Hydroxamic Acids as Chelating Mineral Collectors

Ramanathan Natarajan

Abstract Owing to the ability to form coordination complexes with several metal ions, hydroxamic acids have application in different fields such as analytical chemistry, chelation therapy, nuclear fuel reprocessing, solvent extraction, ion exchange and mineral processing. Application of hydroxamic acids as chelating mineral collectors for ore beneficiation is a unique area of their use and has attracted the attention of limited readers working in the relevant area. A review of the use of alkyl and aryl hydroxamic acids in mineral processing is presented. Some basic information on mineral flotation chemistry is provided for the sake of common readers. Adsorption of hydroxamates on several minerals is compared because mostly the mineral flotation studies are preceded with adsorption studies. Usually, hydroxamic acids take the *trans* conformation about the carbonyl carbon and amine nitrogen bond. However, crystal structures of two aryl hydroxamic acids with *cis* conformation are furnished. Extension of QSAR approach and molecular modelling, hitherto known in drug design, is also covered to present them as scientific tools for design of mineral collectors that are more selective.

Keywords Hydroxamic acids · Froth flotation · Mineral collectors · Ore beneficiation

Abbreviations

CMC	Carboxy methyl cellulose
DCS	Dissimilar cluster selection
HCNPHA	*N*-Hydrocinnamoyl-*N*-phenylhydroxylamine
IR	Infrared
MDS	Maximum dissimilarity-based selection
NAnFPHA	*N*-4-Anisoyl-*N*-(4-flurophenyl)hydroxylamine
NAnPHA	*N*-4-Anisoyl-*N*-phenylhydroxylamine

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NBNXHA	*N*-Benzoyl-*N*-(2, 6-dimethylphenyl)hydroxylamine
NBuXHA	*N*-Butanoyl-*N*-(2, 6-dimethylphenyl)hydroxylamine
NMR	Nuclear magnetic resonance
PANEPHA	*N*-Phenylacetyl-*N*-(4-ethylphenyl)hydroxylamine
PANXPHA	*N*-Phenylacetyl-*N*-(2,6-dimethylphenyl)hydroxylamine
PC	Principal component
PCA	Principal component analysis
PCS	Principal component score
QSAR	Quantitative structure-activity relationship
SCS	Simple cluster-based selection
TBP	Tributylphosphate
tBuAPHA	*N*-t-Butylacetyl-*N*-phenylhydroxylamine
TI	Topological index
TMAPHA	*N*-Trimethylacetyl-*N*-phenylhydroxylamine
TMEPHA	*N*-Trimethylacetyl-*N*-(4-ethylphenyl)hydroxylamine

Contents

1 Introduction

Hydroxamic acids are *N*-acyl derivatives of hydroxylamine (NH_2OH) and act as bi-dentate ligands to complex with several metal ions (Fig. 1). Their ability to form stable complexes with transition, lanthanide and actinide metal ions extends their application in different areas such as analytical chemistry, spectral-colorimetric analyses, solvent extraction, ion exchange, and several other fields. A large number of articles including two early reviews in Chemical Reviews published on

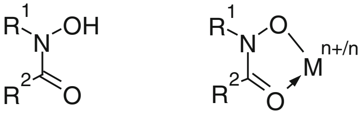


Fig. 1 Generic structures of hydroxamic acids and their metal chelates

the chemistry of hydroxamic acids and their metal chelates highlight the versatility of applications of hydroxamic acids in several fields (Agrawal 1973, 1977, 1979; Agrawal and Tandon 1974; Agrawal and Kapoor 1977; Barocas et al. 1966; Baroncelli and Grossi 1965; Chatterjee 1978; Inoue et al. 2000; Lutwick and Ryan 1954; Natarajan and Nirdosh 2006; Pradip and Fuerstenau 1983, 1985; Shendrikar 1960; Yale 1943; Lipczynska-Kochany 1991; Raymond et al. 1984; Anderegg et al. 1963; Cheng et al. 1982; Majumdar 1972; Verma et al. 1977).

Application of hydroxamic acids extends to fields such as enzyme inhibitors, soil enhancers, fungicides, mutagens, carcinogens, DNA cleavage, artificial metallonucleases, drug delivery systems, malarial research (Ghosh 1997), and analytical chemistry (Brandt 1960). Octyl hydroxamic acid and its salts have also been used in solvent extraction of metals (Vernon and Khorassani 1978; Vernon 1982), and to prevent corrosion of copper (Notoya and Ishikawa 1980). Some naturally occurring hydroxamic acids are involved in microbial iron transport (Neilands 1974), and in the transport and deposition of heavy metals in aquatic metals in aquatic systems (Vuceta and Morgan 1978). Hydroxamate functionalities are also utilised by natural siderophores for the sequestration of iron by fungi in the environment (Raymond et al. 1984; Renshaw et al. 2002a).

Hydroxamic acids form stable coloured complexes with transition metal ions, which form the basis for their usefulness as photometric analytical reagents for the determination of trace metals (Sandell and Onishi 1978). The deep purple or red colour of iron (III) hydroxamate complexes and the violet coloured vanadium (V) complex have been used for the detection of microgram amounts of hydroxamic acids (Agarwal 1973).

