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AFCT/TFCT/ISFS PROGRAM

TECHNICAL PROGRESS REPORT FOR THE PERIOD JULY 1, 1978 - SEPTEMBER 30, 1978

COMPILED BY
O. F. Hill

September 1978

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AFCT/TFCT/ISFS PROGRAM

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O. F. Hill

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ABSTRACT

This is the last in a series of quarterly progress reports on research and development studies performed by the Pacific Northwest Laboratory (PNL) for the Alternate Fuel Cycle Technologies/Thorium Fuel Cycle Technologies/International Spent Fuel Receipt and Storage (AFCT/TFCT/ISFS) Program. This program, sponsored by the Department of Energy (DOE), provided information needed by industry to close the back end of the power reactor fuel cycle. The program included activities in support of specific design studies, as well as activities for general fuel cycle technology. The overall program was managed by Savannah River Laboratory (SRL) under the direction of the Fuel Cycle Program Office of the Savannah River Operations Office of the DOE.

During the last quarter, PNL conducted studies in the following tasks:

<u>Subtask</u>	<u>Project Title</u>
130.4	Thorium Resource Price Analyses
340.3	Investigation of Air Cleaning Processes for Removing Tributyl Phosphate from Off-Gas Streams
350.5	Study of Iodine Chemistry in Process Solutions
610.2	High-Level Waste Treatment
650.1- 650.2	Electropolishing to Decontaminate Metallic Waste from Alternate and Thorium Converter Fuel Cycles
810	U.S. Scale Transport, Dispersion and Removal Model Comparison
840.2	Safety Criticality Experiments
840.3	Criticality Research in Support of Thorium Fuel Cycle Technology Program.

This quarterly report summarizes PNL activities during the months of July, August and September 1978. Previous quarterly reports in this series are BNWL-2052, BNWL-2080-1 through -8 and -10.

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TECHNICAL PROGRESS REPORT FOR THE PERIOD
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INTRODUCTION

In fiscal year 1976, the Fuel Cycle Program Office in the Savannah River Office requested PNL, operated by Battelle Memorial Institute, to conduct studies related to the back end of the light water reactor (LWR) fuel cycle. Steps in the back end of the fuel cycle include the receipt and storage of spent fuel, the reprocessing of spent fuel, the conversion of the uranium and plutonium for recycling, the fabrication of recycled fuel, and waste management. The SRL, administered by E. I. du Pont de Nemours and Company, was assigned lead responsibility for technical management of the fuel cycle program.

In April 1977, the administration announced its policy of indefinitely deferring commercial reprocessing and recycling to permit a reevaluation of the alternatives to the normal LWR fuel cycle--alternatives that would provide proliferation-resistant systems. Alternative fuel cycle systems include coprocessing, spiking, thorium/²³³U cycling and other variants. Investigations were conducted in programs in alternative fuel cycle technology (AFCT), thorium fuel cycle technology (TFCT), and international spent fuel receipt and storage (ISFS).

Our investigations under this program include studies related to:

- the availability of thorium ores and the economics of their mining, milling and processing
- the receipt and storage of spent fuels
- the chemistry of iodine in off gasses and in low activity aqueous streams from reprocessing plants, to eliminate these materials as sources of radioiodine released to the environment
- the conversion of high-level liquid wastes from thorium fuels to vitrified solid waste forms
- the electropolishing of metallic wastes to reduce the quantity of waste that must be disposed of in a federal repository
- the dispersion and deposition of radionuclides using meteorological models
- the assessment of criticality parameters as they apply to the alternative fuel cycles being considered.

At the end of fiscal year 1978, the program was redirected and DOE terminated the funding for the PNL program. The following sections in this report discuss the progress made in each of the above areas during the last quarter.

PROJECT TITLE: THORIUM RESOURCE PRICE ANALYSIS

PROJECT MANAGER: R. M. Fleischman, Fuel Cycle Analysis,
Energy Systems Analysis

PRINCIPAL INVESTIGATOR: C. H. Bloomster, Advanced Energy Analysis
Energy Systems Department

OBJECTIVE

The large scale use of thorium in thermal power reactors is being evaluated by SRL and PNL. The possible ranges of costs for reactor grade thorium oxide (ThO_2) are needed in order to calculate the fuel cycle costs and to determine the economic viability of the various proposed fuel cycles. The purpose of the thorium resource price analysis is to provide the data needed for the fuel cycle economic studies. The supply curve will provide the basis for estimating the price and sources of thorium and will provide the ThO_2 price projections needed for the nuclear fuel cycle cost analysis.

