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Study on the Extraction of Some Metals from Ammonia Solution of Indian Sea Nodules by Using D2EHPA Reagent

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Abstract

The leaching characteristics of sea nodules of Indian Ocean were investigated by leaching of Cu, Ni, Co, and Zn using 0.5 M of the solvent D2EHPA in ammonia solution, and 10% Isodecanol in Kerosene. It was found that Zn recovery almost remained steady after the first contact, i.e (0.017 g/L) while the recovery of Cu, Ni and Co increased even after third contact and reached its maximum value i.e (0.82 Cu , 0.90 Ni , 0.296 Co).

Also the result had revealed that the best time of mixing aqueous solution of metals ions to be recovered was found to be 2min, while the recovery of metals ions decreases as the organic to aqueous ratio was increased from 1:1 to 4:1.

Keywords: Sea nodules, extraction of metals, D2EHPA reagent.

دراسة أستخلاص بعض المعادن من المحلول الأمونياكي لعقيدات البحر في المحيط الهندي بأستخدام كاشف (D2EHPA)

الخلاصة

يتضمن البحث دراسة أمكانية أستخلاص النحاس والنيكل والكوبلت والزنك من عقيدات البحر الموجودة في المحيط الهندي بأستخدام 0.5 مولاري من كاشف ثنائي أثيل هكسيل حامض الفسفوريك في محلول الامونيا و 10% كحول الايزوديكانول والكيروسين، وقد لوحظ أن استخلاص الزنك يبقى ثابت بعد الدورة الاولى للاذابة وبمقدار(0.017 غرام/لتر) في حين أن أستخلاص النحاس والنيكل والكوبلت تزداد حتى بعد الدورة الثالثة من الاذابة لتصل الى اعلى قيمة (0.82 نحاس ، 0.90 نيكل ، 0.296 كوبلت) غرام/لتر.

ولقد أظهرت النتائج بأن أفضل زمن لخلط محلول الاذابة لاستعادة أيونات المعادن هو دقيقتان في حين أن أستخلاص أيونات المعادن يقل عندما تزداد نسبة المكون العضوي الى محلول الاذابة من 1:1 الى 4:1 .

1. Introduction

Over the past two decades, knowledge of submarine hydrothermal systems and the accompanying submarine hydrothermal mineralization at convergent plate margins of the western Pacific has increased enormously [1]. Naturally occurring ores of most valuable metals are being depleted due to increased demand for these metals for various uses. This has led to research in metal extraction from other sources. One such secondary source of these valuable metals is the large amount of ores in sea nodules Factors that influence the extraction of metals in a solid–liquid system include type of leaching agent used, particle size, heterogeneity of the solid matrix in terms of mineral phases, time, temperature, pH, complexation and redox conditions. A careful combination of these factors could lead to selective extraction of metals [2].

Low sedimentation rates, erosional conditions, and seasonal redox cycling favor the formation of ferromanganese concretions at shallow

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water localities of the SW Baltic Sea. These Baltic Sea ferromanganese nodules show an onion-like growth pattern of alternating Fe- and Mn-rich layers. This pattern has been attributed to seasonal cycling variations in bottom water conditions [3].

There is a considerable interest in the potential use of deep-sea manganese nodules for the recovery of copper, nickel, cobalt and manganese, by those countries which have no domestic production of these metals. Such countries, which have partial production of these metals, meet their needs by importing them. Nickel and cobalt are critical components in alloy steel used for jet engine parts, high strength tools, heat and corrosion resistant alloys, magnets, catalysts, drying additives in paints and other chemicals. Cobalt metal is generally used either as a powder, solid metal, or one of its salts. In recognition of the strategic importance of these metals, research has been directed for their extraction from deep-sea manganese nodules as a major source [4]. Nickel powder has important application in industry. It is employed in the manufacture of alkaline batteries. In the Chemical industries as catalyst, as pigment in corrosion paints, etc. [5].