Study of interactions of hydroxamic acids with actinides does not just limit it to stability constant measurements of actinide-hydroxamate complexes (Anderegg et al. 1963; Barocas et al. 1966; Baroncelli and Grossi 1965; Maggio et al. 1966; Sinkov and Choppin 2002) but extends its application towards the extraction of metal ions of nuclear interest, such as zirconium, plutonium and other fission products. Furia et al. (1983) explained the role of hydroxamic acid in the retention of fission products, especially ^{95}Zr, by radiolytically degraded tributyl phosphate in dodecane. Dissolution of αFeO(OH), $ThO_2.2H_2O$ and γ-UO3 by hydroxamate and carboxylate ligands was reported by Renshaw et al. (2002b) while solublisation of actinides by hydroxamic acid-based microbial sideraphores was reported by Brainard et al. (1992). Microbial uptake of uranium and plutonium hydroxamates (John et al. 2001; Renshaw et al. 2003), their solvent extraction (Dasaradhi et al. 1997) and actinide sequestration agents (Durbin et al. 1989) are examples of actinide hydroxamate interactions in radiation chemistry. A mixture of branched chain isomers of 13-carbon atoms, neo-tridecano-hydroxamic acid, had been reported as extractants in nuclear fuel processing (Cao et al. 1973, 1974; Grossi 1970; Mannone et al. 1977). Hydroxamic acids have higher coordinating ability with tetravalent actinides such as Np^{4+}, Pu^{4+} than with hexavalent uranium (Taylor et al. 1998). Hence, hydroxamic acids were tested for the stripping of actinides in Purex flowsheets for Advanced Fuel Cycles (Fox et al. 2006; Birkett et al. 2005, 2007; Zilberman et al. 2002; Todd and Wigelund 2006). Formo- and aceto-hydroxamic acids were also found to be redox-active and therefore can be oxidised by metal ions such as Np(VI) (Colston et al. 2000; Chung and Lee 2006). The redox behaviour exhibited by hydroxamic acids had been utilised in controlling Np and Pu in Purex reprocessing systems both by coordination stripping of tetravalent ions from the TBP solvent phase and by selective reduction of Np(VI) to inextractable Np(V) (Birkett et al. 2005). It was also found that at the acidities used in the process, U(VI) ions were not affected by hydroxamic acids and remain solvated in the TBP phase (May et al. 1998). Carrott et al. (2007) reported the distribution coefficients of Pu(IV) in the presence of hydroxamic acids in order to understand the behaviour of hydroxamate complexes of Pu(IV) under Purex process condition. Saha et al. (2002) tested the use of an aryl hydroxamic acid in the solvent extraction of uranium from acid solution with $pH > 3$.

One of the most interesting fields that utilises the ability of hydroxamic acids to form stable coordination compounds with several metal ions is mineral processing. Hydroxamic acids have been tested as mineral collectors in ore beneficiation by froth flotation. This chapter presents the review of studies on testing hydroxamic acids as mineral collectors. A brief outline of froth-flotation process is given below for the benefit of readers and also certain fundamental concepts of froth flotation process are outlined in some other sections. Though this may appear to be trivial for experts it is deemed necessary for general readers.

2 Mineral Concentration by Flotation

Materials mined from ore deposits within the earth's crust are usually a highly heterogeneous mixture of solidified phases. Crushing and grinding operations are used to free the individual phases from their neighbours, that is, to liberate the mineral species and, occasionally, to reduce their size to a range suitable for the intended separation technique. Once mineral species are liberated, an economic recovery of the valuable components contained in the original mixture depends greatly on the application of the most appropriate separation or concentration process (Leja 1982).

The ultimate goal of ore beneficiation is mineral concentration. This is a separation process that is achieved by techniques exploiting physical and physicochemical characteristics such as specific gravity, shape and size, electrical charge, magnetic susceptibility, radioactivity and surface properties (Leja 1982). Separation processes that exploit the possibility of varying the surface characteristics of minerals make such processes more versatile and universal. Froth flotation is one such process that exploits surface properties of minerals and emerged as the most dominant pre-concentration process in mineral processing.

Though it was initially developed to concentrate sulphides of base metals, it has now been expanded to float oxides and oxidised minerals and non-metallic minerals such as phosphates, fluorites and fine coal. When air is passed through aqueous slurry, hydrophobic mineral particles adhere to the air bubbles. The mineralised air bubbles rise to the surface of the slurry. To prevent the mineral falling back into the slurry, a frother is added to the dispersion. The hydrophobised mineral transferred to the froth phase collects on the surface of the slurry as the concentrate and is periodically removed. All valuable minerals are not naturally hydrophobic. However, hydrophobicity can be imparted to minerals by adding suitable surfactants, called collectors, to the mineral suspension. In addition to collectors and frothers, other auxiliary chemicals are also added to modify the pH or the surface properties of the mineral to effect selective separation (Fuerstenau et al. 1985). Thus, mineral concentration by froth flotation is based on the different affinity for water exhibited by mineral surfaces.

Collectors are organic substances whose molecules may accumulate at the mineral–water interface or react with the mineral surface. Collector molecule has polar group (hydrophilic group) and a nonpolar hydrocarbon back bone. At the mineral water interface the polar part of the molecule faces the mineral surface while the non-polar group (the hydrocarbon part) faces the solution. While collectors are added to make specific minerals hydrophobic, other chemicals are also introduced in the system to keep selected components water-wetted. These “modifying agents” are called depressants. Other modifying agents called activators are added to reinforce the action of the given collector. Though, froth flotation is a multiphase heterogeneous system and is very complex involving several variables the solid/liquid interface and the reaction at the interface plays the most important and primary role (Raghavan and Fuerstenau 1976).

2.1 Measurement of Flotation Behaviour

Flotation is a complex process which is further complicated in the case of ore flotation by the presence of a mixture of minerals. In order to elucidate the complex phenomena involved in flotation, flotation behaviour of individual minerals has to be understood. Flotation studies involving pure samples of minerals can only be accomplished with a laboratory flotation device wherein the physical and chemical variables can be closely controlled. The Hallimond tube is the most extensively used laboratory flotation device that fulfilled the purpose. The device was originally designed by Hallimond (1944), modified by Evans and Ewers (1952), and later by Fuerstneau et al. (1957). Hallimond tube allows only a few milligrams of ores to be tested, hence laboratory bench scale flotation devices that use up to 1 kg of ore are available and scaling up results obtained using such systems are more reliable (Wills 1997).

In flotation research, one of the main objectives is to investigate the surface chemistry of minerals and how the adsorption of surface-active agents affects hydrophobicity. Hence, preliminary investigations are usually carried out by studying adsorption of collectors on pure minerals and their flotation using Hallimond tube followed by bench scale flotation using real complex ores.

2.2 Chelating Agents as Mineral Collectors

Chelating agents attach themselves to a mineral surface by chelate formation. The chelating tendency of the compounds is higher for transition metals which are rendered hydrophobic in preference to alkali and alkaline earth metals. The valuable minerals are normally compounds of transition and inner transition metals while the gangue and clay minerals are that of silica, calcium and aluminium. This makes chelating agents to perform better than conventional collectors and has therefore attracted attention as mineral collectors in flotation research. Chelating collectors suffer from two main defects: (i) absence of long hydrocarbon chain in their molecules and (ii) prohibitively high cost. Marabini et al. (1988) and Natarajan and Nirdosh (2006) had demonstrated that the first defect could be overcome by new synthesis methodologies. Once it is established, a particular chelating agent enjoys good selectivity and has promise to be used, its production in bulk would be potentially economic.

