

ROLE OF IMPURITIES IN SOLVENT EXTRACTION-ELECTROWINNING OF COPPER AND NICKEL FOR THE PROCESSING OF SEA NODULES

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ABSTRACT

During the leaching of roasted nodules from Indian Ocean the soluble amine species of iron, manganese and zinc along with valuable metals such as Cu, Ni and Co enter the ammoniacal solution. Even after the purification step, the metal impurities in small amounts remained in the leach solution. In metal separation using LIX 64N, iron and manganese found their way in the nickel and copper electrolytes. Depending on the feed pH of the nickel spent electrolyte, the selective nickel stripping could be achieved with minimum contamination of copper. A flow sheet based on co-extraction-selective stripping has been developed to process the ammoniacal leach liquor of Indian Ocean nodules. While running the continuous SX-EW circuit, the build-up of metallics (Fe and Mn) and organic impurities in the nickel electrolyte was observed which affected the deposition. The cut-off impurity level in electrolyte for nickel winning was determined as : 0.175 Kg/m³ Mn, 0.010 Kg/m³ Fe and 20 ppm organic reagent. A purification scheme for nickel bleed stream was developed to recycle the electrolyte back to SE-EW circuit. Copper being a more noble metal than nickel, can usually tolerate higher level of impurities. Organic levels of less than 100 ppm in the copper electrolyte produced good sheet deposit. The results showed the possibility of producing electrolytic grade copper and nickel metals of 99.94% and 99.8% purity.

INTRODUCTION

Ammonia leaching technology is considered advantageous for the processing of sulphidic and oxidic ores of important ferrous metals because of selective dissolution of some of these metals leaving iron and manganese in the residue. The process initially developed by Caron¹ for exploiting sulphidic nickel ores^{2,3} has been suitably adopted for the leaching of polymetallic ocean nodules⁴⁻⁶. Copper, nickel, iron and zinc exist as stable soluble amine complexes during the leaching of sea nodules. Small amounts of metallic impurities such as iron and manganese are invariably present in the leach liquor depending on the conditions of leaching^{7,8}. This calls for incorporating purification steps^{9,10} to remove these impurities. The presence of even a small amount (in ppm level) of these metallic impurities causes serious problem¹¹⁻¹⁴ when the leach liquor is subjected to solvent extraction for the separation of copper, nickel and cobalt and subsequent recovery of these metals by electrowinning. Similarly, the organic droplets entrained in the electrolytes during the solvent extraction-leaching step, are reported to affect the quality of metal products and purity in the electro-winning¹⁵⁻¹⁷. It was therefore, considered worthwhile to study the role of these impurities-metallics (Fe & Mn) as well as organic

introduced in solvent extraction step, on the extraction-separation of copper, nickel and cobalt from the ammoniacal leach liquor of Indian Ocean nodules by SX-EW route.

2. EXPERIMENTAL

Polymetallic Ocean nodules, collected by National Institute of Oceanography, Goa, from Central Indian Ocean basin were air dried, crushed and ground to -150 μ m. The powder was mixed with fuel oil and pelletised in a disc pelletiser. The dry pellets were reductive-roasted in a vertical retort furnace and the calcine was leached in ammoniacal-ammonium carbonate solution to dissolve copper, nickel, cobalt and zinc along with small amounts of manganese and iron. Leaching was carried out while passing air in the slurry in lock-cycle mode¹⁸ to enrich the metal content in solution. The clarified leach liquor was mixed with di-ammonium hydrogen orthophosphate and sufficiently aerated to remove manganese and iron¹⁹. The solution was finally filtered and used for metal separation and recovery by solvent extraction-electrowinning method.

