

BENEFICIATION OF INDIAN IRON ORE SLIME AND FINES: EFFECT OF SURFACE-ACTIVE AGENT AND SPECIFIC ION EFFECTS

JYOTIRMOY SARMA*, SANCHAYITA RAJKHOWA*, NAMRATA SARMA*
AND SEKH MAHIUDDIN*

The suspension stability in 10 % slurry of iron ore fines and slime was studied by using three surface-active agents at pH 8. The Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrates are appreciably reduced at the isoelectric point of hematite. The surface-active agent removes and disperses gangue minerals. The hard-water flocculates particles in the dispersed phase and generates roughly clear water for reuse. The specific ion effects in the pH variation have been observed in the hematite suspension.

Introduction

India possesses good quality iron ore reserves of around 14 billion tonnes and the iron ore is generally softer nature with high clay content¹⁻² and the major mines are located in the states of Jharkhand, Orissa, Goa, Karnataka and Chhattisgarh³⁻⁴. During mining and processing, generation of fines and slime typically ~ 35 % and 10-25% of run-of-mines⁵ is a great concern to environment and loss of iron value. Iron ore fines and slime contain ~ 58 % Fe, high amount of alumina (> 8 %) and silica (~ 8 %). Statistics showed that the increase in 1% Fe in the concentrate productivity of the hot metal increases by 2 % and thereby coke and limestone requirements reduced by 1.8 % and 0.9 %, respectively⁶. Considering the feed quality for the blast-furnace and the need to conserve the non-renewable resource, beneficiation of iron ore fines and slime is essential so that the Al_2O_3/Fe and Al_2O_3/SiO_2 ratios are brought down below 0.05 and 1, respectively in the concentrate.

The simple plain water washing alone cannot change Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrate much from the feed. An alternative approach is to use techno-economically cheap and ecofriendly surface-active agent(s) for beneficiation of iron ore fines and slime. In this context several synthetic chemicals are used viz., charged and uncharged polyacrylamide⁷⁻¹², starch¹³⁻¹⁷ humate¹⁸⁻¹⁹ and inorganic or organic additives or both²⁰⁻²¹. The main objective in these studies was to recover iron value from iron ore fines. The surface-active agents, either simple or complex, adsorb onto hematite surfaces resulting in flocculation of hematite particles and dispersion of gangue minerals rich in alumina.

Dewatering and/or recovery of water from waste water/slurry is also an essential step in the iron ore washing. In an iron ore washing plant huge amount of water is required further there is loss of water and fresh water typically ~15 % is added to maintain the total amount of water in the washing circuit. Different kinds of flocculants are used for this purpose²². Moreover, natural hard-water can be used as an alternative because it contains different ions, which are effective flocculating agents. The so-called "specific ion effects" in the metal oxide suspension is important to understand the behaviour of ion to modulate

* Materials Science Division, CSIR-North-East Institute of Science & Technology, Jorhat-785006, Assam, India
(Correspondence to Sekh Mahiuddin, e-mail: mahiuddins@rrl.jorhat.res.in, mahirljt@yahoo.com)

the surface charge of the oxide particles and subsequent change of pH of the suspension. It has already been reported that the pH of ferric hydroxide suspension with aging varies differently depending upon its initial value²³.

In this article, we discussed about the effectiveness of surface-active agents in beneficiation of iron ore fines and slime and also the use of hard-water to flocculate the suspended particles in the suspension and recovery of water for subsequent use in beneficiation. In addition we have also studied the specific ion effect on the change of pH in metal oxide suspension.

