Hindawi

Research Article

Upgradation of Iron Ore Fines and Slime by Selective Flocculation Using Surface-Active Agents, Settling Study, and Characterization of the Beneficiation Waste for Value Addition

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Washing of iron ore fines and slime (10% and 25% w/v, slurry concentrations) with two types of surface-active agents (sodium humate (synthesized) and AD 200 (commercial)) at varying concentrations at pH 8 was conducted for ascertaining the efficacy of dispersants in beneficiating the low-grade iron ores. The beneficiation process follows the "selective dispersion-cum-settling technique." The process results in the formation of a dispersed phase rich in gangue minerals and a settled phase of predominantly active hematite mineral. The stability of dispersed phase (DP) was evaluated by determination of the percentage solid content in the DP. Settling tests were performed. First-order kinetic models have been applied to the dispersion-cum-settling behaviour of both the samples, and evaluated kinetic parameters were found to have good agreement with experimental data. Removal of gangue minerals from iron ore depends on the pH of the slurry, concentration of the slurry, and concentration of the surface-active agent used. The surface-active agents at pH 8 produce ~1.2–1.5 times more stable suspension in the case of iron ore fines and slimes than that of without surface-active agent. They significantly remove gangue minerals and increase the iron value ~2–7% with ~58–74% recovery depending on the experimental conditions. The concentrates collected satisfy the required specifications ($Al_2O_3/Fe < 0.05$ and $Al_2O_3/SiO_2 < 1$). The gangues in the dispersed phase as characterised by "SEM-EDXA" are mostly clay-bearing minerals like kaolinite, goethite, chlorite, and alumina-silicate minerals. Heat treatment causes distortion of clay minerals present in the dispersed phase and also indicates the complex nature of the gangue minerals.

1. Introduction

Upgradation of iron ore is an essential step to meet the quality norms of the feed for the blast furnace in the iron and steel industry. Beneficiation and metallurgical treatment of iron ores depend on their source because of inherent and peculiar mineralogical character. Nevertheless, the selection of the beneficiation techniques/treatments depends on the quality of the gangue/waste minerals present and their inherent embodiment in the ore geometry. Most of the conventional beneficiation techniques are not suitable for mineral mixtures containing fines and slimes [1].

India is rich in iron ore reserves, consisting of around 14 billion tonnes [2]. The principal plants are situated in the states of Jharkhand, Orissa, Goa, Karnataka, and Chhattisgarh [3]. The quality of the iron ore is generally soft in nature associated with high amount of clay minerals [4]. The Indian iron ore processing industry is discarding about 8 to 10 million tons of iron per annum at ~50–60% iron in the form of slimes that results in huge loss of iron value including threat to the environment [5]. The generated low-grade iron ore fines and slime are considered as waste. So, these are stockpiled separately due to less market and industrial value. In general, Indian iron ore fines and slime are

found to contain ~58% Fe, high amount of alumina (>8%), and silica (~8%) [6]. Increasing iron value and simultaneous lowering of gangue minerals in iron ore hence are of prime concern for the industry. The iron ore fines and slime having an alumina-to-silica ratio typically >1 create severe operational problems during sintering and subsequent smelting in the blast furnace. Generally, higher alumina content in iron ore fines causes higher viscous slag throughout the smelting process, which in turn requires a high coke rate. On the other hand, an increase in 1% Fe in the concentrate results in 2% increase in the productivity of the hot metal, which in turn reduces the requirements of coke and limestone by 1.8% and 0.9%, respectively [7]. Keeping in mind firstly about the conservation of this nonrenewable resource and secondly the feed quality for the blast furnace, beneficiation of iron ore fines and slime is essential to keep the Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrate below 0.05 and 1, respectively. During mining and washing operations in the plant, proper care needs to be taken to get good quality iron ore [8]. Moreover, contamination of very fine slime particles with the overflowed water from slime ponds causes serious environmental threats.

Various standard beneficiation techniques *viz.* sizing, classification, hydrocyclone, jigging, magnetic separation, advanced gravity separation, and flotation are employed using only water for beneficiation of the iron ore [9]. The application of reverse cationic floatation technique with mixed collectors/dispersants for beneficiation of iron ores in the dimension of slimes and fines is also noteworthy [10]. Literature revealed that beneficiation of iron ore slime by using hydrocyclone, classification, magnetic separation, and combination of all processes significantly increase the iron value (≥60%) in the concentrate [11, 12]. In addition grinding of the slimes also helps in liberation of the minerals, which when followed by hydrocyclone and magnetic separation results in concentrates with >64% Fe with a recovery of 60% from raw material having 58.13% Fe, located in eastern India [13]. The application of hydrocyclone and magnetic separation techniques in upgrading iron ore slimes both in terms of iron content and recovery was also found effective [14]. However, the performance of air classifier technique in upgrading the low-grade high-goethite content Australian iron ore tailings was found poorer than that of hydrocyclone technique due to agglomerated feed samples [15]. Recently, Nunna et al. also discussed about the application of circulating type air classifier in beneficiating low-grade iron ore fines [16]. Hence, selection of the most effective process for treatment of low-grade iron ores is dependent upon the nature of aggregation of iron with gangue minerals. During washing of the ore, it has been observed that normal plain water washing, as practiced generally, is not very effective in the sense that the Al_2O_3/Fe and the Al_2O_3/SiO_2 ratios do not differ much from that of the feed values [4]. In this context, additive or surface-active agent washing is noteworthy.

Surface-active agents are technoeconomically cheap and ecofriendly in nature. In this connection, several synthetic chemicals are used viz., polar and nonpolar polyacrylamide [17], starch [18], humate [1], and inorganic or organic dispersants or combination of them [19] are used for beneficiation. The surface-active agent, either simple or complex, adsorb onto hematite surfaces of iron ore, resulting in flocculation of hematite particles and dispersion of gangue minerals rich in alumina and silica. In this context, the beneficiation of iron ore tailings with sodium hexametaphosphate as dispersant and starch as flocculant using ultrasonication technique was also significant as it produces concentrate with 65% Fe and 91% recovery from a feed assaying 50.5% Fe with high gangues [20]. The dispersion and settling of minerals is dependent upon the surface charge, slurry, and surface-active agent concentrations. In addition, characterization of the dispersed phase of iron ore slime slurry is essential for proper information of the gangue mineral phases as this in turn helps in selection of suitable beneficiation techniques [21]. In this context, instrumental characterization of iron ore slime confirms the presence of various mineral phases like hematite, gibbsite, goethite, quartz, and kaolinite in a complex way [14]. The lateritic and complex nature of low-grade ores creates problem for effective removal of gangues. Gangues are strongly bound to the active minerals by different sorts of interactions. Moreover, sedimentation processes are ubiquitous in nature and have importance in science and technology. Settling kinetics study in this context is noteworthy for gathering information on the structure and stability of colloidal suspensions [22]. The study of settling behaviour of slimes containing hydrated oxides by flocculants is noteworthy [23].

