

## Selective flocculation of iron oxide-kaolin mixtures using a modified polyacrylamide flocculant

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**Abstract.** High molecular weight polyacrylamides were synthesized and successfully modified to contain up to 8.3% hydroxamate functional groups. The selective flocculation tests carried out on 1:1 iron oxide/kaolin mixtures using parent polyacrylamide, polyacrylic acid and the modified polyacrylamide, confirm the possibility of enhancing selectivity through introduction of iron chelating functional groups in commercially available polymers. Starting with a feed grade of 35% iron, 92% recovery with acceptable grade of 60% iron has been achieved using the modified polyacrylamide.

**Keywords.** Selective flocculation; iron-chelating functional group; modified polyacrylamide; hydroxamates.

### 1. Introduction

Some of the richest iron ore deposits in the world occur in India. These ores, however, suffer from one of the most detrimental characteristics unique to India. They have relatively a high alumina gangue. It is well known that for achieving optimum level of productivity in the blast furnace, the feed should have an iron content > 60%,  $\text{Al}_2\text{O}_3/\text{Fe}$  ratio of < 0.05 and  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio of < 1 (Prasad and Aswath 1983). Indian ores, on the other hand, have  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio much higher than 1. Moreover, the comminution and washing of these ores lead to even more adverse  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio since the free liberated silica particles are rejected during washing.

Detailed phase characterization and liberation studies carried out on Barsua, Rajhara and Kudremukh iron ores (Ravi Shankar and Biswas 1986; Gururaj *et al* 1979) have shown the presence of alumina in the form of illite, kaolinite, montmorillonite, sillimanite, alunite and small amounts of diaspore and gibbsite minerals. The size of aluminium containing grains has been reported to be in the range of 0.03–2  $\mu\text{m}$ . Any physical beneficiation scheme aimed at reducing alumina in Indian iron ore must fulfil the following two important criteria.

- (i) The separation has to be carried out in micron size range.
- (ii) The process should effectively separate iron oxide from clay minerals.

Selective flocculation technology, a recent development in mineral processing, is ideally suited for separation in subsieve size range. The only commercial plant based on this technology is also for iron ore beneficiation. Cliff's Tilden plant in Cleveland, USA uses starch flocculants, having a capacity of 10 million tonnes per annum (Colombo 1977) and has been in operation since 1975. Most of the work in the area

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of selective flocculation of ore slimes has been carried out on the separation of iron minerals from quartz using starches (Gururaj *et al* 1983; Hanumantha Rao *et al* 1985a; Hanumantha Rao and Narasimhan 1985; Sresty *et al* 1978) and polyacrylamides (Drzymala and Fuerstenau 1981, 1986; Gebhardt and Fuerstenau 1986). The presence of clay minerals in the feed has been known to produce disastrous effects on the selectivity of the process (Gururaj *et al* 1983; Iwasaki and Lai 1965; Arol and Iwasaki 1986; Attia *et al* 1986). The attempts to selectively flocculate Indian iron ore slimes, mostly using starch as flocculant have not yielded encouraging results (Gururaj *et al* 1983; Hanumantha Rao *et al* 1985; Hanumantha Rao and Narasimhan 1985).

The present work is a part of an ongoing research programme in our laboratories to develop new selective flocculants/dispersants through the modification of commercially available natural or synthetic polymers for iron oxide/clay separation. The underlying hypothesis is that the use of more selective reagents specific to iron oxide/clay system may be the key to solve this challenging problem.

The selectivity of the reagent can be enhanced by the introduction of chelating type functional groups, which are known to be cation-specific. Amongst the various chelating groups (such as xanthate, GBHA and hydroxamate) which have been used in mineral flotation, hydroxamates appear to be the most promising for iron ore minerals (Fuerstenau and Pradip 1984; Pradip 1987). Clauss *et al* (1976) attempted to selectively flocculate cassiterite using a modified polyacrylamide flocculant containing hydroxamate functional groups. Modified cellulose derivatives having hydroxamic acid groups have also been used for the recovery of ferric and copper ion from solutions containing other ions (Mackawa *et al* 1986). In an interesting study, Winston and Kirchner (1978) reported the synthesis of polymers bearing side chains with varying number of atoms terminating in hydroxamic acid. It has been observed that the optimum side chain length for maximum chelation occurs when the hydroxamic acid groups are separated by 11 atoms.

