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CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

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MINES BRANCH INVESTIGATION REPORT IR 58-173

EXTRACTION TESTS ON SAMPLES OF COPPER-NICKEL ORE
FROM TEMAGAMI MINING COMPANY LIMITED, TEMAGAMI, ONT.

IR 58-173

by

G. THOMAS and T. R. INGRAHAM

MINERAL DRESSING AND PROCESS METALLURGY DIVISION

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SUMMARY OF RESULTS

Pyritic Temagami ore, containing about 1% copper and 0.7% nickel, was leached in ammoniacal solutions under oxygen pressure in an autoclave. Extractions of up to 86% of the copper and 48% of the nickel were obtained. In additional tests, the pyritic ore was thermally decomposed to elemental sulphur and an artificial pyrrhotite. The artificial pyrrhotite, which contained all of the copper and nickel in the original ore, was heated in an autoclave with dilute sulphuric acid under oxygen pressure at about 110°C. From the autoclave, additional elemental sulphur, iron oxide and an acidic solution of copper and nickel were recovered. The extractions of copper and nickel were as high as 86% and 96% respectively, but the metal ion concentrations in the solutions were low, (1 to 2 g/l). Sulphur recoveries of over 90% were obtained.

To increase the copper and nickel ion concentrations in solution, the leach liquors were recycled with fresh samples of the artificial pyrrhotite. The experiments were unsuccessful in producing more concentrated solutions, due principally to the adsorption of metal ions on the iron oxide residue. The successful use of an ion exchange resin to prepare concentrated solutions was hindered by the presence of iron and calcium in the dilute autoclave liquor. Although the recovery of copper, nickel and sulphur from the ore is technically feasible, the standard methods of treating leach liquors are not attractive for the dilute solutions obtainable from this ore.

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**Head, Extractive Metallurgy Section.

INTRODUCTION

Location of Property

The orebody of the Temagami Mining Company Limited is located on the east arm of Lake Temagami, in the Temiskaming Mining Division of Ontario.

Shipments

A 226 lb sample of diamond drill core rejects, selected to represent the main body of ore, was received in April 1956 by the Mineral Dressing Section, for the flotation tests reported in Investigation No. MD 3237. Part of this sample was used for the leaching tests. A second sample of ore, weighing 185 lb, was received in March 1957 by the Extractive Metallurgy Section.

Type of Investigation Requested

The results of Investigation No. MD 3237, indicated that the pyritic copper-nickel ore was difficult to concentrate by flotation methods. Because of this, consultants for the Temagami Mining Company requested that autoclave leaching of the ore be investigated for the recovery of copper, nickel and sulphur. During the course of the investigation, experimental data were discussed frequently with Mr. E. H. Bronson and Dr. M. H. Fröhberg, consultants for the company.

Sampling and Analysis

The samples were ground to minus 100 mesh, and head samples were obtained for analyses. The chemical analyses were as follows:

	Sample 1 (%)	Sample 2 (%)
Copper	1.12	0.72
Nickel	0.63	0.59
Cobalt	0.085	
Iron	32.4	
Sulphur	22.5	
Insolubles	19.5	
Pyrite		36.7

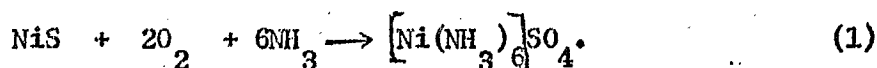
MINERALOGICAL EXAMINATION

The general mineralogical characteristics of the ore were reported previously in Investigation No. MD 3237. The ore contains massive granular pyrite, with small amounts of chalcopyrite. Sphalerite, gersdorffite (sulphide-arsenide of nickel), a linnaeite-type mineral (cobalt-nickel-iron-copper sulphide) and hematite, have been identified. The gangue is mainly chlorite and quartz.

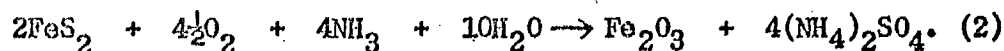
DETAILS OF INVESTIGATION

Ammonia Leaching

Sample No. 1, which contained 1.1% copper and 0.6% nickel, was used in leaching tests with hot ammoniacal solutions under oxygen pressure in an autoclave. The purpose was to dissolve the copper and nickel by reactions of the type:



During the leaching process, part of the ammonia is consumed by undesired reactions with pyrite:



The leaching was done in a four liter stainless steel autoclave equipped with a mechanical stirrer. The 200 g samples of minus 100 mesh ore, together with 1400 ml of aqueous solution containing various amounts of NH_4OH , were heated at various temperatures under air or oxygen pressure for various periods of time. The slurries were cooled and filtered prior to chemical analyses. The experimental data for the leaching tests are given in Table 1.

