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Contaminated Nickel Scrap Processing

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Contaminated Nickel Scrap Processing*

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Abstract

The DOE will soon choose between treating contaminated nickel scrap as a legacy waste and developing high-volume nickel decontamination processes. In addition to reducing the volume of legacy wastes, a decontamination process could make 200,000 tons of this strategic metal available for domestic use. Contaminants in DOE nickel scrap include ^{234}Th , ^{234}Pa , ^{137}Cs , ^{239}Pu (trace), ^{60}Co , U, ^{99}Tc , and ^{237}Np (trace). This report reviews several industrial-scale processes — electrorefining, electrowinning, vapometallurgy, and leaching — used for the purification of nickel. Conventional nickel electrolysis processes are particularly attractive because they use side-stream purification of process solutions to improve the purity of nickel metal. Additionally, nickel purification by electrolysis is effective in a variety of electrolyte systems, including sulfate, chloride, and nitrate. Conventional electrorefining processes typically use a mixed electrolyte which includes sulfate, chloride, and borate. The use of an electrorefining or electrowinning system for scrap nickel recovery could be combined effectively with a variety of processes, including cementation, solvent extraction, ion exchange, complex-formation, and surface sorption, developed for uranium and transuranic purification. Selected processes were reviewed and evaluated for use in nickel side-stream purification.

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1. Introduction

This report presents an evaluation of selected technologies which could provide a basis for development of processes for recovering nickel values from DOE-produced scrap. DOE nickel scrap typically contains small amounts of uranium and trace quantities of cobalt and uranium daughter products. This study was performed early in the project to facilitate process development and to identify areas where research is needed. The DOE is interested in recovery of radiologically contaminated nickel from the perspectives of minimization of legacy wastes and of strategic materials conservation.

Nickel is a relatively scarce, expensive, strategic metal purchased from a variety of foreign sources, most prominently Canada, Norway, and Australia. Its resistance to HF and UF₆ have made nickel and nickel alloys ubiquitous in a variety of nuclear applications. Development of an effective nickel purification process could make 200,000 tons, or nearly \$1 billion, of nickel available from decommissioning the first generation gaseous diffusion plants. As may be inferred from Table 1.1, the nickel potentially available from gaseous diffusion plant decommissioning is equivalent to roughly 3 decades of domestic production, 6 years of recycle, or 17 months of imports.

Although nickel is potentially valuable, its purification is technically demanding. In the DOE system, nickel scrap comes from a variety of sources, including gaseous diffusion

Table 1.1. U.S. nickel production statistics for 1991

Item	Amount, tonnes
Nickel production	7,065
Recovery from ferrous and non-ferrous scrap	32,520
Apparent consumption	137,199
Nickel imports	138,657
Nickel exports	36,902

Source: Kuck 1991.

plants and reactor containment steels.

Radioactive contaminants in this scrap include: ²³⁴Th, ²³⁴Pa, ¹³⁷Cs, ²³⁹Pu (trace), ⁶⁰Co, U, ⁹⁹Tc, and ²³⁷Np (trace).

Present DOE standards for public resale require the absence of contaminants.

However, standards for reuse within the DOE system are

less restrictive and recycled nickel and its alloys could replace a substantial volume of current purchases. If an effective recovery-recycle process is developed, operating experience may permit development of less-restrictive future standards for public resale.

The high volume of DOE scrap encourages the development of a process which uses conventional large-scale nickel purification equipment. Electrorefining and electrowinning, as described by Boldt (1967) are most commonly used for nickel refining. A typical industrial scale electrorefining cell is shown in Figure 1.1. In electrorefining, an impure nickel anode is dissolved into the anolyte (liquid adjacent to the anode) which is subsequently removed from the cell and treated to decrease selected impurities. After treatment, the liquid is reintroduced at the cathode as catholyte. Catholyte purity is maintained by positive pressure through a canvas bag surrounding the cathode. Nickel ions are electrolytically deposited on the cathode. Electrowinning may employ either dissolving anodes of nickel salts, typically nickel sulfide, or the combination of insoluble anodes and dissolved nickel.