The encouraging results of our attempt to introduce iron-chelating hydroxamate groups in polyacrylamide and selectively flocculate iron oxide from synthetic iron oxide/clay mixtures, have been presented in this paper.

## 2. Experimental materials and methods

### 2.1 Materials

Synthetic iron oxide and kaolin used in this study were of AR grade, obtained from Thomas Baker and Co. (USA) having the following characteristics (table 1).

The X-ray diffraction pattern showed that the synthetic iron oxide used in the

**Table 1.** Material characteristics.

Material	Particle size (minus 10 $\mu\text{m}$ )	Surface area sq m/g (BET)	PZC, pH
Iron oxide	70	6.4	6.2
Kaolin	90	16.2	< 3

study, has the same characteristic peaks as observed for mineral hematite. AR grade sodium silicate with  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio of 0.29 was used as dispersant. Double distilled water with a specific conductivity of  $< 10 \mu\text{mho}/\text{cm}$  was used to prepare all the solutions.

## 2.2 Synthesis and modification of polymers

Polyacrylic acid (weight average molecular weight  $M_w, 1 \times 10^6$ ) used in the study was obtained from Polysciences Inc., USA. The polymeric flocculants synthesized are listed along with their corresponding characterization data in tables 2 and 3. Technical grade acrylamide (BDH; min assay  $> 98\%$ ) was polymerized in solution at a pH of 3.5 to 3.7 at  $65^\circ\text{C}$  according to standard procedures. The polyacrylamide (PAM) solution obtained at the end of polymerization was diluted to 3.5% PAM content. An aliquot of the solution containing about 8 g of PAM was reacted with the required quantity of hydroxylamine hydrochloride (in 95% methanol-water solution). The modified polymer was coagulated using methanol and purified by reprecipitation. About 500 ppm KI was used as the stabilizer during the final coagulation step. PAM samples were similarly coagulated and stabilized from the solution at the end of polymerization.

## 3. Characterization of modified polymers

### 3.1 Molecular weights

Viscosity measurements were carried out both for the parent PAM and for modified polymers in 0.12 M NaCl at  $30^\circ\text{C}$  using an Ubbelohde viscometer having a flow of

**Table 2.** Reaction conditions used for introducing hydroxamic acid groups. Polyacrylamide (3.5% solution): 8 g.

Polymer sample	Parent PAM		NaOH 6N (ml)	$\text{NH}_2\text{OH HCl}$ in methanol (ml, M)	Temp. ( $^\circ\text{C}$ )	Time (h)
	$[\eta]$ ( $\text{dl.g}^{-1}$ )	$M_w \times 10^6$				
PAMX-4 (5)	3.04	1.10	—	200, 2.0	95-98	2
PAMX-4 (2)	3.04	1.10	32	200, 0.5	95-98	2
*PAMX-11 (1)	3.04	1.10	40	40, 1.0	Ambient	72
PAMX-9 (3)	5.78	2.36	4	200, 2.0	85-90	2

\*NaOH and  $\text{NH}_2\text{OH HCl}$  were mixed together, NaCl formed, filtered, free  $\text{NH}_2\text{OH}$  was added.

