SEMINAR ON RECOVERY OF VALUABLE BY-PRODUCTS FROM INTERMEDIATE SECONDARIES IN NON-FERROUS INDUSTRIES

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SOLVENT EXTRACTION IN COPPER METALLURGY
RECOVERY OF ACID AND METALS FROM COPPER BLEED STREAM

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ABSTRACT

Solvent extraction in copper metallurgy has been the first major application for producing non-ferrous metals beyond the production of rare earths/nuclear metals. With the advent of solvent extrac-tion (SX), several lean grade, complex, multimetal and pocket deposits including byproducts could be processed to produce copper economically. Though, the SX technology is proven interna-tionally, it has yet to find an industrial application in the Indian context. This paper outlines the possibility of using solvent extraction in copper metallurgy particularly in the Indian scenario. Specific example of the processing of copper bleed stream has also been mentioned. Some of the details and the flowsheet given here shows how the sulphuric acid can be recov-ered from the copper bleed stream for recycling in the system. Besides, the recovery of copper and nickel in convenient form like metal sulphates and electrolytic grade metal cathodes can be taken up

INTRODUCTION

Solvent extraction is considered as the turning point in the history of copper metallurgy, which resulted in the exploitation of oxidic ores that were considered unsuitable earlier for eco-nomic production. This was also applicable for lean grade sul-phidic ores which could be processed through purely hydrometal-lurgical routes. The apprehension of economic viability of any common non-ferrous metal production, other than those of rare earths/nuclear metals, was proved otherwise with the operation of first solvent extraction plant(1) for copper by the year 1968. Since then more than 25 plants came in

to being using leaching-solvent extraction (SX)-electrowinning (EW) route with a share of about 15% copper metal produced world over through this technolo-gy. The domain of the process applicable in the copper metallurgy is widespread (2,3), starting from primary metal production from different leach liquors, to recovery of the metal from various secondaries like dross, wires, rods, electronic components, boards etc. and even effluent treatment. It is interesting to note that the metal of high purity (above 99.9%) could be direct-ly produced by SX-EW technology which is largely suitable for most of the applications envisaged for the primary metal. It has also been possible to extract several other non-ferrous metals on industrial scale in the last three decades.

INDIAN SCENARIO

In our country, Hindustan Copper Ltd., operates two plants at Khetri and Ghatsila using the smelting-refining technology. The basic ingredients of the smelter come from the concentrator plants, where the ore is enriched to a desired level. There are two more plants slated to start production soon in the private sector from the imported concentrates using the smelting route. The application of solvent extraction has yet to start in our countrys' copper plants due to various reasons other than techno-logical problem, though there is tremendous scope. Some of the possible applications of the solvent extraction in copper indus-try may be inumerated below:

(i) Possibility of taping pocket deposits locally by agitated tank / heap / dump/ bioleaching followed by SX-EW, without producing concentrate of desired specifications

particularly with respect to grade and purity.

(ii) Processing of lean grade and complex sulphide ores scattered in the country as the recoveries during concentration may be poor and individual concentrate production may not be viable. Under such conditions, pyro-hydro-metallurgical treatment followed by SX-EW can be the ideal solution.

-Recovery of copper from the processing of mixed oxide-sulphide Malanjkhand deposit by SX-EW route.

-Processing of dirty ore/concentrate from Sikkim.

-Way out can be found for problems in the existing plant at Ghatsila with respect to processing of certain intermediates and byproducts like converter slag, dump slag, anode slime for precious metal recovery, anode slag residue containing nickel and copper etc.,

-Recovery of sulphuric acid and copper and nickel metals from the copper tank house bleed solution by SX technology. This can avoid producing poor quality copper being generated in the decopperisation step which burdens the smelting/melting shop during recycling.

