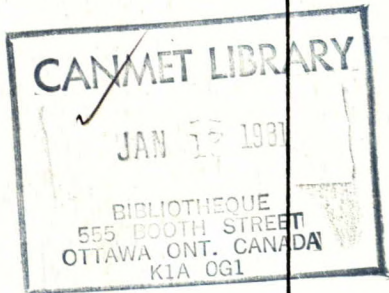CANADA

A LITERATURE SURVEY OF METHODS FOR
TREATING NICKEL AND COPPER ORES
AND CONCENTRATES AND OF
METHODS FOR RECOVERING
COPPER FROM SOLUTIONS

by

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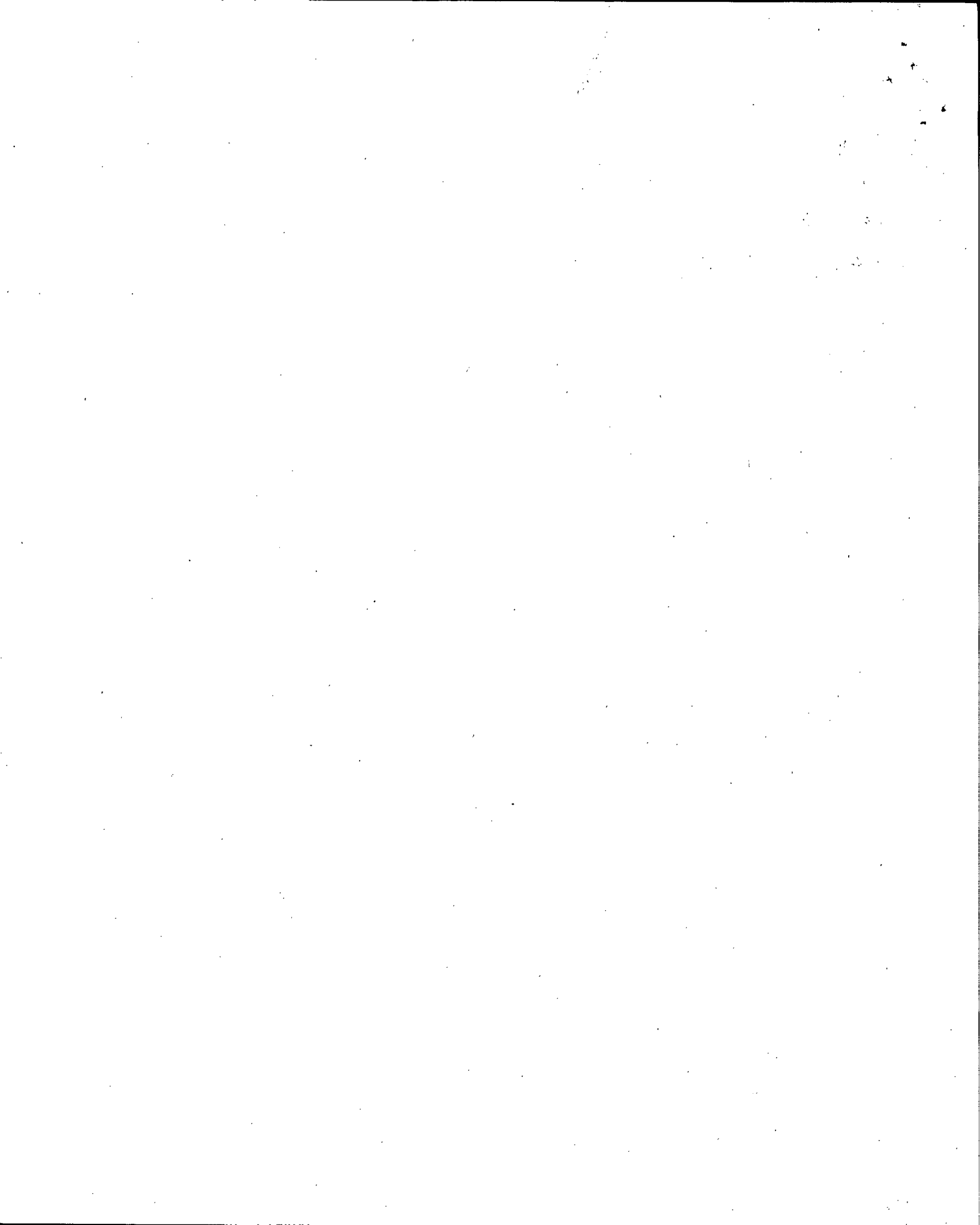
by

J. A. Vezina *

ABSTRACT

This literature survey describes briefly with due acknowledgements, the processes used for extracting nickel and copper from their ores, and the methods used for recovering copper from extraction solutions. The survey is reported in four parts: processes for extracting nickel from nickel-copper sulphide and nickel oxide ores; processes for extracting copper from sulphide and oxide ores; methods for recovering copper from solutions; and a bibliography. Where available, published production and process cost figures are reproduced.

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INTRODUCTION

Part 1, Nickel Ores and Concentrates

The total world production of nickel in 1966 was estimated at 475,000 short tons[70]. Of this production, 51.8 per cent derived from Canadian sulphide deposits, 22.9 per cent from nickel oxide ores from outside Canada, and 24.1 per cent from undisclosed sources mainly in Russia, Indonesia, Poland and South Africa. The remaining 1.2 per cent of the 1966 production is accounted for by producers in Finland and the U.S. operating on sulphide ores.

The most common methods of treating nickel sulphide ores are those based on pyrometallurgical techniques. Ninety-three per cent of the sulphides processed in Canada, Finland and the U.S. are given pyrometallurgical treatment. In addition 72 per cent of the oxide ores mentioned in the literature are treated in pyrometallurgical plants.

Hydrometallurgical techniques are applied in the treatment of nickel sulphide concentrates at the Canadian plant of Sherritt Gordon Mines Limited and the U.S. plant of the National Lead Company. These two plants together produced 17,000 short tons of nickel in 1966. Thirty thousand short tons of nickel were produced from oxide nickel ores by hydrometallurgical methods in the same year in plants in the U.S., Cuba and the Philippines.

Nickel Sulphide Ores and Concentrates

Practice at International Nickel Co. of Canada, Ltd.

In the Sudbury District, the plants of the International Nickel Company of Canada Limited produce three concentrates; a copper concentrate which is flash smelted, a nickel concentrate which is partially roasted and smelted in reverberating furnaces, and a pyrrhotite concentrate which is dead roasted and reduced to produce magnetite,[45][52] metallic nickel, copper and cobalt. At the Thompson, Manitoba plant, of INCO, two concentrates are produced, a nickel concentrate which is partially roasted and smelted in electric furnaces, and a copper concentrate which is flash smelted at Copper Cliff, Ont.[51].

The metallurgical operations of International Nickel Co. of Canada, Ltd., have been described in details in previous publications and will not be discussed in this survey[33,45,50,51,52,67,74,78,79]. However, it may be mentioned that in 1968, Inco announced plans to construct an 85 million dollar plant for processing nickel concentrate using their new "Inco Pressure Carbonyl" process, which will permit increasing production by 30 per cent to 300,000 t/year by 1971 [68][77].

Practice at Falconbridge Nickel Mines, Ltd.

The Sudbury Falconbridge ore consists mainly of pentlandite, chalcopyrite and pyrrhotite. Two concentrates are produced by flotation: a high grade nickel-copper concentrate and a low-grade nickel-pyrrhotite concentrate[53].

The metallurgical operations of Falconbridge Nickel Mines Ltd., have been described in details in previous publications and will not be discussed in this survey[32,47,53,74,77].

It was recently announced[73] by Falconbridge and Allied Chemicals Ltd., that in a joint undertaking, the two companies plan to build a plant at a cost of $35 million for treating low-grade nickel pyrrhotite concentrate produced by Falconbridge to recover elemental sulphur as well as iron and nickel[73]. The method to be used in this proposed operation has not been disclosed, but it is thought that it will consist of roasting the concentrate to produce gaseous sulphur dioxide which will be subsequently reduced to elemental sulphur.