**Table 3.** Polymer characteristics.

Polymer sample	- CONHOH %	- COOH %	$[\eta]$ in	
			0.12 M NaCl $\text{dl.g}^{-1}$	Viscosity-average ( $\text{mol.wt} \times 10^{-6}$ )
PAMX-4 (5)	0.9	2.4	3.20	1.05
PAMX-4 (2)	0.3	44.5	7.90	0.96
PAMX-11 (1)	5.0	11.7	4.65	1.00
PAMX-9 (3)	8.3	23.2	6.31	0.97

$126.5 \pm 0.1$  s for the solvent. Intrinsic viscosities were obtained from linear  $\eta_{sp}/C$  vs  $C$  plots and used to determine molecular weights by using Mark-Houwink constants available (Kulkarni 1981) in the literature. It has been assumed in the calculations of the molecular weights of modified PAMX that hydroxamic acid groups do not significantly contribute to the charge density as the pKa values for hydroxamic acids are higher than those of carboxylic acid groups (Neilands 1966; Chatterjee 1978). The intrinsic viscosities of the PAM samples used were 3.04 and 5.78 dl.g<sup>-1</sup> corresponding to molecular weights of  $1.1 \times 10^6$  and  $2.3 \times 10^6$  respectively. The molecular weights of the first three samples of PAMX listed in table 2 are close to the values obtained for the parent PAM suggesting the absence of main chain degradation during modification. However, the molecular weight of PAMX 9(3) indicates main chain degradation. But PAMX also has molecular weight in the same range as the other three samples. This sample of PAMX 9(3) has been used for flocculation experiments.

### 3.2 Copolymer composition

The synthesized polymers possess, apart from the intended hydroxamic acid groups, unreacted amide and carboxylate groups resulting from the hydrolysis of the amide by the alkali employed. The methods available in literature (Seifter *et al* 1960; Yashpe *et al* 1960) for estimating the concentration of hydroxamate groups in low molecular weight compounds are based on (i) complexation with ferric perchlorate and determining the optical density of the purple coloured complex formed and (ii) hydrolysis of the hydroxamate groups and complexing the liberated hydroxylamine with pyrrole/indole.

In the first method it was observed that, instead of a purple coloured complex, a brown colloidal precipitate was obtained making it difficult to employ the method for quantitative estimation. In the second method no detectable colour developed, perhaps due to the low concentration of the hydroxamate groups.

The method standardized and used for quantitative estimation of hydroxamate groups in this work was based on the quantitative oxidation to nitrite (in acetic acid medium) with iodine, reacting with sulphanilic acid to form a diazonium compound which forms a red coloured complex with naphthylamine. A polymer sample containing 0.15 mole of hydroxamate groups was treated with 4 ml sodium acetate (6% w/v) solution, 0.5 ml sulphanilic acid reagent (1% in 25% acetic acid/water v/v) in a 10 ml volumetric flask, followed by 0.25 ml iodine (1.3% iodine in glacial acetic acid solution). The mixture was allowed to stand for 4–10 min at 10–15°C and sufficient (0.1–25 ml) 0.1 M sodium thiosulphate solution was added, the contents mixed and the volume made up to the graduation mark with distilled water. The mixture was allowed to stand for 10 min and the optical density at 520 nm was determined against a reagent blank. From the experimentally determined optical density, the hydroxamic acid content was calculated using isobutyric hydroxamic acid as the standard.

The extents of hydrolysis were determined by potentiometric titration method (Gunari and Gundiah 1981). Thirty millilitres of 1% (w/v) polymer solution was adjusted to a pH value of 3.30 using 2 M HCl and back titrated to a value of pH 7 using carbonate-free 0.1 M NaOH. From the titre value and the blank titre obtained with 30 ml 1% polyacrylamide solution, the carboxylate contents were evaluated. The amide content in the polymer were evaluated as the difference of 100 and the sum of

the carboxylate and hydroxamate groups. The composition so determined is listed in table 3.

### 3.3 Flocculation tests

One gram of the solid was equilibrated in water after adding the desired quantity of the dispersant. The suspension was conditioned for 30 min before flocculant addition. The volume was made up to 100 ml after flocculant addition. The flocculation experiments were carried out in beakers at a pulp density of 1%. The flocculant was added dropwise from a freshly prepared stock solution (100 ppm). After adding the desired quantity of the flocculant, an additional 3 min conditioning was allowed with stirring at a lower shear, on a magnetic stirrer. The suspension was then allowed to settle for 1 min. The settled portion was separated by decantation, dried and weighed. In the case of mixtures, the iron oxide content was analysed using the standard hydrochloric acid digestion method. The difference between the total settled mass and the residue after digestion was taken as the amount of kaolin present in the floc.

