Separation of Nickel from Technetium

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Kentucky Research Consortium for Energy and Environment
233 Mining and Minerals Building
University of Kentucky, Lexington, KY 40506-0107

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By
Louei El-Azzami, Ph.D. Research Assistant
Dr. Eric Grulke, Professor
Chemical & Materials Engineering Department
University of Kentucky
Lexington, KY 40506-050

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I) Introduction

The recovery of nickel (Ni) from Department of Energy (DOE) gaseous diffusion plant barriers contaminated with radionuclides and specifically, the separation of from Ni from technetium-99 (^{99}Tc), has proven to be difficult. Manufacturing Sciences Corporation (MSC) could not remove ^{99}Tc from volumetrically contaminated Ni utilizing electro-refining approaches to levels that would allow the free release of Ni for commercial and industrial uses. The various methods applied by Manufacturing Sciences Corporation (MSC) are reported in the attached Appendices. The electro-refining methods employed by MSC resulted in Ni containing residual ^{99}Tc. Residual ^{99}Tc in Ni purified by MSC's electro-refining methods resulted in a moratorium being issued by the Secretary of DOE and congressional opposition to the release of Ni from the K-25 plant at Oak Ridge. The present proposal employs an approach that does not rely on electro-refining for the separation of ^{99}Tc from volumetrically contaminated gaseous diffusion plant Ni barriers.

A major obstacle to the free release of surface or volumetrically radioactive contaminated scrap metal originating in radiation impacted areas within the DOE Complex is the scrap metal industry's position of "zero tolerance." The scrap metal industry produces metals that are used in industrial and consumer products. The scrap metal industry position is that the release of scrap metal from radiation impacted areas at DOE facilities into the industry's recycled scrap metal flow path would have both short and long-term negative impacts. It fears the rejection of its products by customers and the contamination of its processing systems. The scrap metal industry supported the decision by the Secretary of DOE to impose a moratorium on the release of volumetrically contaminated metal. This moratorium halted the release of MSC electro-refined Ni, volumetrically contaminated with residual ^{99}Tc, from the K-25 Oak Ridge, TN facility.

The Nuclear Regulatory Commission (NRC) continues to evaluate national standards for the potential release of materials from radiation impacted facilities. The release of DOE scrap metal from radiation-impacted areas, including radiation impact areas at DOE facilities, would be required to meet standards established by NRC and Agreement States. DOE's moratorium on the release of volumetrically contaminated metals remains in place until the NRC and Agreement States establish national standards for the release of radiation-impacted materials. Furthermore, DOE suspended the unrestricted release for recycling of scrap metal from radiological areas within DOE facilities and the suspension will remain in effect until DOE develops release criteria and established release criteria through DOE Order 5400.5.

DOE indicated in its April 2002 draft Guide "DOE G 441.1-XX, CONTROL AND RELEASE OF PROPERTY WITH RESIDUAL RADIOACTIVE MATERIAL for use with DOE 5400.5, *Radiation Protection of the Public and the Environment",* that the DOE's principle requirements for the release of scrap metal from radiation impacted areas are intended to meet the following goals:
  • Property is evaluated, radiologically characterized, and, where appropriate, decontaminated before release.

• The level of residual radioactive material in property to be released is as near background levels as is reasonably practicable, as determined through DOE ALARA process requirements, and meets DOE authorized limits.
• All property releases are appropriately certified, verified, documented, and reported; public involvement and notification needs are addressed; and processes are in place to appropriately maintain records.

Thus prior to release of both surface and volumetrically radiation contaminated scrap metal from DOE and other licensed radiation impact facilities, a number of important concerns must be overcome to ensure the released material will not have a negative impact on both public health and the public perception of the scrap metal industry's use of the material in commercial and industrial products.

II) Problem Statement

The decontamination and radiation decommissioning of the gaseous diffusion process at the Paducah Gaseous Diffusion Plant, in Paducah Kentucky, has generated and will generate vast quantities of nickel and other metals volumetrically contaminated with radioactive materials. The estimated amount of contaminated nickel could reach 44,794 tons (1). The most frequently identified contaminant in the nickel is technetium-99 (99Tc). However, traces of neptunium (Np), plutonium (Pu), protactinium (Pa), thorium (Th), and uranium (U) have also been identified in the nickel.

There is interest in recovering the nickel and recycling it to the industrial sector. However, as indicated above, there are many regulatory issues associated with any use of such material outside of the nuclear industry. The main problem in decontaminating this nickel is an ultrahigh efficiency separation method necessary to separate technetium and nickel. The other radioactive materials can be separated via electrolysis processes. However, the best available electrolysis process still leaves ~ 1 Becquerel of technetium activity per gram for starting materials of 320 Becquerels: this separation does not meet the required release criteria for radioactive materials. This project will explore a new alternative separation method based on the large differences between the vapor pressures of nickel and technetium.

B) Our Solution

This project will develop and demonstrate a technically effective and cost-efficient process using physical vapor deposition to recover pure nickel with no detectable traces of technetium. The slag left behind will be composed of technetium with small levels of nickel. The physical vapor deposition consists of two steps: 1) nickel is preferentially evaporated from solid or liquid solutions of Ni/Tc, and 2) the nickel vapor is deposited on cold surfaces to produce Tc-free nickel plates.

A physical vapor deposition process can be designed only after the fundamental data on the vapor-liquid-solid-solid phase equilibria of the metal mixtures in question are collected. A unique GC/MS system designed for metal vapor evaluation will be

constructed to obtain the needed data. Similar systems were constructed at Lawrence Livermore Lab (1969) and Los Alamos (1983). Bert Lynn of the University of Kentucky (UK) is an expert on GC/MS and a skilled instrument designer. Mr. Lynn will collaborate on design, construction and commissioning of the new GC/MS.

New data obtained with the proposed GC/MS will redefine the phase diagrams for Ni-^{99}Tc and other metallic mixtures and will permit thermodynamic phase equilibria models to be developed and applied to the process design. Data to be obtained includes vapor pressures, heats of vaporization, heats of sublimation, activity coefficients, and separation factors for the Ni-^{99}Tc pair at different temperatures.   The data will be incorporated into phase diagrams that will account for the vapor phases of the constituents. This will revolutionize the ability of material and chemical engineers to determine the feasibility of separation.

The proposed research will investigate the physio-chemical system of Ni-^{99}Tc. Presently, there are no phase diagrams that relate metal vapor compositions to the metallic liquid-solid system.   The proposed research approach will provide data for a relatively unexplored area of metal separation. The proposed research has applications for many non-radioactive systems such as scrap metal recycling and alloy purification. This project will deal with the recovery of nickel from nickel ingots volumetrically contaminated with technetium. Proposals are being prepared for other funding sources to study other metallic systems.

The nickel-rhenium system has been chosen to be a surrogate model system for this method of separation to verify the analytical and physical vapor separation technologies. This system was chosen because rhenium and technetium are in the same chemical group. Rhenium is not radioactive, so one would be able to generate great amount of data to validate the feasibility of the separation without the need for a costly health physics program.

C) Criteria Release of the US and other countries

Tc-99 is a β-emitting radionuclide with maximum beta energy of 297 keV and a half-life of 2.1×10^5 years. Volumetrically contaminated Ni may have a Tc activity of up to about 5000 Bq/g or more, which is at least an order of magnitude above the maximum international release criteria of 74 Bq/g metal total activities. Certain countries have specified lower criteria of 1.0 Bq/g or less total activity. As indicated in the introduction, the U.S. regulatory agencies and federal government would not release scrap metals with any radioactivity detection to the public.

D) Other markets for this technology

The scrap metal industry is a secondary metal industry.   The dismantling and the decommissioning of nuclear facilities along with scrap metal inventories at Department of Energy (DOE) sites would supply the scrap metal industry with millions of tons of metals.   This requires the decontamination of the scrap metals before release to public

use.   The principal administrative authorities responsible for controlling the release of scrap metal from nuclear facilities are the DOE, the Nuclear Commission Regulatory (NCR), Department of Defense (DOD), and Agreement States (1).   These authorities have a jurisdictional authority over 30,000 structures, of which 8,000 are contaminated (1).   The DOE has an estimate of 149,665 tons of contaminated metals in its existing inventory (1).   This inventory consists of carbon steel (119,232 t), Ni (10,699 t), stainless steel (7,462 t), aluminum (Al) (2,353 t), copper (Cu) /brass (1,975 t), and 7,943 tons of other metals (1).

The decommissioning of DOE gaseous diffusion plant facilities commenced with the K-25 plant (1998-2006).   The proposed schedule for decommissioning of the following DOE facilities are the Portsmouth plant (2007-2015), then the Paducah plant (2015-2023), and finally the rest of the plants (2023-2058) (1). The existing and future contaminated scrap metal at DOE facilities will total to 1,068,022 tons (1).   This inventory consists of carbon steel (903,897 t), Cu/brass (53,990 t), Ni (44,818 t), stainless steel (26,960 t), Al (36,070 t), lead (Pb) (291 t), monel (83 t), and 1,913 tons of other metals (1).

E) Prior and present processes

The prior and present processes for removal of Tc from volumetrically contaminated Ni have not been effective for removal of all the residual Tc. The presence of residual Tc in processed Ni metal from K-25 gaseous diffusion plant Ni barriers in Oak Ridge prevented the release of the reprocessed Ni. Such processes include ion exchange, solvent extraction, melt refining, inductoslag refining, and electrolysis. There have been different processes for the recovery of Ni. Ni is selectively stripped by an organic oxime from an acidic solution of Ni & Cu and then Ni electrowinning (2). Another process is the removal of Ni by liquid-liquid extraction (3,4). Muller, et al. extracted Ni from aqueous solutions that contained large amounts of alkali metal ions by contacting the solution with an organic solution of di-2-ethylhexyl phosphoric acid and naphthenic acid (3). Fujimoto et al. used organic mixtures of 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester and/or 3,5,5-timethylhexyl phosphoric acid mono-3,5,5-timethylhexyl ester and/or isodecyl phosphoric acid monoisodecyl ester to separate cobalt (Co) from Ni (4). It is known that metallic Ni, contaminated with fission products, could be decontaminated to remove any actinides present by direct electrorefining based on the differences in reduction potential along the electromotive force (emf) series. Actinide removal is favored by two phenomena during electrorefining. Actinides have a significantly higher reduction potential relative to nickel and they are normally won from molten salt electrolyte rather than from aqueous electrolyte (see U.S. Pat. Nos. 3,928,153 and 3,891,741) (5).

Electrorefining and electrowinning of Ni decontaminated streams have been utilized but these processes encountered problems with the co-deposition of the Tc and Ni on the cathodic cell. This problem was solved by converting Tc(VII) to Tc(IV) which prevents it from co-depositing with Ni (6-10). Other problems arise with the electrowinning and

electrorefining processes because of the generation of large volumes of radioactively contaminated acid wastes especially when large amounts of Ni have to be recovered.

F) Need for an efficient process

There remains a need for an economical and efficient method to refine and decontaminate metals from nuclear facilities. More specifically, there remains a need to separate technetium from contaminated metals in a simple manner.

The radiochemical decontamination art is presented with unique practical problems not shared with traditional extraction technologies. Radiochemical extraction technologies are generally concerned with the economic recovery of radiochemicals. Routine process inefficiencies that result in residual amounts of radiochemicals in process streams, by-products, or waste streams raise only normal economic issues of process yield and acceptable process costs relative to radiochemical recovery. The various process streams and the radiochemicals will continue to be held by the regulated nuclear community in order to minimize the potential for release to the general public.

In contrast to radiochemical extraction technologies are technologies necessary to remove radiochemicals from contaminated materials such as nickel and precious metals. The presence of only residual parts per million concentrations of fission daughter products such as technetium in remediated nickel and other like recycled products will make the products unacceptable to the public The release of material containing residual radioactivity to unregulated non-nuclear markets has been prevented both politically and by regulation. Residually contaminated product must then be employed in less valuable regulated nuclear markets or it must be further decontaminated at great financial cost. (6)

Two of the more important practical considerations in the commercial feasibility of waste processing, recycling, and recovery operations include the effectiveness of so-called "secondary" processing steps and the volume of wastes which are generated by these secondary processing steps. *For example, when strong acid ion exchange resins are employed, adsorbed cations may leak from the resin beads when the pH of the solution is from about 2 to about 5. In addition, the resin beads may be degraded by process reagents such as, e.g., oxidants such as peroxides and ozone that may be added to maintain the oxidation potential of the process streams. Also, it is normally desirable to incinerate contaminated resin beads because they tend to resist compaction and, therefore, volume reduction. However, resin beads cannot easily be incinerated because the resin polymers tend to foul incineration equipment such as incineration grating and also may release noxious offgases. Furthermore, residence time distributions of process streams in ion exchange, carbon beds and the like may result in undesirable side reactions or subsequent reactions which produce other (and perhaps non-extractable) species, such as the reduction of a pertechnetate cation to nonionic technetium oxide. Also, by-passing is a practical concern which may substantially reduce the effectiveness*

of ion exchange and carbon beds and columns.

The Ni reduction process requires high metal concentration in solution during purification. This combined with similarities in properties between Ni and Tc make separation extremely difficult. Accordingly, there remains a need for an economical and efficient method to decontaminate metals and more specifically, to separate technetium from these metals in a simple manner.

The physical vapor deposition of nickel will be more efficient than all the prior and present processes. The advantages of the physical vapor deposition of Ni-Tc are as follows: 1) highly pure nickel can be produce, 2) Tc is also purified in this process and could become a secondary product, 3) the process cost is lower than that of electrolysis, and 4) no additional waste streams are generated.

II) Metal Distillation and Vaporization

A) *Separation of metallic mixtures*

Metal distillation and vaporization has been utilized as a means to purify metals from contaminants. The efficiency of metal distillation depends on the difference of the boiling points and the vapor pressures of the metallic components of the molten mixture. Ginder, et. al., purified zinc (Zn) from cadmium (Cd) by metal distillation (13, 14, and 15). The influent Zn-Cd mixture contained 0.47% Cd (B.P = 767°C) and the remaining Zn (B.P = 905°C). The vapor pressure of Cd is higher than that of Zn. Distilling the Zn-Cd mixture at 975°C, Ginder was able to purify Zn and reduce the content of Cd to 0.0013%.

