

TWO NEW STRUCTURES OF HYDROXAMATE COLLECTORS AND THEIR APPLICATION TO ILMENITE AND WOLFRAMITE FLOTATION

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ABSTRACT

The application of hydroxamic acid as flotation collectors is fast becoming of significant interest for the selective flotation of oxide minerals along with upgrading oxidised based metal ores and minerals. In the hydroxamate molecule, both O and N atoms in the -CONHOH group are identified as coordination atoms in many complexes and their characteristic structure determines the strength of the chelation complex between the hydroxamate and metal ion. The chelating performance of hydroxamates with transition metals including Cu, Ni, Zn, Fe, Cr, Mn and Co, the alkaline-earth metals (Be, Ca) and heavy metal (Pb) has been studied. Cytec has developed and patented a range of alkyl hydroxamates as flotation collectors for oxidised base metal sulphides, metal oxide minerals and precious metals. This paper introduces two new structures of hydroxamate collectors (*Cyclohexyl and 4-tert-butylbenzoyl hydroxamates*) and evaluates their characteristics relative to alkyl and benzoyl hydroxamates. Laboratory small-scale flotation tests were conducted with ilmenite and wolframite. The use of 4-tert-butyl benzoyl hydroxamate resulted in a best flotation performance for ilmenite. A relatively low cyclohexyl hydroxamate dosage was required in the flotation of wolframite to obtain comparable results to the alkyl and benzoyl hydroxamates. It is also shown a significantly improved flotation performance with 4-tert-butyl benzoyl hydroxamate in the flotation of ilmenite plant ore in comparison to the oleic acid or fatty acid collectors typically used for ilmenite flotation.

KEYWORDS

Hydroxamates, Flotation, Collector, Ilmenite, Wolframite

INTRODUCTION

Hydroxamic acid has been reported as an effective collector in small-scale flotation tests for a wide variety of oxide minerals and ores including copper (Lee et al., 1998, Lee et al., 2009), iron (Quast, 2000), tin (Sreenivas and Padmanabhan, 2002; Wu and Zhu, 2006), tungsten (Marinakakis and Kelsall, 1987; Xia et al., 2004), and rare earth metal minerals (Ren et al., 1997; Pradip and Fuerstenau, 1991; Assis et al., 1996; Pavez et al., 1996; Zheng et al., 1996; Chen et al., 2005).

As part of our previous research project, a selected suite of hydroxamic acid collectors including fatty, aromatic and modified hydroxamates (naphthoyl, cyclohexyl, benzoyl, octyl, 4-tert-butyl benzoyl, salicylic hydroxamates) were tested in order to examine their potential for recovery and selectivity of rare earth minerals. In these tests it was shown that the flotation performance with the hydroxamate collectors was significantly better than the phosphoric acid collectors on no slimes removed samples (Brian, et al., 2014; Liuyin, et al., 2014 and unpublished internal technical reports). Furthermore the tests revealed that for most of the hydroxamate reagents tested, their dosage requirements to achieve recoveries at the same levels was less than that for the phosphoric acid collectors. Recovery of both La and Ce was significantly better for the salicylic hydroxamate and that Nb, Y and Zr recovery were favoured by the octyl and benzoyl hydroxamates (Brian, et al., 2014; Liuyin, et al., 2014). Comparison among the hydroxamate collectors showed that the flotation and recovery performance of cyclohexyl (CHH) and 4-tert-butyl benzoyl (TBH) was not as good as the other hydroxamates for rare earth recovery.

CHH is a naphthenic hydroxamic acid. Density Functional Theory (DFT) calculations reveal that in alkaline aqueous solutions, the two oxygen atoms in the CHH molecule possess a greater negative charge relative to the other atoms, and hence become its reactive center. Compared with benzoyl hydroxamate, CHH exhibits higher atomic charge value, HOMO (Highest Occupied Molecular Orbital) energy, bigger dipole moment and binding energy with Ca^{2+} , thus it theoretically has stronger collecting power for the minerals that possibly have bonding configuration of the collectors via Ca^{2+} (Gang Zhao et al 2013). Flotation tests validated that CHH has on the order of 10% greater recovery efficiency for scheelite relative to benzoyl hydroxamate. TBH is a modified benzoyl hydroxamate; the 4-tert-butyl group that is modified on benzoyl changes the charge characteristics. The new structure then could show modestly different flotation characteristics relative to benzoyl hydroxamate. Theoretical calculation on the interaction of CHH (TBH) and Fe^{3+} is underway. In this paper, CHH and TBH as the potential replacement collectors for the fatty acid collector that is currently used to recover ilmenite and wolframite are reported and they are compared with alkyl and benzoyl hydroxamates in small-scale flotation tests.