Separation of nickel, copper and cobalt from the leach liquor was carried out in a mixer-settler unit using 25%

LIX. 64N in kerosene. Metallic impurities viz., iron, manganese and zinc were analysed in leach feed and raffinate. The mixer-settler unit was operated in conjunction with electrowinning of nickel and copper for specific duration while recycling the streams. Due to the recycling of nickel and copper spent electrolytes for metal stripping, the effect of build-up of impurities was examined. The building up of the impurities were periodically analysed and its effect on deposit quality, current efficiency etc., studied. The entrained organic in the electrolytes (due to mixing in the solvent extraction process) was allowed to enter the EW bath to study its role on deposit character. The levels of organic in the electrolytes were controlled by adjusting the agitation rate in the mixer, providing extra retention of the exit pregnant electrolyte and even aeration.

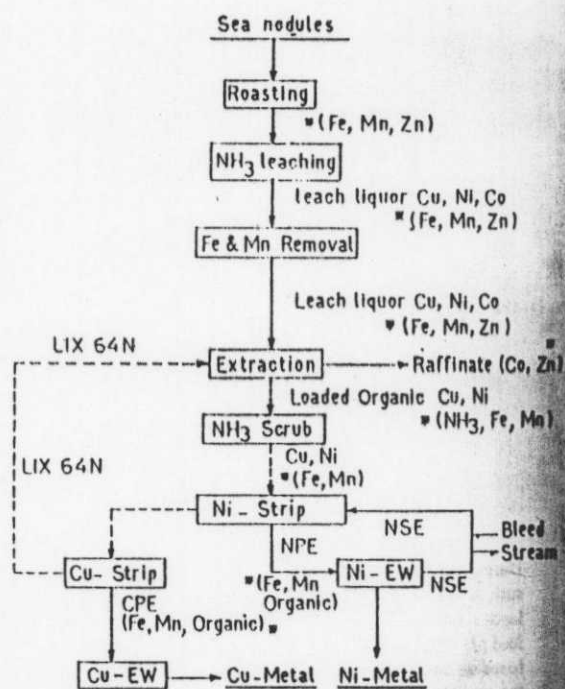
Bleed stream requirements of nickel and copper circuits were worked out depending on the cut-off impurity level. Nickel bleed stream was purified with respect to iron and manganese by oxidation and recycled back to main stream for recovery. Copper bleed stream was also processed by decopperisation, pH adjustment and made alkaline by the addition of ammonia. The ammoniacal solution of copper and nickel could be treated by LIX64N to extract the metals and processed along with the main stream.

The metals in solution were analysed using an Atomic Absorption Spectrophotometer. Ammonia and carbon dioxide were analysed by titrimetry. All the reagents used were of commercial grade chemicals except those for chemical analysis which were AnalaR grade.

3. RESULTS AND DISCUSSION

3.1 Metallic Impurities in Leach Solution

In the processing of sea nodules by roast-leach route, the reduction is carried out at 700°C to selectively reduce⁵ the host lattice of iron (goethite/hydrogoethite) and manganese (todorokite/birnessite) to their lower oxides and oxides of copper, nickel, cobalt and zinc to their metallic states. Yet, certain degree of metallisation of iron takes place (Fig.1). Thus, the metallised iron and zinc become the part of leach liquor along with some amount of manganese. A look at Table-1 shows the presence of different species²⁰ in the ammoniacal-ammonium carbonate solution in the pH range 9-9.5. In the leaching of roasted product air sparging is incorporated to enhance the rate of dissolution which also helps in precipitation of dissolved iron and manganese species due to increase in redox potential (Table-1). However, some amounts of the two metals remain in the



■ - Impurities, CPE & NPE - Cu & Ni Pregnant Electrolytes
CSE & NSE - Cu & Ni Spent Electrolytes

Fig.1 : Flow sheet for separation of metals by SX-EW

leach solution. Zinc forms a stable tetrammine complex and makes a part of the leach solution along with stable

