AN ABSTRACT OF THE THESIS OF

DONALD ANDREW NISSEN   for the Ph.D.   in   Chemistry
    (Name)   (Degree)   (Major)

Date thesis is presented_____

Title   A Fused Salt Electrochemical Method for the

Separation of Cobalt and Nickel

Abstract approved____███████████████████_____
                           (Major Professor)

An ever-increasing demand for metals of higher
and higher purity makes it necessary to either
drastically improve existing separation schemes or
devise new ones. The purpose of this thesis is to
demonstrate an industrially feasible process for
the production of nickel which contains no more
than 20 p.p.m. of cobalt.

Electrochemical methods are perhaps the most
common means of producing pure metals and thus they
formed the basis for this investigation. However,
rather than trying to improve existing methods of
producing cobalt-free nickel, a new approach to the
problem was tried. This consisted of replacing the

conventional aqueous solvent with a fused salt solvent, specifically equimolar NaCl/KCl.

The scheme itself involved electrowinning nickel from a solute which was composed of iron, nickel, and cobalt, in the ratio of about 100:90:1, derived from the chlorination of ferronickel, a readily available nickel containing alloy. In order to effect the desired separation it was necessary to use cathode current in the range of 1.0 to 2.0 x 10^{-2} amps/cm^2 and to use the partially purified product of one deposition as feed material for a second. The iron present in ferronickel caused a drastic lowering of the cathode current efficiency and, therefore, it was necessary to separate it from the remaining constituents of the solute before the electrolytic separation of nickel and cobalt could take place.

A flow-sheet is presented, based on the laboratory scale process, which results in nickel that contains less than 20 p.p.m. cobalt.

A FUSED SALT ELECTROCHEMICAL METHOD FOR THE
SEPARATION OF COBALT AND NICKEL

by

DONALD ANDREW NISSEN

A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements of the
degree of

DOCTOR OF PHILOSOPHY

June 1964

APPROVED:

<div style="border:1px solid black; background:black; width:40%; height:60px;"></div>

Professor of Chemistry

In Charge of Major

<div style="border:1px solid black; background:black; width:40%; height:60px;"></div>

Chairman of Department of Chemistry

<div style="border:1px solid black; background:black; width:40%; height:60px;"></div>

Dean of Graduate School

Date Thesis is Presented 5/8/64

Typed by Sally Huang Nissen

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. W. J. Kroll, not only for his generous financial support of this research but also for freely sharing his vast store of technical knowledge. The contribution of Dr. A. B. Scott to this research problem and the resulting thesis is acknowledged with gratitude. Last, but by no means least, the author wishes to thank his wife Sally for her unfailing support and understanding and for the many hours she spent at a typewriter.

TABLE OF CONTENTS

A FUSED SALT ELECTROCHEMICAL METHOD FOR THE SEPARATION OF COBALT AND NICKEL

I. INTRODUCTION

In order to understand the properties and behavior of metals, the metallurgist and physicist must have materials of high purity with which to work. The difference between metals of extreme purity and those slightly contaminated is remarkable (25.) In addition to the necessity for ultrapure metals for research purposes, it is possible to increase the purity of a number of metals that are in use technically today and in doing so to open up entirely new applications for them (40.) A case in point is the elimination of cobalt in the nickel content of austenitic stainless steel used in certain nuclear applications.

Natural cobalt - ^{59}Co - when bombarded with neutrons undergoes radiative capture to give ^{60}Co; $^{59}Co(n,\gamma)^{60}Co$. This isotope has a half life of 5.2 years and its radiation is intense (1.3 Mev.)(30.)

Thus, once equipment containing cobalt has been exposed to neutron radiation an extended "cooling off" period is necessary before it can be safely approached.

NiO sinter, used in normal practice, has an average cobalt content of .7 per cent, while that of electrolytic nickel is about .1 per cent (60.) The purest commercially available nickel (99.9-99.99 per cent)(77) is that produced by the Mond-Langer carbonyl process; however, it is too expensive for industrial use and the supply is limited.

The purpose of this research is to find a method for producing nickel that is essentially cobalt free, that is, containing less than 20 parts per million cobalt, starting with an inexpensive, readily available nickel alloy. The information thus derived will be used to try to define a flow sheet that would be attractive to industry.

The complete separation of cobalt and nickel is a problem which has plagued the metallurgical industry for years and countless schemes have been proposed. However, when faced with the problem of high recovery with no premium in cost, most of these schemes have failed (76.)

It is first of all necessary to choose a method of separation upon which to center the research. Electrolytic methods seem to be the most desirable; not only are they relatively simple but, in addition, industry possesses a considerable amount of experience upon which it may draw.

At present nickel is refined industrially by electrolysis from a sulfate or mixed sulfate-chloride aqueous electrolyte (65.) It is, therefore, reasonable to expect that electrorefining might offer a promising method of producing pure metal. This has been recognized by those who have studied the problem (90.) Indeed, Wesley (93) has described a process whereby nickel, containing a cobalt impurity of 4 ppm, can be produced. However, in order to reduce the cobalt concentration to the parts-per-million range it is necessary to use Mond metal as a starting material. While this may be reasonable from the standpoint of a laboratory procedure, it is impracticable from an industrial standpoint because of the scarcity and cost of Mond metal.

All of the electrorefining methods for nickel have concerned themselves with aqueous media. A

number of parameters such as bath constituents,
current density, temperature, etc. have been varied
in order to try to achieve the desired results.
None have sought to utilize those properties which
might be available in other solvent systems.

The use of non-aqueous solvents offers a wide
range of possibilities, since in principle all the
properties of the system may change if the solvent
is changed. Thus a suitable choice of solvent
allows electrochemical reactions to be carried out
which are not possible in aqueous systems (2.)
The choice of solvents is limited by the fact that
electrochemical reactions have to be carried out
in them. For this reason it is necessary to choose
a solvent which will not be reduced or oxidized
before the ion or ions of interest have been reduced
or oxidized.

As electrolytes, fused salts have long held a
place in industrial technology. Fused salt electrolysis

is used at present to produce tonnage quantities of aluminum, magnesium, sodium, and calcium, and for the commercial preparation of at least twenty other metals, numerous alloys (65) as well as the purification of a number of others such as thorium and uranium (44, 13.)

Fused salts offer a number of advantages over water as an electrolyte. In general, these are: good electrical conductivity, high decomposition potential of the solvent, the ability of the solvent, because of its nature, to act as a strong complexing agent, and the ability to achieve elevated temperatures without the need of elaborate high pressure equipment. Perhaps the greatest advantage fused salts have to offer is their almost limitless versatility. The general properties stated above, are, for the most part, true for solvents composed of alkali and/or alkaline earth halides. However, the addition of other compounds, or even the alteration of the amount of one constituent of a melt, in relation to the others, may drastically affect the properties of the melt and thus, in essence, provide us with a different solvent.

Molten alkali halides can be considered as liquids that consist entirely of ions. They differ from solutions of electrolytes in solvents such as water because the interionic distances are much less than those which usually exist in aqueous solutions. Hence all molten salt solutions are subject to strong interionic forces due to the close proximity of the charged ions (6.)

X-ray diffraction experiments indicate that a representative configuration in molten alkali halides involves, in comparison with the solid, a collapsed array of anions about cations. The average nearest neighbor coordination number is four to five compared with six in the solid (62.) It appears from this evidence that fused salts consist basically of ion clusters which is to say that short range order is, to a large extent, preserved while long range order is disrupted.

The preceeding remarks indicate that fused salt solvents are capable of exerting a significant influence on the solute. For example, it has been shown that it is possible to stabilize plutonium (IV) chloride at temperatures where it is normally incapable

of an independent existence (in excess of $600^{\circ}C$)(5)
(37) by forming the alkali double chloride with
strong complexing salts such as RbCl or CsCl. With
the aid of spectrophotometric data Morrey (71) has
shown that complexing of the UCl_4 species by the
anion, in a melt of the composition $UCl_4 + MCl$,
where M=Li, Na, K, Rb, or Cs, is a function of the
alkali metal cation. That is, the concentration of
the $UCl_6^=$ species increases as the cation is changed
from Li to Cs.

In fused halides the solvent has been shown to
have a marked influence on the electrode potentials
of the metal cation solute (22.) As the anion is
changed from chloride to iodide the electrode
potential of the metal cation becomes more negative.
This can be explained by a change in the degree of
electrolytic dissociation during the transition from
chloride to iodide (22.)

Elevated temperatures are inherent in fused salt
electrolysis. In general, increases in temperature
increase the conductivity of the electrolyte as well
as the diffusion rates of the electroactive species
(24.) The over-all net effect is a decrease of
polarization and a lowering of the cell voltage (65.)

In addition, the potential at which a metal commences
to deposit changes as a function of temperature and
this fact may aid in a more quantitative separation
of metals which are similar chemically.

Hamby (38) has obtained the values of the standard
potential, E^o, as a function of temperature in the
solvent system LiCl/KCl for the couples $Ni/NiCl_2$ and
$Co/CoCl_2$ and these data are shown in Table 1, along
with their difference, Δ . This data was obtained for
cells of the type

$$M \mid MCl_2 \text{ in LiCl-KCl} \mid C-Cl_2$$

The standard state is taken to be unit mole fraction
of the solute, but the solution having the properties
of infinite dilution.

TABLE 1

The Variation of E^o as a Function of Temperature

| T^oC	680°	700°	750°
E^o_{Co/Cl_2}	1.177	1.169	1.149
E^o_{Ni/Cl_2}	0.980	0.969	0.949
Δ	0.197	0.200	0.200

Data similar to this but for different solvents and
temperatures and other couples has been obtained by
other investigators (28)(56.)

These data show that indeed the potential for the
deposition of the metal does change as a function of

temperature, however, that parameter which is of utmost importance in an electrolytic separation scheme Δ, the difference in potential, remains essentially constant. Therefore, on the basis of these considerations no particular advantage can be gained by going to higher temperatures except those already cited, and these must be weighed against the disadvantages of higher temperatures, namely increased corrosion and lowered current efficiency.

Unfortunately, the use of fused salts presents a number of difficulties. The elevated temperatures tend to increase the reactivity of the constituents of the melt. This increased reactivity not only produces extensive corrosion of materials of construction but also lowered current efficiencies. In most cases, metals are soluble to some degree in their own salts and the solubility increases as the temperature is increased (65 op. cit.) The result of this solubility is a lowered yield of product because of the diffusion of the soluble metal to the anode where it is oxidized. Due to the strongly complexing nature of fused salts and the high temperature it is, in some cases, possible to produce "subvalent" species by

means of the reaction

$$MCl_X + M = MCl_Y \quad (1)$$
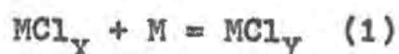
where M is a metal and $X > Y$. This is particular true
in those cases where the anion is a halide. These
"subvalent" states are unattainable in aqueous so-
lution and are usually observed in the case of more
active metals such as the alkaline earths (88, 89)
and the rare earths (17) but lead, bismuth, cadmium,
and nickel also show this behavior. This behavior is
paralleled in aqueous solution, by the couples
Fe/Fe(III) and Cu/Cu(II). The production of subvalent
states is one of the factors responsible for a lowered
current efficiency. If the anode reaction should
result in the production of a strong oxidizing agent,
such as Cl_2, it may diffuse to the cathode where it
will react with the cathode product, causing a
lowered current efficiency. Most of these deleterious
effects can be reduced, some to almost negligible
proportions, by a judicious choice of solvent, the use
of diaphragms, and maintaining the electrolysis cell
at the lowest possible temperature.

Electrolytic metal purification can be done
either by the soluble anode technique or by selective

electrolytic precipitation of the metal ions from the solution using an inert anode. The former is more commonly known as electrorefining and the latter as electrowinning.

A. Electrorefining

Electrorefining is usually done by the soluble anode method. Ideally, in this method the most active of the metallic constituents of the anode goes into solution first; the less active metals drop from the anode as the surrounding portion of the more active metal is dissolved. If the electrolyte does not have access to the underlying portions of the alloy then the next most active metal will dissolve at an electrode potential corresponding to the new process. This newly dissolved component will be plated out at the cathode along with the more active metallic component of the alloy, causing contamination of the cathode deposit.
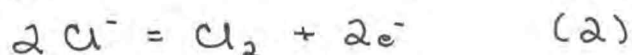
B. Electrowinning

In a cell such as

$C \mid MCl_x$ in $NaCl/KCl \mid C$
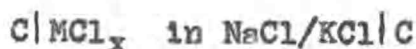
where MCl_x is the chloride of the metal undergoing reduction at the cathode, the electrode reactions are,

for the anode:

$$2 Cl^- = Cl_2 + 2e^- \qquad (2)$$

and, for the cathode:

$$xe^- + M^{+x} = M \qquad (3).$$

The metal ions commence to deposit as soon as the cathode reaches the decomposition potential. The cathode potential is given by

$$E_c = E^\circ - \frac{RT}{xF} \ln \frac{a_M}{a_{M^{+x}}} + \epsilon \qquad (4)$$

where ϵ is the sum of the various overvoltages. Therefore, at constant current, as the electrolyte becomes depleted of metal ions the cathode potential E_c increases in the negative direction. This negative drift of the cathode potential will continue until another reaction is initiated. In the case of the cell shown above this would correspond to the deposition of the solvent cations. If the solute is composed of two or more different species, e.g. MCl_x and $M'Cl_x$, as soon as the cathode potential reaches the reversible potential of M', codeposition of M and M' would occur, assuming M' to be the more active of the two. This negative drift of the cathode potential also will occur if the limiting current density of the ion of interest is exceeded. The limiting current

density is so called because it represents the maximum (limiting) rate at which the particular ion can be discharged under the given experimental conditions. If an attempt is made to increase the current density above this value then the cathode potential must increase until another cathodic process is possible.

C. General Electrochemical Considerations

Nickel and cobalt show complete solid solubility at all temperatures (10.) When two metals form an alloy the activity of each of them usually will be smaller than for the separate pure metals and consequently the potential at which one metal codeposits with another may be considerably different from the potential at which it deposits alone. Therefore, even though the reversible potentials of nickel and cobalt may be far enough apart that a quantitative separation would be obtained, provided the metals naturally were insoluble, (38 op. cit) the alloying tendencies of the two metals may make it impossible to achieve a satisfactory separation.

In any electrowinning operation, particularly where thermal or chemical processes compete, power

cost is an important item; maximum current and energy efficiencies are vital to the economic justification of the method. Increasing the current density of the cell, that is, the current per unit electrode area, augments the capacity of the cell and decreases capital cost, and floor space per unit of product. For any given process, the most desirable current density results from a balance of many factors: power cost, operating charges, value of material in process, and energy consumption per unit of product. On this basis the relationship between current density and electrode potential for non-equilibrium situations is of interest (65 op.cit.)

Since the processes of interest occur at the cathode the following discussion will be centered around that electrode. The following treatment has been discussed by Delahay (19) and in more detail by Bockris (7) and by Glasstone, Laidler, and Eyring (34.) This treatment is, however, only an approximation because the electrode process results in the formation of a solid coating on the electrode and the properties of the coating being formed in the electrolysis determine at least partially the kinetics of the electrode process. The conclusions

which will be drawn are general enough so that the fact that the treatment is only an approximation is no detriment.

When a metal is placed into a solution of its ions there will be a tendency for the ions to discharge onto the metal and for the metal to go into solution. This process may be represented by the following equation:

$$O^{+N} + Ne^- \underset{k_f}{\overset{k_b}{\rightleftarrows}} R \qquad (5)$$
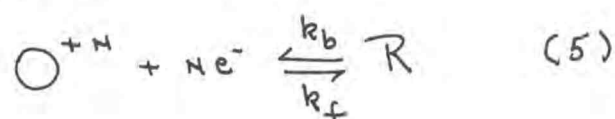
where k_f and k_b are, respectively, the specific rate constants for the discharge step and the dissolution step.

