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Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, Illinois 60439

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ELECTROMETALLURGICAL TREATMENT OF ALUMINUM-BASED FUELS

James L. Willit, A. G. Raraz, S. A. Slater, W. E. Miller, E. C. Gay, J. J. Laidler
Argonne National Laboratory
Chemical Technology Division
9700 South Cass Ave.
Argonne, IL 60439

Background

The U.S. Department of Energy faces a dilemma concerning spent aluminum-matrix reactor fuel. Over the next forty years, 128 metric tons of spent aluminum-matrix fuel will be shipped to the Savannah River Site from U.S. and foreign research reactors. When originally fabricated, this fuel contained over 55 metric tons of uranium at an average enrichment of approximately 20%. Some of this fuel is now corroding in wet storage and must be stabilized. In the past, this fuel would be processed in the Savannah River canyons. However, these facilities will be decommissioned in 2005 under current planning.

In 1996 a task team was formed to recommend to the Department of Energy a technical strategy for the treatment, packaging, and disposal of aluminum-based spent nuclear fuel. The final report was issued in June 1996. Electrometallurgical treatment was the recommended advanced technology backup option for fuel disposition. To a great degree, adapting electrometallurgical treatment to aluminum-based fuels builds on the experience gained in adapting electrometallurgical treatment to treat N-reactor fuel, Single-Pass Reactor (SPR) fuel, oxide fuel, and Molten Salt Reactor Experiment (MSRE) fuel and flush salt.

The task team viewed electrometallurgical treatment favorably for several reasons. The first reason was that it greatly reduces the amount of high level waste since aluminum and uranium are separated from the spent fuel. The high level waste that arises from electrometallurgical treatment of the spent fuel is oxidized to allow incorporation into high-level defense waste glass at the Defense Waste Processing Facility (DWPF) at Savannah River. Many of the electrometallurgical process steps proposed for treating aluminum-based fuel have already been demonstrated with other types of spent fuel. Therefore, electrometallurgical treatment's advanced state of development in treating other types of spent fuel also

contributed to a favorable review of this technology as applied to aluminum-based fuel.

Electrometallurgical Process Flowsheet

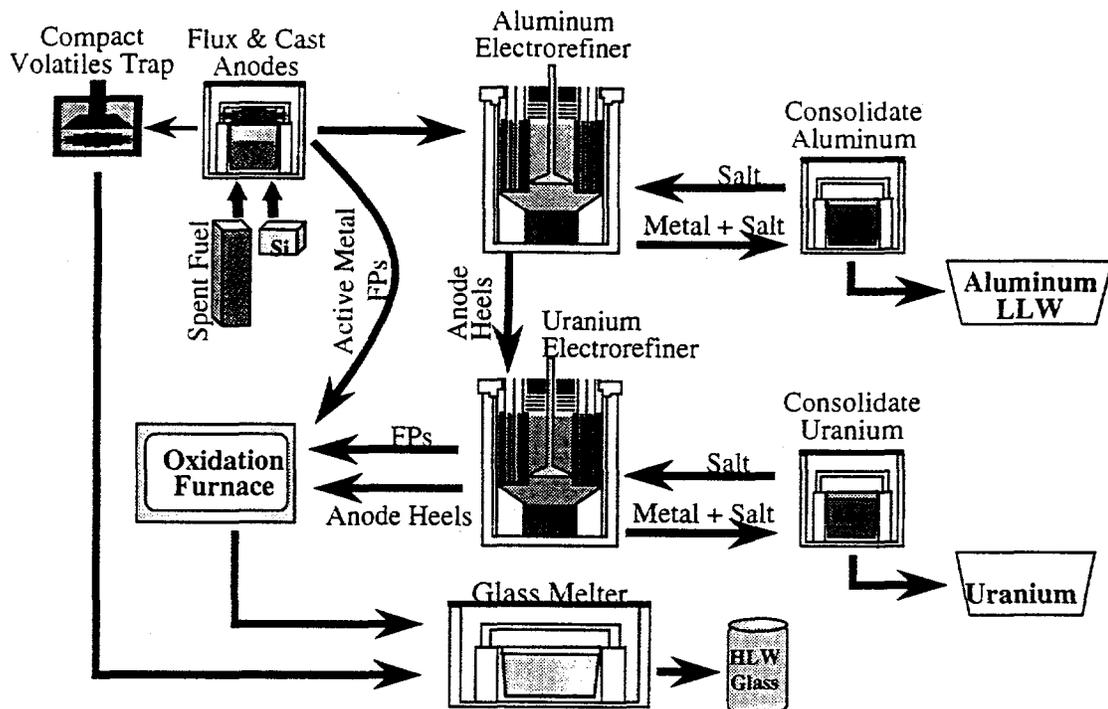
A diagram of the electrometallurgical (EM) process is shown in Figure 1. Because the molten salts used in the process are sensitive to oxygen and water, the entire process will be performed in an inert atmosphere enclosure located in a shielded facility. The inert atmosphere enclosure will have oxygen, nitrogen, and water levels in the ppm range. The process operations can be grouped into three types of operations: (1) head end steps, (2) electrorefining and consolidation steps, and (3) oxidation and glass-forming steps.

