# NICKEL AND COBALT ORES: FLOTATION

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# Introduction

Most of the world's nickel is extracted from the mineral pentlandite, (Ni, Fe)<sub>9</sub>S<sub>8</sub>, which frequently occurs in ores containing predominantly pyrrhotite and various non-sulfides, some of which contain magnesium (Table 1). The nickel content in such sulfide ores is generally low (0.2-3%) and varies from place to place in the same deposit. The low nickel content of the present-day nickel sulfide ores renders them unsuitable for either direct smelting or hydrometallurgical extraction, thus requiring beneficiation.

The usual method of nickel extraction from sulfide ores is through the production of nickel matte after enriching the nickel content of the ore. This is commonly carried out by magnetic separation, flotation, or a combination of both after the ore is comminuted to below 200 µm in size. The enrichment depends upon the degree of rejection of the other sulfide and non-sulfide gangue. The maximum grade of nickel achieved by flotation is around 28% Ni.

#### **Problems Associated with Sulfide Mineral Flotation**

The main problem encountered is selectivity of pyrrhotite and also in some cases chalcopyrite during flotation. A clean and satisfactory separation of pentlandite from pyrrhotite by flotation is difficult in practice since pyrrhotite typically contains intergrown inclusions of pentlandite as well as nickel in solid solution. In fact pyrrhotite often contains 0.5-1% Ni that cannot be separated by physical methods. The common occurrence of both monoclinic (magnetic) and the hexagonal (nonmagnetic) forms of pyrrhotite in association with pentlandite also poses problems. Another type of alteration which adversely effects flotation recoveries is that tochilinite has flotation properties similar to that of pyrrhotite. As a consequence it either reports to the flotation tailings, thereby decreasing the nickel recovery, or, if it is effectively floated, a significant amount of pyrrhotite accompanies it, diluting the nickel grade in the concentrate.

There is a distinct difference in silicate mineralogy between types of host rock, which have their own problems with respect to rejection of gangue by flotation. Talc and other naturally hydrophobic magnesia-bearing minerals have a tendency to float with sulfides, resulting in a concentrate exceptionally high in magnesia. The presence of magnesia causes viscosity problems in the slag during smelting. Magnesia also promotes conditions favourable to hetero-coagulation of minerals, especially fine sulfides with coarse gangue minerals, thus leading to nickel loss.

# **Flotation Practice in Nickel Sulfide** Deposits

Nickel sulfide minerals such as pentlandite can, in general, be separated from their gangue by flotation using a thiol group of collectors like xanthates and alkyl dithiophosphates in the presence of variety of activators, depressants and dispersants. Since nickel sulfides contain other sulfides such as pyrrhotite, pentlandite and chalcopyrite, the enrichment of nickel is generally carried out by two methods:

- 1. production of bulk concentrate containing all sulfides together as smelter feed;
- 2. production of bulk chalcopyrite-pentlandite concentrate by preferentially depressing the pyrrhotite followed by selective flotation of chalcopyrite and pentlandite.

Although bulk flotation of all sulfides is relatively simple the presence of pyrrhotite, which contains minor amounts of nickel but substantial amounts of sulfur (Table 2), causes excessive sulfur dioxide emissions during smelting of the concentrate.

Since most of the sulfur contained in the flotation concentrate is emitted from pyrrhotite, the rejection of pyrrhotite is important, especially in Canada, owing to stringent limits imposed on SO<sub>2</sub> emissions from smelters in that country. The pyrrhotite from the Canadian ores in the Sudbury region occurs in two crystallographic forms having distinct characteristics. The monoclinic pyrrhotite, being magnetic, can be partly rejected by magnetic separation, while the hexagonal pyrrhotite is separated by flotation.