If we now make the electrode more cathodic by applying a potential E to it we will have the situation shown in Figure I by the broken line. The actual potential difference across the electrode-electrolyte interface is symbolized by η and is

16

FIGURE I

Potential - Energy Barrier at

an Electrode Surface
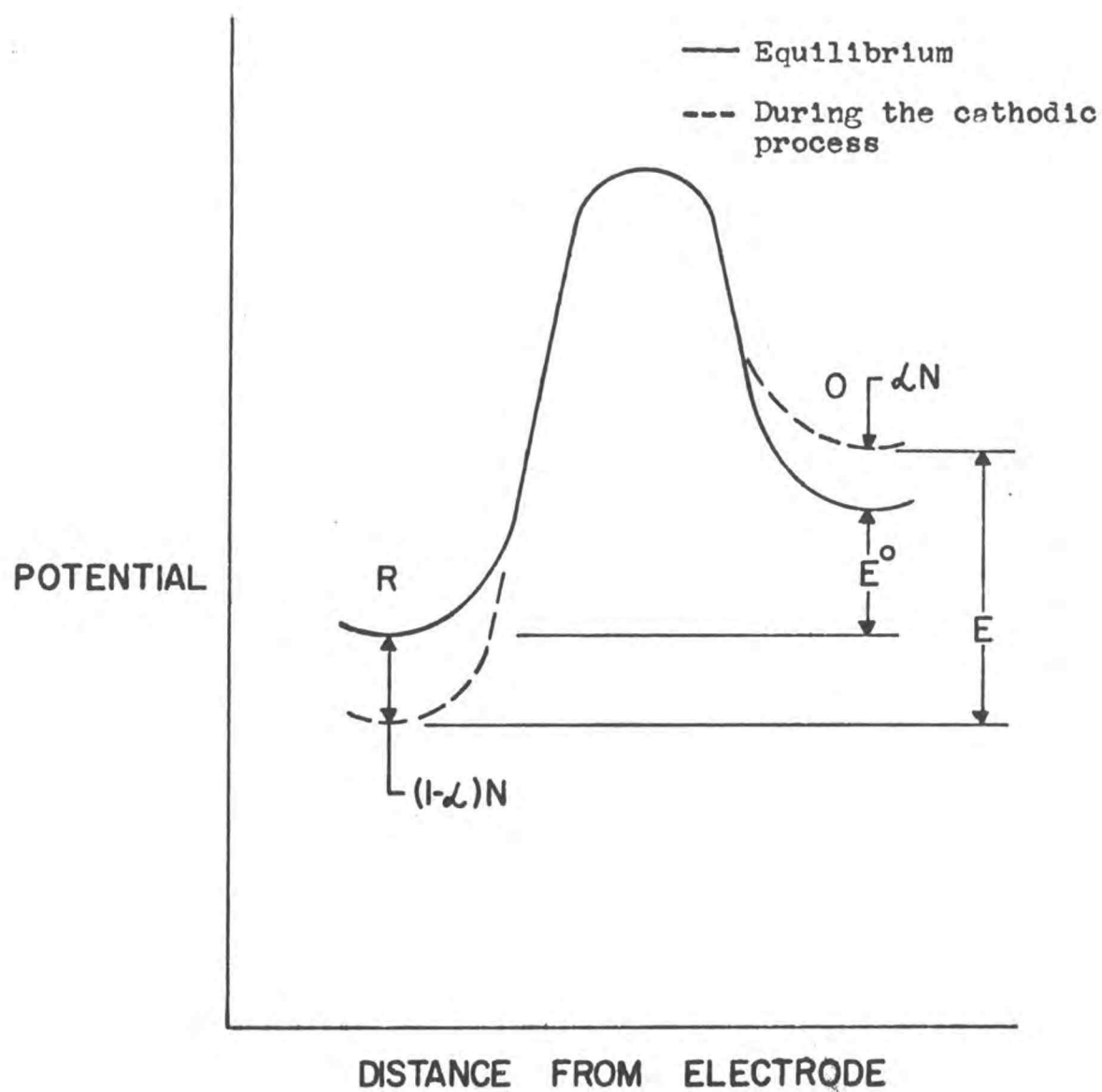
related to E by the equation:

$$E = E^\circ + \eta \qquad (6)$$

where E° is the equilibrium potential. The term η is known as the overvoltage. It is assumed, as shown in Figure I, that a fraction α of the over- voltage facilitates discharge of the ions while the remainder 1- α hinders the dissolution of the metal. We may now write, in terms of the absolute reaction rate theory, that

$$k_f = k_f' \exp\left(-\alpha N F \eta / RT\right) \qquad (7)$$

and

$$k_b = k_b' \exp\left[(1-\alpha) N F \eta / RT\right] \qquad (8)$$

where N is the number of electrons involved in the reaction. The actual rate of the reaction is obtained by multiplying the specific rate by the activity of the reactant and the current for each half reaction is the product of the rate, the electrode area, and the charge involved in that process. Thus:

$$I_0 = N F \sigma a_0 k_f \qquad (9)$$

and

$$I_R = -N F \sigma a_R k_b \qquad (10)$$

where σ is the electrode area and a_i is the activity

of the ith species. Substituting the values of the specific rate constants from equation 7 and 8 we see that

$$I_o = N F \sigma a_o k_f' \exp(-\alpha N F \eta / RT) \qquad (11)$$

$$I_R = -N F \sigma a_R k_b' \exp[(1-\alpha) N F \eta / RT] \qquad (12)$$

at equilibrium $\eta = 0$ so that

$$|I_o| = |I_R| = |I_E| \qquad (13)$$

and thus

$$I_E = N F \sigma a_o k_f' \qquad (14)$$

$$= N F \sigma a_R k_b' \qquad (15)$$

from which it follows that

$$I_o = I_E \exp(-\alpha N F \eta / RT) \qquad (16)$$

and

$$I_R = -I_E \exp[(1-\alpha) N F \eta / RT] \qquad (17)$$

The net current that flows is the sum of the currents for each of the half-reactions:

$$I = I_o + I_R \qquad (18)$$

Inserting the values of I_o and I_R from (16) and (17),

$$I = I_E \left\{ \exp(-\alpha_N F \eta / RT) - \exp[(1-\alpha)_N F \eta / RT] \right\}. \quad (19)$$

Dividing both sides of (19) by σ, the cathode area, and inserting the value of η from (6) we see that:

$$i = i_E \left\{ \exp[-\alpha_N F(E-E^\circ)] - \exp[(1-\alpha)_N F(E-E^\circ)/RT] \right\}. \quad (20)$$

Equation (20) indicates that the higher the value of the current density i the greater the difference in the quantity $(E-E^O)$; or, as the current density becomes larger the electrode potential departs farther from its standard value E^O.

In a situation where two cations are to be separated and their standard potentials are only a few hundred millivolts apart, as in the case with nickel and cobalt, large values of the current density are liable to result in simultaneous deposition of the two cations. Data, which will be presented later will show the dependence of the degree of separation on current density.

Considerable stress has been placed on the importance of current (or current density) to the

success of a separation scheme based on the selective electrolytic reduction of various cations. It should be recognized that, even in those cases in which the cell current is the variable being controlled, it is the electrode potential that controls which ions will be reduced. To say that coreduction of two or more ions depends on the choice of current density, while not a misstatement of fact is a misapplication of logic in that it places the effect - current - before the cause - electrode potential.

In order to insure that as high a degree of separation as possible takes place during an electrolytic metal purification it is necessary that some control be exercised over the course of the electrolysis. This may be done either by controlling the current, the total cell voltage, or the cathode or anode potential, depending on the separation scheme. An excellent discussion of this problem and its ramifications is given by Lingane (63.)

As the name implies, constant current electrolysis means that the current is kept constant during the course of the electrolysis and the cathode potential

is allowed to drift. This method is the one most commonly used by industry since it has the advantage of being the most rapid of the three. It, however, has a disadvantage in that the uncontrolled drift of the cathode reduces the selectivity of the method.

The second method, control of the applied cell voltage, is more selective than the constant current method but it suffers from the disadvantage that the electrolysis time is considerably prolonged. This is due to the fact that when the applied voltage is limited to a value sufficiently small to prevent the potential of the cathode from finally exceeding a desired value at the end of the electrolysis the initial current will be relatively small and as a consequence the electrolysis time is lengthened, in addition, the cell resistance is a very critical factor in electrolyses of this nature (63.)

The third method, electrolysis at a constant cathode potential, has the advantages of having a high degree of selectivity, and the time required for the electrolysis is nearly as short as that in the constant current method. In order to perform an

electrolysis of this sort it is necessary that the potential of the cathode be held constant with respect to a reference electrode. While potentiostatic methods have been applied to fused salts they do present a problem, mainly because of the difficulty of finding a good reference electrode. Satisfactory reference electrodes have been devised for laboratory scale studies (57, 58, 27, 86, 8, 16, 56, 95, 96, 21, 23) but nothing acceptable has been devised for electrolyses on a commercial scale.

On the basis of the above discussion and because of the ease and simplicity of making the measurements, both the electrorefining and electrowinning experiments were done at constant current and all data are compared on the basis of the current density; keeping in mind the injunction that it is the electrode potential which determines the degree of separation.

D. Method of Investigation

Taking into account the desired end, industrial application, and the previous discussion on the advantages of fused salts as solvents for electrolytic applications the method of attack was to investigate

the possibility of separating nickel from cobalt using electrorefining and electrowinning methods in a fused salt system.

The solvent used was a binary mixture of NaCl and KCl with the composition of the eutectic point - a list of the properties of this solvent is given on page 29.

Of the two electrolytic methods available to us, electrorefining and electrowinning, the former is the more desirable. The reason for this lies in the greater simplicity of the electrorefining method. In this method no extensive preparative steps are required and, in the present case, the product may be very simply removed as the anodic residue. On the other hand, electrowinning requires: (1) solution of the metal values; (2) in some cases, purification or conditioning of the electrolyte; (3) electrolytic precipitation of the desired metal; (4) removal of the undesired metal values in order to keep them from eventually appearing in the cathode product as their concentration builds up in the electrolyte. However, under the conditions chosen for this investigation, electrowinning methods appear more attractive for the separation of cobalt from nickel.

II. EXPERIMENTAL

A. Equipment

The furnace was a type 86, multiple unit,
electric crucible furnace manufactured by the Hevi
Duty Electric Company. The throat of the furnace
was three inches in diameter and five inches deep.

Temperature control was effected by a
Thermoelectric Company "Temcometer" which served to
keep the temperature of the salt bath within $\pm$ 1 per
cent of the set temperature, as determined by a
chromel alumel thermocouple immersed in the molten
salt and protected from it by a sheath of Vycor tubing.

A graphite crucible served as a melt container
and in addition as a source of carbon for the melt
chlorination step and as an anode in the electrowinning
experiments. This, in turn, was held in a Vycor
envelope to which was attached a 71/60 Standard Taper
Vycor joint. The upper part of the cell was made
from a Pyrex 71/60 Standard joint and had provision
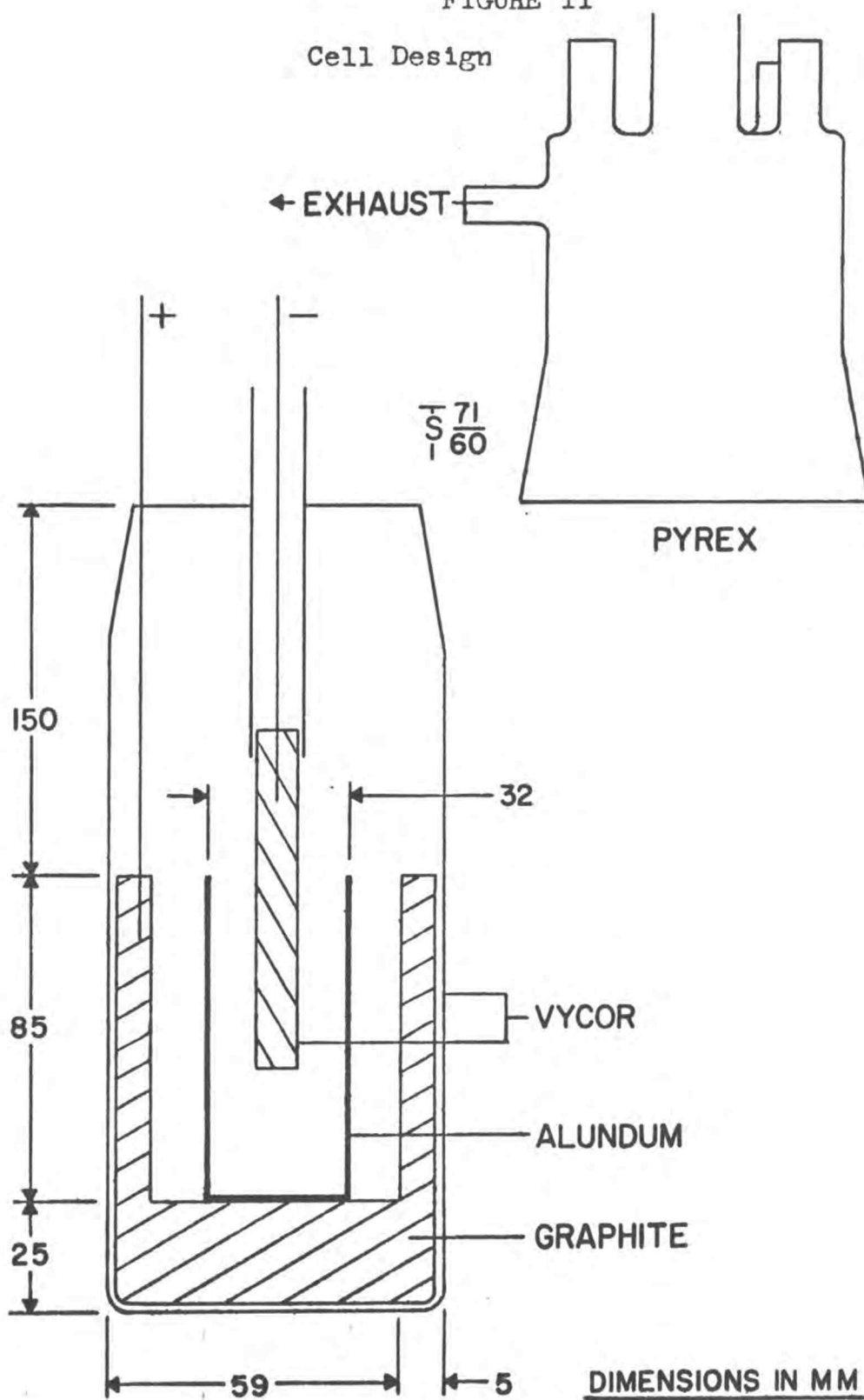for insertion of an anode, cathode, gas inlet tube,

thermocouple sheath, melt sampling tube, and effluent
gas port. Rubber tubing was used to provide an
air-tight connection between the various cell
components and the Pyrex top. In those cases in
which it was desired to stir the melt, this top was
interchanged with one which had a glass bearing
through which a Vycor stirring rod could be inserted.
See Figure II.

The Vycor cell, graphite melt crucible, and
Pyrex top constituted the basic equipment for all
the experiments. Additions or slight modifications
in the basic equipment are either noted later or are
considered to be self-explanatory.

In those cases where the anode reaction was
the discharge of chloride ion to produce chlorine
gas, a diaphragm was necessary to protect the cathode
product from chlorine and thus increase the current
efficiency. The arrangement used is shown in
Figure II. Various materials were used in the
construction of cell diaphragms; alundum, unglazed
porcelain, and graphite. Of those materials alundum
was found to be the most satisfactory and was thus
incorporated into the cell.

FIGURE II

Cell Design

EXHAUST

$\overline{S}\frac{71}{60}$

PYREX

+

—

150

32

85

VYCOR

ALUNDUM

25

GRAPHITE

59

5

DIMENSIONS IN MM

The cathode was made of $\frac{1}{4}$-inch spectrographic rod. In those cases where the electrochemical behavior of the anode was not being investigated the graphite crucible that served as a melt container was made the anode.

Current for the electrolysis was supplied by a six-volt battery charger, regulated by a variable resistor. The complete circuit is shown in Figure III.

B. Chemicals

Materials used were as follows:

1. $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, KCl and NaCl were all Baker's Analyzed Reagent grade chemicals.

2. Nickel metal was in the form of shot obtained from the Matheson-Coleman and Bell Division of Matheson Company with a reported purity of 99.8 per cent.

3. High purity cobalt metal was obtained from Dr. W. J. Kroll.

4. Spectrographic grade iron rod was obtained from the Jarrell-Ash Company.

FIGURE III

Circuit Diagram

VARIABLE RESISTOR

CELL

AMMETER

HIGH IMPEDANCE VOLTMETER
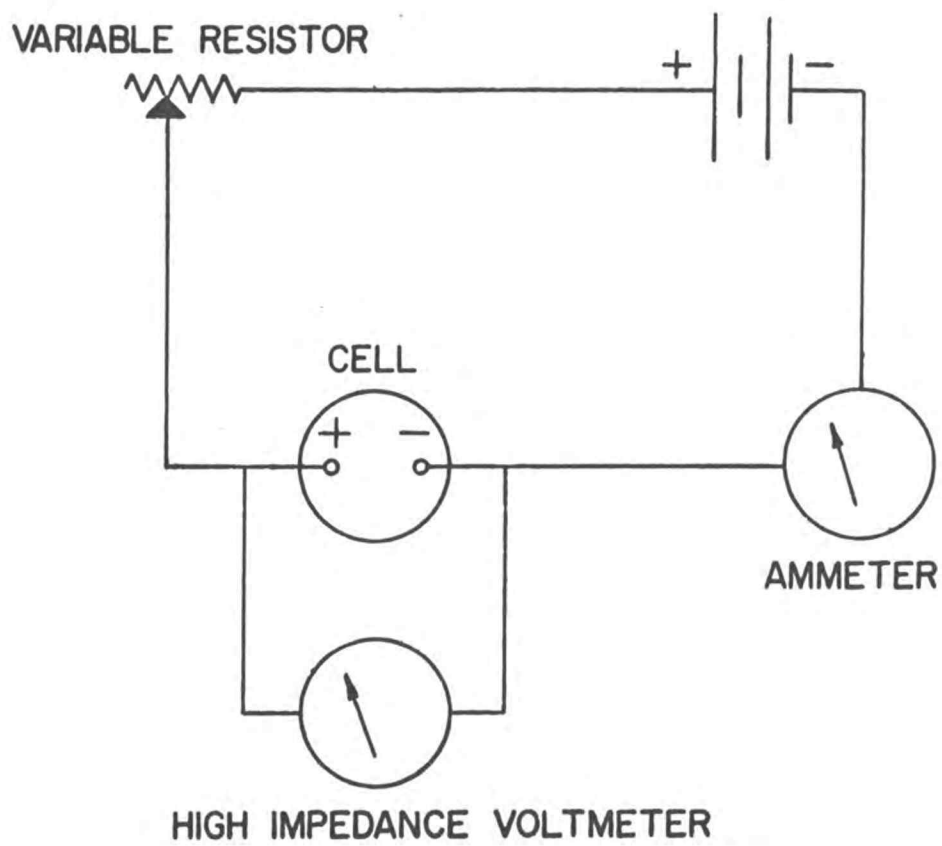
5. The Hanna Nickel Smelting Company of Riddle, Oregon provided the analyzed ferronickel alloy.

