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**EVALUATION OF THE ELECTROREFINING TECHNIQUE
FOR THE PROCESSING OF RADIOACTIVE SCRAP METALS**

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Abstract

This report presents the results of a literature study performed to identify applications of the electrorefining technique to the decontamination of radioactively-contaminated scrap metals (RSM). Upon the completion of the literature search and the review of numerous references, it was concluded that there were applications of this technique that were appropriate for the decontamination of some types of RSM, especially when the desired product is a pure elemental metal of high purity. It was also concluded that this technique was not well-suited for the decontamination of RSM stainless steels and other alloys, when it was desired that the metallurgical characteristics of the alloy be present in the decontaminated product.

Summary

One of the most significant activities in the WINCO Metal Recycle program is the evaluation of processing techniques for the decontamination of radioactively-contaminated scrap metals (RSM). Of special interest are surface and volume decontamination techniques that do not employ aqueous solutions. The volume decontamination techniques include electrorefining, a technique that may be performed at room temperature or high temperature, depending upon the application.

Included among the metals for which this technology has been demonstrated are metals that have applications in the nuclear industry: Al, Cu, Pb, Ni and Zr. Separation of these metals from radioactive contamination has not been demonstrated but should be possible. The Hoopes, Pechiney and ALAG-Neuhausen processes are all mature technologies for the purification of Al. Investigations into the adaptation of one, or all three, of these techniques should be straightforward. The decontamination of RSM Cu, Ni, Pb, and Zr by electrorefining should also be investigated. The technologies associated with the purification of these metals by electrorefining are also mature; adaptation of the techniques applied to the purification of these metals should be developed for the purification of RSM. This technique is not applicable to the processing of alloys, such as cast and stainless steels, when it is desired that the decontaminated product possess the metallurgical properties of the starting material.

During any future RSM electrorefining studies, one of the major concerns will probably be adsorbed contaminants (from the cell electrolyte) on the purified materials. Recontamination of the surface of the electrodeposited metals will result in the incorporation of contamination into the purified metal product (as metal is deposited over surface contaminated metal). In all likelihood it will be necessary to develop divided cells for these applications.

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Introduction

One of the most significant activities in the WINCO Metal Recycle program is the evaluation of processing techniques for the decontamination of radioactively-contaminated scrap metals (RSM). Of special interest are surface and volume decontamination techniques that do not employ aqueous solutions. The volume decontamination techniques are melt refining, slagging decontamination, and electrorefining.^a The first two are high temperature techniques during which the contaminated material is melted; electrorefining may be performed at near-room temperature or at high temperatures, depending upon the application.

Decontamination during melt refining takes place because one or more components of the melt are immiscible in the melt and are subsequently removed by pouring off one fraction of the melt, or because one or more components of the melt are volatile and evaporate. Slagging decontamination employs a solution of additives that remove the undesirable component(s) by selective dissolution. Addition of this solution may result in a separation due to precipitation of the additive and unwanted components, or due to the formation of an immiscible liquid that is subsequently separated from the melt by pouring off one fraction. During electrorefining, an electrical potential is used to preferentially abstract one component (a component may be a pure element or an alloy) from the contaminated material by plating it out onto one electrode of an electrochemical cell.

High purity metals are commonly produced by electrorefining and other techniques that remove the metal to be purified (an abundant component) from a mixture or solution. Melt refining and slagging decontamination remove the contaminants (less abundant components) from a mixture or solution and produce products of lower purity than electrorefining.^b It follows, therefore, that electrorefining has little or no application in the processing of alloys (such as stainless steel and carbon steel) when it is desired that the product retain the metallurgical properties of the starting material. As these alloys are best processed by melt refining and slagging decontamination, the electrorefining of steel will not be discussed further.

a. Electrorefining may be performed with aqueous or non-aqueous electrolytes at a variety of temperatures that depend on the electrolyte.

b. Because the product of electrorefining is of such high purity, the starting materials must also be quite pure. Quite often melt refining is utilized as a pretreatment technique to produce material of adequate purity for electrorefining.