Head End Steps

Sort and compact fuel, melt and cast anodes

In the first head end step the fuel assembly end hardware is removed; the fuel is sorted, and then compacted. Next the fuel is melted in an enclosed tilt-pour furnace beneath a molten salt flux. Thermodynamics calculations predict that the rare earth fission products will be extracted into a $\text{LiF-K}_3\text{AlF}_6\text{-AlF}_3$ flux salt. Plutonium and uranium, on the other hand will remain in the molten aluminum phase. The advantage of using a salt flux is that the active metal fission products can be extracted from the spent fuel at this stage. Without a flux salt, the rare earth and active metal fission products would accumulate in the aluminum electrorefiner. It would be necessary then either to discard the salt or to separate the active metal fission products from the electrorefiner salt. Our works also shows that if the rare earths are oxidized into the electrorefiner salt they contaminate the electrorefined aluminum product.

Because silicon forms very stable intermetallic compounds with uranium and enhances the separation of aluminum and uranium, silicon is added to the molten fuel at this point. The molten fuel is cast into shapes that will form anodes in the next (electrorefining) step of the process. In the



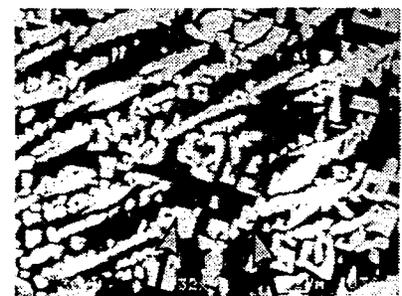
melting step the volatile fission products (cesium, rubidium, bromine, and iodine) will vaporize. These volatile species will be trapped in a fibrous aluminosilicate (fiberfrax) trap above the molten metal. A similar trapping method to trap volatile metals, iodine and bromine was employed in the ANL Melt Refining Process and successfully trapped 100% of the cesium and sodium.¹ After casting the anodes, the trap material is compressed and added to a glass melter at the end of the process. Because the entire process is conducted in an inert enclosure, the xenon and krypton fission gases can be trapped in cryogenic traps as part of the purification system of the inert atmosphere enclosure. Figure 2 shows an SEM image of a U-Al-Si ingot. The composition and temperature program used to melt the components together was selected to obtain a $U(Al, Si)_3$ phase in an aluminum matrix.

Electrorefining and Consolidation Steps

The process has two electrorefining steps, aluminum electrorefining and uranium electrorefining. In the first step, aluminum is collected on a cathode. The alkaline earth fission products accumulate in the electrolyte of the aluminum electrorefiner and the actinides, rare earths, and noble metals remain in the anode. In the second step uranium is collected on a

cathode. The rare earth and transuranic fission products accumulate in the electrolyte of the uranium electrorefiner and the noble metal fission products remain in the anode.