2.2.1 Selection of Chelating Mineral Collectors

The molecule of a chelating collector has two parts, viz., the chelating group (hydrophilic part) and the hydrocarbon backbone (hydrophobic part). Though the chelating group can be decided from literature and experiments done in solvent extraction (liquid–liquid extraction) of metals from process and waste solutions, and also from solution chemistry of metal ions and their interaction with various chelating agents, one has to bear in mind that the metal ion under consideration in a mineral being floated is not present as a completely free metal ion. Rather, it is present on the surface of the mineral as a unionised entity with only some of its valencies liberated during grinding. Therefore, a chelating agent, which is a selective extractant for a *free* metal ion, may not be a selective collector for the mineral of the same metal. For example thenoyltrifluoroacetone, a good extractant for uranium ion, was not found to function as a good collector for uranium minerals (Muthusamy et al. 1983, 1985) and the same is true for tributylphosphate (TBP). Marabini (1993) had laid down a guideline to choose the chelating group based on conditional constants. Conditional constants are nothing but modified form of thermodynamic stability constants where concentrations of hydroxylated metal ion and protonated-ligand are used instead of the concentrations of free metal ion and ligand:

$$\text{Stability constant} \log K = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}] \tag{1}$$

Table 1 Effect of pH on hydroxamate adsorption and flotation recovery

Mineral	pH, maximum adsorption	pH optimum flotation recovery	Reference
Haematite	8.5	8.0–9.0	Fuerstenau et al. (1970); Ragavan and Fuerstenau (1975a, b)
γ-MnO_2	9.0	9.0	Natarajan and Fuerstenau (1983)
Rhodonite(Mn, Fe, Cu) Sio_3	–	9.0	Palmer, Gutierrez, Fuerstneau (1973)
Chrysocolla $CuSio_3 \cdot 2H_2O$	–	6.0	Palmer et al. (1973), Fuersenau and Pradip (1984)
Malachite $CuCO_3.Cu(OH)_2$	9.0 also adsorption below 5	Plateau 6 – 10; 9.5 at 10^{-4} M	Lenormand et al. (1979)
Barite	9.0	9.5	Pradip (1987), Fuerstenau et al.(1983)
Calcite	9.5 also below 8	9.5 also below 8	Pradip (1987), Fuerstenau et al. (1982), Pradip and Fuerstenau (1983)
Bastnaesite(Ce, La)FCO_3	Plateau adsorption decreases above 8.5	Plateau 5–9	Pradip (1987), Fuerstenau et al. (1982), Pradip and Fuerstenau (1983)
Hubnerite	9.0	9.0	Bodanov et al. (1974)
Fluorite	8.5	8.5	Bodanov et al. (1974)
Pyrochlore	–	6.0	Bodanov et al. (1974)
Cassiterite	6.2	6.2–9.0	Sreenivas and Padmanabhan (2002)
Sphalerite	9.0	9.0	Natarajan et al. (2010)
Galena	9.0	9.0	Natarajan et al. (2010)
Pyrite	9.0	9.0	Natarajan et al. (2010)
Chalcopyrite	9.0	9.0	Natarajan et al. (2010)

$$\text{Conditional constant} \log K^1 = [\mathrm{ML}]/[\mathrm{M}^1][\mathrm{L}^1] \tag{2}$$

where [M], [L] and [ML] are concentrations of metal ion *M*, ligand *L* and complex *ML*, respectively, while [M^1] and [L^1] are that of hydroxylated metal ion protonated ligands, respectively.

For a ligand *L* to act as a collector for a mineral that contains the cation M_1 and forms the complex M_1L the conditional constant

$$\log K^1_{\mathrm{M1L}} \geq 6 \tag{3}$$

For the same ligand to act as a selective collector for M1 against the cation M2 in another mineral in a poly mineral dispersion, the difference between the conditional constants for the complexes M_1L and M_2L must be

$$\log K^1_{\mathrm{M1L}} - \log K^1_{\mathrm{M2L}} \geq 5 \tag{4}$$

The first criterion characterises the absolute chelating power towards a cation and the second one defines the relative chelating power of the ligand between two cations.

Once the head group is decided on the basis of the above two criteria, the molecular architecture needs to be designed. Among the congeners (the compounds with the same chelating group), the collector efficiency varies according to the peculiarities of the hydrocarbon part and the substituents in it.

3 Adsorption of Hydroxamates on Mineral/Water Interface

Mineral flotation involves adsorption of collector molecules at the mineral/water interface and the understanding of adsorption of a collector on minerals is necessary before testing the flotation response of minerals towards a particular collector. Adsorption studies on hydroxamates, therefore, precede flotation studies. Hydroxamates adsorb at the mineral surface through electrical double layer interaction and the adsorption peaks around pH 9.0 which is close to the $\mathrm{pK_a}$ of several hydroxamic acids and at this pH hydroxamic acids are in the completely dissociated form, i.e. the highly negatively charged form. Flotation recovery of several minerals by hydroxamic acid collectors is maximum around pH 9.0 (Table 1). Pradip (1987) characterised the adsorption isotherms of alkyl hdyroxamates at mineral/water interface with five distinct regions.

1. Chemisorption occurring in horizontal configuration.
2. Saturation adsorption density corresponding to a horizontal monolayer.
3. Chemisorption leading to a vertical monolayer.
4. Saturation adsorption density corresponding to a vertical monolayer.
5. Multilayer adsorption through chain-chain interaction, hydrogen bonding, surface participation and bulk chelation.

The free energies of adsorption $\Delta G^\circ_{\mathrm{ads}}$ can be computed using the well-known Stern–Grahame equation:

Table 2 Standard free energies of adsorption for mineral-hydroxamate systems

Mineral	Constituent cations	Adsorption energies		
		$\Delta G°_{ads}$ kcal/mole	$\Delta H°_{ads}$ kcal/mole	$\Delta S°_{ads}$ Cal/mole° K
Bastnaesite	Ce^{3+}, La^{3+}	−13.6	42.3	190
Pyrolusite	Mn^{2+}, Mn^{4+}	−8.5	4.4	44
Haematite	Fe^{3+}, Fe^{2+}	−7.4	15.0	76
Calcite	Ca^{2+}	−6.4	7.8	48
Barite	Ba^{2+}	−5.7	7.8	46
Cassiterite	Sn^{4+}	−25.0	−36.8	–

$$\frac{\phi}{1-\phi} = \frac{C}{55.5} \exp\left(\frac{\Delta G^{\circ}_{\text{ads}}}{RT}\right) \tag{5}$$

Where ϕ is the fraction of stern plane sites covered with hydroxamate, C is the equilibrium concentration of collector in solution, R is the universal gas constant and T the temperature in Kelvin. Standard free energies of adsorption for different mineral-hydroxamate systems are given in Table 2.