Table-1

METAL SPECIES AVAILABLE IN THE AMMONIACAL-AMMONIUM CARBONATE LEACH SOLUTION

Predominant species in 9-9.5 pH range

| Metals | Species at different Eh | | |
|--------|-------------------------|-------------------|-------------------|
| | -0.9.50V | 0.25V | 0.75V |
| Cu | $Cu(NH_3)_4^{2+}$ | $Cu(NH_3)_4^{2+}$ | $Cu(NH_3)_4^{2+}$ |
| Mo | $Ni(NH_3)_6^{2+}$ | $Ni(NH_3)_6^{2+}$ | $Ni(NH_3)_6^{2+}$ |
| Co | $Co(NH_3)_6^{2+}$ | $Ni(NH_3)_6^{2+}$ | $Ni(NH_3)_6^{2+}$ |
| Zn | $Zn(NH_3)_4^{2+}$ | $Zn(NH_3)_4^{2+}$ | $Zn(NH_3)_4^{2+}$ |
| Fe | $Fe(NH_3)_4^{2+}$ | FeO.OH | FeO.OH |
| Mn | $Mn(NH_3)_4^{2+}$ | Mn_2O_3 | MnO_2 |

amine complexes of copper, nickel and cobalt. Table-2 gives the composition of the leach liquor obtained in processing of Indian Ocean nodules by roast-leach route. In

Table-2

COMPOSITION OF LEACH LIQUOR OF SEA NODULES

| Before purification(Kg/m ³) | After purification (Kg/m ³) |
|---|---|
| 1.82 | 1.82 |
| 2.075 | 2.07 |
| 0.154 | 0.15 |
| 0.01 | 0.003 |
| 0.15 | 0.075 |
| 0.10 | 0.10 |
| 80.0 | 76.5 |
| 56.6 | 54.0 |

to reduce the levels of iron and manganese in the leach liquor, an aeration step was introduced while adding di-ammonium hydrogen orthophosphate equivalent to four times the stoichiometric requirement for Mn. Typical results of iron and manganese precipitation in a batch operation of 200 L solution through aeration at a rate of 2 L/min for 6 hours are shown in Table-2. At this stage some 2.6% of cobalt was observed with decrease in ammonia level which came down to 76.5 g/L from 80 g/L present before purification.

Impurities in Metal Separation and Recovery

The purified leach liquor contained 0.003 Kg/m³ Fe, 0.075 Kg/m³ Mn and 0.1 Kg/m³ Zn, which was subjected to metal separation by solvent extraction (SX) using LIX64N. Fig. 1 shows the scheme of metal separation by SX and recovery of metal by electrowinning, and also depicts the flow of impurities. It is apparent that iron and manganese were also loaded on the organic solvent along with small amount of ammonia (2.5 g/L) due to the coextraction of copper and nickel. Behaviour of impurities in counter-current extraction in mixer-settler is given in Fig.2. Iron was totally extracted in first stage along with substantial extraction (85.3%) of copper. In the second stage raffinate, the level of

manganese dropped to 0.001 Kg/m³. Thereafter, there was no change in manganese extraction. As regards copper, the first stage was very effective with 99% extraction. Whereas for nickel the extraction level was 54.6% and 43.2% for stage 1 and 2 respectively. In four stages copper and nickel extraction attained optimum level. It may be mentioned that total zinc remained with cobalt in the raffinate.