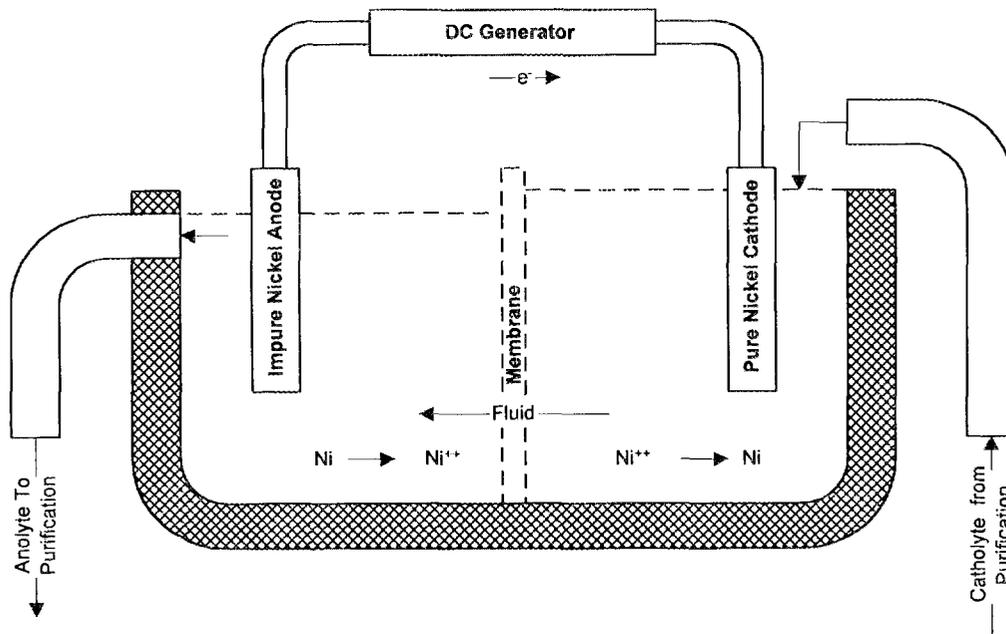


Fig. 1.1. Schematic operation of conventional nickel electrorefining cell. Modified from: Boldt 1967.

Two other processes for nickel purification, vapometallurgy and leaching, are also used at industrial scale. In vapometallurgy, nickel carbonyl formed from reaction of nickel powder and carbon monoxide is decomposed to yield pure nickel. A related process scheme involves ammonia leaching and reduction to form nickel.

Both processes for nickel production by electrolysis are attractive for DOE operations because they provide opportunities to use sidestream processing to remove the contaminants specific to a given lot of scrap. This could maximize process flexibility while minimizing installed capital cost.

Nickel, nickel alloys, and high-nickel steels have historically been used in a wide variety of nuclear process equipment. As facilities are decommissioned, these materials become scrap. The processes discussed in this report are focused on a limited number of nickel products. Different types of nickel-bearing scrap will require other types of processing. Where the nickel is relatively impure or where it is an alloy constituent, conventional practice typically employs successive electrowinning and electrorefining steps. The new molten metal process might also be employed as a first step to separate materials more chemically active than nickel. Where scrap is surface contaminated, washing or leaching is likely to be more appropriate.

Chemical operations of the conventional nickel refining processes will have to be modified to improve removal of the contaminants particular to DOE operations and to meet DOE radiological safety requirements. Conventional systems, for example, typically use a complex electrolyte which contains buffers, such as borate, and salts added to increase current density. Impurities are generally present at levels ranging from 0.01 (lead) to 4%

(copper). These impurities are typically removed by precipitation or cementation. High purity, or 99.9% nickel still contains 0.1%, or 1 gram per kg of impurities. This level would be unacceptably high for the radioactive contaminants in DOE scrap.

To reach very low levels, perhaps less than 1 mg per kg, of contaminants, highly selective modern separations processes can be used in conjunction with less selective, but less expensive, conventional separations. For the radionuclides of interest, selective separations will typically include ion exchange and solvent extraction. In order to permit these separations to operate effectively, process electrolyte concentration will have to be simplified and modified. Otherwise, the electrolyte anions themselves could interfere with the separation. Thus, both sidestream processes and the working electrolyte will have to be reoptimized. The goal is a working electrolyte with a single predominant anion which will produce acceptable electrorefining rates at pH conditions which facilitate separations.