Pyrrhotite is known to float poorly in alkaline media; therefore the general practice is to selectively float pentlandite from pyrrhotite, by maintaining a highly alkaline pH with cyanide as depressant and using thiols like xanthates or dithiophosphates as collectors. Although it is possible to reject significant



| Table 1    | Principal | nickel | and | nickeliferous | minerals | ın | nicke |
|------------|-----------|--------|-----|---------------|----------|----|-------|
| sulfide de | posits    |        |     |               |          |    |       |

|  | Formula   | Nickel<br>content (%)                                |
|--|---|--|
| Nickel minerals<br>Primary   |   |  |
| Pentlandite<br>Millerite<br>Heazelwoodite<br>Geradorffite<br>Nickeline<br>Awaruite | (Ni,Fe) <sub>9</sub> S <sub>8</sub><br>NiS<br>Ni <sub>3</sub> S <sub>2</sub><br>(Ni,Co,Fe)AsS<br>NiAs<br>Ni-Fe  | 25–41<br>65<br>73<br>15–35<br>44<br>25–75            |
| <i>Secondary</i><br>Violarite<br>Bravoite<br>Haapalaite<br>Annabergite             | Ni <sub>2</sub> FeS <sub>4</sub><br>(Ni,Fe)S <sub>2</sub><br>4(Fe,Ni)S.3(Mg,Fe)OH <sub>2</sub><br>(Ni,Co) <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> · 8H <sub>2</sub> O | 33–40<br>17–24                                       |
| Nickeliferous min<br>Primary<br>Pyrrhotite<br>Mackinawite<br>Arsenopyrite          | Fe <sub>(1-x)</sub> S<br>(Fe,Ni) <sub>9</sub> S <sub>8</sub><br>FeAsS   | Up to 1.5<br>Up to 9<br>Up to 0.5                    |
| Secondary<br>Pyrite<br>Marcasite<br>Smythite<br>Tochilinite<br>Magnetite           | $\begin{array}{l} {\sf FeS}_2 \\ {\sf FeS}_2 \\ {\sf Fe}_{3,25}{\sf S}_4 \\ {\sf 6Fe}_{0,9}{\sf S}.5({\sf Mg},{\sf Fe})({\sf OH})_2 \\ {\sf Fe}_3{\sf O}_4 \end{array}$     | Up to 12<br>Up to 6<br>Up to 5<br>Up to 5<br>Up to 1 |

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amounts of pyrrhotite in this way, the concomitant pentlandite losses into flotation tailings are highly unsatisfactory, in addition to the problem of water contamination due to cyanide.

A typical example of a nickel sulfide plant operating with highly floatable talcose gangue is at Trojan mine in Zimbabwe. The Zimbabwean sulfide deposits contain very low grades of nickel (0.6%) and copper (0.04–0.4%). The easily floatable non-sulfide minerals dilute the grade of the concentrate and also result in nickel losses into the tailings. This problem can be overcome by using depressants like carboxymethylcellulose (CMC) and guargum derivatives, although their cost accounts for as much as 60% of the reagent cost incurred in the plant.

# **Developments in Flotation**

#### **Flotation of Nickel Sulfide Minerals**

Collectorless flotation It is known that chalcopyrite and pyrrhotite can be floated without collectors at electrode potentials of +400 mV and +50 mVrespectively, and pyrite does not float even at +700 mV. The underlying mechanism causing hydrophobicity, although obscure, is attributed to surface oxidation, formation of elemental sulfur and partial dissolution of mineral surface, leaving a sulfur-rich layer.

Collectorless flotation studies on three lean nickel sulfide ores, from Outokumpu Finnmines Oy (Enonkoski (0.31% Ni and 0.14% Cu), Vammala (0.9% Ni and 0.45% Cu) and Hitura (0.32% Ni and 0.11% Cu)), ground in steel and ceramic mills at a pH range of 3–12 using polypropylene ether as frother revealed interesting details.

The pentlandite, chalcopyrite and pyrrhotite from Enonkoski ore ground in a steel mill floated easily without a collector at low pH values of 3–5 (Figure 1). The floatability of these three minerals was improved when the same ore was ground in a ceramic mill (Figure 2). This suggests that collectorless flotation in acidic pH can be adopted as a lowcost pre-concentration phase to obtain a bulk sulfide concentrate.