U.S. Patent 5,582,630 demonstrates how to purify magnesium (Mg) from metallic and nonmetallic elements by vacuum distillation (16). The final Mg product contained 5.87 ppm Zn and 0.73 ppm of other metals (25 ppb Al, <10 ppb As, <5 ppb B, <10 ppb Bi, <20 ppb Ca, 18 ppb Cd, <10 ppb Co, <10 ppb Cr, <20 ppb Cu, <10 ppb Fe, <10 ppb Ga, <10 ppb In, <10 ppb K, < 5 ppb Li, 41 ppb Mn, <10 ppb Mo, 36 ppb Na, <10 ppb Ni, 36 ppb Pb, 22 ppb Sb, 226 ppb Si, < 10 ppb Sn, < 1 ppb Th, 10 ppb Ti, <1 ppb U, <30 ppb V, and 23 ppb Zr).

Tayama and Hodozuka used vacuum distillation to purify indium (In) from silicon (Si), iron (Fe), Ni, Cu, gallium (Ga), antimony (Sb), and lead (Pb) (1). The In feed had the following contaminants: 0.14 ppm Si, 0.15 ppm Fe, 2.3 ppm Ni, 0.28 ppm Cu, 0.03 ppm Ga, 0.02 ppm Sb, and 0.2 ppm Pb. The purified In had the following impurities: <0.03 ppm Si, <0.01 ppm Fe, <0.01 ppm Ni, <0.01 ppm Cu, <0.01 ppm Ga, <0.01 ppm Sb, and 0.01 ppm Pb.

Weil distilled a mixture of metals to recover magnesium. The mixture was composed of 85.654% Mg, 10.7% Al, 0.67% Cu, 0.006% Fe, 0.24% Mn, 0.01% Ni, 0.16% Si, and 2.56% Zn. The distillate was composed of >97.805% Mg, <0.01% Al, <0.01% Cu, <0.003% Fe, <0.01% Mn, 0.002% Ni, 0.02% Si, and 2.86% Zn. The residue was composed of 90.16% Al, 0.3% Mg, 5.9% Cu, 0.04% Fe, 2.1% Mn, 0.08% Ni, 1.4% Si, and 0.02% Zn (18).

Historically, metal distillation and vaporization has not been applied to separate radiocontaminated metals from the radioactive contaminants.

B) Proposal: Separation of Nickel and Technetium by Physical Vapor Deposition

1) Theoretical Feasibility of Separation

The physical properties and phase diagram of Ni-Tc system must be investigated to provide the fundamental data needed for the design of separation processes. Figure 1 represents the liquid-solid phase diagram of Ni-Tc. The phase diagram of Ni–Tc system has a simple pertectic phase diagram with a peritectic temperature of 1495°C and composition of 29.4 atomic % Tc. The phase diagram illustrates that the in the region of interest (<10 ppm Tc), the phase of the Tc for the Ni-Tccomposition above the melting point of Ni is liquid. This is critical because the phase diagram shows no formation of alloys in that region, which implies that separation of these metals is possible.

Figure 2 represents the liquid-solid phase diagram of nickel-rhenium. The phase diagram behaves in a similar way to that of nickel-technetium. This one of the main reasons to chose nickel-rhenium system as a surrogate system to model the Ni-Tc system. *The other reason is that the nickel-rhenium system is non-radioactive system and less expensive to work with. This will permit taking a large amount of experimental data to ensure the validity of this work. Tables 1 and 2 show the physical properties and pure component vapor pressures of nickel and technetium.*
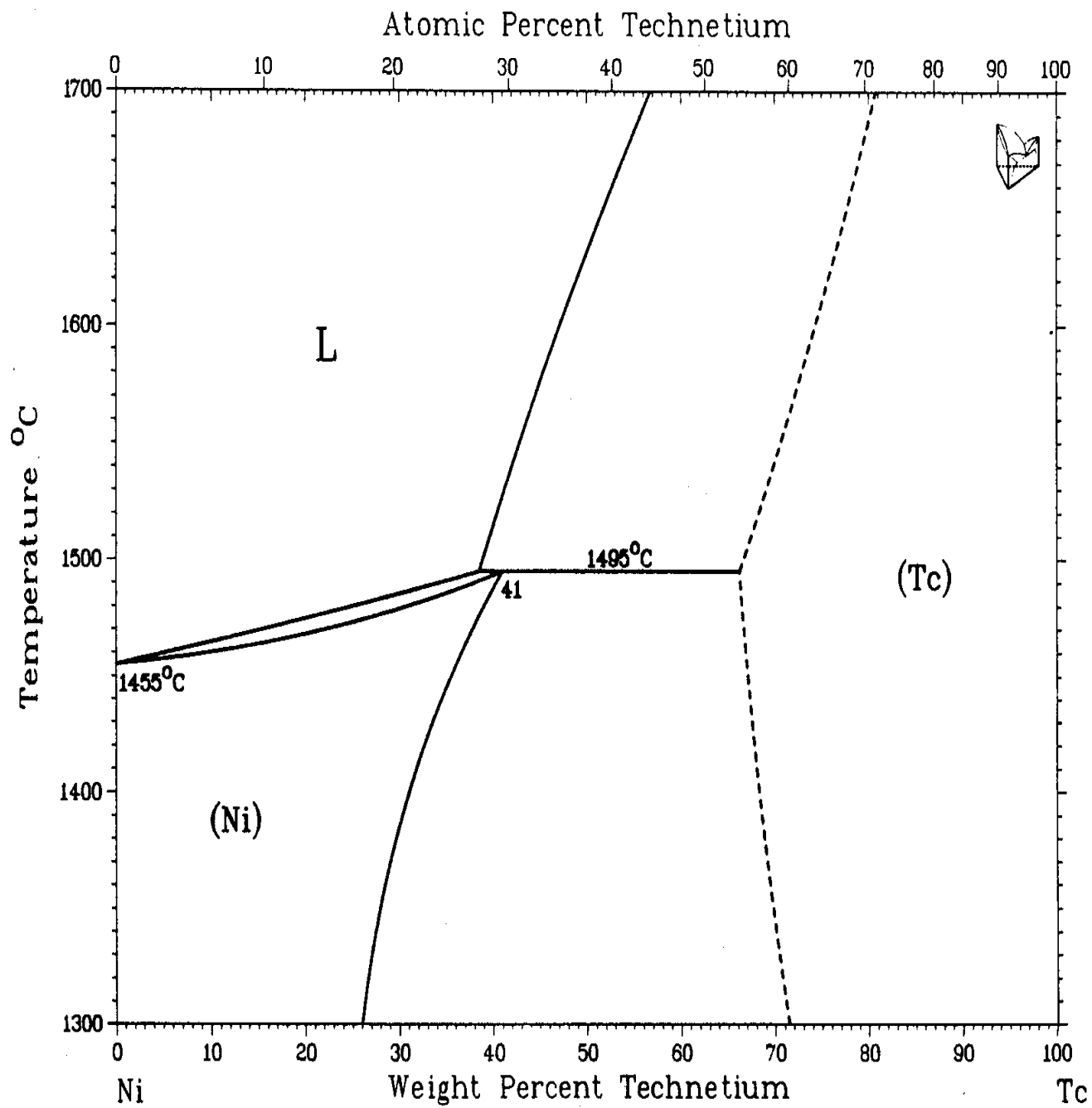
Figure 1. The phase diagram of nickel-technetium (19)
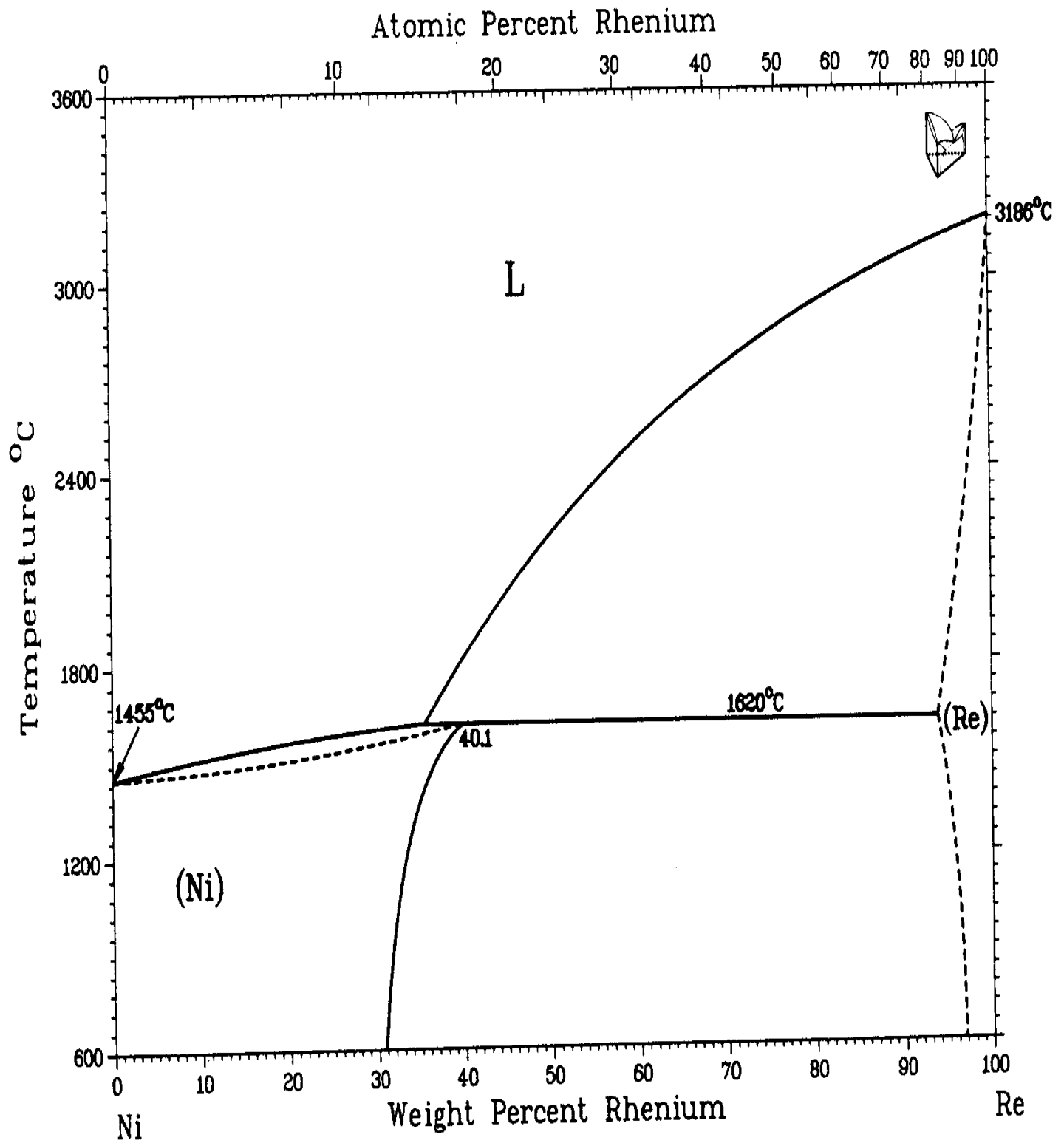
Figure 2. The phase diagram of nickel-rhenium (20)

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Table 1. Physical and thermal properties of nickel and technetium

	M_w (g/mol)	T_m (K)	T_b (K)	T_c (K)	P_c (bar)	V_c (cm^3/mol)	ρ_c (g/cm^{3}l)	Z_c	ω
Ni	58.69	1728.15	2415	6986.15	4918.5	35.4	1.6566	0.3	-0.17
Tc	99	2430.15	5000	17400.8	10183	42.6	2.2992	0.3	-0.31

	M_w (g/mol)	T_m (K)	T_b (K)	$\Delta H_f (T_m)$ (KJ/mol)	$\Delta H_v (T_b)$ (KJ/mol)
Ni	58.69	1728.15	2415	17.6	391.85
Tc	99	2430.15	5000	23.81	587.93

	A	T_c (K)	n	T_{min} (K)	T_{max} (K)	T_b (K)	$\Delta H_v (T_b)$ (KJ/mol)
Ni	460.38	6986.15	0.38	1728.15	6986.15	2415	391.85
Tc	668.703	17400.8	0.38	2430.15	17400.8	5000	587.93

Table 2. The vapor pressures of nickel and technetium

$$\log(P^*) = A + B/T + C\log T + DT + ET^2 \qquad P(mmHg) \quad T(K)$$

	A	B	C	D	E	T range	T_m (K)	T_b (K)
Ni	-57.4301	-13533	23.611	-7.67E-03	7.81E-07	1061-2415	1728.15	2415
Tc	-240.5191	-5792.8	78.794	-1.31E-02	7.46E-07	1660-5000	2430.15	5000

		P^* (atm)		α
T (^{o}C)	T (K)	Ni	Tc	
787.85	1061	1.32E-09		
1455	1728.15	2.43E-03		
1386.85	1660	9.83E-04	1.34E-13	7.35E+09
2141.85	2415	1.00E+00	2.77E-07	3.62E+06
2157	2430.15	1.00E+00	3.37E-07	2.97E+06