Some changes in operating hardware are likely to be required. For example, industrial electrorefining processes like those shown in Fig. 1.1, are typically wood or concrete tanks lined with non-conductive asphalt. Canvas bags are used to contain the catholyte and to provide a slight positive pressure into the electrolyte. In any process which involves radioisotopes, leak prevention and ease of decontamination will drive the choice of tank and membrane materials toward modern, high performance polymers. Any electrolytic processing facility constructed de novo will be expected to reflect improvements in cell design, materials, membranes, and control systems found in current research and operation.

This report is an evaluation of nickel refining and separations processes which, in conjunction, could be used to recover both nickel and radioisotopes from gaseous diffusion plant scrap. A literature review and an evaluation of possible unit processes. These materials will be used to develop process concepts for bench-scale evaluation.

2. Literature Review

To produce pure, high quality nickel from a wide variety of industrial feedstocks has required development of a variety of innovative refining technologies tailored to the feedstock and to the qualities and types of nickel required by the marketplace (Boldt 1967, Tien and Howson 1981). The elements that are removed during refining include antimony, arsenic, bismuth, cobalt, copper, iron, lead, phosphorous, sulfur, tin, and zinc. The removal of cobalt is especially important in materials used in the nuclear industry, since the bombardment of cobalt by neutrons produces a highly radioactive isotope, ^{60}Co , with a half life of approximately 5 years.

Nickel refining practices vary considerably. Refining via electrolysis has been performed using solid anodes of impure nickel metal in a process called electrorefining and using an impure liquid nickel solution or impure nickel sulfide in a process called electrowinning. Additionally, carbonyl (or vapometallurgy) and an ammonia leach/direct hydrogen reduction processes are used at industrial scale. The process used by the Copper Cliff plant to recover nickel by vapometallurgy is detailed in Fig. 2.1. In a typical carbonyl process, impure nickel oxide is reduced to metal with hydrogen; the impure nickel is reacted (50-100 °C) with carbon monoxide to produce gaseous nickel carbonyl, $\text{Ni}(\text{CO})_4$; the gas, in turn, is thermally decomposed (180-300 °C) to yield pure nickel.

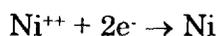
In the ammonia leach/direct hydrogen reduction process, an ammonia leach is employed at high temperature and pressure to dissolve the impure nickel; direct hydrogen reduction of the solution produces nickel in a powder form. The process used by the Fort Saskatchewan hydrometallurgical plant is shown in Fig. 2.2. Ammonia leaching has the advantages of increasing product recovery while reducing process complexity.

The underlying principles of nickel electrolysis are the same for both electrorefining and electrowinning. However, there is a fundamental difference — in electrorefining there is no net cell reaction, whereas in electrowinning there is a net cell reaction.

In electrorefining, the cell consists of an anode of impure nickel and a thin “starting sheet” cathode of pure nickel immersed in an electrolyte, a conducting aqueous solution. As current flows from the anode to the cathode in the external circuit, the nickel and some impurities dissolve from the anode into the surrounding solution, the anolyte. Anolyte is removed from the cell, chemically cleaned of impurities, and returned to the cell around the cathode as catholyte. Impure anolyte is prevented from coming in direct contact with the cathode by means of a porous diaphragm. Nickel from the catholyte is then deposited on the cathode. This completes the electrical circuit of the cell. The overall reaction at the anode can be written as:



And the overall reaction at the cathode can be written as:



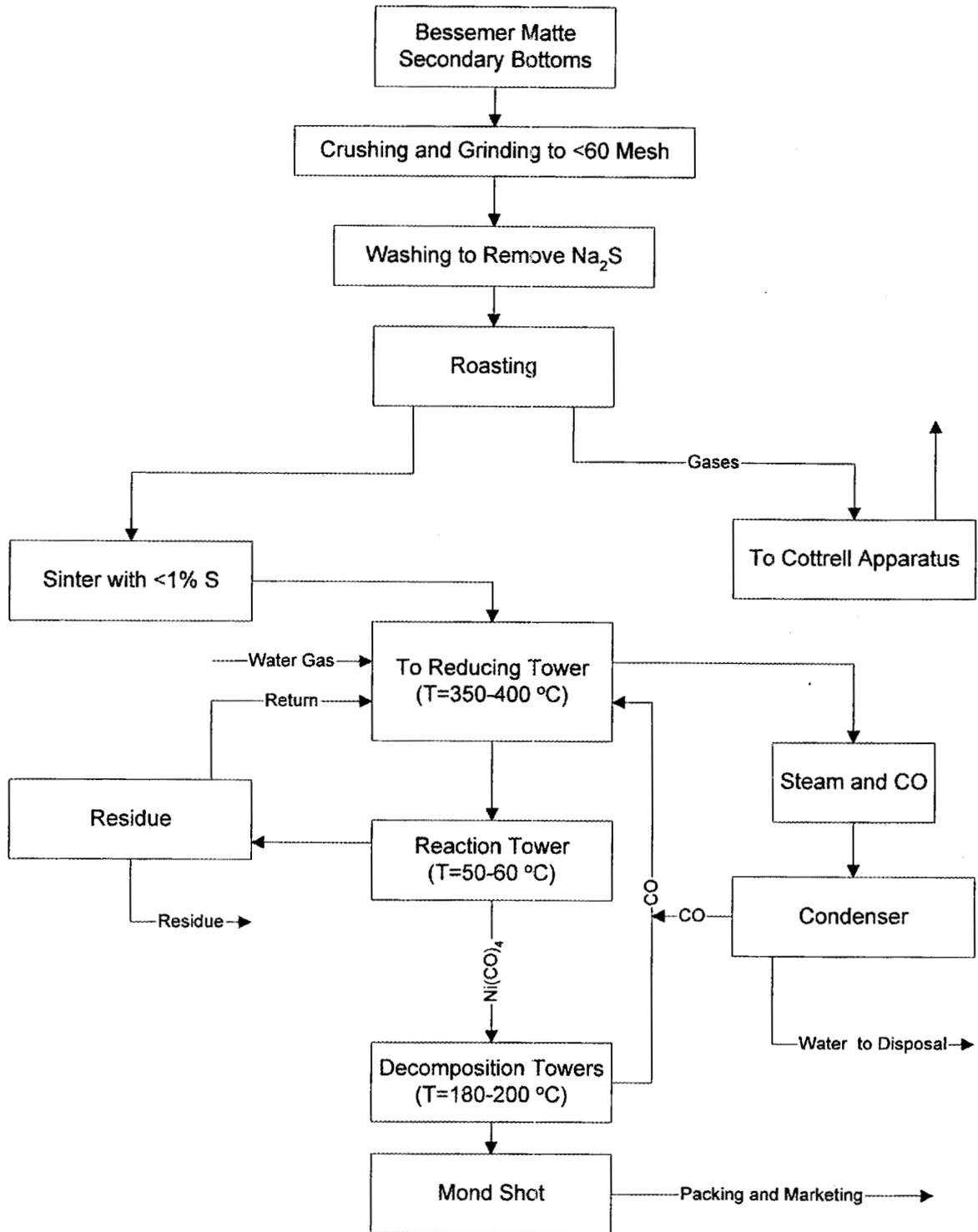


Fig. 2.1. Production of nickel by the carbonyl process. Adapted from Kornilov 1963.

