Selective Flocculation of Dilband Iron Ore, Pakistan

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ABSTRACT

Selective flocculation for long is known as one of the beneficiation techniques applicable to the concentration of finely disseminated ores. The success of this technique is based on the selective adsorption of an organic polymer on the mineral particles to be flocculated. In present study beneficiation of finely disseminated Dilband iron ore using selective flocculation has been attempted. The effect of pH, sodium silicate (Na_2SiO_3), sodium hexametaphosphate ($Na_2OP_2O_5$), sodium trypolyphosphate ($Na_5P_3O_{10}$), ethylediaminetretracetae ($NaCH_2$-CH_2N), flocculant doses, and flocculant mixing method on the selective adsorption of corn starch on hematite, the chief iron mineral, was studied comprehensively. Improvement in grade was assessed by XRF analysis of the flocculation products. The selective flocculation upgraded the ore from 52% hematite (i.e. 39% Fe) to 60% hematite (i.e. 45% Fe) with an average hematite recovery of 15%. Appreciable increase in ore grade with sufficiently poor recovery suggested that selective flocculation process is not adequate beneficiating technique to upgrade the Dilband iron ore due to heavily intergrowth of impurities.

Key Words: **Selective Flocculation, Dilband Iron Ore, SHMP, SS, SPP, EDTA, STPP.**

1. INTRODUCTION

Dilband iron ore is low grade ore containing about 39% Fe with 18-20% SiO_2 and 1.3% P_2O_5 finely disseminated impurities. Petrographic study of the Dilband iron ore revealed that it is typically soft oolitic ore [1] that could not be used directly in blast furnace. The silica to alumina ratio is also undesirable in terms of blast furnace chemistry and would pose serious operational problems during smelting operation in blast furnace. Furthermore gangue mineral specially silica and flourapatite in Dilband iron ore is so finally disseminated that it could not be possible to separate it with conventional beneficiation techniques. Study of mesh of liberation revealed that hematite grain can only be unlocked from gangue minerals when ground down to 5μm [2]. Therefore taking into account all mineralogical, chemical and mesh of liberation attributes of the Dilband ore, selective flocculation process was envisaged for its up gradation [2-3], since it has been found the most promising avenue for beneficiating the finely disseminated ores worldwide [4-8].

It is worth to mention here that before commencing the selective flocculation tests, adequate dispersion tests were conducted in which slurry pH, solid concentration, stirring speed, water quality, dispersant and their doses were optimized [9-10]. Therefore, present paper only reports the results of the selective flocculation tests for up gradation of Dilband iron ore.

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2. EXPERIMENTAL WORK

The materials and methods used in this study are presented as under:

2.1 Dilband Iron Ore

The Dilband iron ore containing averagely 38-40% Fe, 18-20% SiO_2, 5.32% Ca, 1.3% P_2O_5 and 2.262% Al was received from Pakistan Steel Mills Karachi. After mineralogical and liberation study ore was wet grinded in ball mill to achieve 100% 40μm. During the wet grinding the slurry pH was maintained at 10.5 in order to avoid the smearing of impurities on hematite.

2.2 Dispersants and other chemicals.

Technical grade SHMP (Sodium Hexameta Phosphate), SS (Sodium Silicate), SPP (Sodium Pyrophosphate), and EDTA (Ethylene Diamine Tetraacetate Acid), STPP (Sodium Tripolyphosphate), and corn starch were received from Department of Mineral Processing and Petroleum Engineering, Montan University Leoben, Austria. 1M NaOH, and 1M HNO_3 solutions were used as pH modifier.

2.3 Preparation of Corn Starch Solution

500ppm stock solution of corn starch was prepared by dissolving 0.5g corn starch in 100ml distilled water within 30 minutes using autoclave. The temperature and pressure of autoclave was set at 130°C and 30psi respectively. The starch solution was discarded after 24hours. The detail of preparation of corn starch solution is described elesewhere [11].

2.4 Selective Flocculation Tests

To conduct the selective flocculation tests slurry of 7.5% solids was stirred in a 1 liter beaker at 2000rpm for five minutes at 10.5 pH. After stirring the slurry was immediately transferred to the 250ml cylinder where volume and pH adjusted, and shacked 10 times by inverting the cylinder. Thereafter required doses of the starch were added in three intervals. After each addition, the corn starch was mixed by inverting the cylinder 5 times. To modify the flocculant adding method, in some tests the starch was added within the beaker by keeping the stirrer speed low up to 300rpm. In this case the starch was further mixed for 1 min. Thereafter slurry transferred immediately into cylinder and inverted three times before leaving for 2.5 min settling interval. After 2.5 min the supernatantt was siphoned and the floc (sediment) remaining in the cylinder was washed. The sediment obtained after three times floc washing and first supernatantt collected from each selective flocculation test were dried at 100°C, weighed and used for flocculation performance assessment. The grade of flocculation test products was analyzed on XRF.

3. RESULTS

In present selective flocculation study effect of solid concentration, slurry pH, method of flocculant addition, and different dispersants and their doses were evaluated. Initial attempts were made to investigate the effective dispersant and its dose, since in the dispersion tests this parameter could not assessed previously [9-10]. 10ppm corn starch dose was therefore arbitrary selected to evaluate the effect of dispersants and their doses. The result of selective flocculation tests at different doses of EDTA, SS, STPP and SHMP are shown in Figs. 1- 8. It is very clear from the results that none of the dispersant could be effective to improve the grade in any of the test product (i.e. sediment, and supernatant) significantly. Hardly 5% increase in grade with less than 10% recovery could have been achieved either in sediment or in some other cases in supernatant. The marginal improvement in the grade of supernatant was noticed when 90% material flocculated within 2.5 min, while improvement in the grade of sediment took place when approximately 90% material remained suspended. This trend of marginal improvement in the grade of supernatant and sediment remained in all the four dispersants.

