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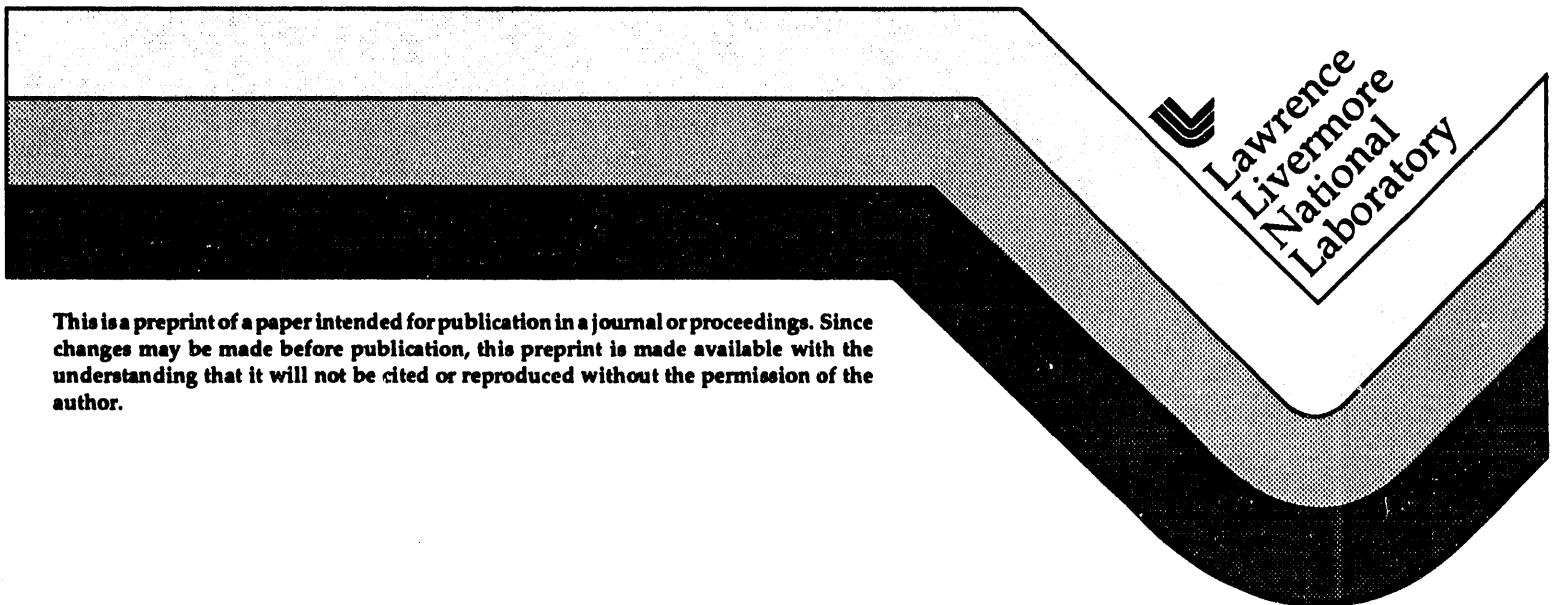
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## Pyrochemical Salt Scrub

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## **PYROCHEMICAL SALT SCRUB**

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### **Abstract**

**A pyrochemical salt scrub process for calcium chloride based salts, that eliminates the waste generated during aqueous processing and the associated chloride corrosion problem, is being developed and tested at Lawrence Livermore National Laboratory. In the scrub process, calcium metal is used to reduce the actinide chlorides present in residue pyrochemical salts to a metal product, called a metal button. The metal button can be stored, converted to an oxide for storage, recycled, or further refined using aqueous processing to separate the plutonium from the americium, if plutonium recovery is required. It has been determined that a calcium titration of molten salt extraction and electrorefining residue salts can be used to determine reaction completion and to prevent the addition of excess calcium to the process. An automated calcium feeder and associated control system have been designed and built to monitor the salt scrub process and to determine when calcium metal should be fed.**

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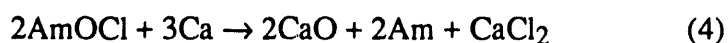
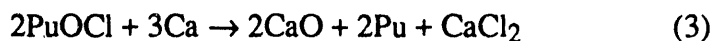
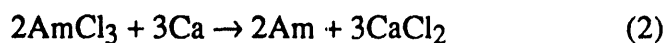
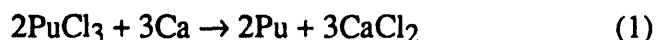
## Introduction