Producing elemental sulphur from sulphur dioxide is not new; in 1936, Consolidated Mining and Smelting Corp. operated a plant for reducing sulphur dioxide with coke. This operation has since been discontinued and the sulphur dioxide is processed now for the production of sulphuric acid which in turn is used to produce fertilizer. In 1961, International Nickel Co. and Texas Gulf Sulphur Co. jointly piloted a process for reducing sulphur dioxide to elemental sulphur using natural gas. A process for reducing sulphur dioxide to sulphur called the "Sulfidin process" was also developed by the German firm, Lurgi, but it was never used on a large commercial scale[50][73].

Practice at Sherritt-Gordon Mines, Ltd.

The Sherritt-Gordon process[30][42][48] was developed during the period 1947-1953 and became a commercial operation at Fort Saskatchewan, Alberta, in 1954. The process cost about $2.5 million to develop. It was originally estimated that this process would produce nickel from sulphide concentrate at a cost less than half of that of conventional smelting and refining. Since 1954, the plant has produced 30 million pounds of nickel per year on a steady, sound, economic and technological basis. The plant also produces 1 million pounds of cobalt per year[44].

It has been announced recently that Western Mining Corporation of Australia[49], plans to build a nickel refinery at Kwinana, Western Australia, which will use the Sherritt Gordon process. It is expected that by 1970, this will be the World's fourth largest nickel producer with an annual capacity of 33 million pounds. The mine has been producing since 1967, and a concentrate produced at the site has been shipped to Sumitamo Metal Mining Co. Ltd., Japan, and Sherritt Gordon for processing. The ore assays 3.8% Ni.

Sulphuric Acid Pressure Leaching

Feasibility tests have shown that chalcopyrite, pentlandite, pyrrhotite and some other sulphides are decomposed in aqueous medium when subjected to pressure oxidation to produce non-ferrous metal sulphates, iron oxides and elemental sulphur[19][20][62][63][64][65][66]. Pilot plant testing with sphalerite and iron monosulphide has demonstrated the economic feasibility of the process for the production of zinc, iron ore, and elemental sulphur.

Conditions for the extraction of copper and sulphur from chalcopyrite, and of iron oxide and sulphur from pyrrhotite, by pressure oxidation have been determined,[19][76] but the extraction of nickel and elemental sulphur from pentlandite has not been studied in detail. It is however, reasonable to assume that the conditions established for the extraction of copper and sulphur from chalcopyrite by this method would also achieve the decomposition of pentlandite for the production of nickel, sulphur and iron oxide.

Results of experiments on the pressure leaching of pyrrhotite, which sometimes contains nickel, in dilute sulphuric acid showed that:[65]

a) at 110°C (230°F) and reasonable pressure, the oxidation of pyrrhotite to elemental sulphur and iron oxide was about complete after a period of one to two hours;

b) agitation of the pulp must be maintained at a rate sufficient to provide good gas-pyrrhotite contact, otherwise it was necessary to use higher pressure to obtain a satisfactory extraction.

c) using oxygen pressure greater than 150 psig resulted in relatively small increase on the rate of sulphur production.

d) the reaction rate obtained by using 30 psig O_2 was identical with that obtained by using $3\frac{1}{2}$ times the theoretical volume of air at 150 psig pressure.

The overall reaction involved in the pressure oxidation of pyrrhotite in sulphuric acid may be expressed by the following equation:

$$FeS + O_2 \longrightarrow Fe_2O_3 + S$$

Practice at Petsamo Nikkeli O/Y., Finland

This operation handles a run-of-mine ore which contains nickel sulphide and pyrrhotite and is not amenable to concentration by flotation or other methods. After intensive testing, it was decided to smelt the ore directly in an electric furnace to produce matte[48]. The following equation would represent the reactions in the furnace:

$$(Fe,Ni)S + FeS + O_2 \longrightarrow FeO.SiO_2 + Ni_3S_2 + FeS + SO_2$$

One advantage to electric smelting compared to flame-fired reverberatory smelting is that the gas composition can be controlled, and it is possible to produce gas containing greater than 10% SO_2; such a gas is excellent for the profitable production of sulphuric acid or liquid SO_2[50].

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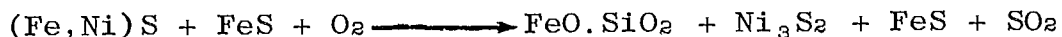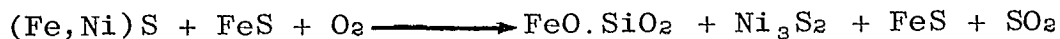
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The Petsamo electric furnace power consumption is 650-700 kWh/t of charge, but for a reason particular to the location of the smelter; suitable limestone for fluxing is not available and the slag produced has a melting temperature 200°C higher than normal for matte smelting. This was also another reason for not using a flame-fired reverberatory furnace for treating Petsamo ore. It has been estimated that with a pre-roasted concentrate the slag temperature could be lowered to 1,100-1,200°C and would require 320 kWh/t; [50] this figure is not far from the actual power consumption required at Thompson's International Nickel plant which is 360-390 kWh/t [58].

The electric furnace matte is then oxidized in a Pierce-Smith converter to produce nickel white metal that contains 58% Ni, 29% Cu, 1% Fe and 10% S.

Practice at National Lead Co., U.S.A.

The National Lead plant treats sulphide concentrate and up to three years ago the concentrate was partially roasted and the calcine was leached in sulphuric acid at 450°F under air pressure of 560 psig. Most of the copper was precipitated from the leach solution as metallic powder by hydrogen under 625 psig pressure at a temperature of 325°F. The solution was stripped of residual copper by cementation with iron and cobalt. The nickel was precipitated from the leach solution as ammonium nickel sulphate and the cobalt was recovered by reduction with hydrogen at temperature 425°F and pressure 600 psig [42].

In 1965, the process was apparently altered and now consists of roasting the concentrate, reducing the calcine with hydrogen in a furnace at 1,350°F for half an hour, digesting the reduced calcine with 1.25 mole H_2SO_4 per mole Co, Ni, Cu at 212°F for three hours, and finally, leaching at 260°F and 20 psig oxygen pressure for 6 hours. The iron oxide residue is removed and the copper is precipitated from the solution as copper sulphide using H_2S. The copper-free solution is then fully stripped of iron by adding oxygen and ammonia. The purified nickel and cobalt sulphate solution is then treated for the recovery of nickel and cobalt [44].

The Caron Process

In his Canadian patent 238,734, [72] Mr. M.H. Caron claims a process for recovering values from nickel and cobalt-nickel ores, whereby the ore is subjected to a preparatory reducing roast and cooled under non-oxidizing or reducing conditions. The nickel and cobalt are then extracted by leaching the roasted product in an ammoniacal ammonium salt solution. The nickel is recovered

from the solution by distillation of the volatile ammonium compounds. This process was applied successfully at the Nicaro nickel plant in Cuba for treating oxidized ores.

Work published in 1948[34] showed that the Caron process can be adapted to treat copper-nickel sulphide concentrates to produce high recovery of nickel and copper. The concentrate was roasted to remove the sulphur. The calcine was reduced with hydrogen at about 900°F to produce metallic nickel and copper as well as magnetite. The calcine was then incubated in an ammonia solution for one hour at 100°F to eliminate the ferrous iron. Extraction of 95% nickel and 80-85% copper were obtained by leaching the digested calcine in an ammonia-ammonium carbonate solution in a 5% pulp at 80°F for 2 hours when oxygen was used for the agitation of the leach. The copper was completely precipitated from the leach solution by cementation with reduced nickel. The purified nickel solution was then boiled to free the ammonia and precipitate basic nickel carbonate.

Nickel Oxide Ores and Concentrates

Blast Furnace Smelting

This process has been used for many years by "La Société le Nickle", New Caledonia. The ore is sintered and then smelted with gypsum. A nickel matte is produced and subsequently converted to separate the iron. The nickel matte is shipped to France, where it is calcined and the resulting oxide is reduced with charcoal. The product is in the form of nickel cylinders which contain 99.6% Ni + Co.[37].