SUMMARY

- A preliminary supply curve for domestic thorium resources was updated to reflect new geological data.
- Mine models were developed to more accurately reflect the cost of underground and surface mining.
- The draft of a topical report is being revised to include data on a new thorium deposit.

TECHNICAL PROGRESS

Conceptual production processes (see Figure 1) for all currently known thorium deposits were evaluated, and preliminary economic analyses were completed. Models of mines were developed to analyze the effects of mining variables on the cost of underground and surface mining. As a result, more complete cost functions were derived

for all deposits. The impact of individual deposits on the supply curve is now more apparent, because factors that affect cost and quantity (i.e., mine recoverability, process efficiency, mine dilution, etc.) are more accurately represented.

Mine Models

The development of two mine models, an underground mine in Lemhi Pass and a surface mine in Palmer, Michigan, has facilitated more accurate representations of mining variables and costs, and their affect on the supply curve. A description of the mine models and the resulting cost considerations will be discussed below.

Underground Mine

The underground mine model is based on the Lemhi Pass thorite deposit. The mine uses resue stoping for veins less than 5 f thick, and cut-and-fill stoping for veins over 5 f thick. The veins are assumed to be 300 f long. Twelve stopes will be constructed, 8 cut-and-fill stopes and 4 resue stopes.

A mining recovery of 69%, and dilution rates of 20% in resue stopes and 10% in cut-and-fill stopes are assumed. The mine employs 142 men including 112 operators, 17 maintenance men, and 13 administrative and supervisory personnel. It operates two shifts/d for 250 d/yr. The mine produces 1,000 tons/d for 14 yr. A backfill system is incorporated into the mine and utilizes a sand slurry to fill mined out stopes.

The two major variables that affect underground mining are mine recoverability and the dilution rate. The mine recoverability

factor indicates the amount of thorium reserves that can be economically obtained using a given mining technique. Thus, the actual quantity of thorium reserves recovered is reflected in the supply curve and not the amount in situ. The dilution rate indicates the amount the average grade of the ore is lowered during mining. Because underground mining costs are based on tons of ore mined, the dilution rate directly influences the unit cost of ThO_2 . As the dilution rate increases, the quantity of ThO_2 /ton mined decreases, and a higher unit cost for ThO_2 results.

Surface Mine

The surface mine model is based on recovering thorium from the Palmer, Michigan deposit by open pit methods. The pit contains approximately 205,000,000 tons of ore and 55 million tons of waste. The walls of the pit dip at a 45° angle. The mine operates 240 d/yr at 3 shifts/d. The average production rate is 41,667 tons/d of ore and 12,500 tons/d of waste for 20 yr. A total of 273 men are employed including 26 general and administrative personnel.

The major variable that affects surface mining is the stripping ratio (i.e., tons of waste/tons of ore mined). Surface mining

costs are based on the total amount of material mined. Thus, the more waste that must be mined to obtain the ore, the higher the unit cost for ThO_2 .

Thorium Resource Overview

With mining costs more accurately represented, more accurate cost estimates for obtaining reactor grade ThO_2 from domestic ThO_2 reserves can be obtained. Results show that the thorite deposits of Hall Mountain, Idaho, Wet Mountain, Colorado, and the larger veins in Lemhi Pass in Idaho and Montana can be recovered for under \$10/lb. Palmer, Michigan offers substantial amounts of ThO_2 at under \$20/lb. However, production costs substantially increase as the less promising reserves are tapped. Additional ThO_2 can be obtained from Conway Granite, Bald Mountain and Piedmont Placers, but the costs exceed \$50/lb.

CONTINUING WORK

Although funding for this task was not available from SRL in FY-1979, the work continued under other DOE funding. A topical report describing this work will be prepared in late FY-1979.