Leach feed = 4.5 l/h, O/A = 1.66

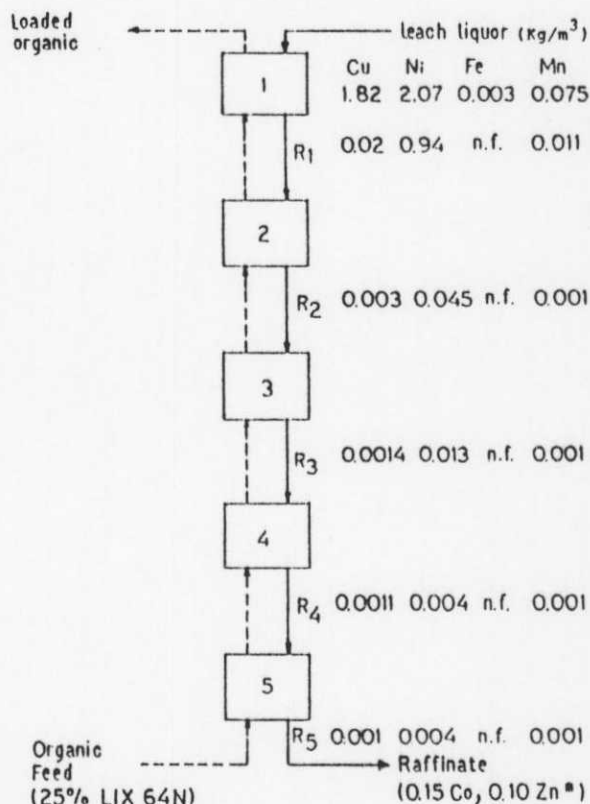


Fig.2 : Behaviour of impurities in counter-current extraction.

Ammonia scrubbing was carried out separately using ammonium bicarbonate and dilute sulphuric acid in two stages each at O/A 1. Removal of ammonia from the loaded organic phase prior to nickel stripping was considered essential to avoid its entry to the nickel electrolyte which could lead to precipitation of double salt of nickel and ammonium sulphate.

In order to achieve selectivity during nickel stripping from the loaded organic phase, effect of aqueous feed pH was examined as shown in Fig.3. At 1.4 pH, almost total nickel stripping was obtained, but the solution was contaminated with as high as 0.30 Kg/m³ Cu. At 1.7 pH the unstripped nickel in the organic phase was found to be 0.12 Kg/m³

with minimum copper contamination (0.04 Kg/m^3). Still higher pH resulted in higher unstripped nickel. Thus, nickel stripping was found to be selective when aqueous

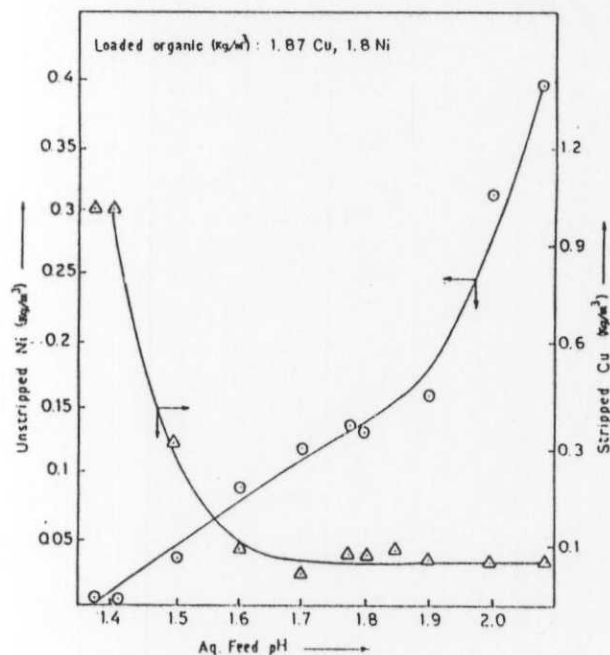


Fig. 3 : Effect of pH on nickel stripping from loaded organic.

feed pH had a value of 1.7 at O/A : 1. As regards copper contamination of nickel electrolyte, it is reported¹² that copper level beyond 0.005 Kg/m^3 will be deleterious for Ni-EW. As such, copper impurity from nickel electrolyte was removed¹⁹ to the desired level by extracting it with a stream of 10% LIX64N in kerosene at O/A 1. The pH (~2.2) of the nickel pregnant solution encountered in the system is considered ideal for copper removal by solvent extraction without extracting nickel. As discussed above, the unstripped nickel entered the copper electrolyte during copper stripping. Entrained organic droplets in the stripping step accompany the nickel and copper electrolytes as another impurity affecting the electrodeposition.

The nickel pregnant electrolyte obtained after copper removal was found to be contaminated with metallic (Fe and Mn) and organic impurities. In a long duration trial run when the electrolyte was recycled in a closed loop of nickel stripping - electrowinning, build-up of the impurities was observed thereby affecting the deposit character. The iron and manganese were carried through the solvent from the leach liquor and a part of it joined nickel electrolyte.