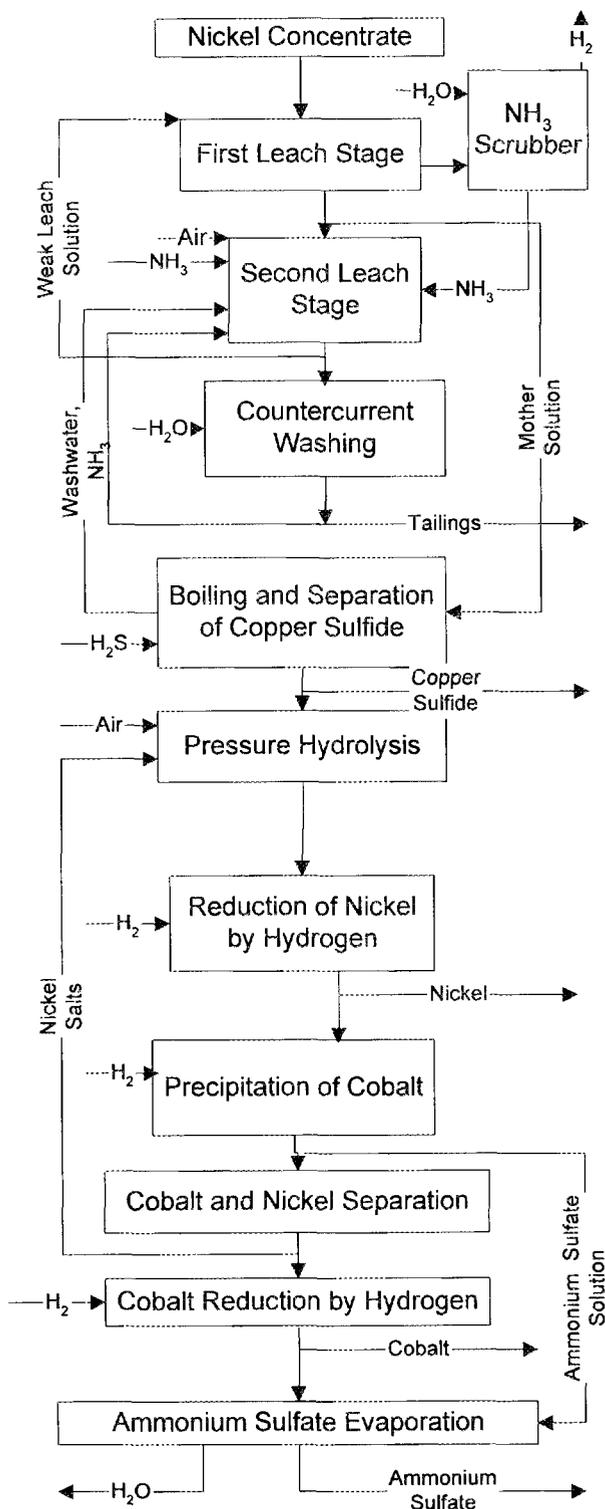
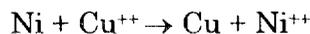


Fig 2.2. Ammonia leach/direct hydrogen reduction process. Adapted from Kornilov 1963.

The net cell reaction is zero, a characteristic of any electrorefining process. It must be noted that not all the current through the cell is used to refine nickel, since other anodic and cathodic reactions may be occurring at the same time.

The electrode potential of a reaction is the sum of three components — reversible potential, concentration polarization potential, and activation potential. The electrochemical series of reversible potentials for reactions generally occurring during nickel refining are presented in Table 2.1. The more negative the potential, the more readily the anodic reaction occurs, and the more positive the potential, the more readily the cathodic reaction occurs.

A typical process flow diagram for recovery of nickel, cobalt, and precious metals from matte is shown in Fig. 2.3. At the normal operating voltage of the electrorefining system, cobalt, iron, lead, zinc, and arsenic go into solution with the nickel. The platinum group, silver, and gold, and the metalloids sulfur, selenium, and tellurium do not dissolve. As the anode dissolves, most of the insolubles fall to the bottom of the tank and are referred to as slime. The anolyte is passed through a chemical purification process to remove the impurities. Copper is usually removed by cementation with metallic nickel which causes copper ions to precipitate in metallic form and nickel atoms to go into solution:



Copper may also be removed by hydrogen sulfide which causes copper to precipitate as copper sulfide:

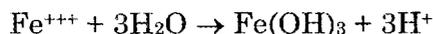


Table 2.1. Standard electrode potentials of selected nickel refining reactions (77 °C)