A residue salt containing actinide chlorides is produced during the molten salt extraction (MSE) and electrorefining (ER) pyrochemical processes. The MSE and ER residue salts contain a substantial amount of plutonium, and the MSE residue salt also contains a relatively high quantity of americium. Aqueous processing is an accepted method for processing the residue salts to recover the actinides; however, aqueous treatment of this salt to meet disposal criteria can generate up to 3 kg of grouted waste per kilogram of plutonium feed. A pyrochemical salt scrub process for calcium chloride (CaCl<sub>2</sub>) based salts, that eliminates the waste generated during aqueous processing, and the associated chloride corrosion problem, is being developed and tested at Lawrence Livermore National Laboratory (LLNL). Successful deployment of the pyrochemical salt scrub process into a future weapons production complex (Complex-21) will reduce the waste volume associated with aqueous processing by approximately 50%, will reduce transuranic (TRU) waste by 20%, and will eliminate the chloride recovery area required for aqueous processing. The construction cost could be reduced by as much as \$42M, and annual operating costs up to \$4.3M.

The pyrochemical salt scrub process can also be used to recover the remains of depleted uranium present in magnesium fluoride salt produced during the reduction of uranium fluoride to metal. A scrub alloy metal would be used to reduce uranium fluoride and uranium oxide compounds to uranium metal. The cleaned salt could be discarded as low level waste and the uranium metal could be reused.

## Chemistry

X-ray diffraction analysis shows that MSE residue salts contain actinide chlorides (PuCl<sub>3</sub> and AmCl<sub>3</sub>), actinide oxychlorides (PuOCl and AmOCl) and plutonium oxide (PuO<sub>2</sub>) (1). Residue ER salts analyzed by x-ray diffraction contain measurable quantities of PuCl<sub>3</sub>, PuOCl, and PuO<sub>2</sub> (2). In the pyrochemical salt scrub process shown in Figure 1, calcium metal is used to reduce the actinide chloride salts and PuO<sub>2</sub> to metal by the following, thermodynamically favorable reactions:



An americium-plutonium-calcium metal button is produced during the MSE salt scrub process, and a plutonium-calcium metal button is produced during the ER salt scrub process. Americium is an intense emitter of gamma radiation. In metal form this radiation is attenuated; therefore, radiation exposure to personnel is minimized because the MSE salt scrub product button is metallic. The metal button can be stored, converted to an oxide for

storage, or further refined using aqueous processing to separate the plutonium from the americium, if plutonium recovery is required. The metal button produced during the ER salt scrub process can be recycled back through ER processing. The cleaned salt can be recycled back through MSE and ER, or can be stored as TRU waste.

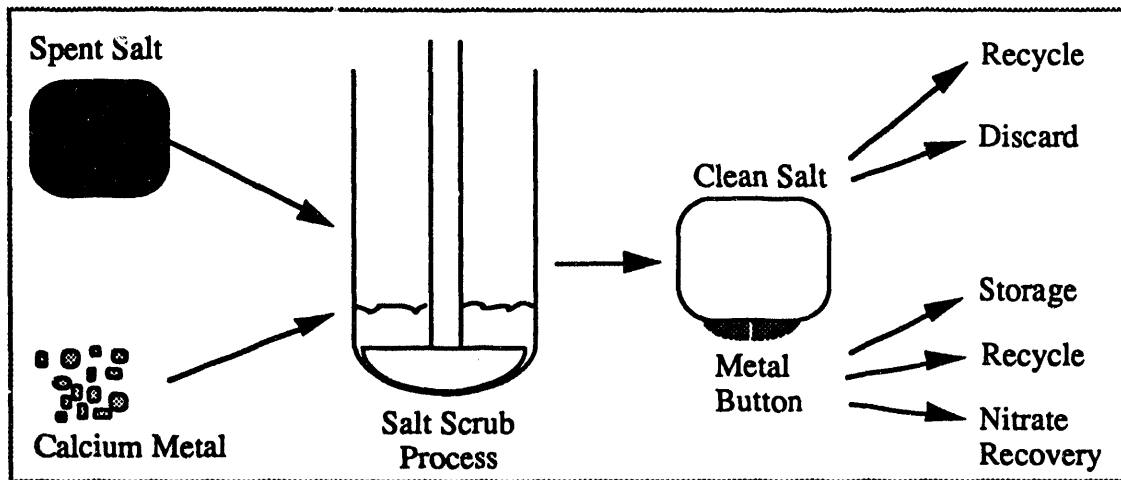


Figure 1. Pyrochemical salt scrub process.