Smelting to Produce Ferro-nickel
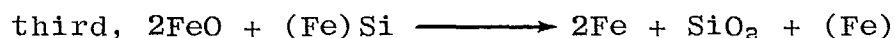
This process is used in a smelter of "La Société le Nickle" in New Caledonia for the treatment of lateritic nickel ore. The ore is dried to zero moisture, and then charged into electric furnaces with coke where a crude ferro-nickel containing 22-23% Ni is produced. This product is then refined by desulphurization with lime and removal of chromium, silica and carbon by oxidation with air [37].

The Ugine Process

This process is used by Hanna Nickel Smelting Co., Riddle, Oregon to produce ferro-nickel[36]. The ore is dried to 3-4% water, crushed and ground. It is then further dried to zero moisture and 30-40% combined water in a kiln. In the Ugine process, the reduction of the nickel and iron in the kiln product is achieved by the addition of a suitable reducing agent to a mixture of molten oxide ore in the presence of molten ferrous metal, using violent agitation for mixing. This process is particularly adaptable to lateritic type low-grade ores containing high magnesia, and is especially attractive for an area where low cost electric power makes electric furnace melting economical.

At Hanna, ferro-silicon in the form of a 45% alloy is used as reductant, and according to the e.m.f. series, the sequence of reduction of the oxides is as follows:

first, $2Fe_2O_3 + (Fe)Si \longrightarrow 4FeO + SiO_2 + (Fe)$

second, $2NiO + (Fe)Si \longrightarrow 2Ni + SiO_2 + (Fe)$

third, $2FeO + (Fe)Si \longrightarrow 2Fe + SiO_2 + (Fe)$

At Hanna in 1959, the nickel recovery was 91.41%

power consumed was 26.32 kWh/lb Ni

nickel production was 20,794,000 lb

ferro-silicon consumed was 1.77 lb/lb Ni

Practice at Nicaro, Cuba

The high magnesia content of the ore treated at Nicaro, prevented the use of an acid leaching process. The technique actually used was essentially the process patented by M.H. Caron[34][72]. The process consisted of drying, grinding and reducing the ore to produce metallic nickel:

$2NiO + H_2 + CO \longrightarrow 2Ni + H_2O + CO_2$; 1,350°F, 83% Ni reduced
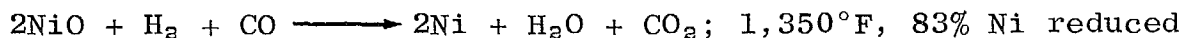
The reduced ore was then leached at atmospheric pressure in a solution of ammonia and ammonium carbonate in Turbo-mixers:

$Ni + \frac{1}{2}O_2 + 6NH_3 + CO_2 \longrightarrow Ni(NH_3)_6 CO_3$; 80% Ni extracted.
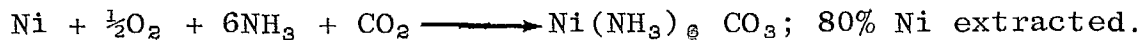
The leached solution was then stripped with steam to precipitate basic nickel carbonate:

$$2Ni(NH_3)_6 CO_3 + 13 H_2O \longrightarrow NiCO_3.Ni(OH)_2 + CO_2 + 12 NH_4OH; 220°F$$
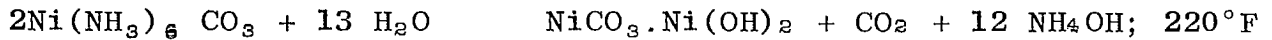
The basic nickel carbonate was calcined:

$$NiCO_3.Ni(OH)_2 \longrightarrow 2NiO_2 + CO_2 + H_2O; 2,000°F$$

The nickel oxide was then sintered and shipped to Wilmington, Delaware;

$$2NiO_2 + \tfrac{1}{2}O_2 + C \longrightarrow NiO.Ni + CO_2; 1,800°F$$

The overall extraction by the Nicaro process was 77-78% Ni[39][40].

Practice at Moa Bay, Cuba

This process was designed particularly for treating the Moa Bay deposit of nickeliferous laterites[38][42]. The ore contained about 1.35% Ni, 0.13% Co and 46.5% Fe. This ore differed from Nicaro in that it contained twice as much cobalt and was low in magnesia. Because of the low magnesium content it was possible to apply an acid leaching process, a technique which was ruled out for high magnesia ore at Nicaro.

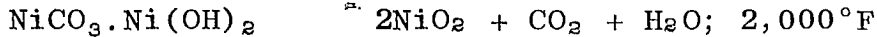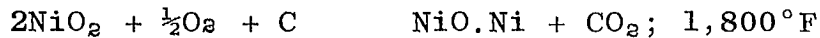The ore was slurried in water and wet screened at 20 mesh. The slurry was thickened to greater than 45% solids. The leaching was carried out by adding 98% sulphuric acid at a temperature between 450 and 500°F and under steam pressure of 650 psig. The nickel extraction was 90-95%. The leach solution was decanted, neutralized with coral mud (90% $CaCO_3$) and treated with enough hydrogen sulphide to destroy chromates and reduce the ferric iron to ferrous iron. The neutralized solution was heated to 170°F and hydrogen sulphide was injected to maintain a total pressure of 150 psig. Under these conditions, 99% of the nickel and 98% of the cobalt in the solution were precipitated.

The sulphide precipitate was then shipped to Port Nickel, Louisiana, where it was dissolved in acid medium to sulphates in autoclaves at 350°F under 700 psig total air pressure. The sulphate solution was purified by adjusting the pH 5-5.5 with ammonia and precipitate aluminum, chromium, and iron. The solution was clarified and acidified to pH 1.5 with sulphuric acid to precipitate the copper, lead and zinc with hydrogen sulphide. Nickel powder was then produced by hydrogen pressure reduction at 375°F and 750 psi. The reduced solution was then evaporated to crystallize the cobalt and the remaining nickel as metal

ammonium sulphates. The crystals were centrifuged and dissolved in strong ammonia. The solution was then oxidized to produce stable cobaltic pentammine and acidified with sulphuric acid. The nickel crystallized out as nickel ammonium sulphate. The nickel-free cobalt solution was then reduced with hydrogen under pressure to produce metal.

The HSO-HTCP Process

This[61] process was designed to treat a variety of so called oxide nickel ores, i.e., laterites, silicates, etc. The ore is mixed with sulphur and slurried. The pulp is then passed through a ball mill to complete the disintegration of the ore to natural particle size and to produce an intimate mixture of the ore and elemental sulphur. The sulphur used varies for different ore types, but normally the required addition is between 300-400 lb/ton dry ore. Pyrite may be used as a source of sulphur.

The slurry is then sulphidized in autoclaves at 230-240°C and 380-480 psig. In the autoclave, most of the elemental sulphur is auto-reduced to sulphide ion which reacts to form iron and nickel sulphides. The balance of the sulphur is auto-oxidized to sulphuric acid which immediately reacts with acid soluble constituents such as the nickel-magnesium silicates. The normal pH of the reacted pulp is between 4 and 6. The contact time is normally about 3 hours.

The pulp is then oxidized in autoclaves at 200°C and 400 psig air pressure. The nickel sulphide is oxidized to soluble nickel sulphate and the iron sulphide is oxidized to sulphuric acid and ferric oxide. The sulphuric acid reacts with the remaining nickel-magnesium silicates and the nickel is taken into solution. In most cases, the terminal pH for optimum nickel extraction is between 1 and 2. It has been found that with silicate ores containing 2% Ni, the extraction was between 85 and 95%.

The solution leaving the oxidation step is primarily a magnesium sulphate solution which contains the nickel, some chromium and iron. The nickel is cemented on iron by heating the solution to 150°C. The nickel and magnetite are recovered by magnetic separation.

The magnetic product is then calcined at 950°C to produce 55% ferro-nickel and slag. The ferro-nickel may be upgraded to 75% by converting.