METHODOLOGY

High purity minerals and small-scale flotation

High purity sample of wolframite was obtained from the Xihua-mountain mine; the samples assayed 71.64% WO_3 , 8.24% Mn and 12.92% Fe. Ilmenite was obtained from the Panzhihua deposit (China) for beneficiation studies. The sample was upgraded by gravity and magnetic separation, the resulting flotation feed of high purity ilmenite contains 47.86% TiO_2 and 35.12% Fe. The two mineral samples were ground separately and screened to collect the -75 microns fraction for the small-scale flotation tests. The flotation tests for high purity minerals were carried out in a XFG type laboratory flotation cell with a volume of 40 mL. In each test one sample (3.0 g) was dispersed in the cell with de-ionized water for 1 min. The pH was adjusted as required and the sample was conditioned for 2 min. Following conditioning the reagents were introduced and the pulp was further conditioned for 3 min, followed by a 5 minute flotation. De-ionized water was used in all tests.

Batch flotation

One ore sample was taken from Panzhihua deposit owned and operated by Panzhihua Iron and Steel Inc. It was ground to 80% passing 200 mesh (75 microns) for testing. Chemical composition of the plant ore is listed in Table 1.

Batch flotation tests were carried out in XFG-C model aeration hanging cell flotation machine. A 0.75 L flotation cell was used for all batch flotation tests. For rougher flotation, approximately 400 mL mill discharge (solid content at around 60%) was added to the cell with a stirring speed set at 1650 rpm, then H₂SO₄ as pH modifier was introduced followed by 2 min of conditioning. After the 2 minute conditioning, the desired dosage of collectors was added followed by another 3 minutes of conditioning. Tap water was used throughout the batch flotation.

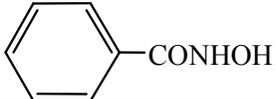
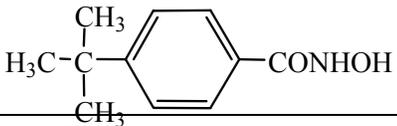
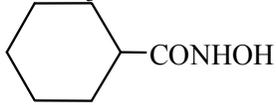
Reagents

CHH, TBH, benzoyl and octyl hydroxamates were all synthesized in Central South University's lab. The chemical structures of them are listed in Table 2. All other reagents, for example H₂SO₄, were purchased from Fisher Scientific.

Table 1 – Panzhihua deposit: Assay of the plant ore mill discharge (P80, 75 um) (data in wt%)

Fe	CaO	TiO ₂	Co	Ni	S	Cu	Al ₂ O ₃	SiO ₂	MgO	P
18.68	6.56	22.09	0.023	0.014	0.13	0.26	7.46	26.23	7.23	0.029

Table 2 – Chemical structures of the hydroxamate collectors used in the flotation tests

Reagents	Chemical structures
Benzoyl Hydroxamate	
TBH	
CHH	
Octyl hydroxamate	CH ₃ -(CH ₂) ₆ -CONHOH

RESULTS AND DISCUSSION

Small-scale flotation of ilmenite

Four hydroxamates listed in Table 2 were employed as collectors in ilmenite flotation tests at dosages of 250 mg/L in the pH range from 2 to 12. MIBC as frother was used as required. Conditioning time (3 min) and flotation time (5 min) was kept constant. The experimental flowsheet is shown in Figure 1 and flotation results are given in Figure 2 and Figure 3.

The results from tests with the four hydroxamate collectors reveal that recovery performance is highest between pH 6 to 10. For example the recovery of ilmenite using TBH decreased from around 90% at neutral pH to less than 20% at pHs less than 4 and greater than 10 (Figure 1). While the maximum ilmenite recovery pH varies between the collectors a similar recovery tendency is indicated; a significant decrease in recovery for ilmenite at high and low pHs. Figure 2 also shows the ilmenite recovery performance in relation to the various collectors. With the same collector dose of 250 mg/L, the highest recovery of ilmenite was reported for TBH (~90%), followed by octyl hydroxamate at ~80%. The performance of CHH is moderate having recovery of about 58% at pH 6. Benzoyl hydroxamate is not so effective for ilmenite having recovery of only ~18% at pH 8. Based on these tests the effectiveness ranking of the four hydroxamates on ilmenite recovery is: TBH>Octyl hydroxamate> CHH > benzoyl hydroxamate.