The Electrorefining Technique

The Chemistry of Electrorefining

The net chemical reaction occurring during the electrorefining process may be represented by the generalized expression in (1), where M(s, contaminated) is the solid, impure metal^c contaminated with radionuclides and M(s, pure) is the solid, purified metal produced from the contaminated metal by electrorefining.

The actual reactions that are summed together to produce the net reaction are often complex and specific to the metal being purified; however, a general description of the overall process is presented in the following paragraphs.

The electrorefining separation is possible because the desired product can be preferentially oxidized and abstracted from the impurities, transported through the electrolyte solution, and subsequently deposited as a purified material. An electric potential provides the driving force to form the products.^d The production of a pure metal by this technique is known as electrodeposition. This process requires that the metal (or alloy) to be purified act as the anode of the electrochemical cell and that the purified metal be deposited on a solid or liquid cathode; the solid cathode is either an alloy, such as stainless steel, that will not react with the deposited material, or the pure metal. Electrical contact of the cell electrodes is provided by an electrolyte solution through which the metal ions are transported; energy to oxidize, transport, and reduce the metal is provided to the cell from a power supply in an external circuit. During room temperature applications, the electrolyte is commonly an aqueous solution that contains the cations of the metal(s) to be purified and is maintained at constant pH or ionic strength. During high temperature electrorefining, the molten salt is quite often a binary or ternary halide salt and includes the metal to be purified as one of the metal halide components of the salt.

The anode and cathode reactions may be described by the generalized expressions (2) and (3), respectively, where e^- is an electron and M^{x+} (in solution) is a metal ion of valence $x +$ in an electrolyte solvent (the molten salt or aqueous electrolyte solution).

c. For the purposes of this report, the term "metal" is meant to denote pure, metallic elements.

d. The electrorefining process is not generally a spontaneous reaction; therefore, work has to be done to overcome the positive Gibbs free energy change for the overall reaction.

The Electrorefining Cell: Description and Operation

The cell, a simplified version of which is shown in Figure 1, generally consists of: (a) a chamber that contains the electrolyte, (b) an anode, which is commonly the material to be purified and is present either as molten material (during high temperature electrorefining) or as solids, and (c) the cathode, which is generally a mandrill of Mo, W, or stainless steel that is immersed into the electrolyte. During high temperature electrorefining, the cell volume above the electrolyte is purged and filled with an inert gas prior to operation. The cell is also fitted with temperature control and monitoring systems, as well as gas inlet/outlet systems.

The performance of the cell is dependent on a variety of operational parameters that include: cell current, cell voltage, purity of starting materials, purity of purge gases, deposition voltages of the various components of the solution, and composition of the electrolyte solution.

Cell current and voltage are chosen to produce the desired product of the desired purity. Because the electrodeposition rate of purified metal is proportional to the current passing through the cell,¹ electrorefining is usually performed in a constant current mode, with the voltage varying with changes in the cell resistance. This operational mode results in a constant deposition rate and a product of fairly uniform purity. When all other factors are held constant, higher current usually produces a product of lower purity, as compared to a lower current, because of contaminant trapping in the electrodeposited product.

The voltage is chosen based on the desired product, and is chosen after experimental investigation. The voltage at which a metal is deposited depends upon the metal, the contaminants and the molten salt. Reduction potentials for aqueous electrochemistry are tabulated for reversible electrode reactions occurring under ideal conditions; however, for a molten salt cell, different molten salt mixtures may lead to different reduction potentials. The result of this phenomenon is that the relative voltages for two metals may be different in different molten salts and/or at different temperatures.^e It follows, therefore, that the molten salt and cell temperature must be carefully chosen so that the reduction potentials of the desired product and undesirable components are different enough to allow adequate separation.

e. An example is the reduction of Zr^{4+} to $Zr(\text{s})$ as compared to the reduction of Ti^{2+} to $Ti(\text{s})$. In a LiCl-KCl eutectic at 732 K, the reduction voltage of the Ti couple is 0.067 volts more positive than the Zr couple; in a 50% NaCl-50% KCl mixture at 973 K, the Ti couple is 0.088 volts more negative than the Zr couple. This result exemplifies the difficulties inherent in molten salt electrorefining. (data from J. C. Sehra et al., *Transactions of the SAEST*, 22(4), p. 223, 1987).