Sulphating Roast

This process[35] was never used commercially. It involved mixing the ground ore with concentrated sulphuric acid in quantity sufficient to sulphate the nickel, cobalt, magnesium and manganese. This was carried out in a pug mill. The mill discharge was dried by direct firing to transform the iron to $Fe(OH)SO_4$ and the non-ferrous oxides to sulphates. The dry product was roasted and the selective sulphatization of the nickel and cobalt was accomplished. The calcine was leached in water and the nickel and cobalt were precipitated from the leach solution by using hydrogen sulphide. With this procedure, 85-90% and 90% of the nickel and cobalt were respectively sulphated.

Ammonia Pressure Leaching

Marinduque Mining and Industrial Corp., Philippines,[71] have announced that they will develop and operate refinery facilities for the recovery of nickel and cobalt from a lateritic ore. Marinduque has been licensed by Sherritt Gordon Mines Ltd., which will provide management and technical assistance for 25 years. The proposed refinery will have a capacity to produce 25,000 s.t./year of nickel and is scheduled to start operations in 1971 or 1972.

Part 2, Copper Ores and Concentrates

Copper Sulphide Ores and Concentrates

The free world copper production for 1960 was 3,970,000 tons at 93 per cent capacity. The distribution of the costs to produce this copper (taxes excluded) was as follows:[54][55]

460,000 tons produced at $0.10/lb and under; mostly by-product copper.

480,000	"	"	$0.10 - 0.15/lb.
1,260,000	"	"	$0.15 - 0.20/lb.
1,000,000	"	"	$0.20 - 0.25/lb.
500,000	"	"	$0.25 - 0.30/lb.
270,000	"	"	$0.30/lb and over; mostly subsidized copper.

The median cost to produce copper was $0.195 per pound of electrolytic copper, delivered. Of this production, 44 per cent came from open pit mining, the remainder from underground mining.

In 1958, 83% of the copper produced came from ores assaying less then 1% Cu.

      7% " " " " " " " " between 1 and 2% Cu.

     10% " " " " " " " " more than 2% Cu.

In general, the lowest grade ores represented the lowest production costs because most low-grade ores were mined open pit.

About 15 per cent of copper ores, mostly oxides, were treated by hydrometallurgical methods, 85 per cent were pre-concentrated by flotation and most of the copper sulphide ores treated by flotation contained other sulphides, usually lead, zinc and molybdenum.

Pyrometallurgical Methods

The smelting of copper ores is similar to that of nickel ores, which has been discussed already in this report. Consequently, only the costs of milling and smelting copper ores and concentrates as published in the literature will be covered in this section on the pyrometallurgy of copper.

In the Southwest USA, in 1957,[3] the approximate costs of mining and milling copper ores were as follows:

	open pit, $/ton	underground, $/ton
mining	0.30	1.50
milling	1.80	1.80
general services	0.70	0.70
investments costs $1,000 - $3,000/t day with interest and amortization	0.20	0.40
total	3.00	4.40

At Jefferson City Flotation Mill in 1963[5], the milling costs were given as:

	$/ton
labor	0.19
supplies	0.27
R and M	0.14
power at ½¢ /kWh	0.09
total	0.55

At Bethlehem Copper Corp. Ltd., a porphyry copper ore processor, in 1963[1], the costs were reported to be:

	$/ton
mining, open pit	1.34
milling a 42% Cu concentrate	1.09
surface and services	0.06
	2.49

In Russia, in 1965,[2] the costs to produce copper concentrates were:

	Asian porphyry copper	Ural Plants
	$/ton	$/ton
mining	1.20	3.50
milling	1.20	2.20
	2.40	5.70

Rottenstone Mining Ltd., a small company operating in an isolated location in Saskatchewan, Canada,[6] produced nickel sulphide concentrate at a total cost of $4.65 per ton of ore, while the U.S. Bureau of Mines[56] estimated that for 1959, the cost to produce mixed oxide-sulfide or oxidized copper concentrate in Arizona, U.S.A., was $1.35 per ton of ore.

In Russia, 1965,[2] the costs of smelting and refining 20 per cent copper sulphide concentrate produced from porphyry deposits were about $0.05 and $0.03 per pound of copper respectively. The costs of smelting and refining 15 per cent copper sulphide concentrate in the Ural smelters were respectively $0.09 and $0.03 per pound of copper. In almost all plants, sulphur dioxide gas was processed to produce either elemental sulphur or sulphuric acid.

In 1957, the custom smelters in Southwest U.S.A.[3] charged $0.06 per pound of copper to smelt concentrates. The charges were as follows:

|		$/ton concentrate
smelter charge	30% Cu concentrate	17.60
metal deduction	2.5¢/lb copper	15.00
metal losses	13% at $0.30/lb Cu	2.30
		34.90

In 1964,[4] custom smelters in the U.S.A. charged about $0.06 per pound of copper to smelt copper concentrates. The charges were as follows:

		$/ton concentrate
smelter charge	30% Cu concentrate	12.50
metal deduction	2.75¢/lb copper	16.50
metal losses	20 lb/ton at $0.32/lb Cu	6.40
total		35.40

These figures apply to copper concentrates containing no other metal values, however, it is important to the producer of concentrates to be familiar with the various smelter schedules and smelting processes in order to control the grade and character of products to obtain maximum returns. While certain secondary elements present in the concentrate may be penalized, others may lead to bonus payments in that they may be advantageous in the smelting process. Lead, zinc and copper smelters each having different smelting practices either give a low return, no payment or a penalty for metals adverse to the particular process. For instance, copper contained in a lead concentrate is paid for at or near the price paid for lead while lead in a copper concentrate will return less than 50% of the current lead price. Zinc contained in lead or copper concentrates is undesirable and is usually penalized when in excess of minimum amounts allowed by the smelter[4].

Cyanide leaching

Cyanide solutions are good solvents for some copper minerals such as malachite, cuprite, chalcocite and bornite; least soluble are chalcopyrite and chrysocolla[15]. The predominant ion species formed when copper is dissolved in cyanide solution is $Cu(CN)_3^{2-}$, and the reaction of cyanide with a typical cuprous sulphide may be written as follows:

$$Cu_2S + 6\ NaCN \longrightarrow 2\ Na_2\ Cu(CN)_3 + Na_2S$$
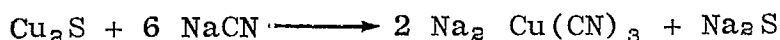
In general, ferric iron is not soluble in alkaline cyanide solutions. Ferrous iron, however, does dissolve to form ferrocyanide, and since ferrocyanides do not decompose readily in cold, dilute sulphuric acid, which is used in the subsequent steps for recovering both copper and cyanide from the leach liquor, the presence of ferrocyanides may result in a cyanide loss. On acidification of the copper cyanide pregnant solution, the free cyanide and the cyanide in the copper complex ion are converted to hydrocyanic acid which is recoverable and the copper is precipitated as Cu_2S[16].

At White Pine Copper Co.,[17] cyanidation of sand tailings which contain sulphide copper has been tested in a 12-24 ton per day pilot plant. The overall copper recovery has been 91.65 per cent on sand tailings assaying 0.228 per cent copper. The cyanide losses were 0.362 pound of equivalent sodium cyanide per pound of copper recovered. Other reagents consumed were 2.06 pounds of lime, 3.60 pounds of spent sulphuric acid and 0.099 pound of sodium bisulphide per pound of copper recovered. The reagents costs were about 9 to 10¢ per pound of copper. It has been estimated that the capital cost of a 7,000 ton per day plant would be about $1,350 per daily ton treated.

Heap leaching

Heap leaching is an old metallurgical process for treating copper ores that has been used extensively in recent years. The practice is widely used in the Southwest U.S.A., where large low-grade deposits, usually containing less than 0.4 per cent copper are mined open-pit and the ore is heap leached. These deposits contain mostly chalcopyrite, chalcocite, pyrite, bornite, etc., but also oxidized copper minerals. Heap leaching is done with natural or artificial solutions of sulphuric acid depending usually on the pyrite content for acid generation[13].

