Selective Dispersion of Rejected Iron Ore Ultra Fines for Feed to Blast Furnace and Minimize Environmental Issues

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Indian iron mines dumps huge quantity of ultra fines containing high gangue minerals resulting in loss of iron values and environmental issues. The major gangue minerals containing alumina, silica and phosphorous are the cause for contamination of Indian iron ore. It has, therefore, become an urgent need to utilize these off-grade ultra fines after making it suitable for blast furnace charging. Due to the fine nature of these ultra fines, selective dispersion studies have been thought of. Two types of dispersants (i) inorganic, sodium hexametaphosphate and (ii) organic, sodium salt of poly acrylic acid have been tried. The performance of these two types of dispersions has been evaluated in separation process. Sodium salts of poly acrylic acid shows better separation of alumino silicate minerals in the ultra fines whereas, sodium hexametaphosphate efficiently separates out silica from the iron bearing minerals.

KEY WORDS: slime; dispersion; waste utilization; alumina removal; iron recovery.

1. Introduction

In India, large quantity of iron ore fines are generated during mining and washing which amounts to about 35% of the total iron ore mineral produced per year. Presently, India produces around 44 million tonnes steel per annum which will be increased to about 110 million tonnes (MT) by 2020 requiring around 190 MT of iron ore. Thus, the huge quantity of these fines will be gradually accumulated with time requiring vast land for dumping which causes environmental problem. Considering the iron ore slimes generated annually and the quantities of slimes accumulated over the years which contains reasonably high %Fe, it is obvious that if properly beneficiated, these slimes can be considered a national resource rather than a waste of nuisance value. These fines contain around 54% Fe and 15% gangue minerals which made them soft and unsuitable for blast furnace charging.1–4) Blast furnace productivity is significantly affected due to the presence of alumina in feed. High alumina slag which is highly viscous requires higher quantity of flux (10% MgO) and relatively large slag volumes resulting in an increase in coke rate consumption and decrease in blast furnace productivity. Due to the very fine nature of the particles, selective dispersion or selective flocculation can be used to upgrade the ultra fines to make them suitable as feed for the blast furnace.5–11) The major gangue materials in the ultra fines contain high alumina and high silica for which the ultra fines are not acceptable as blast furnace feed. The purpose of the present study is to reduce the above two components down to below the maximum limits. Sodium salt of polyacrylic acid12,13) has been found to be a very good dispersant for alumina while dispersing the same for high solid loading as it gives rise to high negative surface potential which forms a highly dispersed phase. Sodium hexametaphosphate is commonly used as a dispersant for such materials.14)

In view of the utilization of these ultra fines which do not need further size reduction requiring high energy and minimizing environment problem, the present study has been undertaken. This paper reports and discusses the results of the dispersion study which shows that gangue minerals could be selectively dispersed leaving behind the valuable iron bearing minerals. This material could be very good feed material for blast furnace after agglomeration and at the same time, the volume of the rejected ultra fines becomes substantially reduced minimizing the environmental problem.

2. Experimental Procedures

Ultra fines of iron ore was collected from Joda slime pond in the state of Orissa (India). As the sample was in lumpy form, it was then disintegrated and subsequently sieved through 100 mesh screen. The ultra fines contain 55.5 wt% Fe, 6.52 wt% SiO₂, 6.91 wt% Al₂O₃ and 0.14 wt% P. The particle size distribution is given in Table 1.

| Particle size (μm) | <0.5 | 0.5–1 | 1–5 | 5–25 | >25 |
|-------------------|------|------|-----|------|-----|
| Weight %          | 2.2  | 45.4 | 13.2| 34.7 | 4.5 |

Laboratory reagent (LR) grade sodium hexametaphosphate (SHMP) and sodium salts of poly acrylic acid (Loba Chemie Pvt Ltd) were used as dispersants. LR grade NaOH was used.
as pH regulator. Tap water was used in the experiments.

The surface charge of clay minerals and feed materials were analyzed using Delta Nano C zeta sizer based on principle of light scattering and electrophoretic mobility.

