METALLURGICAL TESTING OF COPPER-NICKEL BEARING MATERIAL FROM THE DULUTH GABBRO PROGRESS SUMMARY

Coleraine Minerals Research Laboratory

June 1998

By: Blair R. Benner

Blair R. Benner
Program Manager

Approved By: Ronald L. Wiegel

Ronald L. Wiegel
Assistant Director

CMRL/TR-98-17

Natural Resources Research Institute
University of Minnesota, Duluth
5013 Miller Trunk Highway
Duluth, Minnesota 55811

METALLURGICAL TESTING OF COPPER-NICKEL BEARING MATERIAL FROM THE DULUTH GABBRO PROGRESS SUMMARY

INTRODUCTION

The copper and nickel deposits of the Duluth gabbro remain one the world's major copper and nickel resources, as well as having the potential for recovery of platinum group elements (PGEs). While portions of the deposit have been tested in the past, most of the work was aimed at the small high grade areas. Most of the previous testing was conducted in the 1970's and early 1980's. Since then there have been improvements in both flotation equipment and reagents. Also, the recent work on pressure oxidation of refractory gold ore may represent an opportunity for hydrometallurgical treatment of all or part of the sulfides. To determine the effect of the technical improvements since the previous studies and to help promote the development of this resource, the State of Minnesota through the Minerals Coordinating Committee, the University of Minnesota Permanent Trust Fund (PUTF) and Minnesota Technology Incorporated in cooperation with Arimetco, funded metallurgical testing at the Coleraine Minerals Research Laboratory (CMRL) a part of the University of Minnesota-Duluth's Natural Resources Research Institute (NRRI). The objectives of the program were: To determine grade and recovery for a bulk copper-nickel concentrate; to determine if a copper concentrate, low in nickel and suitable for sale to a smelter could be produced; to determine if a nickel concentrate, low in copper could be produced; and to investigate hydrometallurgical treatment of either the bulk copper-nickel concentrate or the sulfide material left after the production of a copper concentrate.

This report summarizes the progress to date and outlines the plan for the ongoing test program being funded under PUTF.

PROJECT WORK PLAN

The original test program consisted of four major stages: laboratory flotation, pilot plant flotation, bioprocessing and hydrometallurgy. These four stages were broken down as follows:

1. Laboratory Flotation
    a. bulk flotation
    b. bulk flotation followed by differential flotation
    c. selective flotation
    d. regrind and retreatment of pilot plant concentrate

2. Pilot Plant Flotation
    a. open versus closed circuit grinding.
    b. circuit configuration and recycles.
    c. conventional versus column flotation for cleaner/recleaner flotation

3. Bioprocessing
    a. Thiooxidans
    b. Ferrooxidans
    c. sequential leaching and washing

4. Hydrometallurgy

    a. scoping studies with various reagents
    b. locked cycle leaching tests
    c. metal recovery from solution

LABORATORY FLOTATION RESULTS

SAMPLE 1

In 1995, a 200 ton sample of copper-nickel ore from the Arimetco lease area (sometimes referred to as the Babbitt Deposit) was shipped to CMRL where it was crushed to minus 3/4-inch. As the material was being crushed a sample was cut for approximately every ton processed. This sample material was composited and blended to provide a head sample and material for bench scale testing. The sample contained about 0.30 percent copper and 0.08 percent nickel.

Laboratory flotation tests were conducted to determine the optimal operating conditions and reagents to produce a bulk sulfide concentrate. The tests indicated that grinding in a stainless steel mill with stainless steel rods to about 95 % minus 65 mesh and floating at the natural ph with sodium iso propyl xanthate (SIPX) in a rougher and scavenger stage produced tailings containing about 0.03 percent copper and 0.03 percent nickel, which corresponds to overall copper recoveries of about 92 percent and overall nickel recoveries of about 62 percent. However it is estimated that only about 68 percent of the nickel is present as sulfide and therefore, recoverable. Using the 68 percent sulfide nickel value, the sulfide nickel recovery is about 91 percent.