Economic evaluation of projects related to multi metal extraction of Cu, Ni, Co & Mn from deep sea nodules have often failed to provide enough incentives to prospective industrial investors for pre-investment planning because of rather high direct costs of metal extraction from sea resources; comparatively, mining & transportation costs for sea nodules are much higher than costs of terrestrial mining / transportation of ores such as nickel late rites. The Indian Program of work considers the manganese recovery option in addition to recovery of Cu, Ni & Co for better process viability & environmental consideration. Three process development approaches have been extensively tested: (a) combined pyrohydrometallurgical process of reduction roasting and ammoniacal leaching (b) direct leaching process in ammoniacal medium with dissolved sulfur-dioxide as aqueous reducing agents and (c) high temperature reductive sulphuric acid leaching. Several cost saving technologies were introduced during pilot scale of operation : these include minimization of chemicals for reducing operating cost attained through judicious change of process parameters, process water conservation through hot raffinate wash, reduction of process effluents such as sodium sulphate through the use of state-of-the-art extraction reagents etc. Research programs recently commenced include evelopment of a modified high pressure acid leaching system for Indian nodules for attaining energy economy. Sulfuric acid based leaching processes are likely to be less energy intensive [6]. In present work, an effective chemical process has been developed for the extraction of copper, nickel, cobalt and recovery of manganese as manganese carbonate. Manganese nodules from the Indian Ocean basin are abundant in water depths of around 2000 to 5000 meters. They are rough surfaced, contain todorokite as the dominant mineral phase, have a thicker oxide layer and are rich in Mn/Fe and Cu/Ni ratio.

They range from 0.625 to 7.25 cm in size and are composed of MnO_2 and Fe_2O_3 or hydroxides (40% to 70%) as the main component associated with relatively minor amounts (0.1% to 1.0 %) of copper, nickel and cobalt. The mineralogy is basically fine-grained oxides mixed with layers of silicious gangue minerals [7]. Haynes gave comprehensive flow sheets for the processing of the nodules in (1983) [8].

On reviewing the details of these methods, it is evident that the cuprion ammoniacal leach process is not appropriate for cobalt extraction, and the other four methods are complex, expensive and hazardous to the environment. Mn-nodules contain up to 30% water even when drying in air [9].

Thus hydrometallurgical processes will be superior and economical to the pyrometallurgical ones due to saving of energy. In order to develop a suitable, separate process for the extraction of Cu, Ni and Co with a high grade of purity at a much-reduced cost (less than 50% of the present cost), the main objectives should be:

(i) Search for an effective reducing agent as Cu, Ni and Co are present as oxides and hydroxides of manganese and iron phases so that complete dissolution of the metals may be achieved under ambient temperature and pressure using the hydrometallurgical method.

(ii) The three metals Cu, Ni and Co may be separated using simple chemical processes rather than the solvent extraction method or an ion exchange device.

Fig. (1) show the recovery process of Cu, Ni, Co and Mn from sea nodules [4].

2. Experimental work

The reduction roast – ammonia leach being developed at National Metallurgy Laboratory (NML) is a combination of pyro and hydrometallurgical methods which consists of:

* Material preparation.
* Leaching.
* Solvent extraction and electrowinning.
* Metals recovery.

This work is focusing on studying the utilization of Polymetallic sea nodules which are one of important and potential sources of certain non – ferrous metals like copper, nickel, cobalt and manganese. Nodules samples found in the Central Basin of the Indian Ocean (CIB) and mind by National Metallurgical Laboratory (NML).

2.1 Material preparation.

As the copper, nickel and cobalt are not homogenously distributed, the nodules after air/oven drying is crushed and ground to fine size (<125 µm) and mixed with a carbon source (nodules and charcoal 4.5: 1). The mixture is palletized in a disc Pelletier with speed of 18 r.p.m and time 10 min [10] and the palletized milled ore were used for reduction purpose.

2.2 Reduction roasting.

The main objective of the reduction roasting is to break the manganese lattice structure, also reduce the oxide of copper, nickel and cobalt to their metallic states. Based on the available thermodynamic data for reduction of oxides of copper, nickel and cobalt which is carried out in a suitable furnace. The parameter such as temperature of reduction (900 ^{o}C), retention time (1 hr), and percentage reluctant is important. About 180kg of nodules can be processed per day in the reactor designed for this purpose. The reactor consist of big closed flask with three holes, the first used to pass (NH_3), the second used to pass (SO_2), and the third for the sea nodules powder.