The molten salt in the high temperature process is also chosen for operational ease. Viscosities and corrosivities are among the important considerations addressed during the selection of the molten salt, with the chemistry of the components of the mixture to be separated being of paramount importance.

The starting materials often are pretreated to remove oxide coatings or other surface contaminants that lead to impurities in the product. Usually, the purge gas (for high temperature cells) is free of oxygen and nitrogen because these two impurities lead to embrittlement of the metallic products (due to dissolution of oxygen and/or nitrogen that results in the formation of metal oxide and/or nitride phases in the deposited material).

Lastly, selectivity is of great importance. Optimum operation of the electrorefining cell is dependent on the selectivity of the oxidation and reduction processes occurring at the anode and cathode, respectively. The ideal cell will remove metal from the impure anode at the same rate as it deposits purified metal at the cathode. A consequence of this optimum condition is an essentially constant concentration of that metal ion in the electrolyte. Codeposition of impurities by reduction at the cathode occurs when a component of the electrolyte is more easily reduced (reduces from an ion to an atom at a lower voltage) than the desired metal ion; this condition may limit the selectivity of the electrorefining process for some mixtures. As described above, these problems may often be alleviated by a judicious choice of electrolyte.

Electrorefining as Compared to Other Techniques

The application of electrorefining to the decontamination of RSM is a logical extension of this technology; melt refining has already been adapted and demonstrated for the decontamination of alloys when a high degree of purity is not necessary. The melt refining technique is not, however, well suited for the production of high purity materials because even when the distribution coefficient for separation of the impurity is high, it is still very difficult to quantitatively remove trace impurities from a solution

Electrorefining is utilized for the production of high purity metals, when greater than 99 weight % (w/o) purity is desired. It is well suited for this application because the most abundant component in the impure material is being removed, leaving behind a mixture that is less abundant in the desired material. It is common to recover up to 90-plus w/o of the desired material by electrorefining, with the product usually greater than 99 w/o pure.

Applications of Electrorefining^f

Electrorefining has been applied to a variety of scrap metal recovery problems. One common application is the recovery of scrap material produced during manufacturing. The starting materials might include lathe turnings, casting skull, and a variety of scraps of random sizes and shapes produced during cutting and shaping activities. Among the metals recoverable by this technique^g are aluminum,^{2,3} beryllium,⁴ copper,^{5,6} gold,⁷ lead,⁸ molybdenum,⁹ plutonium,¹⁰ silver,¹¹ Ni,¹² Ni and Co in superalloy^{13,14} (to recover them as a binary alloy), titanium,¹⁵ uranium,¹⁶ vanadium,¹⁷ and zirconium,^{18,19} from zircaloy scrap. Of these, only the processing of those metals and alloys of interest as candidates for RSM recycle will be addressed in more detail.

Aluminum

Aluminum is commonly-used structural material because of its high strength, low density, and its resistance to corrosion in air. Its applications in the nuclear industry have been primarily as a structural material and as a cladding for nuclear reactor fuel. There is presently an estimated 195,000 tons of RSM Al at Department of Energy facilities that will be available for recycling, valued at \$115 million (based on the nominal 1990-91 value of \$600/ton for uncontaminated Al);²⁰ the gaseous diffusion plants (GDPs) at Oak Ridge, TN, Paducah, KY, and Portsmouth, OH will be among the largest contributors to the RSM Al inventory in the DOE complex. Decontamination of this material would lead to its reuse, as opposed to its burial in a waste repository.

Aluminum is an excellent candidate for recycling by electrorefining. Aluminum can be produced, in varying purities, by processes based on four electrolytic processes: the Hall-Heroult process, the Hoopes process, the Pechiney process, and the AIAG-Neuhausen process; aluminum produced by these processes have maximum purities of 99.9%, 99.98%, greater than 99.99%, and greater than 99.9%, by weight, respectively.