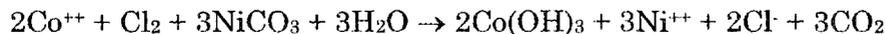
Element	Reversible Reaction	Reversible Potential (V)
Sodium	$\text{Na} \leftrightarrow \text{Na}^+ + \text{e}^-$	-2.71
Zinc	$\text{Zn} \leftrightarrow \text{Zn}^{++} + 2 \text{e}^-$	-0.76
Iron	$\text{Fe} \leftrightarrow \text{Fe}^{++} + 2 \text{e}^-$	-0.44
Cobalt	$\text{Co} \leftrightarrow \text{Co}^{++} + 2\text{e}^-$	-0.28
Nickel	$\text{Ni} \leftrightarrow \text{Ni}^{++} + 2\text{e}^-$	-0.25
Lead	$\text{Pb} \leftrightarrow \text{Pb}^{++} + 2\text{e}^-$	-0.13
Hydrogen	$\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$	0.00
Copper	$\text{Cu} \leftrightarrow \text{Cu}^{++} + 2\text{e}^-$	+0.34
	$\text{Cu} \leftrightarrow \text{Cu}^+ + \text{e}^-$	+0.52
Silver	$\text{Ag} \leftrightarrow \text{Ag}^+ + \text{e}^-$	+0.80
Palladium	$\text{Pd} \leftrightarrow \text{Pd}^{++} + 2\text{e}^-$	+0.99
Platinum	$\text{Pt} \leftrightarrow \text{Pt}^{++} + 2\text{e}^-$	+1.2
Oxygen	$2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	+1.23
Chlorine	$2\text{Cl}^- \leftrightarrow \text{Cl}_2 + 2\text{e}^-$	+1.36
Gold	$\text{Au} \leftrightarrow \text{Au}^{+++} + 3\text{e}^-$	+1.50

Source: Boldt 1967.

Iron is normally removed by aerating the solution to oxidize the ferrous iron and precipitate it as ferric hydroxide. The ferric hydroxide also incorporates other impurities such as lead and arsenic. The precipitate which is filtered from the solution is formed by the reaction:

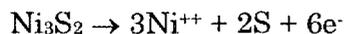


Cobalt is normally precipitated as a hydroxide by treatment with chlorine, with nickel carbonate added for pH control:

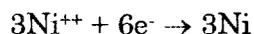


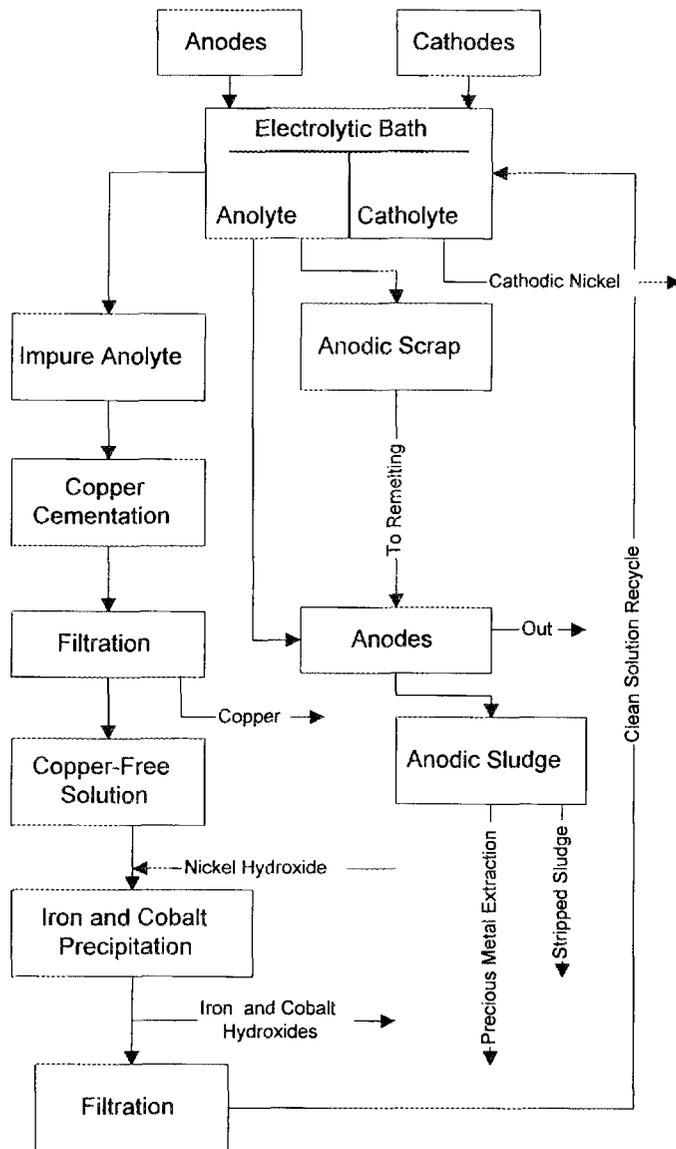
Two different methods of electrowinning are generally employed. One uses soluble anodes of nickel sulfide, and the other uses insoluble anodes to extract the nickel from a leach solution. In all cases there is a net cell reaction.