#### Process Description

At LLNL, two different solvent salts have been used for MSE -- eutectic KCl - 74 mole percentage CaCl<sub>2</sub> (627°C melting point), and pure CaCl<sub>2</sub> (782°C melting point). Because the melting temperature of calcium metal is 839°C, all tests were conducted at a temperature between 850 and 950°C to ensure that the salt and calcium were molten. All experimental work was conducted in stationary furnaces located in high purity (less than 1 ppm O<sub>2</sub> or H<sub>2</sub>O), argon glove boxes. Tantalum flat or opposed-pitch dual propeller paddles were used to stir the molten materials at a rate of 200 - 400 rpm. Magnesium oxide (MgO) ceramic crucibles were used for the reactor vessel. As much as 4 kg of residue salt can be easily processed per batch run.

The process steps include adding the black colored residue salt to the MgO crucible, loading the crucible into the stationary furnace, melting the salt, stirring, and adding the calcium in approximately 10 g increments. The calcium is incrementally added to prevent thermal shock and failure of the crucible resulting from the exothermic reactions (equations 1-5). After the calcium is added, the crucible is allowed to cool. The crucible containing the frozen salt and metal is removed from the furnace. The crucible is broken away from the salt and metal, and the heavy, metal button is split from the lighter, scrubbed salt.

#### Results

Since January 1989, LLNL has processed approximately 27 kg of residue MSE and ER salt using the pyrochemical salt scrub process, from which more than 6 kg of actinides were recovered. The americium concentration in the metal buttons ranged from 8 to 22 weight percent. All the salt met TRU waste discard limits. The scrub efficiency ranged from 91.2 to

99.8 weight percent actinides recovered. The lower efficiency runs occurred when there was less than 50 g of actinides initially present in the residue salt. With small quantities of actinides, a molten metal pool is not produced that provides a mechanism to coalesce metal droplets. Starting the process with a pool of metal, or scrubbing with a zinc-magnesium (Zn-Mg) scrub alloy should improve the actinide recovery of the lower actinide concentrated residue salts. The Zn-Mg alloy has been shown to be effective for scavenging residual plutonium metal out of residue direct oxide reduction (DOR) salts to form an intermetallic compound (3).

In initial salt scrub tests, a calculated quantity of calcium was added to each batch run. The calcium addition was calculated with the assumption that all the actinides were chloride compounds (equations 1 and 2). An additional 10% calcium was added to the stoichiometric quantity to ensure reaction completion. However, it is difficult to accurately determine the quantity of actinides in residue salts. MSE residue salts are concentrated in americium that generates high radiation fields that the analytical laboratory at LLNL is not equipped to handle. Additionally, MSE and ER salts are inhomogeneous and extracting a sample representative of the entire salt cake was not possible; therefore, the salts were analyzed nondestructively by calorimetry and isotopic measurements. The actinide values generated by this method are often in error due to metal shot being dispersed throughout the salt (i.e., inhomogeneity of the actinides) (4). The initial calcium addition produced a 10 to 15°C temperature spike due to the exothermic reaction of producing  $\text{CaCl}_2$ . The temperature was allowed to stabilize before another calcium addition was added. This process was continued until all the predetermined quantity of calcium was added.

More than 10% excess calcium was being added to each run because some of the plutonium in the salt was already metal shot (i.e., not all the plutonium and americium were present as chlorides). This procedure increased the residue stream, excessively contaminated the product metal, and left unreacted calcium metal that had to be separated from the salt before it could be discarded. It was determined that a more accurate quantity of calcium could be added by monitoring the temperature change of the exothermic reaction. A typical temperature profile of a salt scrub process is shown in Figure 2. With each 10g increment of calcium, the increase in temperature is less until finally there is no increase. There is often a decrease in temperature with the last calcium addition because the calcium is cold (room temperature) compared to the molten salt.