Both the aluminum and uranium electrorefiners are a high throughput design that has been developed at ANL². The anodes are mounted in a circular array and rotate in the channel between two cylindrical cathodes. Dendritic uranium



$U(Al, Si)_3$

Al matrix

Figure 2 Scanning electron photomicrograph of the U-Al-Si alloy used in electrorefining experiments.

or aluminum deposits at the cathode and then is scraped off the cathode by scrapers attached to the anode baskets. The dendrites then sink to the bottom of the electrorefiner where they are collected. When all the aluminum or uranium has been electrorefined out of the anodes, the current is turned off, the dendrites are compressed, and the dendrites are removed from the electrorefiner.

Consolidate dendrites

Because there will be some salt adhering to the dendritic aluminum and uranium electrorefiner product, a melting step is necessary to coalesce the aluminum and uranium into a single metal. Because the melting point of the salt is below that of aluminum and uranium, the salt can be poured off after cooling the melt below the melting point of aluminum yet above the melting point of the salt. The salt is then returned to the respective electrorefiner and the consolidated aluminum or uranium ingots can be disposed of as low-level waste or sold to fuel fabricators.

Periodic salt scrubbing

Over time there will be a buildup of transuranic element (TRU) chlorides in the uranium electrorefiner. If left unaddressed, eventually this buildup will result in an undesirable carryover into the electrorefiner product. Thus it will be necessary to periodically scrub these metal chlorides from the salt or discard the salt. Salt scrubbing is the preferred choice because it will allow a single batch of salt to be used in each electrorefiner for the entire campaign. Several different approaches are available for this periodic scrubbing including chemical reduction, and nitride or oxide.

Oxidation and Glass Forming Steps

Oxidize uranium electrorefiner anode heels and scrubbed fission products

The scrubbed alkaline earths, rare earths, and TRUs are then converted to oxides along with the metal that remains in the anode after uranium electrorefining. The operation is similar to an oxidation performed at ANL in the past.¹ The conversion is performed in an air oxidation furnace. The output from the furnace is an oxide powder with noble metal fines dispersed throughout the oxide.

Melt fission product oxides and fabricate waste glass

A small glass melter will be used to melt the oxide powder from the oxidation furnace, together with the compressed aluminosilicate trap and additional glass formers. The intent is to formulate a glass within the specifications of the Defense Waste Processing Facility (DWPF) glass. A concerted effort has been made to minimize waste volumes throughout the process by adding only glass forming oxides (fibrous aluminosilicate) and silicon, which is converted to silica in the oxidation furnace. Alumina and silica are components of DWPF glass. The glass can then be poured into DWPF waste canisters that will later be bundled into a waste package.

Experimental Results

Because many of the proposed process steps have been demonstrated, this paper will focus on those steps that have not yet been demonstrated, namely aluminum electrorefining and fluxing the molten fuel alloy to remove the active metal and rare earth metal fission products.

Electrorefining U-Al-Si alloy

To date we have performed several laboratory-scale studies in which the anode feed alloy was a U(32.4 wt%)-Al(59.8 wt%)-Si(7.8 wt%) alloy. Scanning electron

Table 1. Experimental results from stirring test. Cathode data refers to analysis of cathode product. Anode data refers to analysis of anode material remaining at the end of the experiment

Test	Sample	Al (wt%)	U (wt%)	Si (wt%)
UAL-11	cathode	96.1	2.64	1.26
(no stirring)	anode	--	--	--
UAL-13	cathode	93.05	5.67	1.28
(no stirring)	anode	6.02	80.12	13.86
UAL-14	cathode	97.92	<0.05	2.03
(with stirring)	anode	3.09	82.94	13.97

microscopy revealed that the alloy is comprised of a $U(AlSi)_3$ phase imbedded in an aluminum metal matrix. The two phases are shown in Figure 2.

It is clear from this picture that most of the aluminum that is electrotransported is from the aluminum matrix. The balance of the aluminum must be extracted from the $U(AlSi)_3$ phase of the alloy.

Table 1 shows test results from some U-Al-Si alloy electrorefining experiments that highlight the effect of stirring the cell during the experiment. These tests were conducted with a constant cathode vs. anode voltage of -0.20 V. The cathode data refers to analysis of the cathode deposits for that particular experiment. The anode data refers to analysis of the anode material that is remaining at the end of the experiment. From this table it is clear that a stirred cell results in a lower uranium concentration in the electrorefined aluminum product.