Effect of sulfur dioxide It is possible to effectively separate Cu–Ni ores from pyrrhotite gangue in the absence of a collector, but with  $SO_2$  and an effective complexing agent such as diethylenetriamine (DETA) and a frother. The depressant action of  $SO_2$ , which is greatly enhanced in the presence of DETA, does not affect the recovery of chalcopyrite. Figure 3 shows that 93% of chalcopyrite can be recovered in 12 min in the presence of  $SO_2$ , but the co-recovery of 12% pentlandite and 23%

Table 2 Distribution of Ni and S in sulfide ores

| Ore source  | Nickel distribution (%) |            | Sulfur distribution (%) |              |            |  |
|-------------|-------------------------|------------|-------------------------|--------------|------------|--|
|             | Pentlandite             | Pyrrhotite | Pentlandite             | Chalcopyrite | Pyrrhotite |  |
| Sudbury     | 87.0                    | 13.0       | 12.5                    | 9.8          | 77.7       |  |
| Thompson    | 94.8                    | 5.20       | 20.1                    | 1.5          | 78.4       |  |
| Shebandowan | 91.8                    | 8.20       | 16.0                    | 7.6          | 76.4       |  |

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**Figure 1** Effect of pH on collectorless flotation recoveries on Enonkoski noritic ore after grinding in steel mill. (Reprinted from Heiskanen *et al.* (1991) with permission from Elsevier Science.)

pyrrhotite makes the grade unacceptable. The overall recovery of pentlandite and pyrrhotite could be restricted to 4.1% and 2.5% respectively by introducing DETA in combination with SO<sub>2</sub> (Figure 4).

The differential separation of pentlandite and pyrrhotite from the resulting flotation tailings with sodium isobutyl xanthate collector and Dow froth -250 can also be achieved in the presence of SO<sub>2</sub> and DETA. By using 1.4 kg SO<sub>2</sub> per tonne of ore in combination with 300 g DETA per tonne a concentrate with an overall pentlandite recovery of about 89% could be produced, while restricting pyrrhotite recovery to less than 12.5% (Figure 5).

**Problems due to process water** The difficulty of selective depression of pyrrhotite at Canadian plants was found to be due to the process water containing heavy metal ions such as Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ag<sup>2+</sup>, which were causing the inadvertent activation. By using a small amount of DETA the separation effici-



**Figure 2** Effect of pH on collectorless flotation recoveries on Enonkoski noritic ore after grinding in ceramic mill. (Reprinted from Heiskanen *et al.* (1991) with permission from Elsevier Science.)



**Figure 3** Collectorless flotation kinetics after treatment with sulfur dioxide (1.1 kg t<sup>-1</sup> SO<sub>2</sub>; 35 g t<sup>-1</sup> Dow froth -250, pH  $\approx$  9.5). (Reprinted with permission from the Canadian Institute of Mining, Metallurgy and Petroleum.)

ency was greatly improved (Figure 6); however, the depressing effect is more effective when the ore is oxidized.

The activation products formed on pyrrhotite may be sulfides of Ni, Cu and Ag, which are usually insoluble under reducing conditions. When the mineral is oxidized, the activation products convert to oxides, increasing the solubility in the presence of DETA and thus causing its depression.

Effect of pulp potential Pentlandite can be floated selectively from pyrrhotite by maintaining the pulp



**Figure 4** Collectorless flotation kinetics after treatment with sulfur dioxide and DETA (1.1 kg t<sup>-1</sup> SO<sub>2</sub>; 200 g t<sup>-1</sup> DETA; 35 g t<sup>-1</sup> Dow froth -250, pH  $\approx$  9.5). (Reprinted with permission from the Canadian Institute of Mining, Metallurgy and Petroleum.)



**Figure 5** Flotation selectivity in the separation of pentlandite from pyrrhotite using sulfur dioxide and diethylenetriamine with sodium isobutyl xanthate (pH  $\approx$  9.2, 25 g t<sup>-1</sup> Dow froth – 250). (Reprinted with permission from the Canadian Institute of Mining, Metallurgy and Petroleum.)

pH at a sufficiently alkaline value and with minimal quantities of collector. Careful grinding and classification are essential for retrieving the coarse pentlandite while restricting the entry of pyrrhotite into the concentrate. Interestingly, the influence of pulp potential on flotation recovery of pentlandite and pyrrhotite is virtually the same (Figure 7), and the possibility of achieving satisfactory selective flotation from such mineral mixtures by means of differential pulp potential can be ruled out.