During the test period, NRRI geologists determined that the mineralogy and texture of the 200 ton sample were not typical of the deposit. Therefore, it was decided to suspend testing of the sample and to procure a more representative sample.

SAMPLE 2.

In May of 1996 a second bulk sample of approximately 125 tons was obtained from the Babbitt deposit. The sample was crushed and screened to minus 3/4-inch and stockpiled inside. During the crushing and screening the final product was sampled and composited to produce a sample for chemistry and for laboratory processing. The head sample contained 0.363 percent copper and 0.085 percent nickel. A series of rougher scavenger tests were run using SIPX to determine the effect of grind time and to produce sufficient bulk concentrate for regrinding and selective flotation of the bulk sulfide concentrate. The total copper and nickel recoveries in the rougher and scavenger stages as a function of grind time are shown in Figure 1, which indicates an improvement in recovery with increased grinding time. The rather large scatter in nickel recovery is due in part to analytical accuracy. A difference of 0.005 percent nickel in the scavenger tail can change the recovery calculation by about 4 percent. In general the laboratory rougher-scavenger tests have indicated that over 90 percent of the copper can be floated along with about 68 percent of the total nickel, which should be over 90 percent of the sulfide nickel.

Because of the low weight recovery in the bulk sulfide concentrate, between 2 and 4 percent, it was difficult to produce sufficient material for regrinding and selective flotation tests. Therefore, it was decided to set up a small pilot scale rougher-scavenger circuit without any recirculating and to grind in a ball mill in open circuit. Before the pilot plant was run, the effect of grinding in a mild steel mill with mild steel ball compared to grinding in a stainless steel mill and stainless balls was tested in the laboratory. The laboratory tests showed the flotation response was not effected by grinding with mild steel. The small pilot plant flowsheet consisted of 30-inch by 40-inch ball mill which fed a conditioning tank ahead of a four-cell rougher bank. The rougher concentrate was collected in plastic lined drums and was stored under water to reduce surface oxidation. The rougher tails were fed to another conditioner which fed a two-cell scavenger bank. The scavenger concentrate was also collected and stored. The scavenger tails were decanted, dried and stored for disposal. Samples of the various stream were taken during periods of smooth operation. The material collected in the drums included periods of upset which diluted the concentrates. In general, the pilot plant recoveries were similar to the laboratory results with over 90 percent copper recovery and about 67 percent total nickel recovery.

Laboratory regrind and selective flotation tests were run on the pilot plant bulk sulfide concentrates to make a separate copper concentrate and a separate nickel concentrate. Making the copper concentrate was fairly straight forward. It was possible to make a copper concentrate containing approximately 24 percent copper and 0.30 percent nickel. The copper concentrate contained over 70 percent of the total copper in the feed. It was not possible to produce a nickel concentrate with a low copper content. In general there was as much or more copper than nickel in the "nickel" concentrate.

To assess the potential for PGE recovery, samples of crude ore, copper concentrate and "nickel" concentrate were sent to the University of Quebec for analysis. The results are shown in Table I. The analysis indicates that the PGEs are fairly evenly distributed between the copper and nickel concentrates, which suggests that producing a bulk sulfide concentrate and then treating the bulk concentrate hydrometallurgically would maximize the PGE recovery.

CONTINUOUS PILOT PLANT

To facilitate running the pilot plant about 20 tons of minus 3/4-inch crude was crushed to minus 20 mesh in a high pressure roller press (HPR) and was stored in drums. The pilot plant as originally configured, Figure 2, consisted of a ball mill in closed circuit with a density classifier, followed by conditioning of the classifier overflow with the conditioned slurry going to a three-cell bank of rougher flotation machines. The rougher froth went to a two-cell bank of cleaners with the cleaner tails being recycled back to the conditioner. The rougher tail went to a second conditioner which fed a two-cell bank of scavengers. The scavenger concentrate was cleaned in a two-cell bank while the scavenger tails went to a thickener. The tails from the scavenger cleaner went back to the second conditioner. The pilot plant was constructed to allow for changing the destinations of the various recycled streams and various configurations were tested. The two concentrates from the pilot plant, cleaner concentrate and scavenger cleaner concentrate, were collect in plastic lined drums and stored under water to await laboratory regrinding and selective flotation and/or hydrometallurgy.