In processes that use nickel sulfide anodes, the anodic reaction is:

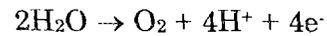


And the cathodic reaction is:

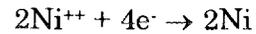




In processes that use insoluble anodes, the nickel in a leach liquid is recovered, and the only function of the anode is to transfer electrons to the external circuit. Thus there is no requirement for casting impure nickel anodes or to collect tank slimes. The leach liquid is generally an aqueous solution of nickel sulfate, sodium sulfate, and boric acid. The principal anodic reaction is:



The principal cathodic reaction is:



Nickel streams evince considerable variability in composition. Because many of the contaminants in these streams are profitably recovered as byproducts, a wide range of process configurations have been developed. Cobalt is recovered in both of the processes detailed above. As discussed earlier, separation of cobalt from nickel is of particular concern because of the presence of ^{60}Co in previously irradiated scrap. The process detailed in Fig. 2.3 recovers copper and precious metal concentrate.

Figure 2.4 illustrates conventional industrial separation and recovery of nickel and cobalt.

Fig. 2.3. Nickel electrorefining from matte. Adapted from Kornilov 1963.

New Electrolyte Developments

In earlier practice (Boldt 1967), nickel electrorefining was typically performed using a sulfate-based electrolyte like that detailed in Table 2.2. This practice evolved because of the sulfur content of nickel ores and nickel concentrates, and because of the limited