The flocculation efficiency of starch noticed to decrease with increase of % dose of the dispersants except STPP. Because of marginal variation in the grade of the products again selection of optimal dispersant remained unresolved. Therefore, 0.04% EDTA (i.e. 4.8kg EDTA/ton of ore), 0.1% SS (i.e. 2.4kg SS/ton of ore), 0.1% STPP (i.e. 2.4kg STPP/ton of ore) and 0.02% SHMP (i.e. 2.1kg SHMP /ton of ore) were arbitrary selected to survey the optimal dose of corn starch.

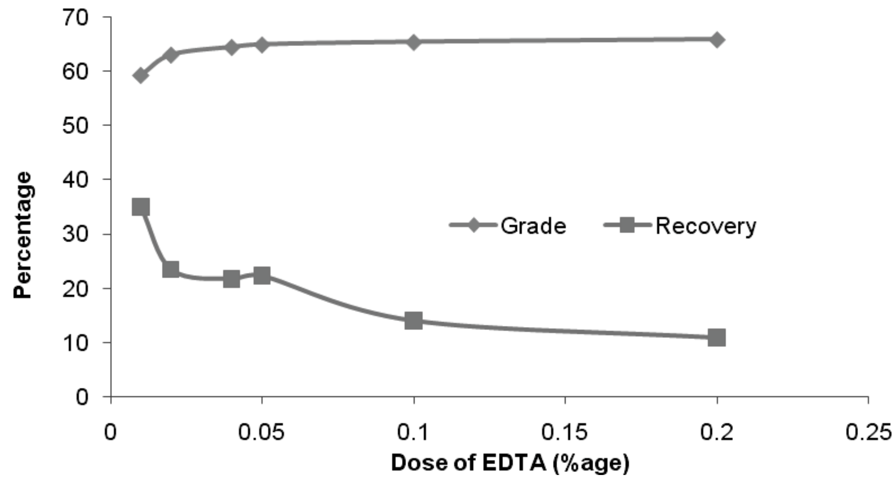


FIG. 1. EFFECT OF EDTA DOSES ON GRADE AND RECOVERY OF SEDIMENT AT 10PPM CORN STARCH AND 10.5pH

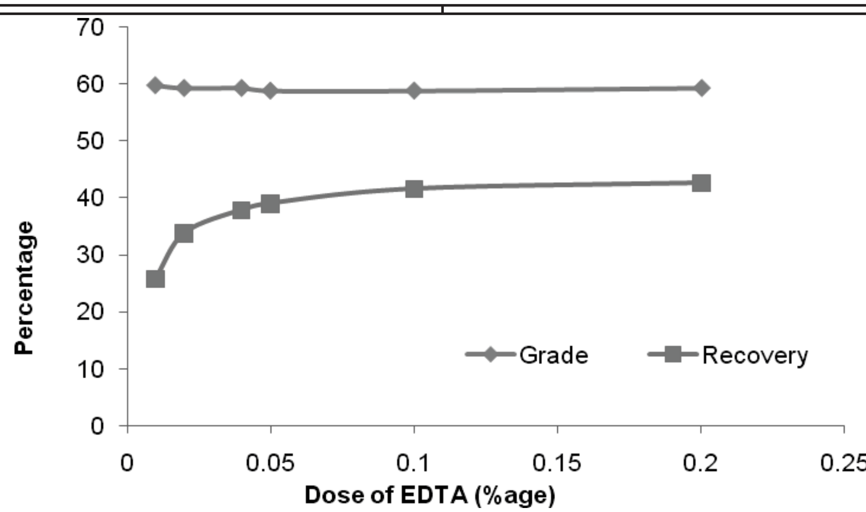


FIG. 2. EFFECT OF EDTA DOSES ON GRADE AND RECOVERY OF SUPERNATANT AT 10PPM CORN STARCH AND 10.5pH

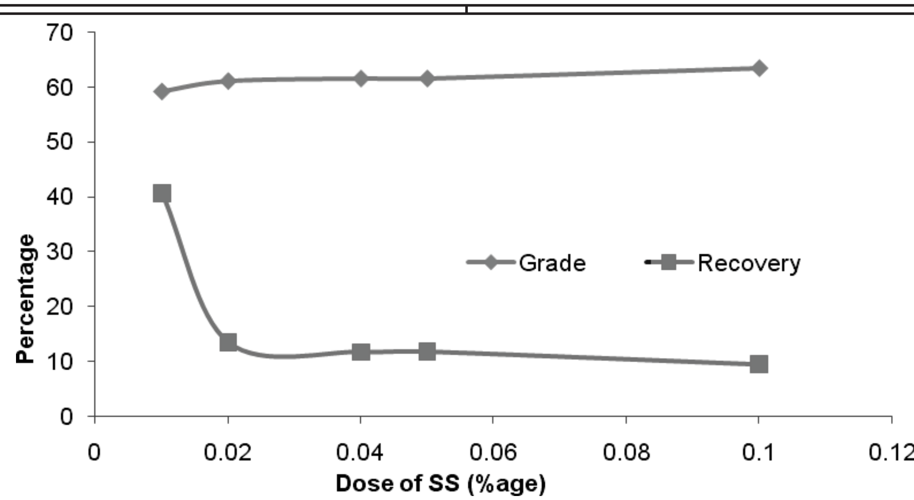


FIG. 3. EFFECT OF SS DOSES ON GRADE AND RECOVERY OF SEDIMENT AT 10PPM CORN STARCH AND 10.5pH