Therefore, in this paper, we report the selectivity of two novel surface-active agents, which are environment friendly and cheap towards iron ore fines and slimes, and examine their efficacy for removal of clay-bearing gangue minerals. The particle size distribution and chemical analysis is mentioned in the Materials and Methods sections. A theoretical attempt have been made in the scope of settling kinetics study with the help of the first-order kinetic model, which seems to be a novel study in the scope of settling of iron dispersions. Moreover, detailed mineralogical characterization of the dispersed phase is also reported here for the waste management approach, though brief introduction was reported in an earlier conference paper [24]. In this present communication, the DRIFT spectroscopic characterization of the dispersed phase is extended by thermal treatment on the same and the XRD results are supported by SEM-EDXA analysis.

2. Experimental

2.1. Materials. Iron ore fines and slime of different sizes used in this study were collected from the CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, India. The selection of slime with ~60% iron value was made in the sense to check the applicability of two-stage beneficiation to increase the iron value. Hydrochloric acid (AR grade; Fisher Scientific, India) and sodium hydroxide (97%; Nice Chemicals, India) were used as received. One surface-active agent with identification number AD 200 was received as a gift from Dai-Ichi Karkaria Ltd., Mumbai, India, and

another was sodium humate, an anionic dispersant prepared in this laboratory [25], and also starch was used in combination with the surface-active agents. The distilled water was used in all experiments. The particle size distribution of both iron ore fines and slimes is shown in Table 1. The particle size analysis was carried out by the standard laboratory sieving method with standard screens.

2.2. Methods.

The stability of the 10% slurry (25 g/250 mL water) of iron ore fines and slime in the presence of the surface-active agents was studied at different concentrations and pH 8. The slurry was shaken in a 250 mL stoppered cylinder with the wrist action for 10 min and then allowed to settle to obtain settled dispersed phase. The pH of the suspension was adjusted with either dilute HCl (aq) or NaOH (aq) solution and was monitored with a digital pH meter-802 (Systronics, India). A suspension of 25 mL was withdrawn from the midpoint of the total suspension height at different intervals, and the solid matter was estimated after drying at 110 C in an air oven. For higher scale experiments, 25 wt. % (500 g/2000 mL water), the slurry was mixed properly in a 5 L container with a stirrer for about 20 minutes at a fixed additive dose and pH 8. After mixing, the slurry was allowed to settle for 20 minutes and then the dispersed phase was decanted in a 2 L measuring cylinder and the concentrate was washed once with water before drying. The dispersed phase (DP) has solid content of ~4–6% w/v. The chemical analyses of the concentrates were performed as per the IS method (1493-Part I, 1981). However, for qualitative analysis, the dispersed phase was collected by using surface-active agents (AD 200 and humate) at pH 8 and also without using any surface-active agent at pH 8 maintained by using aqueous sodium hydroxide solution. The dispersed phases so collected under above conditions are termed as DPAD200, DPHU8, and DPNAOH8, respectively.

The dried mass of the dispersed phase was characterised by using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, X-ray diffraction (XRD) technique, and scanning electron microscopy (SEM) along with energy dispersive X-ray (EDX). Heat treatment was performed upon the dispersed phase, and the effect was monitored by DRIFT spectroscopic characterization.

2.3. Settling Test.

The settling test following the dispersion-cum-settling technique was carried out in a 250 ml graduated cylinder by recording the slurry concentration from the midpoint of the cylinder as function of time. The slurry concentration was made 10% (w/v).

2.4. Theory.

A simple first-order kinetic equation has been applied to fit the curves obtained with respect to the settling of iron ore slime dispersions.

For a simple first-order chemical reaction (e.g., A ⟶ P), we know that

$$[A] = [A]oe^{-kt}. \tag{1}$$

where $[A]_o$ and $[A]$ are the initial and final concentrations of the reactant, k is the first-order rate constant, and "t" is the respective time.

In accordance to the above, we use the following similar equation [26]:

$$y = yoe^{-kt}. \tag{2}$$

where "y" is the amount of solid in the dispersed phase at different settling times (in percentage), "y_o" is the initial amount of solid present in the dispersed phase (in percentage), k is the first-order rate constant, and t is the settling time. The value of "y_o" can be obtained from the result of exponential one-phase decay nonlinear regression fit that has been applied in our case.

2.5. Characterization.

DRIFT spectra of DPAD200, DPHU8, and DPNAOH8 were recorded with the IRAffinity-1 system (Shimadzu Corporation, Japan) using DRS 8000A accessory and IR Solution, version 1.40, software. In all cases, the spectra were recorded with 200 scanning and 4 cm^{-1} spectral resolution.

XRD patterns of DPAD200 were recorded using an X-ray diffractometer (ULTIMA IV; Rigaku, Japan) with Cu-Kα X-ray source ($\lambda = 1.54056$ Å) at a generator voltage of 40 KV and current 40 mA with a scanning rate of 2 min^{-1}.

The SEM image of DPAD200 was recorded by SEM S430I (LEO, UK) coupled with the ISIS EDX detector (Oxford Instruments, UK). The powder sample was dispersed ultrasonically in distilled water. A small drop of the sample was put on a small piece of cleaned glass substrate and dried under an IR lamp and then mounted on the SEM stubs using conducting tape. A thin layer of carbon coating was applied to make them electrically conducting.

3. Results and Discussion

3.1. Dispersion-Cum-Settling Technique.

The dispersed phase formed during beneficiation of iron ore fines and slime using surface-active agents is rich in alumina- and silica-containing minerals. For the iron and steel industry, iron content of the feed should be more than 60% Fe. A typical snapshot exhibiting a stable dispersed phase using 5 ppm AD 200, recovered concentrate, and the feed sample is shown in Figure 1. After treatment of iron ore slime using 5 ppm AD 200 and 10 min of settling, the recovery of the concentrate rich in hematite was found to be 62.35%. The chemical analysis of the slime feed was 60.06% Fe, 3.00% Al_2O_3, and 4.00% SiO_2 (Table 2). Upon treatment with the surface-active agent AD 200 at 5 ppm, the concentrate becomes rich in iron value with respect to the feed and assaying 64.25% Fe, 2.50% Al_2O_3, and 2.38% SiO_2 with $Al_2O_3/Fe = 0.04$ and $Al_2O_3/SiO_2 = 1.05$. The gangue minerals present in the dispersed phase are characterised by DRIFT, XRD, and SEM-EDXA. The effect of heat treatment of the "DP" was also investigated by DRIFT technique.

TABLE 1: Particle size distribution of feed.

Size analysis							
Sample	$-10 + 8$ mm	$-8 + 6.5$ mm	$-6.5 + 4$ mm	$-4 + 2$ mm	$-2 + 1$ mm	$-1 + 0.5$ mm	$-0.5 + 0.25$ mm	-0.25 mm
Iron ore fines	9.48	6.74	10.36	22.77	10.44	18.62	8.67	12.92
Tailings	$+70\,\mu m$	$-70 + 50\,\mu m$	$-50 + 40$ mm	$-40 + 20\,\mu m$	$-20 + 10\,\mu m$	$-10\,\mu m$		
	4.90	2.28	1.75	11.37	27.48	52.22		

FIGURE 1: Snapshot of (A) iron ore slime suspension with 5 ppm AD 200, (B) suspension without surface-active agent, (C) dispersed phase, (D) concentrate, and (E) feed.

TABLE 2: Chemical analysis (wt. %) of the feed of iron ore fines and slime (wet chemical analysis).