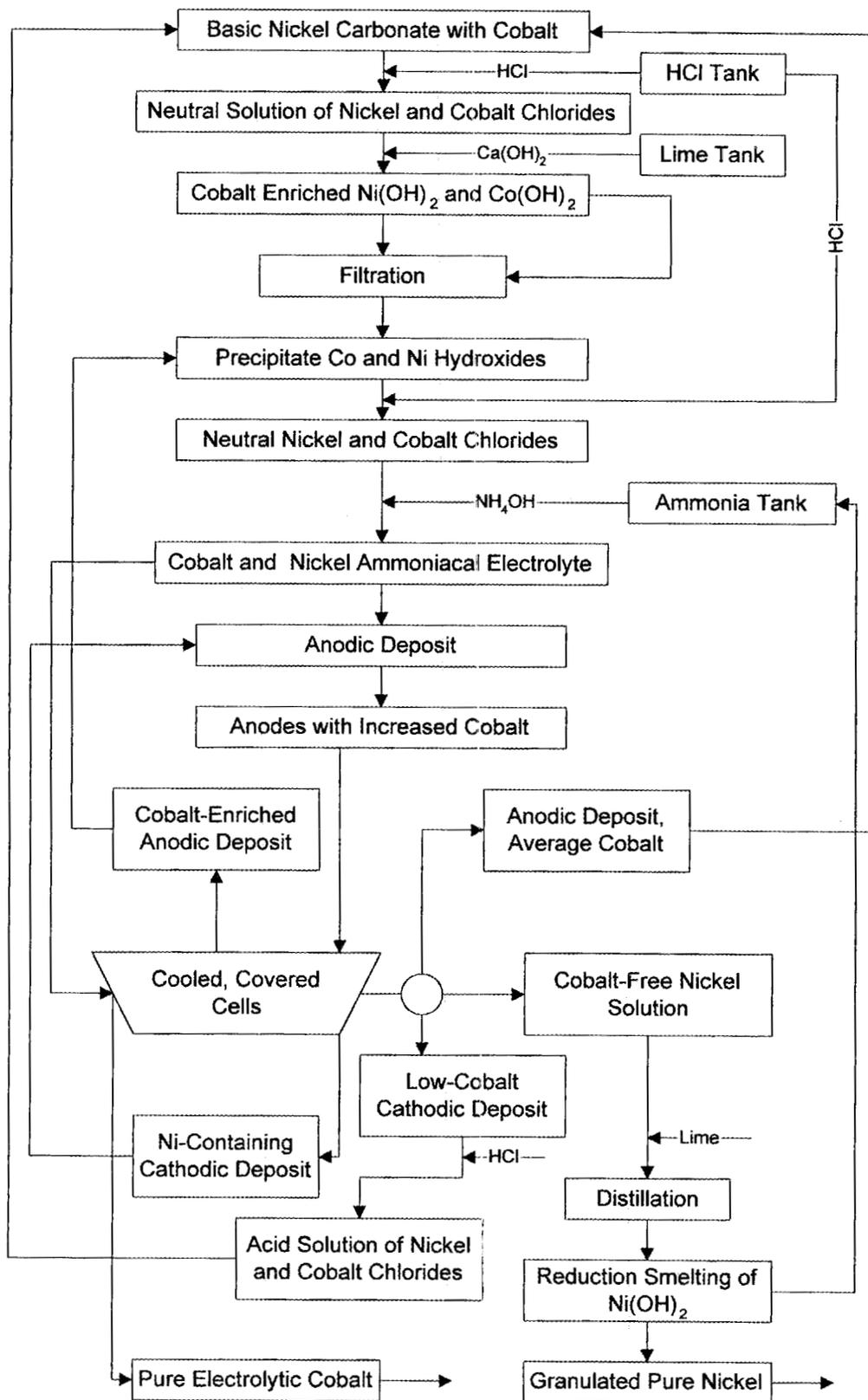


Fig. 2.4. Electrolytic separation of nickel and cobalt. Adapted from Kornilov 1963.

evolution of gas in tankhouse operations. However, Ettl (1983) indicated that new and increasingly stringent environmental regulations may require collection of gas from sulfate-electrolyte tanks. This is encouraging the adoption of chloride-based leaching

Table 2.2. Electrolyte for conventional nickel electrorefining

Ion	Concentration, M
Ni ⁺	1.022
SO ₄ ⁻	0.989
Na ⁺	1.522
Cl ⁻	1.551
H ₃ BO ₃	0.258

Adapted from Boldt 1967.

leaching, to chloride-based operations (Conard 1994). There has also been French interest in developing chloride-based processes (Demarthe, Gandon, and Goujet 1983).

The Falconbridge Nikkelverk at Kristiansand, Norway is the first large-scale plant employing an electrowinning process to use a chloride electrolyte (Stensholt and coworkers 1988). As shown in Fig. 2.5, chlorine leaching is used to selectively dissolve nickel from the incoming matte. This leaves a solid sulfide high in copper. The nickel solution is treated to remove iron and arsenic and solvent extracted to remove cobalt. Following a final precipitation to remove lead and other residual impurities, nickel is recovered from the solution by electrowinning. Chlorine gas produced during electrowinning is recycled to matte leaching. Cobalt is back-extracted from the solvent stream and recovered by electrowinning. The nickel produced by the Falconbridge Nikkelverk is very pure.

Radioactive contaminants in DOE nickel scrap include: ²³⁴Th, ²³⁴Pa, ¹³⁷Cs, ²³⁹Pu (trace), ⁶⁰Co, U, ⁹⁹Tc, and ²³⁷Np (trace). As discussed below, chloride-based systems have good potential for simplifying ion exchange and solvent extraction separations of radiological contaminants from nickel. Chloride, as opposed to sulfate, systems may facilitate separations of uranium, the major radiological contaminant, from nickel.

Nitrate systems could also be used for nickel recovery by electrolysis. These systems have historically been used in uranium operations. For that reason, separations of a variety of daughter products and transuranics from nitrate solutions into various organic extractants have been well studied.

Advances in Cell Architecture

Conventional nickel electrowinning and electrorefining cells usually employ parallel plate geometry. Materials of construction are typically concrete or wood tanks coated internally to minimize damage by the electrolyte (Boldt 1967). Because materials and processes have evolved throughout a plant's history, often for several decades, changes can be both difficult and expensive.

As a startup operation, the nickel scrap electrorefining process should selectively employ modern technology to meet the difficult operating conditions likely to be imposed on the facility. These may include: minimization of leaks; minimization of radioactive contamination; provisions for safe handling of radioisotopes, including any criticality