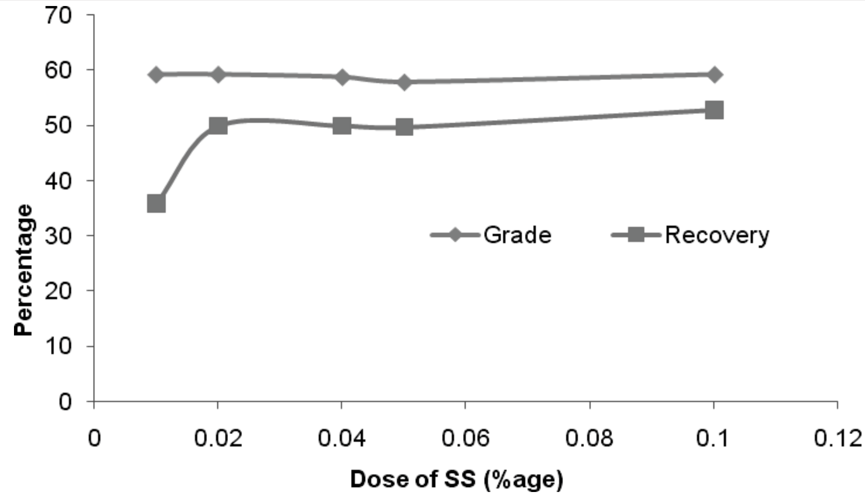


FIG. 4. EFFECT OF SS DOSES ON GRADE AND RECOVERY OF SUPERNATANT AT 10PPM CORN STARCH AND 10.5pH

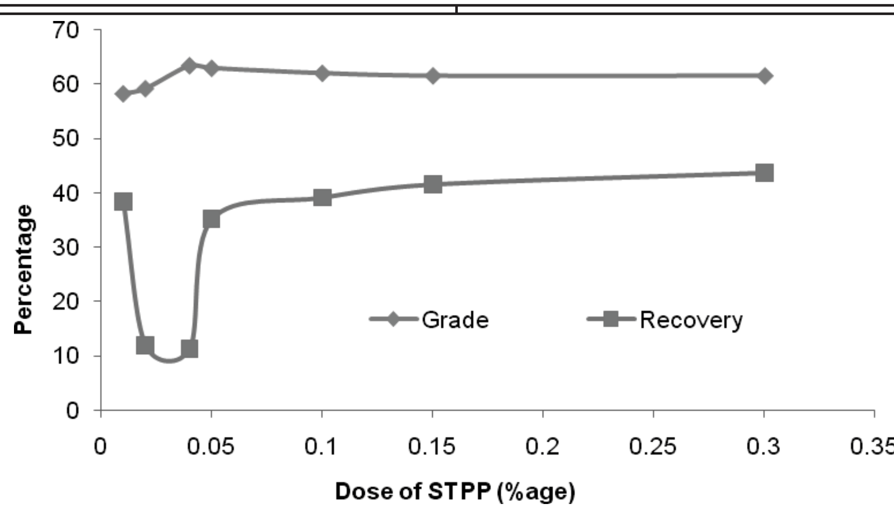


FIG. 5. EFFECT OF STPP DOSES ON GRADE AND RECOVERY OF SEDIMENT AT 10PPM CORN STARCH AND 10.5pH

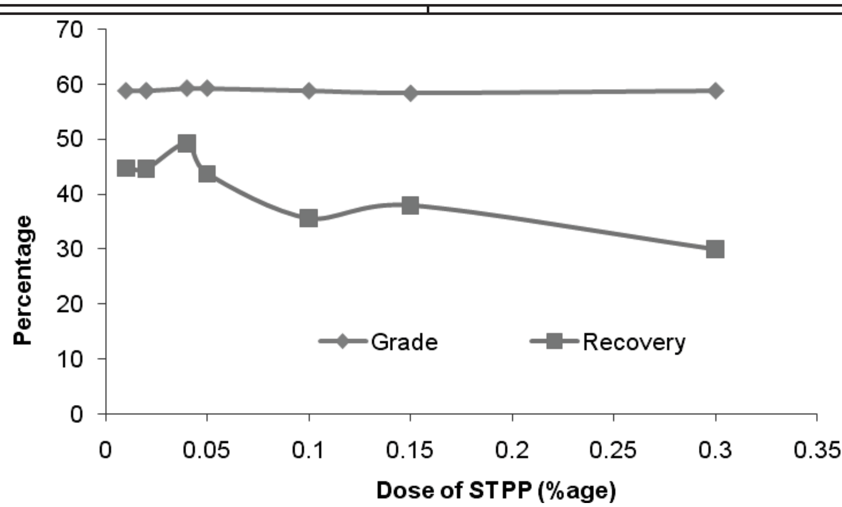


FIG. 6. EFFECT OF STPP DOSES ON GRADE AND RECOVERY OF SUPERNATANT AT 10PPM CORN STARCH AND10.5pH

The results shown in Figs. 9-14 indicate that grade of each product of test remained poor at all starch doses. With increase in starch dose increase in percent recovery at the cost of percent decrease in grade resulted. The grade and recovery of sediment and supernatant remained reciprocal in all dispersants. Grade of supernatant increased with decrease in grade of sediment. Similarly vise versa case remained for their respective percent recoveries.