TABLE 1

Ammonia Leaching of Ore Sample No. 1
(200 g ore, 1400 ml alkaline solution)

Test	$\text{NH}_4\text{OH}^{\text{N}}$ (ml)	Gas (psi)		Temp (°C)	Time (hr)	% Extraction		Pyrite (% reaction)
						Cu	Ni	
1	50	air	100	80	6.0	25	7	14
2A	350	air	100	80	6.8	43	36	
2B**	350	O ₂	50	80	5.2	86	48	
3	200	O ₂	20	70	6.5	65	34	16
4	350	air	200	80	4.8	85	42	14
5	350	O ₂	300	110	5.0	89	23	54

* Reagent was 28% NH_3 of sp.gr. 0.90

** In Test 2B, residue from 2A was released.

Table 1 shows that low extractions of copper and nickel were obtained in Test 1, in which a small amount of ammonia and a low gas pressure were used. Calculations indicate that of the 50 ml of NH_4OH for Test 1, (which is twice the theoretical amount required to leach all of the copper and nickel) approximately 15 ml was consumed by reaction with pyrite. By the use of more ammonia, as in Test 2A, higher extractions of copper and nickel were obtained. By releasing

the residue, as in Test 2B, the over-all extractions of copper and nickel were 86% and 48% respectively. Similar extractions were also obtained in Test 4.

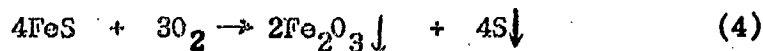
In attempting to increase the nickel extraction by using the severe leaching conditions of Test 5, the nickel extraction decreased to 23%. During Test 5, the nickel concentration of the leach liquor was found to increase initially, and then to decrease. Hence the low nickel extraction was probably due to the adsorption of dissolved nickel on the freshly precipitated iron oxide, formed from the oxidation of the pyrite. Due to the low extraction of nickel and to the high consumption of ammonia, the leaching tests with ammonia were discontinued.

Thermal Decomposition and Acid Leaching

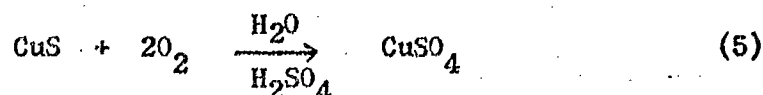
Since the ore contains pyrite, it is a potential source of elemental sulphur. Part of the sulphur can be recovered by thermal decomposition of the pyrite in the absence of air.



Additional elemental sulphur can be obtained by heating an aqueous slurry of this artificial pyrrhotite with dilute sulphuric acid under oxygen pressure in an autoclave.



The latter process for the recovery of sulphur is also suitable for the extraction of copper and nickel. These metals report as sulphates in the leach liquor.



A few experiments were done to note the effect of temperature on the thermal decomposition of the ore. The 350 g samples of minus 100 mesh ore were placed in a 3 in. iron pipe.

Nitrogen was passed over the charge, which was heated at different temperatures, for various periods of time, in an electric furnace. The results of these tests are given in Table 2.

TABLE 2
Thermal Decomposition of Ore Sample No. 1

Test	Temp (°C)	Time (hr)	Decomposed ore	
			wt (g)	FeS (%)
6	750	3	284	42
7	650	4	297	43

Table 2 shows that "pyrrhotite" was formed by the decomposition of the Temagami pyrite. Most of the elemental sulphur, formed during the decomposition tests, escaped as a fine dust with the nitrogen stream. This elemental sulphur could be recovered by the use of suitably designed equipment.

The thermally decomposed ore, from the above tests, was leached with dilute acid under oxygen pressure in an autoclave. The sulphur nodules, formed during the autoclave treatment, were removed by means of a 100 mesh screen, and the iron oxide residue was separated from the leach liquor by filtration. The autoclave products were washed with water, and were analyzed for copper, nickel, and sulphur. The results are shown in Table 3.