Data given in Table-3 show the effect of metallic impurities on the type of deposit, purity of metal and energy consumption of 8-10 h electrowinning. It may be seen that good sheet deposit with satisfactory energy requirement (3.65 kWh/kg) was obtained upto Fe and Mn levels of 0.004 and 0.175 Kg/m^3 respectively in electrolyte. The deposited nickel cracked at Fe and Mn concentrations of

Table-3

EFFECT OF METALLIC IMPURITIES (Fe & Mn) IN NICKEL ELECTROWINNING

Ni electrolyte feed : 70 Kg/m^3 Ni, 0.004 Kg/m^3 Cu, 2.3 pH

| Sl. No. | Electrolyte feed (Kg/m^3) | Deposit character (%) | Purity of metal (%) | Carbon in metal | Energy consumption (kWh/Kg) |
|---------|--------------------------------------|-----------------------|---------------------|-----------------|--|
| 1. | 0.001 Fe 0.010 Mn | (B) | 99.77 | 0.026 | 3.55 |
| 2. | 0.004 Fe 0.175 Mn | (A) | 99.68 | 0.062 | 3.65 |
| 3. | 0.013 Fe 0.225 Mn | (C) | 99.60 | 0.073 | 3.9 |
| 4. | 0.005 Fe 0.170 Mn | (B) | 99.70 | 0.053 | 3.67 |

(A) Adherent sheet deposit
(B) Bright adherent sheet deposit
(C) Cracked deposit with peeling

0.013 and 0.225 Kg/m^3 respectively with corresponding energy consumption of 3.9 kWh/Kg . Prior to this stage, electrolyte bleed-off was required to control the metallic impurities for getting proper cell operation, improving metal purity and conserving energy.

Table-4 summarised the data on effect of metallic impurities (Fe and Mn) on copper electrowinning in continuous SX-EW runs while recycling the electrolyte. The increase in iron and manganese from $0.031-0.17 \text{ Kg/m}^3$ and $0.002-0.17 \text{ Kg/m}^3$ respectively had no effect on deposit character, as, bright sheets were obtained under above conditions. Copper being more noble than nickel had no change in purity (99.92-99.95%) including carbon content (0.03-0.06%) even at 5.0 Kg/m^3 concentration and energy consumption ($2.08-2.20 \text{ kWh/Kg}$).

in the winning. Also 5.0 Kg/m³ nickel concentration in the copper electrolyte did not affect the copper deposits. It is reported that copper winning is not sensitive to lower amount of metallic impurities and their allowable limits¹² are 20 Kg/m³ Ni, 2 Kg/m³ Fe and 1-2 Kg/m³ Mn.

Table-4

EFFECT OF METALLIC IMPURITIES (Fe & Mn) IN COPPER ELECTROWINNING

Copper electrolyte : 40 Kg/m³ Cu, 5.0 Kg/m³ Ni, 164 Kg/m³ H₂SO₄

| Sl. No. | Electrolyte feed | Deposit character | Purity of metal (%) | Carbon in metal (%) | Energy consumption (kWh/Kg) |
|---------|----------------------|-------------------|---------------------|---------------------|-----------------------------|
| 1 | 0.031 Fe 0.002 Mn | (B) | 99.94 | 0.038 | 2.09 |
| 2 | 0.050 Fe 0.103 Mn | (B) | 99.92 | 0.058 | 2.2 |
| 3 | 0.068 Fe 0.150 Mn | (B) | 99.95 | 0.033 | 2.13 |
| 4 | 0.240 Fe 0.160 Mn | (B) | 99.93 | 0.04 | 2.10 |
| 5 | 0.510 Fe 0.170 Mn | (B) | 99.95 | 0.03 | 2.08 |