To measure the concentrations of the metal vapors at high temperature, a quadrupole mass spectrometer coupled to a Knudsen effusion cell must be assembled. Figure 3 shows the schematic diagram of a Knudsen effusion cell mass spectrometer (21). Figure 4 shows a physical vapor deposition apparatus to purify Ni.
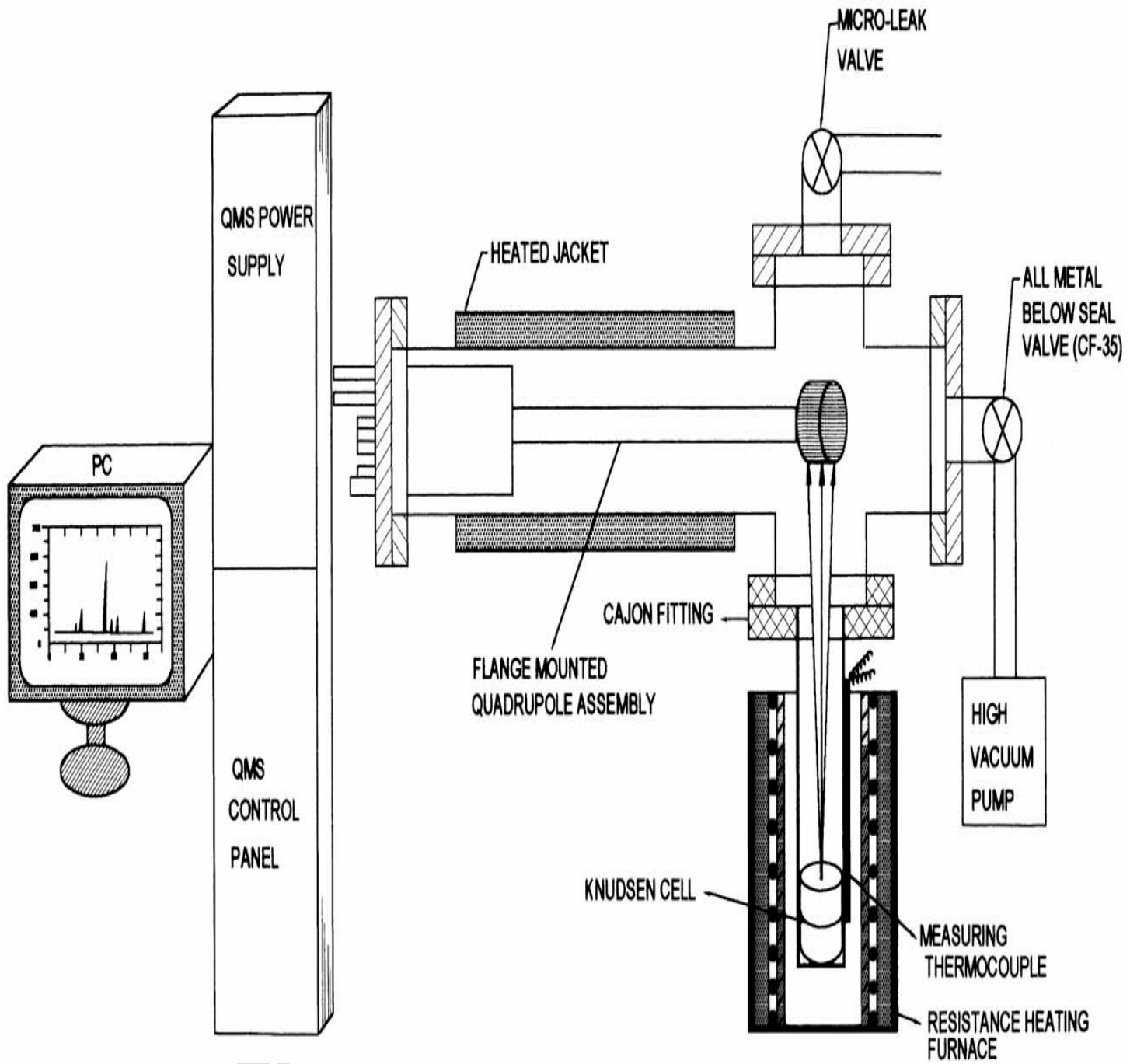
Figure 3. The schematic diagram of a Knudsen effusion cell mass spectrometer
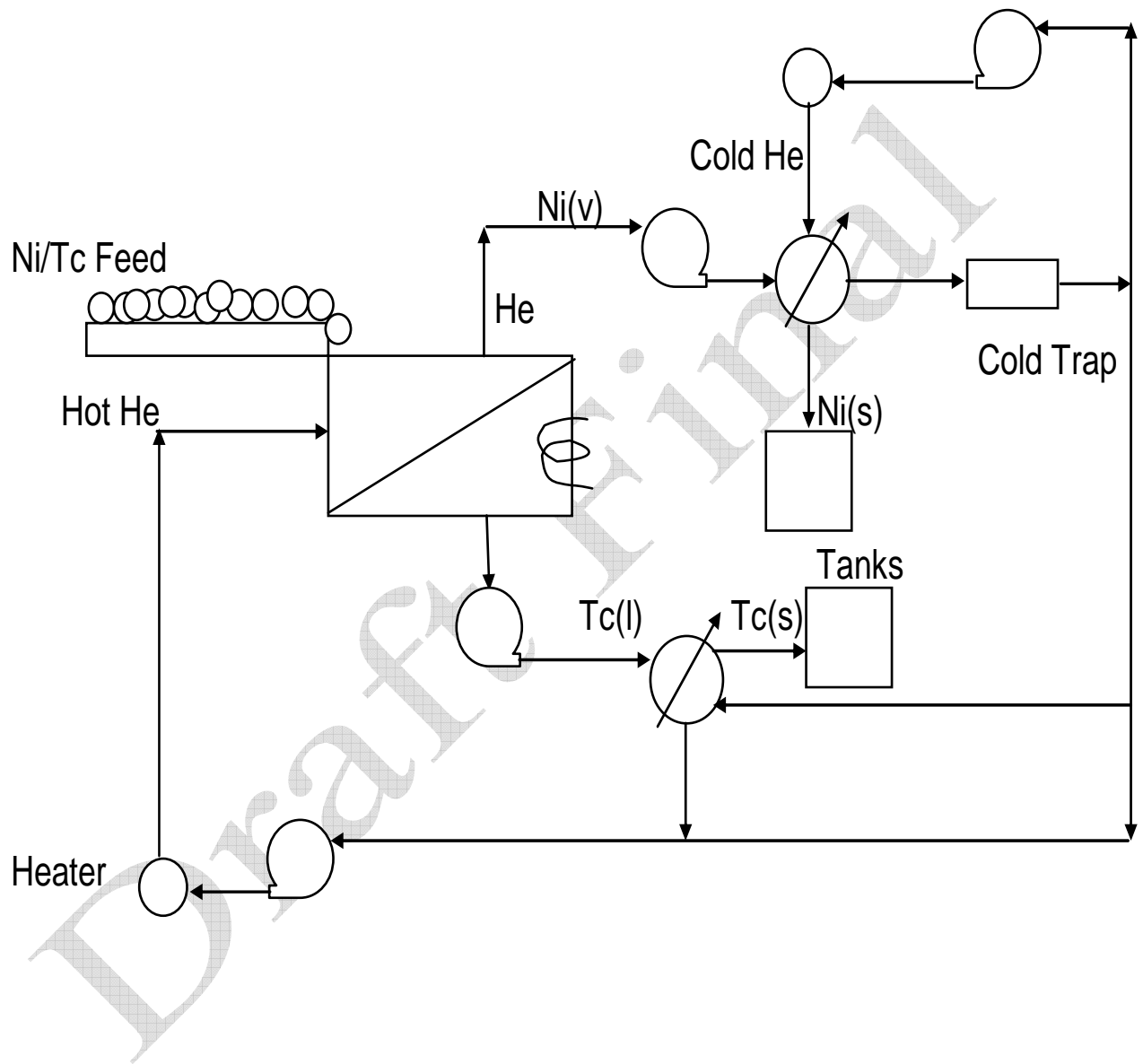
Figure 4. Vaporization apparatus for the recovery of nickel from Tc-contaminated nickel ingots.

2) Proposed Concepts

The proposed concepts are:

a) Separation of metals from metal mixtures due to the difference of vapor pressures.

b) Constructing vapor-liquid-solid phase diagrams of metallic mixtures.

c) Developing correlations for vapor pressures, activities, and enthalpies as a function of temperature for the metallic systems.

d) Design of metal-metal separation processes such as physical vapor deposition, batch distillation, or continuous distillation.

3) Economic Benefit Estimates

There are three ways of dealing with radioactive materials: which are dumping, storing, and the BNFL electrolysis method.   The cost of the physical vapor deposition method vs. the cost of the above methods is tabulated in Table 4.   The cost is based on the decontamination of 9700 tons of contaminated nickel. The London Exchange Metal quoted the price of nickel to be $6.64/lb ($14.62/kg). The price of Tc was quoted by the National Lab. at Oak Ridge to be $50/g. The costs of the electrolysis process, Nevada and Envirocare disposal sites were quoted from DOE/EM-0567 Report (22).

Table 4. Cost of decontamination of 9700 tons of contaminated nickel

	Price($)/kg	mass (kg)	Price ($)
Ni Price/Kg	14.61944	9,699,960	141,807,980
Tc Price/Kg	50,000	40	2,011,780
Ni / Tc		9700000	143,819,760

	Cost($)/kg	Cost($)/Prod	Profit	Savings *	Savings **
Electrolysis					
Ni (1Bq)	**5.61**	**54,417,000**	**87,390,980**	**121,961,780**	**127,432,580**
Sold Ni & Tc			**89,402,760**	**123,973,560**	**129,444,360**
Nevada (disposal)	3.564	34,570,800			
Envirocare	4.128	40,041,600			
Our Process					
Ni (>> 1Bq)	**1.14**	**11,021,260**	**130,786,720**	**165,357,520**	**170,828,320**
Sold Ni & Tc			**132,798,500**	**167,369,300**	**172,840,100**

* Disposal at Nevada
** Disposal at Envirocare

4) Environmental Benefits

Tables 5 and 6 illustrates that the process of physical vapor deposition can reduce Tc levels in Ni much lower than the electrolysis method.   In addition, Tc is purified with only 4 ppm Ni.   The electrolysis method produces large amounts of radioactive acidic and basic wastes, which have to be treated by the Purex method or dumped or stored.

Table 5. The number of moles and mole fractions of nickel and technetium in the liquid and vapor phases.

n_{Tc}	n_{Ni}	V_{Tc}	V_{Ni}	x_{Tc}	x_{Ni}	y_{Tc}	y_{Ni}
0.40643	164406	0	0	2.5E-06	1	0	0
0.40643	16440.6	3.2E-07	147965	2.5E-05	0.99998	2.1E-12	1
0.40643	1644.06	6.3E-07	162762	0.00025	0.99975	3.9E-12	1
0.40643	164.406	9.5E-07	164242	0.00247	0.99753	5.8E-12	1
0.40643	16.4406	1.3E-06	164390	0.02412	0.97588	7.7E-12	1
0.40643	1.6E-06	3.5E-06	164406	1	4E-06	2.1E-11	1

Table 6. The radioactivity of technetium vs. nickel recovery.

Tc		Ni
ppb	Bq	Rec (%)
2.13E-03	3.58E-04	90.00
3.87E-03	6.50E-04	99.00
5.76E-03	9.66E-04	99.90
7.67E-03	1.29E-03	99.99
2.11E-02	3.54E-03	100.00

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III) Appendix: Prior & Present Arts of Electrorefining & Electrowining

A) Introduction

Electro-refining using aqueous acid electrolytes is known to be effective for the removal of actinides from contaminated Ni; in such a technique the Ni is deposited selectively on a cathode, with the actinide ions remaining in solution due to their lower electrochemical reduction potential. Conventional electro-refining is however ineffective for reducing Tc concentrations in Ni; Tc is found to co-deposit with Ni at the cathode in a ratio that is the same as, or higher than, that in which it is found in the electrolyte. To reduce the concentrations of Tc in Ni ingots, new techniques were implemented. These techniques are listed below

1) A technique in which solvent extraction is combined with electrorefining is described in Snyder et. al. U.S. Pat. No. 5,156,722. Solvent extraction is used to separate heptavalent Tc from the electrolyte in which radio-contaminated Ni is dissolved, followed by electrowinning to recover Ni.

2) The process described in Snyder et. al. U.S. Pat. No. 5,183,541 and U.S. Pat. No. 5,156,722 employs an electro-refining cell that utilizes a semi-permeable membrane. Tc is chemically precipitated in the anodic compartment, using a variety of agents to reduce it to its tetravalent state, and is removed by filtration. A hydrochloric acid-based electrolyte is used because it is more amenable than sulfuric acid to the chemical precipitation of Tc.

3) U.S. Pat. No. 5,217,585, also to Snyder et. al., describes an electrorefining process in which the Tc-containing Ni is again electrolytically dissolved in an acid electrolyte. The electrolyte is contacted with activated carbon to absorb pertechnetate ions, after which the solution is filtered and transferred to an electrowinning cell, where the Ni is recovered at the cathode. The contaminated carbon is subsequently incinerated to produce Tc-containing ash, which can be encapsulated for disposal.

4) In U.S. Pat. No. 5,262,019, Snyder et al address the foregoing(contaminated ash?) problem by providing an electro-refining process with separate electrolytic dissolution and electrowinning steps. Contaminated nickel is first electrolytically dissolved in a sulfuric acid electrolyte, followed by treatment of the filtered nickel-laden electrolyte with an ion exchange resin to remove pertechnetate and other ions; the treated electrolyte is then processed in an electrowinning cell to deposit purified Ni at the cathode.

5) In U.S. Pat. No. 5,439,562, Snyder et al developed a novel method for decontaminating radio-contaminated nickel comprising, in an electrorefining cell having a semi-permeable membrane, cathodically depositing Ni from an alkaline solution containing electrolyte, Ni ions, and radioactive ions. Preferably, the electrolyte solution is ammonium sulfate maintained at a pH of least about 10.

6) In U.S. Pat. No. 5,458,745, Hardil et al employs a three-step process to separate Tc from radio-contaminated metal. The contaminated metal is dissolved in an acid solution; the Tc, present in the resultant solution as pertechnetate ions, is quantitatively reduced to its metallic state through a metal displacement (cementation) reaction with a base metal of lower reduction potential; and the desired metal is electrolytically recovered from the solution.

All these techniques were not capable of meeting the release criteria for radioactive materials.

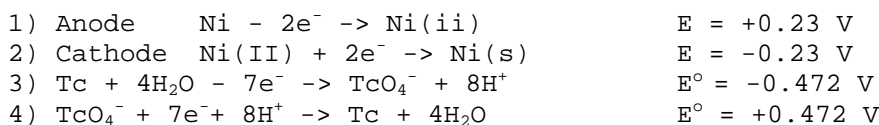## B) US patent 5,156,722: Decontamination of radioactive metals (5)

1) Method

Figure 1. shows the process of the decontamination of radio(actinide?)-contaminated Ni. The contaminated Ni ingots are fabricated into electrodes. The electrode is dissolved in sulfuric acid (H_2SO_4) to produce a solution containing actinide ions and at least 30 g/L of Ni to oxidize Tc to produce pertechnetate anions. The pertechnetate anions and actinides are removed by countercurrent solvent extraction with a barren solution containing tri-n-octylphosphine oxide (TOPO), and di-2-ethyl hexyl phosphoric acid (D_2EHPA) mixtures dissolved in a long-chained aliphatic hydrocarbon such as kerosene. The organic-to-aqueous phase contact ratios for the extraction are between 0.25 and 20 to produce a decontaminated Ni containing raffinate and a contaminated, loaded solvent stream. The Tc-rich solvent stream is diluted by 2-6N HCl and incinerated. The organic-to-aqueous phase contact ratios for the stripping circuit are 0.10-10. The decontaminated, Ni is passed through an absorbent (carbon column) to remove residual organic solvents. The raffinate is electrowon in an electrolysis cell with acidic electrolyte to remove residual actinides present, and Ni is recovered at the cathode.

The electrolysis cell operating range preferably includes a current density of 10-300 A/ft^2 with an efficiency of 80-98%, pH = 1-6, and a cell-operating voltage of 2-4 V/cell. The electrolysis cell is preferably operated at a temperature in the range of 25°C-60°C. The electrolyte additives can include 0-30 g/L free H_2SO_4, 60 g/L H_3BO_3 and 20-40 g/L Cl$^-$ to improve both the plating rate and the character of the plated deposit. Suitable examples of Cl$^-$ sources which may be used include NaCl, $CaCl_2$ and $NiCl_2$.