To evaluate the effect of pH on grade of Dilbnad iron ore, the selective flocculation tests using the different doses of corn starch was studied at 10.5 and 11.5pH values. The results shown in Fig. 15 indicate that with increasing slurry pH to 11.5 the selectivity of the corn starch for the hematite present in Dilband iron ore could not improved significantly and starch almost behaved similarly in both pH values.

The effect of solid concentration on selective role of corn starch for Dilband iron ore was also studied. For this two more 5 and 7% solid concentrations were tried. The results shown in Fig. 16 indicate that with decreasing the solid concentration marginal decrease in wt% of the material flocculated has taken place.

Study on the effect of corn starch addition method did not improve the grade significantly. However addition of starch at 600rpm indicated marginal increase in % recovery. This shows that proper mixing of starch would have been achieved at 600rpm.

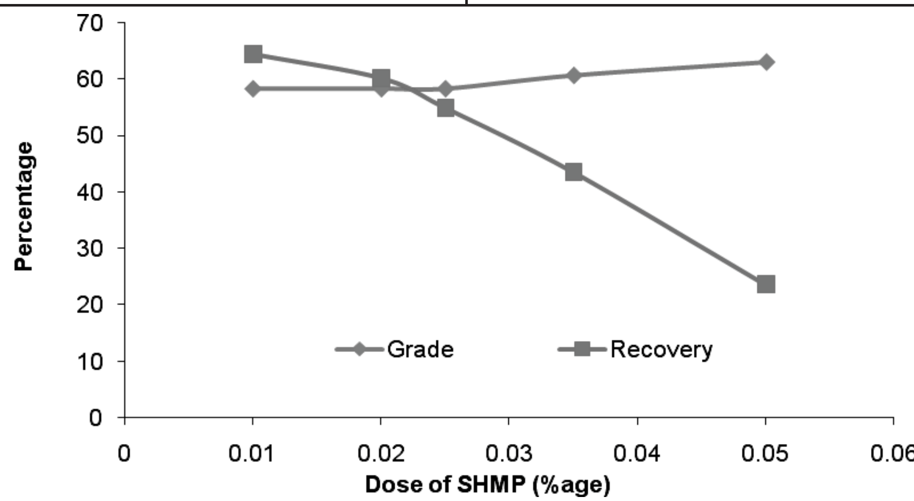


FIG. 7. EFFECT OF SHMP DOSES ON GRADE AND RECOVERY OF SEDIMENT AT 10PPM CORN STARCH AND 10.5pH

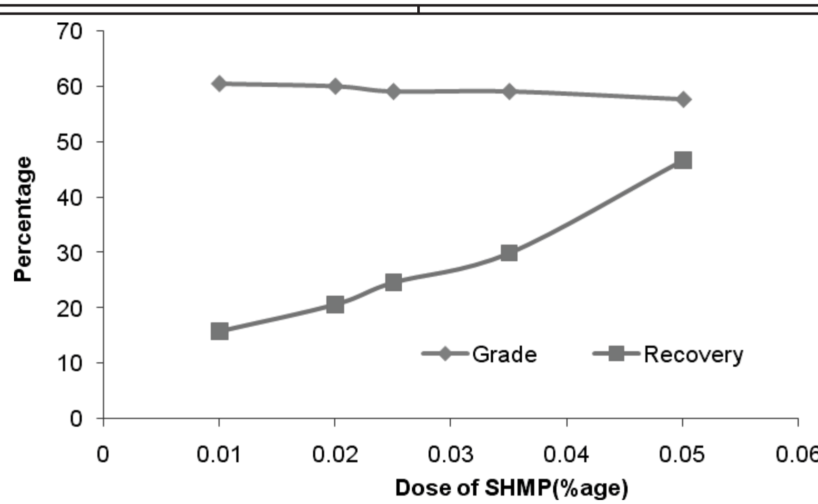


FIG. 8. EFFECT OF SHMP DOSES ON GRADE AND RECOVERY OF SUPERNATANT AT 10PPM CORN STARCH AND 10.5pH