The Hall-Heroult process, and processes based on it, are essentially the only widely used smelting processes for the production of Al(s). The starting material for this process is alumina produced from bauxite ore by the Bayer process. The alumina is loaded into an electrolytic cell that has carbon (graphite) anode electrodes, a

f. The references cited for the applications of electrorefining include chemical systems that utilize aqueous electrolytes. These cells operate at considerably lower temperatures than the molten salt electrolyte cells. The references cited do not include all of the literature identified; they merely include a representative sample of the literature on this topic.

g. The metals listed are not the only metals that may be processed by this technique; this is merely a representative sample. It is likely that many other alkali, alkaline earth, d-transition and f-transition metals could be refined by this technique, depending on the contaminants present with the metal to be purified.

carbon (graphite) housing that acts as the cathode, and a molten salt electrolyte that is a solution of 5-7 w/o CaF_2 , 5-7 w/o AlF_3 , and 0-7 w/o LiF , with the balance cryolite Na_3AlF_6 . Joule heating from the passage of current through the cell keeps the molten salt within its limits of operation, 1213 - 1253 K. During operation, the alumina dissolves in the molten salt, $\text{O}_2(\text{g})$ is liberated from the solution at the anode (and consumes the anode to produce $\text{CO}_2(\text{g})$ which exits the cell), and $\text{Al}(\text{l})$ is formed at the bottom of the melt on the cathode.²¹

The Hoopes process was the first of the three subsequently developed processes designed to produce higher purity Al than the Hall-Heroult process. The starting material for the Hoopes process is an Al alloy (usually with Cu), which contacts a carbon electrode and acts as the anode, a molten salt electrolyte of fluoride salts of Na, Al, and Ba that also contains 7 w/o or less Al_2O_3 , and a graphite cathode that contacts the product, $\text{Al}(\text{l})$. As current passes through the cell, the aluminum in the anode alloy is oxidized and passes into the electrolyte, as the $\text{Al}^{3+}(\text{l})$ species in the melt are reduced at the cathode to form $\text{Al}(\text{l})$, which floats on the surface of the molten salt because of its low density. Cell temperatures are usually in the range 1223 - 1273 K, and while the voltage of the cell is moderate, at 5 - 7 volts, it is not uncommon for the cell to operate at currents of 20 kiloamperes (kA).²²

The Pechiney and AIAG-Neuhausen processes are quite similar to the Hoopes process. The Pechiney process employs a mixed fluoride-chloride molten salt and operates at temperatures near 1025 K; the AIAG-Neuhausen process employs a fluoride molten salt electrolyte and operates at temperatures near 1015 K. Both furnaces are lined with magnesia brick. Their advantages over the Hall-Heroult process are lower operational temperatures and higher product purity; the AIAG-Neuhausen process also has the additional advantage of lower power consumption.²³

Within the last two decades, laboratory-scale investigations have addressed the recycle of scrap aluminum contaminated with a variety of elements. Singleton and Sullivan²⁴ recovered 99.9 w/o pure Al (an average of the results of 16 experiments) from electronic equipment scrap materials that were 69.69 w/o Al with 19.98 w/o Cu and lesser amounts of Pb, Sn, Ag, and Au. The impure (anode) materials were first consolidated into an ingot by melting and loaded into the cell (which was of a similar design to that in Figure 1), where they resided in the bottom of the refining cell because of their density, which was greater than that of the molten salt. The molten salt electrolyte was 60 w/o BaCl_2 , 17 w/o NaF , and 23 w/o AlF_3 . The refined aluminum floated to the top of the electrolyte because of its low density and was subsequently removed at the conclusion of each experiment.

Pemsler and coworkers²⁵ more recently addressed the purification of Al scrap Materials. Their experimental setup was slightly different from that of Singleton and Sullivan. In the Pemsler investigations, a cell with two anodes suspended from

the top of the cell on either side, and adjacent to the cathode, was utilized. The anode was Alcoa alloy 380.^h The molten salt used during these experiments was NaAlCl_4 . The mean Al purity over three experiments was 99.97 w/o.