The sample of known weight was collected in a beaker and pulped with either tap or distilled water in such a way that the resultant mixture was 1 liter in volume and had the desired (5 wt%) pulp density. After addition of the different dosages of dispersants, the suspensions were magnetically stirred at about 150 rpm for 10 minutes; the suspensions were then allowed to settle for the specified time. The settling rates of the mixtures could not be measured as there was no visible mud line due to high turbidity. The supernatant was decanted and settled mass was collected. Supernatant and settled mass were separately dried, weighed and chemically analyzed and reported as total iron, alumina, silica and phosphorous. Dispersants were added with respect to solid mass. The recovery of iron value was calculated.

Iron recovery was calculated by the formula,

\[
\text{Iron recovery} \% = \frac{\text{Concentrate Weight} \times \text{Fe (T) \% in conc.} \times 100\%}{\text{Weight of conc. after drying} + \text{Weight of Tailing after drying} \times \text{Fe (T) \% in feed}}
\]

The results reported here are within the error limit of 2%. The agglomerated samples were powdered and analyzed in PANalytical X-Ray Diffractometer to identify the possible phases present in the concentrates and tailings. About 1 g of dried ultra fines of iron ore before and after dispersion study was powdered and placed in a mould. A mixture of 11 ml Biphenol A and 2 ml of Epoxy hardener was poured on the sample and thoroughly mixed to remove any air bubbles. The mixture was then allowed to dry (either 1 h in vacuum or 6 h in open air) and the top of the hardened mass containing the dried sample was polished. Finally, the hardened mass was gold coated in vacuum for 40–60 seconds to make it conductive and observed under Scanning Electron Microscope (SEM).

3. Results and Discussion

3.1. Characterization of Iron Ore Ultra Fines

The iron ore ultra fines sample was characterized by particle size analyzer as well as SEM-EDS techniques. It is evident from particle size analyzer that particle size of iron ore ultra fine varies significantly as shown in Table 1.

The SEM-EDS analysis confirms that iron ore ultra fines are well liberated (see Fig. 1) and both iron bearing minerals as well as gangue minerals are clearly distinguishable. The X-ray diffraction (XRD) study of the feed material was conducted as received condition as well as after acid leaching to identify the minerals present in ultra fines of iron ore. Leaching of ultra fines by concentrated HCl has been done to dissolve iron bearing minerals to identify the acid insoluble minerals present in the ultra fines by XRD. It is evident from the Fig. 2 that ultra fines of iron ore consist of hematite, goethite, zeolite and quartz phases. No pure Al₂O₃ was present in the ultra fines.

| O wt% | Al wt% | Si wt% | P wt% | Fe wt% |
|-------|--------|--------|-------|--------|
| Pnt1  | 48.69  | 23.2   | 23.95 | 3.73   |
| Pnt2  | 48.07  | 23.38  | 23.04 | 0.43   |
| Pnt3  | 30.43  | 0.23   | 0.00  | 0.04   | 69.34 |
| Pnt4  | 40.92  | 14.5   | 13.29 | 0.32   | 31.07 |
| Pnt5  | 50.08  | 24.11  | 24.41 | 0.42   | 0.98  |
| Pnt6  | 29.8   | 0.00   | 0.00  | 0.00   | 70.2  |
| Pnt7  | 46.85  | 21.65  | 21.07 | 0.45   | 9.98  |

Fig. 1. SEM-EDS results of feed material under magnification of 1000.

Fig. 2. XRD analysis result of feed material (a) as received and (b) after concentrated HCl acid leaching.
detected in the feed material. Al and Si content are represented as \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \), respectively.