## 4. Results and discussions

The objective of this study was to evaluate polymers having hydroxamate functional groups (known to be highly specific for iron ions (Fuerstenau and Pradip 1984; Pradip 1987)) for selective separation of iron oxide. The polymer modification method employed invariably leads to the hydrolysis of the amide group and hence the polymeric flocculants used have varying proportions of  $-\text{COOH}$ ,  $-\text{CONH}_2$  and  $-\text{CONHOH}$  groups. In order to establish the role of these three functional groups in the selectivity of separation of iron oxide/kaolin mixtures the flocculation tests were also conducted with pure polyacrylamide (100%  $\text{CONH}_2$ ) and polyacrylic acid (100%  $\text{COOH}$ ).

The results of the flocculation tests have been presented as cumulative weight percent settled vs pH plots at varying flocculant dosages. These plots were superimposed on the blank curves obtained with no flocculant. Unless otherwise specified, a constant dispersant (Na silicate) concentration of 40 ppm was used. The experimental points are not shown for the blank for the sake of clarity. A perfect separation in these figures would correspond to 100% settling of iron oxide (denoted by solid lines) and no settling of kaolin (dotted line).

Figure 1 illustrates the effect of PAM flocculant (molecular weight  $2.36 \times 10^6$ ) on the settling of a 1:1 synthetic mixture of iron oxide/kaolin. As compared to about 70% settling obtained without flocculant, the addition of a 5 ppm dosage of PAM resulted in almost 100% flocculation of the iron oxide at pH 8. However, kaolinite also flocculated equally well under these conditions and hence, there was no selective separation. In fact, it is observed from figure 1 that the settling of kaolinite closely follows that of iron oxide. Even for pure minerals, similar trends have been observed (figure 1).

In contrast to PAM, PAA brought about almost total flocculation of iron oxide while only less than 10% of kaolin was flocculated (figure 2) during single mineral study. Thus selectivity could be expected. With 1:1 mixtures, the recovery of iron oxide increased with increasing flocculant dosages. In all cases, the recovery of iron

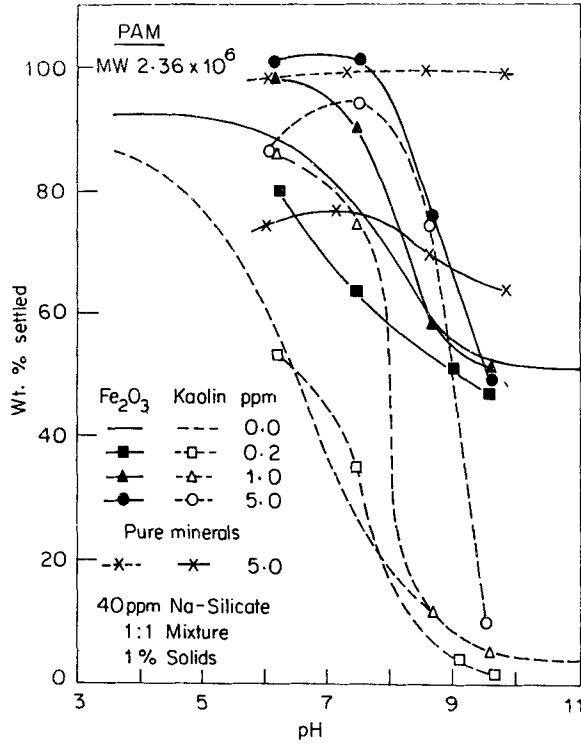


Figure 1. Effect of pH on selectivity at various flocculant dosages: polyacrylamide (PAM).