Heap leaching is still in the "art" stage because precise knowledge of the chemistry of the process is lacking, and it is only recently that intensive experimentation has begun with a view of lifting the process out of the category of a minor side-line and elevating it to an integral part of copper producing operations. Producers in Southwest U.S.A. account for one fifth of the world copper production. Selective mining in that area has all but ceased to be a copper source of consequence and the great source of copper is now from the expanding number of open-pit mines, the "great waste mines"[7].

The recent interest in heap leaching can be attributed to various factors. Experimental work carried out at Kennecott Copper Corp. showed that the efficiency of copper leaching could be raised by the growth of bacteria in solutions, regulation of solution temperature, control of oxygen in solution, and relationship to iron salts. The opportunity for heap leaching has been vastly increased because of the great tonnages of low grade material mined and dumped each day at new mines and as a result of stripping ratios at older mines. Heap leaching requires relatively small investment compared to the expansion of milling facilities required to produce the same amounts of copper. The manpower required in heap leaching is low. Finally, heap leaching and copper precipitation from solutions is a simple process that requires little reagents and does not need continuous and close supervision by trained operators[13].

Ammoniacal Pressure Leaching

The Sherritt Gordon process for the ammoniacal leaching of nickel-copper ores has been described in the previous section in the Treatment of Nickel Ores and Concentrates. Although the Sherritt Gordon process was designed for the treatment of the company's nickel-copper ores, the process can be used for treating copper ores as well.

Copper sulphide minerals are altered and dissolved in ammoniacal solutions when subjected to pressure oxidation and high temperatures[29]. Complex reactions occur during the leaching of sulphide minerals with ammonia. Generally, the major reaction may be expressed by the following equation:

$$MS + x\ NH_3 + 2O_2 \longrightarrow M(NH_3)_x\ SO_4,$$
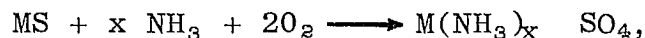
where M represents a metal capable of forming a soluble amine, eg., copper, nickel, cobalt, and x is the number of molecules of ammonia, which varies according to the valence of the metal M.

Experimentation with the leaching of specimen-grade copper sulphides with ammonia under oxygen pressure has shown the following results[29].

    (a)   vigorous agitation of the pulp was required to obtain good leaching rates;

    (b)   the leaching of bornite, chalcocite and covellite in ammonia was not complete, even when a large excess of the reagent was used. This was attributed

to sulphate deficiency in the liquor because the sulphur in bornite and chalcocite is stoichiometrically inadequate to convert the copper to soluble ammonia complex ion. The leaching of chalcopyrite in ammonia was good. Adding ammonium sulphate to the leach solution resulted in high copper extractions from all copper sulphides;

(c) high copper extractions were achieved from bornite, chalcocite and covellite at 50°C in reasonable time, but to obtain similar extractions with chalcopyrite required a temperature of 200°C. Generally, increasing the leach temperature increased the leaching rate of copper from all copper sulphides;

(d) reasonable extractions of copper were obtained from bornite, chalcocite and covellite using an oxygen pressure of 25 psi, but to obtain similar extraction with chalcopyrite required an oxygen pressure of 100 psi;

(e) reasonable extraction of copper from chalcopyrite required a grind of minus 270 mesh;

(f) and again with chalcopyrite, it was necessary to maintain the pulp density at a maximum 15 per cent solids to obtain a reasonable copper extraction.

The same source of information[29] also showed that experimentation with the leaching of chalcopyrite concentrate with ammonia under oxygen pressure resulted in the following:

(a) 96.4 per cent of the copper was leached from a chalcopyrite concentrate in 60 minutes when the pulp which contained 5 per cent solids, 2 pounds of free amonia and 1.5 pound of ammonia as ammonium sulphate per pound of copper was subjected to a temperature of 75°C and an oxygen pressure of 100 psi;

(b) Under the same conditions, the copper extraction was 98.7 per cent in 90 minutes.

Marinduque Iron Mines, in the Philippines[18], proposed to take advantage of the fact that copper sulphide minerals may be leached in ammonia solution under oxygen pressure, and to erect a plant for the production of 42 tons per day of copper and 275 tons per day of ammonium sulphate from a complex ore
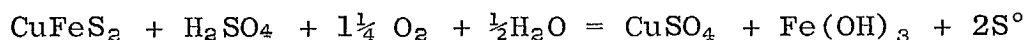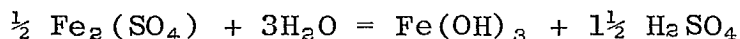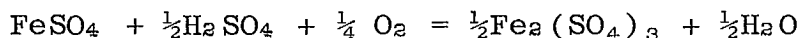
containing 16-25 per cent copper and varying amounts of zinc. The technology is to be provided by Chemetals Inc. and Sherritt Gordon Mines Ltd. The process is basically similar to Sherritt Gordon's at Fort Saskatchewan. From the point of view of the Philippines, the process is advantageous because the operation is designed to be economical at one fifth the capacity and one sixth the investment of a conventional copper smelter.

At Silver Bell, Arizona[7], the mixed oxides and oxidized material encountered in stripping for open pit mining, and which contain about 1 per cent copper and less, are segregated pending results of ammonia leaching tests in a 10 ton pilot plant. The contents prohibit acid leaching.

Sulphuric acid pressure leaching

Chalcopyrite is dissolved in aqueous solution by the action of oxygen under pressure at temperatures both below and above the melting point of sulphur. However the distribution of the products of the reactions varies considerably upon the temperature at which the leaching is done. Generally, leaching chalcopyrite under oxygen pressure at temperatures below 240°F appears to take place at a rate slower than at higher temperatures, and favors the formation of elemental sulphur, while the latter favors the formation of acid. Severe corrosion of the stainless steel autoclave was observed when the leaching was done at temperature about 200°C and above.

Low temperature (210-240°F) leaching of chalcopyrite under oxygen pressure has been said to take place through a set of reactions that may be expressed ideally by the following equations:[19]

$$CuFeS_2 + 2H_2SO_4 + O_2 = CuSO_4 + FeSO_4 + 2S° + 2H_2O$$

$$FeSO_4 + \tfrac{1}{2}H_2SO_4 + \tfrac{1}{4}O_2 = \tfrac{1}{2}Fe_2(SO_4)_3 + \tfrac{1}{2}H_2O$$

$$\tfrac{1}{2}Fe_2(SO_4) + 3H_2O = Fe(OH)_3 + 1\tfrac{1}{2}H_2SO_4$$

$$CuFeS_2 + H_2SO_4 + 1\tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O = CuSO_4 + Fe(OH)_3 + 2S°$$

Laboratory test work[19] has shown that the reaction expressed by this ideal overall equation does not give the complete picture since;

(a)   small quantities of H_2SO_4 (1-3g/1) and $Fe_2(SO_4)_3$

(1-5g Fe^{3+}/1) remained in the leach solution;

(b)   the oxidation of the sulphide sulphur to elemental sulphur was not complete and 10 to 15 per cent of the sulphur was oxidized to sulphate;

(c)   about half of the sulphide sulphur oxidized to sulphate remained in solution, while the other half formed basic ferric sulphate presumably the result of the hydrolysis of the iron in the presence of sulphate;

In determining the optimum conditions for the acid pressure leaching of chalcopyrite, favoring the production of elemental sulphur, it was found that;

(a)   increasing the oxygen pressure from 30 to 500 psi. increased the leaching rate of the copper by a factor of four, while increasing the oxygen pressure to values greater than 500 psi. had no noticeable effect on the rate;

(b)   leaching rates of practical interest could only be obtained when the mineral was ground to minus 325 mesh;

(c)   to obtain practical leaching rates it was essential that the pulp should be initially acidic;

(d)   increasing the temperature of the pulp from 210 to 240°F increased the rate of leaching by a factor of two, while a further increase in the leaching temperature appeared to decrease the leaching rate.

In summary then, it has been shown[19] that the optimum conditions favoring rapid leaching of chalcopyrite and the formation of elemental sulphur by oxidation-pressure leaching were as follows: initially acid pulp, a pulp density of 5 per cent solids, a grind of minus 325 mesh, an oxygen pressure of 500 psi, and a temperature of 240°F. Under these conditions, 97.8 per cent of the copper was dissolved and 85 per cent of the sulphur was oxidized to elemental sulphur[19].