TABLE 3

Effect of Preliminary Decomposition Temperature
on the Autoclave Process

(140 g decomposed ore, 1400 ml H₂O, 10 ml H₂SO₄,
300 psi O₂, 120 min at 110°C, 15 min at 130°C)

Test	Decomp temp (°C)	% extraction in liquor		% recovery in nodules		Elem. S recovery (%)
		Cu	Ni	Cu	Ni	
8	750	75	94	9	1	84
9	650	36	87	57	9	85

Table 3 shows that high yields of sulphur, copper, and nickel were obtained by autoclaving the decomposed ore. Recoveries of sulphur of up to 85%, were obtained and the purity of the nodules ranged from 81% to 96% elemental sulphur. Table 3 also shows that the lower the decomposition temperature, the lower was the dissolution of copper and nickel. However, this lower dissolution was compensated by the higher amounts of copper and nickel recovered in the sulphur nodules. The average over-all recoveries of copper and nickel, in the liquors and nodules, were 89% and 96% respectively. The removal of elemental sulphur from the nodules gave nodule residues containing up to 18% copper.

Cyclic Leaching

In the recovery of metal from leach liquors, it is economically desirable to have concentrated solutions. However, due to the low grade of the ore, there was a low concentration of copper and nickel in the autoclave leach liquor. To increase the metal ion concentration of the leach liquors, a series of tests was done, in which the leach liquor was recycled, with fresh ore, to the autoclave.

TABLE 4

Cyclic Leaching of Decomposed Ore Sample 1

(600 g ore, 1800 ml liquor, 300 psi O₂,
120 min at 110°C, 15 min at 130°C)

Cycle	Analysis				Recoveries				Elem. S recovery (%)
	Iron oxide		Leach liquor		% extraction liquor + wash		% recovery in nodules		
	Cu (%)	Ni (%)	Cu (g/l)	Ni (g/l)	Cu	Ni	Cu	Ni	
1	0.23	0.12	1.60	1.44	78	82	15	3	78
2	0.39	0.10	2.56	2.45	57	73	15	3	80
3	0.53	0.10	2.42	3.84	3	89	14	2	73
4	0.53	0.10	2.00	4.68	-34	51	12	2	81

For the recycle tests, a 4000 g lot of ore Sample No. 1 was ground to 100 mesh. The ground ore, after thermal decomposition at 800°C, contained 37% FeS. The results of these cyclic tests are given in Table 4.

Table 4 shows that the recycling process did not build up high concentrations of metal in the leach liquor. The percent metal extraction decreased in successive cycles, and in the fourth leaching cycle, copper was actually removed from the liquor. Because of this unexpected result, and partly because of unsatisfactory metallurgical balances, the recycle tests were repeated.

For the second series of recycle tests, a 4000 g lot of Sample 2 Tomagami ore was decomposed for 3 hr at 850°C. During the decomposition, a high rate of flow of nitrogen was used to remove the sulphur vapour from the ore. The decomposed ore contained 24% FeS, 0.75% Cu, 0.58% Ni and 0.08% Co. In the recycle tests, the experimental autoclave conditions were the same as those used in the previous series.

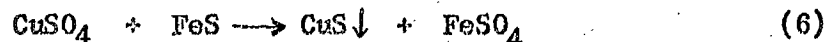
TABLE 5

Cyclic Leaching of Decomposed Ore Sample 2

(600 g ore, 1800 ml liquor, 300 psi O₂,
120 min at 110°C, 15 min at 130°C)

Cycle	Analysis				Recoveries				
	Iron oxide		Leach liquor		% extraction liquor + wash		% recovery in nodules		Elem. S recovery (%)
	Cu (%)	Ni (%)	Cu (g/l)	Ni (g/l)	Cu	Ni	Cu	Ni	
1	0.25	0.08	1.76	1.45	80	85	3	1	88
2	0.27	0.11	2.08	1.75	54	65	5	2	93
3	0.32	0.15	2.86	2.50	47	61	5	2	91
4	0.39	0.21	2.52	2.37	37	55	5	2	82

Table 5 shows that the percentage extractions of copper and nickel decreased with successive cycles of the recycle process. In this series of tests, satisfactory metallurgical balances were obtained, due to more accurate analytical data. The average elemental sulphur recovery was 89%, and the nodule purity sometimes exceeded 97%. As shown by the table, progressively smaller proportions of the copper and nickel were extracted into the liquors, while progressively larger amounts of copper and nickel appeared in the iron oxide residues. These observations are applicable to both Sample 1 and Sample 2. These results indicate that the copper and nickel of the leach liquors were adsorbed from solution by the freshly precipitated iron oxide formed in successive cycles. The sharper decrease in the extraction of the copper may have been due, in part, to some of the copper, but not the nickel, being replaced from the acidic solution by the pyrrhotite.