2.3 Leaching.

The roasted product is leached in ammonia-ammonium carbonate solution. Concentration of leaching media, solid-liquid ratio, oxygen partial pressure, time of leaching are maintained in such a way that the desired concentration of metal in solution is obtained.

The shake out experiments was carried out in a stirring vessel using agitator grooved at the bottom. Mostly 50ml of aqueous solution was mixed for stipulated time with LIX 64N an organic reagent diluted with kerosene. Isodecanol was mostly used as the third phase modifier. The RPM of the agitator was perfectly controlled to avoid emulsion formation. The mixed phase was allowed to settle in a separating funnel and two aliquots (phase) analyzed for knowing the metal contents.

Aqueous phase was mostly analyzed to know the metal extraction/stripping. Loaded organic phase was mixed with 100g/L sulphuric acid to check the material balance.

Atomic Absorption Spectrophotometer (AAS) was used at NML to analyze the metals. Ammonia and carbon dioxide of the aqueous phase were analyzed volumetrically by ANC. All the chemical used in the experiments were AnaIR grade. D2EHPA was fluke make (Germany).The leach liquor produced earlier at NML with its composion is given in table (1).

2.4 Solvent extraction and electrowinning.

In general, solvent extraction offers the possibility of selective recovery of the designed metals by choice of extraction conditions like (particles size, exposed surface area for chemical reaction, temperature, group of chemical agents used for metal leaching, (O/A) ratio, No. of contact, (NH_3) amount in aqueous feed and time of mixing). Considerable concentration effect can also be achieved by variation of the flow ratio of organic to aqueous phase (O/A) by amount of (1,2,3 and 4). Thus, solvent extraction is technically well-suited for the recovery of metals, as it can selectively transfer a metal into a concentrated product solution. In addition, solvent extraction processes are often environmentally acceptable, are flexible with respect to the composition of initial materials and size of operation, and can be made economically in a small-scale operation.

The Leached solution is purified and treated for metal recovery by solvent extraction and electrowinning operation. LIX 64N has been used to separate copper, nickel and cobalt from the leach solution and metals are produced by electrowinning.

The technical feasibility of reduction roast-ammonia, leach process developed on a 100kg/day scale that has been established at NML.

The ammonical leach liquor of Indian Ocean nodules is subjected to solvent extraction using LIX 64N. The solvent co-extracts copper and nickel leaving cobalt in the raffinate. The selective stripping of nickel and copper produce pregnant solution of these metals while regenerating the solvent.

Generally Fig. (2) explain the block diagram of extraction of Cu, Ni and Co from Indian Ocean nodules.

3. Results and discussion

The recovery of different metals in nitrate solution (0.1M $NaNo_3$) by using D2EHPA reagent is given in table (2). It is thus obviously shown that separation of Cu, Ni, Co, Zn, Fe, and Mn from acidic solution can be achieved by perfect control of pH for extraction as explained in table (2) , scrubbing and stripping. The separation of Co and Ni from such solutions requires highest control of pH. As such D2EHPA is usually applied for separation of leach metals from acidic solutions by converting it to sodium or ammonium form mainly to control the pH during extraction. It was thus considered appropriate to attempt the application of the solvent for ammonical leach liquor of ocean nodules produced at NML. The ammonia available in the leach liquor may be advantageous for deprotonating D2EHPA which may be extracting the metal in situ.

Extraction studies were initially carried out with leach solution using 0.5M (16.1% v/v) D2EHPA and 10% Isodecanol (ID) in kerosene. The results given in table (3) indicates that 0.7g/L Cu, 0.6g/L Ni, 0.116g/L Co, and 0.017g/L Zn was loaded in the solvent during the first contact at O/A=1 (O/A the ratio between organic to aqueous) and mixing time of 10 min. Extraction of these metals in organic phase increased in successive contacts with the fresh aqueous solutions. In four contacts of organic phase, the amount of metals loaded were found as 0.82g/L Cu, 0.90g/L Ni, 0.296g/L Co and 0.019g/L Zn. Data further indicate that zinc extraction remained almost steady after first contact whereas Cu and Ni extraction increases even after third contact.