This calcium titration, with the endpoint based on the temperature of the mixture, proved to be effective in the salt scrub process. The salts no longer had to be analyzed for actinide concentration, thus decreasing hands-on operations, total processing time, and potential radiation exposure. To eliminate the need for manual addition of calcium, an automated calcium feeder and associated control system have been designed, manufactured, and are presently undergoing testing.

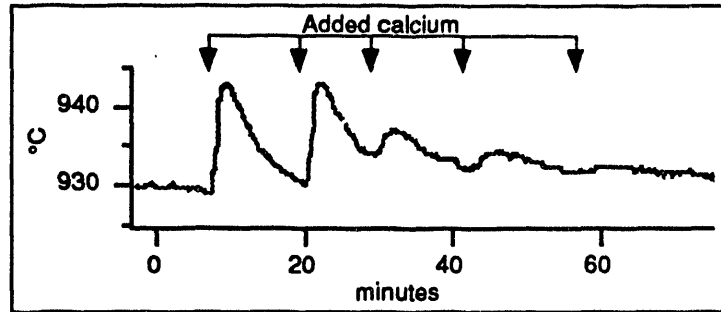


Figure 2. Temperature profile of salt scrub process.

### Calcium Titration

A schematic of the calcium feeder is shown in Figure 3. The feeder/titrator has been designed to fit onto the top of a stationary furnace head typically used throughout the Department of Energy (DOE) Complex for pyrochemical processing operations; however, it could be easily adapted for use with most furnaces. The hopper and piston assembly are constructed of stainless steel and viton gaskets. A 24 VDC solenoid is used to actuate the piston.

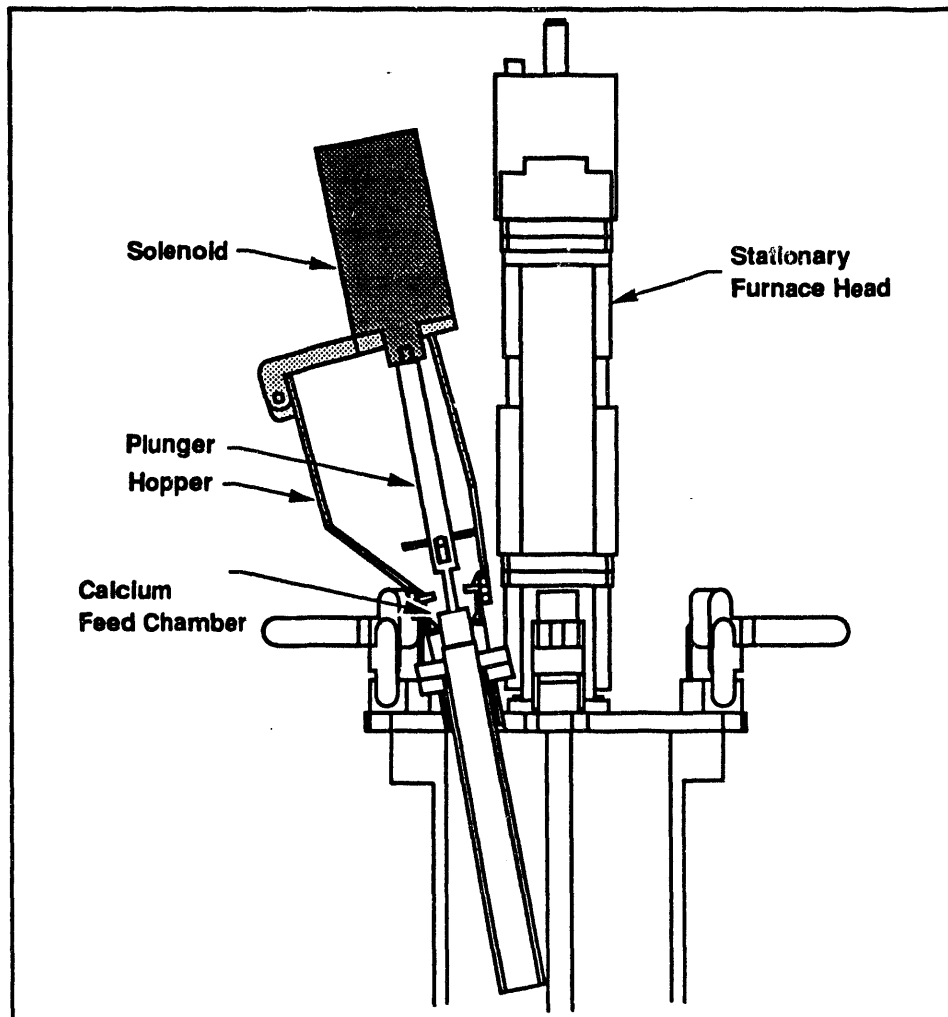


Figure 3. Calcium feeder schematic.