Feed	% Fe	% Al_2O_3	% SiO_2	Al_2O_3/Fe	Al_2O_3/SiO_2	Loss on ignition (LOI)
Iron ore fines	48.37	9.61	12.99	0.199	0.740	8.62
Slime	60.06	3.00	4.00	0.050	0.750	5.86

3.2. Stability of Suspension (10 wt. %) Using Different Surface-Active Agents

3.2.1. Stability of Suspension in 10 wt. % Slurry of Slime and Fines. The stability of dispersed phase versus time at pH 8 with different dispersant (AD 200 and humate) concentrations and without surface-active agent is shown in Figures 2 and 3.

In the case of slime, the stability of the suspension for all surface-active agents at all concentrations and at pH 8 is comparable. However, humate produces a comparatively more stable DP than AD 200 in the case of iron ore fines (Figure 3). The efficacy of sodium humate as an additive in iron ore beneficiation via selective dispersion-cum-settling technique was also reported [1]. The results show a uniform pattern in the variation of solid content of the dispersed phase with time for all the systems. The variation is exponential in nature, finally attaining a plateau. Hence, the settling kinetics data were fitted to equation (1), which is relevant to our present case. The details of equation (1) are discussed in the Theory section above. Estimated values of the parameters of equation (1) are listed in Tables 3 and 4.

The goodness of fit of the theoretical equation (equation (1)) to the experimental kinetics result is justified by the respective "R^2" (R-squared values) almost above 0.9 in all cases. The surface-active agents are found to be effective in producing a stable dispersed phase than that of without
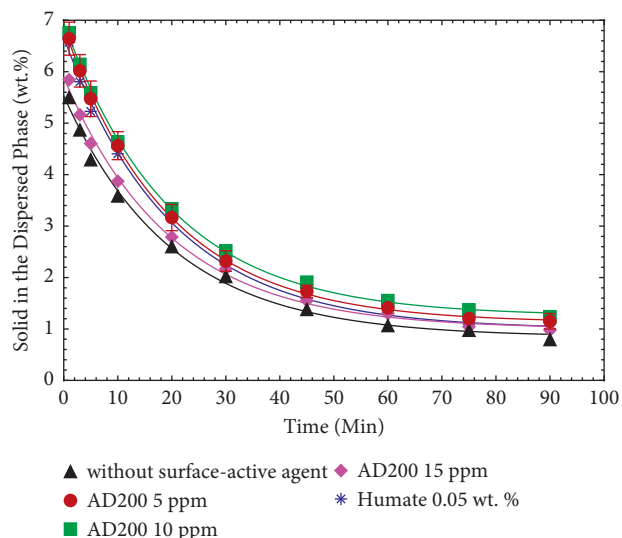

FIGURE 2: Stability of the dispersed phase (% solid) of slime versus time at pH 8 with different concentrations of AD 200 and humate and without surface-active agent. Data points represent minimum duplicate experiment. The solid lines represent equation (1).

additive (Figures 2 and 3). The values of the plateaus observed in the range of 0.9 to 1.1 for slime (Table 3) are reasonable in the context of stability of dispersed phase with
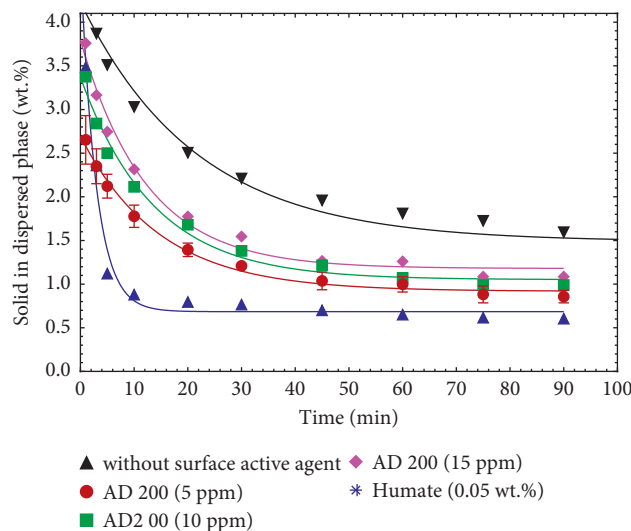
FIGURE 3: Stability of the dispersed phase (% solid) of iron ore fines versus time at pH 8 with different concentrations of AD 200 and humate and without surface-active agent. Data points represent minimum duplicate experiment. The solid lines represent equation (1).

TABLE 3: Values of the parameters of equation (1) for beneficiation of 10 wt. % slurry of slime.

Experiment	System	Rate constant (k) in min^{-1}	Half-life time ($t_{1/2}$) in min.	Y_o (wt. %)	Plateau	Goodness of fit (R^2)
	AD 200 ppm 5, pH 8	0.0518	13.38	6.866	1.121	0.9860
	AD 200 ppm 10, pH 8	0.0507	13.67	6.954	1.252	0.9986
Stability of suspension in 10 wt. % slurry of slime (Figure 2)	AD 200 ppm 15, pH 8	0.0508	13.62	5.893	1.001	0.9958
	Sodium humate (0.05 wt. %), pH 8	0.0503	13.76	6.672	0.9935	0.9979
	Without additive, pH 8	0.0501	13.84	5.535	0.8433	0.9956

TABLE 4: Values of the parameters of equation (1) for beneficiation of 10 wt. % slurry of fines.

Experiment	System	Rate constant (k) in min^{-1}	Half-life time ($t_{1/2}$) in min.	Y_o	Plateau	Goodness of fit (R^2)
	AD 200 ppm 5, pH 8	0.0679	10.20	2.697	0.9180	0.9462
	AD 200 ppm 10, pH 8	0.0736	9.410	3.372	1.051	0.9861
Stability of suspension in 10 wt. % slurry of fines (Figure 3)	AD 200 ppm 15, pH 8	0.0813	8.518	3.799	1.179	0.9861
	Sodium humate (0.05 wt. %), pH 8	0.0463	14.95	4.232	1.486	0.9824
	Without additive, pH 8	0.3469	1.998	4.728	0.6846	0.9786

dispersants. The resulted plateaus represent the stability saturation. The same for iron ore fines is observed in the range 0.9 to 1.5 (Table 4) with dispersant than that without dispersant, which appears at around 0.6. This clearly indicates the efficacy of surface-active agents in beneficiation of iron ore slime and fines. The values of the rate constant and half-life time are in accordance with the nature or more specifically slopes of the settling curves. In the present systems, the settling rate for without surface-active agent is comparatively higher than those for with surface-active agents. This can be attributed to the higher stability of dispersed phase for systems in presence of dispersants because of selective adsorption onto mineral phases [23, 27]. The settling nature of slimes is different from that of fines, which is probably because of the size and aggregation of particles [22].