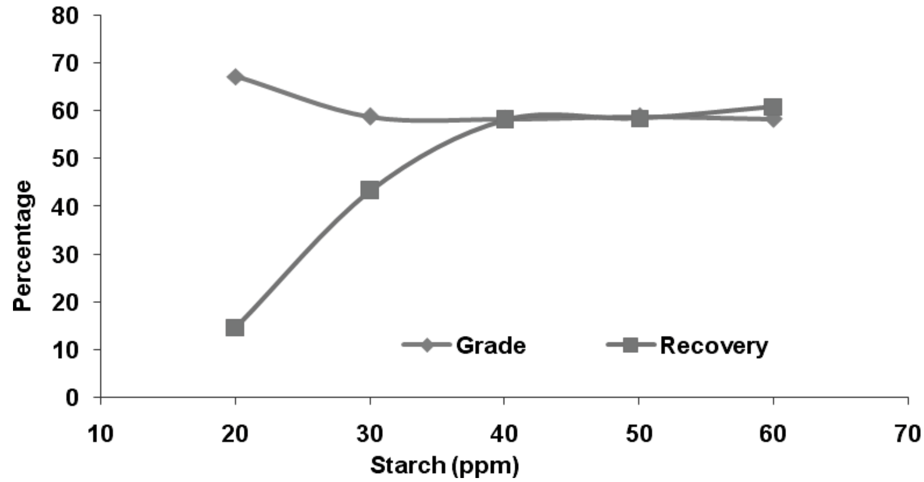


FIG. 9. EFFECT OF CORN STARCH DOSE ON GRADE AND RECOVERY OF SEDIMENT AT 0.04% EDTA AND 10.5pH

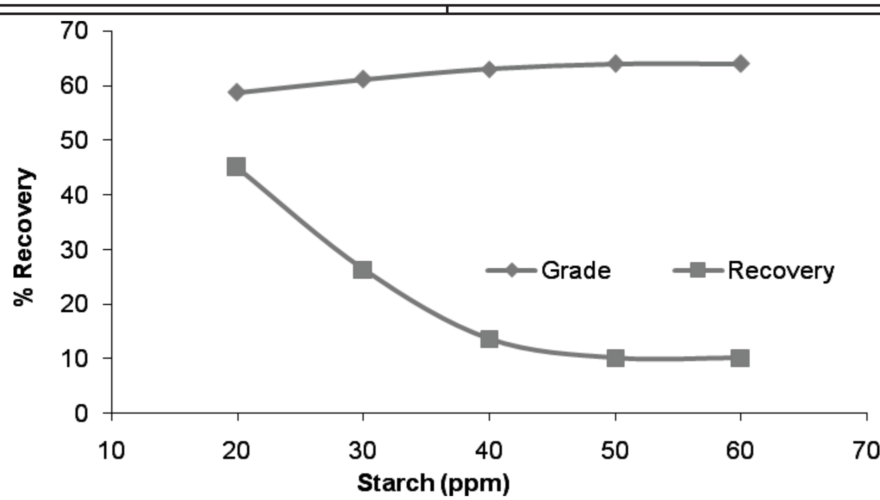


FIG. 10. EFFECT OF CORN STARCH DOSE ON GRADE AND RECOVERY OF SUPERNATANT AT 0.04% EDTA AND 10.5pH

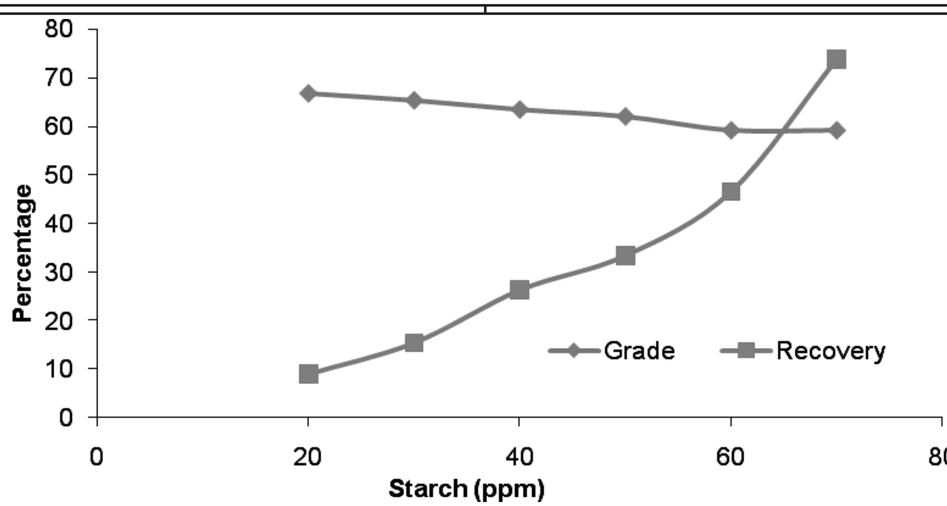


FIG. 11. EFFECT OF CORN STARCH DOSE ON GRADE AND RECOVERY OF SEDIMENT AT 0.1% SS AND 10.5pH

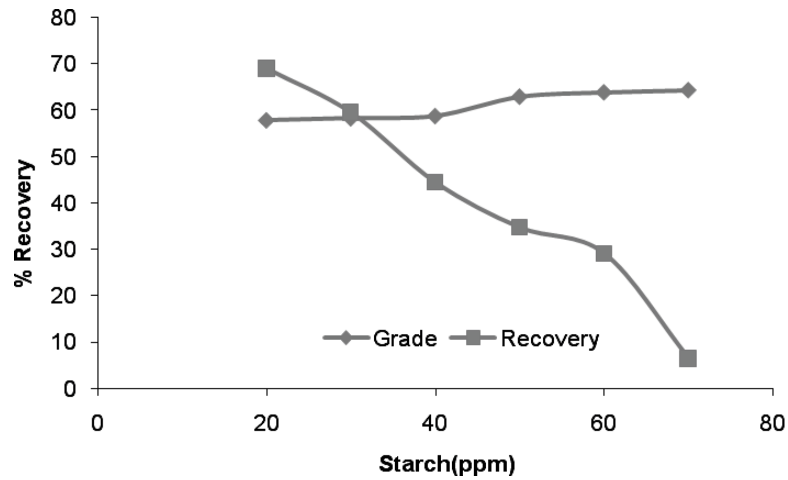


FIG. 12. EFFECT OF CORN STARCH DOSE ON GRADE AND RECOVERY OF SUPERNATANT AT 0.1% SS AND 10.5pH

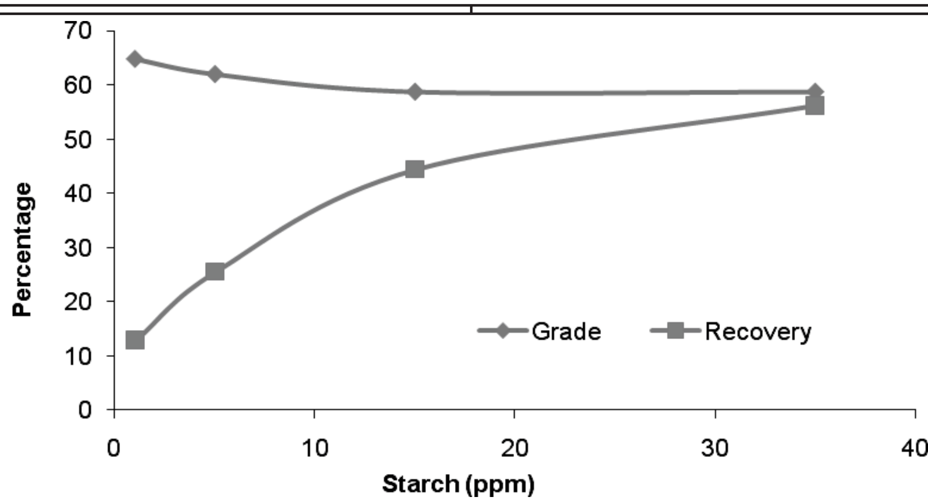


FIG. 13. EFFECT OF CORN STARCH DOSE ON GRADE AND RECOVERY OF SEDIMENT AT 0.1% STPP AND 10.5pH

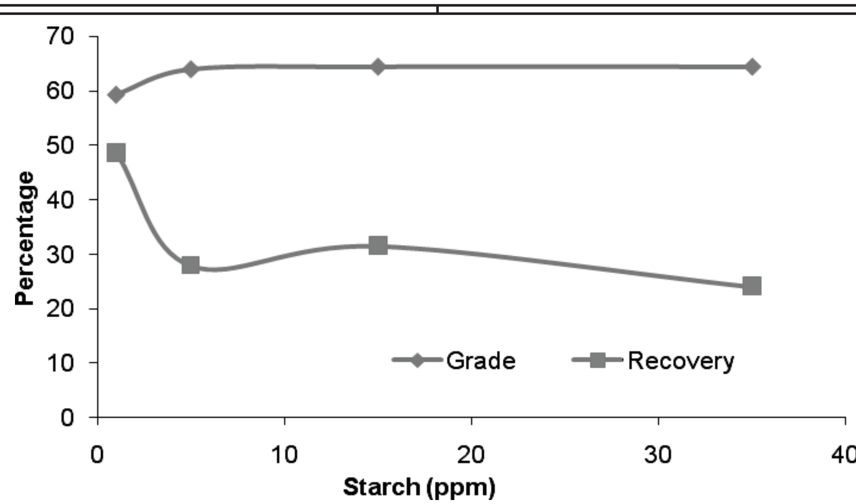


FIG. 14. EFFECT OF CORN STARCH DOSE ON GRADE AND RECOVERY OF SUPERNATANT AT 0.1% STPP AND 10.5pH

4. DISCUSSION

In order to flocculate Dilband iron ore selectively all the major process parameters were studied. The results indicated that selective adsorption of corn starch on hematite could not achieved due to one or another reason. The improper selection of dispersants and their doses, less selective flocculant, improper slurry solid concentration and pH