2) Chemistry

The Ni and the Tc half-cell reactions are given by reactions 1, 2. 3, and 4:

```
1) Anode     Ni – 2e⁻ -> Ni(ii)              E  = +0.23 V
2) Cathode   Ni(II) + 2e⁻ -> Ni(s)           E  = -0.23 V
3) Tc + 4H₂O – 7e⁻ -> TcO₄⁻ + 8H⁺            E° = -0.472 V
4) TcO₄⁻ + 7e⁻+ 8H⁺ -> Tc + 4H₂O             E° = +0.472 V
```

Controlling pH, temperature and anolyte oxidation potential, metallic Ni is won at the cathode. The problem arises due to the fact that Tc will track Ni and co-deposit at the cathode. Employing a reducing acid (preferably HCl (aq)) reduces Tc in the feedstock

solution at the anode.

Equations (5) and (6) potentially describe the half-cell reactions that allow TcO_2 precipitation without influencing Ni recovery at the cathode. In a highly concentrated Ni solution (particularly in a chloride electrolyte in which nickel forms no chloride complexes but remains as bare Ni (II)), at least one possible pertechnate-nickel complex can be formed with which is positive: $[(TcO_4)^-.XNi^{+2}]^{2x-1}$.

Not only does this complex provide a positive charge which would be attracted to the cathode but, if x equals 1 or 2, then it would explain why Tc concentrates in the cathodic Ni product relative to the Tc contaminated level in the Ni feedstock. Note also that cationic Tc complexes can form as well.

In a strong oxidizing acid, Tc, present either as a pertechnate-Ni ion complex or a lower valence, positive Tc complex, migrates from anode to cathode during nickel electrorefining where it is reduced chemically with the cathodic Ni product, and equations 5 and 6 do not occur anodically.

Anodic Reactions in Reducing Electrolyte	Cathodic Reaction in Reducing Electrolyte
(5) $Tc - 7e^- + 4H_2O + TcO_4^- + 8H^+$	$4e^- + 4H^+ \rightarrow 2H_2$
(6) $TcO_4^- + 4H^+ + 3e^- \rightarrow TcO_2 + 2H_2O$	

The complete electrochemical formation of TcO_2 in solution would force insoluble TcO_2 to the precipitate in the slimes at the anode by equations 5 and 6, but complete precipitation is unlikely using oxidizing electrolyte conditions because reactions 5 and 6 are difficult to drive to completion in oxidizing media. Further, both the heptavalent Tc state and its pertechnate ion are quite stable in oxidizing electrolytes. Therefore, a chemical reduction of Tc must boost the strictly electrochemical behavior to drive reactions 5 and 6 to completion.

A reducing acid such as aqueous HCl is substituted by the present invention for the oxidizing acid to promote the formation of TcO_2 by anodic reaction shown in equations 5 and 6. Moreover, the oxidation potential of the electrolyte must be controlled to maintain conditions favoring TcO_2 formation. Further, increasing anodic half cell voltages to ≥ 0.8 V provides an overall cell voltage of ≥ 1.2 V to enhance this reaction.
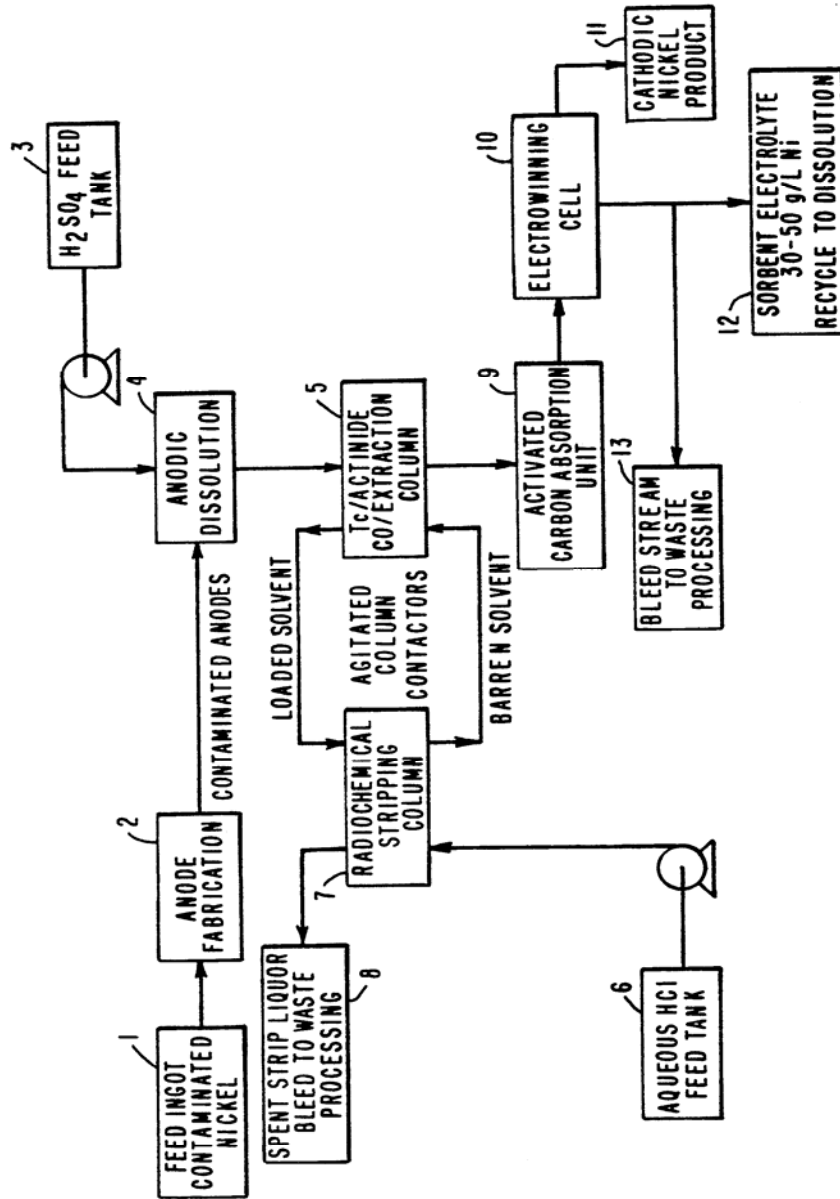
Figure 1. The first radio-decontamination method of the present invention--namely, solvent extraction of Tc and Co combined in the electrowinning.

C) US patent 5,183,541: Decontamination of radioactive metals (6)

1) Method

Ni contaminated with radioactive Tc is dissolved in HCl(aq) to produce a solution that contains pertechnetate ions and Ni ions. Fe^{+2} and Sn^{+2} are added continuously to the aqueous solution (0.05-5N) externally of an electrochemical cell to reduce the pertechnetate ions to a TcO_2 precipitate. The TcO_2 precipitate is continuously separated from the aqueous solution externally of the cell and then the separated aqueous solution is introduced into the cell for cathodically depositing metal from the aqueous solution.

The TcO_2 precipitate has a residence time of <1 hr in the aqueous solution. The multivalent metal ion is added to the aqueous solution at a low valence by applying a voltage between an anode comprised of the multivalent metal and a cathode in an electrochemical cell. The aqueous solution has a pH < 2.

The reductive electrorefining method allows Tc and other radioactive contaminants to be removed in the course of the electrorefining step.

2) Chemistry

The complete electrochemical formation of TcO_2 in solution would force insoluble TcO_2 to the precipitate in the slimes at the anode but complete precipitation is unlikely using oxidizing electrolyte conditions because reactions 5 and 6 are difficult to drive to completion in oxidizing media. Further, both the heptavalent Tc state and its pertechnetate ion are quite stable in oxidizing the electrolytes. Therefore, a chemical reduction of Tc must boost the strictly electrochemical behavior to drive reactions 5 and 6 to completion. Further, increasing anodic half cell voltages to ≥ 0.8 V provides an overall cell voltage of ≥ 1.2 V to enhance this reaction. Chemical reductants are added to the anodic chamber to enhance Tc valence reduction from VII to IV.

3) Process Flow

Figure 1. shows the process of decontamination of Ni by the use of HCl as a reducing agent. The electrochemical cell 10 has an anode 12 in an anode chamber 14 and a cathode 16 in a cathode chamber 18 which are electrically connected by a voltage source 20. The anode 12 is normally comprised of the metal to be recovered at the cathode 16. The anode chamber 14 and the cathode chamber 18 are separated by a semipermeable membrane 22 which permits the transfer of the electrolytic solution from one chamber to the other chamber. Preferably, the solution is circulated through an external circuit from the anode chamber 14 to the cathode chamber 18 and then back to the anode chamber 14 through the membrane 22. Alternatively, the solution may circulate within the cell 10 between the chambers (not shown). The cell 10 may have a drain line 24 for removing

anode slimes, including TcO_2 in some practices, which form in the anode chamber 14. The cell 10 typically operates at a temperature range of 25-60°C and at a current density of 10-300 A/ft^2 with an efficiency of about 80% or more at a cell voltage of 2-4 V/cell.

The electrochemical cell 10 employs HCl having a pH=1-4.5 where Ni is to be recovered. The solution may contain 40-105 g/L metal. Boric acid or other plating agents are added in an amount of 60 g/L to improve the plating rate and the character of the plating deposit.

Preferably, a reductant is added to an aqueous hydrochloric acid solution in the case where the contaminated metal is Ni or its alloy. Reductants such as Fe^{+2}, Cu^{+2}, Sn^{+2}, Ti^{+2}, V^{+2} or other multivalent ions may be advantageously added to the solution in the form of soluble salts such as chlorides, as is indicated by addition arrow 26. Gaseous reductants alternatively may be added by sparging the gases into the HCl solution in the anode chamber 14.

The process can be altered to substantially reduce the codeposition of the reductant at the cathode, titanium or vanadium ions are added as reductants for nickel. Advantageously, these multivalent metal ions will form cations having a low valence state of +2 which reduce the pertechnetate ions and concomitantly are themselves oxidized to a higher valence state of +3 or +4 in the anode chamber 14. The precipitated TcO_2 generally reports to the anodic slimes. The cations in the higher valence state are reduced from the high valence state to the low valence state in the cathode chamber 18 without cathodically depositing on the cathode 16. Then the reductant may be recirculated to the anode chamber 14 to repeat the cycle. Also, the reductant concentration may be closely maintained within a controlled range with little loss of reductant to the slimes and low volumes of waste may be generated. In addition, a dimensionably stable electrode may be deposited. In practice, deposited cathodes may be subject to scaling or flaking where the reductant is a transition metal which codeposits with the metal to be recovered. Thus the selection of the candidate reductants (such as ferrous, stannous or cuperous ions in the case of nickel) include this consideration.

Preferably the aqueous solution in the anode chamber 14 is pumped from the electrochemical cell 10 via a pump 28 in an external line 30 through a strong base anion exchanger 32 for capturing pertechnetate ions which may not have been reduced or may have been generated. The polished aqueous solution from the anion exchanger 32 flows into a holding tank 34 where the activity of the solution may be continuously analyzed. The solution may then be introduced into the cell cathode chamber 18 via a pump 36 in a line 38.

Another adaptation of the process can be made to remove substantially all of the Tc-containing species from the metal-containing solution in the cathode chamber 18. The aqueous solution in the anode chamber 14 containing pertechnetate ions and metal ions is pumped via a pump 40 in an external line 42 into a pipeline reactor 44 or other substantially plug flow reactor for closely controlling the concentration of added technetium reductants and the residence time of the TcO_2 precipitate in the metal-

containing solution. A reductant such as Fe^{+2}, Sn^{+2} or Cu^{+2} ions in an aqueous solution may be pumped by a pump 46 from a make-up tank 48 or other suitable source into the reactor 44. In addition, an aqueous suspension of filter aid may be conveniently added from a make-up tank 52 by a pump 54 to the precipitate-containing solution in the reactor 44. The filter aid preferably contains graphite or activated carbon and also a powdered anion exchange resin so that Tc which reoxidizes to the pertechnetate species and goes back into solution may be adsorbed. The suspension flows from the pipeline reactor 44 into a rotary drum filter 56 or other suitable (and preferably continuous) separating device for separating the precipitate and the filter aid from the aqueous solution. The precipitate and filter aid are discharged as a sludge, as is shown by discharge arrow 58. Preferably the residence time of the precipitate in the reactor 44 and in the filter 56 is > 1 hr, and more preferably < 0.5 hr. The metal-containing solution is then pumped through the anion exchanger 32 to the cathode chamber 18. Data indicates that the activity of the solution of the metal-containing solution after the anion exchanger 32 will be from about 1% to about 10% of the activity of the solution before the anion exchanger 32.

4) Experimental Data

Beaker tests have shown that the precipitate begins to redissolve as complex ions into the aqueous solution shortly after the precipitate forms. Thus, the anode slimes may be a significant source of Tc contamination in the case where TcO_2 precipitates from the solution inside the cell anode chamber 14. The beaker tests were conducted on HCl solutions at a pH=2 and at a temperature of $25^{o}C$. The solutions generally contained 90 g/L Ni and 3000-4000 ppm Tc.

In one series of tests, ten samples of the contaminated solution were each charged with up to 50 g $FeCl_2$/50 mL solution or 50 g $SnCl_2$/50 mL solution to precipitate TcO_2. The samples were not filtered immediately after precipitation. Several weeks were permitted to lapse between precipitation and analysis of the activity and of the technetium concentration of the solutions. The analyses of the samples with initial activities over 4000 Bq/g charged with $FeCl_2$ indicated the following concentrations with week long residence times in the filtrates:

Sample	g FeCl$_2$ 50ml soln	g-mole FeCl$_2$ L	Tc Activity (Bq/g Fe)	Conc. Tc (ppb)
1	0.5	0.08	566	908
2	1.25	0.2	591	947
3	2.5	0.4	386	947
4	5.0	0.8	370	620
5	50	8.0	1910	3086

The analyses of similar feed samples charged with $SnCl_2$ indicated the following concentrations at long residence times in the filtrates:

Sample	g $SnCl_2$ 50ml soln	g-mole $SnCl_2$ L	Tc Activity (Bq/g Sn)	Conc. Tc (ppb)
6	0.5	.053	257	413
7	1.25	0.13	333	535
8	2.5	0.263	434	697
9	5.0	0.525	528	848
10	50.	5.25	837	1347

This series of tests indicates that as the concentration of the reductant is increased, the Tc activity and concentration increases.