R&D WORK AT NML
Processing of copper bleed stream:

At the instance of Indian Copper Complex, Ghatsila, a systematic R&D work was initiated to develop a suitable process to treat copper bleed stream. The aim of this study was to work out the details for recovery of acid, iron, nickel and copper in suitable form producing useful end products. It was also expected to be applicable under the conditions projected for recovery of these metals from the liquor of nickel rich anode slag residue. The literature search on the subject shows that several solvent extraction processes were developed to recover the metals

from copper bleed stream. Japanese researchers developed (4,5) and implemented the SX and ion exchange based recovery systems in some plants. Similarly, several others from copper plants of western companies (6-8) have also applied the SX technology for the purpose. It was thus considered worthwhile to develop a scheme specially suitable in Indian context. The typical composition of the bleed solution was 40 g/L Cu, 20 g/L Ni, 1 g/L Fe and 180 g/L H_2SO_4. The initial experiments were carried out to extract sulphuric acid by organic reagent viz the tertiary amine. These were Alamine 336, a solvent produced by M/s Henkel Corporation (USA) and Tri-isooctyl amine (TIOA) diluted in Kerosene 10% isodecanol (ID) was added as the third phase modifier.

The results of the acid extraction from an aqueous feed containing 167.6 g/L sulphuric acid by 25% Alamine 336 at different organic to aqueous ratio (O/A) are given in Figure-1. It is apparent that 50% acid was extracted at O/A 2 and 90% extraction at O/A 4. It also shows the quantitative acid extraction in single contact at O/A 6. Figure-2 shows the extraction of sulphuric acid in different contacts at O/A 1. Data clearly reveal the drop in acid content of aqueous feed with the simultaneous extraction in Alamine 336. In four contacts the acid left in the aqueous raffinate was found at 17 g/L.

In order to see the rate of acid extraction, the kinetics experiments were also carried out and results are shown in Figure-3. At O/A of unity, the kinetics was found to be very rapid and favourable. In 30 seconds also, the acid extraction was fairly high with no major effect on extraction by increasing the mixing time. The rapid rate of acid transfer to the organic phase is therefore ideal for running any mixer-settler unit to achieve the objective of acid recovery from such aqueous solutions. Loading of Alamine 336 with sulphuric acid at two different phase ratios was studied for a contact time of 5 minutes and results are depicted in Figure-4. In two contacts, maximum acid loading was observed at O/A 4 whereas five contacts resulted in maximum

loading at O/A 8. These results are critical from the point of extracting and recovering acid so that the condition can be implemented in a continuous operating system.

The kinetics of stripping of loaded acid from the 25% Alamine 336 is shown in Figure-5. Data on stripping showed the requirement of about 2 minutes at O/A 1 at room temperature which is also suitable for a continuous extractor. Further studies were carried out to strip the loaded acid from the solvents and results are listed in Table1.

Table- 1 Stripping of acid from the Loaded Organic

Extraction :-

Organic phase : 25% Alamine 336/TIOA and 10% isodecanol (ID) in Kerosene

Aq. feed : 170.58 g/L H_2SO_4

O/A=1   t= 5 min   No of Contact = 1
Stripping
Acid loaded Alamines 336 =47.04 g/L
Acid loaded in TIOA =49.08 g/L
O/A =1   t= 5 min   Temp. 30° C

Sl No	Cont-act No	Alamine 336		TIOA	
		Acid Stripped (%)	Acid Un-Stripped (g/L)	Acid Stripped (%)	Acid Un-Stripped (g/L)
1	1	31.25	32.34	31.50	33.64
2	2	41.04	27.73	42.90	28.05
3	3	46.25	25.28	49.20	24.96
4	4	49.49	23.76	53.50	22.83
5	5	52.06	22.54	56.70	21.25
6	6	54.53	21.39	59.10	20.05
7	7	56.32	20.54	61.20	19.03

The conditions for extraction and water stripping with 25% Alamine 336 and 25% TIOA are also given. The stripping at room temperature (30° C) in different contacts for Alamine show that 56.32% acid was recovered with 20.54g/L acid being still attached to the solvent in seven contacts. Acid recovered by water stripping of

the acid from TIOA was 61.2% with 19.03 g/L acid left in the solvent due to equilibrium effect. As some amount of acid remained attached with the solvent, it was considered worthwhile to examine the recycling characteristic of the regenerated solvent. The results given in Table.2 clearly indicate that the loading of acid in Alamine 336 as well as in TIOA in 4 cycles was almost the same, the acid extraction being slightly higher for the latter. Thus, two solvents can be used conveniently to recover acid and recycle the same in the plant if desired.