The pilot plant ball mill was operated in both open and closed circuit. There was no significant difference in copper and nickel recoveries between the two modes of operation. The copper and nickel losses occur in both the coarse and the fine fractions as shown in Table II for open and closed circuit. Therefore changes in grind will have little effect on recovery.

During the pilot plant operation, very little scavenger concentrate was produced and therefore, there was no need for a cleaner stage in the scavenger circuit. In fact, recirculating the scavenger concentrate to the conditioner ahead of the roughers had no significant effect on recovery. Therefore, the bulk of the pilot plant tests were run with the production of only one product, the cleaner concentrate. This flowsheet is shown in Figure 3 along with the copper and nickel grades and recoveries. The cleaner concentrate contains about 2.5 percent of the weight with 91.1 percent copper recovery and 58.6 percent nickel recovery. These results are close to those obtained in the laboratory, although the nickel recovery is lower. Part of the lower recovery may be because the nickel head was also lower (0.075 compared to 0.085 percent), which may mean that the percentage of sulfide nickel is lower and therefore, overall nickel recovery would be lower.

Selective flotation of the copper from the pilot plant bulk cleaner concentrate when the scavenger concentrate was recycled was not successful. It may be that recycling the scavenger concentrate allows the nickel to adsorb too much SIPX and is still hydrophobic after regrinding and retreatment. Tests run with lower reagent dosages in the pilot plant have shown that a selective copper concentrate containing 24.21 percent copper and 0.40 percent nickel can be produced from the pilot plant bulk sulfide concentrate. If a selective flotation is desirable in the commercial operation then the scavenger concentrate should not be recycled and should be cleaned and used as part of the leach plant feed.

BIOPROCESSING

For the bioleaching of crude ore, five cultures of Thiobacillus bacteria were obtained from the American Type Culture Collection (ATCC). Two cultures of Thiobacillus Thiooxidans (oxidize sulfur) and three cultures of Thiobacillus Ferrooxidans (oxidize iron) were obtained along with one culture of Leptosprillium Ferrooxidans. Samples of crude ore from Sample #2 were crushed and screened to produce feeds that were minus 6 mesh, minus 20 mesh, and minus 200 mesh. Each of these samples were split into 25 gram samples for testing. The minus 6 mesh and minus 20 mesh samples were inoculated with the 3 Thiobacillus Ferrooxidan cultures and the Leptosprillium Ferrooxidan culture. The minus 200 mesh material was inoculated with all 6 cultures.

Each bioleach solution was analyzed on a daily basis for Eh (oxidation-reduction potential) and ph and on a weekly basis for Cu, Ni, and Fe concentrations. The Thiobacillus Thiooxidans were generally ineffective with little or no leaching. The four Ferrooxidan cultures extracted both copper and nickel and produced sulfuric acid. Leaching of the two coarser fractions was quite slow, less than 20 percent copper and less than 50 percent nickel dissolved. Therefore, the bulk of the work concentrated on the minus 200 mesh fractions. Each of the four bioleaches of the 200 mesh ore "leveled off" at 30 percent copper dissolution after 80 days with a nickel dissolution of about 70 percent. The leach slurries with the four Ferrooxidan cultures were filtered and rinsed in either 1 normal hydrochloric acid or in one case, deionized water After the rinse the ores were re-inoculated with the appropriate cultures and the leaching continued. Rinsing of the samples increased the copper leaching to between 42 and 57 percent (see table below) with corresponding nickel dissolution of between 78 and 90 percent. The table below gives the recoveries after 180 days for the various cultures:

Culture Name	ATCC Number	% Cu Leached	% Ni Leached	Rinse
Leptosprillium Ferrooxidan	29047	57	90	HCl
Thiobacillus Ferrooxidan	23270	46	81	H_2O
Thiobacillus Ferrooxidan	14119	48	87	HCl
Thiobacillus Ferrooxidan	19859	42	78	HCl

The rinse was necessary to remove a coating of dead bacteria which tend to coat the surface and stop the bioactivity. It appears that the increase in leaching was due to the mechanical rinsing and reinoculation and not to a chemical reaction with the HCl

Under PUTF funding, the bioleaching of bulk sulfide concentrate will be tested. The testing is planned for the summer of 1998.