In another series of tests, five samples of contaminated solution were each charged with 5 grams of ferrous chloride per 50 mL of contaminated solution (such as Sample 4 above). These samples were held for 0.5-6 hr and then filtered. The analyses of the samples indicated the following activity and Tc concentration of the filtrates:

Sample	Residence Time (hours)	Activity Tc (Bq/g Sn)	Conc. Tc (ppb)
11	0.5	10.2	16
12	1	9.2	15
13	2	26.9	43
14	4	20.9	33
15	6	30.3	49

A comparison of Samples 11 and 12 with Samples 13-15 indicates that the Tc concentration of the filtrate was substantially less when the residence time was less than about one hour. Thus, the TcO_2 should be precipitated and separated from the aqueous solution within a residence time of about one hour if the redissolution of Tc from the oxide is to be minimized. Preferably, the addition and separation steps are performed continuously to closely control the reductant concentration and to minimize the redissolution of the Tc.

In another practice of the process to efficiently reduce the pertechnetate ions as they are anodically dissolved, multivalent metal ions in a low valence state are added to the solution in the anodic chamber by applying a voltage between a secondary anode

comprised of the multivalent reductant metal and a cell cathode. The reductant anode may be located near the contaminated anode so the pertechnetate anions are reduced before they have a substantial opportunity to form more stable complex ions, which are not repelled by the cathode and disperse throughout the solution. In addition, the voltage supplied to the reductant anode may be controlled to minimize the addition of excessive amounts of reductant to the solution.

In the demonstration test, Ni ions and pertechnetate ions were anodically dissolved into an electrolytic solution 80 provided as a 2 N HCl solution containing 30-60 g/L boric acid. The Ni feed activity was over 4000 Bq/g. The anodic slimes which formed were filtered from the solution and their activities (disintegrations/minute) were analyzed as follows:

pH	°C	Filtrate DPM	Filtercake DPM
0	25	--	2200
0	60		
		--	2500
2	25	1000	180000
2	60		
		800	320000
4	25	1000	280000
4	60	500	310000

Thus this practice may be employed to efficiently reduce the pertechnetate ions to a TcO_2 which may be separated to provide a relatively clean metal-containing filtrate. It is noted that a commercial-type cell having an anode in an anode chamber and a cathode in a cathode chamber would provide an even cleaner filtrate.

A beaker test was conducted without the use of added reductants such as multivalent metal ions, reducing gases and the like to demonstrate the net behavior difference between a hydrochloric acid solution (a reducing environment) and a sulfuric acid solution (a mildly oxidizing environment) in the anodic dissolution of contaminated nickel. Nickel anodes contaminated with about 0.7 ppm Tc were dissolved in 2 N acid solutions at about room temperature. The solutions were permitted to sit prior to filtration of the slimes from the solution and analysis of their activities. The analysis indicated the following activities:

Acid	Filtrate DPM	Sludge DPM
H_2SO_4	1200	1500
HCl	0	400

Thus, although H_2SO_4 may be employed in the decontamination of metals containing Tc,

this test demonstrates that a reducing acid such as HCl (and/or another reductant) will more effectively separate the Tc from the solution and thereby permit the cathodically recovered metal to be more completely decontaminated.
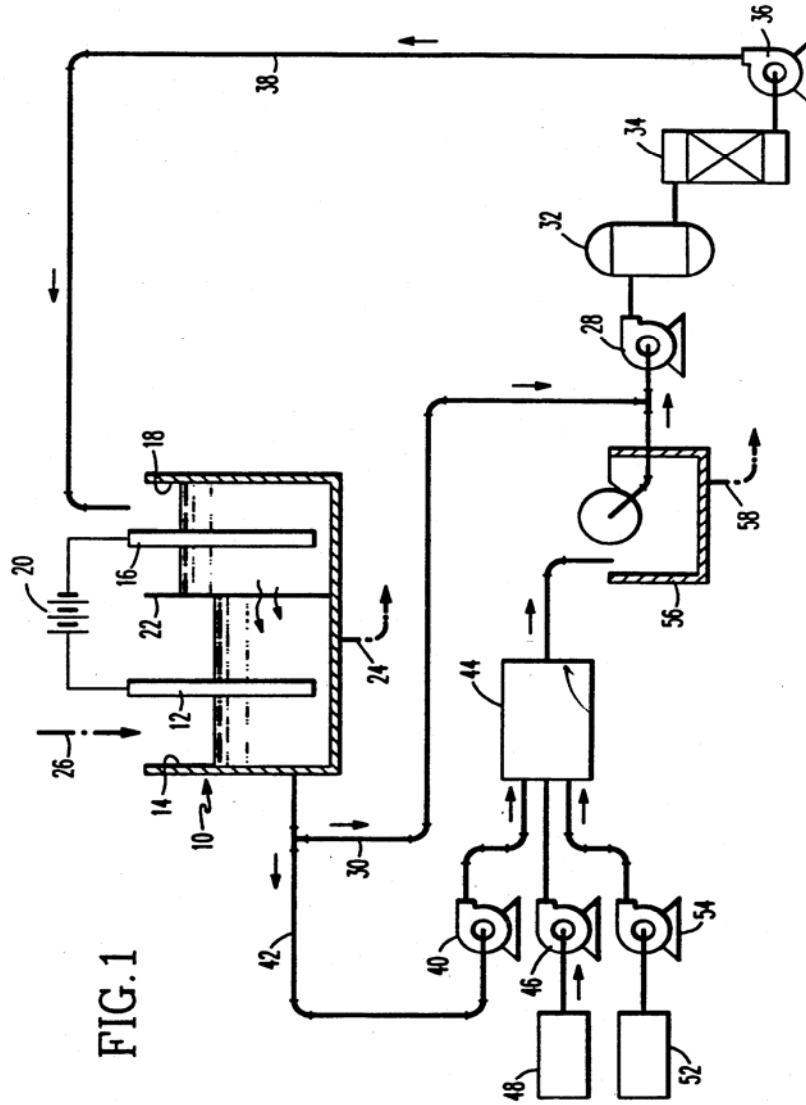
Figure 1. A schematic representation of an electrochemical cell which may be employed in the practice of the present invention

D) US patent 5,217,585: Transition metal decontamination process (6)

1) Process Flow

Figure 1. shows the removal of Tc from contaminated Ni. A transition metal such as Ni which may be contaminated with up to about 10 ppm or more of Tc, U, Th and other transuranic elements is introduced (as indicated by addition arrow 10) into an anodic dissolution tank 12.

The transition metal in the dissolution tank 12 is dissolved in an aqueous sulfuric acid solution. The acid solution may be fresh and/or recycled acid. The diagram shows two recycle streams introduced into the dissolution tank 12 via a recycle line 14 and a bleed line 16.

The bleed line 16 is employed to introduce an adsorbent powder such as graphite or activated carbon into the dissolution tank 12 for adsorbing the Tc as it dissolves. The Tc-carbon bond is sufficiently strong that the adsorbed Tc will not leak from the powder at the process temperatures experienced by the aqueous acid solution. Preferably, the powder is introduced by any suitable distributor 17 in close proximity to a dissolution anode 18 (and other dissolution anodes where employed) so that the Tc is immediately adsorbed as it dissolves. The pertechnetate ion is the primary Tc complex in solution at that point. However, it may be reduced if the potential of the electrolyte solution is not maintained.

The powder size is in the range of from about 0.1-100 micron and the slurry in a process line 19 from the dissolution tank 12 comprises from about 0.1-50 g/L of powder. Assuming a surface area of about 500 m^2/g, it will be seen that the dissolving Tc will be exposed to a large total surface area. Such powders do not tend to clog and do not tend to interfere with the electrical properties of the electrolyte solution in the dissolution tank 12.

The powder-containing slurry may be fed to a premix tank 20 where it is mixed with known filter aids such as diatomaceous earth, powdered anion and/or cation exchange resins, from a filter aid make-up tank 22 and flocculants from a flocculent make-up tank 24 (which flocculants may consist of polyelectrolytes, Al or Zr complexes). The slurry is then fed to a filter 26 or other suitable device for separating the Tc-containing solids from the aqueous acid solution. The Tc-containing filter cake may then be washed with water to remove residual acid and ions. About two bed volumes of water or more will sufficiently wash the cake in any instances. Preferably, the filter cake is then incinerated in a high temperature incinerator 28 to produce a technetium-containing ash, which most preferably is encapsulated in a glass structure by known means for permanent disposal. U.S. Pat. No. 4,792,385 provides the method of incineration and encapsulation systems (10). Similarly, the wash water may be neutralized, evaporated and the evaporator bottoms encapsulated. The total volume of radioactive wastes produced by this practice is

substantially reduced.

The metal-containing acid filtrate from the filter 26 may optionally be fed to an ion exchange polishing column 30 (as shown) and then to an electrochemical cell 36 where the dissolved metal may be electrowon. The filtrate from the filter 26 may be analyzed on-line to verify the decontamination efficiency of the previous operation free of self-shielding due to the presence of the dissolved metal. If the activity of the filtrate is too high, then the process can be easily taken off-stream and corrected before off-specification nickel is plated.

The electrochemical cell 36 may operate at 25-60 $^{\circ}$C and at a current density of 10-300 A/ft^2 with an efficiency of about 80% or more at a cell voltage of 2-4 V/cell. The aqueous acid solution in the electrochemical cell preferably has a pH of between 1 and 6 and, in the case where nickel is recovered from a hydrochloric acid solution, preferably between 1 and 4.5. The solution in the electrochemical cell contains from about 40-105 g/L of contaminated metal. The solution may also contain up to about 60 g/l of boric acid or other suitable plating agent to improve the plating rate and the character of the plating deposit. It is these operating conditions that depart from traditional radiochemical decontamination conditions and necessitate the intimate contact of the electrolyte with the adsorption/exchange media.

The metal-depleted aqueous acid solution from the electrochemical cell 36 may be recycled to the dissolution tank 12 via process line 14. Preferably, the oxidation potential of the aqueous solution in the dissolution tank 12 is controlled by injecting a peroxide into the solution by a suitable means. Thus, e.g., a water soluble peroxide may be dissolved in metal-depleted acid and then added via an addition line 40 to the process line 14.

The metal-depleted recycle stream may be employed to introduce graphite or activated carbon powder into the dissolution tank 12. Thus, e.g., a metal-depleted solution bleed stream may be diverted via process line 42 from the process line 14 to an in-line mixer 44, which may be a turbine impeller of an injection pump, for intimately mixing the solution with the carbon powder. The powder may be fed from a feed bin 46 by a solids feeder 48 or by other suitable means to the mixer 44, which may then pump the slurry into the dissolution tank 12. In a preferred practice, graphite or activated carbon powder is added in amounts sufficient to produce a slurry in the aqueous solution from the dissolution tank 12 containing 0.1-50 g/L powder. Preferably, the powder size is between about 0.1 microns and 100 microns.

The carbon powder may be introduced into the aqueous solution by other suitable means. In an alternative practice, low grade graphite anodes may be employed as an inert anode in either the dissolution tank 12 (in processes where the contaminated metal is anodically dissolved) or in the electrochemical cell 36. These anodes will disintegrate over time to provide the required adsorbent. In another practice, a graphite frame may be employed to hold the contaminated metal anodes.

In a full scale pilot plant test of a prototype process, a technetium-contaminated nickel sample from the Oak Ridge uranium diffusion cascade was dissolved in a sulfuric acid solution and then slurried with between 0.1 g/L and 50 g/L of a 0.1 micron to 100 micron graphite powder. The slurry was mixed with conventional filter aids and flocculants in a premix tank and then filtered. The filtrate was then fed to an electrochemical cell where decontaminated nickel was electrowon from the sulfate solution. The plated nickel was analyzed at less than 1 Bq/g (total activity).

In addition, bench scale tests were performed in which Tc-contaminated nickel was dissolved in a sulfuric acid solution that was then slurred with less than about 1 g/100 cc solution of graphite powder. The graphite was filtered from the solution and the activity of the filtrate and the adsorbent determined to be:

SAMPLE NO.	FILTRATE ACTIVITY	ADSORBENT ACTIVITY	KD
1	400	76	0.19
2	1600	753	0.47
3	1100	179	0.16

Thus the, practice of the present procedures/method will effectively decontaminate metals such as nickel so that they may be released to commercial markets.
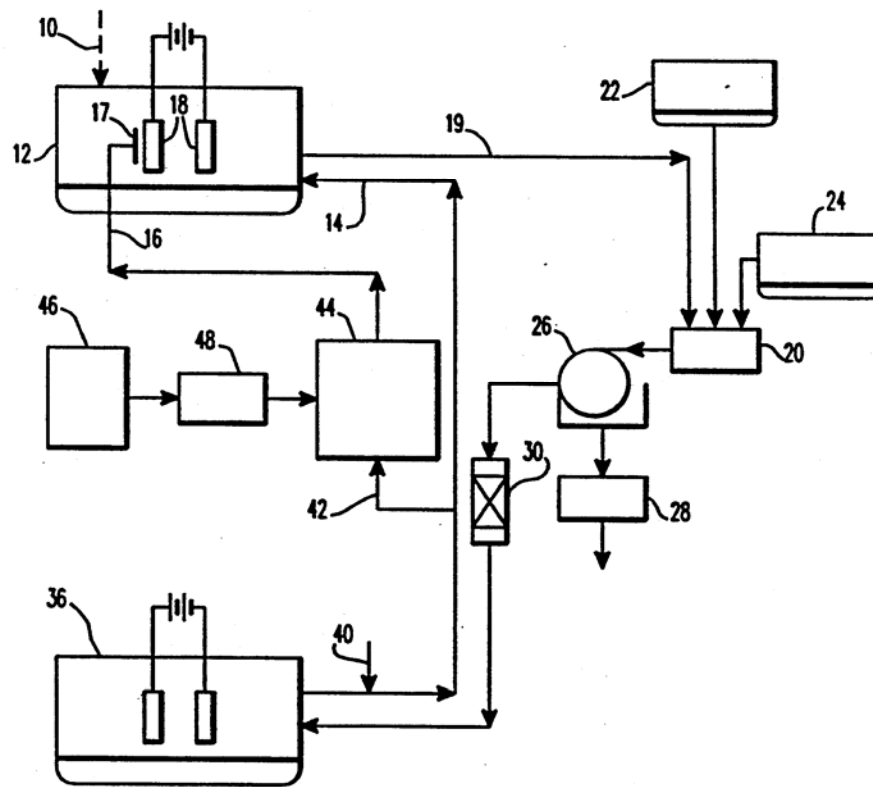
Figure 1. Process flow diagram of Ni Recovery from Tc-contaminated Ni..