Another series of tests was conducted to examine the uranium concentration in the aluminum product as a function of the fraction of aluminum removed from the alloy. It was expected that the uranium concentration in the aluminum product would slightly increase as more aluminum is removed from the alloy. The results from this test are shown in Table 2.

Table 2 Purity of cathode product vs. charge passed.

Cathode Sample	Charge Passed (A-hrs)	Deposit Composition (wt %)
1	2.33	Al: 99.93 Si: 0.062 U: 0.003
2	10.56	Al: 99.93 Si: 0.053 U: 0.016

Fluxing molten alloy to remove active metal and rare earth metal fission products

Equilibrium thermodynamics calculations predict that the alkali metal and alkaline earth metal fission products will be oxidized into the salt of the

aluminum electrorefiner. Fortunately, these fission products should not contaminate the aluminum product. These calculations also predict that the rare earth metal fission products will likewise be oxidized into the salt of the aluminum electrorefiner. However, the rare earth metal fluorides will be reduced back to metals at the cathode because they form very stable intermetallic compounds with aluminum.

Therefore, in order to verify the prediction that the rare earth metals will co-deposit with aluminum we added yttrium, strontium, neodymium, samarium, lanthanum, and calcium fluorides to the molten salt in the cell and electrorefined a sample of U-Al-Si alloy. Analysis of the product confirmed that metals did not co-deposit with aluminum at the cathode and that the active metals, calcium and strontium did not deposit at the cathode whereas detectable amounts of yttrium, neodymium, samarium, and lanthanum were all present in the cathode deposit.

Scale-up of Aluminum Electrorefining

Because aluminum is such a light metal, an aluminum electrorefiner will require 3000 Amp-hrs of charge to refine 1 kg of aluminum. Therefore a high-throughput electrorefiner will be needed to handle large amounts of spent

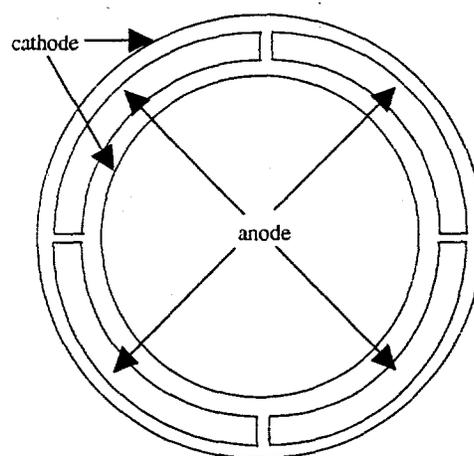


Figure 1. Cross section diagram of high-throughput electrorefiner.

fuel. The scaled-up aluminum electrorefiner will be similar to the high-throughput uranium electrorefiner developed at ANL. A simplified top view of the electrorefiner is shown in Figure 3. The anodes are mounted in a circular array and rotated in the channel between two cylindrical cathodes. Dendritic aluminum deposits at the cathode. The dendrites are scraped off the cathode by scrapers attached to the anode baskets. The

dendrites then sink to the bottom of the electrorefiner where they are collected. When all the aluminum has been electrorefined out of the anodes, the current is turned off, the dendrites are compressed, and the dendrites are removed from the electrorefiner.

Concluding Remarks

We have successfully demonstrated aluminum electrorefining from a U-Al-Si alloy that simulates spent aluminum-based reactor fuel. The aluminum product contains less than 200 ppm uranium. All the results obtained have been in agreement with predictions based on equilibrium thermodynamics. We have also demonstrated the need for adequate stirring to achieve a low-uranium product.

Most of the other process steps have been demonstrated in other programs. These include uranium electrorefining, transuranic fission product scrubbing, fission product oxidation, and product consolidation by melting. Future work will focus on the extraction of active metal and rare earth fission products by a molten flux salt and scale-up of the aluminum electrorefining.

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- ² E. Gay, W. Miller, and J. Laidler, "Proposed High Throughput Electrorefining Treatment of Spent N-Reactor Fuel," Proceedings of Spring 1996 American Nuclear Society Meeting, Reno, NV.