Natarajan et al. (2010) studied the adsorption of an *N*-aryl hydroxamic acid on several minerals and the adsorption isotherms are fitted very well with Langmuir model (Giles et al. 1960) and this confirmed the formation of monolayer, whereas the adsorption of alkyl hydroxamates followed multilayer mechanism. Pradip and Fuerstenau (1983, 1985) proposed that adsorption of hydroxamates on semi soluble minerals such as bastnaesite, barite and calcite occurs via the formation of hydrolyzable cationic species. The metal ions from mineral surface hydrolyse in bulk solution and hydroxycomplexes formed then re-adsorb at the interface assisting adsorption. The surface reaction and bulk precipitation which lead to the formation of multilayers in the case of alkyl hydroxamates appeared to be least probable during the adsorption of aryl hydroxamates on minerals. In the case of alkyl hydroxamates, the hydrocarbon backbone is linear and has much more conformational flexibility to allow multilayer adsorption. The specific adsorption of the aryl hydroxamic acid studied was lower at pH 10.0 than at pH 9.0 and this might be due to hydroxylation of mineral sites at higher OH^- ion concentration. Iron-containing ores were found to have very high specific adsorption and this is due to the high affinity between the iron and hydroxamates. The adsorption on quartz was nearly one-tenth of that on sphalerite and galena which indicated that aryl hydroxamic acids will not float silica minerals. Comparison of specific adsorption of octyl hydroxamates and aryl hydroxamates is given in Table 3.

4 Hydroxamic Acids as Mineral Collectors

The first application of hydroxamic acids in mineral processing appears to have been proposed in 1940, when Popperle (1940) obtained a patent in Germany for the use of hydroxamic acids or their salts as collectors in the flotation of ores.

Table 3 Comparison of specific adsorption of octyl hydroxamate and *N*-phenylcinnamohydroxamate

Adsorbent	Adsorbate	PH	Conc. (mmol/L)	µmol/g	Reference
Haematite (0.5 m^2/g)	Octylhydroxamate	7.5	1.0	5	Raghavan et al. (1975a), Fuerstenau et al. (1970)
Malachite (<3 µm)	Octylhydroxamate	6.6	0.11	113	Lenormand et al. (1979)
Chrysocolla (<75 µm)	Octylhydroxamate	9.0	0.17 1.13	415.0 685.0	(Urbina 1985)
Calcite (2.15 m^2/g)	Octylhydroxamate	9.0	0.6	1.7 (µmol/m^2)	Pradip and Fuerstenau (1983)
Barite (2.4 m^2/g)	Octylhydroxamate	9.0	1.0	1.3 (µmol/m^2)	Pradip and Fuerstenau (1983)
Sphalerite (<75 µm)	HCNPHA	9 10	0.24 0.25	30.5 10.0	Natarajan et al. (2010)
Galena (<75 µm)	HCNPHA	9 10	0.24 0.27	26.9 8.8	
Pyrite (<75 µm)	HCNPHA	9 10	0.54 1.45	145.4 119.5	
Chalcopyrite (<75 µm)	HCNPHA	9 10	0.22 0.22	112.3 90.4	
Quartz (<75 µm)	HCNPHA	9 10	0.20 0.24	2.9 0.7	

However, Peterson et al. (1965) reported the use of potassium octyl hydroxamate as a collector for chrysocolla only after 25 years. Since then, numerous investigations on alkylhydroxamate flotation of minerals have been reported.

Promising flotation results were obtained in the laboratory with minerals such as chrysocolla (Fuerstenau and Pradip 1984; Peterson et al. 1965; Barbaro et al. 1997), malachite (Lenormand et al. 1979), haematite (Fuerstenau et al. 1967, 1970; Ragavan and Fuerstenau 1975a), pyrolusite (Natarajan and Fuerstenau 1983), rhodonite (Palmer et al. 1973), bastnaesite (Pradip 1987) copper oxide (Rule 1982), copper-cobalt oxide ores (Evard and De Cuyper 1975) and oxidised zinc lead ores (Kiersznicki 1981). Hallimond tube microflotation test using alkyl hydroxamic collectors showed that the flotation response of different minerals towards these collectors increase in the order spheen > ilmanite > pyrochlore > pyrolucite > bastnaesite > malachite > calcite > cassiterite > barite. As mentioned in the previous section, maximum flotation recoveries occur at pH 8.0–9.0.

The reagent IM-50 (a mixture of alkyl hydroxamic acids and their salts containing 7–9 carbon atoms) was developed in the Soviet Union and has shown to effectively float wolframite, cassiterite and pyrochlore (Bogdanov et al. 1973), as well as quartz in the presence of iron salts (Koltunova et al. 1978). This reagent was also used for processing tin and rare metal ores (Bogdanov et al. 1977). Hydroxamate collectors with 6–9 carbon atoms are also being used in China for the flotation of copper oxide ores.

Fuerstenau et al. (1970) developed octyl hydroxamate-based collector for the beneficiation of iron ores and showed that the new collectors performed better than the conventional tall oil fatty acids. Pradip and Fuerstenau (1989) tested hydroxamate collectors for the beneficiation of rare earth ores. Hydroxamates were found to be more selective than fatty acids for the separation of bastnaesite, a serium lanthanum fluoro carbonate. This ore from California had calcite, barite and celestite as gangue minerals and was successfully suppressed by using ammonium lignin sulphonate and washing soda. A rare earth ore from China that could not be beneficiated using fatty acids was successfully beneficiated using a hydroxamate reagent scheme (Ref. 26 in Pradip 1987).

Many sulphide minerals of copper have oxidised copper minerals, such as malachite, associated with them. The oxidised copper minerals such as malachite, azurite, cuprite, tenorite and chrysocolla do not respond to the traditional xanthate collectors used to float sulphide minerals of copper and require alternative flotation methods. Generally, the oxide minerals are treated by sulphidisation using reagents such as sodium hydrogen sulphide and then floated with conventional collectors. Hydroxamate collectors were found to float the oxidised copper minerals (Peterson et al. 1965) without sulphidisation. Ausmelt Ltd developed a hydroxamate-based flotation reagent AM 28 for the recovery of copper and gold from sulphide ore bodies that contain oxidised copper ore. Several mines are currently using Ausmelt hydroxamate collectors for the flotation of copper oxide deposits. Hydroxamates are also used in conjunction with xanthate collectors for improved copper recovery (Lee et al. 2009). A copper cobalt oxide ore which failed to float even after sulphidisation was successfully beneficiated using laurohydroxamate collector.