The control system for the calcium titration is shown in Figure 4. A personal computer measures the molten salt temperature, operates the feeder, and regulates the set point of the Micristar (Research, Inc., Minneapolis, Minnesota) temperature controller. The data flow is managed through a program written in LabVIEW™ (National Instruments Corp., Austin, Texas) operating on a Macintosh personal computer. The program is based on a While Loop that runs until the titration endpoint is detected or the user clicks a STOP button.

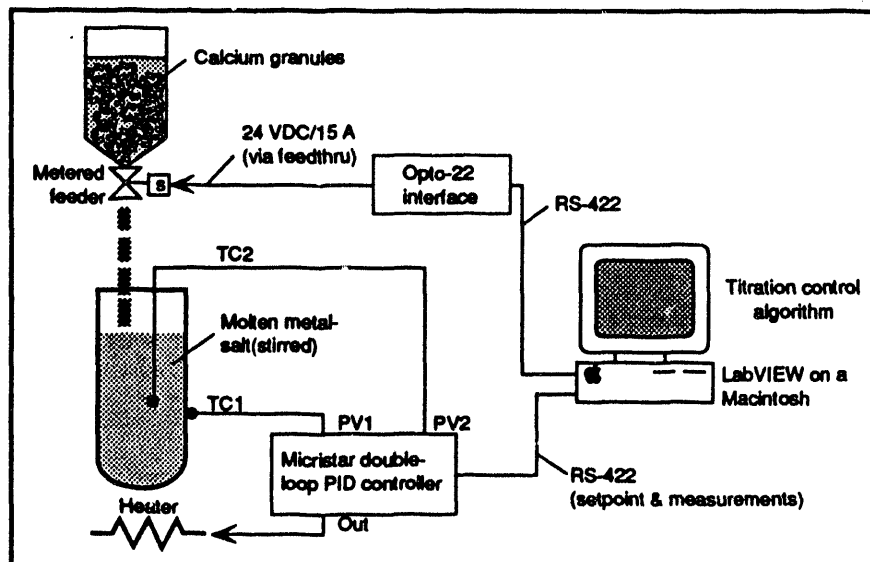


Figure 4. Calcium titration control system.

The computer sends commands to and receives data from the Micristar temperature controller through an RS-422 serial interface. One channel of the Micristar controls the furnace temperature, while the other measures the salt temperature. A LLNL developed control algorithm analyzes the temperature of the salt and metal mixture in real time, looking for indications that an exothermic reaction is happening. Control of the solenoid actuator is through Opto-22 (Opto22 Corporation, Huntington Beach, California) interface modules.

After the residue MSE or ER salt is molten, an initial calcium addition is made. The temperature will increase due to the exothermic reaction. The temperature is measured over time, and the control algorithm determines when to feed calcium again. A second calcium addition is made when the temperature is at steady state. This process continues until there is no longer a temperature increase upon calcium addition. The algorithm determines that the titration is complete, the operator is notified, and the program stops.

Operational status, current data, and user controls appear on the computer screen as shown in Figure 5. Controls are available to change display attributes such as the channels being displayed and the update interval. During a run, all measurements are stored in a tab-delimited text file with time stamps for loading and analyzing with almost any application. Another LabVIEW™ program is available for post-run plotting. A separate run log-file contains information entered by the operator and a running list of control algorithm status

messages. This file can be viewed and edited with a word processor and printed out for a permanent record of the run.