There were high extractions of copper and nickel in single stage tests, but the over-all extractions of these metals decreased sharply and progressively when cyclic leaching was used. The differences in extraction in the single and cyclic tests may be explained on the basis of the relative rates of reaction of the copper, nickel, and iron sulphides, and on the highly adsorptive properties of freshly precipitated iron oxide.

In the single stage tests, the oxidation of pyrrhotite to form hydrated iron oxide is rapid and precedes the oxidation of the copper and nickel sulphides. As a result, the iron oxide has passed through its most active adsorbing stage before appreciable concentrations of copper and nickel sulphate have accumulated in the solution.

Hence, in single stage tests, adsorption of copper and nickel by the iron oxide is slight. However, in the cyclic tests, appreciable amounts of copper and nickel are present in the solution (from the previous test) at the time when the iron oxide is being formed from the fresh ore charge and is passing through its active adsorption stage. Hence, in the cyclic tests, marked adsorption might be expected and was in fact observed. The adsorption was so effective that copper and nickel were actually lost from the solution during tests where, barring adsorption, they might have been expected to accumulate.

Recovery of Copper, Nickel and Cobalt

There are numerous methods which can be used for the recovery of copper, nickel and cobalt from aqueous leach solutions. An increased recovery, at decreased cost, can usually be obtained by the use of concentrated leach solutions instead of dilute leach solutions. To compare recoveries, tests were done with a strong synthetic liquor, and with the autoclave leach liquor from the first recycle series.

In the recovery process, the solutions were heated and aerated, to oxidize iron to the ferric state. The ferric hydroxide, formed by the addition of NaOH to give a pH of 3, was removed by filtration. Metallic copper was removed from the liquor by cementation with iron fillings. Residual iron from the cementation stage was precipitated as the hydroxide, by raising the aerated solution to a pH of 4.5. Cobaltic hydroxide was precipitated by the addition of sodium hypochlorite. By adjusting the pH to 9.5, nickel was precipitated as the hydroxide.

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TABLE 6Recovery of Metals from Leach Liquors

Metal	Synthetic liquor		Recycle liquor	
	(g/l)	(% recovery)	(g/l)	(% recovery)
Fe	13.1		5.6	
Cu	21.5	96	2.0	89
Ni	14.0	95	4.7	86
Co	2.2	96	0.7	81

Table 6 shows that high recoveries of copper, nickel and cobalt were obtained with the concentrated synthetic liquor. With the dilute recycle autoclave liquor, the recoveries were less satisfactory, but were in excess of 80%. With more experience in the separation technique, somewhat higher recoveries might be obtained.

Ion Exchange Resin Tests

The recycling of autoclave liquors was unsuccessful in producing concentrated leach liquors. This failure was due, possibly, to the adsorption of metal ions on the iron oxide formed from the pyrrhotite. The possibility of using a modified adsorption phenomenon, to advantage, was investigated with an ion exchange resin.

For the ion exchange experiments, the sulfonated cation exchange resin, Permutit Q, was placed in a vertical glass burette of 1 in. diameter. Dilute leach liquor, containing various amounts of copper, nickel, iron and calcium, was passed slowly down through the tube. In this passage, the metal ions were removed from the dilute liquor, and replaced by hydrogen ions from the resin. After the loading stage, the ion exchange process was reversed by the passage of

a strong 10% v/v H_2SO_4 solution down through the tube, to give an effluent containing a high concentration of metal ions. Water was then passed upward through the column to expand the resin bed prior to re-use of the resin.

The presence of calcium in the liquors was found to be harmful. The calcium ions, which were eluted by the strong sulphuric acid, formed a precipitate of calcium sulphate that blocked the passage of solution through the resin bed. Two methods of preventing this blockage were tried. One method was to expand the resin bed by the upflow of water, immediately prior to eluting the resin by the upflow of acid through the expanded bed. The second method was to use the resin in a stainless steel wire basket, and to elute the resin by moving the basket up and down, piston-wise, in a glass cylinder containing the sulphuric acid.

In each ion exchange test, the metal ion concentration in the eluate changed progressively during the elution stage. The metal concentration was initially zero, rose to a certain maximum value, and then decreased to zero when the elution was complete. The maximum metal concentrations, that were obtained in the various tests, are given in Table 7.