HYDROMETALLURGY

Due to unanticipated problems and costs in setting up the pilot plant, the hydrometallurical portion of the project was delayed and the program is being fundED by PUTF. The initial test work has focused on pressure oxidation of the bulk sulfide concentrate. The test work is being conduction in a one liter Parr autoclave. To date the results have been encouraging. Over 99 percent of the copper and nickel has been leached with less than 1 percent of the iron reporting to the leach liquor, when leaching at 200 °C with 50 psi oxygen overpressure for 2 hour. Increasing the oxygen pressure slightly improves the leach kinetics. The sulfide sulfur is converted to sulfate with no elemental sulfur being detected. The iron precipitates as an easily filtered material which appears to be hematite.

If the selective flotation of copper from the bulk sulfide concentrate is successful, then the tailings from the selective float will be leached also. Work is continuing on leaching the bulk sulfide with the focus switching to metal recovery from solution and locked cycle tests to determine impurity buildup and to produce sufficient residue for PGE analysis.

CONCLUSIONS AND FUTURE WORK

The test work on the low grade ore from the Babbitt deposit has indicated that it is possible to recovery over 90 percent of the copper and over 80 percent of the sulfide nickel into a bulk sulfide concentrate.

The standard xanthate reagents work as well as some of the newer more expensive reagents.

Using stainless steel rods in a stainless steel mill, produced essentially the same metallurgy as using conventional rods and mill.

Single stage laboratory flotation tests produced essentially the same recovery as did continuous pilot plant tests.

It appears to be possible to produce a smelter grade copper concentrate from the bulk sulfide concentrate. If a copper concentrate is desired, then the scavenger concentrate should be treated separately and not recycled. It was not possible to produce a nickel concentrate which was low in copper, which is typical of all other tests on Duluth gabbro ores.

Bioleaching with Ferrooxidans shows promise and will be continued with the testing of a bulk sulfide concentrate instead of crude ore. Especially promising is the rinse and reinoculation practice to improve recovery.

Oxidation pressure leaching of the bulk concentrate has produced greater than 99 percent copper and nickel extractions with less than 1 percent iron co-extraction. Work is continuing in this area to look into metal recovery, impurity build up, and disposition of the PGEs.

Table I - Metal and PGE Analysis for
Crude Ore, Copper Conc and Nickel Conc

Element	Crude Ore	Copper Conc	Nickel Conc
S(%)	0.79	35.31	19.19
Cu(%)	0.38	23.67	4.74
Ni(%)	0.085	0.36	1.59
Co(%)	0.04	0.02	0.075
Ir(ppb)	0.44	7.40	9.55
Rh(ppb)	0.93	14.29	30.89
Pt(ppb)	8.6	349.2	322.7
Pd(ppb)	52.7	682.6	1138.3
Re(ppb)	2.85	13.96	74.41
Au(ppb)	5.39	172.47	93.49

Table II - Comparison of Copper and Nickel by Size for Scavenger Tails Produced from Open and Closed Circuit Operation

Open Circuit					
Mesh	Wt %	% Cu	% Ni	Cu Dist, %	Ni Dist, %
65	8.1	.052	.075	11.41	16.03
100	7.3	.039	.039	7.71	7.51
150	10.5	.029	.029	8.25	8.04
200	14.0	.024	.024	9.10	8.87
270	12.0	.024	.024	7.80	7.60
400	10.6	.023	.023	6.60	6.43
500	7.9	.031	.031	6.63	6.46
-500	29.6	.053	.050	42.49	39.06
Calc head	100.0	.037	.038	100.0	100.0
Closed Circuit					
Mesh	Wt %	% Cu	% Ni	Cu Dist, %	Ni Dist, %
65	0	-	-	-	-
100	1.4	.057	.039	2.39	1.39
150	11.1	.011	.011	3.74	3.18
200	19.2	.024	.020	14.14	10.03
270	15.3	.018	.028	8.46	11.19
400	12.1	.020	.033	7.46	10.47
500	8.4	.023	.035	5.96	7.72
-500	32.5	.058	.066	57.85	56.02
Calc head	100.0	.033	.038	100.0	100.0