In order to improve the extraction/recovery level of the metal in solvent, the ammonia concentration of the aqueous feed was varied. The final loading pattern of the solvent with the metals in four contacts with aqueous solution is given in table (4).

From the result it can be seen that extraction of the metals, in general, favorable at lower ammonia concentration in the aqueous feed.

With 17g/L ammonia in the aqueous solution the amount of different metals extraction was 1.695g/L Cu, 1.7g/L Ni, 0.225g/L Co and 0.055g/L Zn.

Kinetics of metal extraction from the leach liquor was carried out for different durations and results are given in table (5). The time required for extraction of the metals in solution of sea nodules was 2 min at O/A 1 which is ideal for operating a continuous extractor like mixer-settler unit. It may be noticed that metals (Cu, Ni, Co and Zn) extraction remained constant after 2 min. of mixing.

Organic to aqueous ratio(O/A) was varied from 1/1 to 4/1 with the aim of extracting maximum amount of metals from the aqueous solution. The results given in table (6) show that metals left in the raffinate at O/A=4/1 were minimum as the aqueous phase contained 0.7g/L Cu, 0.8g/L Ni, 0.06g/L Co and 0.023g/L Zn.While at lower ratio for example at O/A=1, the metals left in the raffinate were 1.1g/L Cu, 1.40g/L Ni, 0.09g/L Co and 0.07g/L Zn.

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Table (1)Chemical composition of the ammonical leach liquor of Indian Ocean nodules.

Metal	g/L
Cu	1.800
Ni	2.000
Co	0.206
Zn	0.087
NH_3	68.30
CO_2	49.60

Table (2) Reagent: 0.5M D2EHPA in Xylene

Aqueous feed: Metal nitrate (0.1M NO_3).

Metal ion	pH for 50% extraction
Cu(II)	2.90
Ni(II)	4.12
Co(II)	3.70
Zn(II)	1.42
Fe(II)	3.56
Fe(III)	0.32
Mn(II)	2.82

Table (3)Metal extraction in various contacts with actual leach solution.

Solvent:0.5M(16.1%) D2EHPA and 10% Isodecanol (ID) in kerosene.

Aqueous feed: Metal nitrate (0.1M NO_3)

t(mix): 10 min ; No. of contacts:4

No. of contacts	Metal in organic phase (g/L)			
	Cu	Ni	Co	Zn
1	0.70	0.60	0.116	0.017
2	0.75	0.70	0.206	0.020
3	0.80	0.85	0.215	0.020
4	0.82	0.90	0.296	0.019

Table (4) Extraction of metal at different ammonia level in aqueous feed.

Aqueous feed: Metal nitrate (0.1M NO_3).

Organic phase: 0.05M D2EHPA and 10% Isodecanol in kerosene

t(mix): 10 min; No. of contacts:4 ; O/A=1

NH_3 in Aqueous Feed (g/L)	Metal in organic phase (g/L)			
	Cu	Ni	Co	Zn
17.0	1.695	1.700	0.225	0.055
34.0	1.675	1.250	0.268	0.049
68.0	0.820	0.900	0.296	0.019

Table (5) Kinetics of extraction with D2EHPA

Aqueous feed (g/L): Metal nitrate (0.1M NO_3).

Organic feed: 0. 5M D2EHPA and 10% Isodecanol in kerosene

O/A=1; t(mix): varied; No. of contacts: 1

Time of mixing (min)	Metal in organic phase (g/L)			
	Cu	Ni	Co	Zn
0.5	0.63	0.53	0.116	0.08
1.0	0.68	0.55	0.116	0.007
1.5	0.70	0.62	0.116	0.014
2.0	0.70	0.60	0.116	0.017
5.0	0.70	0.60	0.126	0.017
10.0	0.70	0.60	0.116	0.017

Table (6) Effect of O/A ratio on extraction

Aqueous Feed: Metal nitrate (0.1M NO_3).