Bogdanov et al. (1973) concentrated wolframite, cassiterite and pyrochlore using IM-50, a hydroxamate-based collector developed in previous USSR. In the flotation of the tungsten minerals higher flotation recoveries were obtained at low acidic pH. A niobium-tantalum ore was preconcentrated by flotation using hydroxamic acids in combination with transformer oil (Ref. 26 in Pradip 1987), Sreenivas and Padmanabhan (2002) studied the surface chemistry and flotation of cassiterite using alkylhydroxamic acid of carbon chain length 8, 10 and 14. Unlike several other studies, octyl hydroxamate adsorption was found to be in an acidic pH indicating the involvement of undissociated hydroxamic acids. Similar phenomenon was reported in the alkyl hydroxamate-ferric oxide-manganese dioxide systems by Raghavan and Fuerstenau (1975b) and Natarajan and Fuerstenau (1983).

Carboxylic acids were conventionally used to remove coloured impurities (TiO_2) from kaolin clay. Yoon and Hilderbrand (1986) developed a hydroxamate-based process for clay flotation and patented the technology. The hydroxamate collector has many advantages over the conventional fatty acids flotation. The amount of hydroxamate collector required is far less than the carboxylic acid (tall oil) and moreover, no frother is needed owing to the frothing properties of hydroxamic acid (Willis et al. 1999). Cytec industry developed a new hydroxamate-based commercial collector under the name S-6493 Promotor and this is currently used by several kaolin industries. Hydroxamates were found to yield higher kaolin recoveries with better grade in reverse flotation of kaolin clay (Yoon et al. 1992; Clifford 1998); Yordan et al. (1993) and Yoon et al. (1992) showed that direct flotation of anatase using hydroxamates gave higher yields with faster flotation kinetics. The clay product obtained using hydroxamates were better in quality and the hydroxamate-based process could be extended to different kinds of kaolin clays. Cytec's S-6493 has been shown to recover oxide copper minerals.

4.1 Arylhydroxamic Acids as Mineral Collectors

Natarajan and Nirdosh (2001a) preferred to synthesise and test *N*-aryl hydroxamic acids with wide structural variations that might affect electronic and steric parameters. Sphalerite (ZnS) is associated with galena (PbS) and in the conventional xanthate flotation of scheme galena is floated first by suppressing sphalerite using NaCN. Suppressed sphalerite is activated by copper sulphate and then floated with potassium amyl xanthate (PAX). Amount of copper sulphate required for activation depends on the grade of the ore and it varies from 500 g to 1 kg per tonne of ore. Copper sulphate is corrosive and expensive. Natarajan and Nirdosh (2006) synthesised several arylhydroxamic acids (Table 4) and tested for the flotation of sphalerite without copper sulphate activation. Though they successfully floated sphalerite without copper sulphate activation, concomitant flotation of iron minerals, pyrite and pryrrhotite, owing to the strong affinity of hydroxamic acids towards iron, the reduced grade of zinc concentrate was obtained. Hamilton et al. (2009) went on to improve the zinc grade by suppressing pyrrhotite using carboxy methyl cellulose (CMC).

4.2 Flotation Kinetics Using Arylhydroxamic Acids

It is generally accepted that froth flotation follows first order kinetics (Wills 1997), and the rate expression therefore leads to

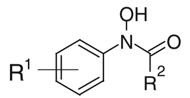
$$\ln \frac{Co}{C_t} = kt \tag{6}$$

On rearrangement, this gives

$$C_0 - C_t = C_0(1 - e^{-kt}) \tag{7}$$

C_0 in the above equation is the initial concentration of the mineral in the ore at time zero, i.e. the *maximum theoretically flotable amount* or the *theoretically maximum possible recovery* of the mineral. However, the complete recovery of the entire mineral present in the ore feed is never achievable because some mineral

Table 4 Structures of hydroxamic acids synthesised and tested with abbreviated names



No.	R^1	R^2	Name	Abbreviation
1	H	n-C_3H7	*N*-Butanoyl-*N*-phenylhydroxylamine	NBuPHA
2	4-C_2H_5	n-C_3H7	*N*-Butanoyl-*N*-(4-ethylphenyl)hydroxylamine	NBuEPHA
3	H	$C(CH_3)_3$	*N*-Trimethylacetyl-*N*-phenylhydroxylamine	TMAPHA
4	H	$CH_2C(CH_3)_3$	*N*-t-butylacetyl-*N*-phenylhydroxylamine	tBuAPHA
5	2,6-diCH_3	n-C_3H7	*N*-Butanoyl-*N*-(2,6-dimethylphenyl)hydroxylamine	NBuXHA
6	2,6-diCH_3	$C(CH_3)_3$	*N*-Trimethylacetyl- *N*-(2,6-dimethylphenyl)hydroxylamine	TMAXHA
7	2,6-diCH_3	$CH_2C(CH_3)$	*N*-t-Butylacetyl-*N*-(2,6-dimethylphenyl)hydroxylamine	tBuAXHA
8	4-C_2H_5	$C(CH_3)_3$	*N*-Trimethylacetyl- *N*-(4-ethylphenyl)hydroxylamine	TMAEPHA
9	H	n-C_5H11	*N*-Hexanoyl-*N*-phenylhydroxylamine	NHexPHA
10	4-Br	n-C_3H7	*N*-Butanoyl-*N*-(4-bromophenyl) hydroxylamine	NBuBPHA
11	H	C_6H_5	*N*-Benzoyl-*N*-phenylhydroxylamine	NBPHA
12	H	4-$CH_3O–C_6H_4$	*N*-4-Anisoyl-*N*-phenylhydroxylamine	NAnPHA
13	H	4$NO_2–C_6H_4$	*N*-(4-Nitrobenzoyl)-*N*-phenylhydroxylamine	NNBPHA
14	4-F	C_6H_5	*N*-Benzoyl-*N*-4-(fluorophenyl)hydroxylamine	NBFPHA
15	2-OCH_3	C_6H_5	*N*-Benzoyl-*N*-(2-methoxyphenyl)hydroxylamine	NBoMPHA
16	4-F	4-$CH_3O–C_6H_4$	*N*-4-Anisoyl-*N*-phenylhydroxylamine	NAnFPHA
17	4-C_2H_5	C_6H_5	*N*-Benzoyl-N-(4-ethylphenyl)hydroxylamine	NBEPHA
18	2,6 -diCH_3	C_6H_5	*N*-Benzoyl-*N*-(2,6-dimethylphenyl)hydroxylamine	NBXHA
19	4-n-C_3H_7	C_6H_5	*N*-Benzoyl-*N*-(4-propylphenyl)hydroxylamine	NBPPHA
20	4-i-C2H_7	C_6H_5	*N*-Benzoyl-*N*-(4-i-propylphenyl)hydroxylamine	NBiPPHA
21	4-t-C_4H_9	C_6H_5	*N*-Benzoyl-N-(4-t-butylphenyl)hydroxylamine	NBtBuPHA
22	H	$C_6H_5CH_2$	*N*-Phenylacetyl-*N*-phenylhydroxylamine	PANPHA
23	H	$C_6H_5CH_2CH_2$	*N*-Hydrocinnamoyl-*N*-phenylhydroxylamine	HCNPHA