**Figure 6** Flotation results obtained with Clarabelle ore from Canada in the presence and absence of DETA, with amyl xanthate collector. (Reprinted from Yoon *et al.* (1995) with permission from Elsevier Science.)



**Figure 7** Influence of pulp potential on the flotation of pyrrhotite with potassium ethyl xanthate at pH 7. (The broken curve shows the corresponding data for pentlandite.) (Reprinted from Senior GD, Shannon LK and Trahar WJ (1994) The flotation of pentlandite from pyrrhotite with particular reference to the effects of particle size. *International Journal of Mineral Processing* 42: 169–190 with permission from Elsevier Science.)

# **Recovery of Valuable Slimes**

#### By High Intensity Conditioning

The recovery of valuable metal being lost in slimes is of paramount importance. It has been estimated that recovering 15% of the metal lost in the less than  $10 \,\mu\text{m}$  fines in Canada would increase revenue by approximately \$100 m.

High intensity conditioning of slimes in the presence of collector and frother substantially improves the flotation kinetics of pentlandite slimes. The floatability of fine particles by high intensity conditioning, however, largely depends on the nature of the ore and the power input per unit volume of pulp treated. Maximum recoveries are obtained at a power input exceeding 1.5 kWh m<sup>-3</sup> of pulp. High intensity conditioning of slurry adopted at the Trojan mill in Zimbabwe has improved nickel recoveries by 2–4%, owing to the increased flotation response of oxidized and tarnished nickel-bearing sulfides.

#### Depression and Activation by Slimy Gangue Minerals

Many hydrophobic silicate minerals such as talc, chlorite, kaolinite and serpentinite activate other minerals by forming slime coatings. It is also known that the serpentine slimes, containing chrysotile and lizardite, form slime coatings on unoxidized pentlandite and such coatings depress nickel flotation. The formation of these slime coatings is directly related to the magnitude and sign of surface charges of the slimes and sulfide particles.

Crysotile is known to depress nickel sulfide more than lizardite. Addition of small amounts of chrysotile to the flotation pulp  $(0.05 \text{ g L}^{-1})$  dramatically decreases pentlandite flotation recovery, from 90% to 5%.

#### **Dispersion of Slime Coatings**

The reagents generally known to modify the slime surface charge and reduce their adverse influence on pentlandite flotation are dextrin, sodium pyrophosphate, sodium silicate, sodium carbonate, guargum and CMC. Among these reagents CMC has been found to be the best, despite the high concentration required (more than  $2 \text{ kg t}^{-1}$ ). CMC treatment of an Australian ore containing a number of magnesium silicate minerals improved the flotation rate of pentlandite when using amyl xanthate as a collector. The carbonate ions derived from soda ash enhanced dispersion in the pulp, while CMC facilitated the removal of slime particles from pentlandite, thereby allowing the xanthate to coat the surface. The pentlandite fines flotation was found to be improved with either soda ash or CMC but the synergistic effect of both proved beneficial for intermediate sizes.

#### **Effect of Saline Water**

The extent of slime coating is related to the zeta potential, being greatest when slime and particles have a high zeta potential of opposite sign. The zeta potential of the particles can be decreased by increasing the concentration of counterions. A highly saline pulp produces a high concentration of counterions, Na<sup>+</sup>, and Cl<sup>-</sup>, which influence the slime dispersion, besides enhancing hydrophobicity due to modification of the hydration layer around the mineral particles and air bubbles.

In the presence of 10% saline solution, fine nickel sulfide flotation is promoted, whereas flotation with 1 kg t<sup>-1</sup> CMC does not result in upgrading the nickel sulfides. Flotation tests on the whole feed and cyclone overflow of a transition ore, from Western Australia, in saline pulp gave better results (Figure 8) than the addition of 1 kg t<sup>-1</sup> of CMC.