The effect of collector dosage on ilmenite recovery was investigated at each collector's optimal pulp pH as determined in the preceding testing (Figure 2). The amount of collectors varied from 50 mg/L to 450 mg/L; all other parameters were maintained from the preceding tests. Results on the flotation recovery of ilmenite as a function of hydroxamate dose are shown in Figure 3. Ilmenite recovery increases from 50 mg/L to 150 mg/L for octyl hydroxamate, and to 250 mg/L for TBH and CHH. After these points, the recoveries remain relatively consistent after which increasing the collector dose does not affect the ilmenite recovery. Benzoyl hydroxamate on the other hand shows continuous increase in ilmenite recovery in response to a dose increase. Although the maximum recovery shown in Figure 3 is at around 40%, it seems likely that increasing the collector dose would lead to further ilmenite recovery. This indicates that the dose required to achieve ilmenite recoveries at similar levels to the other three collectors is significantly higher for benzoyl hydroxamate.

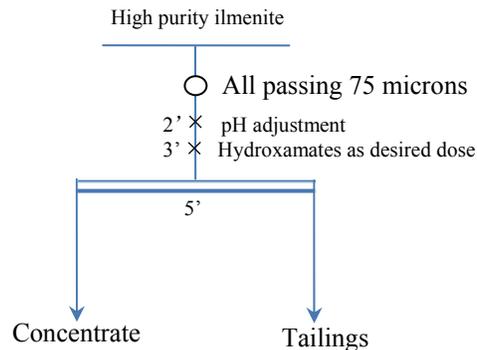


Figure 1 - Simplified flowsheet of small scale rougher flotation of high purity ilmenite

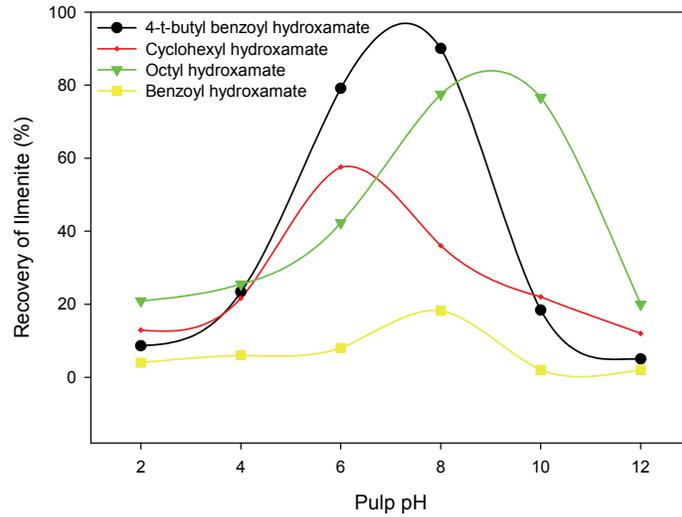


Figure 2 - Effect of pulp pH on the recovery of ilmenite with different hydroxamates as collectors.

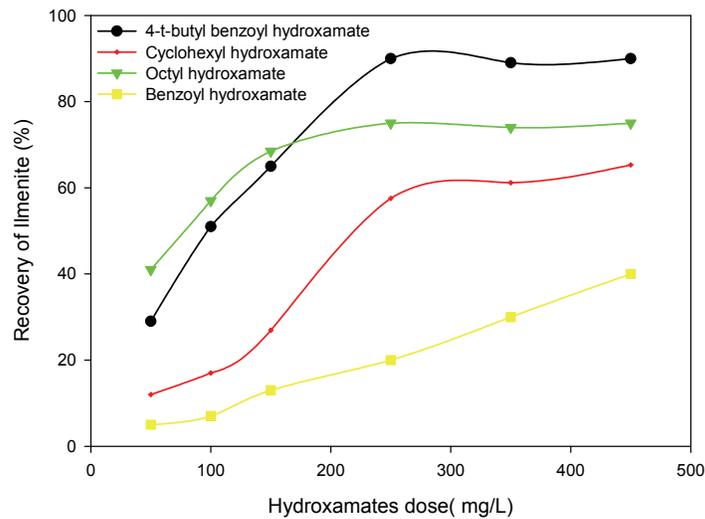


Figure 3 Flotation recovery of ilmenite as a function of the concentration of hydroxamates

Small-scale flotation of wolframite

Small-scale flotation was carried out with a high purity sample of wolframite and the modifier lead nitrate. Figure 4 shows the flotation flowsheet reveals the order of reagent addition, their dosage and the conditioning time after each addition. In the tests with variable pulp pH, the collector dosage was kept at 100mg/L. In the tests with different collector dose the pulp pH was kept at pH 8-8.5.