(continued)

Table 4 (continued)

No.	R^1	R^2	Name	Abbreviation
24	4-C_2H_5	$C_6H_5CH_2$	*N*-Phenylacetyl-*N*-(4-ethylphenyl)hydroxylamine	PANEPHA
25	4-C_2H_5	$C_6H_5CH_2CH_2$	*N*-Hydrocinnamoyl-*N*-(4-ethylphenyl)hydroxylamine	HCNEPHA
26	2,6-diCH_3	$C_6H_5CH_2$	*N*-Phenylacetyl-*N*-(2,6-dimethylphenyl)hydroxylamine	PANXHA
27	2,6-diCH_3	$C_6H_5CH_2CH_2$	*N*-Hydrocinnamoyl-*N*-(2,6-dimethylphenyl)hydroxylamine	HCNXHA
28	H	CH_2–C(= O)	*N*,*N*-Diphenylmalanodihyroamic acid	MALDHA
29	H	$(CH_2)_2$–C(= O)	*N*,*N*-Diphenysuccinonodihyroamic acid	SUCDHA
30	H	$(CH_2)_3$–C(= O)	*N*,*N*-Diphenylglutarodihyroamic acid	GLUDHA
31	H	$(CH_2)_4$–C(= O)	*N*,*N*-Diphenyladipodihyroamic acid	ADIDHA

particles will remain inaccessible due to their being locked inside other matrices such as quartz or in very coarse particles. Hence, C_0 on the right hand side of Eq. (7) is replaced by the term R_∞, where R_∞ is the *maximum recovery achievable* or the *cumulative recovery at infinite time*. Noting that C_t is the concentration of the mineral at time t during flotation, $C_0 - C_\mathrm{t}$ is therefore equal to the cumulative recovery, R_t, at time t. Thus, Eq. (7) can be rewritten as:

$$R_t = R_\infty (1 - e^{-kt}) \tag{8}$$

A plot of cumulative recovery *versus* time is an asymptotic curve and the cumulative recovery corresponding to the asymptotic portion is the maximum recovery achieved, R_∞. Agar (1985) introduced a time correction factor φ in Eq. (8) for the first order flotation kinetics. The modified rate equation is:

$$R_t = R_\infty (1 - e^{-k(t+\phi)}) \tag{9a}$$

The changes in flotation variables such as airflow rate and collector dosage alter the numerical values of R_∞ and/or k. The effect of an operating variable on flotation characteristics is usually interpreted from the trend observed in the change in the values of these parameters. However, in a batch flotation test, a change in one flotation variable may have opposing effects on the parameters. Since selectivity of a collector for a certain mineral over others depends on the value of R_∞ and k, it becomes difficult to interpret the change in selectivity between a valuable mineral and a gangue mineral. In order to overcome this, Xu (1998) suggested a modified rate constant, K_m, which is a combination of R_∞ and k and is given by the equation:

$$K_m = R_\infty \times k \tag{9b}$$

It is known that for a first order kinetics,

$$\text{rate} = C_t \times k \tag{10}$$

when time $t = 0$, $C = C_0$ (but $C_0 \approx R_\infty$), therefore

$$\text{rate} = R_\infty \times k \tag{11}$$

Hence, the modified rate constant, $K_{m,}$ is the rate of the reaction at time $t = 0$.

The modified rate constants were used by Xu (1998) to define a new quantity, viz., the *selectivity index* (SI) or the relative rate constant of one mineral (M_1) over that of the other mineral (M_2). The selectivity index therefore may be given by the following expression:

$$\mathrm{SI}_{(M_1/M_2)} = \frac{K_m of\, M_1}{K_m of\, M_2} \tag{12}$$

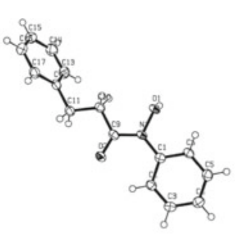
Thus, the selectivity index between a valuable mineral M and a gangue mineral G may be calculated by the equation:

$$SI_{(M/G)} = \frac{K_{m_M}}{K_{m_G}} \tag{13}$$

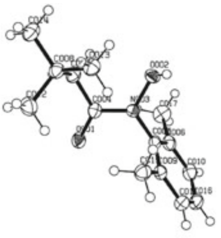
Selectivity index (SI) is the quantification of the selectivity of a collector for a particular mineral over another mineral under the given set of process variables. It is therefore helpful to identify the factors that have positive effects on SI in order to maximise the separation between the two minerals. Effect of substituents on the kinetics of flotation of a copper–nickel ore from Canada by *N*-arylhydroxamic acids was studied. Seven *N*-arylhydroxamic acids were synthesised and tested to float a nickel ore containing pentlandite (4–5 %), chalcopyrite (4–5 %) and pyrrhotite (30–35 %). *N*-phenylacetyl-*N*-(2,6-dimethylphenyl)hydroxylamine (PANXPHA) was found to have highest first order rate constant for the kinetics of flotation of pentlandite and this was higher than that for potassium amyl xanthate, the conventional collector for sphalerite. Amongst the seven *N*-arylhydroxamic acids, PANXHA was also found to have the highest selectivity index for pentlandite. Modified rate constants were linearly related to calculated dissociation constants (pK_a) of the *N*-arylhydroxamic acids used in the study. It may be interesting to note that the compound found to have the highest first order rate constant and the highest selectivity is the one detected to have the *cis* (*E*) conformation even in the solid state.