The dispersing ability and stability of the suspension depend on the types of surface-active agent used and also the pH of the medium that reflects in Al_2O_3/Fe and Al_2O_3/SiO_2 ratios (Figure 4). The effect of surface-active agent on the suspensions is best realized at pH 8 that corresponds to the isoelectric point of hematite (pH 8.5). The zeta potential study gives an idea about the surface charge. The importance of zeta potential and surface chemistry on flotation and desliming of iron ore slime was well discussed in a recent review article [28]. So, comparison of surface-active agent concentrations at pH 8 indicates that, at all concentrations, a dispersed phase with almost equal stability is obtained. The concentrates obtained after dispersion were then analysed for Fe_2O_3, Al_2O_3, SiO_2, and LOI. Chemical analyses for the slime showed that the surface-active agents (AD 200 and humate) significantly remove gangue minerals and increase
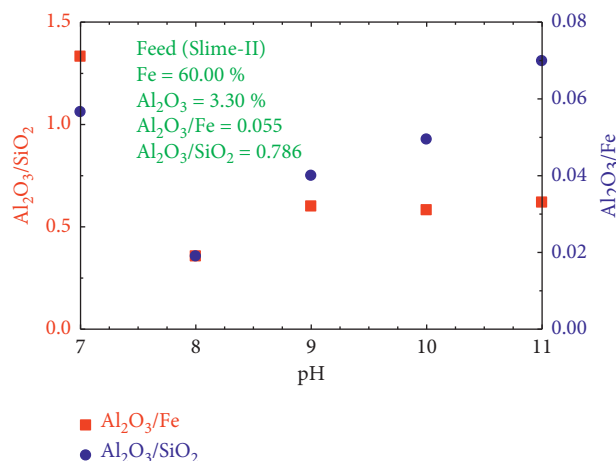
FIGURE 4: Plot of the pH effect on the Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrate obtained from 10 wt. % slurry of slime at 5 ppm AD 200.
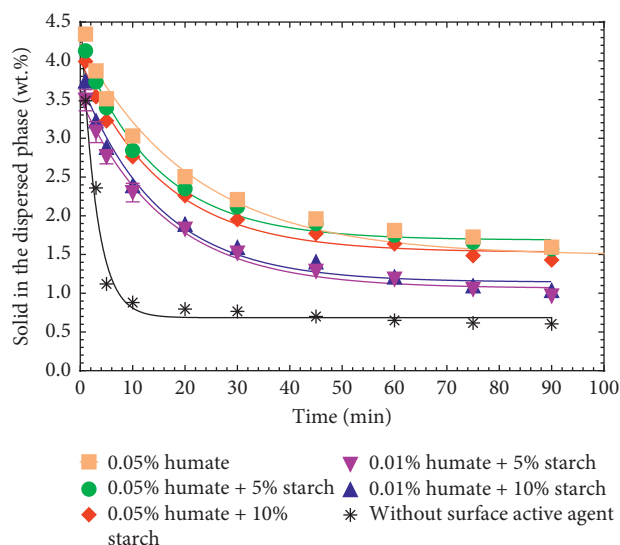

FIGURE 5: Stability of suspension in 10 wt. % slurry of iron ore fines at pH 8.

FIGURE 6: Stability of suspension in 10 wt. % slurry of slime at pH 8.

the iron value 2–7% with 58–74% recovery depending on the pH of the suspension. A bench-scale beneficiation study also produces a concentrate of 2.2% alumina from slime of 7–9% alumina [29]. Nevertheless, the application of magnetic separator technique results in an iron concentrate with 65% Fe from the raw slime having 59.22% Fe and with 50% recovery from a 10% slime slurry [30].

Better quality of the concentrate (Fe > 60%) is obtained at pH 8 that satisfies the blast furnace requirement ($Al_2O_3/Fe < 0.05$ and $Al_2O_3/SiO_2 < 1$). The stable DP containing gangue minerals is due to the surface propensity of the surface-active agent. The surface-active agent binds with the positively charged hematite particles (at pH 8.0), resulting in flocculation. On the other hand, clay-bearing minerals present in the DP (at pH 8.0) are negatively charged and are dispersed in the presence of surface-active agent, which in turn increases the iron value in the concentrate [24]. This is believed to be the adsorption phenomena of the reagents.

The effect of humate alone and in combination with starch on the stability of suspension (10% w/v) of iron ore fines and slime was also investigated in the context of natural surface-active agents and is shown in Figures 5 and 6.

It is apparent from Figure 5 that humate (0.05 wt. %) alone and humate + starch (5 and 10 wt. %) at pH 8 produce ~1.2–1.5 times more stable suspension in the case of iron ore fines than that of without surface-active agent at a time interval that was kept for better beneficiation efficiency. The stability of DP using humate at 0.01 wt. % and 5 and 10 wt. % starch is comparatively lower. Recent literature also reveals the application of starch as depressant in iron ore floatation and the study of starch iron oxide interaction mechanism [20, 31]. Nevertheless, the importance of various reagents viz. collectors, activators, depressants, dispersants, flocculants, and frothers in iron ore processing industries is substantial [28]. In our case of slime, both sodium humate and mixed (humate + starch) produce roughly equal stable suspension but slightly higher than that of without surface-active agent. The settling kinetics data were fitted to equation (1) and estimated values of the parameters of equation (1) are listed in Tables 5 and 6. The observed R^2
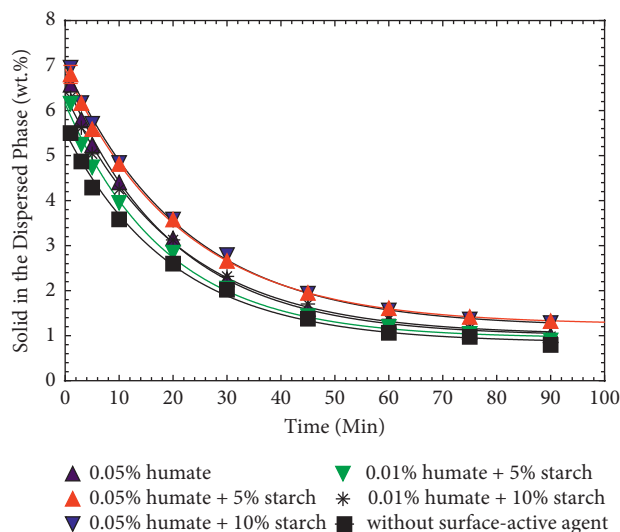
(R-squared) values above 0.9 indicate good fit of the proposed equation to our experimental settling data.

The deviation of the rate constant and half-life time values from the normal stability trend in case of iron ore fines without dispersant corresponds to the unstable dispersed phase. However, the comparison of kinetic parameters in case of slimes both in the presence and absence of surface-active agents indicates roughly equal stable suspension but slightly higher than that of without dispersants. Nevertheless, it should be kept in mind that nonlinear first-order kinetics is superior to the linear first-order kinetics in settling kinetics [26].

3.2.2. Stability of Suspension in 25 wt. % Slurry of Iron Ore Slime. The efficacy of surface-active agent (AD 200) at higher scale on slime slurry (25 wt. %) at pH 8 was examined.

TABLE 5: Values of the parameters of equation (1) for beneficiation of 10 wt. % slurry of fines.

Experiment	System	Rate constant (k) in min^{-1}	Half-life time ($t_{1/2}$) in min.	Y_o	Plateau	Goodness of fit (R^2)
Stability of suspension in 10 wt. % slurry of iron ore fines (Figure 5)	With 0.05% humate, pH 8	0.0463	14.95	4.232	1.486	0.9824
	With (0.05% humate + 5% starch), pH 8	0.0688	10.07	4.203	1.686	0.9656
	With (0.05% humate + 10% starch), pH 8	0.0642	10.79	4.015	1.529	0.9675
	With (0.01% humate + 5% starch), pH 8	0.0616	11.25	3.517	1.063	0.9800
	With (0.01% humate + 10% starch), pH 8	0.0663	10.45	3.747	1.143	0.9881
	Without additive, pH 8	0.3469	1.998	4.728	0.6846	0.9786

TABLE 6: Values of the parameters of equation (1) for beneficiation of 10 wt. % slurry of slime.