In another investigation[21] using specimen-grade chalcopyrite which was leached under oxygen pressure at temperatures greater than 240°F, the following results were reported:

(a) using pulp densities greater than 25 per cent solids lowered the leaching rate of chalcopyrite rapidly;

(b)   to obtain practical leaching rates, the particle size must be fine, say, minus 270 mesh;

(c)   the rate of leaching deteriorated when the temperature was below 200°C;

(d)   the leaching rate was halved when air was used instead of oxygen;

(e)   high copper extractions were obtained only when oxygen partial pressures of 90 psig or higher were used;

(f)   vigorous agitation of the pulp was essential to obtain practical extraction rates;

(g)   elemental sulphur was not detected in the leach residues;

(h)   with specimen-grade chalcopyrite, 98 per cent of the copper was extracted in 15 minutes when using a pulp of density 5 per cent solids, a grind of minus 270 mesh, an oxygen pressure of 115 psi and a temperature of 200°C.   The copper extraction was about complete in 30 minutes;

(i)   with chalcopyrite concentrate, and using the conditions specified in (h) above, 97.2 per cent of the copper was extracted in 15 minutes; 99.1 per cent in 30 minutes;

(j)   with chalcopyrite concentrate containing 10 per cent zinc, it was necessary to add acid to the pulp to obtain a good extraction in reasonable time.

Recent work[46] has shown that the reactivity of chalcopyrite was enhanced by thermal treatment, thus decreasing its resistance to oxidation leaching.   The results of comparative tests have shown that leaching chalcopyrite of size 95 per cent minus 325 mesh at 90°C and 70 psi oxygen pressure extracted 62 per cent of the copper in 10 hours, while heating the chalcopyrite in an inert atmosphere at 825°C, prior to leaching under these same conditions resulted in 91.5 per cent of the copper being extracted in 10 hours.   Heating the chalcopyrite in the pressence of sulphur in an inert atmosphere at 475°C, and then leaching as before, resulted in an extraction of 97.5 per cent of the copper in 3 hours and 99.5 per cent in 10 hours.

Bacterial leaching:

It is now recognized that microorganisms have been responsible for the extraction of copper from sulphide ores through centuries. It was confirmed in 1962, for instance, that the extraction of copper at Rio Tinto, Spain, is effected through the action of bacteria[41].

The success of the giant heap leaching operations in Southwest USA is also attributable, at least in part, to bacteria which have been identified in the leach streams. Kennecott Copper Corp., Utah, has carried out extensive experimental work in that field and considerable interest has been shown in heap leaching by many other copper producers[41]. Kennecott have found the efficiency of heap leaching could be increased by the growth of bacteria in solution, and the control of oxygen in the solution[43]. The importance of these operations is reflected by the fact that, in 1965, 10% of the world production of copper originated from heap leaching.

Studies of the many variables that control the leaching of sulphide minerals by the action of microorganisms have resulted in the development of techniques that have increased the rates of leaching and extraction. For instance, chalcopyrite which is only very slightly soluble in sulphuric acid at atmospheric pressure can be dissolved to liberate its copper in sulphuric acid containing bacteria at a rate of 50 mg/hr/l of solution[41]. However, it appears that some types of chalcopyrite cannot be dissolved completely with bacterial action, and as much as 10 to 60% of the copper cannot be dissolved in these cases.

As of 1967, the only commercial operations making use of bacteria for extracting metals were the heap leaching of waste copper ores and the extraction of uranium at Elliot Lake, Ontario and in South Africa[41].

Copper Oxide Ores and Concentrates

Sodium hydroxide leaching

At Banner Mining, Arizona[8] work has been carried out to leach oxide copper from carbonate ores; high acid consumptions put acid leaching out of the question with these ores. The copper minerals are dissolved with sodium hydroxide, forming sodium cuprate. Static or batch leaching have proven impractical because of silica gel which coated the minerals and prevented further leaching. Recovery is accomplished at the relatively coarse 10 mesh size. Slimes must be removed continuously from

the solution to avoid an ion-exchange reaction; slimes from an oxide copper ore containing limestone gangue will adsorb cuprate anions from the leach solution. The solution is electrolyzed, decomposing the sodium cuprate and precipitating the copper as a sponge at the cathode. The sponge is separated, dried, melted and purified with a reducing agent to produce copper anode containing about 99.5% Cu.

Hydrochloric acid leaching

This process has been developed at Universidad Technica del Estado, Chile[9][10]. It is based on dissolution of the copper minerals with hydrochloric acid, and raw materials consisting of salt, sulphuric acid and calcium carbonate. Hydrochloric acid is produced from the salt-sulphuric acid reaction, and the oxidized copper is leached yielding copper chloride in solution. Copper carbonate and hydroxide are precipitated from solution with calcium carbonate, and then reduced with carbon in a fusion to metallic copper.

Sea Water leaching

A new joint company has been formed to bring the Michilla copper deposit, Chile[11], into production. The ore is oxide and sulphide copper. A 600 t/day leaching plant using sea water will be built to treat the oxide copper, the sulphide copper will be concentrated by flotation.

Copper ores are not especially soluble in a solution of salt, but a salt solution impregnated with sulphuric acid[9][10] or with sulphur dioxide gas[58] is able to leach copper oxide minerals.

Leaching-precipitation-flotation

The idea of concentrating mixed oxide sulphide copper ores by the LPF method was conceived and developed at Miami Copper Co., Arizona[12], by F.W. Maclennan and H. Keyes between 1929 and 1934. At Miami, a sulphide concentrate is produced for pyrometallurgical treatment. The flotation cell tailing containing copper oxides is leached with sulphuric acid. The dissolved copper is recovered by cementation with iron. The cemented copper is then floated and combined with the sulphide concentrate.
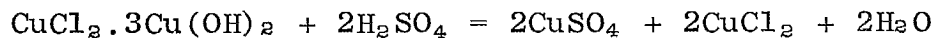
At Morenci, Arizona,[7] the crushed concentrator feed
is leached with sulphuric acid to dissolve the oxide copper.
The dissolved copper is precipitated with a "unique sulphide
precipitant" to a mixture of cupric sulphide and sulphidized
metallic copper. The precipitated copper is then circulated
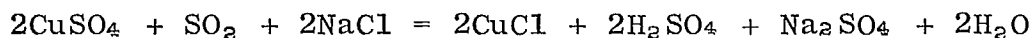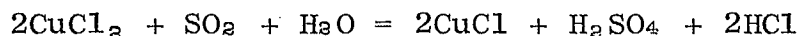with the rest of the ore through grinding and flotation.

Sulphuric acid leaching

Sulphuric acid leaching is used by Nchanga Consolidated
Copper Mines Ltd., for treating oxide copper ores[42]. The ore
is a mixed oxide-sulphide grading 4.69% Cu. The most common
non-sulphide copper mineral is malachite, a carbonate. Direct
leaching followed by flotation of the sulphide was not feasible
because of high acid consumption, and the poor response of
sulphides to flotation from the leach residue. Consequently a
sulphide concentrate is recovered by flotation and smelted,
while two oxide concentrates are produced; a high grade
containing 30% Cu, which may be either smelted or leached, and
a low grade containing 12-14% Cu, which is leached with
spent electrolyte from the refinery. The retention time for
the leaching step is about 5 hours, and the acid concentration
is maintained at 9-11 g H_2SO_4/l. The solubilized iron is oxidized
with MnO_2 and precipitated to a maximum concentration of 1.2 g/l
of solution. The solution is then electrolysed until the copper
concentration is reduced to about 23 g/l copper and then
recirculated. This procedure results in 99% of the copper being
extracted in leaching where the acid consumption is equivalent
to 0.31 lb H_2SO_4/lb Cu. In electrolysis the current efficiency
is 92% and the power consumption is equivalent to 1.05 kWh/lb
Cu.