#### Separation of Nickel from High Nickel Matte

The separation of chalcocite  $(Cu_2S)$  and heazlewoodite  $(Ni_3S_2)$  from high nickel matte can be



**Figure 8** Comparison of dispersant regimes on nickel recovery from cyclone overflow material with CMC and NaCl. (Reprinted from Wellham *et al.* (1992) with permission from Elsevier Science.)

achieved by maintaining the proper pH and pulp potential while using xanthates as collectors. The flotation recovery of Cu<sub>2</sub>S and Ni<sub>3</sub>S<sub>2</sub> has been studied by adjusting the oxidation–reduction potential of the flotation pulp with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and KMnO<sub>4</sub>. The recovery of Ni<sub>3</sub>S<sub>2</sub> is almost zero either at pH 8.5 where  $E_h > 500 \text{ mV}$  or at pH 11.2 with  $E_h > 400 \text{ mV}$ , whereas the potential has little effect on Cu<sub>2</sub>S at pH 8.5. The depression of Ni<sub>3</sub>S<sub>2</sub> can be improved by employing Ca(ClO)<sub>2</sub>, as modifier of potential, and Ca<sup>2+</sup> ions. As the potential of Ni<sub>3</sub>S<sub>2</sub> is increased, with increase in dosage of Ca(ClO)<sub>2</sub> the recovery decreased, but the potential appears to have little effect on the flotation behaviour of Cu<sub>2</sub>S (Figure 9).



**Figure 9** Flotation recovery of  $Cu_2S$  and  $Ni_3S_2$  and  $E_h$  as a function of  $Ca(CIO)_2$  in the presence of a mixture of butyl xanthate and ethyl xanthate  $(10^{-4} \text{ mol } L^{-1})$ . (Reprinted with permission from International Academic Press.)

# Lateritic Nickel Resources

Lateritic nickel resources are formed when peridotite, an igneous rock comprising predominantly the mineral olivine, which contains around 0.25% Ni, are exposed to prolonged and intense chemical weathering. During such prolonged weathering, the magnesium and silica are leached out of the rock to leave a residue rich in ferric oxide, nickel and other minor constituents such as aluminium and chromium. The type of weathering which dissolves silica and metallic elements from rocks to produce limonite and silicate nickel ores occurs most frequently in tropical climates with a high rainfall, and with decomposing vegetable matter to provide organic acids and carbon dioxide in the ground water.

Lateritic nickel deposits are classified on the basis of differences in the essential make-up of the profiles. The differences between limonitic and silicate minerals influence the methods by which they are treated for nickel recovery.

## **Developments in Laterite Flotation**

Flotation studies on an ore from New Caledonia with a variety of collectors did not give any substantial upgrading with appreciable recoveries (**Table 3**). Laboratory investigations on garnierite samples from the Pomalaa mine, Indonesia, indicated that by using sodium oleate in combination with a chelating reagent like dimethylglyoxime or  $\alpha$ -diphenylglyoxime the flotability of garnierite could be markedly increased at high pH. Between pH 11 and 12 stable nickel chelate complexes are believed to be formed, causing maximum flotability (**Figure 10**). However,

**Table 3** Significant minerals in nickel laterites



**Figure 10** Effect of pH on the floatability of garnierite using dimethylglyoxime (DMGO) or  $\alpha$ -diphenylglyoxime (DPGO) as chelating reagents along with sodium oleate. (Reprinted from Nakahiro Y, Saburi H and Wakamatsu T (1987) Fundamental study on the flotation of garnierite using chelating reagents and anionic collectors. *International Journal of Mineral Processing* 19: 69–76 with permission from Elsevier Science.)

other anionic collectors like mercaptobenzothiazole and sodium diethyldithiocarbamate show no favourable effects on garnierite collection even when the same chelating reagents are used in combination.