Materials and Experiments

Materials: Iron ore fines and slime used in these studies were collected from Institute of Minerals and Materials Technology, CSIR, Bhubaneswar, India. Hydrochloric acid (AR grade, Fisher Scientific, India) and sodium hydroxide (97%, Nice Chemicals, India) were used as received. Sodium chloride (99.5 %, Merck, India), sodium bromide (99%, Rankem, India), sodium iodide ($\geq 99\%$, Merck, India), sodium thiosulphate (99%, Qualigens, India), sodium sulphate (99.5%, Merck, India), sodium thiocyanate (99%, Sisco, India), sodium nitrate (99%, Merck, India), sodium formate (99.5%, Loba Chemie, India) and sodium acetate (99%, Spectrochem, India) were recrystallized from double-distilled water. Two surface-active agents with identification numbers AD200 and AN103(P) were received as a gift from Dai-Ichi Karkaria Ltd., Mumbai, India and humate was prepared in our laboratory. The double-distilled water was used in all experiments.

Experiments – Stability of suspension : The stability of the 10 % slurry (25 g/250 mL water) of iron ore fines and slime in the presence of three 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. A suspension of 25 mL was withdrawn from the mid-point of the total suspension height at different intervals and the solid matter was estimated after drying at 110 °C in an air-oven. The pH of the suspension was monitored with a digital pH meter-802 (Systronics, India) and was adjusted with either dilute HCl(aq) or NaOH(aq) solution.

Efficacy of surface-active agent : The efficacy of the surface-active agents in removing the gangue minerals in the suspension of iron ore fines was studied at higher scale (500 g iron of fines/2000 mL water) at pH 8. The

slurry was mixed properly in a 5 L container with a stirrer for about 15-20 minutes at a fixed additive dose and pH 8. After mixing, the slurry was allowed to settle for 10 minutes and then the dispersed phase was decanted in a 2 L measuring cylinder and the concentrate was washed once with water before drying.

Characterization of waste : The dried dispersed phase collected from the iron ore slime suspension using AD 200 as additive was characterized using X-ray diffractometer (ULTIMA IV, Rigaku, Japan) with Cu-K α X-ray source ($\lambda = 1.54056 \text{ \AA}$) at a generator voltage 40 KV and current 40 mA with the scanning rate 2° min^{-1} .

Water recovery from iron ore fines suspension : In a 2 L measuring cylinder containing 1 % dispersed phase 5 % hard-water was added and the suspension was mixed thoroughly for about 10 minutes and was allowed to settle. The water was collected after 12 h and was used for the beneficiation of iron ore fines using 0.05 % humate at pH 8.

Specific ion-effect in metal oxide suspension : Specific ion-effects were examined in hematite-buffer suspension in the presence of simple and different background electrolytes having a common cation. The initial pH of the suspensions was 6.00 ± 0.02 . Different background electrolytes (NaCl, NaBr, NaI, NaNO₃, Na₂SO₄, Na₂S₂O₃, HCOONa and CH₃COONa) were added to the suspension at varying ionic strength upto 500 mM. The suspension was equilibrated for 2 h at 298.15 K and then the pH of the suspension was noted.

Results

The chemical assay of the feed iron ore fines and slime is given in Table 1. The stability of the suspensions of iron ore fines and slime as functions of time and concentration of three surface-active agents at pH 8 is shown in Fig. 1. The effect of surface-active agent (e.g., AN103(P)) on the recovery of the concentrate typically from 25 % slurry of iron ore fines and on the Al₂O₃/Fe

TABLE 1: Chemical analysis of feed (wt %)

Component	Slime	Fines
Fe (Fe ₂ O ₃)	60.03 (85.84)	48.37 (69.17)
Al ₂ O ₃	3.15	9.61
SiO ₂	4.17	12.98
Al ₂ O ₃ /Fe	0.052	0.199
Al ₂ O ₃ /SiO ₂	0.755	0.740

and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios as function of AN103(P) concentration is shown in Fig. 2. The XRD pattern of the gangue minerals in the dispersed phase is shown in Fig. 3 along with the d -spacing values in Table 2. A typical snapshot exhibiting the effect of hard-water for flocculating