The extraction of copper from Chuquicamata, Chile,[75],
oxide ores, is effected by sulphuric acid leaching in which a
batch percolation system is used. The ore assays about 1.35% copper
and is mostly antlerite, (3 $CuO.SO_3.2H_2O$), of which 1.03% is
soluble. The ore used to generate sufficient acid for the
process, but since the head has dropped to about 1%, sulphuric
acid must be added periodically. The overall copper extraction
is 77%, and the extraction of soluble copper 94%.

A process which was designed for the particular treatment
of atacamite, $CuCl_2.3Cu(OH)_2$ ore is used at Mantos Blancas, Chile[14].
Basically the process consists of the following:

$$CuCl_2.3Cu(OH)_2 + 2H_2SO_4 = 2CuSO_4 + 2CuCl_2 + 2H_2O$$

the leach solution is then treated with SO_2:

$$2CuCl_2 + SO_2 + H_2O = 2CuCl + H_2SO_4 + 2HCl$$

$$2CuSO_4 + SO_2 + 2NaCl = 2CuCl + 2H_2SO_4 + Na_2SO_4 + 2H_2O$$

The precipitation of CuCl decreases the copper concentration of the leach solution from 35 to 13 g Cu/l. Cementation is used to recover the copper not precipitated by SO_2. The precipitated CuCl is mixed with coke and limestone and smelted:

$$4\ CuCl + 3CaCO_3 + C = 4\ Cu + 2\ CaCl_2 + 3CO_2$$
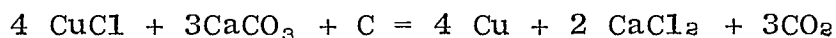
Cyanide leaching[16]

Oxide copper minerals dissolve readily in cyanide solution.

$$Cu_2O + 6NaCN + H_2O = 2Na_2Cu(CN)_3 + 2NaOH$$
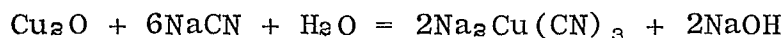
from which the copper and hydrocyanic acid can be recovered.
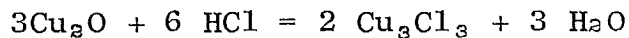
The Segregation process

Sulphide copper ores are normally concentrated by flotation, while oxide copper ores are either leached with sulphuric acid or concentrated by flotation. Some oxide-sulphide ores are refractory to both methods. Some mixed oxide-sulphide ores may be processed by a combination of flotation and leaching while oxide or mixed ores that have calcareous gangue with acid consumption have been treated by sulphidization or ammonia leaching. When these methods fail to give simple and economical solutions, the segregation process presents possibilities since with this technique both oxide and mixed ores with or without calcareous gangue yield good recoveries of the copper and reasonable recoveries of gold and silver[57][61].

Three reactions of major importance occur in the segregation process, and simply expressed, they are:[60]

1. The production of HCl by the reaction of water vapor, silica, silicates and certain chlorides, e.g.,

$$SiO_2 + H_2O + 2NaCl = 2\ HCl + Na_2SiO_3$$
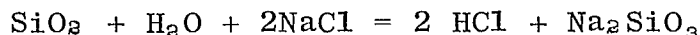
2. The chlorination of copper minerals by the diffusion of HCl to volatile cuprous chloride,

$$3Cu_2O + 6\ HCl = 2\ Cu_3Cl_3 + 3\ H_2O$$

3. The reduction of cuprous chloride to metallic-copper and the regeneration of HCl,

$$2\ Cu_3\ Cl_3 + 3\ H_2 = 6\ Cu + 6\ HCl$$
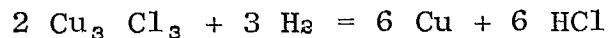
The segregation process was discovered by accident in 1923 by Moulden and Toplin while working for Minerals Separation Ltd. They found that with Chilean Sagasca ore, when using solid carbon as a reductant at 600-800°C, the copper segregated from the ore minerals and was deposited on the carbon. This was traced to the presence of NaCl in the ore, and it was shown that a similar effect could be achieved by adding a small amount of any of the halogen chlorides. The original letter patents were awarded to J.C. Moulden, B. Toplin and Minerals Separation Ltd., British Patent 250, 991 in 1924[58].

Following its discovery in 1923, two attempts were made to apply the process to mixed oxide and sulphide ores in the early 1930's[58]. Both of these plants closed down because of the unfavorable economic climate prevailing at that time. In 1954 a 50-75 tpd segregation plant was built and operated for the treatment of a 3 per cent copper ore in Mauritania[59]. The plant closed after eight months of operation due to operating problems on the desert location.

In 1956 the U.S. Bureau of Mines conducted further research on the segregation process,[59] and concluded that the process was feasible for treating certain types of copper ores at a cost of about $3.00 per ton of feed. Based on this work, a 175 tpd plant was built by Transarizona Resources Inc. near Tucson, Arizona in 1960. In 1961 another 500 tpd plant was built, but unfortunately, faulty design of the two-furnace exhaust system precluded adequate fring rate. The financial resources of the company were not sufficient and the plant was closed in July 1962[64].

More recently, in 1960, Project Torco[60] was started and has progressed to a 500 ton per day plant. It is the code name given by Anglo American Corporation of South Africa Limited, for the project undertaken in Zambia to develop a plant capable of treating large tonnages of copper-bearing ores by the segregation method. Twelve oxide copper ores and two mixtures of oxide-sulphide ores were tested. In the two mixed ores, the oxide to sulphide ratios were greater than 2:1 and the copper recoveries were 85-90% copper. The Torco process offers a solution to the problem of treating refractory ores, but in the words of their technical people: "it is not under normal circumstances competitive with conventional methods for the treatment of sulphide ores".

The costs to operate the Torco process are shown below. They include crushing, drying, dry rod milling of the ore, the Torco furnacing and concentrate drying.

		1,000 t/day	10,000 t/day
Supervision and maintenance	man-hours/day	232	680
Operating labor	" " "	568	2,120
Power	kWh/ton	27	25
Water	gal/ton	1,300	1,300
Drying	Btu/ton water	3,500,000	3,500,000
Roasting	Btu/ton ore	1,430,000	1,430,000
Reagents	lb/ton	0.42	0.42
Lime	lb/ton	2.0	2.0

Finally in the last few years, a combination process of segregation, roasting and flotation-or-magnetic separation was developed to recover nickel from lateritic and oxide nickel ores. Recoveries of 85-90% nickel were achieved.

The segregation process was close to success several times; it was defeated in 1931 by the economic depression and on other occasions by financial troubles. This was because the refractory ores have often belonged to small mining companies with insufficient financial resources. As for the technical aspect of the process, there are several techniques possible for segregation, but each must be worked out before it is considered a viable metallurgical operation[57].

## Part 3, Recovery of Copper From Solutions

Cementation

The oldest, most common method of precipitating copper from copper-bearing solutions has been the gravity-flow launder charged with scrap iron[24]. This installation can effectively recover over 90% of copper in solution, but the iron consumption can vary between 2 and 4 times the quantity required theoretically to precipitate the copper, depending on the ferric iron and free acid in the solution. Launder plants, although simple to construct and operate, require much hand labor and produce an impure cement copper which is usually blended with concentrate as smelter feed.

Gravity drum precipitators have been modified by laying one or more manifolds along the bottom of the launder to inject the copper-bearing solutions into the mass of iron. This has shown a definite improvement over the gravity-type plant. Here again, the cleaning required for removing the accumulation of copper precipitate and trash require high labor costs.

For the efficient recovery of cement copper, the system must have a high volumetric capacity, the capability of treating solutions of variable concentrations with high recoveries, and be amenable to a high degree of mechanical handling and automatic control.