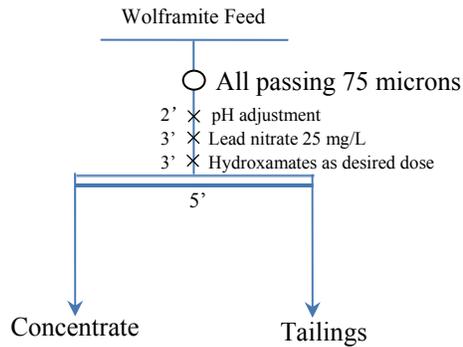


Figure 4 - Simplified flowsheet of small scale rougher flotation of high purity wolframite

Wolframite recovery as a function of pulp pH is shown in Figure 5. The data show that the best wolframite recovery with CHH and benzoyl hydroxamate occurs in the pH range of 8 to 10, whereas for octyl hydroxamate the best recovery occurs between pH 6 and 8. The highest wolframite recovery for CHH, benzoyl hydroxamate and octyl hydroxamate are 92.7%, 63.1% and 77.3% respectively indicating that CHH is the best collector for wolframite recovery among the four investigated.

Figure 6 shows the effect of collector dose on the wolframite recovery. It is obvious that flotation recovery of wolframite is much higher by using cyclohexyl hydroxamate as the collector. At 100 mg/L CHH, wolframite recovery was significantly higher than that observed for octyl and benzoyl hydroxamates, moreover at this dose of CHH the recovery of wolframite was the same or even higher relative to octyl and benzoyl hydroxamates at 200 mg/L. The results indicate that CHH shows a much better flotation performance for wolframite relative to the other two traditional hydroxamates.

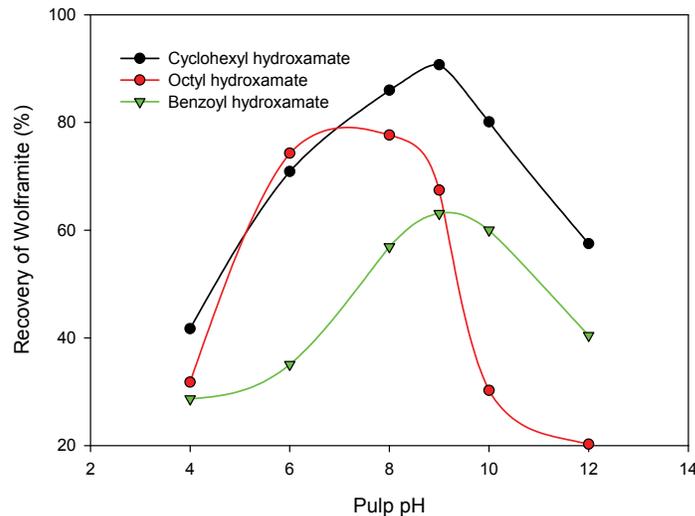


Figure 5 - Effect of pulp pH on the recovery of wolframite with the three hydroxamates as the collector.