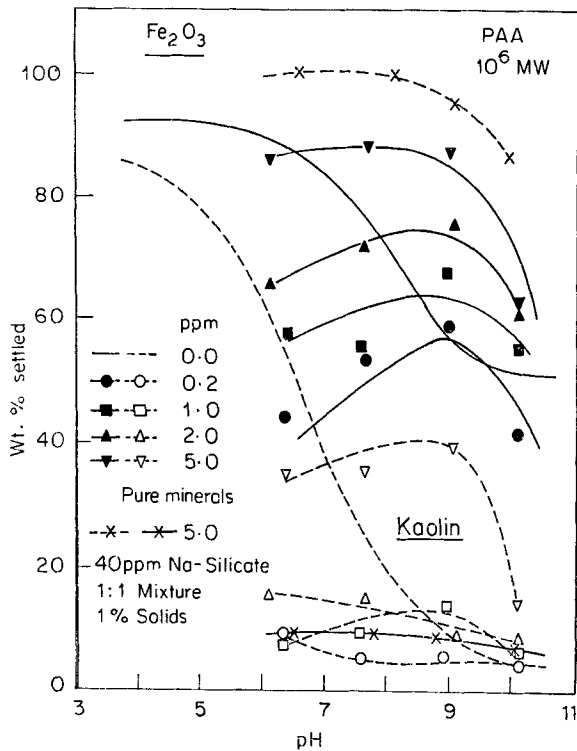


Figure 2. Effect of pH on selectivity at various flocculant dosages: polyacrylic acid (PAA).

oxide decreased above pH 9.0. The kaolin contamination was minimum at lower polymer dosage and at higher dosages where iron oxide recoveries were very high, kaolin contamination was also high. Thus, the pronounced selectivity was not observed.

The results of flocculation tests conducted with a modified polymer, PAMX, containing 8.3% hydroxamate and 23% carboxylate groups are shown in figure 3. As compared to the results shown in figures 1 and 2, flocculation of the iron oxide was enhanced considerably by the use of PAMX. Almost 100% of the iron oxide could be flocculated at pH around 8.5–9.0 and at flocculant dosages in the range 1–5 ppm. Kaolin under similar conditions remained largely dispersed. It is interesting to note that there is a sharp drop in the settling curve for the kaolin at alkaline pH ranges in the presence of PAMX. For instance at a polymer dosage of 5 ppm, kaolin recovery in the settled fraction drops from 80% at pH 7.5 to about 10% at pH 9 whereas iron oxide recovery remains at around 85–90% under similar conditions. The beneficial effect of the polymer is illustrated in figure 4. The settling curves for iron oxide and kaolin with the parent polyacrylamide flocculant (1,1') when compared with (2,2'), the corresponding curves for the modified polymer, demonstrates remarkable enhancement in selectivity. With the modified polymer, the drop in kaolin flocculation occurred at lower values of pH whereas for the iron oxide it occurred relatively at a higher pH values, thus also enhancing the pH range of selective separation.

The introduction of higher percentage of hydroxamate functional groups helps in enhancing the selectivity of separation. Two effects are clearly noticeable in figure 5.

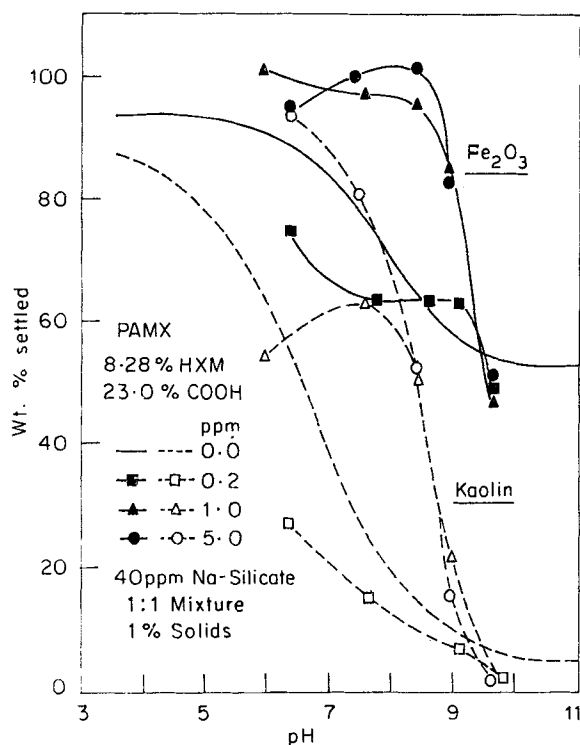


Figure 3. Effect of pH on selectivity at various flocculant dosages: modified polyacrylamide (8.3% hydroxamate).