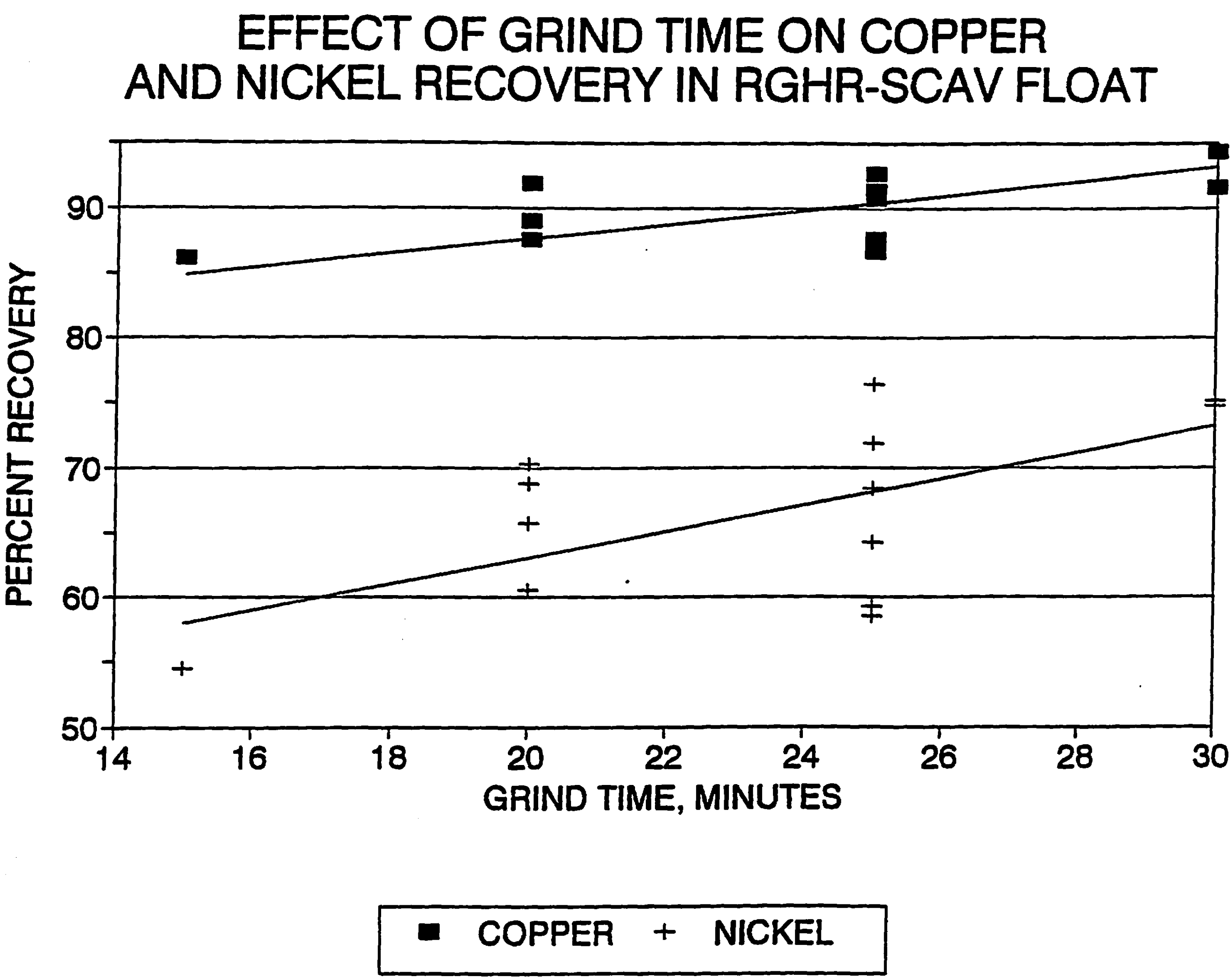

EFFECT OF GRIND TIME ON COPPER
AND NICKEL RECOVERY IN RGHR-SCAV FLOAT
PERCENT RECOVERY
90
80
70
60
50
14
16
18
20
22
24
26
28
30
GRIND TIME, MINUTES
COPPER
NICKEL