### **Treatment of Limonitic Ores**

In India, substantial quantities of nickel-bearing lateritic material containing 0.5% Ni are available at Sukinda, Orissa, which is the country's largest chromite deposit. During chromite mining, nearly 10 t of

| Minerals                 | Formula  | % Ni    |  |
|--------------------------|--|---------|--|
| Periditite rock          |  |         |  |
| Olivine                  | (Mg,Fe,Ni) <sub>2</sub> SiO <sub>4</sub>   | 0.25    |  |
| Orthopyroxene            | (Mg,Fe)SiO <sub>3</sub>  | 0.05    |  |
| Serpentine               | Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>                                 | 0.25    |  |
| Saprolite zone           |  |         |  |
| Nickeliferous serpentine | (Mg,Fe,Ni) <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>                         | 1–10    |  |
| Garnierite               | $(Ni,Mg)_3Si_4O_{10}(OH)_2$  | 10–24   |  |
| Intermediate zone        |  |         |  |
| Nontronite               | (Ca,Na,K) <sub>0.5</sub>   |         |  |
|                          | (Fe <sup>3+</sup> ,Ni,Mg,Al) <sub>4</sub> (Si,Al) <sub>8</sub> O <sub>20</sub> (OH) <sub>4</sub> | 0–5     |  |
| Quartz                   | SiO <sub>2</sub>   | 0       |  |
| Limonite zone            |  |         |  |
| Goethite                 | (Fe,Al,Ni)OOH  | 0.5–1.5 |  |
| Asbolite                 | Mn,Fe,Co,Ni oxide  | 1–10    |  |
|                          |  |         |  |

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**Figure 11** Effect of pH with sodium petroleum sulfonate collector (0.4 kg t<sup>-1</sup>). (Reprinted with permission from Society for Mining, Metallurgy and Exploration, Inc.)

waste overburden, containing on average 0.5% Ni, 0.02% Co and 25% Fe, are currently being rejected for every tonne of chromite mined. The nickel in such waste materials is found to be in association with goethite, which is the predominant iron mineral and tends to become enriched in the fines along with iron.

Flotation of goethite has been attempted to enrich nickel in proportion to iron enrichment. The nickel could be enriched to above 1.1% Ni with around 75% recovery at pH between 3.5 and 5 on a variety of samples studied by using a commercial grade (SPS 430) anionic petroleum sulfonate collector. The flotation response of the lateritic nickel-bearing iron with different collectors and their mixtures can be seen in Figures 11 and 12. The flow chart suggested for enriching nickel to above 1.1% from lean lateritic chromite overburden is given in Figure 13.

The pertinent details concerning the flotation response of a variety of samples drawn from a wide cross-section of the overburden dumps, including scrubbing, are given in Table 4.

# Cobalt

Cobalt is present in many rocks, soils and sea water in very low concentration and exploitable deposits occur only in a few places. As a result cobalt-containing ores are not mined primarily for their cobalt content, but rather cobalt is produced as a by-product, particularly from the production of copper, nickel, silver, gold, lead and zinc. The cobalt minerals which are exploited mostly for their recovery as by-products are given in **Table 5**.

The only beneficiation plant put up exclusively to recover cobalt is in Morocco, treating the complex cobalt-bearing ores from the Bou-Azzer deposit. The principal ores at Bou-Azzer are skutterudite and erythrine. The specific gravity of these cobalt-bearing minerals being high (5.7–6.8), they are recovered first by gravity concentration followed by flotation of the middlings of the gravity circuit and the fines using amyl xanthate collector subsequent to activation with sodium sulfide and copper sulfate. A mixed cobalt concentrate containing 10% Co can be obtained by combination of gravity and flotation from a feed containing 0.9% Co.

Cobaltite can be separated from pyrite, chalcopyrite and pyrrhotite by initial separation of chalcopyrite, followed by an acidic bulk flotation of all the remaining sulfides using amyl xanthate. Pyrite and pyrrhotite are subsequently floated by depressing the cobaltite with monocalcium aryl sulfonate. Another known flotation separation of cobaltite, from a similar ore containing the same type of minerals, is by direct flotation of all the sulfides other than cobaltite at mildly alkaline pH followed by flotation of cobaltite from tailings with ethyl xanthate at acidic pH after activation with copper sulfate.

By utilizing nitrosonaphthol-based collectors, the flotation of two oxide minerals – erythrite  $(Co_3(AsO_4)_2 \cdot 8H_2O)$  and smolyaninovite (Co,Ni,



**Figure 12** (A) Effect of pH with Flotinor<sup>®</sup> P195 collector (0.25 kg t<sup>-1</sup>). (B) Effect of pH with a mixture of SPS 430 and Flotinor<sup>®</sup> P195 (1 : 1 at 0.25 kg t<sup>-1</sup>). (Reprinted with permission from Society for Mining, Metallurgy and Exploration, Inc.)