E) US 5,262,019: Decontamination of radioactive metals (7)

1) Process Flow

Figure 1. lays out the process flow diagram designed for the decontamination of ORNL Ni. The ORNL Ni is contaminated with about 0.85 ppm Tc, < 0.5 ppb Np 237, < 0.005 ppb Pu 239, 0.93 ppm U 235 and 1.74 ppm total U and has a gross beta activity of about 4000 Bq/gm.

The ORNL nickel is generally available in the form of 24 inch diameter by 18 inch high 2,200 pound ingots, which must be converted to electrodes having a much higher surface area per unit weight geometry for effective electrolytic dissolution. Desirably, the electrode preparation involves a minimum amount of reprocessing, product losses and waste generation. Accordingly, contaminated feed electrodes may be prepared by "shot" production or thin sheet rolling from the contaminated ingots.

Shot production generally involves the steps of induction melting, screening, free-fall through a shot tower and collection. Induction melting is preferred over arc melting due to health physics constraints to control the spread and volatilization of radioactive contaminants. The particle size should be sufficiently small that the product "flowers" can be loaded into titanium baskets for electrolytic dissolution. The chief advantages of a shot process are the generation of high surface area particles, ease of reloading and minimal rework. In addition, various known "slags" can be introduced during the melting operation to extract radiochemicals such as uranium and transuranics.

Planar electrodes may be produced by rolling thin sheets of about one-quarter inch to about 2 inch thicknesses to generate high surface areas. Planar electrodes may be preferred to "flowers" because anodic slimes which tend to form during the dissolution step can be readily removed from planar anodes in most cases. In addition, a rolling process is inherently simpler than shot production and substantially eliminates dust control problems of shot production.

Once the electrode geometry is established, a suitable number of contaminated nickel electrodes 8 are loaded into a dissolution tank 10 in a "side-by-side" configuration. Up to 60 or more electrodes may be employed as shown in the tank 10. Half of the electrodes may be connected together as anodes and the other electrodes may be connected together as cathodes. Thus, inert cathodes need not (but could) be employed to complete an electrical circuit. The side-by-side contaminated electrodes are preferably connected to the dissolution process power supply through a reversing switch, which alternates polarity on the electrodes so each electrode spends half of its time as an anode and half as a cathode. The polarity may be reversed at 5-30 s intervals. Preferably, the electrode polarity is reversed when the initial current flux drops by about 10% due to the rise in electrode polarization. Concentration polarization is eliminated and anodic slimes are removed by the frequent polarity reversal. A voltage of 2-5 V is applied per cell, and preferably, about 3 V, to dissolve the transition metal and the radioactive contaminants

with the reduction of protons to $H_2(g)$ at the cathodes. Gases and vapors from the tank 10 may be vented via an overhead hood 12 and piping 14 to an off gas scrubber (not shown). Also, the acid solution in the dissolution tank 10 may be re-circulated by a pump through a carbon filter for removing slimes and particulates from the acid solution (not shown).

Preferably, nickel is dissolved into an acid solution having a pH=0.5-2. Because the acid solution is comprised of recycled acid solution from the electrowinning step, which generally does not economically plate nickel at substantially lower concentrations, the acid solution will typically contain at least about 60 g/L Ni. Anodic dissolution and hydrogen reduction are efficiently affected under these conditions. The acid solution from the tank 10 contains 70-100 g/L Ni. The acid solution may have a gross beta activity > 100 Bq/gm. [Sulfuric acid and contains 145-245 g/L sulfate??]. The acid solution may also contain up to about 30 g/L boric acid, which functions as a plating agent in the electrowinning step. The temperature of the acid solution may vary between 35-75°C.

The redox potential of the acid solution in the dissolution tank 10 is maintained at about 0.3 V so that the Tc (+4) species is oxidized to the Tc (+7) species. The contaminated acid solution from the dissolution step is transferred by a pump 20 via a pipe 22 to an oxidation tank 24 where it is contacted with an oxidizing agent. Ozone is employed as the oxidizing agent, the acid solution from the oxidization tank 24 contains from 2 ppm to 10 ppm ozone. In the process shown, some of the acid solution in the oxidization tank 24 is recycled by pump 26 in pipe 28 and a second pipe 30 back to the dissolution tank 10 for maintaining the acid solution in the dissolution tank 10 at the proper redox potential.

The contaminated acid solution in the oxidization tank 24 may be transferred downstream via the pump 26 in the pipe 28 and another pipe 32 to a stripping tank 34 for removing unreacted oxidizing agents such as ozone from the acid solution by sparging regenerative air or steam supplied by a pipe 36 into the stripping tank 34. Alternatively, where hydrogen peroxide or the like is employed as the oxidizing agent, ion exchange "blocking" (not shown) may be employed in place of gas stripping to remove the unreacted oxidizing agent. Removal of such unreacted oxidizing agents protects downstream equipment such as ion exchange resins and the like from oxidation.

The contaminated acid solution in the stripping tank 32 may be transferred via a pump 40 in a pipe 42 to a pH adjustment tank 44 where boric acid or other buffer may be added via a pipe 46 to the acid solution for adjusting the solution pH=2.5-4.5. Analysis of pilot plant operating data (for decontaminating ORNL nickel) indicates that the gross beta activity of the acid solution may be as high as about 150 Bq/g at this point in the process.

The contaminated acid solution in the pH adjustment tank 44 may be pumped downstream by pump 50 in pipe 52 through particulate filter 54 for removing radioactive particulates from the acid solution thereby reducing the gross beta activity of the acid solution to $\leq$ 20 Bq/g. Preferably, the filter 54 is a hybrid sand-powdered ion exchange resin filter. In a preferred practice, filter 54 is a downflow filter with a layer of sand over a layer of powdered ion exchange resins having a fabric mesh extending horizontally through the resin.

The contaminated acid solution may be transferred downstream via pump 56 in pipe 58 through one or more anion exchangers 60, cation exchangers 62 and mixed ion exchangers 64 (which are shown as one exchanger each) to one of two hold tanks 66. Preferably, sulfate resins are employed at an operating temperature of less than about 60°C. Mixed ion exchangers 64 may be employed to eliminate the effects of any localized pH variations that may occur in a pure anion or cation column. Both radioactive anions and cations may be sorbed from the acid solution. Analysis of pilot plant operating data (for decontaminating ORNL nickel) indicates the gross beta activity of the solution after the anion exchangers 60 may be as low as 10 Bq/g and as low as 8 Bq/g after the cation exchangers 62 where the gross beta activity of the acid solution before the filtration step is as high as 150 Bq/g.

Preferably, at least two anion exchangers 60, cation exchangers 62 and mixed ion exchangers 64 are employed on-line in series. Each on-line ion exchanger 60, 62, and 64 is monitored to determine radiochemical activity breakthrough. When the first (i.e., the upstream) ion exchanger bed in tandem breaks through, it is taken off-line and regenerated while the second bed in tandem is "moved-up" to the first position and a fresh bed is installed in the second position.

The radioactivity of the acid solution in the hold tanks 66 is verified before charging the solution to the downstream electrowinning step. If the gross beta activity exceeds approximately 20 Bg/L the acid solution may be recycled via a pump 70 in a pipe 72 and a pipe 74 to upstream of the anion exchanger 60. Preferably, the recycled acid solution is returned to the oxidation tank 24 for adjusting its redox potential to assure complete oxidization of Tc to the Tc (+7) species. If the gross beta activity is less than about 20 Bq/g, the acid solution may be transferred via pump 70 and pipe 76 to an electrowinning tank 80. Preferably, the acid solution is not charged to the electrowinning tank 80 unless its gross beta activity is less than about 10 Bq/g. In a preferred practice of the present procedure/method, and after the gross beta activity of the acid solution in a hold tank 66 has been verified to be below about 20 Bq/g, the pH of the solution may be buffered with boric acid or other suitable buffer to between about 4.0 and 4.5 before charging the solution to the electrowinning step.

The electrowinning tank 80 is operated at ~2-6 V/cell, and preferably at about 3 V/cell to plate nickel product at the cathode while generating oxygen gas at the anode. The electrowinning tank 80 as shown has three cells with 20 anodes/cell, although other configurations may be employed. Inert anodes must be employed to maintain clean electrolytes in the electrowinning step. Thus, commercially available titanium anodes coated with a platinized layer or iridium oxide layers are preferably employed. Conventional graphite electrodes are not acceptable as they tend to spill submicron particles into the solution, which may adsorb technetium complexes and pass through ion exchangers then be adsorbed on the cathode product. Also, "inert" stainless steel anodes are not employed because they contaminate the plating bath with chromium, which tends to inhibit plating by increasing the surface stresses on the cathodic deposits. Analysis of pilot plant data (for decontaminating ORNL nickel) indicates that Ni plated in accordance

with this practice has beta activities due to Tc from 1.6 Bq/g to 17.0 Bq/g or less.

The off gases from the electrowinning tank 80 may be vented via a hood 82 and piping 84 to a gas scrubber or other waste treatment facility (not shown). In addition, the acid solution in the electrowinning tank 80 may be recirculated by centrifugal pumps through external carbon filters for removing particulates in the solution (not shown).

The barren acid solution from the electrowinning tank 80, now containing about 60 g/L-75 g/L Ni and up to about 30 g/L boric acid is transferred via pump 86 in pipe 88 to recycle tank 90 for recycling the barren acid solution to dissolve additional contaminated nickel. The barren acid solution will inherently have a lower pH than does the acid solution charged to the electrowinning tank 80 because of the electrowinning step. Preferably, sulfuric acid or other suitable acid is added via a pipe 92 to the barren acid solution in the recycle tank 90 in order to further reduce the pH of the barren acid solution to the pH of the solution in the dissolution step, which is about 0.5 to about 2. In addition, and as shown, the barren acid solution is transferred via pump 94 in pipe 96 back to the oxidation tank 24 (for adjusting the redox potential of the recycled acid solution to about 0.3 V) and then to the dissolution tank 10 via pipe 26.

Accordingly, the technical risks of product contamination are managed by an effective process screen (comprising a particulate filter for trapping TcO_2 colloidal sized and larger particles out of aqueous acid solutions, and an anion exchanger and a cation exchanger for trapping both positive and negative pertechnetate complexes) between the dissolution step and the electrowinning step and recycling of all excessively contaminated solutions to upstream of the screen. Importantly, the decontamination is verified at the process screen before the electrowinning step.
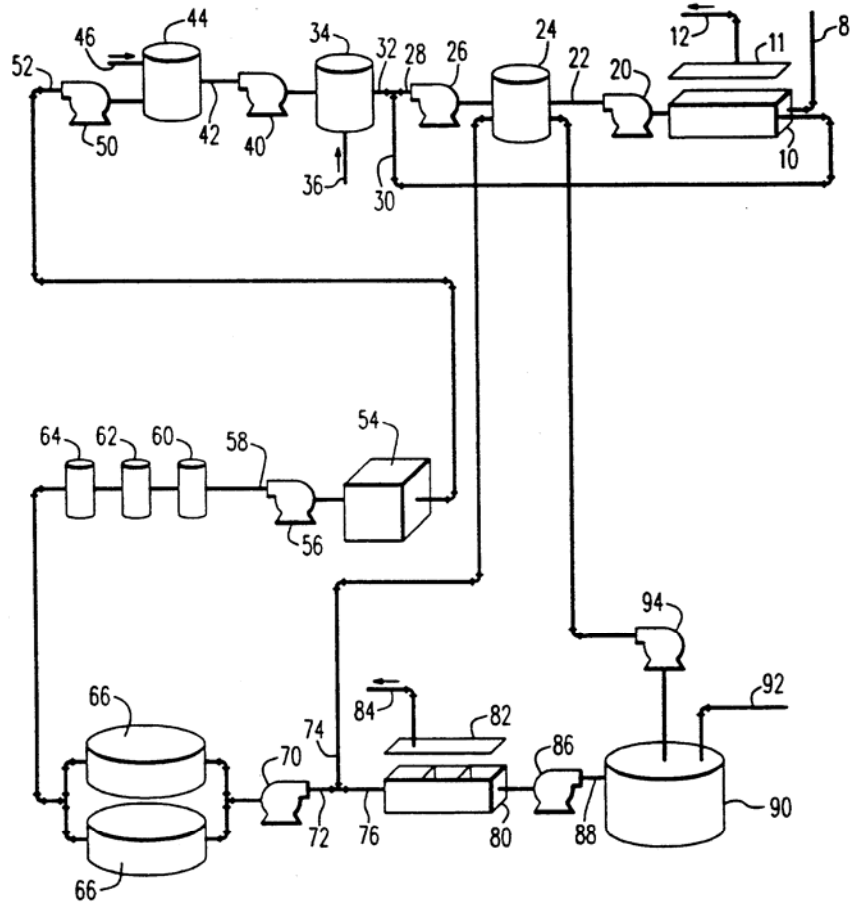
Figure 1. Process flow diagram to decontaminate transition metals.

F) US 5,439,562: Electrochemical decontamination of radioactive metals by alkaline processing (9)

1) Method

Ni metal contaminated with Tc is dissolved in ammonium sulfate in an electrolytic cell containing a semi-permeable membrane. The electrolyte has a pH in the range of 10-13. The solution contains nickel ions and radioactive ions. Ni is selectively recovered from the solution by cathodically depositing substantially radioactive-free Ni from the solution in the electrofining cell.

The electrodes of the cell are driven by a common current and controlled by a single rectifier. The oxidation potential of the radioactive contaminants in the solution is adjusted by the addition of ozone.

The electrolyte is maintained at a temperature of 40-60°C., and the electrochemical cell is operated at a current density of about 10-300 A/ft^{2} with an efficiency of about 80% or more at a cell voltage of about 1-4 V/cell.

2) Process Flow

Figures 1 & 2 depict a conventional single electrowinning dissolution system and an entire plant layout, respectively. In figure 5 the contaminated metal is first dissolved in anodic dissolution tank 10. The contaminant-containing solution is then transferred out of the dissolving tank to oxidation tank 12, which is equipped with a dispersion system and optionally a blower 26, where the oxidation potential of the radioactive contaminants is adjusted. Next, the solution is transferred from the oxidation tank to tank 14, which is equipped with a gas dispersion system and optionally a blower, where oxidants are removed from solution. Then, the solution is transferred through filter 16 which removes solids, and then through a series of ion exchangers 18, 20 which remove the radioactive contaminants from solution. Next, the solution is transferred to a series of holding tanks 22, 24, and subsequently to an electrowinning plating cell (not shown) where nickel is cathodically plated.