Figure 1

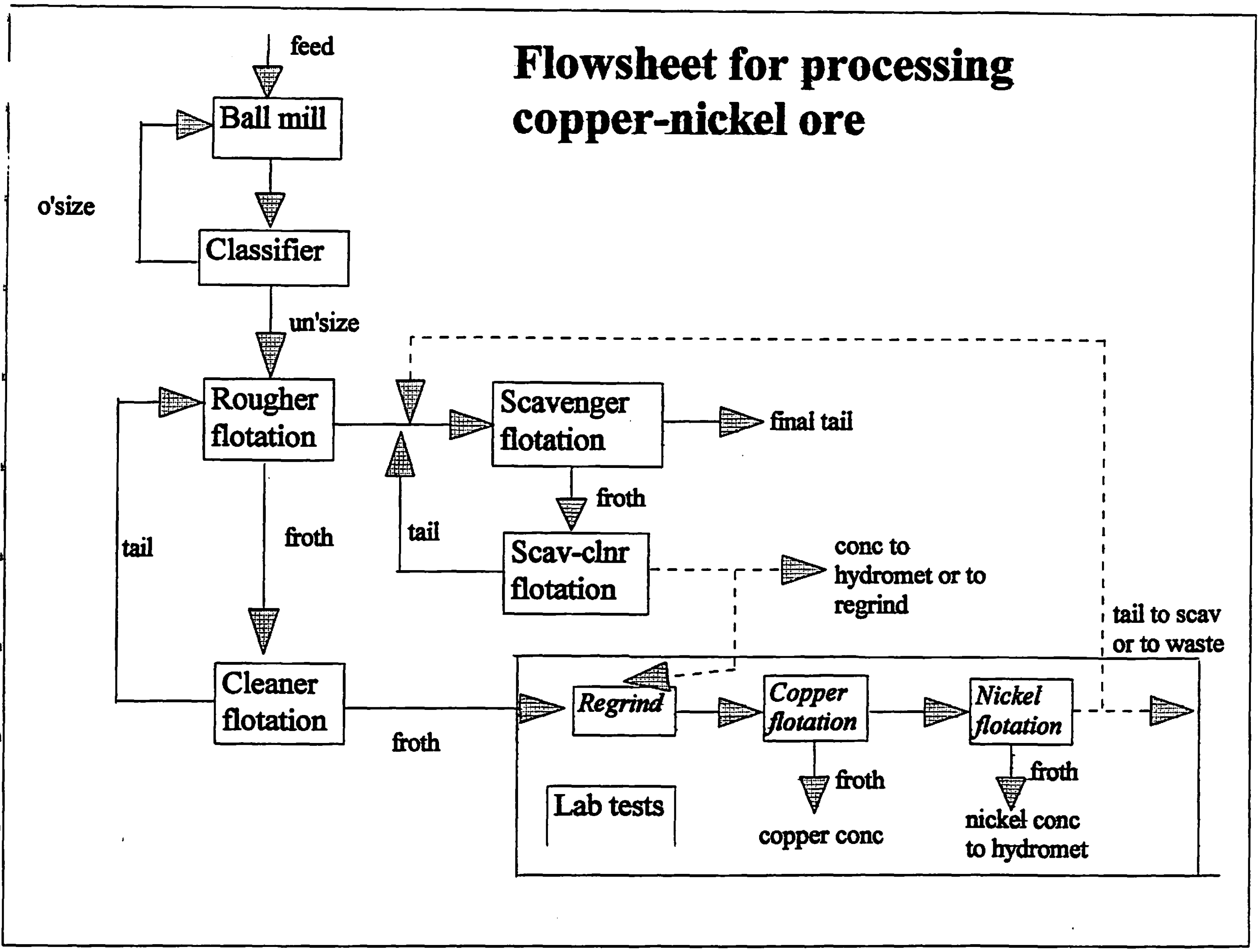
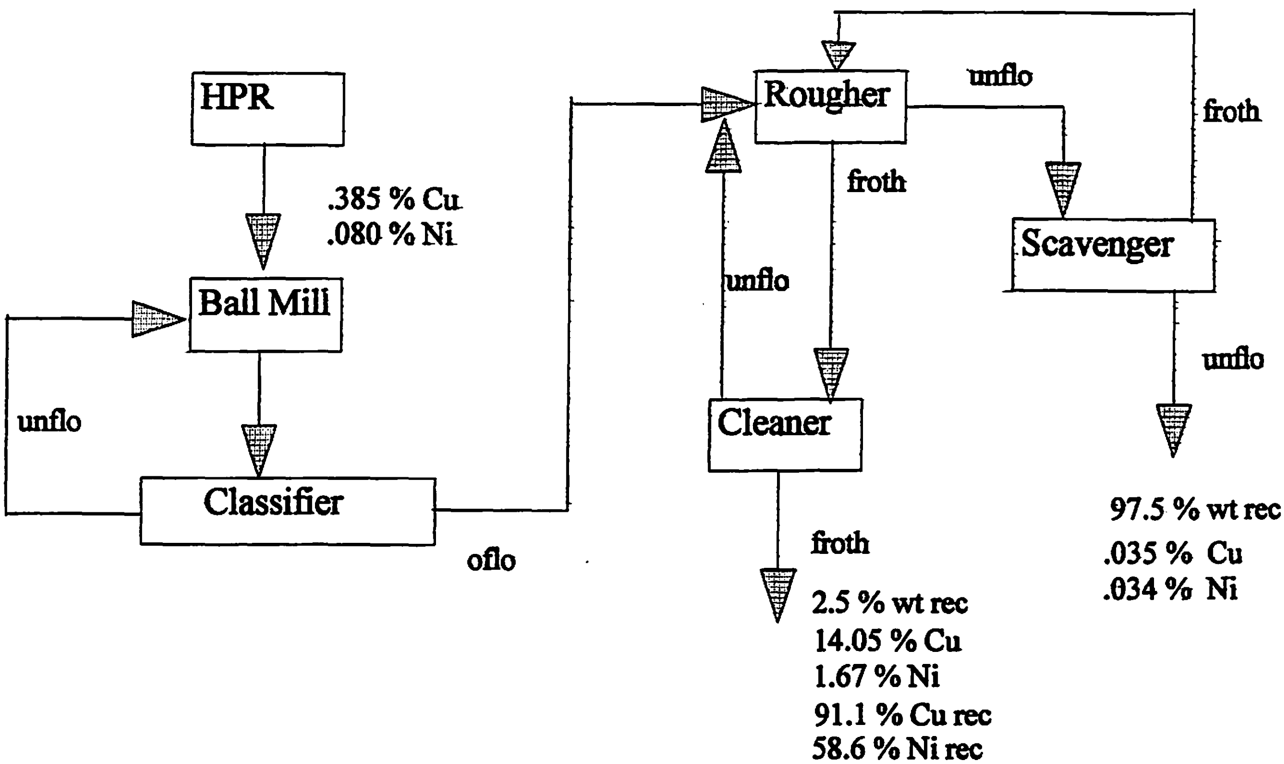

Flowsheet for processing copper-nickel ore
feed
Ball mill
o'size
Classifier
un'size
Rougher flotation
Scavenger flotation
final tail
froth
tail
froth
Scav-clnr flotation
conc to hydromet or to regrind
tail
tail to scav or to waste
Cleaner flotation
froth
Regrind
Copper flotation
Nickel flotation
froth
froth
Lab tests
copper conc
nickel conc to hydromet

Figure 2



SUMMARY OF PILOT PLANT FLOTATION TESTS

Figure 3