Experiment	System	Rate constant (k) in min^{-1}	Half-life time ($t_{1/2}$) in min.	Y_o	Plateau	Goodness of fit (R^2)
Stability of suspension in 10 wt. % slurry of slime (Figure 6)	With 0.05% humate, pH 8	0.0503	13.76	6.672	0.9935	0.9979
	With (0.05% humate + 5% starch), pH 8	0.0462	14.98	6.929	1.245	0.9961
	With (0.05% humate + 10% starch), pH 8	0.0453	15.29	7.017	1.188	0.9981
	With (0.01% humate + 5% starch), pH 8	0.0534	12.97	6.160	0.9456	0.9953
	With (0.01% humate + 10% starch), pH 8	0.0478	14.50	6.358	1.015	0.9973
	Without additive, pH 8	0.0501	13.84	5.535	0.8433	0.9956

The efficacy of surface-active agent was also examined on the recovery of hematite concentrate from the slime slurry (Figures 7 and 8) and primarily on the Al_2O_3/Fe and Al_2O_3/SiO_2 ratios (Figure 9) with respect to varying amount of AD 200.

The surface-active agent AD 200 recovers a good amount of concentrate (~53 wt. %). The results show an increasing trend in the recovery of the concentrate with an increase in AD 200 concentration. Roy and Das have reported an effective recovery of the concentrate with significant removal of gangues for Ukraine slimes via an environment-friendly physical beneficiation process [32]. Nevertheless, it was also reported that pellet-grade concentrates can be produced from low-grade slimes via physical separation [33]. The Fe values and Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrates (Figures 8 and 9) showed that 5–10 ppm of AD 200 is sufficient for the beneficiation at pH 8 from iron ore slime.

3.3. DRIFT Spectra of Dispersed Phase.
The DRIFT spectra of dispersed phases (DPAD200, DPHU8, and DPNAOH8) as collected by using dispersing agents (AD 200 and humate) and NaOH (aq) at pH 8 and after drying at 110°C are shown in Figure 10. A brief analysis of the IR characterization parts has been reported in our earlier conference proceeding [24]. The DRIFT spectra of all dispersed phases are comparable to each other with negligible shift (± 2 cm^{-1}) of the characteristic peaks. The characteristic peaks of kaolin clay are in good agreement with the reported values [34, 35]. The bands at 801–803 and 695 cm^{-1} correspond to Si-O stretching vibration of quartz and 472 and 473 cm^{-1} is assigned to Si-O-
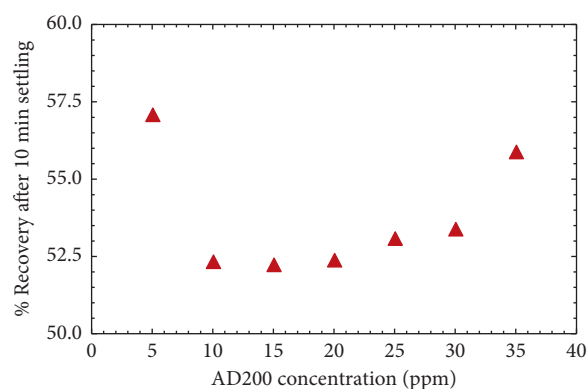

FIGURE 7: Recovery of concentrate from 25 wt. % slurry of slime at different doses of AD 200 at pH 8.

Si bending [35,36]. The medium peaks at ~801 and ~910 cm^{-1} represent Al-O-H stretch from kaolinite clay-like minerals. The strong peaks at 472 and 473 and 538–541 cm^{-1} represent complex systems that represent Fe-O and Fe_2O_3 in addition to Si-O stretch [36]. A strong peak at 1032–1035 cm^{-1} along with a weak peak at ~1007 cm^{-1} represents asymmetric or antisymmetric and symmetric, respectively, stretching vibration of Si-O-Si and nevertheless represents kaolinite [36,37]. For pure silica, strong bands appear at ~1105 and ~805 cm^{-1}, but in the present system a weak peak in the region 1101–1105 cm^{-1} appears and represents Si-O stretching hydrogen bonded to water [38]. The medium sharp peak at ~1380 cm^{-1} and very weak peaks at ~1580 and ~1815 cm^{-1} represent organic moieties. In the
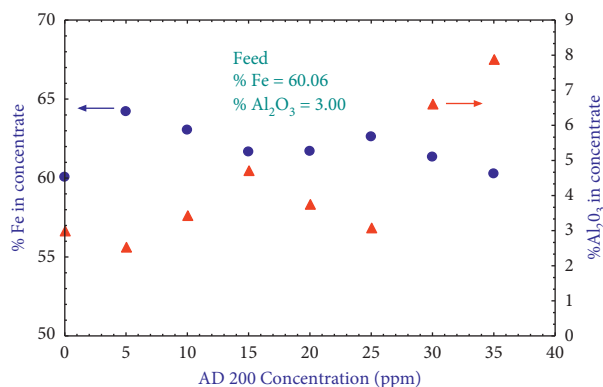
FIGURE 8: Amount of Fe and Al_2O_3 in the concentrate from 25 wt. % slurry of slime at different doses of AD 200 at pH 8.
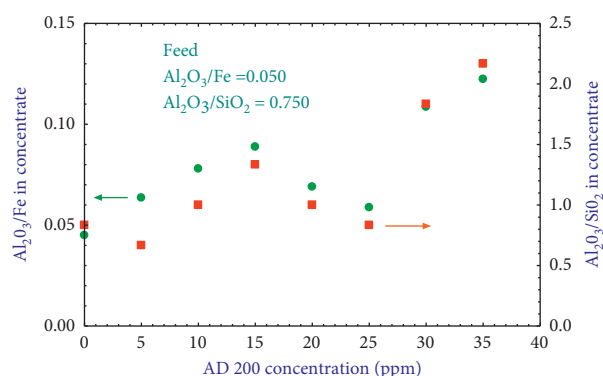

FIGURE 9: Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrate from 25 wt. % slurry of slime at different doses of AD 200 at pH 8.

spectra, the small peaks in the range ~1635 to 1660 cm^{-1} due to bending and a broad stretching band at 3145–3149 cm^{-1} appear from H-bonded water that adsorbed in the interlayer of the kaolin clay [38]. The broad band at ~3145 cm^{-1} corresponds to the lateral hydrogen bonding with the hydroxyl group.

The bands due to O-H stretching in the region 3618–3694 cm^{-1} are the signature of the kaolin clay. The relatively strong peak at ~3694 cm^{-1} represents the internal surface-free O-H stretching for Al-O-H, the peak with medium intensity at ~3618 cm^{-1} is due to the internal O-H stretching for Al-O-H, and the low-intensity peak at ~3654 cm^{-1} indicates the degenerate internal surface-free O-H asymmetric or antisymmetric stretching in Al-O-H. The results are in tune with the reported values [34, 38]. The presence of kaolin clay is roughly confirmed by the appearance of bands at 3694, 3619, 1032, 912, 541, and 473 cm^{-1} [39]. It is interesting to note that the peak at ~3420 cm^{-1} representing the H-O-H stretching of absorbed water in natural kaolinite [34, 35] is appeared as a very weak band (Figure 10).