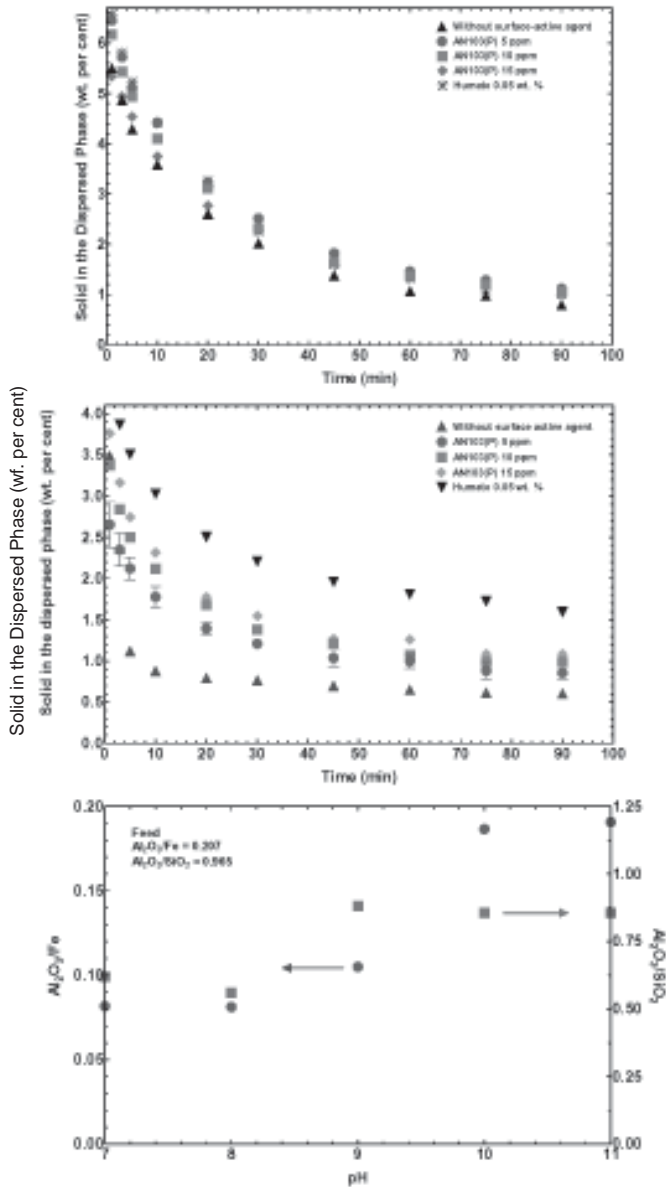


Fig. 1. Variation of solid content in the dispersed phase of 10 wt. per cent slurry of (upper panel) slime and (middle panel) fines as a function of time at pH 8 and different concentrations of AN103(P) and (lower panel) the effect of the pH on the $\text{Al}_2\text{O}_3/\text{Fe}$ and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios in the concentrate obtained from 10 wt. per cent slurry of fines at 5 ppm AN103(P).

the suspended particles and the recovery of water for subsequent use of the same for beneficiation of iron ore fines is shown in Fig. 4. The effect of different electrolytes on the pH variation of the Fe_2O_3 -buffer suspensions is shown in Fig. 5.