### 3.2. Dispersion Study

The ultra fines have been conditioned with dispersants and the settled mass is designated as “concentrate” whereas the dispersed particle after the predetermined time in the supernatant is called as “tailing”. Two dispersants used in the present study are sodium hexametaphosphate and sodium salt of poly acrylic acid. The effect of pH on dispersion of the ultra fines without the above dispersants shows only very marginal variation of both alumina and silica contents in the settled mass. In case of alumina, the minimum level is attained at about 6.5% from 6.91% and that of the silica is 6.2% from 6.52% at a pH of 6.7 \((\text{Fig. 3})\), when sodium hexametaphosphate is used as a dispersant alumina is reduced to about 5.8% and silica is reduced to about 4% at a pH of 8.5 whereas the addition of sodium salt of poly acrylic acid as dispersant alumina is reduced to about 4% and silica to 5% at a pH of 9.5. \(\text{Figures 4(a) and 4(b)}\) show the results using sodium salt of poly acrylic acid and sodium hexametaphosphate as dispersants, respectively.

Sodium salt of poly acrylic acid is a typical dispersant for alumina\(^{13}\) works better for alumina bearing minerals whereas sodium hexametaphosphate works better for silica removal. This shows that there is some degree of selectivity of the dispersants towards silica and alumina which could be utilized for efficient separation of the mineral matters. Due to the increased amount of alumina and silica in the dispersed phase, the iron value in the settled portion gets enriched. Zeta potential data as plotted in \(\text{Fig. 5}\) for both the dispersants used in the present study shows that the dispersion of gangue minerals is expected to be high at the higher pH around 8 or above due to high repulsive forces between the particles. Sodium hexametaphosphate as adsorbed onto the ultra fine particles shows higher zeta potential compared to sodium salt of acrylic acid on the particles. \(\text{Figures 6(a) and 6(b)}\) show the results using sodium salt of poly acrylic acid and sodium hexametaphosphate as dispersants, respectively.

The addition of both dispersants shifts the iso-electric point towards acid side as shown in \(\text{Fig. 6}\). This means that there is a specific adsorption on the ultra fines. Since the effect is pronounced in the separation of silicate minerals of the ultra fines, it can be predicted that the hematite mineral in the mixture (ultra fines) retains its characteristic PZC and due to this, there is a maxima at pH 6.7 where the repulsive forces become zero and the particles are agglomerated and settled. The iron recovery as shown in the \(\text{Fig. 7}\) indicates that there is a maxima near point of zero charge of hematite. \(\text{Figure 7}\) shows that the maximum iron is recovered at a pH around 6.7. As the points of zero charge

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**Fig. 3.** \(\text{Al}_2\text{O}_3, \text{SiO}_2, \text{P}\) and \(\text{Fe}\) content on concentrate and tailing under varied pH of the solution for without addition of any dispersing agent.

**Fig. 4.** \(\text{Al}_2\text{O}_3, \text{SiO}_2, \text{P}\) and \(\text{Fe}\) content in concentrate and tailing when 5 000 ppm (a) sodium salt of acrylic acid or (b) sodium hexametaphosphate used dispersing agent.

**Fig. 5.** Zeta potential characteristics of clay mineral for 5 000 ppm of dispersing agent under varied pH conditions.
of most of the iron bearing minerals especially hematite is around 6.7, it can be predicted that due to the zero charge on to the hematite surface, hematite particles agglomerate efficiently in absence of any mutual repulsive force and settle faster. Therefore iron recovery goes up. But at higher pH, the particles are strongly dispersed due to high negative zeta potential as shown in Fig. 6. Further increase in pH leads to high negative potential causing hindrance to agglomeration. Hence, the total concentrate amount decreases and the iron recovery go down.

Figures 8(a) and 8(c) show the results using sodium salt of poly acrylic acid as a dispersant and Figs. 8(b) and 8(d) depict the results using sodium hexametaphosphate as a dispersant. The effect of dispersant dosage on the separation of the quartz and aluminium silicate min-

Fig. 6. Zeta potential characteristics of feed material under varied dosages for (a) Na salt of acrylic acid and (b) Sodium hexametaphosphate used as dispersing agent.

Fig. 7. Wt% iron recovery in concentrate under varied pH and dispersing agents.