The reactions of importance that occur in the cementation of copper from acidic iron-copper solutions with iron, are as follows:

$$CuSO_4 + Fe^{\circ} = Cu^{\circ} + FeSO_4$$

$$Fe_2(SO_4)_3 + Fe^{\circ} = 3\ FeSO_4$$

$$H_2SO_4 + Fe^{\circ} = FeSO_4 + H_2$$
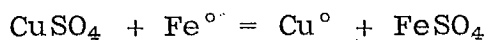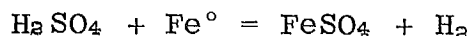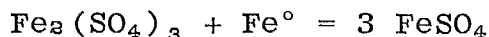
Scrap iron is a major cost item in the cementation process, and it is important that the conditions of operations must favor the reaction between iron and copper sulphate and depress the other two. Kennecott Copper Corp. have made a thorough study of the mechanism of these reactions and have found that the rate of each of these three reactions may be controlled to decrease the iron consumption. Their investigation has led to the development of a system that meets the three previously mentioned requirements for the efficient and economical cementation of copper with iron. Its operating characteristics are based on a high velocity, rapid through-put of the copper-bearing solutions and an intimate contact of the solution with clean active iron. Pilot plant tests which have been expanded to plant scale, have shown that the new system permits the recovery of 95 per cent of the copper contained in solutions assaying 1.5 to 15 lbs Cu/1000 gallons with an iron consumption of 1.5 lb Fe/lb Cu. Discounting the reactions of iron with ferric iron and sulphuric acid, which in practice cannot be eliminated, the iron required theoretically to cement the copper is of course 56/64 = 0.88 lb/lb Cu. Assuming the cost of scrap iron as $50.00/t, they therefore can cement copper with a reagent cost of $0.0375/lb copper.

Electrowinning[24]

The direct electrowinning of copper from relatively dilute solutions of copper-bearing mine waters and heap leaching solutions, containing 10-20 lb copper/1000 gallons, has always been an attractive possibility because high-purity copper can be produced at a relatively cheap cost of about 3.5 kWh/lb. However, once the solutions have been depleted to about 5 lb Cu/1000 gallons, the current efficiency drops rapidly, requiring the use of other methods to recover the remainder economically.

Electrowinning plants are expensive and require a large supply of power, but from an operating viewpoint they produce high purity copper directly at a cost that is probably cheaper than any other method providing that the solutions contain more than about 5 lb copper/1000 gallons (and that the solutions can be pumped and circulated.)

Precipitation of copper sulphide

At Sherritt Gordon's Fort Saskatchewan plant, the ammoniacal leach solution of nickel, copper and cobalt is processed for the copper recovery[31]. The copper recovery consists of two steps. First, the solution is boiled, the ammoniacal copper sulphate is converted to insoluble copper sulphides and the ammonia is recovered. The solution is filtered and the copper sulphides are smelted. About 80 per cent of copper is recovered in this first step. In the second step, the solution is treated with hydrogen sulphide and the remaining copper is precipitated as a mixed sulphide carrying an equal amount of nickel. This precipitate is recycled to the process ammonia pressure leach.

Precipitation of copper oxide

At Calumet and Hecla[28], the ore treated is a conglomerate containing native copper. Free copper is removed by gravity concentration. The leaching sand remaining contains about 8 to 14 pounds of copper per ton. The solvent employed in leaching is a water solution of cupric ammonium carbonate. As native copper is the only valuable mineral in the ore, advantage is taken of the two valences of copper in water solution to effect its oxidation to a soluble form; native copper is nearly insoluble in ammonium carbonate in the absence of an oxidizing agent. A portion of the cuprous solution is regenerated to the cupric condition for use as a new leaching solution by oxidizing it with air. Copper recovery from the remainder of the cuprous solution is effected by distillation whereby the ammonium carbonate is volatilized and recovered and the copper precipitated as copper oxide, which is shipped to the smelter for refining.

Pressure Hydrogen reduction

Arizona Chemicopper Corp's acid leach - hydrogen reduction route to yield high-purity products became operational in June 1966[25][26]. It is the first commercial scale operation of its type. It will produce 25 tons per day of high purity copper powder and cost $3,350,000 to build. Starting with cement copper precipitate from the heap leach step at the Mine, a slurry is made with recycled reduction-end solution. This leach solution contains sulphuric acid, ammonium sulphate, copper, iron and oxygen. The leaching is done at 175°F and pH 2.0. The leach solution is filtered and reduced with hydrogen at 425 psig and 280°F. The copper precipitate is dried and finished according to customer specifications.
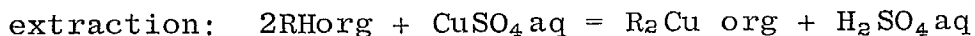
Liquid ion-exchange

The major objectives of a liquid ion-exchanger are defined as follows:[22]

(a)   the purification of a metal from unwanted contaminants; the separation of metals;

(b)   the concentration of metal values for further processing;

(c)   the conversion of metal values to forms which simplify eventual recovery.

Considerable research has been done to develop reagents for the extraction of metal values from solutions. A giant step toward reaching this objective was reached in 1963 with the development of LIX-63 reagent by General Mills Inc. This is a highly selective reagent for the extraction of copper. Unfortunately, because of limitations of the reagent to operate successfully with solutions at pH below 3.0, the treatment of acid heap leaching solutions with this reagent would not be economical. However, recently, General Mills Inc. has introduced to producers a new reagent called LIX 64, that corrects the drawback of LIX 63. It is reasonably priced, has good selectivity for copper and is effective at the normal pH of heap leaching solutions[22].

The chemistry of LIX 64, operating on a hydrogen cycle may be represented by the following equations:

extraction: $2RH\,org + CuSO_4\,aq = R_2Cu\,org + H_2SO_4\,aq$

stripping: $R_2Cu\,org + H_2SO_4\,aq = 2RH\,org + CuSO_4\,aq$

In the large industry of heap leaching low grade copper ores with natural or artificial acidic solutions the standard method for processing the resulting copper-bearing solutions has been to precipitate the copper with iron. The copper is then either electro-refined or smelted. The high cost of this method seems to have been the major driving force behind the intensive work carried out with LIX 64, since this reagent would provide the industry with the means to concentrate and purify dilute copper solutions which could then be electrolysed to high purity copper. The solvent extraction step could thus eliminate the cementation step[23].

However, Kennecoh Copper Corp.[24] which has carried out a detailed investigation to find substitutes for copper cementation with iron, have found that in the field of liquid extractants, improved reagents resisting emulsification were available, but that sufficient experience with these reagents had not yet been obtained to safely justify a major installation. Presently available reagents have a rather low loading factor and would require a large capital expenditure for plants of the size envisioned by Kennecott. A small plant, and in particular, one which does not have a readily available low-cost source of scrap iron would appear to be the logical next step in this development[24].

It has been estimated that a full plant installed would cost for the solvent extraction equipment only, between $200. and $600 per g.p.m. of aqueous feed for dump leaching operations[24][25].

When operated in conjunction with an electrolytic refinery, the chemical and power costs of the LIX 64 process are as follows:[22]

solvent losses @ $2.50/lb LIX 64	1.0 - 2.5 ¢ /lb copper
acid	0.1
scrubbing	0.0 - 0.2
power @ 90% C.E., 1 ¢ /kWh	1.0
	2.1 - 3.8 ¢ /lb copper

The cost is comparable to that of iron cementation operating with a typical dump leaching solution containing 10 pounds of copper per 1000 gallons. The iron consumption would be about 1.5 lb per pound of copper, and with scrap iron at $50.00 per ton, the cost would be 3.75¢ per pound of cement copper [22].

Ion-exchange [27]

Taking $12.00 at the operating cost of the ion-exchange process for the recovery of one pound equivalent of metal (formula weight of the substance/valence of the ion adsorbed by the resin) which does not include amortization costs or the recovery of the metal in a desired form in the eluate, it has been estimated that the cost to process copper and nickel with an ion-exchanger would be: for nickel, $0.41/lb, for copper $0.38/lb. Capital costs are high and it is evident that for metals with low atomic weights, such as copper and nickel, recovery by ion-exchange is high cost and not economical.

Kennecott Copper Corp.[24] have found that technically,
the use of ion-exchangers for the concentration of copper-bearing
dilute mine solutions, has not proven feasible because of the
lack of selectivity of resins and fouling with iron and aluminum.

Part 4

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