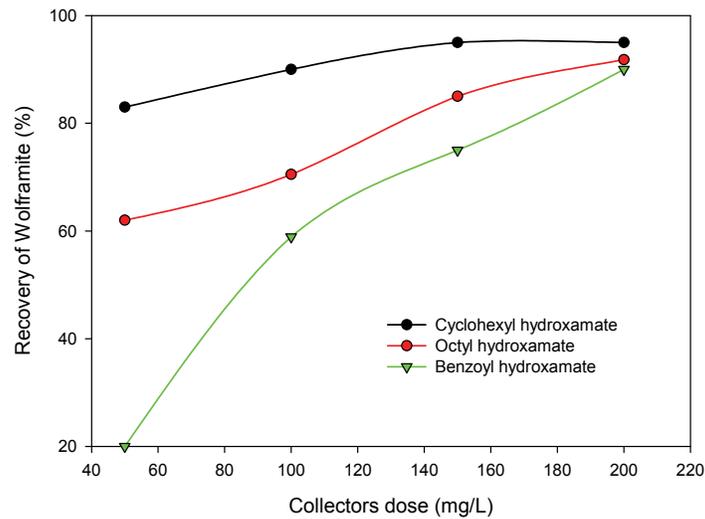
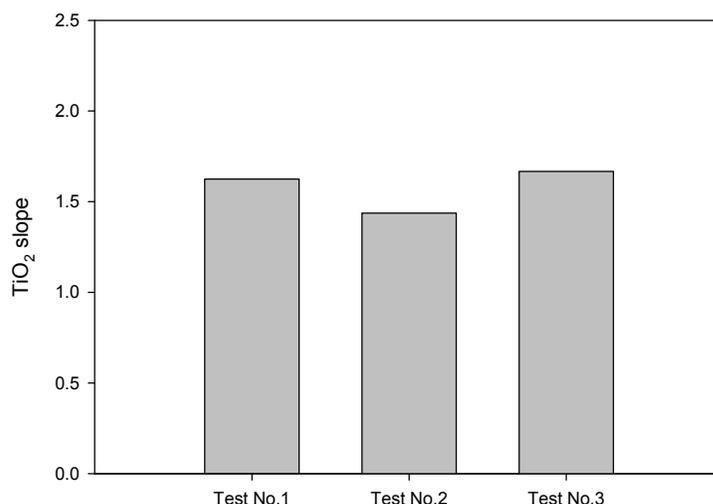


Figure 6 - Flotation recovery of wolframite as a function of the concentration of hydroxamates

Batch-scale flotation of ilmenite plant ore

Batch scale rougher flotation tests were conducted on an ilmenite plant ore sample with hydroxamate collector (TBH) and the traditional fatty acid and oleic acid collectors. Flotation tests were done at ~30% solids and pH of 8.0. Froth was scraped for a total of 5 min. The dosage of each collector is shown in Table 3, which also includes the grade and recovery of TiO_2 for each concentrates and tailings. The results were also calculated for the TiO_2 slope that is the ratio of TiO_2 recovery to mass pull of rougher concentrate (Figure 7). The higher the slope, the better the separation selectivity. As can be seen from Fig.7, separation of TiO_2 from the gangue minerals was achieved for all the flotation tests. Separation efficiency of the test with hydroxamate collector (Test No.1) is almost identical with that using fatty acid as a collector (Test No.3). However, within the 5 min rougher flotation time, more TiO_2 was recovered in test No. 1; over 80% of TiO_2 was recovered in test No.1 whereas only 72% of TiO_2 was recovered in test No.3 (Table 3). In test No.2, with oleic acid as the collector, more solid recovery was achieved relative to the other two tests, resulting in the lowest rougher concentrate TiO_2 grade but still a moderate TiO_2 recovery among the three tests. The tests suggest that TBH could be considered a valid alternative to the oleic acid or fatty acid collectors typically used for ilmenite flotation.

Figure 7 - TiO₂ slope of wolframite flotation testsTable 3 – Comparison of TiO₂ recovery with the new structure of hydroxamate and the anionic collectors that is currently used

Test No.	Reagents	Dose(g/t)	Products	Mass pull	Grade of TiO ₂ (%)	Recovery of TiO ₂ (%)
1	TBH	1500	Con.	51.76	36.07	84.09
			Tals.	48.23	7.30	15.91
			Feed (Calc.)	100.00	22.19	100.00
2	Sodium oleic acid	1500	Con.	54.29	31.29	78.03
			Tals.	45.71	10.48	21.97
			Feed(Calc.)	100.00	21.77	100.00
3	Mix of tall oil and paraffin	1500	Con.	43.33	37.38	72.24
			Tals.	56.67	11.1	27.76
			Feed(Calc.)	100.00	22.66	100.00

CONCLUSIONS

Small scale flotation testing cyclohexyl and 4-tert-butyl benzoyl (CHH and TBH) hydroxamates show significant merit towards the flotation recovery of ilmenite and wolframite in the context of both recovery and dose requirements. In particular a relatively low CHH dose was required in the flotation of wolframite to obtain comparable results to the alkyl and benzoyl hydroxamates. TBH was further tested in the batch flotation in comparison with fatty acid and oleic acid collectors, typically used commercially available reagents. The tests revealed that TBH gave the highest recovery of TiO₂ indicating that TBH may be a valid alternative to oleic acid or fatty acid for wolframite flotation. In companion research we have found that the collecting ability and selectivity of hydroxamates varies distinctly with different minerals. We suggest that more effort be made to link the selectivity and recovery performance of specific

hydroxamate collectors to various minerals with an ultimate goal of designing and developing potentially more effective hydroxamic acid reagents.

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