(B) Bright adherent sheet deposit

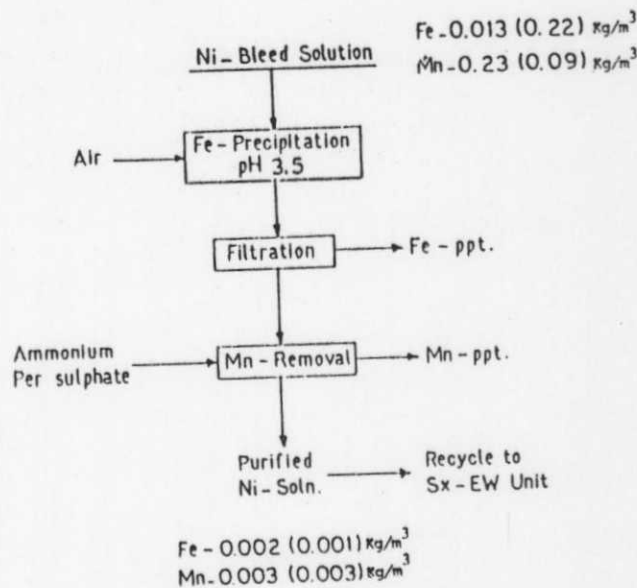
Entrained organic in the electrolyte affected the deposit as given in Table-5. For a specific composition of the electrolyte, the nickel deposit was found to be coarser when organic level in the solution was more than 150 ppm. The metal purity was 99.78% with carbon content of 0.03%. Deposit character and metal purity improved substantially with 50 ppm organic in the electrolyte which was obtained by giving longer settling times of 12 h for the electrolyte. With 20 ppm organic entrainment in electrolyte obtained by aeration and adsorption over activated carbon, very good deposit was produced with 99.81% purity including 0.012% carbon.

Effect of organic in electrolyte on the purity of copper deposit (99.91-99.94%) was not very severe. Perforation in electrodeposit was observed when 500 ppm organic due to higher rate of agitation (1800 rpm) in the stripping circuit

was present in the copper electrolyte. The deposit quality improved drastically when organic level was less than 100 ppm in the electrolyte. The amount of carbon found in deposit was also decreased with decrease in entrained organic of the electrolyte.

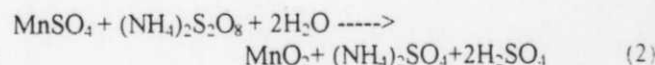
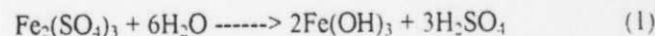
3.3 Bleed Stream Treatment

The metallic impurities in the electrolytic bath could be controlled by bleeding off a part of the electrolyte and replenishing it with a pure solution. For nickel, two typical composition with respect to Fe and Mn given in Fig.4 were produced in different runs. The purification scheme that was adopted shows the removal of iron at pH 3.5 by aeration and precipitation of Mn by ammonium persulphate as per reactions :



Figures in bracket correspond to different solution.

Fig.4 : Purification and recycling of nickel bleed stream



The purified nickel sulphate solution contained iron and manganese level of 0.001-0.002 and 0.003 Kg/m³ respectively, which was found suitable to produce good quality nickel metal. For processing copper bleed stream containing 40 Kg/m³ Cu, 20 Kg/m³ Ni and 1 Kg/m³ Fe, a

Table-5

EFFECT OF ORGANIC IMPURITY ON THE ELECTROWINNING OF NICKEL AND COPPER

Ni electrolyte : 80 Kg/m³ Ni,
 Cu electrolyte : 40 Kg/m³ Cu, 155 Kg/m³ H₂SO₄

| Metal | Composition of electrolyte (Kg/m ³) | Organic in the electrolyte (ppm) | Deposit character | Metal purity | Carbon in bath/ in metal (%) |
|-------------|---|----------------------------------|-------------------|--|------------------------------|
| Sl.No. | | | | | |
| Nickel Bath | 1. trace 0.005 0.02 | Cu Fe Mn | >150 ** | Coarser adherent sheet deposit | 99.78 . 0.03 |
| | 2. 0.001 0.007 0.02 | Cu Fe Mn | 50 | Adherent smooth sheetdeposit | 99.80 0.02 |
| | 3. 0.010 0.005 0.02 | Cu Fe Mn | 20 | Bright adherent sheet deposit | 99.81 0.012 |
| Copper Bath | 1. 6.22 0.08 0.17 | Ni Fe Mn | 500 * | Perforated deposit | 99.91 0.04 |
| | 2. -do- | -do- | >200 ** | Adherent deposit with organic tears and burn | 99.93 0.02 |
| | 3. -do- | -do- | <100 | Brigfht adherent sheet deposit | 99.94 0.01 |