6. Carbon electrodes were $\frac{1}{4}$-inch spectrographic grade rods manufactured by the National Carbon Company.

7. Graphite crucibles were machined from United Carbon Products Company's Ultra-Purity Graphite grade UF-4-S.

The eutectic mixture of 60 wt% KCl and 40 wt% NaCl was chosen as the electrolyte because of its desirable properties. These are:

Relatively slight corrosive nature

Melting point: 650°C

Specific conductivity: $K = 2.2$ ohm^{-1}cm.$^{-1}$ [91]

Decomposition Potential: KCl 3.5 volts

NaCl 3.3 volts

(based on the free energies of formation)[39]

Ease of purification.

Furthermore, none of the principal metals, i.e. iron, cobalt, or nickel, are soluble to any appreciable extent in this particular solvent (18, 46, 47.)

All salts were vacuum dried for periods ranging from six to eight hours at 120°C. The drying salts were held under reduced pressure, about 15 inches of water, with a constant flow of nitrogen, during the drying period. This treatment served to change nickel chloride from its green hexahydrated form to the yellow anhydrous form, and cobalt chloride from its pink hexahydrated form to its blue anhydrous form.

Nitrogen, which was used as a purge and as an inert cover for the melt, was passed over copper turnings held at 500°C, to remove any oxygen, before being passed through sulfuric acid and magnesium perchlorate. The chlorine gas used in all experiments was passed through sulfuric acid and magnesium perchlorate to remove water vapor before being passed into the cell. In all cases the effluent gases were passed through a sulfuric acid trap.

In some cases it was desired to use ferronickel
as a solute; it was added to the melt in the form of
the metal chlorides, produced by chlorination of
ferronickel turnings. Chlorination of the turnings
was done in eight-inch Pyrex test tubes that had
previously been thoroughly dried and purged of all
air by a stream of chlorine. The turnings were
strongly heated in a chlorine atmosphere until the
reaction was started. Once this point had been
reached the external heating could be removed since
the turnings burned very vigorously in chlorine. The
iron could be very simply removed from this mixture,
if this was desired, by continued heating. This was
possible because of the low boiling point of
$FeCl_3$ (319°C) (55.) The Pyrex tubes were stoppered
and their anhydrous products stored, under a chlorine
atmosphere, over magnesium perchlorate.

In some cases it was necessary to add iron to the
melt as $FeCl_2$. This was done *in situ* by anodizing a
spectrographic grade iron rod.

C. Procedure

Glassware to be used in the experiment was all
thoroughly cleaned and dried. The graphite crucible
was boiled in concentrated hydrochloric acid, until
nothing more could be leached from the crucible, and
then twice more in distilled water. Before it was
used the crucible was thoroughly dehydrated by
drying in a vacuum oven under the same conditions
used for the salts.

The solvent, NaCl/KCl, was mixed with the
desired amount of solute and the prepared charge was
then poured into the previously assembled cell, the
top put on, and the thermocouple sheath, and gas
inlet tube, were inserted into their appropriate
receptacles. Following this, the furnace was raised
to the desired temperature, the charge melted and
treated with chlorine to convert any oxides or
oxychlorides to chlorides (52) via the reaction

$$MO + C + Cl_2 \rightleftharpoons MCl_2 + CO \quad (21.)$$
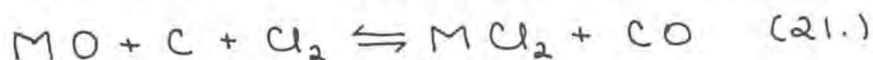
After treatment of the melt was complete, it
was purged of any dissolved chlorine by passing
nitrogen through it for approximately one-half hour.

When this treatment was finished the gas inlet tube was pulled out of the melt to a position just above the surface of the melt so that the nitrogen could provide an inert cover for the melt. Now the graphite cathode was added, after having first been heated to redness to expel all adsorbed water.

D. Analytical Methods

A sensitive, reliable, and reasonably rapid analytical method was of prime importance to this research. The method chosen must be of such a nature that it may be used for the quantitative determination of iron, cobalt, and nickel, alone and in combination with one another.

Unfortunately, cobalt and nickel, because of their very similar chemical properties, interfere with one another to some extent in almost any analytical method and, therefore, a complete separation is necessary before analysis. This was especially the case in this research where the concentration of nickel may be anywhere from one to several orders of magnitude greater than that of cobalt.

Polarography, because of its versatility and
sensitivity, offered considerable promise. Numerous
methods were tried (48, 68, 70, 49) but were rejected
for one reason or another. In general these methods
involved a tedious and complicated separation of the
interfering cations, making accurate and reproducible
analyses very difficult.

Solvent extraction procedures employing organic
solvents, such as chloroform and amyl alcohol-ethyl
ether, were investigated as a means of separating
nickel from cobalt (80, 81.) However, all of the
extraction methods that were tried suffered from the
disadvantages cited above. A simple and completely
satisfactory separation scheme was finally evolved
using ion exchange coupled with colorimetry.

The separation scheme is based on data presented
by Kraus and Moore (51,) which showed that $Fe(III)$,
$Co(II)$, and $Ni(II)$ form chloride complexes of
differing stability, where the order of complex
stability is $Fe(III) > Co(II) > Ni(II)$, and that these
cations can be eluted from the chloride form of an
anion exchange resin in the reverse order of their
chloride stabilities.

Cathode deposits were prepared for analysis by first leaching in distilled water to remove any occluded salt, scraping the deposit off the graphite cathode, leaching again in distilled water, decanting off the liquid, washing in acetone, drying and weighing. The samples were then dissolved in a mixture of 9 M HCl plus a few drops of nitric acid. This solution was boiled to incipient dryness to remove the nitric acid and taken up in 9 M HCl. The solution was gently warmed to dissolve the solids and then brought to a definite volume with 9 M HCl.

Melt samples were dissolved in the mixture of 9 M HCl plus nitric acid, which served to oxidize the iron to the trivalent state, and then treated as above.

The anion exchange resin, Dowex-1, was prepared by converting it completely to the chloride form by passing 9 M HCl through the column. Next the sample, containing cobalt, nickel, and sometimes iron, made up in 9 M HCl, was loaded onto the column. After loading was completed nickel was eluted from the column by passing about one to 1.5 column volumes of 9 M HCl, at the rate of one milliliter per minute, through the column. The eluted nickel solution was

evaporated to incipient dryness, neutralized with
NaOH, taken up in 20 milliliters of 0.1 molar KCN,
and made up to 100 milliliters with distilled water.
This solution containing the tetracyano complex of
nickel was analyzed spectrophotometrically. Figure IV
shows the standard curve determined at 268 mμ. Cobalt
and iron, if present, were then eluted from the
column with distilled water. The eluted cobalt was
then analyzed spectrophotometrically using the
Nitroso-R (1-nitroso-2-hydroxy-3, 6-napthalene
disulfonic acid) complex (97.) Iron caused no
interference problem with this method. Figure V shows
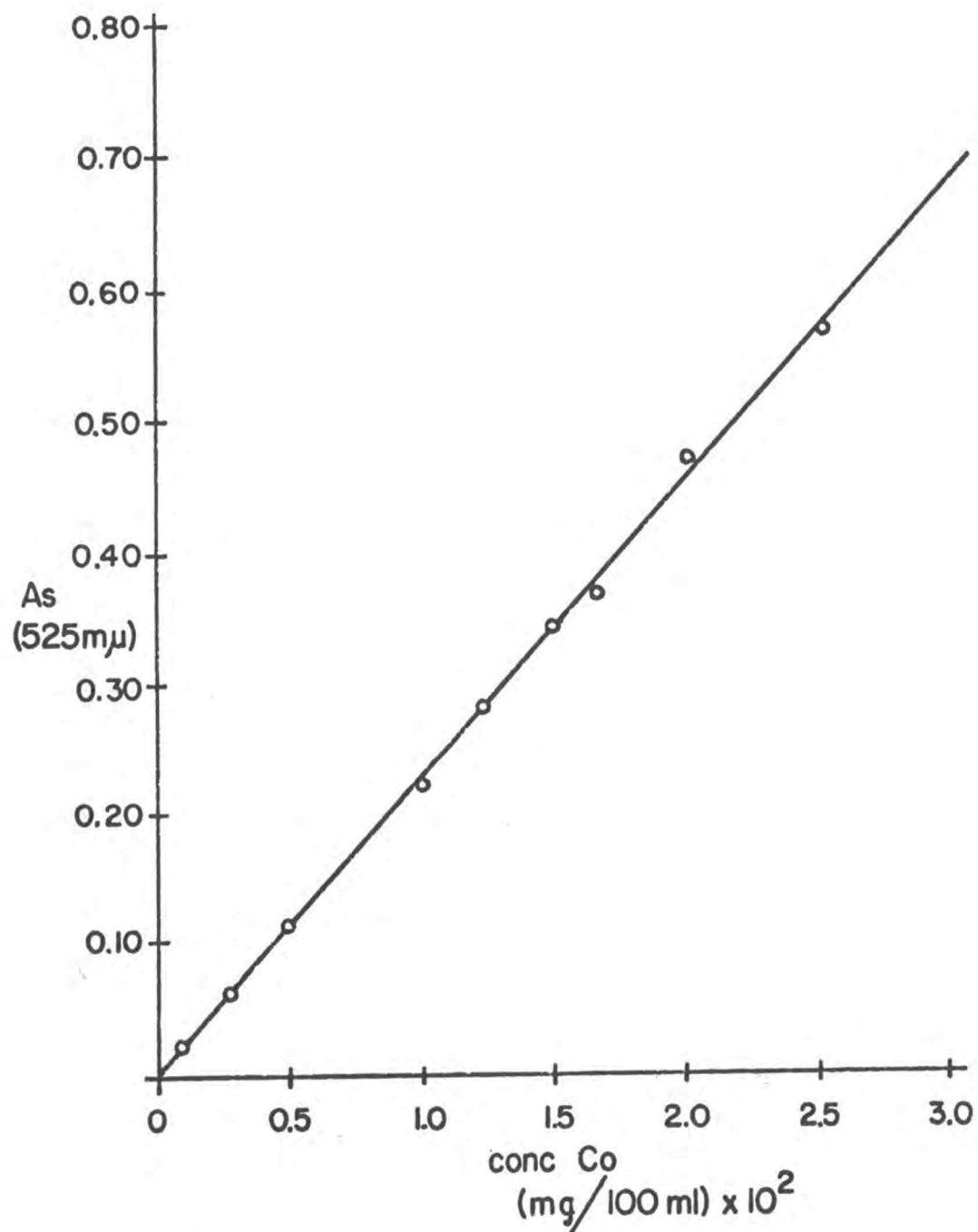the standard curve for cobalt determined at 525 mμ.

Iron was determined colorimetrically as the
thiocyanate complex, a method practically free from
interference from cobalt and nickel (1;) Figure VI
shows the standard curve determined at 475 mμ. An
aliquot of the dissolved sample was taken and
analyzed directly without subjecting it to ion
exchange separation.

As an independent check on the accuracy of this
analytical method some standard samples, containing