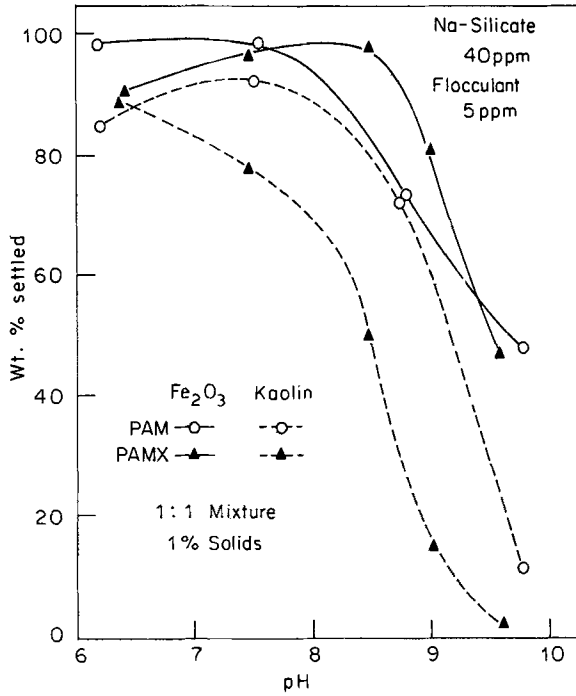


Figure 4. Enhancement of selectivity in separation through modification of polyacrylamide: PAMX (8.3% hydroxamate).

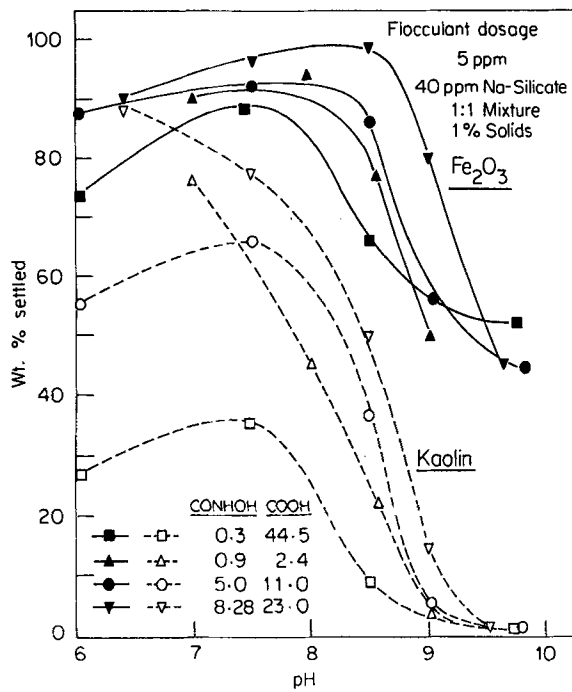


Figure 5. Effect of increasing content of hydroxamate group on the selectivity of separation.



For a polymer having as high as 44.5% of  $-COOH$  groups and almost negligible hydroxamate content, a drop in the iron oxide flocculation occurs at pH around 7.5–8. With 8.3% introduction of hydroxamate groups, on the other hand, and with only 23% of  $-COOH$  groups this drop was shifted to pH around 9. This observation of a progressive shift in flocculation peak towards alkaline pH (when iron oxide is highly negatively charged) in the modified polymers as a result of hydroxamate introduction suggests that these groups are indeed chemisorbing at the interface.