The bands at 3693, 3615, 1635, 1029, 909, and 801 cm^{-1} indicate the possible presence of illite [35]. A band at 695 cm^{-1} is an indicative of the presence of calcite [40]. The band assignments of the different minerals present in the beneficiation waste are presented in Table 7. Briefly, the band

at 475 cm^{-1} corresponds to Si-O str. and Si-O-Fe stretching vibrations; 543 cm^{-1} Si-O str. and Si-O-Al str.; 696 cm^{-1} Si-O str. and Si-O-Al str.; 801 cm^{-1} Si-O str., Si-O-Al str., (Al, Mg)-O-H, and Si-O-(Mg, Al) str.; 909 cm^{-1} Al-O-H str.; 1029 and 1005 cm^{-1} asymmetric and symmetric stretching modes of Si-O-Si; 1101 and 1029 cm^{-1} Si-O-Si and Si-O str.; 1635 cm^{-1} H-O-H str.; 3189 cm^{-1} hydrogen-bonded O-H stretch; 3615 cm^{-1} internal O-H stretch (Al$_2$O-H); and 3693 cm^{-1} corresponds to internal surface-free OH stretch (Al$_2$O-H) vibrations of alumina-silicate-bearing clay minerals present in the beneficiation wastes.

Note that, upon heat treatment, the structure of kaolin is distorted due to dehydroxylation and no characteristic peaks for the -OH group appears at ≥600°C in the DRIFT spectra (Figure 11(c)) [41, 42]. Taking this observation as a guide, the DRIFT spectra of the dispersed phase produced by AD 200 at three different temperatures are shown in Figure 11. The characteristic peaks for -OH stretching vibration in the range 3618–3696 cm^{-1} (Figure 10) and the peaks for the Si-O stretch at ~1035, ~1003, and ~911 cm^{-1} (Figure 10) disappear at ≥ 450°C, which can be clearly seen in Figures 11 and 12. In contrast, the peak for -OH of pure kaolin disappears at ≥ 600°C. The possibility of metakaolinite upon heating is ruled out as no broad peak at ~1145 cm^{-1} appears [42]. The results suggest that the clay in the iron ore slime dispersed phase exists in a complex environment, i.e., the -OH groups are hydrogen bonded that causes dehydroxylation at a relatively lower temperature [41]. Further, the strong peaks at 472 and 473 and 538–541 and 1032–1035 cm^{-1} upon heat treatment in the temperature range $270 \leq t/°C \leq 600$ shifted to the higher frequency region without losing the noticeable intensity. In contrast, these characteristic peaks in pure kaolin are blue shifted upon heating [43]. The peaks for asymmetric and symmetric stretching vibrations of the Fe-O bond in natural Fe_2O_3 appear in the range (541–556 cm^{-1}) (Figures 10 and 11) [44]. Therefore, the peaks at an average of ~472 and ~545 cm^{-1} (Figures 10 and 11) represent both Si-O and Fe-O stretching vibrations.

3.4. XRD of the Dispersed Phase. XRD characterization of the dispersed phase of slime using DPAD 200 was carried out for further confirmation of the mineral phases present in the iron ore beneficiation waste. This has been reported in one of our conference papers [24]. Quantitative phase analysis in conjunction with SEM and EDX, which are analysed in the subsequent section, confirmed that hematite and goethite to be the major iron-bearing mineral phases and kaolinite clay and goethite as gangue minerals in the beneficiation waste. A similar type of characterization also reveals the presence of quartz and kaolinite as major gangue phases of iron ore slime [45].

3.5. SEM and EDX of the Dispersed Phase. The iron ore beneficiation waste of slime (DPAD200) was also characterised by SEM with EDX spectra and is shown in Figure 13. Further, we noted that the morphology of other beneficiation wastes DPHU8 and DPNAOH8 is found to be same and not shown.
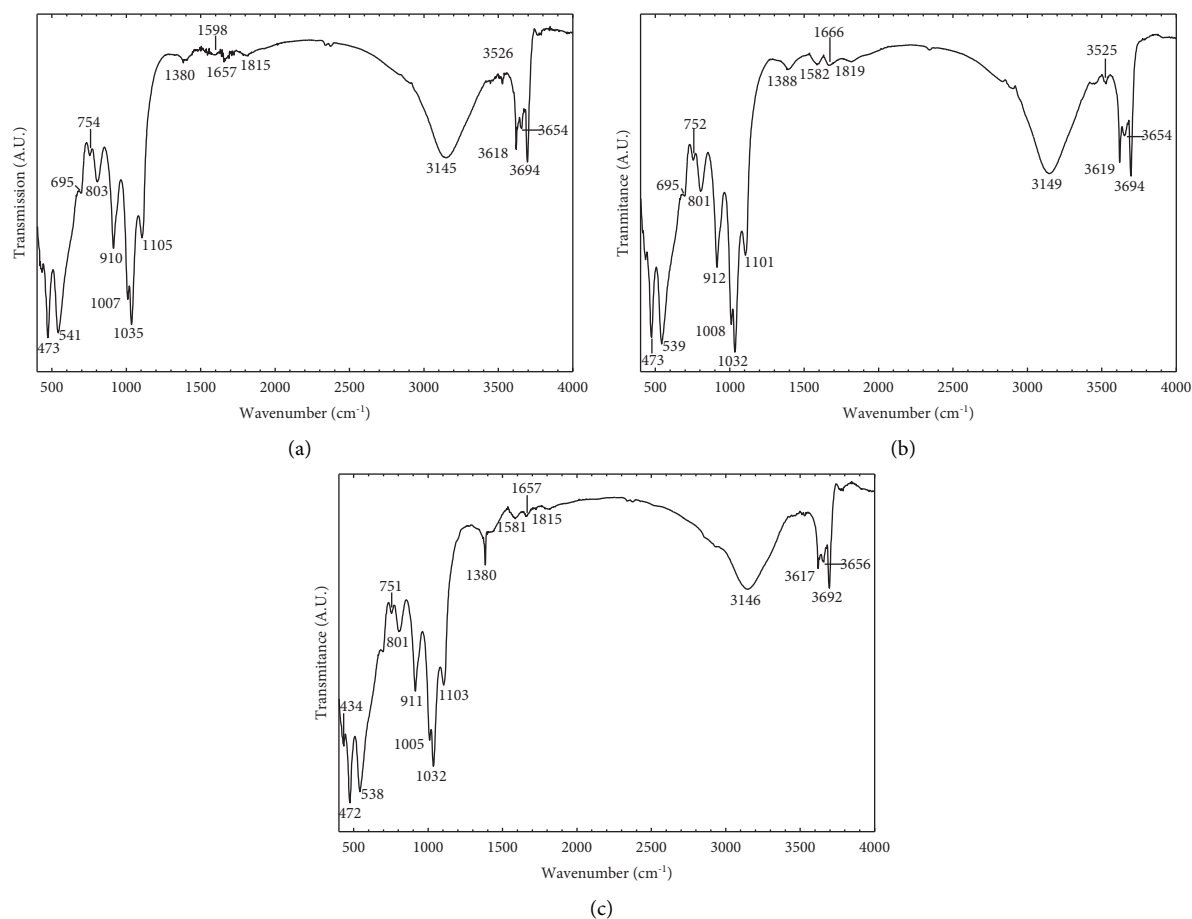
(a)

(b)

(c)

FIGURE 10: DRIFT spectra of dispersed phase of iron ore slime: (a) DPAD200, (b) DPHU8, and (c) DPNAOH8.