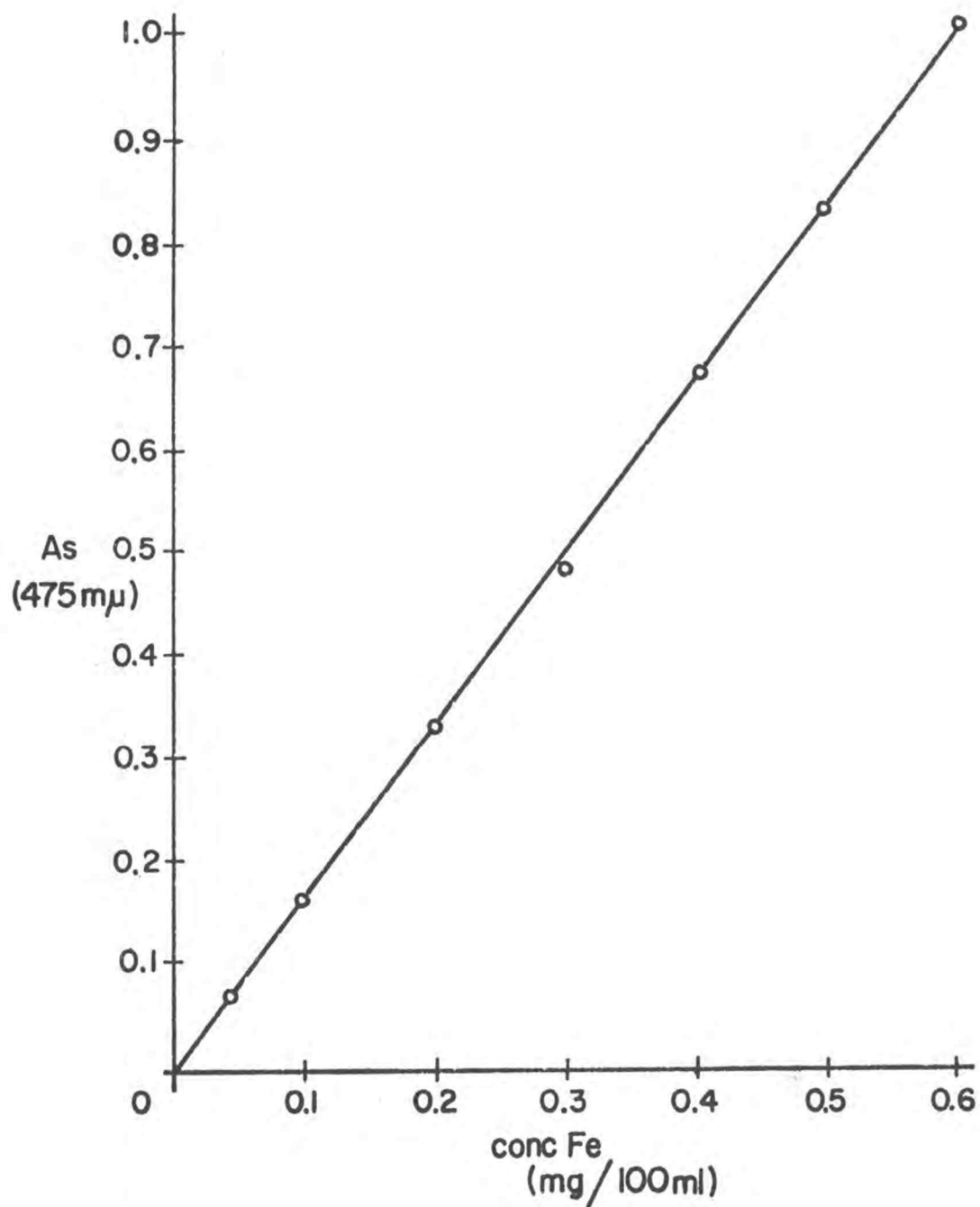FIGURE IV   37

Standard Curve for the Determination

of Nickel as the Tetracyano Complex at 268 mμ

FIGURE V   38
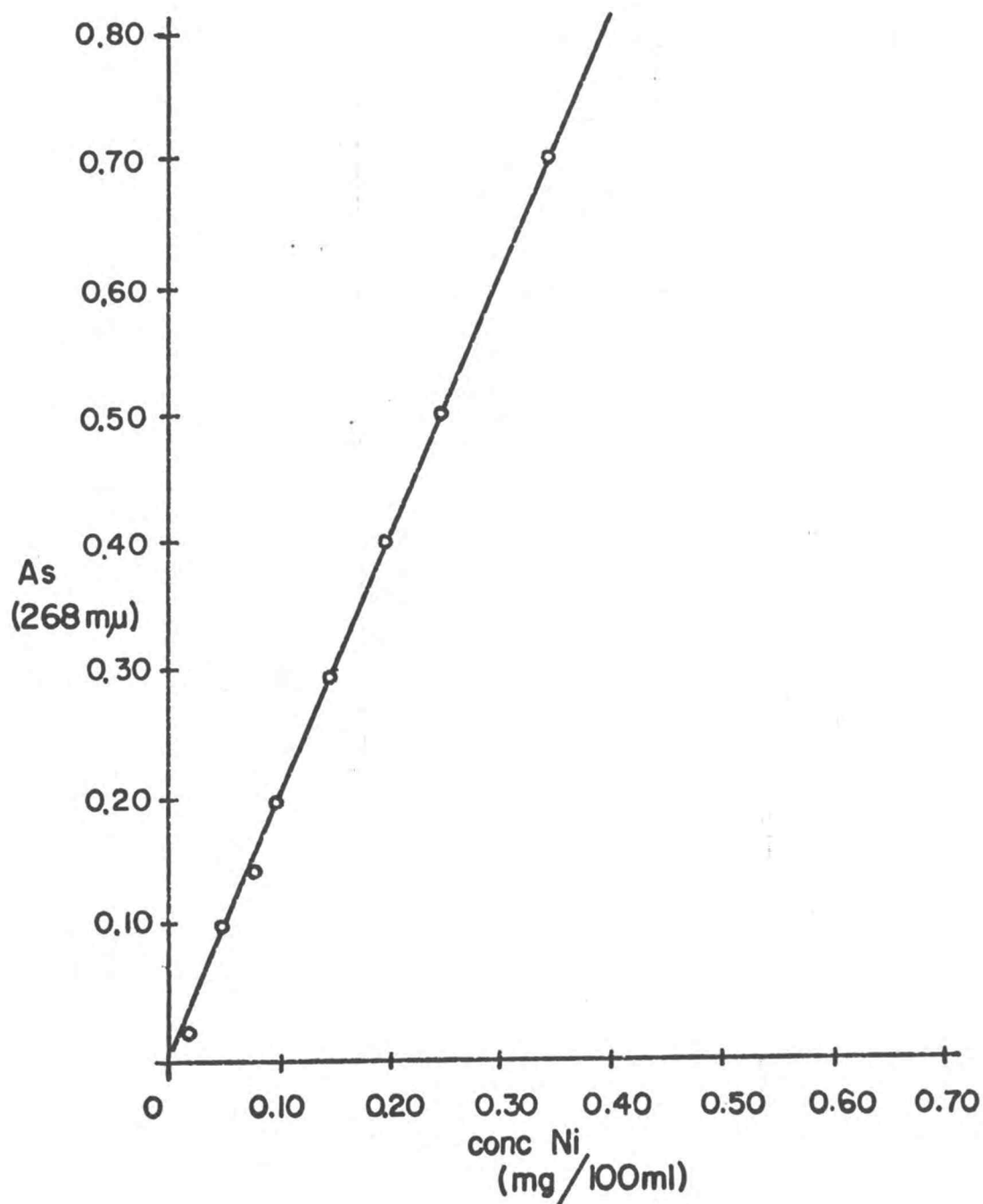
Standard Curve for the Determination
of Cobalt as the Nitroso-R Complex
at 525 mμ

FIGURE VI   39

Standard Curve for the

Determination of Iron as the

Thiocyanate Complex at 475 mμ

iron, cobalt, and nickel, were obtained from the
Bureau of Mines in Albany, Oregon and were analyzed
by the method described above. The results of these
analyses are presented in the table below.

TABLE 2

Number Sample	Element	Bureau of Mines Analysis (%)		Found Experi.	Average Deviation
		Chem.	Spec.		
48724	Fe	1.63 1.70 1.68	1.63	---	---
	Co	3.29 3.29 3.30	3.26	3.38	.0045
	Ni	95.50	95.17	94.88	.0036
48729	Fe	73.80 74.10	74.45	---	---
	Co	0.56 0.64 0.63	0.60	0.63	.0059
	Ni	25.3	24.95	25.02	.0013

III. RESULTS

A. Electrorefining Studies

As was stated earlier most electrorefining is done by the soluble anode method. Therefore, experiments of this nature were conducted using pieces of ferronickel alloy, supplied by the Hanna Nickel Smelting Company, as anodes. This material is produced from lateritic type ore. Reduction of nickel and iron from the ore is accomplished by the Ungine process, which involves the addition of a suitable reducing agent, in this case silicon in the form of ferrosilicon, to a mixture of molten oxide ore (15.) Analysis of the ferronickel product indicates the following average composition: (15)

Ni	45.94%
Fe	52.38%
S	.006%
P	.024%
C	.029%
Cr	.02%
Si	.9%
Co	.5%
Cu	.2%

Reference to the values of the electrode potentials given in Table 3 for the oxidation of the several metals to their respective divalent cations indicates, as a first approximation, that, in the case of a ferronickel anode, iron would go into solution first leaving nickel and cobalt behind, and plate out at the cathode. After the iron had been removed the cobalt would follow, leaving the nickel behind.

TABLE 3

Electrode Potentials for the Oxidation
of Several Metals to Their Respective Divalent
Cations in 1:1 LiCl/KCl at 700°C

Reaction	E^O*
$Fe=Fe(II) + 2e^-$	1.365
$Co=Co(II) + 2e^-$	1.169
$Ni=Ni(II) + 2e^-$	0.985

*measured against the Ag/AgCl reference electrode

In order to gain as much information as possible from the electrorefining experiments the cathodes were removed for analysis at periodic intervals. This allowed one to follow the course of the electrolysis - to determine at what point nickel began to appear in the deposit. As has been stated

previously, according to EMF data (viz. Table 3) one
would expect iron to dissolve from the anode first
and plate out at the cathode. When the concentration
of iron in the anode dropped to a low enough value
cobalt would be expected to appear on the cathode
deposit leaving nickel behind. The appearance of
nickel in the cathode deposit, before all of the iron
had been removed, cannot be tolerated since this means
not only less of the product but also poor separation.

The procedure itself consisted of removing the
cathode from the melt and inserting a new one at
periodic intervals.

The results of two of a number of experiments
are shown in Figure VII and VIII. These results showed,
in contrast to the ideal situation, that the cathode
deposit was always contaminated with nickel. These
experiments were picked because they show the gradual
but increasingly rapid built-up of nickel in the
cathode deposit and apparently that higher anode
current densities tended to accelerate the process of
solution of the nickel and its subsequent appearance
in the cathode deposit. For current densities in the
region of 1.0-1.5 amps/cm^2 iron and nickel deposited
on the cathode in about the same ratio as that which
existed originally at the anode.

FIGURE VII 44

Variation of Nickel Concentration

in the Cathode as a Function

of Time

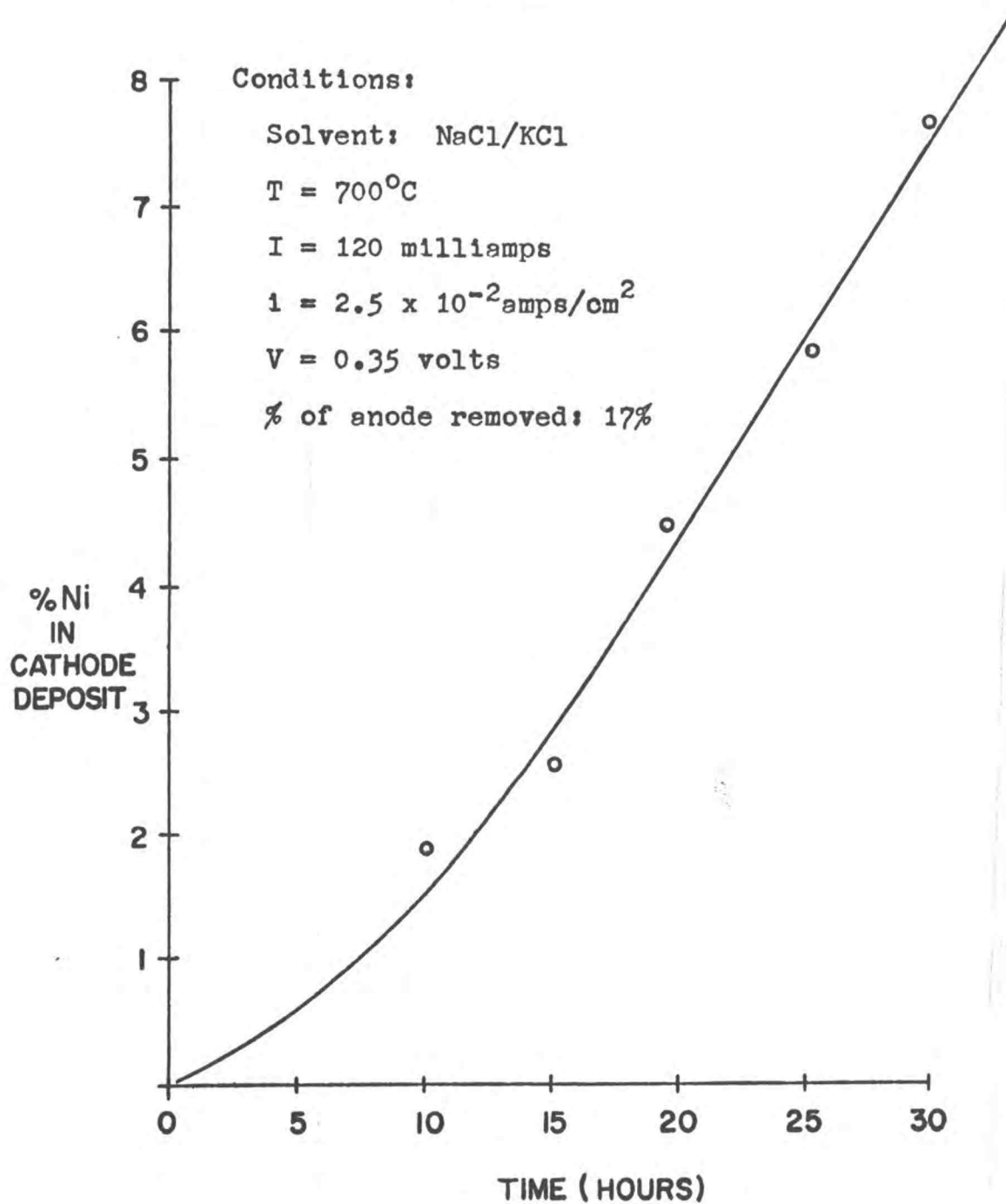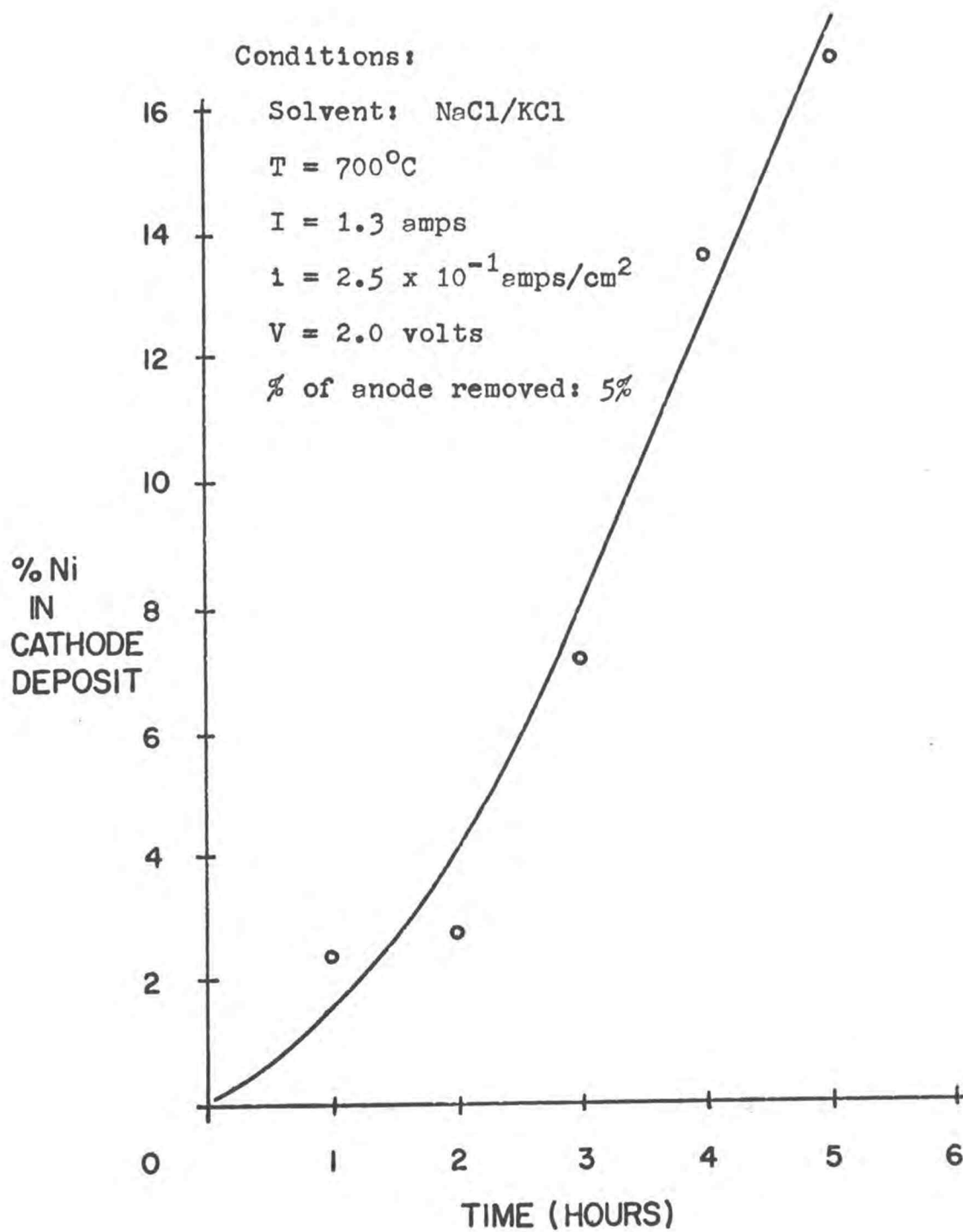Conditions:

Solvent: NaCl/KCl

$T = 700^{\circ}C$

$I = 120$ milliamps

$i = 2.5 \times 10^{-2} amps/cm^2$

$V = 0.35$ volts

% of anode removed: 17%

%Ni IN CATHODE DEPOSIT

8

7

6

5

4

3

2

1

0   5   10   15   20   25   30

TIME (HOURS)

FIGURE VIII

Variation of Nickel Concentration in the
Cathode as a Function of Time

Conditions:

Solvent: NaCl/KCl

$T = 700°C$

$I = 1.3$ amps

$i = 2.5 \times 10^{-1}$ amps/cm^2

$V = 2.0$ volts

% of anode removed: 5%

% Ni IN CATHODE DEPOSIT

TIME (HOURS)

The results of those electrorefining experiments, which were done at relatively low current densities - 2.5×10^{-1} to 2.5×10^{-2} amps/cm^2, - seemed to indicate that as the boundary layers of the anode became depleted of iron nickel began to go into solution and was subsequently codeposited with iron at the cathode. One possible explanation for this result is the fact that the diffusion coefficient of iron in iron-nickel alloys, at the temperature of the experiments, is very small - $10^{-16} cm^2$/sec (32.) This would mean that iron from the interior portions of the anode could not diffuse to the surface fast enough to replace that which was lost by oxidation and as a result nickel began to go into solution.

At current densities in the region of 1 amp/cm^2 it was noted that appreciable bubbling took place at the anode surface and that the effluent cell gas was acid to moist litmus paper. These observations indicate that discharge of the chloride ion was taking place at the anode. It can be inferred from these observations that the ferronickel anode exhibited considerable polarization in the 1 amp/cm^2 region, a phenomenon which may

extend to lower values of the anode current density.
If the anode were polarized strongly enough to be
able to discharge chloride ion it is reasonable to
assume that nickel was being oxidized simultaneously
with the iron.

It is apparent that the processes which occur
at the anode are of a complicated nature, seemingly
dependent to some degree on the anode current
density. The difficulties apparently result from the
inability of the iron to diffuse rapidly enough to
the surface of the anode and from the polarization
of the anode. In any event, the results of these
soluble anode experiments indicated that this
technique was unsuitable for the separation of iron
and nickel and as a corollary nickel and cobalt at
least under the conditions used in these experiments.
Therefore, the electrowinning method which later
formed the basis for the proposed separation
scheme was tried.

B. Electrowinning Studies

Deposition was carried out at 700-750°C from a
NaCl-KCl eutectic mixture which contained approximately

6-10 wt% $NiCl_2$ plus the chlorides of cobalt and, in some cases, iron. Since the object was the separation of nickel from cobalt these experiments concerned themselves initially with the electrolysis of synthetic mixtures of anhydrous $NiCl_2$ and $CoCl_2$, made up with approximately the same Ni/Co ratio as is present in ferronickel. In order to follow the course of the electrolysis the cathode was removed at periodic intervals and replaced with a fresh one, following the procedure outlined previously. At the same time melt samples were taken by drawing up small samples into a previously flamed Pyrex tube. In later experiments the artificial mixtures of $NiCl_2$ and $CoCl_2$ were replaced by $NiCl_2$ and $CoCl_2$ made by chlorinating turnings made from Hanna ferronickel. The deposits themselves were composed of very small shining needles, which adhered well enough to the graphite cathode to allow the frozen melt to be leached away, but not so strongly that they could not be removed with ease by gentle scraping.