value, and inadequate flocculant addition method can be speculated behind poor selectivity of corn starch. Therefore, in this section role of each parameter playing in Dilband iron ore slurry is discussed in detail in order to trace the possible root cause behind the poor selective flocculation results.

In order to find out most effective dispersant for the Dilband iron ore almost all well known dispersants EDTA, SS, SHMP, and STPP at different doses were tried in present study. The marginal improvements in the grade of sediment suggested that none of the dispersant can effectively dispersed the gangue minerals present in Dilband iron ore slurry. Literature pertaining to basic purpose of using dispersants in selective flocculation process is to enhance the zeta potential of the slurry constituents in general and to develop significant difference between the surface potentials of mineral of interest (hematite) and gangue minerals in particular. The significant difference in surface potentials is required just to facilitate the corn starch molecules to adsorb on mineral surface of least zeta potential. From present set of results

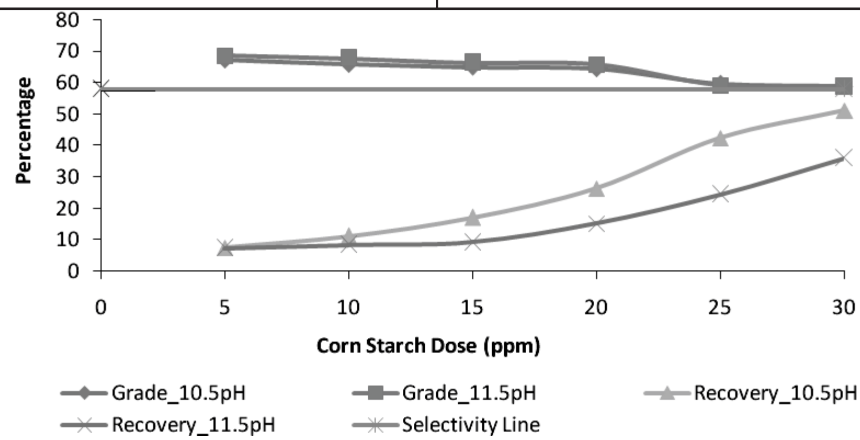
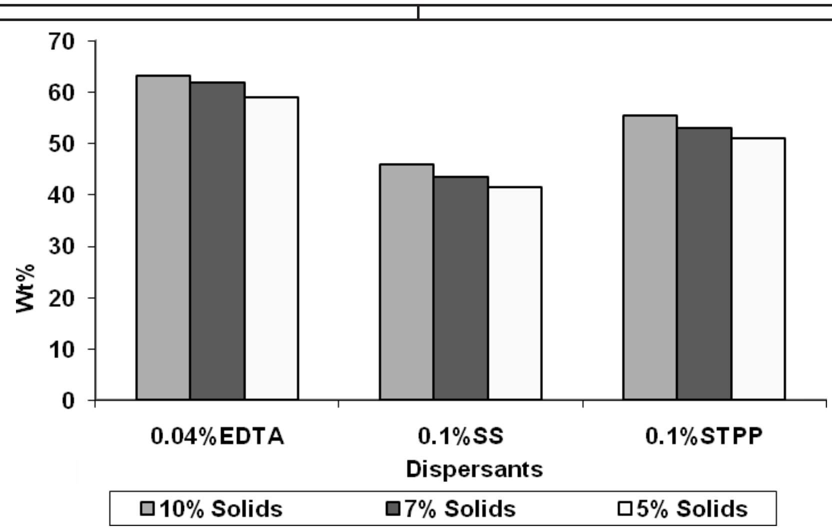