Table- 2 :Recycling of the regenerated solvent (Alamine 336/TIOA)

Extraction :-

Loading : 25% TIOA/Almamine 336 and 10% ID in Kerosene

Aq. feed : 176.4 g/L H_2SO_4
O/A=1   t= 5 min   No of Contact = 1
Stripping
O/A =1   t= 5 min   No of Contacts = 4

Recycle	TIOA		Alamine 336	
	Acid loaded (g/l)	Acid in regenerated Solvent (g/L)	Acid Loaded (g/l)	Acid re-grnerated solvent (g.)
Cycle 1	50.96	24.38	47.04	23.76
Cycle 2	53.78	26.85	53.16	29.25
Cycle 3	55.27	28.10	56.69	27.48
Cycle 4	56.52	29.66	52.96	25.58

As regards extraction and separation of iron, copper and nickel from the raffinate obtained in acid extraction, the iron may be first precipitated out at 3.5 - 4 pH by neutralisation and aeration. The studies on copper extraction from acidic solution by partially saponified Napthenic acid (sodium salt) were carried out and results are given in Table 3.

Table- 3
Extraction of Copper By Naphthenic Acid at Different pH

Aq. feed	: 4.86 g/L Cu
Org Phase.	: 25% Naphthenic Acid, 10% ID Kerosene.

O/A=1   t= 10 min   No of Contact = 1

Sl No	pH		Cu Loaded g/L	Loading (%)
	Initial	Equilibrium		
1	3.8	2.6	0.09	1.85
2	3.8	3.0	0.87	17.90
3	3.3	3.15	2.73	56.17
4	3.3	3.8	3.89	80.14
5	3.8	4.0	43.48	92.18

It thus shows the possibility of copper extraction without major nickel loading under the conditions optimised. The nickel could then be extracted at still higher pH. The pregnant solutions of copper and nickel sulphates could be used to produce the respective metals by electrowinning or metal sulphate crystals as desired by conventional technology. An indigenous solvent viz. di-2ethyl hexyl phosphoric acid (D2EHPA) now available was also found quite suitable for recovery of copper and nickel as discussed above. The bench scale and continuous facilities on large scale available at the NML can be used to test the process described earlier. A flowsheet is given in Figure-6 which shows the scheme for separation and recovery of acid and metals in respect of processing copper bleed stream. The scheme can also be applicable for treating the sulphate solution of nickel rich anode slag residue.

CONCLUSION

The solvent extraction-electrowinning - a state of the art technology opens up the possibility of exploiting several low grade complex and pocket deposits in our country which may not require the concentration plant or the bulk concentrate can be treated. Even the dirty concentrates like those produced in Sikkim and mixed oxide-sulphide ore that is available at Malanjkhand can be processed on the site by following suitable leaching approach followed by SX-EW route. Though, it is a thirty years old technology world over, India has yet to start and use the vast experience gained in the field at the national laboratories to utilise the approach wherever it is possible. Some of the existing problems of the Hindustan Copper Limited can be directed towards this end. One such example discussed in the text shows how efficiently the acid, nickel and copper can be recovered in the desired form by processing copper tank bleed stream and leach liquor of anode slag residue. Though data generated showed promise, some more experiments on bench and large scales need to be carried out to test the scheme developed.