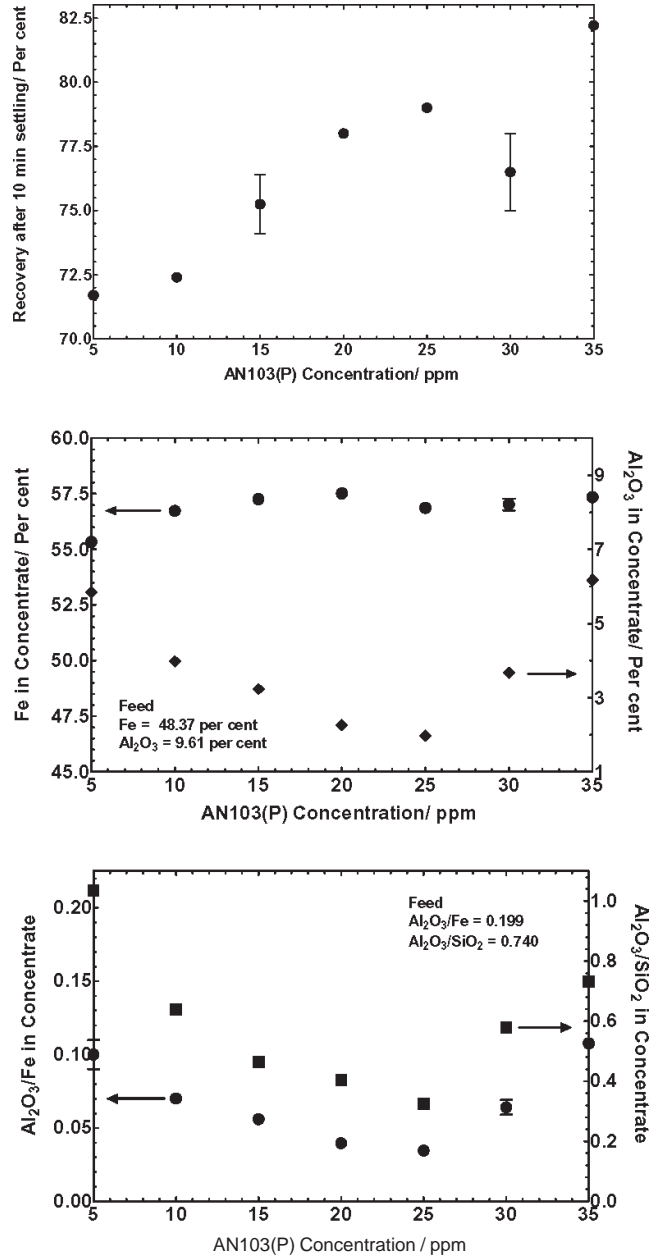


Fig. 2. (Upper panel) recovery of concentrate obtained from 25 wt. per cent slurry of fines (middle panel) variation of Fe and Al_2O_3 in the concentrate obtained from 25 wt. per cent slurry of fines and (lower panel) Variation of $\text{Al}_2\text{O}_3/\text{Fe}$ and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios in the concentrate obtained from 25 wt. per cent slurry of fines after treating with different concentrations of AN103(P) at pH 8.

Discussions

Stability of suspension : The surface-active agent, typically AN103(P), produces a stable suspension at pH 8 (Fig. 1). The stability of the suspensions of the slurry of slime at different intervals in the presence of three surface-active agents under similar conditions is comparable. The stability of the suspension of 10 % slurry of slime at pH 8 without surface-active agent is also added in Fig. 1 (upper

panel). The results suggest that pH of the medium is also one of the controlling parameters for producing a stable suspension. The solid contents in the dispersed phase of slime after treatment with AD200, AN103(P) and humate are roughly comparable and ~ 1.4 times higher than that of without surface-active agent.

Interestingly, the stability of the suspension of fines in 10 % slurry is different, we have shown only for AN103(P) (Fig. 1, middle panel). The humate produces ~ 1.5 times stable suspension in comparison to AD200 and AN103(P), which also produce ~ 2.4 times stable suspension in comparison to without surface-active agent. The differences in the stability and solid content of the dispersed phase of slurry are due to complex nature of the gangue mineral in iron ore slimes and fines.

Beneficiation of slime and fines : The efficacy of the surface-active agents (AN103(P) and AD200) was examined at pH 8 for beneficiation of iron ore slime and fines and vis-à-vis the removal of gangue minerals. A typical example on the use of AN103(P) showed that the surface-active agent significantly removes and disperses alumina containing gangue minerals in the suspension and increases the iron value in the concentrate of iron ore fines. The Al_2O_3/Fe and Al_2O_3/SiO_2 ratios are minimum at pH ~ 8 (Fig. 1, lower panel), which coincides with the isoelectric point of hematite particle²⁴⁻²⁶. Therefore, the application of surface-active agent(s) is best realized at ~ pH 8.