Organic feed (g/L): 0.5M D2EHPA and 10% Isodecanol in kerosene

t(mix): 10 min; No. of contacts =1

O/A ratio	Metal in aqueous phase (g/L)			
	Cu	Ni	Co	Zn
1	1.10	1.40	0.09	0.070
2	0.85	1.15	0.07	0.043
3	0.80	1.05	0.075	0.035
4	0.70	0.80	0.060	0.023

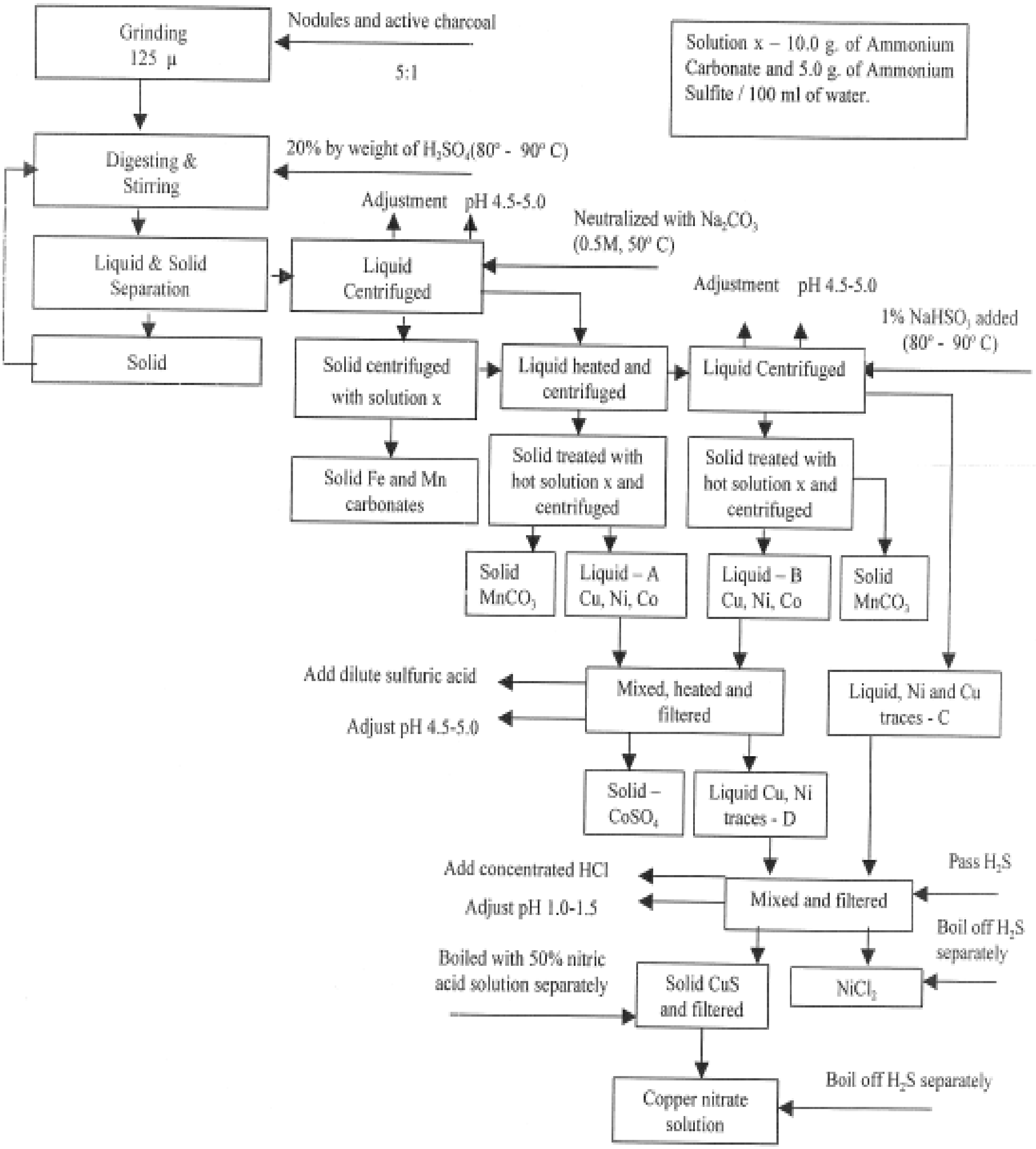

Fig. (1) recovery process of Cu, Ni, Co and Mn from sea nodules [4].