Fig. 8. Wt% of Al₂O₃, SiO₂, P and Fe in concentrate and tailing after dispersion experiment under varied dispersion dosages using (a) & (c) Na salt of acrylic acid and (b) & (d) Sodium hexametaphosphate as dispersing agent.
erals is shown Figs. 8(a) and 8(b) which indicates a gradual widening of the separation curves of alumina in the concentrate and that in the tailings and finally it reaches maxima at 5 000 ppm, further increase in concentration converges. Similar situation is arrived with SiO₂ but at a lesser extent. Fe-value goes high with increasing amount of salt of acrylic acid. When sodium hexametaphosphate is used as dispersant, SiO₂ reduces more compared to Al-silicate minerals as shown in Fig. 8(b). Fe in the concentrate gets enriched as the gangue minerals are depleted. It can therefore be seen that there is some degree of selectivity towards Al- silicate component as far as sodium salt of acrylic acid is concerned whereas sodium hexametaphosphate shows selectivity more towards SiO₂ component. Figures 8(c) and 8(d) show that higher dosage of the dispersants leads to a stable suspension due to high negative charge at the surface-water interface and therefore settlement of the particles drastically reduces for which recovery of iron in the settled part also reduces.

It is further seen in Fig. 6(a) that with increasing amount of sodium salt of acrylic acid shifts the iso-electric point towards acid side. This means dispersant specifically adsorb onto the surface with a preference towards Al-silicate minerals resulting in selective separation of these minerals as shown in Fig. 8(a). Furthermore, it is seen that sodium hexametaphosphate also shifts the iso-electric point towards acid side and the extent of this shifting is maximum at 5 000 and 10 000 ppm. Such a high dosage of sodium hexametaphosphate makes the suspension very stable due to high negative charge even at a pH of 7. This shifting of iso-electric point indicates specific adsorption of the dispersant for which SiO₂ rich components are better separated.

### 3.3. Characterization of Concentrate and Tailing

Both the concentrate and the tailing were characterized by SEM-EDS and XRD techniques. The particle size is coarser in concentrate than in tailing. ‘Al’ lean concentrate is obtained using sodium salt of acrylic acid as dispersing agent whereas ‘Si’ lean concentrate is obtained using sodium hexametaphosphate as dispersing agent. Tailing generated after both the types of dispersion experiment consists of more clay minerals compared to feed material. Alumino silicates have higher degree of dispersibility than iron bearing minerals. The tailing generated after dispersion experiment using sodium salt of acrylic acid as dispersing agent, consists of alumino silicates with higher level of ‘Al’ whereas tailing generated after dispersion experiment using sodium hexametaphosphate as dispersing agent consists of aluminium silicates with higher level of ‘Si’. It can be concluded that sodium salt of poly acrylic acid separates alumino silicates minerals whereas sodium hexametaphosphate separates SiO₂ from the ultra fines containing iron bearing minerals (hematite and goethite), zeolite and quartz more efficiently.

### 4. Conclusions

(1) The gangue minerals present (15 wt%) in feed could drop down to 7.8 wt% in concentrate which expected to be useful material for sinter making after selective dispersion process with reasonably good yield 50 wt%. So, 50 wt% materials can be reduced in dumping yard.

(2) The efficiency of dispersion process strongly depends on pH and dispersant dosage. Optimum pH is identified to be 8.5 at which the siliceous gangue minerals can be efficiently separated when sodium hexametaphosphate used as dispersing agent whereas, the same is identified to be 9.5 for sodium salt of acrylic acid used as dispersing agent.

(3) Increasing concentration of sodium salt of acrylic acid and sodium hexametaphosphate shifts the iso-electric point indicating specific adsorption of the dispersion on to the constituents of the ultra fines.

(4) Sodium salt of poly acrylic acid specifically adsorb more onto the aluminium bearing mineral surface for which these minerals are better separated as compared to the siliceous materials. Sodium hexametaphosphate adsorbs specifically on the siliceous mineral resulting in better silica separation from the bulk.

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