TABLE 7

Ion Exchange Experiments to Form Concentrated Solutions

Test	Elutriant (% H ₂ SO ₄)	Elutriant flow	Apparatus	Influent solution (grams per litre)					Eluate solution (grams per litre)				
				Cu	Ni	Fe ⁺⁺	Fe ⁺⁺⁺	Ca	Cu	Ni	Fe ⁺⁺	Fe ⁺⁺⁺	
10	10	Downflow	Burette	2						19			
11	"	"	"	1	1					8	8		
12	"	"	"	2		2				8		9	
13	"	"	"	2			2			7			10
14	"	"	"	1		1	3			3		3	10
15	5	"	"	1	1	1	4			1	1	1	5
16	10	"	"	1	1	1	3			2	2	2	9
17	15	"	"	1	1	1	4			4	4	4	17
18	10	"	"			4						15	
19	15*	"	"			4						45	
20	10	Upflow	"	1				1		6			
21	10**	Upflow	"	1				1		17			
22	10		Basket	1				1		5			

* Elutriant contained acid plus 22 g Fe⁺⁺/l.

** Elutriant contained acid plus 20 g Cu/l.

The synthetic solutions used in these tests were made from reagent grade metal sulphates, and the acidity was adjusted to a pH of 1 with H_2SO_4 . The composition of certain of these synthetic solutions was similar to that of autoclave leach liquors. The Permutit Q was found to have a capacity of about 16 lb copper/ft³ of resin bed. On eluting the resin bed, approximately 65% of the metal in the loaded bed was removed by the passage of 4 bed volumes of 10% v/v H_2SO_4 .

Tests 10 to 14 show that, with 10% v/v H_2SO_4 for elution, the concentration of the eluate liquor was approximately 17 g metal ion/litre. This same total concentration was reached whether one or several metals were present in the liquors. The presence of metals, such as iron, in the influent liquors was undesirable, since these metals lowered the concentration of the desirable metals in the eluate liquors.

The use of strong acid was found to be effective in forming concentrated eluate liquors. Tests 15 to 17 show that by increasing the acid concentration from 5% to 15%, the metal ion concentration in the liquor was increased approximately three-fold.

A second method of producing concentrated eluates is shown by Tests 18 and 19. By using an elutriant solution containing dissolved metal ions, as in Test 19, the metal ion concentration of the liquor was increased, by its passage through the resin, to a value of 45 g/l. This procedure is useful in stripping a loaded resin. As previously noted, the final portions of eluate solutions have a low metal concentration. The mixing of the final with the initial portions of the eluate, would cause an undesired lowering of the metal

concentration. However, if the final portions are kept separate, and are used for the initial elution of a subsequently loaded resin, then concentrated eluate liquors would be recovered.

Calcium presented a serious problem, due to the plugging of the column with insoluble calcium sulphate. The upflow of elutriant solution expanded the resin bed, and prevented this plugging. However, this expansion, as shown by Tests 20 and 21, was accompanied by dilution of the liquor, so that concentrated eluates were not obtained. In Test 22, the piston-like action of a wire basket in a glass column shook the calcium sulphate from the resin, but was unsuccessful in producing a strong eluate solution. In this investigation, no suitable method was devised for eliminating the calcium problem.

CONCLUSIONS

The leaching of Temagami ore, in ammoniacal solutions under oxygen pressure, was unattractive. Although the extraction of copper was almost 90%, the nickel extraction was less than 50%. Attempts to increase these extractions caused an undesired oxidation of the pyrite, and the wasteful consumption of ammonia.

The pyritic ore samples were changed, endothermally, to elemental sulphur and pyrrhotite, by heating the ore in the absence of air. An aqueous slurry of the pyrrhotite, when heated under oxygen pressure in an autoclave, formed iron oxide, elemental sulphur nodules, and an autoclave liquor; the copper and nickel were distributed among these three products. A low temperature of 650°C, during the thermal decomposition stage, led to the appearance of about 60% of the copper in the autoclave sulphur nodules. A high thermal decomposition temperature of 850°C led to a high proportion of the copper appearing

in the autoclave liquor. Under suitable conditions, up to 80% of the copper and 94% of the nickel was dissolved. The sulphur nodules were of up to 97% purity, and recoveries of over 90% were obtained,

To improve the economics of metal recovery, by forming concentrated leach liquors from the low grade ore, the leach liquors were recycled to the autoclave with additional ore. These experiments were unsuccessful. This was probably due to the adsorption of copper and nickel, from the recycle liquor, by the freshly formed iron oxide in the autoclave.

The use of an ion exchange resin was found to be unsuitable for concentrating the copper and nickel. The presence of iron and calcium in the autoclave liquors lowered the capacity of the resin, and also lowered the concentration of copper and nickel in the eluted solutions. Calcium formed calcium sulphate and plugged the resin bed during the elution.

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