TABLE 7: Important bands of clay minerals along with their possible assignments.

Band (cm^{-1})	Assignments
3693	Internal surface-free OH stretch (Al$_2$O-H).
3615	Internal O–H stretch (Al$_2$O-H)
3189	Hydrogen-bonded O-H stretch
1635	H-O-H str.
1101, 1029	Si-O-Si, Si-O str.
1029 and	Asymmetric and symmetric stretching modes of
1005	Si-O-Si
909	Al-O-H str.
	Si-O str., Si-O-Al str.
801	(Al, Mg)-O-H
	Si-O-(Mg, Al) str.
696	Si-O str., Si-O-Al str.
543	Si-O str., Si-O-Al str.
471	Si-O str., Si-O-Fe str.

In the SEM micrograph, four particles are marked as 1, 2, 3, and 4(Figure 13, SEM) and are chosen for the EDX analysis. Variation in elemental compositions (qualitative) from particle to particle can be seen from the recorded EDX spectra shown in Figures (13(b)–13(e)). The EDX analysis showed that iron, silicon, aluminium, and oxygen are found as the major elements present in the dispersed phase and are considered the basic composition of alumina-silicates. The

EDX spectra also indicate the presence of elements like calcium, magnesium, and sodium in low content that are also the elemental composition of calcite, chlorite, and illite minerals [43]. EDX analysis of Figure 13(b) shows that particle "1" showed the emission of oxygen, aluminium, silicon, and iron in higher magnitude. Here, almost a similar ratio of aluminium and silicon (1 : 1) indicates the presence of kaolinite phase [46]. The SEM image also reveals that particle 1 is composed of some plate-like structure, which is a characteristic of kaolinite. Particles "2" and "4" (Figures 13(c) and 13(e)) show the presence of silicon and oxygen in higher amount, and it is the characteristic of silica as the major phase. Silica present as major phase is the tridymite mineral [47, 48]. The particle marked as "2"(Figure 13(c)) also showed the presence of the elements sodium and magnesium that indicate the presence of illite and chlorite minerals as the minor phase in combination with the major tridymite phase [47, 48]. In particle "3" (Figure 13(d)), oxygen is present in higher amount with aluminium, silicon, and iron in approximately same quantity. But here emission of iron comes out at three different energies, indicating the presence of iron-containing minerals in the beneficiation waste. The EDX analysis of particle "1" (Figure 13(b)) shows that the emission of elements oxygen, aluminium, and silicon was found to be higher than that of the other elements. A similar ratio of aluminium and silicon indicates this
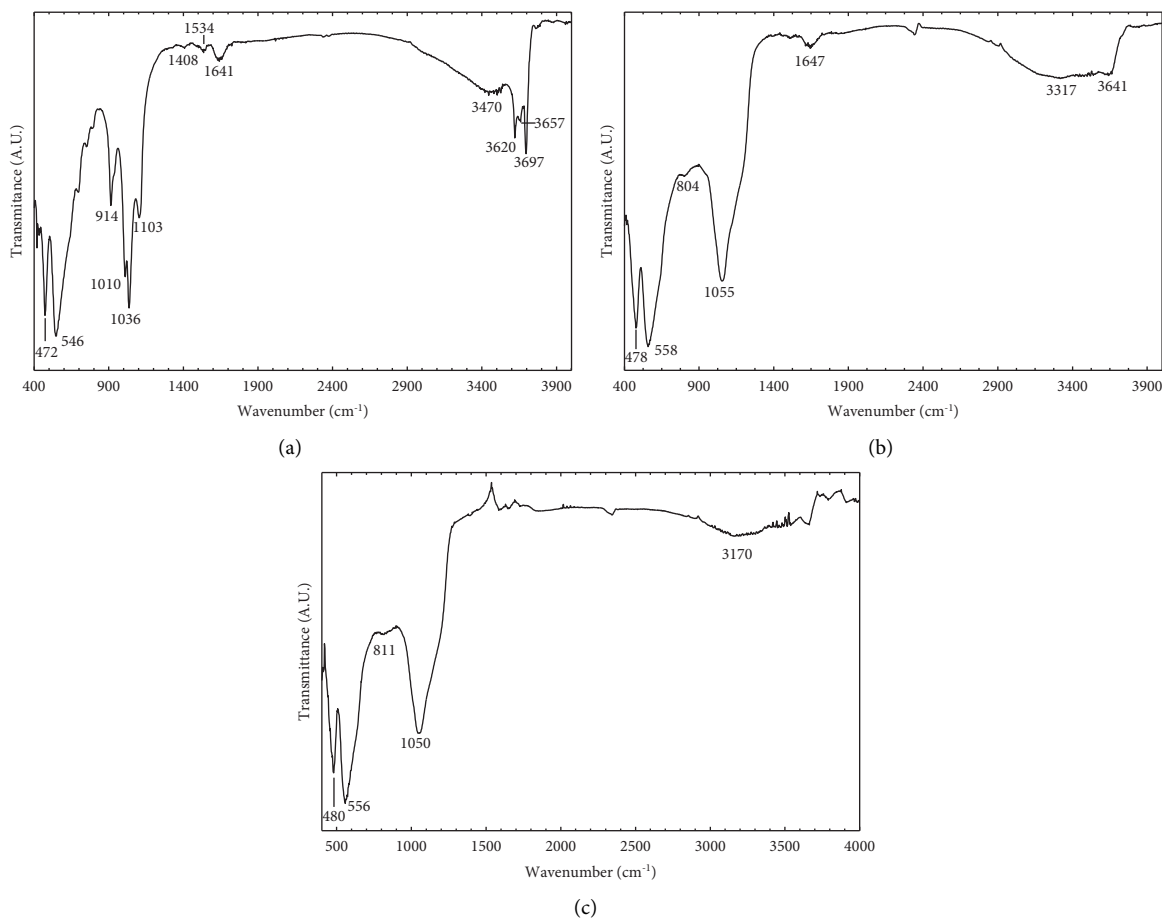
(a)

(b)

(c)

FIGURE 11: Effect of heating on the DRIFT spectra of DPAD200: (a) 270°C, (b) 450°C, and (c) 600°C.
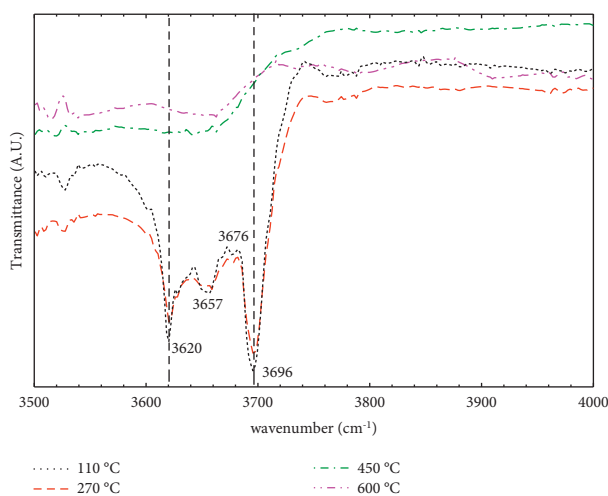