Figure 2 is a schematic representation of a full scale plant layout utilizing the dissolution system of Figure 1. A series of dissolving tanks 100 (as described above) are serially connected to each other electrically (heavy lines) and via electrolyte piping (thin lines). The dissolving tanks are also connected to holding tanks 120,122 and electrolyte return tanks 130. The dissolving tanks are driven by power supplies 124. Upon dissolution, the solution is transferred to a series of electrowinning plating tanks 126, which are serially connected to power supplies 128, for cathodic deposition of nickel. Thus, while such electrowinning methods are generally effective, but they require the use of separate, multiple tanks and power supplies, with a concomitant high cost in capital and operating expense.

The methods of recovering nickel in accordance with the procedures/method are illustrated in the accompanying drawings. Referring to figure 3, the electrorefining electrochemical cell 202 has an anode 200 in an anode chamber 201 and a cathode 204 in a cathode chamber 205 which may be electrically connected by a voltage source 208 and controlled by a single rectifier (not shown). The anode chamber 201 and the cathode chamber 205 are separated by a semi-permeable membrane 206 which permits the transfer of the electrolytic solution from one chamber to the other, and completes the electrical circuit. The semi-permeable membrane may be comprised of any material which permits ionic flow, but prohibits bulk or osmotic flow, between anode chamber 201 and cathode chamber 205. Preferred materials include polymers such as polysulfone, sintered glass frit, and finely powdered ceramic particles compressed between porous membranes. The cell 202 may have a drain line 214 for removing anodic slimes, including technetium oxide, which form in the anode chamber. The cell may also be equipped with a blower 212 for agitation and/or aeration of the solution.

The anode 200 is normally comprised of the metal to be recovered at the cathode 204. The nickel to be decontaminated is generally available in the form of 24 inch diameter by 18 inch high 2,200 pound ingots, which must be converted to anodes having a much higher surface area per unit weight geometry for effective electrolytic dissolution. Preferably, the electrode preparation involves a minimum amount of reprocessing, product losses and waste generation. Accordingly, contaminated anodes are preferably prepared by "shot" production or thin sheet rolling from contaminated ingots. Methods for preparing such electrode are described in U.S. Pat. No. 5,262,019. Alternatively, the contaminated anode may be in powder or bar form.

The cathode employed to evaluate the methods may be comprised of one or more materials selected from the group consisting of titanium, platinum, stainless steel, graphite and nickel. Ni is preferred.

The electrochemical cell typically operates at 40-60°C, and at a current density of about 10-300 A/ft^2 with an efficiency of about 80% or more at a cell voltage of 1-3 V/cell.

The electrochemical cell 202 may employ any suitable aqueous solution having a pH above 7 as an electrolytic solution, including for example, ammonium sulfate, ammonium chloride, ammonium hydroxide, ammonium carbonate, with ammonium sulfate being preferred. Initially, the contaminated anode may be dissolved in an acidic solution of sulfuric or hydrochloric acid, having a pH=1-3, and a temperature of 30-75°C. The amount of anion in solution is not critical, as long as there is a sufficient amount to support nickel dissolution. Preferably, the electrolyte contains from 100-250 g/L SO$_4^{2-}$, and preferably 145-245 g/L sulfate, added as H$_2$SO$_4$. Next, a balancing cation may be added to the solution in an amount sufficient to increase the pH of the electrolyte to the desired alkaline range. Preferably, the pH of the electrolyte is adjusted by adding at least one cation selected from the group consisting of ammonium, sodium, calcium with ammonium being preferred. For example, the pH of the electrolyte may be adjusted by adding sodium hydroxide, calcium hydroxide, and/or by sparging with NH$_3$ Alternatively, the contaminated anode may be placed directly in an alkaline solution

having the appropriate pH.

The alkaline electrolyte may contain 30-280 g/L Ni. Preferably, the alkaline electrolyte contains 60-130 g/L, and preferably 70-100 g/L Ni. The alkaline electrolyte may also contain up to ~30 g/L boric acid, which functions to improve the plating rate and the character of the plating deposition.

Other electrolytes, such as fluoroboric acid, fluorosilicic acid, hydrochloric acid, nitric acid and the like, and other suitable process conditions may be employed in other applications of the this method, as long as such materials and process conditions support nickel plating, are compatible with the cellular construction materials, and do not substantially increase the amount of secondary waste generated. The alkaline electrolyte may have a gross beta activity of 2000-6000 Bq/gm prior to treatment.

In the preferred application of the method depicted in figure 3, the solution is circulated within cell 202 between chambers 201 and 205. In evaluating this particular embodiment, the alkaline solution in the cathode chamber 205 may be maintained at a slighter higher pressure (1-1.2 atm), to promote flow/transfer of the alkaline solution from the cathode chamber to the anode chamber to dissolve additional contaminated nickel. The alkaline solution in electrochemical cell 202 also may be recirculated by pumps 210 which may be equipped with carbon filters (not shown) for removing organics and other particulates in the solution. In addition, a blower device 212 may be utilized for cell agitation and aeration.

Unprecipitated contaminants remain in solution, accumulating in the anolyte, which is periodically removed and treated. Any precipitated contaminant, such as TcO_2, generally reports to the anodic slimes, which may be periodically removed from the cell, treated and buried. For example, recirculating carbon beds may be placed in both the anolyte and catholyte chambers to receive hydrocarbon and radioactive contaminants. Thus, there is no requirement for any separate processing step using ion exchange means or solvent extraction to remove the radioactive contaminants, and any process step to separate the radioactive contaminants from the Ni-containing solution external to the electrochemical cell is optional. As a result, low volumes of waste are generated.

In another modification of this application substantially radioactive-free nickel is electrorefined at the cathode by controlling pH and adjusting the oxidation potential of the radioactive contaminants in a separate step, which occurs externally of the electrochemical cell. This approach is particularly effective in the removal of trace amounts of radioactive-contaminants from the nickel-containing solution prior to the deposition of nickel in the cathode chamber. In this alternative of the method which is shown in figure 7, the solution may be circulated through an external circuit from the anode chamber 201 to the cathode chamber 205 and then back to the anode chamber 201 through the membrane 206. The composition of the electrolyte solution and operating conditions of the electrolytic cell generally are as described above.

The contaminate-containing solution in the anode chamber 201 is pumped from the electrochemical cell 202 (via pump 216) in an external line 218 into a vessel 220 where the oxidation/reduction potential of the radioactive contaminants in solution may be adjusted. Preferably, the contaminate-containing solution is contacted with an oxidizing agent that oxidizes the contaminants to a valence state where the contaminants may be readily precipitated and removed from solution in later processing steps. Preferably, the radiocontaminant-containing solution is contacted with an oxidizing agent selected from the group consisting of hydrogen peroxide, ozone, oxygen gas, nitric acid-nitrous acid mixtures, and permanganate. Preferably, oxidizing agents such as peroxide and ozone are used to oxidize any Tc species in the alkaline solution to Tc (+7). Depending upon the oxidizing agent, any unreacted oxidizing agent remaining in solution after the oxidation step, may be removed to protect downstream filters and ion exchangers from possible oxidation. In those practices where ozone is employed as an oxidizing agent, air or steam is preferably employed to strip the ozone from the alkaline solution following the oxidation step. In practices where hydrogen peroxide is employed as the oxidizing agent, ion exchange "blocking" may be used to remove residual impurities.

Following the oxidation adjustment (or redox) step, the nickel-containing solution may be pumped (via pump 221) through a contaminant polishing means 222, which may consist of, for example, a filtering means and/or an ion exchange means, for removing contaminants from the solution. For example, the nickel-containing alkaline solution may be filtered through a particulate filter to separate particulates from the alkaline solution. The particles may be colloidal sized particles stemming from the contaminant metal itself (such as TcO_2) or processing contaminants such as resin fragments or the like. Preferably, the filter is a hybrid sand-powdered ion exchange resin filter. Alternatively, or in addition to the filtration step, the alkaline solution may flow through one or more ion exchangers having an anionic or mixed resin bed, for sorbing cationic technetium complexes and other radioactive/transition/actinide metal ions. Preferably, resins are employed at an operating temperature $> 60^{o}C$. Mixed ion exchangers may be employed to eliminate the effects of any localized pH variations that may occur in a pure anion column and which may be deleterious to the reaction.

Preferably, at least two ion exchangers are employed on-line in series. Each on-line ion exchanger is monitored to determine radiochemical activity breakthrough. When the first (i.e., the upstream) ion exchanger bed in tandem breaks through, it is taken off-line and regenerated while the second bed in tandem is "moved-up" to the first position and a fresh bed is installed in the second position.

If desired, after the contaminant polishing step and before the alkaline solution is reintroduced into the cathode chamber, the solution may be pumped to one or more holding tanks 224, where the contamination level/activity of the alkaline solution may be monitored so that an excessively contaminated alkaline solution is not fed into the cathode chamber. If the contaminant level or radioactivity of the alkaline solution is too high, say > 40 ppb (75 Bq/g), the alkaline solution may be recycled via a pump 228 in an external line 226 to upstream of the redox vessel. The recycled solution is returned to the

vessel 220 for adjusting its oxidation potential to assure, for example, complete oxidation of Tc to the Tc +7 species. The oxidation/reduction and contaminant polishing steps may be repeated until the desired level of contaminant has been removed. When the contaminant/activity level of the alkaline solution is considered acceptable, the nickel-containing alkaline solution may be reintroduced to the cathode chamber of the electrorefining electrochemical cell.

3) Experimental Data

A solution containing about 90 g/L of Ni and 5.4 mg/L of U was plated under the operating conditions set forth in Table 1. Results are set forth in Table 2.

During Experiments 1 and 2, which were conducted in an acidic electrolyte, the seed cathode surfaces were passivated by oxidation when the cathodes were removed from the bath to establish the weight gain, rendering the cathodes substantially inoperable for additional runs. Electrode passivation did not occur during Experiments 3 and 4 which were conducted in an alkaline electrolyte. As the data for Experiments 3 and 4 indicates, over 99% of the Ni was recovered by cathodic deposition in an alkaline electrolyte. The purity of the recovered Ni was not analyzed.

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                   TABLE 1
_____
TEST CONDITIONS
NUMBER      ANODE       CATHODE     pH
_____
1           GRAPHITE    STAINLESS   ACIDIC
2           INERT       NICKEL      ACIDIC
3           GRAPHITE    STAINLESS   BASIC
4           INERT       NICKEL      BASIC
_____


              TABLE 2
_____
RESULTS
BASIC TESTING - EXPERIMENTS 3 AND 4
          U     Ni        EFF.    NITRATE
          mG/L  mG/L      %       G/L
_____
TEST 3    5.4   24        99.5    157
TEST 4    5.4   12.5      99.8    194
_____
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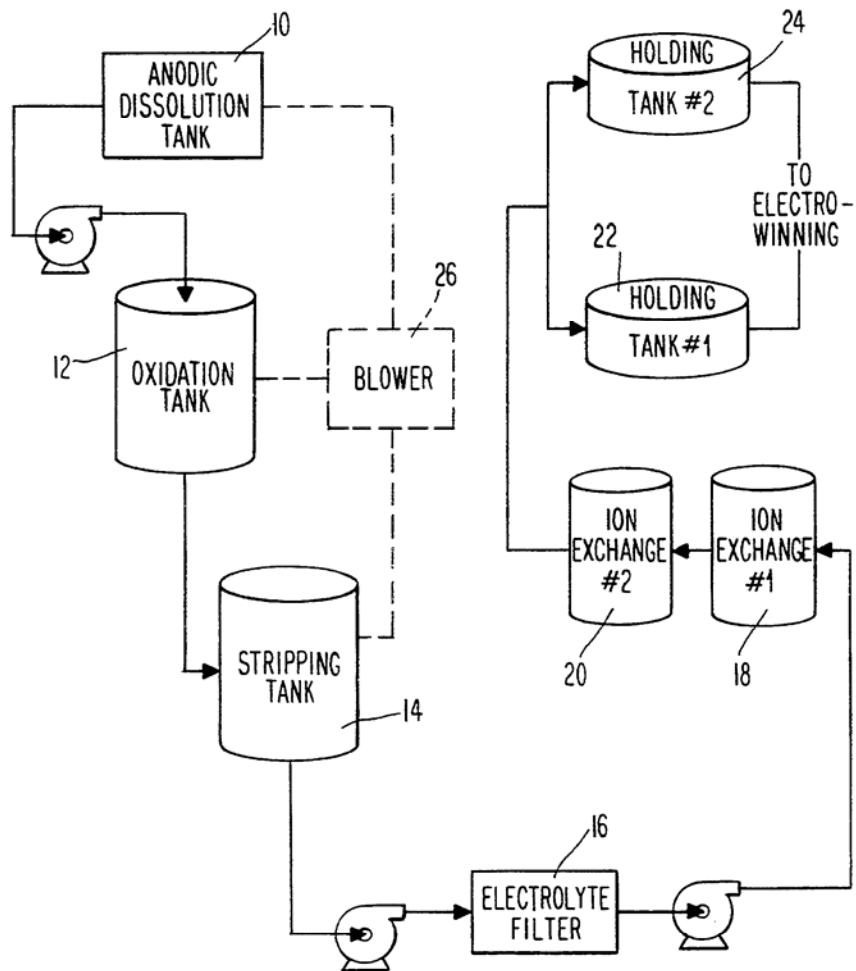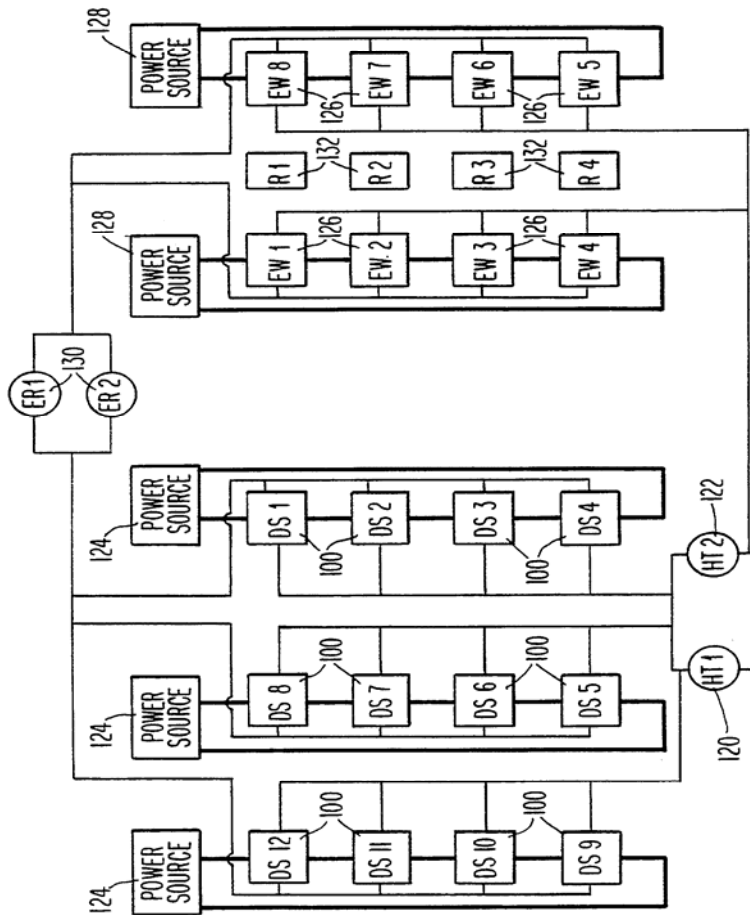
Fig.1