Of primary concern was the purity of these deposits. The results of experiments in which the cobalt concentration of the cathode deposit was followed as a function of the nickel concentration of the melt are shown in Figure IX. Examination of these results enables us to draw a number of conclusions. According to these data, cobalt begins to codeposit with nickel to a noticeable extent when the nickel concentration of the melt has decreased by a factor of about 5. This is very much in contrast with the behavior one would predict from Hamby's data.

The Nernst equations for the two reactions of interest:

$$NiCl_2 = Ni + Cl_2 \qquad (22)$$

and

$$CoCl_2 = Co + Cl_2 \qquad (23)$$
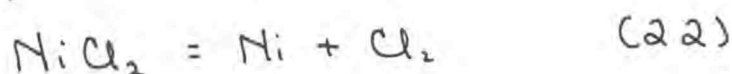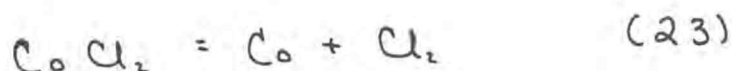
are

$$E_{Ni} = E^\circ_{Ni} - \frac{RT}{nF} \ln \frac{[a_{Ni}][a_{Cl_2}]}{a_{NiCl_2}} \qquad (24)$$

and

$$E_{Co} = E^\circ_{Co} - \frac{RT}{nF} \ln \frac{[a_{Co}][a_{Cl_2}]}{a_{CoCl_2}} \qquad (25.)$$

20

15

%Co IN
CATHODE
DEPOSIT

$(\times 10^2)$

10

5

INITIAL CONDITIONS:
[Ni(II)] = 2.4 x 10^{-2} g/g solvent
[Co(II)] = 3.0 . 10^{-3} g/g solvent

Solvent = NaCl/KCl   T = 700° C

I = 110 milliamps (Constant)
i = 1.5 x 10^{-2} amps/cm^2

0   10   20   30   40   50   60   70   80   90   100

% Ni REMAINING IN THE MELT

FIGURE IX

Percent Cobalt in the Cathode Deposit
as a Function of the Nickel Concentration
of the melt

50
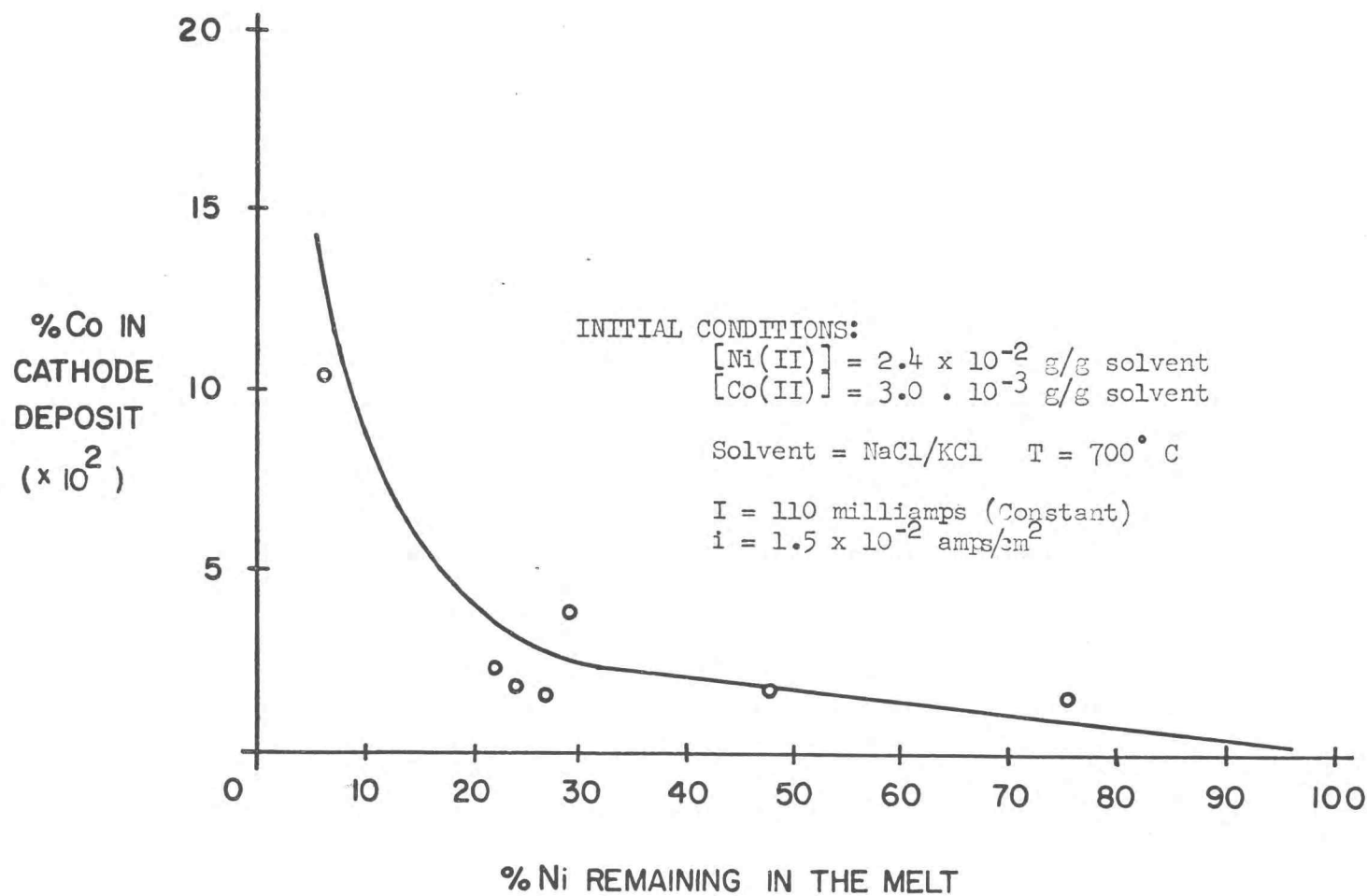
neglecting overpotential, which is assumed to be small. When cobalt codeposits with nickel it follows that

$$E_{Co} = E_{Ni} \qquad (26)$$

or

$$E^{\circ}_{Co} - \frac{RT}{NF} \ln \frac{[a_{Co}][a_{Cl_2}]}{a_{Co Cl_2}} = E^{\circ}_{Ni} - \frac{RT}{NF} \ln \frac{[a_{Ni}][a_{Cl_2}]}{a_{Ni Cl_2}} \qquad (27)$$

Assume that the activity of the pure metals equals one and that

$$a_{Cl_2} = P_{Cl_2} = 1 \qquad (28)$$

since the standard state for Cl_2 is taken to be the pure gas under one atmosphere pressure. Rewriting equation (27) we see that for $T=700^{\circ}C$

$$E^{\circ}_{Co} + .0965 \log a_{Co Cl_2} = E^{\circ}_{Ni} + .0965 \log a_{Ni Cl_2} \qquad (29)$$

This may be rewritten to give

$$\log [N_{Ni Cl_2}][\gamma_{Ni Cl_2}] = \frac{E^{\circ}_{Co} - E^{\circ}_{Ni}}{.0965} + \log [N_{Co Cl_2}][\gamma_{Co Cl_2}] \qquad (30)$$

where N_{MCl_2} is the mole fraction of the metal chloride and γMCl_2 is the activity coefficient of the metal chloride on the mole fraction scale. Hamby gives the values $\gamma CoCl_2 = 1.1$ and $\gamma NiCl_2 = 1$ at $700^{\circ}C$ for the concentration range 4×10^{-2} to 4×10^{-4} mole fraction. For the cases illustrated in Figure IX,

$$N_{Co Cl_2} = 1.6 \times 10^{-4}$$

so that

$$N_{NiCl_2} = 1.5 \times 10^{-6}$$

whereas, in fact, the simultaneous deposition of cobalt started when $N_{NiCl_2} = 5.0 \times 10^{-3}$, a difference by a factor of approximately 10^3. The assumption has been made, in arriving at these numbers, that the limiting current density for nickel was not exceeded; a reasonable assumption considering the magnitude of the current density, 1.5×10^{-2} amp/cm^2. This striking difference is attributed to the extensive alloy formation that takes place between the two metals.

It appeared, on the basis of these data, that using the experimental conditions employed here, i.e., NaCl/KCl solvent and temperature of 700-750°C, and starting with a solute whose Ni/Co ratio is 90, as it is in commercial ferronickel, it is not possible to deposit a product whose cobalt content falls within the prescribed limits of less than 20 part per million. However, these data also hint at a solution - using the product of one deposit as the starting material for a second. That is, redissolving the first cathode product in a melt composed only of the solvent NaCl/KCl, by chlorination, and then performing the electrolysis

a second time. The question remained, how much
nickel might be removed from the melt before the
cobalt concentration of the deposit became too
large to achieve the desired purity in the second
deposit? Using the data presented in Figure IX and
assuming that it was desirable to carry over into
the second electrolysis as little cobalt as possible
we see that about 80 per cent of the nickel present
in the bath could be removed. The results of some
of these two-stage experiments are presented in
Table 4. In two of these cases the starting material
was chlorinated ferronickel turnings from which most
of the $FeCl_3$ had been sublimed. These results show
that it is indeed possible to produce nickel which
contains less than 20 p.p.m. cobalt. The optimum
recovery seems to be in the region of 75 per cent
to 85 per cent of the original nickel but most
certainly less than 90 per cent.

Current density, as might be predicated, plays
an important role in determining the effectiveness

TABLE 4

The Effect of a Two-stage Electrolysis on the Purity of the Nickel Deposit

Initial Bath Analysis (g.)	Analysis of 1st Product	Ni Recovery	Current Efficiency 1st Deposition	Analysis of Second Product	Ni Recovery	Current Efficiency 2nd Deposition
Ni-3.47	Ni-99.984%	77%	----	Ni-99.998%	70%	71%
Co-0.0385	Co- .016%			Ni-99.988%	95%	
Ni-3.61	Ni-99.988%	74%	30%	Ni-99.9984	74%	70%
Co-0.0316	Co- 0.012%					
Fe-0.532						
Ni-3.07	Ni-99.978%	79%	45%	Ni-99.9982	72%	71%
Co-0.0221	Co- 0.022%					
Fe-0.3795						

Cathode Current Density: 1.5×10^{-2} amps/cm^2.

Melt Temperature: $700^{\circ}C$

Weight of Solvent: 165g

Anode & Cathode: Graphite rods

Cathode Diaphragm: Perforated Alundum cylinder

of the separation. Table 5 presents data which show
the effect of current density.

TABLE 5

Effect of Cathode Current Density
on the Codeposition of Nickel and Cobalt

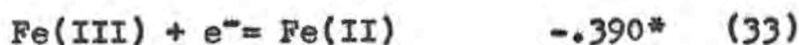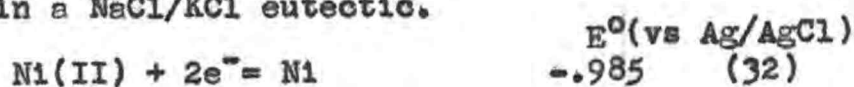| Current Density ($amps/cm^2$)	$\frac{(Ni/Co)\ Deposit}{(Ni/Co)\ Melt}$	% Nickel Removed
1.46×10^{-2}	84.6	25%
1.5×10^{-2}	82.1	55%
5.4×10^{-2}	42.6	35%
5.4×10^{-2}	40.2	60%

Thus it may be seen that low values of current
density aid in effective separation of nickel and
cobalt. Since there is only a very small separation
between the deposition potentials of nickel and
cobalt any drastic departure from equilibrium
conditions, as occasioned by high current density,
would cause an increase in the amount of cobalt
present in the deposit.

While the cathode current densities necessary
to achieve the required separation of nickel and
cobalt ($1.5 - 2.0 \times 10^{-2}$ amps/cm^2) are lower than
those normally used in fused salt electrowinning
(65,) they are still within the range used by
industry in a number of conventional, aqueous,
electrowinning operations. Cathode current densities
of 50 - 100 times as high are necessary in fused
salt electrolysis in order to keep the electrolyte
molten; the cell current is used to maintain the
cell at the proper operating temperature by I R
heating. In view of the necessarily low cathode
current densities in the present process it
probably would be necessary to use an externally
heated cell. This has some disadvantages from an
economic viewpoint, however. The resolution of
this problem must await a thorough economic study
perhaps coupled with more detailed research.

The data presented in Table 4 reveal a serious problem, however, this being the drastic lowering of the current efficiency due to the presence of iron in the melt. As little as 13 per cent iron can cause a 50 per cent drop in the current efficiency. The reason for this may be seen by referring to the electromotive force values given by Flengas and Ingraham (28) for the reaction:
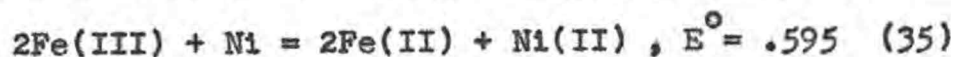
$$M = M^{+x} + xe^- \qquad (31)$$

at 700°C in a NaCl/KCl eutectic.

	E^o(vs Ag/AgCl)	
$Ni(II) + 2e^- = Ni$	-.985	(32)
$Fe(III) + e^- = Fe(II)$	-.390*	(33)
$Fe(II) + 2e^- = Fe$	-1.365	(34)

*Calculated from the data of Flengas and Ingraham, op.cit. and Hamer et. al. (28, 39.)

We see from these data that, in those melts which contain iron in the trivalent state, the reaction

$$2Fe(III) + Ni = 2Fe(II) + Ni(II) , \quad E^o = .595 \qquad (35)$$

will take place; resulting in a dissolution of the deposited nickel metal. Eventually, of course, the reaction will come to equilibrium and the dissolution

of nickel metal will stop. However, it must be kept
in mind that the divalent iron may diffuse to the
anode, be oxidized to the trivalent state and
diffuse back to the cathode to be reduced back to
the divalent state. The net result is observed as
a lowering of the current efficiency. Due to the
fact that a prime requisite of this process is a
rather low current density, in the vicinity of
$1.5-2.5 \times 10^{-2}$ amps/cm^2, it is necessary that the current
efficiency be as high as possible. Since the cell
design, Figure II, included a refractory diaphragm
intended to reduce the diffusion of chlorine through
the melt as much as possible the only alternative we
have to attain the maximum current efficiency possible
for this process (70 per cent) is to remove es-
sentially all the iron prior to deposition of the
nickel. The question now remains how best to effect
this removal. While not an end in itself it is
desirable to keep the process simple and to keep the
volume of wastes as low as possible and thus it is
preferable to try to effect the removal of iron
in situ. Any attempts to effect iron removal by

chemical means, such as precipitation, would lead to the removal of nickel and cobalt not only because of their similar chemistry, but also because of entrainment in the precipitate.

The easiest solution to this problem would be to remove the iron from an anode and to let the nickel drop into the anode sludge. However, a clean separation has been shown to be impossible to achieve with this method, at least at reasonable current densities (0.5-1.5 amps/cm^2) with an anode containing 45 per cent nickel.