FIG. 15. EFFECT OF pH AND STARCH DOSES ON GRADE AND RECOVERY OF SEDIMENT AT 0.1% SS



FIG, 16. EFFECT OF SOLID CONCENTRATION ON WT% OF SEDIMENT AT 30 PPM CORN STARCH AND 10.5pH

(Figs. 1-8) increase in zeta potential with addition of dispersants can be witnessed from increasing and decreasing trend of % recovery. Therefore at higher concentration of dispersants it would become difficult for starch molecules to adsorb on to the mineral surface. The flocculant conformational changes from extended to flattened can also be attributed with increase in % dose of dispersants due to increase in zeta potential. Keeping in view the basic role played by dispersants in present study poor results of selective flocculation cannot be attributed with improper selection of the dispersant.

Another possible reason behind the poor results of selective flocculation of Dilband iron ore can be lower selectivity of corn starch for hematite. Selectivity of corn starch for hematite in a system containing gangue mineral chiefly quartz is widely acknowledged in the literature [12-19]. Therefore authors could not find supporting literature for authentication of corn starch poor selectivity speculation for hematite in present case. To elucidate the poor selectivity of corn starch for hematite in present case, flocculation tests at different doses of corn starch at optimal doses of EDTA, SS, and STPP dispersants were attempted. Results, shown in Figs. 9-14, indicated that although the percent recovery increased with increasing the starch doses the improvement in the grade was, however, minimum. No significant improvement in the grade suggested that corn starch dose is not the cause of poor selectivity.

Upon realizing the problem of poor selectivity of starch for Dilband iron ore, poor flocculant mixing in the cylindrical tests can also be attributed. To look into this issue, the starch addition during stirring the slurry and sonicating ultrasonically was made. Results of these tests did not differ in terms of the improvement in the selectivity. During flocculation tests conducted without sonicating or stirring, at the time of starch addition, it was thought that perhaps particles of the quartz or fluorapatite might be so close that starch couldn't find way to reach hematite surface. But this conjecture remained invalid and the selectivity remained poor even after modifying the flocculation addition method.

The slurry pH is well recognized to play a significant role in altering the flocculants selectivity [5,7,20-22]. Keeping in view the governing role of slurry pH, the selective flocculation tests for Dilband iron ore were attempted at 10.5 and 11.5pH. At this pH range starch selectivity for hematite in comparison with quartz is widely recognized in the literature [4,6,16,18,21-25]. Since Dilband iron is composed of two main gangue minerals namely quartz and fluorapatite, it would be therefore worth to discuss aetiology of poor selectivity of starch at these pH values individually. In a natural ore containing only hematite and quartz, smearing effect or poor liberation can only be the cause of poor selectivity of corn starch for hematite at highly alkaline conditions. In present case smearing effect cannot be anticipated, because Dilband ore was wet grinded at 10.5pH. However, poor liberation may be the major cause, because the gangue minerals are finely disseminated in the ore body. In addition, the poor selectivity of corn starch, in case of hematite and fluorapatite, is the major issue because of their very close zeta potential value.

5. CONCLUSIONS

In present paper major factors behind the poor selective flocculation of Dilband iron ore are discussed. Each operating parameter is critically observed and finally the two major root causes responsible of poor performance of selective flocculation are outlined. These are:

(i) The Dilband iron ore is not completely liberated, specially quartz is so heavily intergrown into the grains of hematite that all the selective flocculation parameters failed to separate it.

(ii) The fluorapatite, if it is liberated, might have the equivalent zeta potential to the zeta potential of hematite at operating pH and dispersants doses. Therefore starch could not preferably adsorbed onto hematite.

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REFERENCES

[1] Abro, M.I., Pathan, A.G., Mallah, A.H., and Böhm, A., "Mineralogical Characterization of Dilband Iron Ore Deposits of Balochistan, Pakistan [Mineralogische Beschreibung der Dilband-Eisenerzlagerstätten in Balochistan, Pakistan]", BHM Berg-und Hüttenmännische Monatshefte, Springer Wien Publisher, Volume 153, No. 6, pp. 206-210, June, 2008.

[2] Abro M.I., Pathan, A.G., and Mallah, A.H., "Assessment of Mesh of Liberation of Dilband Iron Ore, Pakistan", Mehran University Research Journal of Engineering & Technology, Volume 29, No. 3, pp. 455-464, Jamshoro, Pakistan, July, 2010.