In this direction, the beneficiation of iron ore fines at higher slurry concentration (25 %) was studied at pH 8 and different concentrations of AN103(P) and the results are shown in Fig. 2. The results showed that the recovery of the concentrate increases with the increase in AN103(P) concentration. The Fe values and Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrates indicate that 15-25 ppm of AN103(P) is sufficient for the beneficiation at pH 8 for this particular type of iron ore fines. The Al_2O_3/Fe and Al_2O_3/SiO_2 ratios in the concentrate were decreased by ~ 5.7 and ~ 2.3 times, which ($Al_2O_3/Fe = 0.035$ and $Al_2O_3/SiO_2 = 0.324$) meet the blast furnace requirement for the production of the hot metal.

Characterization of dispersed phase : The XRD patterns (Fig. 3 and Table 2) indicate that the gangue minerals in the dispersed phase contain chlorite, kaolinite,

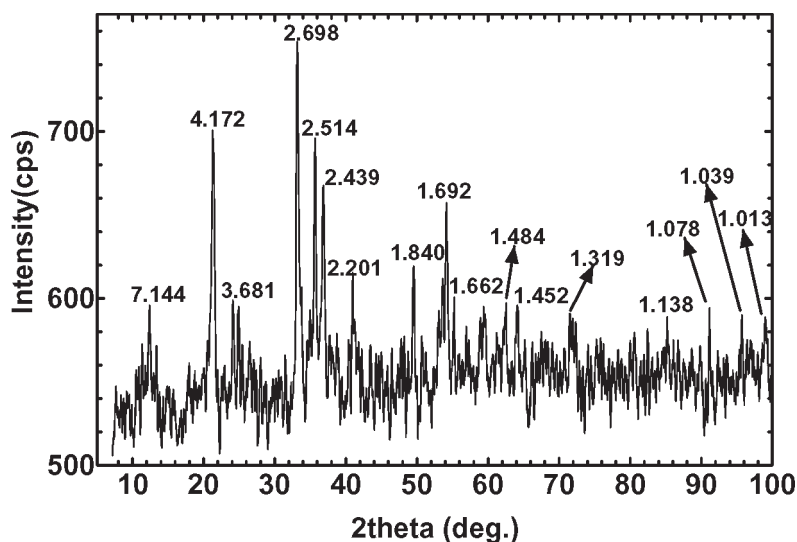


Fig. 3. XRD diffractogram of dispersed phase of 25 wt percent slurry of iron ore slime with AD 200 as dispersing agent.

hematite, goethite, alumina and trydimite based on the d -spacing value in the literature²⁷. It is observed from the Table 2 that most of the d -spacing values are resembled with the hematite and alumina. From the XRD study it can be concluded that the hematite and goethite are the major iron bearing mineral phases and kaolonite clay is present as a gangue mineral in the beneficiation waste.

TABLE 2: d -spacing value of different mineral phases present in beneficiation waste

d (Å°)	Possible minerals
7.144, 4.172, 1.484, 1.662, 1.452	Kaolinite
4.172, 2.439, 2.698	$Fe(OH)_2$, Iron hydroxides
3.68, 2.698, 2.517, 2.205, 1.8406, 1.6949, 1.4852, 1.4536	Hematite
3.579, 2.570, 1.311	Alumina
2.514, 2.439	Tridymite

Water recovery and its applicability : The typical snapshot (Fig. 4b) showed that the hard-water can flocculate the suspended particles and produce clear water. The hard-water contains different ions which modulate the surface properties of the particles resulting in flocculation of particles. The particles in the dispersed phase are mainly clay, hydroxyl/(oxy)hydroxyl containing minerals, which are good adsorbent for all ions present in the hard-water.