Chlorination of ferronickel turnings in the melt at 700°C was also tried as a method of iron removal. Since the temperature of the melt was about 400°C higher than the boiling point of $FeCl_3$ (319°C) it was hoped that the iron might be driven off by a prolonged chlorination of the melt; Figure X shows the rate of removal of $FeCl_3$ from a NaCl/KCl melt at 700°C. While it was possible to remove $FeCl_3$ from the melt by this method the rate was too slow to be practicable. The $FeCl_3$ that was driven from the melt, and which condensed on the cooler portions of the apparatus, had a bright yellow color, in contrast to the usual black color of

FIGURE X

Rate of Removal of Fe(III) from a
NaCl/KCl Melt at 700°C Using a Chlorine Sparge
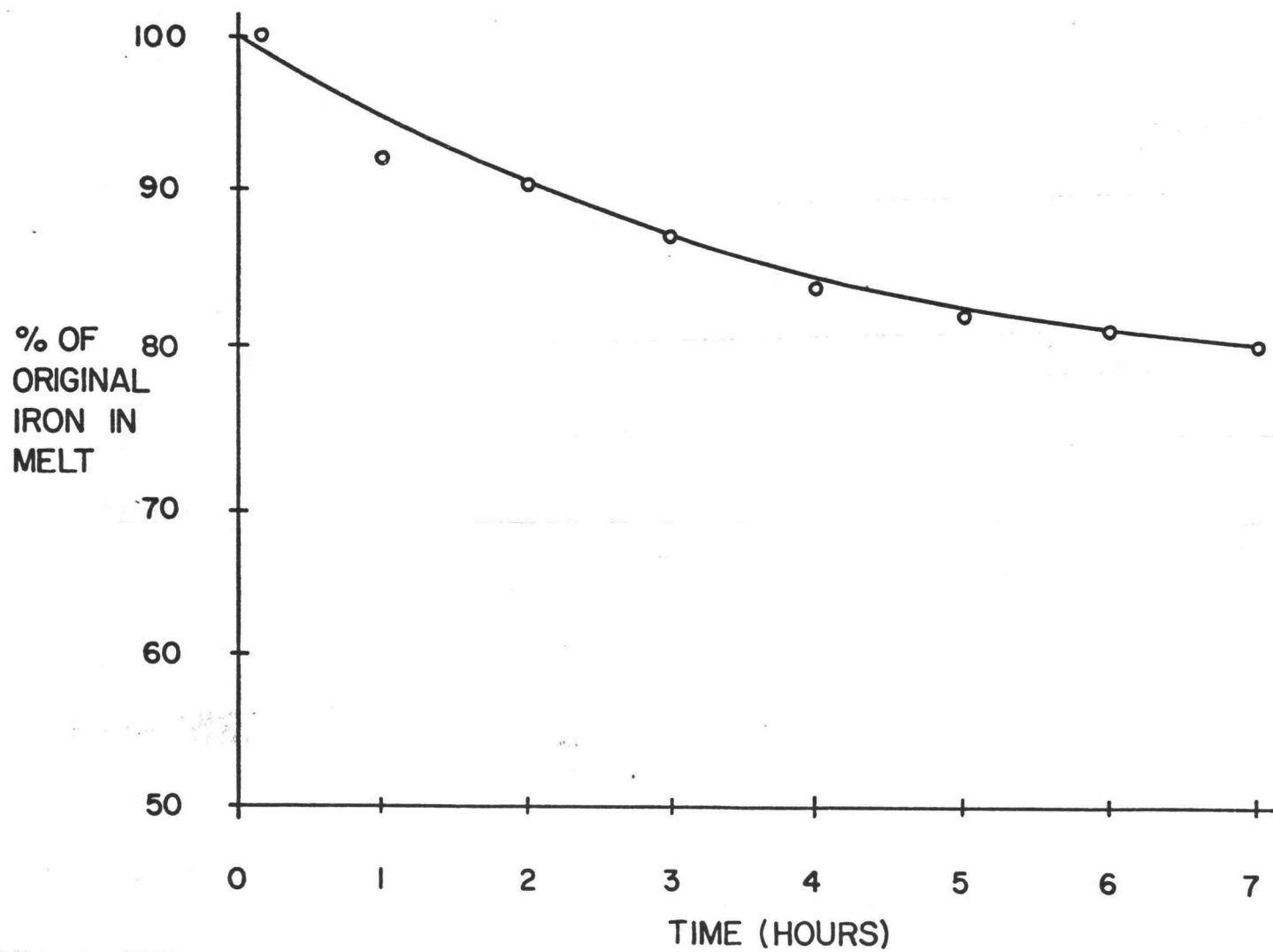
anhydrous $FeCl_3$. This yellow material was probably
a complex compound of $FeCl_3$ with the alkali chlorides
which would probably account for the unusual
stability of $FeCl_3$ in the melt.

Another method that suggested itself was the one
used for the laboratory preparation of cell feed,
chlorination of ferronickel turnings and sublimation
of the iron as $FeCl_3$. In order to obtain complete
conversion of the metal to the chloride a high
surface to volume ratio was necessary; chlorination
of massive pieces was not successful. This meant that
the large ferronickel ingots must be reduced to small
pieces, either by turning on a lathe, which would be
prohibitively expensive, or by adding sulfur which
would make the metal brittle and allow it to be
crushed (54.) From an industrial standpoint, however,
it is improbable that this would be an economically
feasible process. Chlorine is used as a reagent and
its cost would have to be offset by selling the
by-product $FeCl_3$. It is doubtful that the market
for $FeCl_3$ would favor this solution.

The difference in the standard electrode
potential E^o (p.42) between the iron and nickel couples
suggested yet another method for removing iron;
equilibration of divalent nickel and metallic iron.

C. Equilibration Studies

It can be seen from the standard potentials for
reaction (32) and (34) that E^o for the reaction

$$Fe+Ni(II) = Ni + Fe(II) \qquad (36)$$
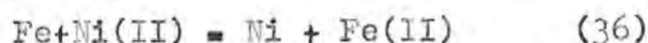
in the NaCl/KCl eutectic, at $700^o C$ is 0.380 volts.
This indicates another method which may be available
to us for separating iron from nickel; equilibration
of a melt containing divalent nickel with iron metal.

We may relate the standard potential for
reaction (31) to the equilibrium constant for that
reaction by the equation:

$$E^o = \frac{RT}{nF} \quad \ln K \qquad (37)$$

where in this case

$$K = \frac{[a_{Fe(II)}][a_{Ni}]}{[a_{Ni(II)}][a_{Fe}]}.$$

After inserting the values of the constants we find
that at $750^o C$, $K=6.9\times10^3$. Thus it appeared that if
pure iron metal were put into a melt containing
divalent nickel, essentially all of the nickel ion
would react to give the metal putting an equal
quantity of iron into solution. This suggested that
perhaps the nickel present in ferronickel could be easi-
ly separated from the iron by precipitation and then the

precipitated nickel could be reworked to remove the cobalt. While this procedure appeared to be possible from a thermodynamic point of view, nothing was known about the rate of reaction, so experiments were performed in order to obtain this information and at the same time obtain an independent value of K, the equilibrium constant.

These experiments consisted simply in bringing either pure iron or nickel metal, in a finely divided form, into contact with the chloride of the other member of the couple depending upon the direction from which the equilibrium was approached, in a NaCl/KCl flux with constant stirring. In all cases the solvent was pretreated as described previously.

The variation of the ratio of $\frac{a_{Fe(II)}}{a_{Ni(II)}}$ with time is shown in Figure XI. From these data we can see that the equilibrium constant for reaction (36) is about 3×10^2. This value is more than one order of magnitude smaller than that calculated from EMF data.

It is assumed that because the concentration of the solute is so small (5×10^{-3} mole fraction or less) that the concentration is equal to the activity, that is, the activity coefficient is equal to one. Now in

FIGURE XI

Variation of the Ratio $\frac{a_{Fe(II)}}{a_{Ni(II)}}$ as a Function of Time

64

Fe(II)+Ni ⇆ Ni(II)+Fe (shaded circles)

$$\frac{a_{Fe\,(II)}}{a_{Ni\,(II)}}$$

T = 750°C

Solvent : NaCl/KCl

Ni(II)+ Fe ⇆ Fe(II)+Ni (open circles)

TIME (HOURS)
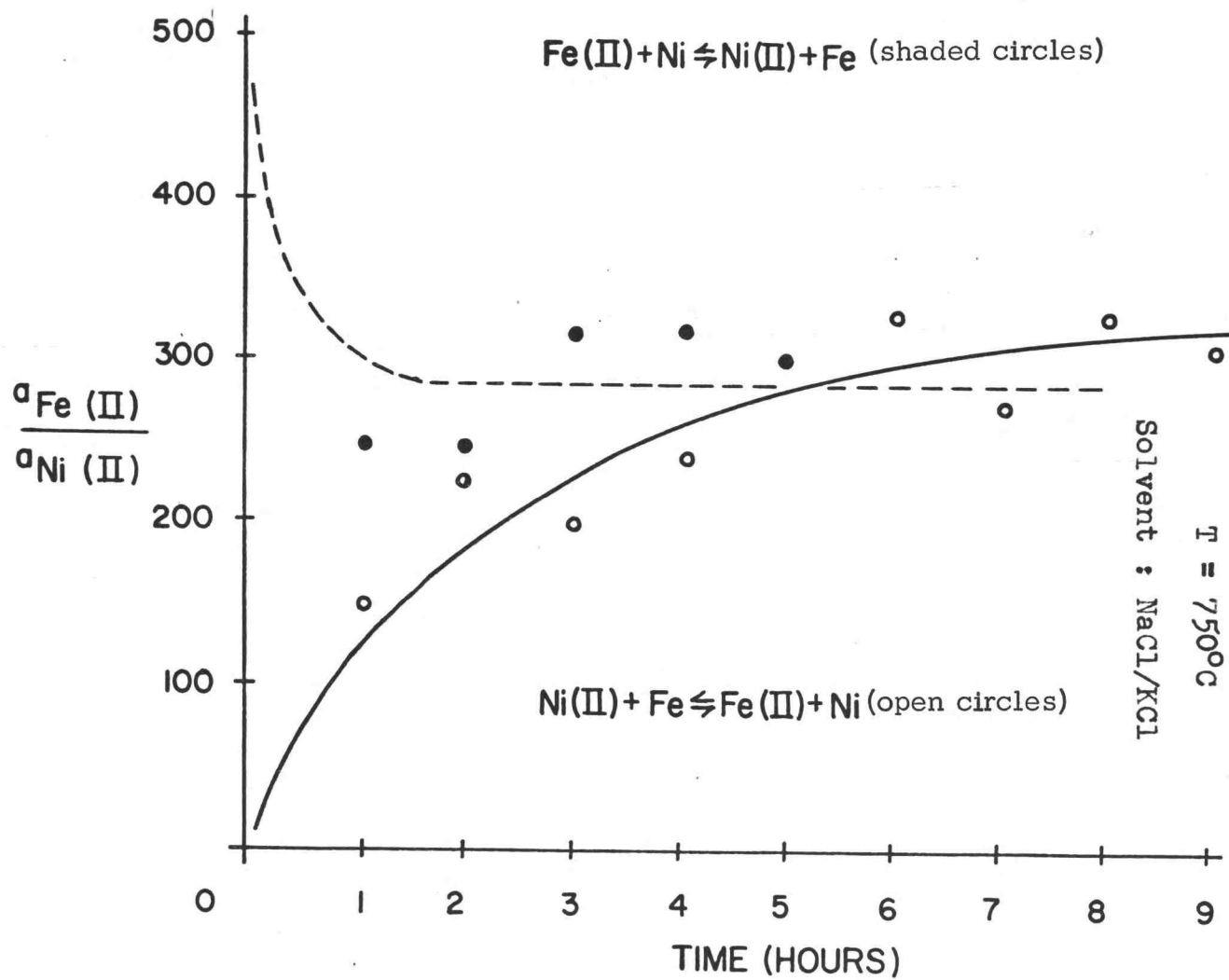
the case of divalent nickel in the NaCl/KCl solvent and in the concentration range of interest Hamby (38) has shown that the activity coefficient is equal to one. This information is not available for divalent iron but it seems reasonable to assume that its behavior is similar to that of nickel, in which case we would expect the activity coefficient of divalent iron in the NaCl/KCl solvent system at $700^{\circ}C$ in the concentration range 5×10^{-3} or less to be about one. Thus it does not appear that the discrepancy between the value of the equilibrium constant calculated from EMF data and that found experimentally can be attributed to deviations of the solute from ideal behavior. A more probable explanation is that the values of the equilibrium electrode potentials used to calculate the value of the equilibrium constant for the reaction under consideration were determined for the individual reactions

$$2e^- + Fe(II) = Fe \qquad (38)$$

and

$$2e^- + Ni(II) = Ni \qquad (39)$$

separately. It was indicated earlier that iron and nickel form a series of solid solutions with one another which will tend to lower the potential at

which Ni(II) will discharge on an iron electrode and vice versa. The discrepancy, therefore, probably lies in values of the electrode used theoretically to determine the values of equilibrium constant for reaction (36.)

Regardless of the reasons for the discrepancy in the theoretical value of the equilibrium constant for reaction (36) and that found experimentally, the data indicated that it was possible to remove in excess of 99 per cent of the nickel in an equimolar mixture of NaCl and KCl at 750°C in about one hour by equilibration with iron metal. The question still remained: How well would this process work when the iron powder used in the equilibration experiments was replaced by massive iron? Replacing the iron powder used in the equilibration experiments by more massive pieces was desirable because it would prove difficult to remove the precipitated nickel from the former.

In order to answer the question posed above short pieces of steel bar stock were mounted on a Monel rod and slowly revolved, to promote stirring, in a NaCl/KCl flux containing $FeCl_2$ and $NiCl_2$ derived from in situ chlorination of comminuted ferronickel. This comminution was done electrolytically, that is, a large

piece of ferronickel was made the anode, in a
NaCl/KCl melt, and by the passage of current through
the cell the iron and nickel were deposited on the
cathode as small crystals in which state the material
was easily chlorinated. Table 6 gives an indication
of the results that were obtained.

TABLE 6

The Effect of Time and Temperature on
the Oxidation of Iron by Divalent Nickel

T	Total Ni in Melt,g	Ni Recovered g	Percent Ni Recovered	Equilibration Time,hr.	Ni/Co[**] in Recovered Product
700°C	4.5[*]	3.65	81%	.5	--
700°C	2.97	2.82	95%	1.0	95.4
750°C	2.24	2.22	99%	1.0	132

[*] Ni was added as anhydrous $NiCl_2$.

[**] Ni/Co ratio in original ferronickel=92.

The precipitated nickel completely covered the
outside of the iron pieces and had a very porous
structure. It was black in color and apparently
composed of very small crystals. This precipitated
nickel could be removed easily and completely from
the underlying iron by one or two sharp blows.

Following this, the precipitate was crushed and leached with water. Data on the nickel/cobalt ratios was included to show that this procedure resulted in a slight improvement of this value. This was due to the reaction

$$Ni(II) + Co = Co(II) + Ni, \qquad (40)$$
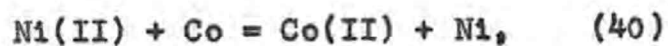
the cobalt having been precipitated by the reaction between $CoCl_2$ and iron.

IV. DISCUSSION OF RESULTS

As stated earlier the purpose of this research
was to show that nickel containing less than 20 p.p.m.
cobalt could be produced and to devise an industrially
attractive scheme for doing so. A scheme employing
electrochemical separation in a fused salt medium
has been demonstrated and the effect of various
parameters such as current density, impurities, etc.
has been shown. The separation scheme itself employs
a number of individual operations, and in order to
complete the proposed task it is necessary to unite
the separate processes into a feasible, unified
process. These operations and their inter-
relationship is shown in Figure XII.

In the process outlined in Figure XII there are
two major by-products whose recovery is desirable,
the chlorides of iron and cobalt. From an economic
standpoint the commercial feasibility of the process
outlined above may be entirely dependent upon, (1)
an inexpensive method of iron elimination from the
solvent salt, and (2) the ability to reclaim
by-product metals for which there may be a ready or
potential market. From a chemical standpoint both of
these metal chlorides, iron and cobalt, occur as
contaminants and thus their removal is essential if
the process is to accomplish its desired end.