ACKNOWLEDGEMENT

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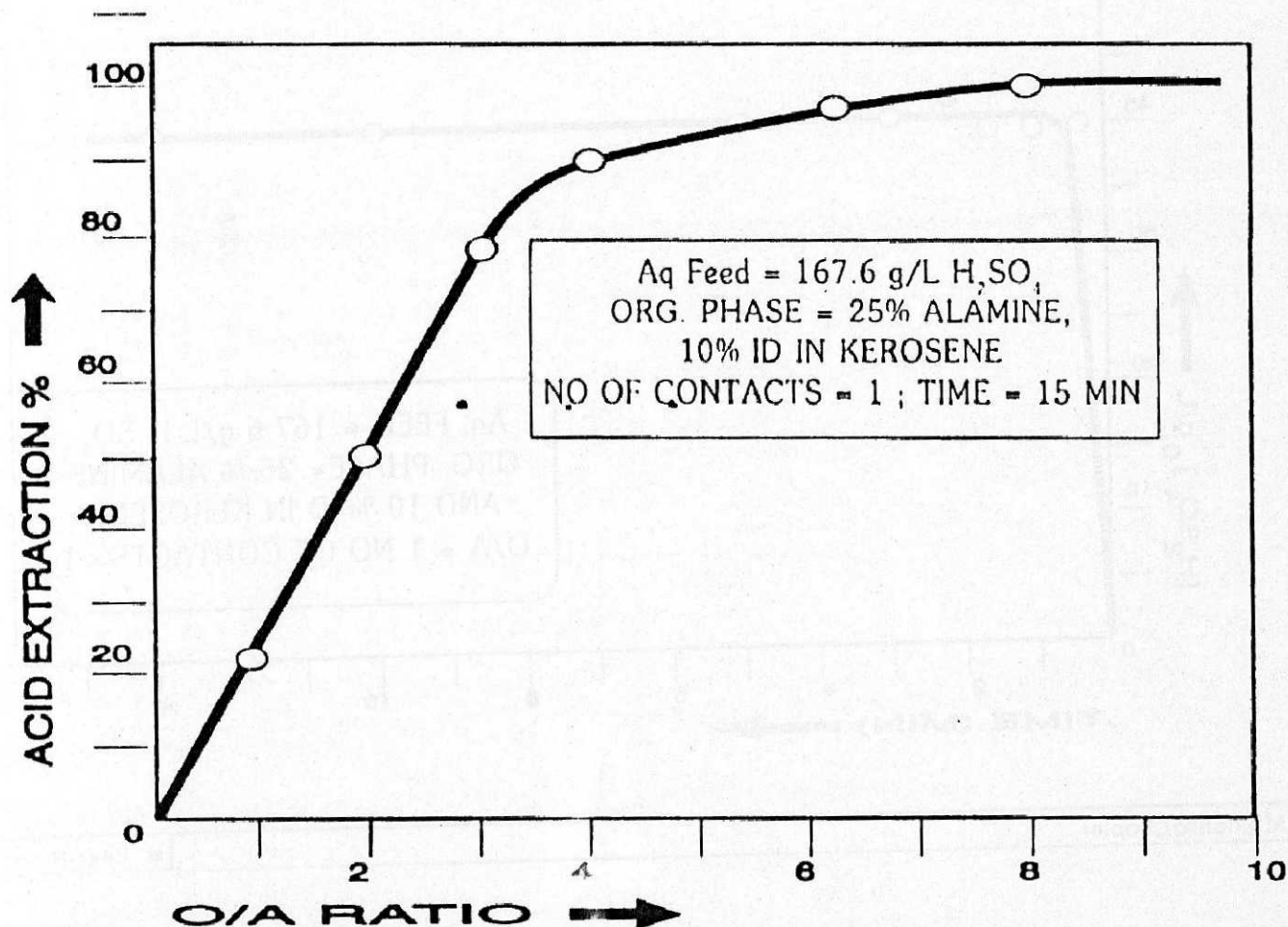FIGURE 1 EFFECT OF O/A VARIATION ON SULPHURIC ACID EXTRACTION BY ALAMINE 336

Aq Feed = 167.6 g/L H_2SO_4
ORG. PHASE = 25% ALAMINE,
10% ID IN KEROSENE
NO OF CONTACTS = 1 ; TIME = 15 MIN

FIGURE 2   SULPHURIC ACID EXTRACTION BY ALAMINE 336 FROM COPPER BLEED STREAM

FIGURE 2 chart. Y-axis labeled H_2SO_4 with values 100, 200, 150, 100, 50, 0. X-axis labeled NO OF CONTACTS with values 1, 2, 3, 4, 5.