Specific ion-effect in hematite-water suspension : The pH change of α - Fe_2O_3 -buffer suspensions (0.2%) was studied with varying ionic strength of different electrolytes



Fig. 4. A typical snapshot showing (a) dispersed phase (b) flocculation/settling of suspended particles in 1 % DP of slime slurry in the presence of natural hard water and (c) stable dispersed phase of 25 % iron ore fines using water from (b) and 0.05 % humate.

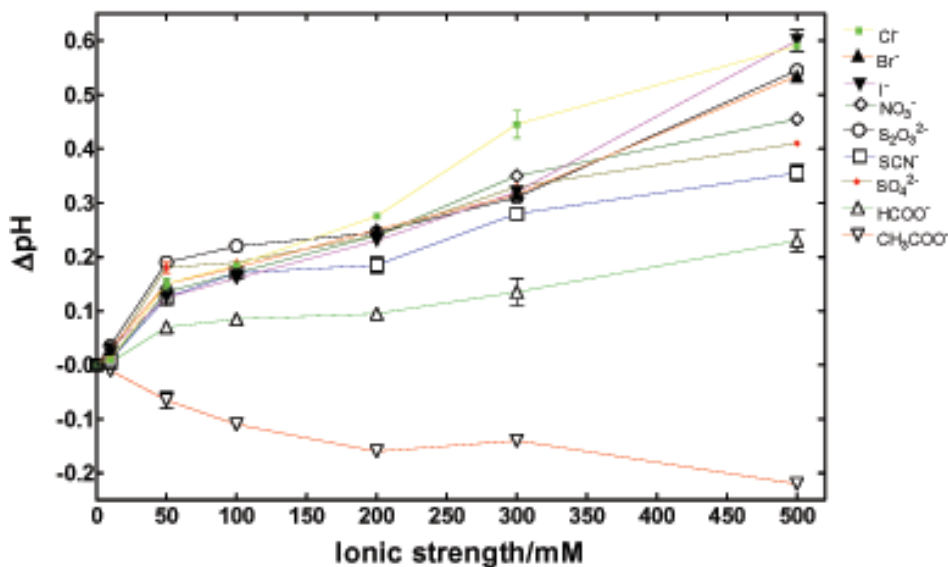


Fig. 5. pH variation of hematite-buffer suspensions (0.2% w/V) in the presence different background electrolytes at 298.15 K.

at 298.15 K. The change in pH of the suspension thus solely depends upon the nature and concentration of the background electrolyte and their adsorption at the solid-water interface. The observed trend is due to the effect of different ions on the iep of the metal oxide suspension. The observed specific ion effects are roughly in tune with the polarizability of the different ions and the ion-ion effect.

Conclusion

The surface-active agents produce a stable dispersed phase in the aqueous slurry of iron ore slime and fines. The surface-active agents are effective in increasing the iron value in the concentrates and subsequent removal of gangue minerals. The dispersed phase bears the gangue minerals like kaolinite, goethite. The hard-water is found to be an effective flocculating agent for recovery of water from the suspension and the recovered water can be used for further beneficiation. Different inorganic ions are responsible for the change in pH of metal oxide suspensions. □