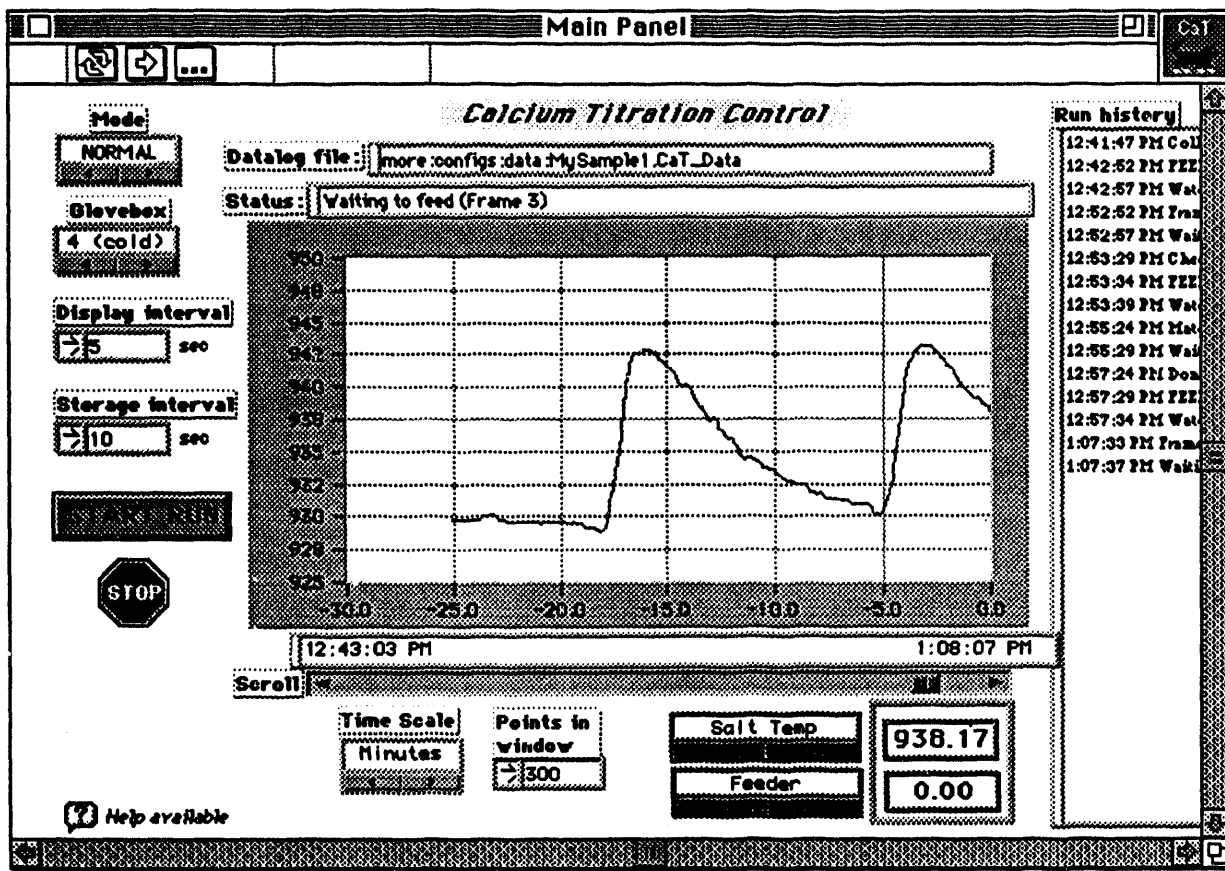


Figure 5. Main panel of LabVIEW control program.

By monitoring the temperature and regulating the addition of calcium, the temperature spikes are controlled thus eliminating thermal shock to the crucible. Additionally, excess calcium is not required to assure reaction completion. A reduction in radiation exposure to the operator will also be realized because the addition of calcium to the furnace is automated, and assay of the residue salts before processing is not required. Preliminary tests have resulted in automated operations that were comparable to manual operations.

### Summary

The development of a pyrochemical salt scrub process for recovering actinides from residue MSE and ER salt is ongoing at LLNL. In initial salt scrub tests, a calculated quantity of calcium was added to each batch run. Because some of the actinides were present as metal rather than chlorides, an excess quantity of calcium was added. By monitoring the temperature of the exothermic reaction of calcium metal with the actinide chlorides, the addition of excess calcium has been eliminated. An automated calcium feeder and associated control system have been designed and built. The control system monitors the process and automatically feeds calcium to the molten salt mixture. The calcium titration endpoint is determined when there is no longer an increase in process temperature after calcium metal is

fed. The calcium titration system is presently undergoing testing. Test results have shown that the automated operations are comparable to those obtained manually.

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