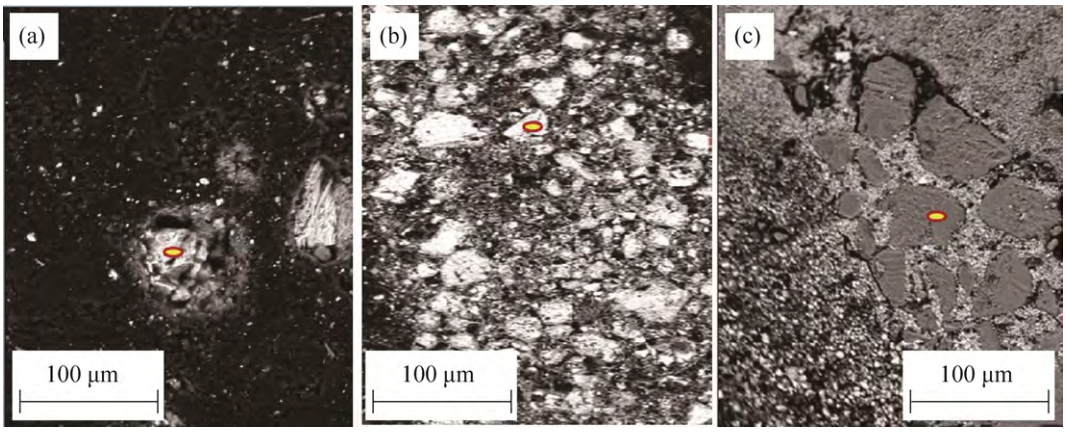

Fig. 9. Electron microanalysis images of (a) feed, (b) concentrate (obtained using AP-g-PAA), and (c) tailings (obtained using AP-g-PAA).

Table 1. Elementary analysis of EPMA study wt%

Sample	SiO_2	FeO	Al_2O_3
Feed	7.04	69.30	6.20
Concentrate	0.89	94.23	0.11
Tailing	12.36	45.44	7. 29

concentrate contains 94.23wt% FeO, 0.89wt% SiO_2, and 0.11wt% Al_2O_3, and tailing analysis shows the existence of 45.44wt% FeO, 12.36wt% SiO_2, and 7.29wt% Al_2O_3 using the graft copolymer.

4. Conclusions

(1) The graft copolymer of AP with PAA was synthesized in laboratory by a free radical polymerization technique in an inert atmosphere of nitrogen using KPS as an initiator. The results of analyses conducted in this study confirm that a lower zeta-potential (−17.62 mV) can be obtained using a graft copolymer (AP-g-PAA) at a concentration of 0.5 mg/g than with the other polymers tested in the study.

(2) The results of flocculation studies show the possibility of iron grade enhancement from 58.49% to 67.52% with 95.08% recovery using an AP-g-PAA dosage of 0.5 mg/g. However, using 2.0 mg/g starch AP and 3.0 mg/g PAA, maximum grades of iron at 64.45% and 63.46% can be obtained with recoveries of 88.79% and 82.10%, respectively.

(3) Characterizing the concentrate using various techniques ascertain that the graft copolymer selectively flocculates iron minerals more effectively than other flocculants used in the study.

Acknowledgements

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References

[1] A.C. Araujo, P.R.M. Viana, and A.E.C. Peres, Reagents in iron ores flotation, *Miner. Eng.*, 18(2005), No. 2, p. 219.

[2] M. Ma, Froth flotation of iron ores, *Int. J. Min. Eng. Miner. Process.*, 1(2012), No. 2, p. 56.

[3] M. Dworzanowski, Maximizing the recovery of fine iron ore using magnetic separation, *J. South Afr. Inst. Min. Metall.*, 112(2012), No. 3, p. 197.

[4] S. Roy, Recovery improvement of fine iron ore particles by multi gravity separation, *Open Miner. Process. J.*, 2(2009), p. 17.

[5] P. Pradip, Beneficiation of alumina rich Indian iron ore slimes, *Met. Mater. Processes*, 6(1994), No. 3, p. 179.

[6] N.R. Mandre, Selective flocculation of low-grade iron ore fines, [in] *XXVI International Mineral Processing Congress*, New Delhi, 2012, p. 3220.

[7] L.O. Filippov, V.V. Severov, and I.V. Filippova, Mechanism of starch adsorption on Fe–Mg–Al-bearing amphiboles, *Int. J. Miner. Process.*, 123(2013), No. 6, p. 120.

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

[9] M. Dash, R.K. Dwari, S.K. Biswal, P.S.R. Reddy, P. Chattopadhyay, and B.K. Mishra, Studies on the effect of flocculant adsorption on the dewatering of iron ore tailings, *Chem. Eng. J.*, 173(2011), No. 2, p. 318.

[10] R. Kumar and N.R. Mandre, Characterization and beneficiation of iron ore tailings by selective flocculation, *Trans. In-*

dian Inst. Met., 69(2016), No. 7, p. 1459.

[11] 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.

[12] S. Mathur, P. Singh, and B.M. Moudgil, Advances in selective flocculation technology for solid-solid separations, *Int. J. Miner. Process.*, 58(2000), No. 1-4, p. 201.

[13] M. Schintu, P. Meloni, and A. Contu, Aluminum fractions in drinking water from reservoirs, *Ecotoxicol. Environ. Saf.*, 46(2000), No. 1, p. 29.

[14] J. Xiao and Q. Zhou, *Natural Polymer Flocculants*, *Chemical Industry Press*, *Beijing*, 2005.

[15] A.K. Sarkar, N.R. Mandre, A.B. Panda, and S. Pal, Amylopectin graft with poly (acrylic acid): Development and application of a high performance flocculant, *Carbohydr. Polym.*, 95(2013), No. 2, p. 753.

[16] W.P. Talmage and E.B. Fitch, Determining thickener unit areas, *Ind. Eng. Chem.*, 47(1955), No. 1, p. 38.

[17] 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.