Figure 13 Flow chart to preconcentrate nickel from lateritic chromite overburden material from Sukinda, India.

 $Ca,Mg)_3(Fe,Al)_2(AsO_4)_4 \cdot 11H_2O)$  – and a sulfide mineral – arsenosulfide cobaltite (CoAsS) – could be improved.

The flotation response of cobaltite (CoAsS) from Mount Cobalt with nitrosonaphthol indicated an optimum response between pH 8 to 9 (Figure 14) whereas its flotation response with xanthates is known to be best at pH 4–4.5.

The flotation results obtained with xanthate and nitrosonaphthol can be seen in Table 6. Nitrosonaphthol collectors are found to be pH-dependent and specific for cobalt-bearing minerals. The availability of cobalt ions on or near the mineral surface may be the determining factor for the selectivity of nitrosonaphthol collectors. Alkyl group attachment on to the naphthalene ring increases the hydrophobicity of the cobalt-bearing minerals on to which these compounds adsorb, thereby increasing the collecting capability of nitrosonaphthol, but at the expense of selectivity.

A combination of xanthates and nitrosonaphthol collectors is suitable for the recovery of cobalt sulfide

| COB assay |        | Flotation f | eed assayª | % Ni expected in | % Ni obtained in | Fe/Ni in flotation |
|-----------|--------|-------------|------------|------------------|------------------|--------------------|
| Ni (%)    | Fe (%) | Ni (%)      | Fe (%)     | product*         | product          | leed               |
| 0.58      | 28.5   | 0.87        | 38.5       | 1.13             | 1.10             | 44.2               |
| 0.40      | 19.0   | 0.82        | 35.7       | 1.15             | 1.08             | 43.5               |
| 0.78      | 28.0   | 1.20        | 42.0       | 1.43             | 1.35             | 35.0               |
| 0.55      | 22.0   | 0.90        | 40.0       | 1.13             | 1.15             | 44.4               |
| 0.57      | 32.0   | 0.78        | 40.6       | 0.96             | 0.91             | 52.0               |
| 0.36      | 14.9   | 0.57        | 23.0       | 1.24             | 1.11             | 40.0               |

Table 4 Flotation results on nickeliferous chromite overburden (COB) materials of Sukinda

 $^a\text{The}$  fines obtained after scrubbing the COB ( - 210  $\mu\text{m}$  size).

<sup>*b*</sup>% Ni expected in product = (% Ni in feed/% Fe in feed)  $\times$  50.

COB, chromite overburden.

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deposits that are partly oxidized, whereas nitrosonaphthol collector alone is effective for oxide cobalt deposits.

# Conclusions

The nickel extraction process is dictated by the mineralogical assemblage of the ore. Pyrrhotite rejection has been of no real importance in many mills treating sulfide ores except in countries having strict restrictions on  $SO_2$  emission. Pyrrhotite rejection from pentlandite is not very satisfactory in the plants adopting differential flotation, but recent investigations indicate the possibility of employing  $SO_2$  and DETA besides adopting starvation flotation. The problems often encountered in sulfide flotation are the fast floating magnesia-bearing minerals and coatings of crysotile and lizardite. Such problems can be addressed successfully by adding soda ash, CMC or sodium chloride. Plants where  $SO_2$  emissions are not

| Table 5 Principal cobalt mineral | ls |
|----------------------------------|----|
|----------------------------------|----|