[3] Abro, M.I., and Pathan, A.G., "Determination of Physico-Chemical Characteristics of Dilband Iron Ore" Mehran University Research Journal of Engineering & Technology, Volume 29, No. 2, pp. 291-296, Jamshoro, Pakistan, April, 2010

[4] Colombo, A.F., "Concentration of Iron Oxides by Selective Flocculation-Floatation", US Department of Interior, Chapter 42,Bur of Mines, Reno, NV, USA, 1986.

[5] Drzymala, J., and Fuerstenau, D.W., "Selective Flocculation of Hematite in The Hematite-Quartz-Ferric Ion-Polyacrylic Acid System, Part-I. Activation and Deactivation of Quartz", International Mineral Processing Journal, Volume 8, Issue 3, pp. 265-277, July, 1981.

[6] Kafali, L., Cuhadaroglu, D., and Kizgut, S., "Selective Flocculation-Flotation of Camdag Iron Oxides", Innovation In Mineral & Coal Processing, Proceeding of The 7th International Mineral Processing Symposium, pp. 177-182, Turkey, September, 1988.

[7] Khan, M.M., "Selective Flocculation of Lead Zinc Concentrate", Ph.D. Thesis, University of Nottingham, 1985.

[8] Somasundaran, P., and Runkana, V., "Selective Flocculation of Fines", Transaction of Nonferrous Metals Society China, Volume 10, Special Issue, pp. 8-11, June, 2000.

[9] Abro, M.I., Pathan, A.G., Bohm, A., and Mallah, A.H., "Effect of Various Parameters on the Dispersion of Ultra Fine Iron Ore Slurry Part-I", Pakistan Journal of Analytical and Environmental Chemistry, Volume 10, Nos. 1-2, pp. 34-38, December, 2009.

[10] Abro, M.I., Pathan, A.G., Bohm, A., and Mallah, A.H., "Effect of Various Parameters on the Dispersion of Ultra Fine Iron Ore Slurry Part-II", Pakistan Journal of Analytical and Environmental Chemistry, Volume 10, Issue 2, December. 2010.

[11] Abro, M.I., “Upgradation of Dilband Iron Ore”, Ph.D. Thesis, Department of Metallurgy & Materials Engineering, Mehran University of Engineering & Technology, Jamshoro, Pakistan, 2009.

[12] Mohamed, I., Khalil, Amal, A.A., "Preparation and Evaluation of Some Anionic Starch Derivatives as Flocculants", Starch-Stärke International Journal for the Investigation, Processing and Use of Carbohydrates and Their Derivative, Volume 54, Issue 3-4, pp. 132-139, April, 2002.

[13] Montes-Sotomayor, S., Houot, R., and Kongolo, M., "Flotation of Silicated Gangue Iron Ores: Mechanism and Effect of Starch", Minerals Engineering, Volume 11, Issue 1, pp. 71-76, January, 1988.

[14] Pavlovic, S., and Brandao P.R.G., "Adsorption of Starch, Amylose, Amylopectin and Glucose Monomer and Their Effect on The Flotation of Hematite and Quartz", Minerals Engineering, Volume 16, Issue 11, pp. 1117-1122, November, 2003.

[15] Peres, A.E.C., and Correa, M.I., "Depression of Iron Oxides With Corn Starches", Minerals Engineering, Volume 9, Issue 12, pp. 1227-1234, December, 1996.

[16] Ravishankar, S.A., Pradip, and Khosla, N.K., "Selective Flocculation of Iron Oxide From its Synthetic Mixtures With Clays: A Comparison of Polyacrylic Acid and Starch Polymers", International Journal of Mineral Processing, Volume 43, Issue 3-4, pp. 235-247, June, 1995.

[17] Subramanian, S., and Natarajan, K.A., "Flocculation, Filtration and Selective Flocculation Studies on Haematite Ore Fines Using Starch", Minerals Engineering, Volume 4, Issue 5-6, pp. 587-598, August, 1991.

[18] Weissenborn, P.K., "Selective Flocculation of Ultrafine Iron Ore", Ph.D. Thesis, School of Applied Chemistry, Curtin University of Technology, 1993.

[19] Yong, Raymond, N., and Sethi, A.J., "Process For Making Starch Flocculants of Improved Efficiency", United States Patent 4508627, 1985.

[20] Hogg, R., Bannual, P., and Suharyono, H., "Chemical and Physical Variables in Polymer-Induced Flocculation", SME Transactions, Minerals and Metallurgical Processing, Volume 294, Issue 10, pp. 81-85, May, 1993.

[21] Mathur, S., Singh, P., and Moudgil, B.M., "Advances In Selective Flocculation Technology For Solid-Solid Separations", International Journal of Mineral Processing, Volume 58, Issue 1-4, pp. 201-222, February, 2000.

[22] Paananen, A.D., and Turcotte, W.A., "Factors Influencing Selective Flocculation-Desliming Practice at The Tilden Mine," Mining Engineering, SME Littleton, Colorado, Volume 32, No. 8, pp. 1244-1247, August, 1980

[23] Arol, A.I., "The Effect of Clay Minerals on Selective Flocculation of Iron Ores", Ph.D. Thesis, University of Minnesota, Turkey, 1984.

[24] Gururaja, B., Sharmaa, J.P., Baldawaa, A., Aroraa, S.C. D., Prasad, N., and and Biswas, A.K., "Dispersion-Flocculation Studies on Hematite-Clay Systems", International Journal of Mineral Processing, Volume 11, Issue 4, pp. 285-302, December, 1983.

[25] Jones, F., "The Mechanism of Bayer Residue Flocculation", Ph.D. Thesis, School of Applied Chemistry, Curtin University of Technology Australia, 1988.