References

1. B. Gururaj, N. Prasad, R.N. Ramachandran, and A.K. Biswas, In: Proceedings 13th International Mineral Processing Congress, Warsaw, 2, Part A, p. 447, (1979).
2. S.J. Roychoudhury, and D.N. Dash, In: Proceedings National Seminar on Beneficiation of Raw Materials for Iron Making, R&DC, SAIL, Ranchi, India, (2003)
3. K.V. Rao, T.V.V. Kumar, K.K. Bhattacharyya and S.C. Maulik, In: Proceedings International Seminar on Mineral Processing Technology, Goa, India, February 6-8, pp159-162 (2003).
4. G.B. Raju, S. Prabhakar, S.S. Rao, D.S. Rao, T.V.V. Kumar, Y.S. Reddy and A. Timblo, In: Proceedings International Seminar on Mineral Processing Technology, Goa, India, February 6-8, pp 174-182, (2003).
5. P.K. Sengupta, S.K. Mukherjee, and N. Prasad, In: Proceedings National Seminar on Beneficiation of Raw Materials for Iron Making, (R&DC, SAIL, Ranchi, India), (2003).
6. N. Prasad, In: Proceedings International Seminar on Mineral Processing Technology, Goa, India, February 6-8, pp 153-158, (2003).
7. B.M. Moudgil and P. Somasundaran. In SME-AIME Annual Meeting, Dallas, Texas, Paper 12p. (1982).
8. D.M. Bagster, In: Proceedings 12th Australian Chemical Engineering Conference, Melbourne, 26-29 August, Paper 25e, (1984).
9. D.M. Bagster, *Int. J. Mineral Process.* **14**, 21-32 (1985).
10. D.M. Bagster and J.D. Mellvenny, *Int. J. Mineral Process.* **14**, 1-20 (1985).

11. R. Jin, W. Hu and X. Hou, In: *Flocculation in Biotechnology and Separation Systems* (ed: Y.A. Attia), pp 639-657 (Elsevier: Amsterdam 1987).
12. R. Jin, W. Hu and X. Hou, *Colloids Surf.* **26**, 317-331 (1987).
13. H.O. Lien and J.G. Morrow, *CIM Bulletin*, **71**,109-120 (1978).
14. M. Zuleta, L.V. Gutierrez and J.A. Matar, In *Regents in the Mineral Industry Conference* (Rome) (eds: M J Jones and R Oblatt), pp 277-285 (Institute of Mining and Metallurgy: London 1984).
15. S. Subramanian and K.A. Nataraj, *Mineral Engineering*, **4**, 587-598 (1991).
16. M.V. Biber and W. Stumm, *Environ. Sci. Technol.* **28**, 763-768 (1994).
17. P.K. Weissenborn, L.J. Warren and J.G. Dunn, *Int. J. Mineral Process.* **42**, 191-213 (1994).
18. S. Mahiuddin, S. Bondyopadhyay and J.N. Baruah, *Int. J. Mineral Process.* **26**, 285-296 (1989).
19. N.N Dutta and S. Mahiuddin, In: *Proceedings of the International Conference on Advances in Chemical Metallurgy*, Bombay, India, 9-11 January, 1991, Paper no: 3AC5.
20. B. Gururaj, N. Prasad, T.R. Ramachandran and A.K. Biswas, In: *Proceedings 13th International Mineral Processing Congress*, Warsaw, Vol 2, and Part A, pp 447-471 (1979).
21. B. Gururaj, J.P. Sharma, A. Baldawa, S.C.D. Arora, N. Prasad and A.K. Biswas, *Int. J. Mineral Process.* **11**, 285-302 (1983).
22. M.J. McGuire, J. Addai-Mensah and K.E. Bremmell, *Asia-Pac. J. Chem. Eng.*, **3**, 18-23 (2008)
23. R.W. Lahann, *Clays clay miner.* **24**, 320-326 (1976).
24. G.A. Parks, The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems, *Chem. Reviews.* **65**: 177-198 (1965).
25. M. Kosmulski,. The pH-dependent surface charging and the points of zero charge, *J. Colloid Interface Sci.* **253**: 77-87 (2002).
26. M. Kosmulski, E. Maczka, E. Jartych, and J.B. Rosenholm,. Synthesis and characterization of goethite and goethite-hematite composite: experimental study and literature survey, *Advances in Colloid Interface Sci.*103: 57-76 (2003).
27. L. R. Bernstein, W.E. Mayo, H.F. McMurdie, F.J. Rotella, M.E. Mrose, (Eds.), In: *Powder Diffraction File, Alphabetic Index, Inorganic Phases, Sets 1-46*, International Centre for Diffraction Data, Pennsylvania, USA, (1996).