The primary source of RSM Al is probably the GDPs and it is expected that this material would probably be contaminated with U and Hg.ⁱ The removal of Hg from the RSM Al should be relatively straightforward, whether it is removed prior to electrorefining or during the electrorefining process. Mercury present as surface contamination could be easily removed by chemical techniques; however, such preprocessing is probably not necessary. The mercury halides all have low decomposition and/or boiling points; the most refractory is HgF_2 , which decomposes at 918 K.²⁶ This temperature is well below the normal operating temperatures of Al electrorefining cells, so it is likely that most of the Hg would be collected in the cell offgas system.

The removal of U will occur during the electrorefining process. The potential for the oxidation of U^{3+} to U(s) , in a LiCl-KCl eutectic at temperatures near 700 K, is about -1.2 volts,²⁷ which is about 0.562 volts more positive than the Al^{3+} - Al(s) couple in the same solvent system.²⁸ The result will be that the Al in an Al-U mixture can be separated from the U contamination by electrorefining, with Al(s) collected at the cathode of the cell.

Copper

Copper is another candidate for electrorefining. It is widely used as an electrical conductor in a variety of applications throughout industry, including the nuclear industry. It is estimated that DOE holds title 38,000 tons of RSM Cu, valued at an estimated \$57 million (based on the nominal 1990-91 value of \$1500/ton for uncontaminated Cu).²⁹

The copper electrorefining method is a well understood, mature technology, and should be very applicable to the separation of Cu(s) from a variety of radionuclide contaminants. During the mass production of Cu, electrorefining is a widely-used method of refining Cu. In this process, the impure copper is introduced to the electrorefining cell as the anode, a Cu-alloy, with contaminants including Zn, Ni, Se and Te, depending on the source. The electrolyte in this cell is aqueous sulfuric acid-copper sulfate solution. The copper is deposited onto high purity copper sheets that act as the cathode. These electrolytic cells generally operate at 0.2 - 0.4 volts and 175 - 230 amperes/meter². Generally, the cathodic deposits are

h. The elemental composition of Alcoa alloy 380 is: 83.81 w/o Al, 8.08 w/o Si, 3.17 w/o Cu, 2.88 w/o Zn, 0.90 w/o Fe, 0.54 w/o Ni, 0.48 w/o Mn and 0.14 w/o Ti. (from Pernsler et al., "Electrorefining of Aluminum," from Energy Reduction Techniques in Metal Electrochemical Processes, The Metallurgical Society/AIME, Warrendale, PA, 1985)

i. The Hg contamination is present because Hg has been used in the pumping systems of the GDPs.

dendritic in nature and can include considerable amounts of electrolyte material in the occlusions. To remove these contaminants, the electrolytic deposition is often performed with additives blended into the molten salt that cause the elimination of most major surface imperfections.^{30,31}

While it is not known what the primary contaminants in RSM Cu are, it is likely that Cu used at a reprocessing facility would be contaminated with fission products and actinides, which would include the metals Cs, Sr, Pu, U, Nb, Mo, and Ni. The standard reduction potentials for these metals (in aqueous solution) are each more negative than that of Cu; therefore, they are more easily oxidized than Cu.³² For surface contamination, some of this material is probably present as oxides, the balance as metals. Both the metals and metal oxides can be removed, prior to electrorefining, by chemical treatment or electropolishing. The volume contamination dissolved from the anode could be removed from the anolyte by precipitation or separated by complexing the contaminant in the anolyte subsequent to dissolution.

Nickel

Radioactively contaminated nickel is another metal that is a candidate for electrorefining decontamination. There is an estimated 245,000 tons of RSM Ni available in the DOE complex with an estimated value of \$1.47 billion (based on a nominal 1990-91 market value of \$6000/ton).³³ Nickel metal is produced by a variety of techniques; the choice of processing technique is a function of the desired purity of the product. The highest purity material is produced by the carbonyl and electrorefining processes (exceeding 99.9 w/o Ni).