FIGURE XII 70

Outline of the Separation Scheme

71
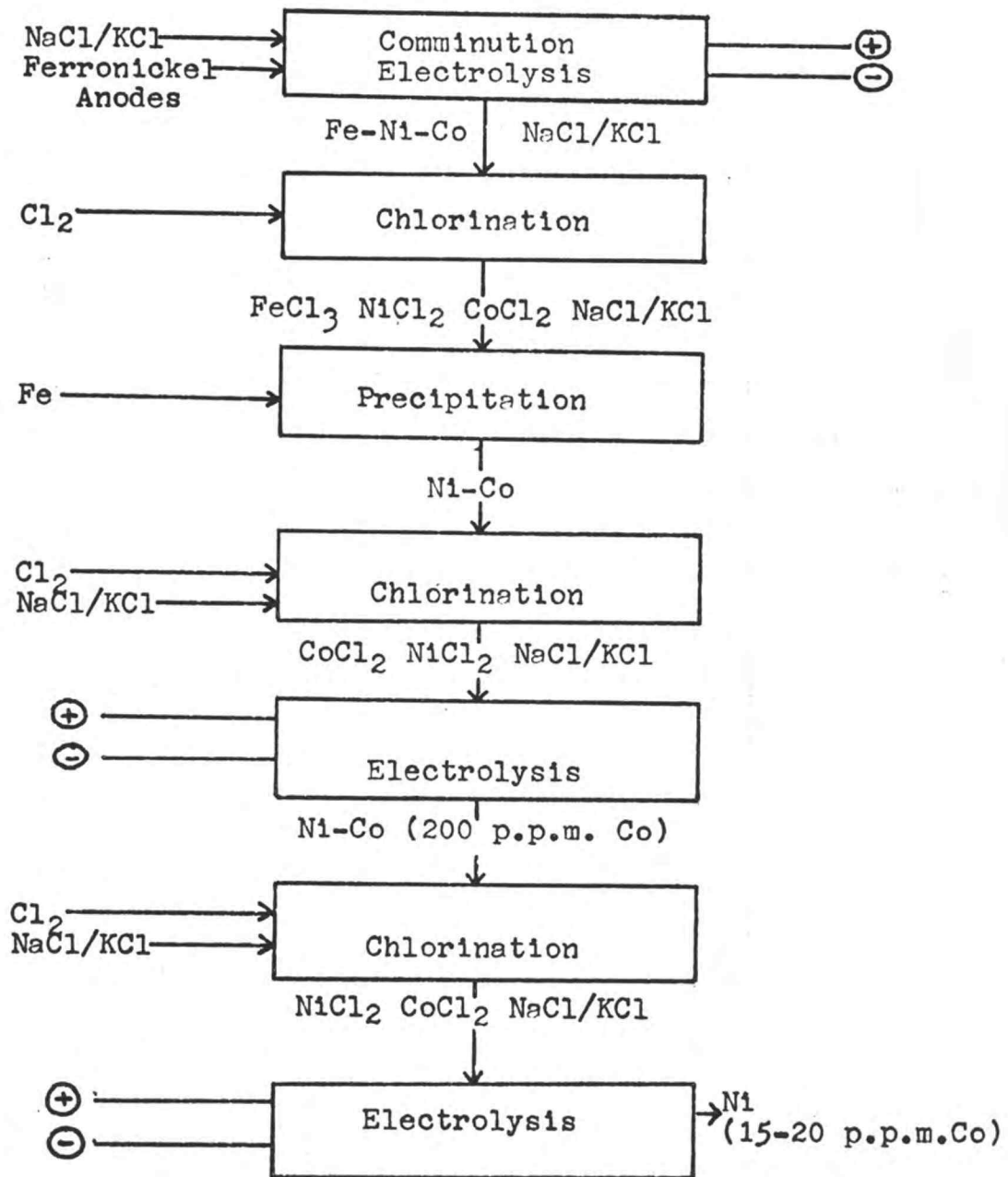
Iron, as the chloride, occurs in two of the operations shown in Figure XII, chlorination of the comminuted alloy and precipitation of Ni-Co by reaction (31.) The problem of iron removal from the melt has been briefly considered, where it was shown that removing iron, as $FeCl_3$, by blowing chlorine through the melt was not feasible. Due to the fact that neither nickel nor cobalt would be present in the melt, having been removed previous to these steps, it would be possible to use chemical means to remove the iron. Chemical methods which might be used are:

1. Blowing dry air into the melt to form Fe_3O_4 and Cl_2 and then decanting the oxide.
2. Blowing H_2S into the melt and decanting the FeS, HCl occurring as a by-product.
3. Adding Na_2S and decanting FeS.
4. Reducing with H_2 and decanting the iron powder, HCl occurring as a by-product.
5. Adding NaOH or Na_2Co_3 and decanting Fe_3O_4.
6. Electrolyzing.

Iron is used as a reagent and thus it is desirable to recover it as a metal so that it may be reused. Methods 4 and 6 are therefore to be preferred. Number 4 is the less attractive of the two because of the formation of HCl which, due to its corrosive action,

72

is very undesirable. On the other hand, electrolysis
is not an altogether satisfactory choice, in view of
the fact that iron can exist in two different valence
states which cause a drastic lowering of the current
efficiency by redox cycling. Studies were undertaken
to determine what degree of current efficiency might
be expected for the deposition of iron from a
NaCl/KCl melt at 750°C. In contrast to previous
practice the cathode was not protected by any
diaphragm. The results indicated that a current
efficiency of about 20-25 per cent was the best that
could be expected. This figure could probably be
improved to some degree by a different cell geometry
and by utilizing a barrier to prevent the anode
products from diffusing to and reacting with the
cathode product. This barrier might take the form of
refractory diaphragm or a nickel gauze screen.

There remained the problem of removing the cobalt
and nickel remaining after the final two electrolysis
operations (Figure XII.) In this case the best
solution seemed to be to continue the electrolysis,
with a new cathode, until these metals had been
completely removed. How could we know when this

process was completed without performing a series of
analyses of the melt? The answer to this question
was presented earlier during the discussion of
insoluble anode electrolysis. Here it was shown, in
equation (4) that at constant current as the concen-
tration of the electroactive cations-Co(II) and Ni(II)-
decreases, the potential of the cathode will increase.
This increase continues until a potential is reached
at which another reaction can take place; in this
case the reduction of the solvent cations sodium and
potassium. Thus the depletion of Co(II) and Ni(II)
from the melt, at constant current, would be signaled
by a rapid increase in the cell voltage. In the
present situation the cell voltage rose from a value
of approximately 1.5 volts for the deposition of
cobalt and nickel in NaCl/KCl at 750°C to about
3.2-3.4 volts when sodium and potassium began to
deposit. The cathode deposit, instead of being com-
posed of small shiny metallic needles, was then a
voluminous black mass in which no crystals were
apparent. When this deposit was placed in water it
produced a violent evolution of gas and the aqueous
solution was basic which indicated that the deposit

contained metallic sodium and potassium. The Table
below shows the amount of nickel and cobalt that
remained in the melt after the deposition of the
solvent cations had commenced.

TABLE 7

Percent of Original Nickel(II) and Cobalt(II)
Remaining in a NaCl/KCl Melt at the Inception
of Sodium Deposition at 700°C

Cathode Current Density (amp/cm^2)	% of Original Nickel Remaining in Melt	% of Original Cobalt Remaining in Melt*
1.5×10^{-2}	0.2	0.59%
1.5×10^{-2}	0.55	0.65%
3.0×10^{-2}	1.2	0.92%

* This figure represents the maximum concentration
of cobalt that could be present in the melt. In
all cases the amount actually present was below
the detection limit of the analytical method and
thus the minimum concentration of cobalt that could
be detected was taken as that present.

From these results it was seen that the amount of
cobalt and nickel remaining in the melt at the point
at which the solvent cations began to deposit was less

than 1 per cent of that originally present. The
results of Table 7 also showed the effect of current
density upon the amount of residual nickel and cobalt.
This was in keeping with expectations; the larger the
value of the cathode current density the more nickel
and cobalt left in the melt when their limiting
current densities were exceeded. It appeared possible,
therefore, to render a melt reusable by the simple
expedient of continuing the electrolysis after the
product had been removed, until alkali metal began
to be deposited; a point which was signaled by an
abrupt increase in the cell potential.

It would be desirable to simplify the process
outlined in Figure XII by combining some of the
individual steps into one operation. The most likely
would be a combination of the first three steps,
comminution electrolysis, chlorination, and precipi-
tation of Ni-Co, into one operation. The process
envisioned was one in which the comminution
electrolysis and the precipitation of Ni-Co took
place in the same melt and at the same time, thereby
doing away with the necessity for a separate
chlorination step. This scheme involved interposing

an iron screen between the ferronickel anode and the
graphite cathode; as the Ni(II) migrated from the anode
to the cathode it would come into contact with the
iron screen. When this happened reaction (36)

$$Ni(II) + Fe = Ni + Fe(II)$$

would take place, plating nickel out upon the surface
of the iron plate. The Fe(II) produced by this
reaction would then travel to the cathode to be
deposited.

In order to test the proposed scheme a large scale
electrolysis cell, holding about 3 kg. of salt, was
constructed. The reason for constructing a larger cell
was that the proposed experiments could be more easily
conducted on this scale. A piece of ferronickel bar
stock served as the anode and the cathode was a
graphite plate. Using this apparatus a number of
different screen designs and various cell geometries
were tried. However, in all cases this scheme failed
to accomplish its desired result, the production of
iron-free nickel. Table 8 presents a compilation of
the results along with some pertinent experimental
details.

TABLE 8

The Extent of the Separation of Iron and Nickel
from an Anode Containing 52 per cent Iron

% Fe in Screen Deposit	% Fe in Cathode Deposit	Form of Metal Screen and Cell Geometry
34.9%	----	perforated cylinder completely surrounding anode
47.7%	58.1	perforated plate between anode and cathode
34.6%	67.5%	perforated plate between anode and cathode, perforations larger than above
53.1%	52.2%	Solid plate behind anode. Melt stirred vigorously

It appeared from the results presented in Table 8
that iron was deposited along with nickel on the
metal screen. Since it was postulated that deposition
on this screen would occur only by means of reaction
(36) this behavior was rather puzzling. The only
reasonable explanation seemed to be that because of the
ability of the screen to act as a conductor of
electricity a voltage drop existed between it and the
anode, in other words, the screen behaved as a cathode.
This supposition was confirmed by placing a high
impedance voltmeter between the screen and the anode.

Approximately 50-75 per cent of the total cell voltage appeared between the anode and the screen, depending upon, among other things, the length of time the electrolysis had been carried out.

Examination of Table 8 also revealed the fact that the less resistance the screen offered to ionic conduction the less it acted as a cathode. This was shown by the smaller percentage of iron which appeared in the screen deposit. Apparently the increased resistance to migration of the current-carrying ions offered by certain screen designs or by the filling of perforations in the screen by deposited metallic crystals tended to enhance the cathodic nature of the screen.

Undoubtedly it would be possible, by proper design of the iron screen and by a careful adjustment of its potential, to cause it to perform its intended function of complete separation of iron and nickel. However, this would, in all probability, be extremely difficult in practice and thus did not warrant any further study.

V. CONCLUSION

Based on the experimental results and discussion given earlier, a scheme is presented in Figure XIII for the preparation of cobalt-free nickel.
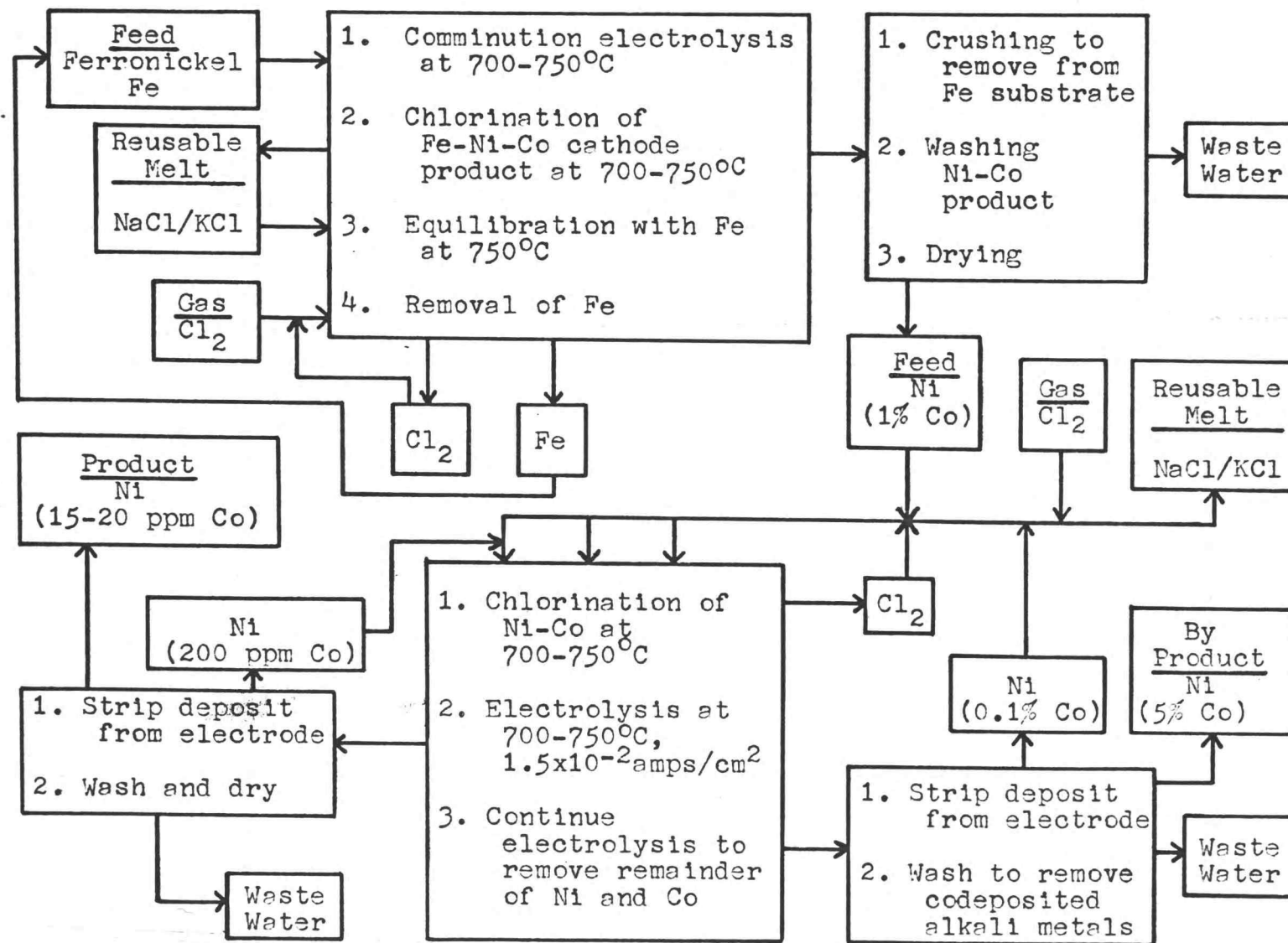
FIGURE XIII

Outline of the Nickel-Cobalt Separation Scheme

The process shown in Figure XIII is composed of three main operations, namely: separation of nickel and cobalt from the bulk of the iron via chlorination of the comminuted starting material and equilibration with iron metal, a primary electrolysis to separate nickel from most of the cobalt, and finally, a second electrolysis to yield the nickel product. Coincidental with these three main steps are auxiliary operations such as chlorination, washing the deposit to remove occluded salt, and electrolyses designed to make melts reusable by removing contaminants and to produce consumed reagents such as iron.

The first operation, separation of nickel and cobalt from the large quantity of iron present in the ferronickel starting material consists of the following steps:

1. Comminution, by electrolysis, of the Fe-Co-Ni alloy cathode to make it suitable for chlorination.

2. Chlorination of the cathode product in situ to give $FeCl_2$, $CoCl_2$, and $NiCl_2$ in NaCl/KCl.

3. Equilibration of this system with iron
   metal to precipitate nickel and cobalt,
   via equation (31,) on an iron substrate
   and a melt which is composed of NaCl/KCl
   and $FeCl_2$.

4. A scavanging step to render the melt
   reusable and to recover the iron reagent
   by either chemical or electrochemical means.

The iron substrate with the precipitated nickel
and cobalt is subjected to a crushing operation that
serves to remove the precipitated metal which is
then washed free of any occluded salt.

A preliminary separation of nickel and cobalt
is the second major operation. It involves the
following steps:

1. The nickel-cobalt product from the first
   operation is chlorinated at about $700^{o}C$
   in a NaCl/KCl melt. During the chlorination
   it is advantageous to stir the melt.

2. An electrolysis of the $NiCl_2$, $CoCl_2$, NaCl/KCl
   system at a cathode current density of
   $\sim 1.5 \times 10^{-2}$amps/cm^2 and removal of about
   80 per cent of the nickel which now
   contains $\sim$ 200 p.p.m. cobalt.

3. The deposit is stripped from the electrode
   and washed to remove any occluded salts
   preparatory to the third major operation.

4. In order to recover the remaining 20 per
   cent of the nickel and cobalt and also
   to render the melt reusable the melt is
   subjected to further electrolysis until
   alkali metal begins to be deposited.

The third operation, the final purification
electrolysis, involves the same steps as above. In
this the nickel product contains 15-20 p.p.m. cobalt.

As outlined above, the process has the following
assets:

1. A minimum waste problem. The only
   significant waste is wash water and
   this would not need to be processed
   since it contains no valuable products
   or reagents.

2. Low cost of reagents. The reagents are
   either a by-product of various electrolytic
   steps, e.g. chlorine, or can easily be
   recovered. Only water is expended. It

is necessary to add additional NaCl and
KCl to make up losses due to volatilization
and washing; however, this is only a
minor expense.

3. The technology and equipment involved
in this process are all familiar to
the electrochemical and metallurgical
industries.

For all the positive features this process
offers it has some disadvantages; these are discussed
below and possible solutions are given and might act
as guidelines for further research.

Chief among the disadvantages is the necessity
for operating at a low cathode current density, a
problem briefly touched upon earlier. This require-
ment not only necessitates the use of auxiliary
heating equipment to maintain the cell at its proper
operating temperature - 700°C - but also prolongs the
electrolysis time with a resultant increase in the
cost per unit of product. Associated with this and
certainly a disadvantage is the requirement that only
80-85 per cent of the nickel present in the melt
may be recovered before the cathode potential becomes

cathodic enough to cause the codeposition of cobalt.
While this latter problem does not represent a
direct loss, since the 15-20 per cent of the nickel
which is left may be easily recovered, it means a
smaller return than might otherwise be realized.

It may be possible to overcome these
difficulties to some extent by controlling the cathode
potential at some fixed value relative to a reference
electrode. In this way cobalt would be prevented
from codepositing with nickel. This approach would,
however, require considerable research to determine
not only its feasibility but also whether it
represented a distinct advantage over the present
constant current method.

Additional research expended on a method of
simultaneously comminuting the ferronickel alloy and
removing the nickel, as was attempted briefly by the
use of an iron screen, might repay the effort since
it would eliminate at least one operation.