| Mineral      | Formula   | Cobalt content (%) |  |
|--------------|---|--------------------|--|
| Cattierite   | CoS <sub>2</sub> (pure)   | 47.8               |  |
| Linnaeite    | Co <sub>3</sub> S <sub>4</sub> (pure)                                     | 58.0               |  |
| Siegenite    | (Co,Ni)₃S₄  | 20.4-26.0          |  |
| Carrollite   | (Co <sub>2</sub> Cu)S <sub>4</sub>  | 35.2-36.0          |  |
| Cobaltite    | (Co,Fe)AsS  | 26.0-32.4          |  |
| Safflorite   | (Co,Fe)AsS <sub>2</sub>   | 13–18.6            |  |
| Smaltite     | (Ca,Ni)As <sub>2</sub>  | 21                 |  |
| Glaucodot    | (Co,Fe)AsS  | 12–31.6            |  |
| Skutterudite | (Co,Fe)As <sub>3</sub>  | 10.9–20.9          |  |
| Heterogenite | CoO(OH) (pure)  | 64.1               |  |
| Asbolite     | Со  | 0.5–5.0            |  |
| Erythrite    | (Co,Ni) <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> · 8H <sub>2</sub> O | 18.7–26.3          |  |
| Gersdorffite | (Ni,Co)AsS  | Low                |  |
| Pentlandite  | (Fe,Ni,Co)₀S <sub>8</sub>   | Up to 1.5          |  |
| Pyrite       | (Fe,Ni,Co)S <sub>2</sub>  | Up to 13           |  |

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a problem can adopt collectorless flotation at acidic pH as a cost-effective pre-concentration process. New flotation reagents like nitrosonaphthol can be adopted in circuits containing oxidized sulfide ores.

There seems little prospect of upgrading nickel from oxide ores since the nickel values are finely dispersed. Marginal upgrading is possible by using dioxime collectors. In view of the contemporary technological practices being followed elsewhere in the world and the Ni content of ores utilized by such processes, flotation of limonitic ores with anionic collectors like petroleum sulfonates is likely to play



**Figure 14** Recovery of cobalt from cobaltite-containing sample as a function of pH with 1-nitroso-2-naphthol as collector  $(-105 + 75 \,\mu\text{m})$ . (Reprinted with permission from The Institution for Mining and Metallurgy.)

| Flotation products    | pН   | Collector | Wt (%) | Co (%) | Recovery (%) |
|-----------------------|------|-----------|--------|--------|--------------|
| Rougher concentrate   | 8.2  | NN        | 19.0   | 16.16  | 88.7         |
| Scavenger concentrate | 8.5  | BNN       | 18.6   | 1.69   | 9.0          |
| Scavenger tailing     |      |           | 62.4   | 0.13   | 2.20         |
| Calculated head       |      |           |        | 3.47   |              |
| Rougher concentrate   | 4.5  | SEX       | 9.0    | 30.74  | 82.6         |
| Scavenger concentrate | 4.4  | PAX       | 1.80   | 19.68  | 10.5         |
| Scavenger tailing     |      |           | 89.2   | 0.26   | 6.9          |
| Calculated head       |      |           |        | 3.35   |              |
| Rougher concentrate   | 4.20 | PAX       | 9.50   | 31.13  | 96.4         |
| Scavenger concentrate | 8.5  | NN        | 2.70   | 3.22   | 2.8          |
| Scavenger tailing     |      |           | 87.8   | 0.03   | 0.8          |
| Calculated head       |      |           |        | 3.09   |              |

 Table 6
 Comparison of flotation results of Mount Cobalt sulfarsenide cobalt-mineralized sample with nitrosonaphthols and xanthates

NN, 1-nitroso-2-naphthol; BNN, tert-butyl-1-nitroso-2-naphthol; SEX, sodium ethyl xanthate; PAX, potassium amyl xanthate. Conditioning time, 20 min; flotation time, 5 min; collector concentration,  $5 \times 10^{-4}$  M; frother, MIBC; % solids, 10; feed, 100% – 105  $\mu$ m. (Reprinted with permission from The Institution for Mining and Metallurgy.)

a vital role in raising the nickel content to above 1.1% from lean limonitic deposits abundantly available in various tropical zones. Processing such flotation concentrate by hydrometallurgical routes needs to be explored.

Cobalt minerals are generally recovered as byproducts during the extraction of zinc, copper, nickel, silver etc. Flotation of cobalt sulfide ores can be best achieved at acidic pH ( $\sim 4$ ) with xanthate collectors and at pH of about 7.5 for oxide ores with nitrosonaphthol chelating reagents, while their mixture is recommended for oxidized sulfide ores.

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