The electrorefining process involves the use of a divided cell, with an aqueous electrolyte solution. In the divided cell, the cathode is protected from direct contact with the electrolyte solution by a porous diaphragm that protects it from insoluble materials in the cell (anode sludge) and decreases the rate of codeposition of contaminant metals.³⁴

The electrolyte is recirculated through a purification loop to remove soluble contaminants, such as ferrous ion (it is first oxidized to ferric ion) and $\text{Cr}^{3+}(\text{aq})$, by precipitation with NaOH prior to its contacting the cathode; precipitation and complexing techniques could also be used to remove radionuclide contaminants as well. The draw-off point for the recirculation loop is near the anode; the purified anolyte returns to the cell at the cathode, where the Ni is abstracted. The solution then passes through the porous membrane in to the anode region. One possible electrolyte might be a hydrochloric acid/sulfuric acid/boric acid mixture of pH 1, with a $\text{Ni}^{2+}(\text{aq})$ concentration of about 0.75 M. The anode residues can subsequently be processed to abstract metals of value.³⁵

The major sources of contaminated Ni are expected to be the GDPs. This material would be contaminated with Hg and U. The removal of Hg would be easily performed without pretreatment as the reduction potential of the Hg^{2+}/Hg couple is more positive than that of the Ni^{2+}/Ni couple,³⁶ and the Hg is not removed from the anode during electrorefining.

Surface contaminant U could be removed by a chemical treatment (or electropolishing) prior to the electrorefining process. Uranium present as volume contamination could be removed from the anolyte during the purification process described above.

Lead

Lead metal has been extensively used throughout DOE nuclear research and production for personnel shielding. At the Idaho National Engineering Laboratory (INEL) alone, there is an estimated 2800 tons of radioactively-contaminated lead metal. Of this amount, about 500 tons is considered excess.³⁷ While there are not extensive applications for decontaminated lead (except in the battery industry), removal of the radionuclides would result in the conversion of the RSM lead from a mixed-hazardous waste to a hazardous waste and alleviate some of the obstacles associated with waste disposal.

Lead has traditionally been refined by smelting; however, electrorefining has been investigated for the recycling of Pb from scrap batteries because of the environmental concerns related to pyrometallurgical processing of Pb. The electrorefining process purified lead by cathodically depositing Pb of purity 99.6 - 99.9-plus w/o Pb onto high purity Pb electrodes. The anodes were formed by melting battery wastes that included Pb, sludge, plastic and rubber. The major metallic contaminants in the anode feed material were As (about 2 w/o) and Sb (about 4.5 w/o). The electrolyte was prepared from PbO(s) , $\text{H}_2\text{SiF}_6(\text{aq})$, and $\text{H}_2\text{O(l)}$, and the cell was operated at 308 K; the resulting solution was 0.34 M in $\text{Pb}^{2+}(\text{aq})$ and 0.62 M in $\text{H}_2\text{SiF}_6(\text{aq})$. To promote the growth of cathodic deposits with smooth surfaces, bone gelatin and calcium lignin sulfonate were added.³⁸

As is the case during most electrorefining processes, the $\text{Pb}^{2+}(\text{aq})$ concentration remained essentially constant throughout each experiment. The cell operated at 0.27 - 0.30 volts at current densities of 170 A/m². The product purity, 99.6 w/o Pb or better, is pure enough for a variety of applications in the battery industry, including maintenance-free batteries.³⁹

The types of radionuclides to be found in RSM Pb from the INEL should include Cs, Sr and Co. Surface contaminants can be removed during preprocessing by electropolishing or other chemical means. During the electrorefining process, removal of contaminants can be accomplished by treating the anolyte with

complexants (to change the activity of the metal ions, thus prohibiting them from depositing on the cathode) or by precipitation from the anolyte during a purification step as was described for Ni.

Zirconium

Zirconium metal is widely used as a fuel cladding material as a component of various Zircaloy alloys. While there probably is not a large amount of RSM Zr present at DOE facilities in the form of structural materials, there is a considerable amount of Zircaloy present in both irradiated and unirradiated reactor fuel assemblies. Reclamation of the Zr present in these fuels would reduce significantly the volume of material that would be deposited in a high level waste repository if zircaloy-clad fuels were ultimately dispositioned to such a facility.