The enhancement in selectivity as a result of the introduction of hydroxamate group in PAM is also illustrated in figure 6 where the recoveries of the individual component settled at pH 9 is shown as a function of flocculant dosage. At lower dosages of PAA and PAM, the iron oxide recoveries are lower. With higher dosages, however, kaolin also flocculated and hence selectivity suffered. In contrast, with the modified polymer the initiations of kaolin flocculation was shifted to relatively higher dosages and thus facilitated higher recovery of iron oxide of acceptable grade. It is also possible to achieve further improvement in recovery at an acceptable grade by increasing the dispersant concentration as shown in the figure.

Thus it could be seen that with introduction of hydroxamate functional groups, the selectivity of separation in iron oxide/kaolin mixtures could be markedly increased. In table 4 the best results obtained with each of the polymers are tabulated along with the corresponding optimum experimental conditions. Without any flocculant, in the presence of 40 ppm of Na-silicate dispersant only, about 50% iron oxide could be recovered at a grade of 91%. With PAM, only a marginal increase in the recovery could be achieved at the cost of precipitous drop in the concentrate grade. With PAA, the recovery was higher but the grade was still not comparable to

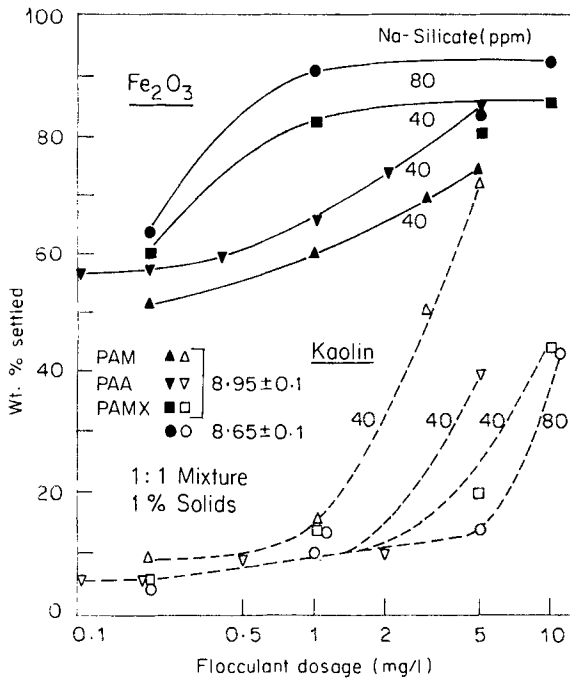


Figure 6. Effect of flocculant dosage on the selectivity.

**Table 4.** Enhancement in selectivity in iron oxide/kaolin system by the introduction of hydroxamate functional groups in polyacrylamide. Feed grade 35% Fe, 1:1 mixture; dispersant 40 mg/l Na-silicate; pulp density 1%.

Polymer	Experimental conditions		Selective flocculation results			
	pH	Flocculant dosage (ppm)	Grade %Fe <sub>2</sub> O <sub>3</sub>	Grade %Fe	Recovery %	S.I***
No flocculant	10	—	91	63.6	50.0	4.35
PAM	9	1	79.3	55.5	57.5	3.01
PAA	9	2	88.0	61.6	74.0	5.06
*PAMX	9.2	5	95.1	66.5	72.0	6.98
	8.6	2**	85.2	59.6	92.0	10.17

\*8.3% – CONHOH and 23% – COOH.

\*\*80 mg/l Na-silicate dispersant.

\*\*\*Selectivity index =  $[(R_{vm}/100 - R_{vm}) (R_{lvm}/100 - R_{lvm})]^{\frac{1}{2}}$ .

$R_{vm}$  and  $R_{lvm}$  are the recoveries of the valuable mineral and the less valuable minerals in the concentrate and tailings respectively.

what was obtained with dispersant alone. In contrast, with modified polymers both the grades and the recovery could be improved. Thus the order of selectivity for Fe<sub>2</sub>O<sub>3</sub>/kaolin separation was observed to be PAMX > PAA > no flocculant > PAM.