Box text:
Aq. FEED = 167.58 g/L H_2SO_4
ORG. PHASE= 25 % ALAMINE,
10 % ID IN KEROSENE
O/A = 1   TIME = 15 MIN
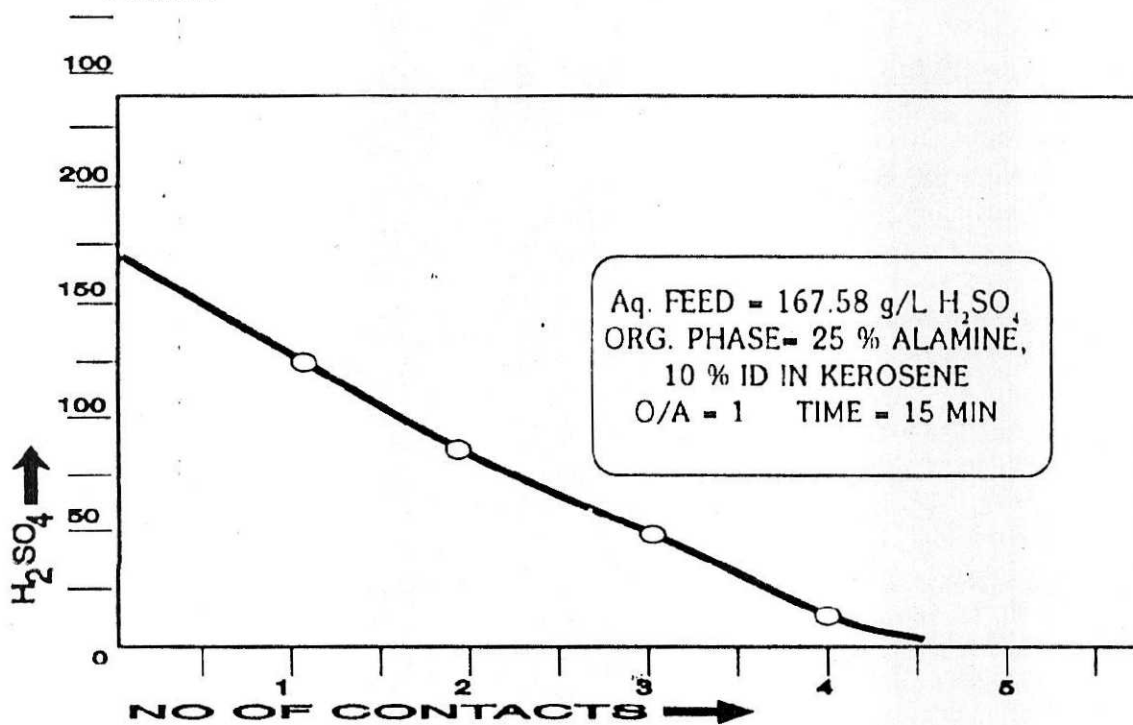
FIGURE 3   KINETICS OF ACID EXTRACTION BY ALAMINE 336

FIGURE 3 chart. Y-axis labeled $[H_2SO_4]_{0}$ g/L with values 50, 40, 30, 20, 10, 0. X-axis labeled TIME (MIN) with values 2, 4, 6, 8, 10, 20.