* agitated speed = 1800 rpm

** agitators speed = 1400 rpm

Average energy consumption : Ni = 3.70 kWh/Kg
 Cu = 2.08 kWh/Kg

treatment scheme is given in Fig.5. This consisted of²² decopperisation to bring the level of copper equal to nickel. pH adjustment by lime addition to remove iron and acid. and ammoniation to bring copper and nickel into ammoniacal solution with 70 Kg/m³ NH₃. This solution after dilution could be treated by LIX 64N to coextract

copper and nickel which may then be diverted to main stream for separation. Alternatively, the lime neutralization step may be followed by crystallising Cu-Ni mixed sulphate after decopperisation and redissolving the sulphate. to avoid high consumption of lime. Table-

shows the purity of copper and nickel produced in a typical run with purified electrolytes.

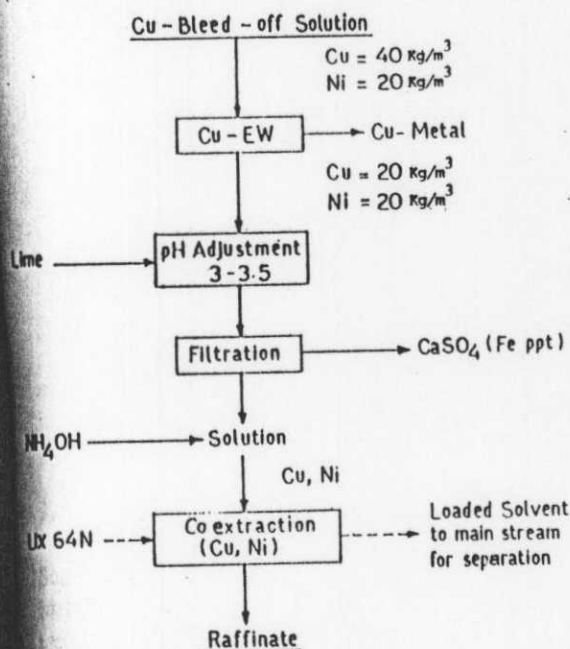


Fig. 3: Treatment of copper bleed stream for recovery of metallic values.

Table 6

PURITY OF METALS PRODUCED BY SX-EW

| Element | Nickel(%) | Copper(%) |
|---------|-----------|-----------|
| | 0.02 | 99.94 |
| | 99.81 | 0.011 |
| | 0.076 | n.f |
| | 0.05 | 0.015 |
| | 0.002 | 0.002 |
| | 0.009 | 0.002 |
| | n.f. | n.f. |
| | n.f. | n.f. |
| | 0.01 | 0.02 |
| | 0.0003 | 0.001 |

4. CONCLUSIONS

In the reduction roast-ammonia leach process for Indian Ocean nodules, metallic impurities in different amounts were found along with copper, nickel and cobalt even after purification step. When metal separation and recovery were carried out by solvent extraction-electrowinning method, metallic impurities like Fe and Mn entered the electrolytic bath. The entrained organic along with the metallic impurities present in the electrolytes affected the deposition of metals. For nickel winning, the effect of the impurities was extremely severe calling for introducing bleed stream to control their concentration. These studies were helpful in deciding the cut-off level of impurities in a recycling operation. The nickel bleed stream was treated through a scheme comprising of iron and manganese removal by precipitation to obtain a purified solution suitable for recycling back to the circuit. The effect of metallic and organic impurities were much less pronounced for copper winning due to the higher tolerance limits. A scheme was also worked out for copper bleed stream treatment to augment the metal recovery. The results may be useful for producing electrolytic grade copper and nickel metals from these resources.

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