High purity Zr is often produced by the Kroll process, in which Zr metal is chlorinated, followed by reduction of the $ZrCl_4$ product by $Mg(s)$. The mixture is subsequently distilled to remove $MgCl_2$ and residual $Mg(s)$. Electrorefining has been investigated as an alternative to the Kroll process for the processing of zircaloy scrap and offgrade Kroll process product. For these investigations, molten salts have been utilized as the electrorefining cell electrolyte. Electrolyte solutions, deposition voltages, and operating temperatures, included: NaCl with 6.0 w/o K_2ZrF_6 at 0.2-0.7 volts and 1103 K;⁴⁰ NaCl with 31 w/o K_2ZrF_6 at less than 8 volts and 1123 K; and NaCl with 7.8-8.3 w/o NaF and 7.8-8.3 w/o $ZrCl_4$ at 1.2 volts and 1123 K.^{41,42} Zirconium recovery efficiencies were 87%, 60% and 60%, respectively, for these processing conditions.

This technique could have promise for the decladding of spent reactor fuels. During such an operation, the cladding would be preferentially removed from U metal fuels, leaving the U. For UO_2 fuels, it is also expected that decladding should be possible. Other radionuclides expected to be present in uranium fuel include Cs, Sr, Pu, Nb, Mo, and Ni. Many of these trace components (as compared to the masses of the U and Zr in zircaloy-clad fuels) will likely have reduction potentials such that they will not codeposit with Zr during a decladding operation.

Conclusions

Electrorefining is a well-known process for producing high purity metals; the product is generally of higher purity than the products from melt refining or slagging decontamination. As it is likely that high purity of product will be of paramount importance when processing RSM metals, electrorefining would probably be preferred to either of these techniques when recovering pure metals.

j. No voltage was specified; however, the power supply was an 8 volt, 300 A direct current supply.

Included among the metals for which this technology has been demonstrated are metals that have applications in the nuclear industry: Al, Cu, Pb, Ni and Zr. Separation of these metals from radioactive contamination has not been demonstrated but should be possible. The Hoopes, Pechiney and AIAG-Neuhausen processes are all mature technologies for the purification of Al. Investigations into the adaptation of one, or all three, of these techniques should be straightforward. The decontamination of RSM Cu, Ni, Pb, and Zr by electrorefining should also be investigated. The technologies associated with the purification of these metals by electrorefining are also a mature; adaptation of the techniques applied to the purification of these metals should be developed for the purification of RSM.

During any future RSM electrorefining studies, one of the major concerns will probably be adsorbed contaminants (from the cell electrolyte) on the purified materials. Recontamination of the surface of the electrodeposited metals will result in the incorporation of contamination into the purified metal product (as metal is deposited over surface contaminated metal). In all likelihood it will be necessary to develop divided cells for these applications.

Recommendations

It is recommended that the electrorefining decontamination of RSM be investigated. The investigation should address both economic and technical considerations of RSM electrorefining. Such a program might be organized as follows.

1. Cost-benefits analyses to elucidate the economic aspects of this decontamination method as compared to other methods. (These analyses would be based on the application of the already published techniques to RSM).
2. Market analyses to identify demand for decontaminated RSM and products fabricated from RSM.
3. Experimental, laboratory-scale testing to demonstrate the applicability of this technique for the decontamination of RSM Al, Cu, Ni, Pb and Zr; the purpose of this activity would be to produce data to support process flowsheet development. (These activities would be based on the nonradioactive studies published in the literature. Also, non-aqueous electrorefining processes should be investigated for the decontamination of RSM Cu, Ni, and Pb, as the published work addresses only the aqueous electrolyte process for purifying these metals.)
4. Further cost-benefit analyses to identify the cost effectiveness of the technique after the initial experimental testing has identified technically feasible process flowsheets.

(a) cell chamber and insulation, (b) anode, (c) cathode,
 (d) impure metal, (e) electrolyte, (f) purified metal,
 (g) monitoring ports/gas inlet/outlet, (h) cathode
 connection to power supply, (i) anode connection
 to power supply

Figure 1

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