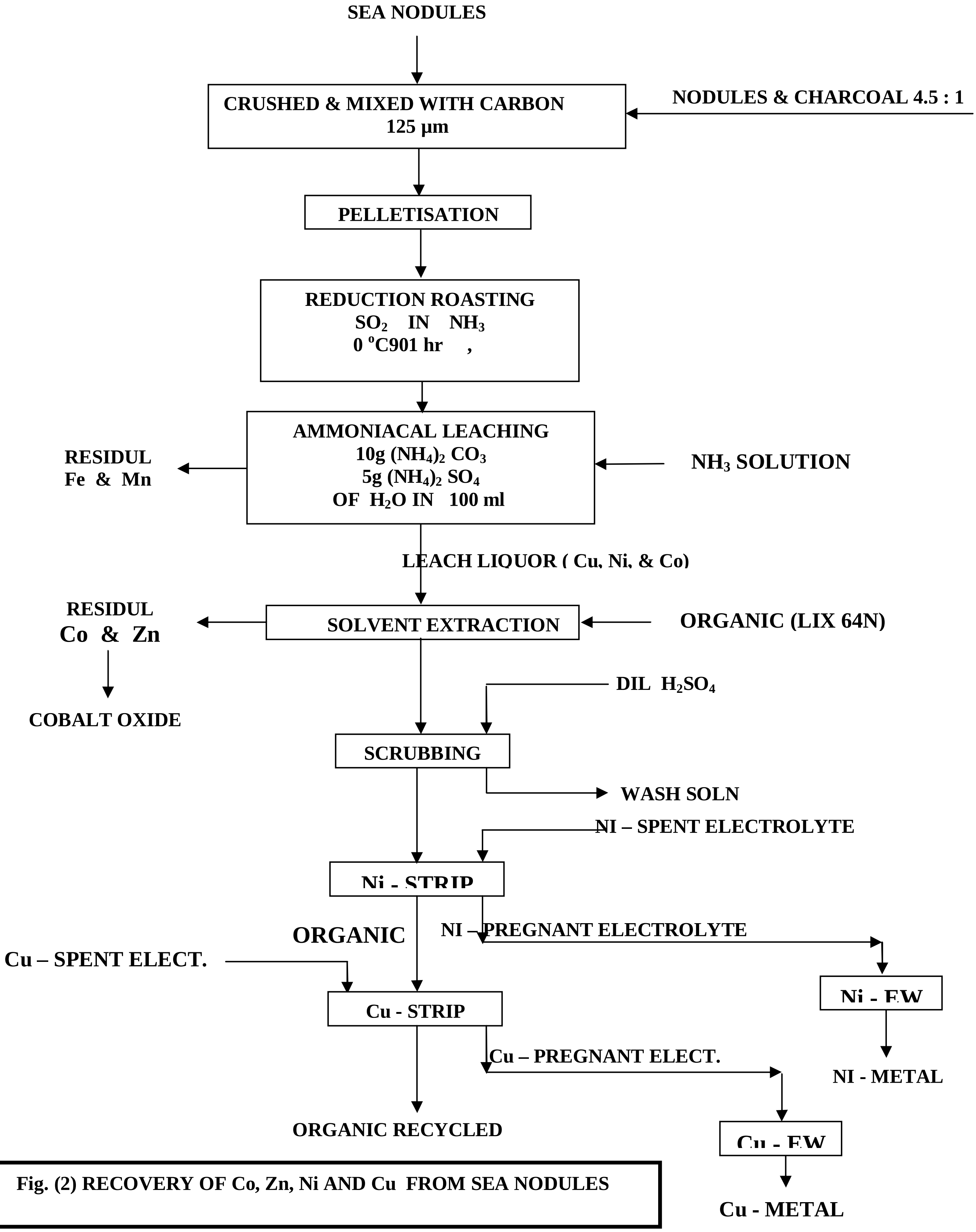

Fig. (2) RECOVERY OF Co, Zn, Ni AND Cu FROM SEA NODULES