5 Crystal Structure of Hydroxamic Acids

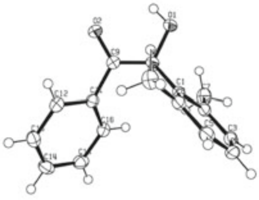
The hydroxamate group has to be in the *cis*(*Z*) conformation to form the chelate ring with metal ions. However, in free hydroxamic acid the C(=O)NHOH group is usually in the trans conformation and this had been confirmed in the case of several aryl-hydroxamic acids by X-ray crystal structure determination (Raman et al. 1984; Bryde and Kjoeller 1993; Andreas et al. 1990; Jaroslav 2000; Urbina 2003; Fuerstenau et al. 2000; David et al. 1996). Brown et al. (1996) studied the conformational behaviour of hydroxamate group using ab initio calculation, NMR and IR spectroscopy, and X-ray crystal structure determination. IR and NMR studies showed the presence *E* and *Z* isomers in chloroform while the *Z* form was found to be the predominate isomer in DMSO. The ab initio calculations indicated the stabilisation of the *cis(Z)* conformation in water by hydrogen bonding with water molecules. On the other hand, the X-ray crystal structure of p-$CH_3C_6H_4N(CH_3)OH$ confirmed the trans conformation of the molecules in the solid state. In spite of being crystallised from the same solvent mixture, two unique hydroxamic acids were identified to have the *cis(E)* form even in the solid state among the six arylhydroxamic acids investigated using single crystal X-ray crystallography. This was a very rare instance where the *cis*(*E*) form was detected even in the solid state. The two *N*-aryhydroxamic acids (NBNXHA and PANXHA) in the *cis* form were found to have 2,6-dimethylphenyl group attached to the nitrogen atom. This group on nitrogen appeared to be bulky enough to restrict the



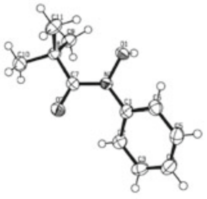
N-hydrocinnamoyl-*N*-phenylhydroxylamine (HCNPHA)



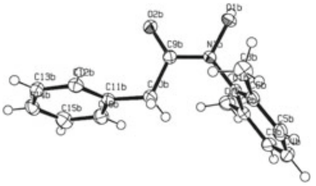
N-tert-butylacetyl-*N*-2,6-dimethylphenylhydroxylamine (tBuNXHA)



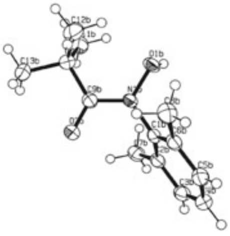
N-Benzoyl-N-2,6dimethylphenylhydroxylamine (NBNXHA)



N-Trimethylacetyl-*N*-phenylhydroxylamine (TMANPHA)



N-Phenylacetyl-*N*-2,6-dimethylphenylhydroxylamine (PANXHA)



N-Trimethylacetyl-*N*-2,6-dimethylphenylhydroxylamine (TMANXA)

Fig. 2 Crystal structures of *N*-aryl hydroxamic acids. PANXHA and NBNXHA in unusual *cis* form

free rotation around the C–N bond provided a sterically bulky group or an anchoring group such as phenyl (C_6H_5-) or benzyl ($C_6H_5CH_2$-) is attached to the carbonyl carbon. The *trans* conformation of TMAXHA clearly indicated that bulky substituents should be present on both the nitrogen and the carbonyl carbon of the hydroxamate group to restrict free rotation and lock the conformation in the *cis* form (Fig. 2).

6 QSAR Approach for the Selection of Hydroxamic Acid Collectors

Though the dependence of efficiency of chelating collectors on their molecular structures had been studied (Nagaraj 1987; Marabini et al. 1988; Marabini 1993; Das et al. 1995; Fuerstenau et al. 1967; Ackerman et al. 1984, 1987, 1999; Nirdosh

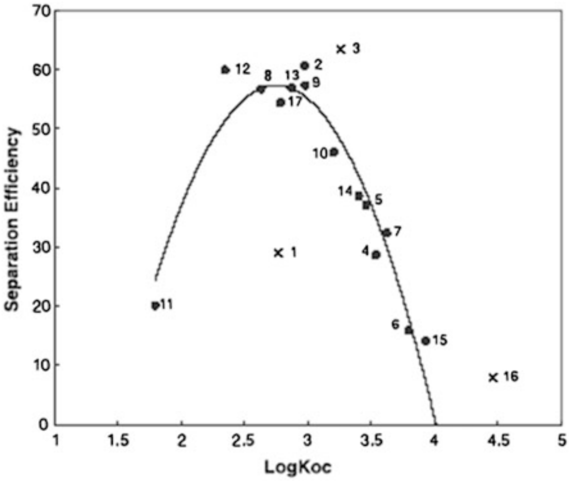


Fig. 3 Quadratic fit of separation efficiency against logKoc (data points 1, 3 and 16 are not included in curve fitting)

et al. 1994; Natarajan and Nirdosh 2001a, 2006), no quantitative treatment had been reported. There is implicit dependence of efficiency of a chelating agent (organic compound) as flotation collector on the molecular architecture, and QSAR is the approach that quantifies this intuitiveness. Natarajan et al. (1999; 2002a, b; 2003) extended the QSAR approach to model the efficiency of chelating collectors. They successfully showed that the separation efficiencies of chelating collectors are amenable to QSAR modelling and topological indices (Natarajan et al. 2001b). Separation efficiencies of aryhydroxamic acids used to float a Canadian zinc ore was modelled (Natarajan and Nirdosh 2003) using electronic parameters, physicochemical properties such as octanol–water partition coefficient (log$P$) and soil–water partition coefficient (logK_{oc}), and geometrical parameters that describe the molecular surface area and volume. Several of the computed parameters were found to fit in a second-order polynomial regression with the separation efficiencies (SE) of the collectors (Fig. 3). Soil–water partition coefficient, logK_{oc} and Connolly solvent-excluded volume gave good correlation for the complete data set. The quadratic fit showed that the collector performance peaks at particular structural feature optimum to give the best flotation response.