Box text:
Aq. FEED = 167.6 g/L H_2SO_4
ORG. PHASE= 25 % ALAMINE
AND 10 % ID IN KEROSENE
O/A = 1 NO OF CONTACTS= 1
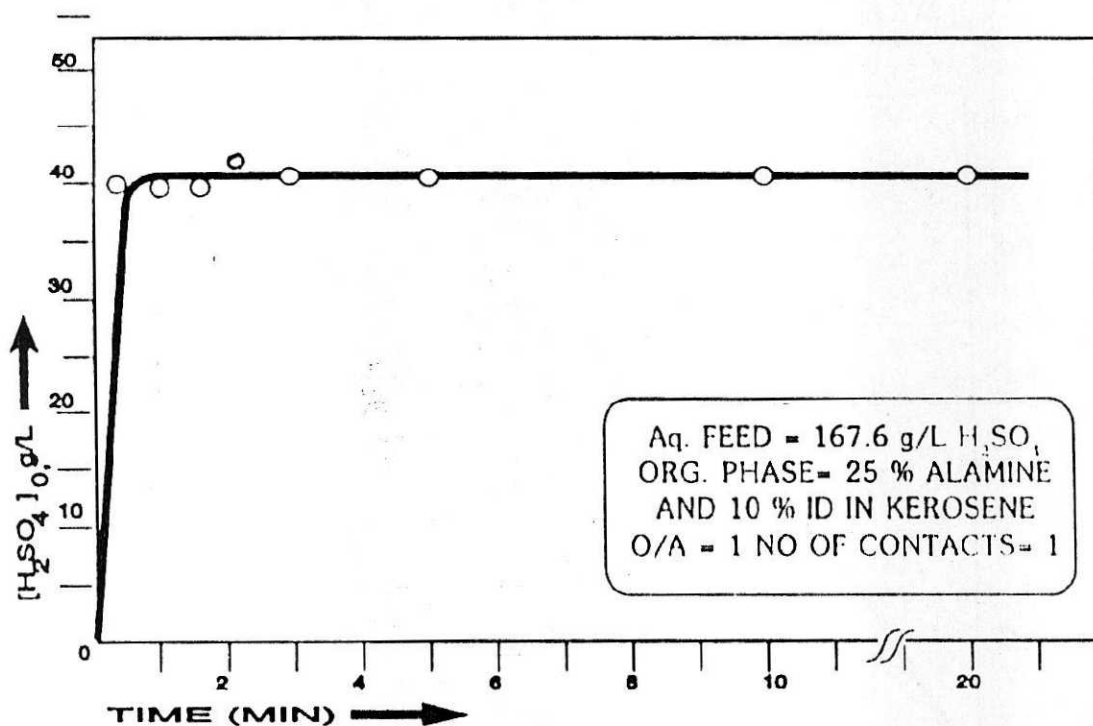
FIG 4 : LOADING OF H_2SO_4 IN ALAMINE 336 AT DIFFERENT PHASE RATIOS

Aq. FEED = 170.5 g/L H_2SO_4
ORG. PHASE= 25 % ALAMINE
10 % ID IN KEROSENE
⊕ O/A= 4; ▲ O/A= 8 TIME=5 MIN
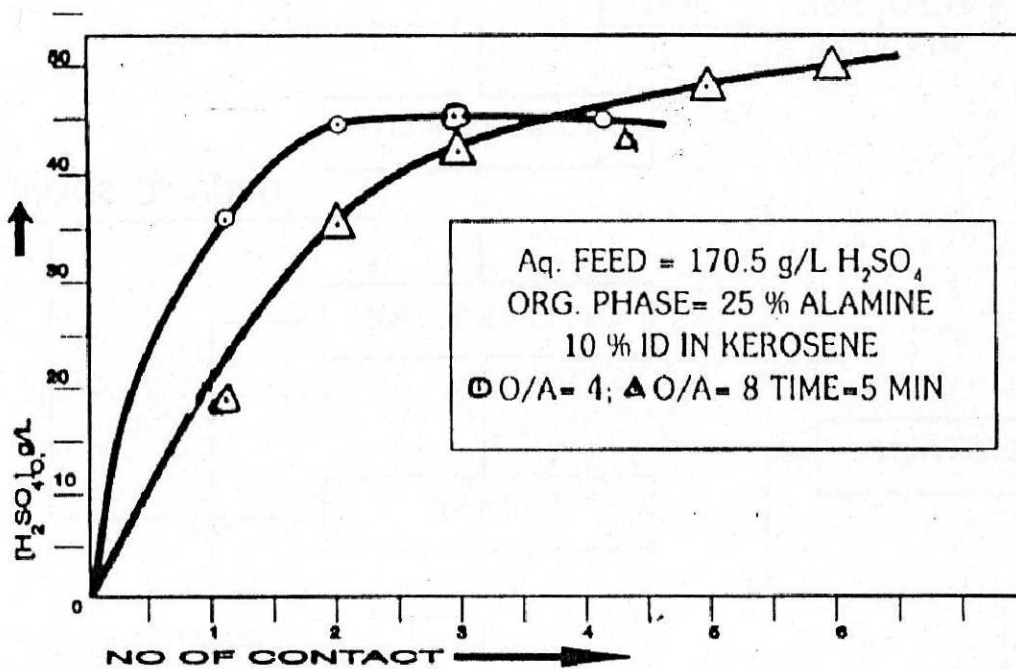
FIG 5 : EFFECT OF TIME ON ACID STRIPPING FROM THE LOADED ALAMINE 336