## 5. Conclusions

Our results indicate that selective flocculation is possible in iron oxide/kaolin system. A judicious combination of carboxylic acid (–COOH) and hydroxamate (–CONHOH) functional groups is required to achieve optimum recovery and grade. It is important to recognise that both these groups are known to be specific to iron minerals. At alkaline pH where hydroxamates strongly chelate with iron, the presence of –COOH group in the flocculant is likely to prevent the flocculation of kaolin due to repulsive electrical double layer interactions.

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## References

- Arol A I and Iwasaki I 1986 SME Annual Meeting, preprint # 86–12 New Orleans, Louisiana
- Attia Y A, Deason D M and Krishnan S V 1986 *Flocculation in biotechnology and separation systems* (ed.) Y A Attia (Amsterdam: Elsevier) pp. 717–727
- Chatterjee B 1978 *Coord. Chem. Rev.* **26** 281
- Clauss C R A, Appleton E A and Vink J J 1976 *Int. J. Miner. Proc.* **3** 27
- Colombo A F 1977 *Proc 50th Annu. Meet. Min. Section Am. Inst. Min. Met. Eng.* **8** pp. 18
- Dryzmala J and Fuerstenau D W 1981 *Int. J. Miner. Proc.* **8** 267

- Dryzmala J and Fuerstenau D W 1986 *Flocculation in biotechnology and separation systems* (ed.) Y A Attia (Amsterdam: Elsevier) p. 45
- Fuerstenau D W and Pradip 1984 *Reagents in mineral industry* (eds) M J Jones and R Oblatt (London: IMM) p. 161
- Gebhardt J E and Fuerstenau D W 1986 *Miner. Metall. Process.* **3** 164
- Gunari A A and Gundiah S 1981 *Macromol. Chem.* **182** 1
- Gururaj B, Prasad N, Ramachandran T R and Biswas A K 1979 *XIII Proc. Int. Miner. Process. Congr.* (ed.) J. Laskowski (New York: Elsevier) IMPC Warszawa Poland Vol. I Sec II Fine Particle Technology pp 153–182
- Gururaj B, Sharma J P, Baldawa A, Arora S C D, Prasad N and Biswas A K 1983 *J. Miner. Process.* **11** 285
- Hanumantha Rao K, Nayak A, Mahapatra S N and Narasimhan K S 1985a *Mining Engg.* **37** 1312
- Hanumantha Rao K and Narasimhan K S 1985b *Int. J. Miner. Process.* **14** 67
- Iwasaki I and Lai R W 1965 *Trans. AIME* **235** 364
- Kulkarni R A 1981 *Expansion coefficient of polyelectrolyte—A viscosity and light scattering studies of hydrolysed polyacrylamide in solution* Ph.D. thesis, Univ. of Poona, India
- Kulkarni R A and Gundiah S 1984 *Macromol. Chem.* **185** 549
- Maekawa E M, Kousaki T and Koshyima Sen'i and Gakkaushi T 1986 **42** T-460–467 (1986 *Chem. Abstr.* **105** 154896)
- Neilands J B 1966 *Struct. Bonding* **1** 59
- Norris M V 1967 in *Encycl. Ind. Chem. Analy.* (ed.) F D Snell Vol. 4 (New York: Int. Sci. Publ.) p. 160
- Pradip 1987 *Trans. Indian Inst. Met.* **40** 287
- Prasad N and Aswath H S 1983 *Silver Jubilee Workshop on research needs in mineral processing and chemical metallurgy* (ed.) R Mallikarjunan
- Ravishankar S A and Biswas A K 1986 *Trans. Indian Inst. Met.* **39** 75
- Seifter S, Gallop P M, Michaels S and Meilman E 1960 *J. Biol. Chem.* **235** 2613
- Sresty G C, Raja A and Somasundaran P 1978 *Recent developments in separation science*, Vol. 4 p. 93
- Winston A and Kirchner D 1978 *Macromolecules* **11** 597
- Yashpe J, Halpern Y S and Grosswicz N 1960 *Anal. Chem.* **32** 518