FIGURE 12: Magnified version of Figure 11 in the range 3500–4000 cm^{-1}.

particle to be kaolinite [44, 46]. Particles "2" and "4" (Figures 13(c) and 13(e)) indicate the presence of silicon and oxygen in higher amount than the others and is a characteristic of tridymite phase [47, 48]. Moreover, their EDX analysis also reflects (Figures 13(c) and 13(e)) the presence of calcium and carbon in addition to silicon and oxygen. The emission of calcium, carbon, and oxygen is significantly prominent and

is almost similar for calcium and carbon. This observation indicates the presence of calcite mineral in the beneficiation waste. The presence of sodium and magnesium indicates the presence of illite and chlorite as minor phases in combination with the major calcite phase [43]. DRIFT and XRD studies revealed that goethite was found to be a major phase in the waste. The SEM-EDX analysis also supports the
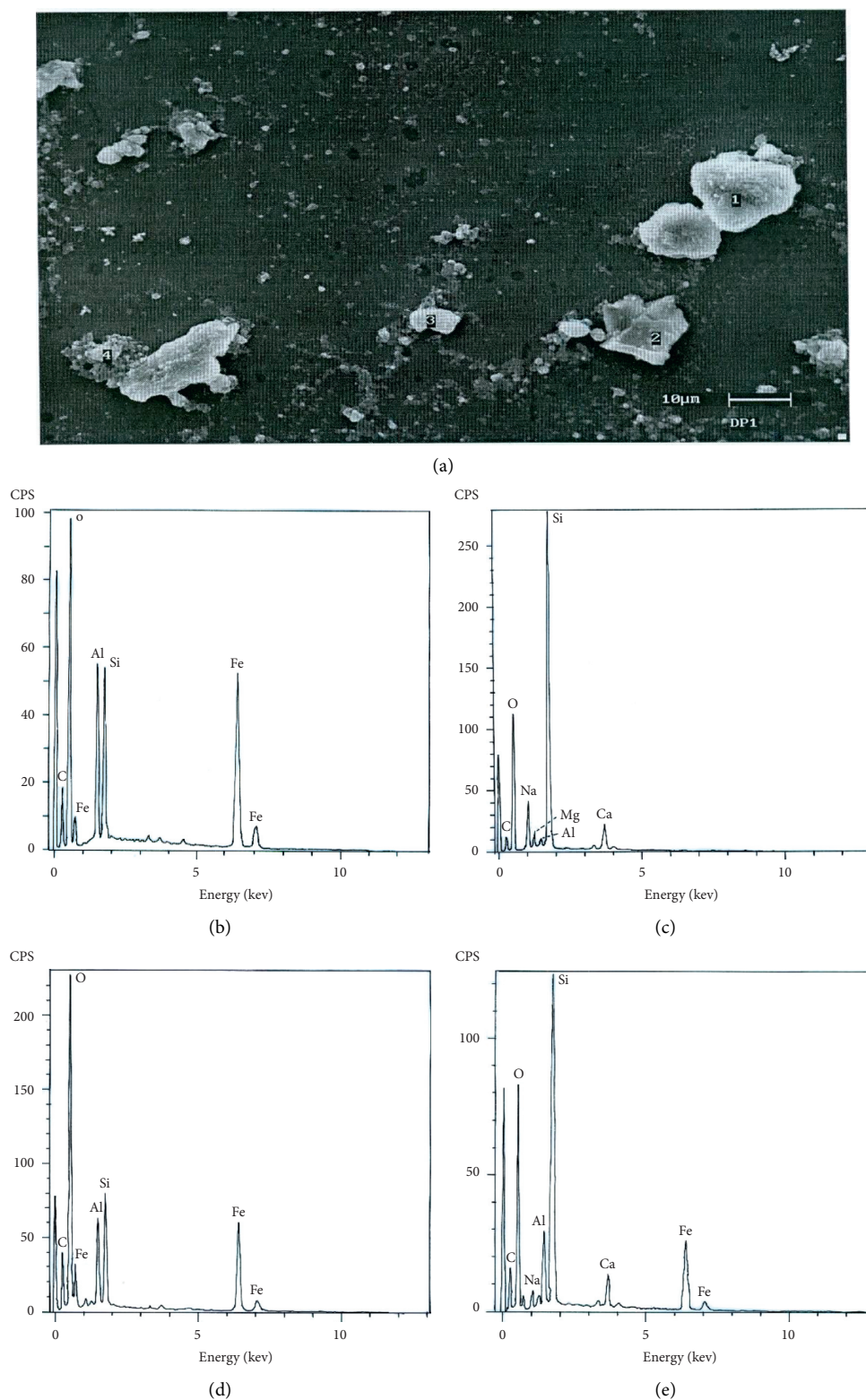
(a)

(b)

(c)

(d)

(e)

FIGURE 13: SEM snapshot of DPAD200 (a) and the corresponding EDX (s) of particles 1, 2, 3, and 4 are shown in (b), (c), (d), and (e), respectively.
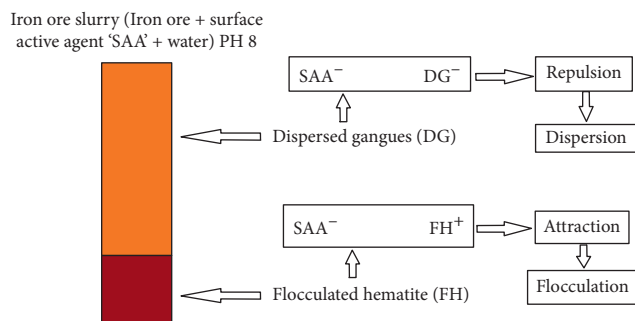
Figure 14: Model diagram for the overall process.

presence of the major iron-containing mineral, i.e., goethite in the beneficiation waste [45].

4. Conclusions

The selective flocculation process for iron ore fines and slimes using surface-active agents was found to be effective for enrichment of hematite in iron ore fines and slime. Washing of iron ore fines and slime with surface-active agent removes the gangue minerals effectively. A typical snapshot of the brief understanding of the process involved is shown in Figure 14. The concentrates recovered are found to be rich in iron value. The settling rate is dependent upon the dose of dispersants. The experimental settling kinetics data are well supported by the proposed exponential one-phase decay nonlinear regression theoretical fit. Characterization of the dispersed phase confirms the existence of clay- and iron (oxy hydroxide)- bearing minerals. These present beneficiation results provide ways for proper application of surface-active agent in iron ore washing plants and to increase iron value in iron ore fines and slime; and nevertheless, the dispersed phase may be converted to a value-added product, such as pigment. The results of present beneficiation of slime further suggest that two-stage beneficiation using surface-active agents can increase the iron value significantly in the concentrate.

Data Availability

The data that are collected during experimentation are mentioned in the manuscript.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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