ORG. PHASE= 25 % ALAMINE
AND 10 % ID IN KEROSENE
(42.14 g/L H_2SO_4)
O/A = 1 NO OF CONTACT= 1

ORGANIC SOLVENT
(O₁) ──────────→

Cu- BILEED SYSTEM

ACID EXTRACTION

ACID STRIP

H₂SO₄ FOR
RECYCLE

pH ADJUSTMENT

ORGANIC SOLVENT(O₂)

Cu- EXTRACTION

CRYSTALN.

CuSO₄
CRYSTALS

Cu-STRIP

ORGANIC SOLVENT (O₃)

Cu-EW

Ni-EXTRACTION

Cu-METAL

Ni-STRIP

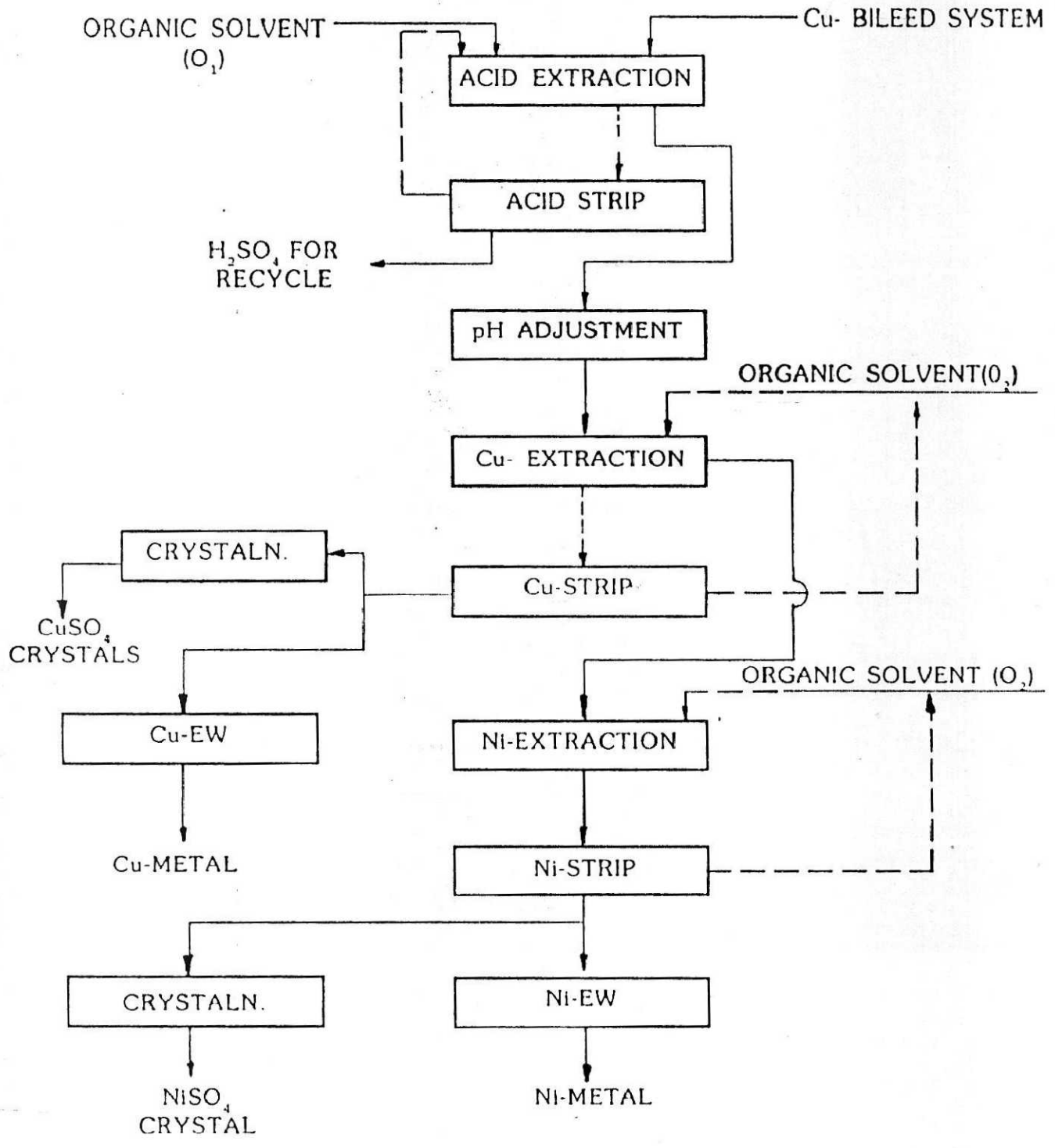**CRYSTALN.**

Ni-EW

NiSO₄
CRYSTAL

Ni-METAL
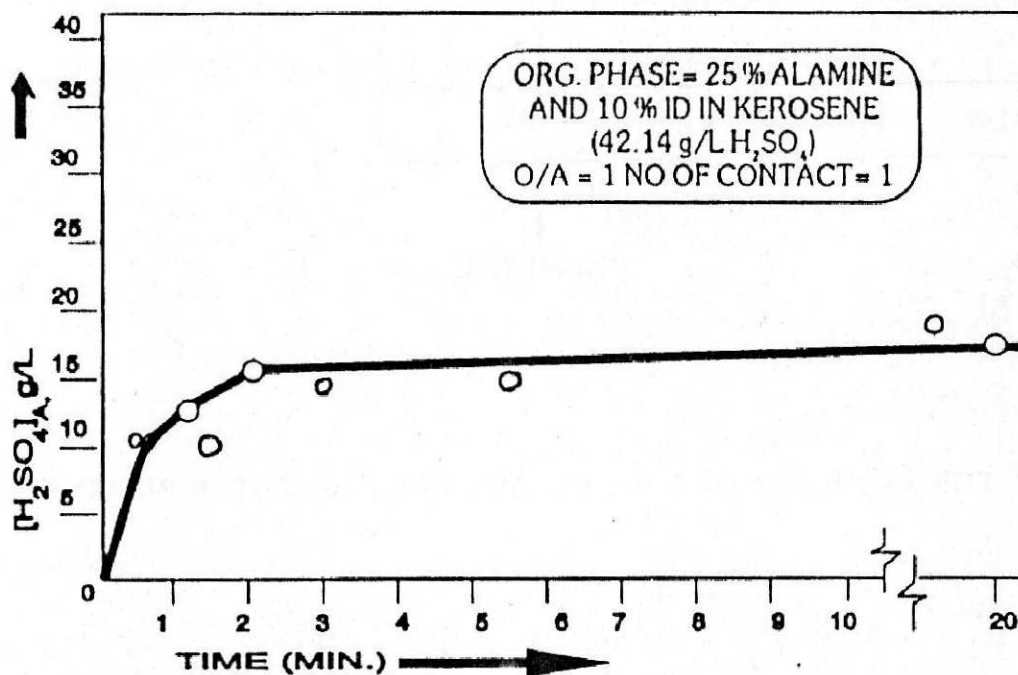
FIG.6 SCHEME FOR RECOVERY OF ACID, Cu AND Ni FROM COPPER BLEED STREAM.