6.1 Selection of Hydroxamic Acid Collectors by Molecular Similarity Method

The success in the extension of QSAR modelling approach to flotation chemistry indicated that efficiency of chelating collectors for a given mineral is a function of molecular structure assuming the other conditions (variables) such as pH, particle size, air-flow rate, etc., are constant. Hence, it may be concluded that compounds with similar structure have comparable flotation efficiency for a mineral. In the case of a chelating collector, the molecule can be visualised to consist of two parts, namely the chelating group (polar group) and the hydrocarbon backbone. The polar group can be decided using the difference in stability constants discussed in Sect. 2.2.1 (Marabini 1993). Once the molecular skeleton with a polar group is decided, the combinatorial library of possible structures can be explored for the selection of a small number of compounds for synthesis and testing.

6.1.1 Molecular Dissimilarity/Similarity Clustering

Johnson and Maggiora (1990) showed that molecular similarity clustering was an efficient method in the selection of compounds and prediction of biological and physicochemical properties, and Lajiness (1990) found this method useful for the selection of a small number of compounds from a virtual library (a database of compounds that contain all possible structures) in the process of identification of new therapeutic agents. To create a similarity space for the selection of compounds, an appropriate measure of molecular similarity is needed. Physicochemical properties, topological indices and substructures, called atom-pairs, had been used in constructing structure spaces for selections. Use of experimental data has a very restricted application due to the limitation in their availability for all the chemicals under consideration. Computable properties are always preferred for the purpose.

Let us consider that t numbers of topological indices are calculated for the given set of m structures. The data set is very large, hence the ($t \times m$) data matrix is subjected to data reduction by principal component analysis (PCA). Principal components with Eigenvalues ≥ 1 are extracted. Before performing PCA, the calculated topological indices are transformed into $\log_e(\mathrm{TI} + 1)$. This is necessary because the magnitudes of some topological indices are several times greater than those of the others. Principal Components (PCs) derived from Topological Indices (TIs) are efficient in clustering structurally similar compounds. The similarity space is an n-dimensional space, where n is the number of PCs extracted from TIs and the compounds are clustered based on their structural similarities encoded by the PCs. The principle component scores of the extracted factors are standardised. The standardised scores are used to form similarity spaces by a nonhierarchical cluster analysis. Thus, the m chemicals in the virtual database are classified into a few clusters of related compounds. The clusters are formed around a centre point, the centroid, and have a set radius based on the molecular density around the centroid. The number of clusters to which the chemicals are to be grouped is decided on the basis of the selection method. One or more compounds are selected from the clusters based on the distance from the cluster centre. There are three methods for the selection of chemicals by cluster analysis. They are:

1. Simple cluster-based selection (SCS)
2. Maximum dissimilarity-based selection (MDS)
3. Dissimilar cluster selection (DCS)

In the SCS method, the cluster analysis based on the similarity measures is performed to generate a given number of clusters. One compound can then be chosen from each cluster either randomly or on the basis of the distance from the centroid. In the MDS method, compounds are chosen such that they are maximally different from the compounds already chosen or tested. This can be achieved by ordering the set of compounds in the selection list. In the DCS method, cluster analysis is performed on the dataset to generate $D + S$ clusters where D is the number of compounds decided for testing and S is the number of compounds already tested or selected. Clusters containing screened compounds are then eliminated and one compound from each of the remaining clusters is chosen. The DCS method was found to be superior to the other two methods (Lajiness 1990).

A library of 3,800 *N*-arylhydroxamic acids was created, this being a virtual library of compounds because most of the chemicals were not even synthesised while preparing the database. Ninety-four topological indices were calculated for these 3,800 compounds. Data reduction was performed using Principal Component Analysis (PCA) extracted seven principal components (PCs) and they explained 95 % of the variance. Thus, the 600 compounds were clustered in a seven-dimensaional space. The ten *N*-arylhydroxamic acids selected were synthesised and tested as mineral collectors for two different types of ores. Results of flotation tests indicated that out of the ten aryl hydroxamates tested in the zinc-rougher stage, same four collectors namely HCNPHA, PANEPHA, TMEPHA, tBuAPHA were found to be the top performers for both the ores. The collectors NAnPHA, NAnFPHA,

NBuXHA and TMAPHA did not show any promise in the flotation of sphalerite. Hence, other compounds in the clusters to which each of the four chemicals was a member were not pursued further in testing. HCNPHA was found to give the best results in both the cases and in addition its synthesis was found to give the best percentage yield. Results of the study indicated that molecular similarity-based selection could be used to select a desired number of compounds for synthesis and testing as mineral collectors from a large database. This offers a scientific tool for the selection of compounds and avoids the trial-and-error method and saves considerable amount of laboratory testing as one explores a large structural database by testing a few compounds.

7 Molecular Modelling Approach for Mineral Collector Design

Molecular modelling and docking ligands onto protein molecules are very common tool in drug design. Pradip et al. (2002) extended this approach for the design of mineral collectors. In the molecular modelling approach the geometry of the collector molecule is optimised using quantum chemical calculation. The optimised geometry is docked on to the cluster model of mineral surface generated to represent the cleavage plane of the mineral under consideration. The mineral collector interaction energies are calculated to simulate adsorption of the collector on to the mineral surface. (Pradip et al. 2002) studied octyl hydroxamate-calcium minerals interactions. The theoretical predictions were compared with the results of the laboratory microflotation tests. There was excellent correlation between theoretical prediction and experimental results.

The success of molecular modelling approach in designing mineral collectors and the molecular similarity-based selection of compounds for synthesis and testing offer scientific tools for the designing mineral collectors. A combination of both these computational approaches is expected to make the significant contribution in the design of tailor-made mineral collectors that are better selective than commercially available ones. With the depletion of easy to handle high grade ores it is necessary to find new collector molecules that are selective to effectively separate valuable minerals from low grade ores from complex ore deposits.

8 Conclusion

Xanthate reagent scheme is widely used in the mineral processing industry and is the most studied system over a few decades. Hydroxamate-based reagent schemes are relatively new and most of the research is still to attract the attention of the industry and at present appears to be simple laboratory tests. As more and more of the high grade easy-to-process mineral resources are depleting and complex low grade ores need to be processed, new reagents such as hydroxamate reagents are expected to find more application. Moreover, xanthates are cheaper than hydroxamates and several of the hydroxamic acids are not ready to be used as commercial chemicals. They are specialised reagents and are apparently expensive in the absence of a demand to manufacture in large quantities. Chemical industries such as Cytec started bringing in reagents based on hydroxamates to process oxidised ores either alone or in combination with xanthates. It appears as lot more research has to be carried out to develop hydroxamate-based reagent scheme that includes proper combination of frother, suppressant, activator and other modifiers.

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