In order to get current efficiencies of 70 per
cent it was necessary to include a refractory
diaphragm in the cell design to avoid contact of the
cathode with chlorine. At present such diaphragms

cannot be used on a large scale; therefore, unless a satisfactory substitute could be found, a nickel gauze diaphragm perhaps, an undesirable decrease in current efficiency would result.

A large-scale demonstration of the process would be useful not only to show its commercial feasibility but also to establish costs and to point out areas where further research should be done.

A scheme, which is felt to be industrially feasible, has been successfully demonstrated on a laboratory scale for the production of nickel containing at most 20 ppm cobalt starting from a commercially available ferronickel alloy. This scheme utilizes electrolysis in a fused salt medium as the means of effecting the separation. In addition to developing a scheme for the separation of iron, nickel and cobalt the possibilities that the use of fused salts can open to the fields of chemistry and metallurgy have been explored.

BIBLIOGRAPHY

1. American Society for Testing Materials.
   A.S.T.M. Methods of chemical analysis of
   metals. 1950. 476 p.

2. Audrieth, L. F. and H. W. Wilson.
   Electrodeposition of metals from non-aqueous
   solvents. Chemical Reviews 8:335-351. 1931.

3. Bander, R. B. Bibliography on extractive
   metallurgy of nickel and cobalt January 1929-
   July 1955. 1957. 159 p. (U. S. Bureau of
   Mines. Information Circular 7805.)

4. Benoit, Robert L. et. al. Separation of Nickel
   from cobalt. U. S. Patent 2,822,262.
   Feb. 4, 1958.

5. Benz, R. and R. M. Douglas. Some observations
   on plutonium (IV)-alkali double chlorides.
   Journal of Inorganic and Nuclear Chemistry
   23:134-136. 1962.

6. Bloom, H. and B. J. Welch. Molten salt mixture.
   Part 5. Activity determinations from
   vapor-pressure measurements in molten salt
   systems. Transactions of the Faraday Society
   57:61-68. 1961.

7. Bockris, J. O'M ed., Modern aspects of
   electrochemistry. London, Butterworth

8. Bockris, O'M, et. al. An all glass reference
   electrode. Journal of Scientific Instruments,
   33, 438 (1956)

9. Boston, G. P. and G. P. Smith. Visible and
   ultra-violet absorption spectra of $NiCl_2$
   dissolved in fused LiCl-KCl mixture. Journal
   of Physical Chemistry 62:409-414. 1955.

10. Brick, R. M. and Arthur Phillips. Structure
    and properties of alloys. 2nd ed. New York,
    McGraw-Hill, 1949. 485 p.

11. Caron, M. H. Separation of nickel and cobalt.
    Transactions of the American Institute of
    Mining Engineers 188:91-103. 1950.

12. Charlot, G., J. Badoz-Lambling and B. Tremillion.
    Electrochemical reactions. Elsevier Publishing
    Co., New York, 1962. 376 p.

13. Chauvin, G., H. Coriou and J. Hure.
    Electroraffinage de certains métaux nucléaires
    en bain de sels foudus. Métaux, Corrosion,
    Industries 37(439):112-126. 1962.

14. Clasing, M. and F. Sauerwald. Concerning the
    production of the heavy metals by molten
    electrolysis. Zeitschrift für elektrochemic
    54:358-361. 1950.

15. Coleman, E. E. and D. N. Vedensky. Production
    of ferronickel at Riddle, Oregon. Paper read
    before the meeting of the American Institute
    of Mining, Metallurgical and Petroleum
    Engineers, New York, Feb. 15-18, 1960.

16. Coriou, Dirian, and Hure. Une electrode de
    reference utilisable dans des bains fondus de
    fluorures. Journal of Chemical Physics 52, 479.
    1955.

17. Corbett, J. D. et al. Metal and metal-halide
    systems for lanthanum, cerium and praseodymium
    iodides. Discussions of the Faraday Society
    32:79. 1962.

18. Cubiciotti, D. Solutions of metals in fused
    salts. Transactions of the American Institute
    of Mining Engineers 197:1106-1108. 1953.

19. Delahay, P. New instrumental methods in
    electrochemistry. 1st ed. New York, Interscience,
    1954. 437 p.

20. Delimarskii, Yu. K. Electrode potentials of metals in molten salts. Zhur. Fiz. Khim. 29(1), 28(1955) AEC-tr-2217.

21. Delimarskii, Yu. K. Electrochemical series of metals in molten salts. Ukr. Khim. Zhur. 16, 414(1950). AEC-tr-1969.

22. Delimarskii, Yu. K. On the effect of the anion on electrode potentials of metals in fused salts. Ukrainian Journal of Chemistry 21:449-456. 1958.

23. Delimarskii and Kolotti. The reversible glass-tin-sodium reference electrode in fused salts. Ukr. Khim. Zhur. 16, 438(1950). AEC-tr-2475.

24. Delimarskii, Yu. K. and B. F. Markov. Electrochemistry of fused salts. Washington D.C. Sigma Press, 1961. 338 p.

25. Desch, C. N. Preparation of pure metals. Vortrage Hauptversammlungen. Deutsche Gesellschaft Metallkunke. Pp. 1-5. 1938.

26. Fink, C. G. and F. A. Rohrman. The preparation of pure electrolytic nickel. Transactions of the American Electrochemical Society 59:359-369. 1931.

27. Flengas and Ingraham. Voltaic cells in fused salts. Canadian Journal of Chemistry
35, 1139. 1957.
35, 1254. 1957.
36, 780. 1958.
36, 1103. 1958.
36, 1662. 1958.

28. Flengas, S. N. and T. R. Ingraham. Electromotive force series of metals in fused salts and activities of metal chlorides in 1:1 molar KCl-NaCl solutions. Journal of the Electrochemical Society 106:714-721. 1959.

29. Freeman, M. L. Electrolytic production of zirconium in a fused salt voltaic cell. Journal of Electrochemical Society 107:934-936. 1960.

30. Friedlander, Gerhart and Joseph W. Kennedy. Nuclear and radiochemistry. New York, John Wiley & Sons, 1956. 449 p.

31. Garfinkel, H. M. and F. R. Duke. Complexions in fused salts. Effect of solvent cation. Journal of Physical Chemistry 65:1629-31. 1961.

32. Gerischer, H. Mechanism of electrolytic deposition and dissolution of metals. Analytical Chemistry 31:33-39. 1959.

33. Glasstone, Samuel. The electrochemistry of solutions. London, Methuen & Co. Ltd., 1930. 405 p.

34. Glasstone, Samuel and K. J. Laidler and H. Eyring. The theory of rate processes. 1st ed., New York, McGraw-Hill, 1941. 611 p.

35. Gruen, Dieter M. and Robert L. McBeth. Tetrahedral $NiCl_4^=$ ion in crystals and in fused salts. Spectrophotometric study of chloro complexes of nickel (II) in fused salts. Journal of Physical Chemistry 63:393-397. 1960.

36. Gruen, Dieter et al. The chemistry of fused salts. In: Proceedings of the 2nd U. N. International Conference on the Peaceful Uses of Atomic Energy, Basic chemistry in atomic energy. P. 112-124. (Paper 940) Geneva, 1958. Vol. 28.

37. Gruen, Dieter et al. Oxidation states of the elements and their potentials in fused-salt solutions: The Actinide Elements. Annals of the New York Academy of Science 79:941-949. 1960.

38. Hamby, Drannan. Electrode potentials of nickel and cobalt in a fused electrolyte. Master's thesis. Corvallis, Oregon State College 1961. 56 numb. leaves.

39. Hamer, Walter J. and Marjorie S. Malmber and Bernard Rubin. Theoretical electromotive forces for cells containing a single or solid or molten chloride electrolyte. Journal of the Electrochemical Society 103:8-16. 1956.

40. Hansel, Gunther. Electrolytic processes for the preparation of pure metal from ore and crude metal. Elektrochemische Zeitschrift 64:579-584. 1943.

41. Hyman, M. B. and A. Ya. Shinyayev. An investigation of the diffusion of iron in iron-nickel alloys. Doklady Adakemii Nauk S.S.S.R. 102:969. 1955.

42. Inman, D. and J. O'm. Bockris. The reversible electrode potential of the system U/UCl_3 in molten chloride solvents. Canadian Journal of Chemistry 39:1161-1163. 1961.

43. Johnson, J. W. and M. A. Bredig. Miscibility of metals with salts in the molten state. Journal of Physical Chemistry 62:604-607. 1958.

44. Johnson, R. E. Thorium fused salt electro-deposition into a molten zinc cathode. 1962. 10 p. (U. S. Atomic Energy Commission NAA-SR-6802)

45. Kellogg, H. H. Thermodynamic relationship in chlorine metallurgy. Transactions of the American Institute of Mining Engineers 188:863-872. 1950.

46. Kocheigin, V. P. et al. Solution of iron in fused chlorides of alkali and alkaline earth metals. Journal of Applied Chemistry, U.S.S.R. 27:188. 1954.

47. Kocheigin, V. P. and G. I. Stolyarova. The solution of iron in fused mixtures of the chlorides of lithium and potassium and sodium and potassium. Journal of Applied Chemistry, U.S.S.R. 28:18-21. 1955.

48. Kolthoff, I. M. and J. J. Lingane. Polarography. New York, Interscience, 1941. 510 p.

49. Kolthoff, I. M. and J. I. Watters. Polarographic determination of cobalt as trioxalatocobaltate (III.) Analytical Chemistry 22:1422-1426. 1950.

50. Kraus, C. A. Electrolytes: from dilute solution to fused salts. Journal of Physical Chemistry 58:673-683. 1954.

51. Kraus, K. A. and G. E. Moore. Adsorption of iron by anion exchange resins from HCl solutions. Journal of the American Chemical Society 72:5792-3. Anion exchange studies. I. Separation of zirconium, etc.; IV. Cobalt & nickel, etc.; V. Adsorption of HCl; Journal of the American Chemical Society 73:9-13. 1951; 74:843-844. 1952; 75:1457-1460. 1953.

52. Kroll, W. J. Chlorine metallurgy. Metal Industry 81:243-245, 252;269-271, 284-286, 307-311, 325-326, 341-343, 365-368. 1952.

53. Kroll, W. J. Fused salt electrolysis for the production of metal powders. Transactions of the American Electrochemical Society 87:551-569. 1945.

54. Kroll, W. J. Private communications.

55. Kubaschewski, O. and E. L. Evans. Metal thermochemistry. New York, John Wiley & Sons, 1956. 409 p.

56. Labrie and Lamb. A porcelain reference electrode conductive to sodium ions for use in molten salt systems. Journal of Electrochemical Society 106:895. 1959.

57. Laitinen, H. A. and Liu. An electromotive force series in molten LiCl-KCl eutectic. Journal of the American Chemical Society 80:1015. 1958.

58. Laitinen, H. A. and Pankey. Halogen, iron, and vanadium potentials in LiCl-KCl eutectic. Journal of the American Chemical Society 81:1053. 1959.

59. Laity, R. W. Electrochemistry of fused salts. Journal of Chemical Education 39:67-73. 1962.

60. Lane, J. R. Is cobalt harmful in stainless steel? Metal Progress, December 1957. P. 86-87.

61. Latimer, Wendell M. Oxidation potentials. 2nd ed. Englewood Cliffs, N. J., Prentice Hall, 1956. 392 p.

62. Levy, H. A., et al. X-ray and neutron diffraction studies of molten alkali halides. Annals of the New York Academy of Science 79:762-780. 1960.

63. Lingane, J. J. Electroanalytical chemistry. 2nd ed. Interscience, New York, 1959. 669 p.

64. Littlewood, R. W. and E. J. Argent. The effect of aqueous contamnants on the redox potential of chloride melts. Electrochimica Acta 4:114-128. 1961.

65. Mantell, C. L. Electrochemical engineering. 4th ed. New York, McGraw-Hill, 1960. 680 p.

66. Markov, B. F., J. K. Delimarsky and I. D. Panchenko. Thermodynamic properties of some fused chlorides. Journal of Polymer Science 31:263-268. 1958.

67. Meister, G. and W. C. Lilliendahl. Preparation of uranium metal by fused salt electrolysis. American Institute of Mining Engineers, Transactions 209:1445-1447. 1957.

68. Meites, Louis. Polarographic techniques. New York, Interscience, 1955. 317 p.

69. Menzies, I. A. et al. The mechanism of the electrodeposition of Ti. Journal of Electroanalytical Chemistry 1:161-170. 1959.

70. Milner, G. W. C. The principle and applications of polarography and other electroanalytical processes. New York, Longmans, Green, 1957. 728 p.

71. Morrey, J. R. and R. L. Moore. Thermodynamic evidence for complex formation by actinide elements in fused KCl-AlCl$_3$ solvents. 1961. 20 p. (U. S. Atomic Energy Commission HW-SA-2597)

72. Nies, N. P. Preparation of bismuth by fused salt electrolysis. Journal of the Electro-chemical Society 107:817-820. 1960.

73. Potter, E. C. Electrochemistry, principles and applications. London, Cleaver-Hume Press, 1956. 418 p.

74. Proceedings of the 7th International Committee on Electrochemistry, Thermodynamics in Kinetics, 1957. 409 p. Electrochemical behavior of nickel. London, Butterworth Scientific Publications.

75. Queneau, Paul, ed. Extractive metallurgy of copper, nickel and cobalt. Metallurgical Society of the American Institute of Mining Engineers. New York, Interscience, 1960. 647 p.

76. Queneau, Paul and J. E. Magner. Extractive metallurgy of copper, nickel and cobalt. New York, Interscience, 1960.

77. Remy, H. Treatise on inorganic chemistry. Armsterdam, New York, Elsevier Pub. Co., 1956. 2 vol.

78. Richardson, F. D. and C. W. Dannatt. Extraction metallurgy. Metal Industry 83:63-66. 1953.

79. Rotinan, A. L. Experience in production of electrolytic nickel. Tsvetnye Metally 31(7):23-30. 1958.

80. Sandell, R. B. Colorimetric determinations of traces of metals. 2d ed. New York, Interscience, 1950. 673 p.

81. Sandell, R. B. Colorimetric metal analysis. 2d ed. New York, Interscience, 1950. 673 p.

82. Senderoff, Seymour and Abner Brenner. The electrolytic preparation of molybdenum from fused salts. I. Electrolytic studies. Journal of the Electrochemical Society 101:16. 1954.

83. Smirnov, M. V. and N. Ya. Chukreev. The anodic dissolution of metals in molten salts. Zhur. Fiz. Khim. 32:2165-2173. 1958.

84. Smirnov, M. V. and L. E. Ivanovskii. Cathodic processes in the deposition of be from molten electrolytes. Zhurnal Fizicheskoi Khimii 32:2174-2182. 1958.

85. Soine, Tyler Sylvester. Utilization of potassium cyanide as a spectrophotometric reagent, with particular attention to the determination of nickel. Master's thesis. Corvallis, Oregon State College, 1957. 62 numb. leaves.

86. Stern, Kurt H. Electrode potentials in fused systems. Journal of Physical Chemistry 60:679. 1956; 60:1443. 1956; 62:385. 1958; 63:741. 1959.

87. Straumanis, M. E. and A. W. Schlechten. Electrochemical behavior of Ti-fused salt-platinum cell. Journal of the Electrochemical Society 102:131-136. 1955.

88. Suskii, L. The mechanism of the cathode process in the electrolysis of a fused $NaCl-CaCl_2$ mixture on an iron cathode. Zhurnal Fizicheskoi Khimii 32:1785-1795. 1958.

89. Suskii, L. Studies of the cathodic process during electrolysis of the pure molten chlorides of Ca, Na, and K. Zhurnal Fizicheskoi Khimii 32:1393-1403. 1958.

90. van Arkel, A. E. Reine Metalle. Berlin. Julius Springer, 1939. 574 p.

91. van Artsdalen, E. R. and I. S. Yaffe. Electrical conductance and density of molten salt systems. Journal of Physical Chemistry 59:118-127. 1955.

95

92. Wartenberg, H. Anode effect in the case of
    molten electrolysis. Zhurnal Fizicheskoi
    Khimii 32:330-336. 1926; 41:448-450. 1935.

93. Wesley, W. A. Preparation of pure nickel by
    electrolysis of chloride solutions. Journal of
    the Electrochemical Society 103:296-301. 1956.

94. Willard, H. H., L. L. Merritt and J. A. Dean.
    Instrumental methods of analysis. Princeton,
    New Jersey, Van Nostrand, 1958. 3rd ed. 626 p.

95. Yang and Hudson. Some investigations on the
    Ag/AgCl in LiCl-KCl eutectic reference
    electrode. Journal of Electrochemical Society
    106:986. 1959.

96. Yang, L. and R. G. Hudson. Equilibrium
    electrode potentials of some metal chlorine
    galvanic cells and activities of some metal
    chlorides in LiCl-KCl eutectic melts.
    Transactions of the Metallurgical society
    of the American Institute of Mining Engineers,
    215:589-598. 1959.

97. Young, R. S., E. T. Pinkney and R. Dick.
    Colorimetric determination of cobalt in
    metallurgical products with nitroso salt.
    Industry and Engineering Chemistry 18:474-476.
    1946.