Figure 1. A schematic representation of a dissolution system for practicing an electrowinning process to plate nickel;

Figure 2. A schematic representation of a plant layout for practicing an electrowinning process to plate nickel, using a series of dissolution systems depicted in FIG. 1.
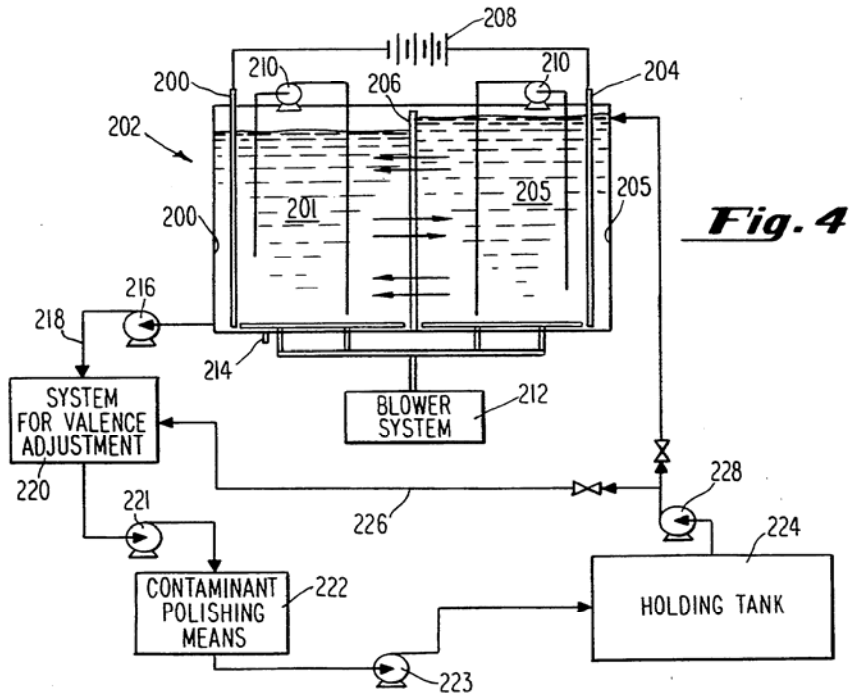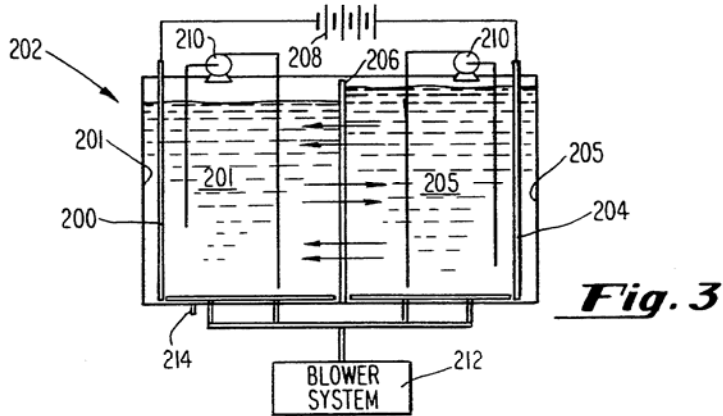
Figure 3. A schematic representation of an apparatus and an abbreviated flow diagram of an embodiment of the process employed in the practice of the present invention, and FIG. 4 is a schematic representation of an apparatus and an abbreviated flow diagram for an alternate embodiment of the process employed in the practice of the present invention.

G) US 5,487,748: Method for removal of technetium from radio-contaminated metal (10)

1) Chemistry

To best understand the electrolytic separation of Ni and Tc, the oxidation/reduction potentials of those elements should be considered. In an acidic solution, Tc exists predominantly in a heptavalent form, as pertechnetate ions (TcO_4^-), and Ni exists as Ni^{2+}. The reduction of these ions to the metallic state is governed by the following half reactions:

$$TcO_4^- + 8H^+ + 7e^- \Leftrightarrow Tc + 4H_2O \qquad\qquad E^o = 0.477V$$

$$Ni^{2+} + 2e^- \Leftrightarrow Ni \qquad\qquad E^o = -0.250V$$

The magnitude of the standard potential indicates the driving force of the reaction to proceed from left to right. Therefore, the pertechnetate ions are more readily reduced to the metallic state than are the nickel ions. Additionally, the standard potentials indicate that metallic Ni will act as a strong reducing agent with respect to pertechnetate ions. Combining the two foregoing half-reaction equations yields the following reaction:

$$TcO_4^- + 16H^+ + 7Ni \Leftrightarrow 7Ni^{2+} + 2Tc + 8H_2O \qquad\qquad \Delta E^o = 0.727 \ V$$

The equilibrium constant for the foregoing reaction can be determined from the Nernst equation:

$$\Delta E = \Delta E^o - (0.059/n) \log [Ni^{2+}]^7 / [H^+]^{16} [TcO_4^-]^2$$

wherein n is the number of electrons (14 in this case) transferred. At equilibrium, de=0, and the equilibrium constant can be expressed as:

$$k = [Ni^{2+}]^7 / [H^+]^{16} [TcO_4^-]^2$$

$$\Delta E^o = (0.059/n) \log k$$

$$\log k = n \Delta E^o / 0.059$$

$$k = 10^{(n \Delta Eo/0.059)}$$

$$k = 10^{(14*0.727/0.059)} = 3.22 * 10^{172}$$

$$[TcO_4^-] = ([Ni^{2+}]^{7/3.22} \times 10^{172} [H^+]^{16})^{1/2}$$

In a typical sulfate-based electrolyte, the Ni concentration would be about 1 M and the

pH would be about 4 ($[H^+] = 0.0001$ M). This yields a pertechnetate concentration of $5.5\text{x}10^{-55}$ M. Thus, for all practical purposes the displacement reaction can be considered to go to completion, such that the removal of technetium is quantitative.

The level of Tc contamination in feedstock nickel is typically 0.3 ppm, which is approximately 1 g Tc for every 3300 kg of feedstock Ni. In the displacement reaction, 2 moles Tc are reduced for every 7 moles Ni oxidized; to reduce 1 g Tc, therefore, 2 g of Ni would be dissolved.

Since the displacement reaction tends to encapsulate the reducing metal, it is beneficial to use a powder, or other high surface area medium, to maximize the surface area and, in turn, Tc loading on the metal. In metal-displacement reactions, the metal ion subjected to reduction forms a metallic layer approximately 0.25 micron thick before the reaction ceases, due to encapsulation of the base metal. Powdered nickel is widely available in a range of particle sizes, with 5 microns being typical. Assuming a spherical geometry, this provides, as a conservative estimate, a surface area of 1348 cm^2/g. A 0.25 micron coating of Tc deposited over the calculated surface area translates to approximately 0.4 g of Tc reduced per gram of powdered Ni. Since approximately 2 g Ni are oxidized to reduce 1 g Tc, this indicates that the nickel will be almost completely displaced by Tc.

2) Experimental Data

Distilled water, with a pH of 3 and having an initial activity of $3.9\text{x}10^3$ Bq/ml due to the presence of Tc 99 as ammonium pertechnetate, is contacted with 5 g/l of activated nickel powder. The resultant solution, at 25°C, is agitated for 20 minutes to allow sufficient solid-liquid contact for the heterogeneous displacement reaction to proceed. After an additional period of 20 minutes, the solution is settled and the clear solution is decanted. It is found to have an activity of 16 Bq/ml, representing a technetium removal of 99.2%. Allowing the reaction to proceed for a full hour produces an activity level of 7 Bq/ml, representing 99.8% removal.

An acid solution (pH = 2), containing 5.25 g/l of Ni, as $NiSO_4$, and having an initial activity of $0.935\text{x}10^3$ Bq/ml due to the presence of Tc 99 as ammonium pertechnetate ions, is contacted with 5 g/l of activated Ni powder. The resultant solution, at 25°C, is agitated for 20 minutes to allow sufficient solid-liquid contacting for the heterogeneous displacement reaction to proceed. After an additional period of 20 minutes, the solution is settled and the clear solution is decanted. It is found to have an activity of 5.1 Bq/ml, indicating that 99.43% of the Tc has been removed.

3) Process Flow

Figure 1 shows a single cell, generally designated by the numeral 1, suitable to use in carrying out an electrorefining process embodying the present invention. Although the decontamination of radio-contaminated nickel is specifically discussed, it will be appreciated that the system illustrated is suitable for carrying out a wide range of decontamination reactions, within the scope of the instant invention.

The depicted cell 1 is divided into cathodic and anodic compartments 3 and 2, respectively, by a semi-permeable membrane 6, which may consist of a chemically impervious cloth. The radio-contaminated metal (e.g., Ni) is employed as the anode 4, which is electrolytically dissolved in a sulfuric acid-based electrolyte contained in the anodic compartment 2. The electrolyte for nickel decontamination will typically comprise 50-100 g/L of Ni ion, 65-120 g/L of sulfate radical, an effective amount (generally up to 40 g/L) of boric acid as a plating agent, and optionally up to 50 g/L of chloride ion. The pH of the electrolyte will normally be maintained between 1 and 4; a pH value of about 1.5 will generally be optimal in the absence of chloride in the electrolyte, and a pH of 3.0 will generally be optimal if chloride ion is present in significant concentrations. The cell will normally be operated at a solution temperature maintained between 20°C, and 80°C, with 60°C often producing the best results.

Anolyte is transferred from the anodic compartment 2 by way of line 8 and pump 9, through a filter 11 to remove particulates, and then through a bed 13 of Ni powder, where the pertechnetate ions are reduced to the metallic state. The solution then passes through a second filter 16 to remove any suspended matter, which may include nickel powder carried over from the bed 13. A fraction of the treated solution is returned to the anodic compartment 2 through line 17, with the balance flowing through line 14 to the cathodic compartment 3. In this manner Tc is removed from the anolyte solution on a continuous basis.

The portion of the anolyte solution diverted to the cathodic compartment 3 through line 14 serves to maintain the desired nickel concentration therein, while also maintaining the solution level above the level in the anodic compartment 2. This forces the electrolyte to flow from the cathodic compartment 3 to the anodic compartment 2 through the semi-permeable membrane 6, due to the resultant hydrostatic pressure differential. Because the anolyte diverted to the cathodic compartment has been subjected to the metal displacement reaction in bed 13, and because hydrostatic pressure prevents flow from the anodic chamber 2 to the cathodic chamber 3, the technetium concentration in the catolyte will be maintained at a very low level (e.g., below 10 Bq/ml). The flow of treated anolyte is so proportioned as to maintain the Ni concentration in the cathodic compartment 3 sufficiently high for effective nickel deposition on the cathode 5, which will desirably be of seed nickel or stainless steel construction. Ni deposited from the catolyte will normally have an activity below 17 Bq/g, and U and other actinides will not codeposit due to their low reduction potentials; rather they will accumulate in the electrolyte. Drainage for maintenance and cleaning of the cell may be affected through line 15.

The cell is operated under steady or pulsating direct current, delivered to the electrodes 4 and 5 from the power supply 7, usually at a level of 2 to 6, and preferably 3, volts.

Current density will normally be maintained at 50-250 A/ft^2.

The system will usually be so designed that the liquid will be subjected to intimate contact with the treating metal for a period of about 10-30 minutes, so as to allow the displacement reaction to approach equilibrium concentrations. Initially, it may be necessary or desirable to activate the metal surface by acid flushing, such as with concentrated sulfuric acid or sulfurous acid, as taught in U.S. Pat. No. 3,117,000 (12). Particles of any powder employed will generally have a diameter of 2 microns or larger; it is believed however that 5 micron particle will to afford almost complete utilization of the base metal for the displacement reaction, while at the same time minimizing the difficulties that would be encountered in the handling of ultra-fine powders.
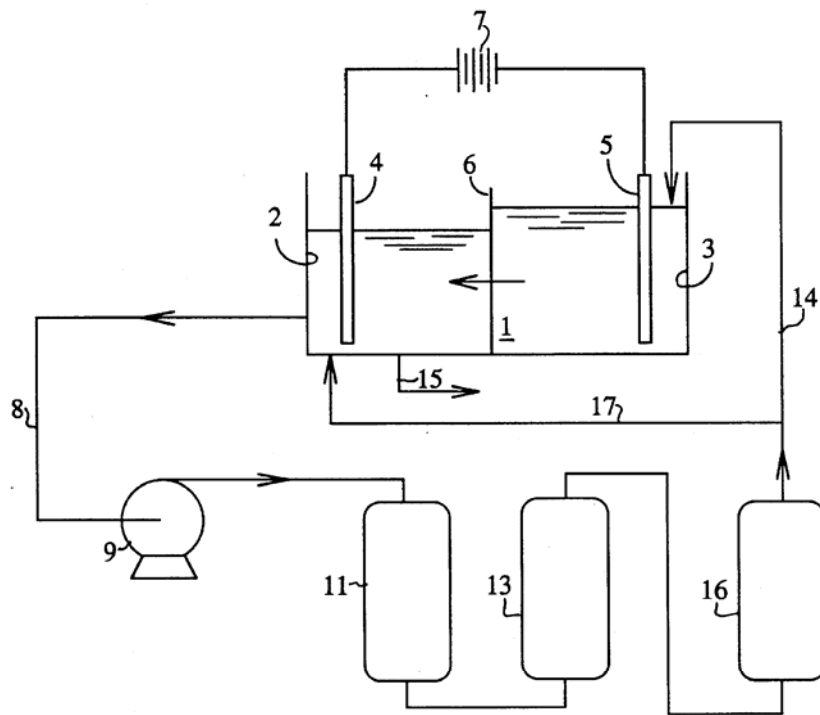
FIG. 1

Figure 1. The process flow diagram for the decontamination of Ni.