FIGURE 1. Thorium Production Processes

PROJECT TITLE: INVESTIGATION OF AIR CLEANING PROCESSES FOR REMOVING
TRIBUTYL PHOSPHATE FROM OFF-GAS STREAMS

PROJECT MANAGER: L. C. Schwendiman, Particulate and Gaseous Waste Research,
Atmospheric Sciences Department

PRINCIPAL INVESTIGATOR: G. B. Parker, Particulate and Gaseous Waste Research,
Atmospheric Sciences Department

OBJECTIVE

The objective of this project is to provide a suitable air cleaning process for removing low concentrations of tributyl phosphate (TBP) vapors from nuclear fuel reprocessing off-gas streams.

SUMMARY

- A bench-scale demonstration unit was used in an experiment that was run using a 14 wt% Ag impregnated iodine sorbent to determine the effectiveness of an alumina catalyst material (material H) to trap TBP and to protect iodine sorbent. Iodine retention of columns with and without the TBP sorbent, material H, was nearly the same.
- The TBP vapor concentration measured by the PA460-2 analyzer in the feed stream of the demonstration unit was found to be $\sim 10^{-5}$ g/L, or about 80 times less than predicted by calculations of mass loss. The TBP generator apparatus was modified to increase the concentration to 5×10^{-4} g/L, which is more near that expected in actual off-gas streams.
- A similar experiment, using the modified demonstration unit at the increased TBP concentration, was run with material H and an 18% Ag substituted mordenite iodine sorbent. Breakthrough data showed that material H reduced the deleterious effect of the TBP. The calculated iodine retention at a 1% breakthrough in 10 cm of the iodine sorbent was 0.14 g for the column that was not protected by material H compared to 4.4 g for the protected

column. The ultimate iodine retention capacity in 10 cm of iodine sorbent was greater for the protected column compared to the unprotected column.

- An experiment was conducted using a 7 wt% Ag sorbent. The sorbent was loaded with iodine in the presence of TBP normal paraffin hydrocarbon (NPH) vapor and then subjected to 2 vol% NO_2 in air. Visual examination of the iodine sorbent after it was subjected to the NO_2 indicated that the NO_2 regenerated the sorbent. The iodine appeared to wash off the iodine sorbent, leaving the material in its original state. No quantitative analysis was performed to confirm this conclusion.

TECHNICAL PROGRESS

Two experiments were completed this quarter using the bench-scale demonstration unit to evaluate material H as a sorbent to remove TBP and to protect iodine sorbent beds. The experiments were conducted using two 2.5-cm-dia stainless steel columns. Each column consisted of several 5-cm-deep segments of the selected sorbent materials. The columns were placed in an oven and maintained at 130°C. Air at 2% relative humidity containing methyl iodide and TBP/NPH was metered to the columns in each experiment. The breakthrough of methyl iodide, measured by gas chromatography, was followed to determine the efficiency of the TBP sorbent to protect the iodine beds.

In the first experiment, column I contained two 5-cm segments (Sections A and B) of material H followed by three 5-cm segments (Sections C, D and E) of a 14 wt% Ag

impregnated silica gel sorbent; column II contained five 5-cm segments (Sections A through E) of the 14 wt% Ag iodine sorbent. The columns were conditioned with air at 2% relative humidity for 24 h, and air plus TBP/NPH vapor for 1.5 h before metering methyl iodide to the air stream. During the experiment, the average airflow was 1.85 L/min and the average methyl iodide concentration was 210 mg/m³.

The breakthrough of methyl iodide was followed until a total of 9.5 g of iodide had been metered to column I and 9.7 g to column II. Methyl iodide was retained by material H (column I, sections A and B) so breakthrough was also followed in material H. Figure 2 shows the breakthrough curves for column I. Figure 3 shows the breakthrough curves for column II, sections A and B. No breakthrough was noted in sections C, D, and E of column II.

To determine the effectiveness of the TBP sorbent to protect the iodine sorbent, a comparison of breakthrough data was made between Section C in column I and Section A in column II, and between Section D in column I and Section B in column II. Table 1 summarizes the breakthrough data.

The iodine retention in Section C of column I and Section A of column II is nearly the same when adjustments are made for error, and breakthrough in Section C is

extrapolated to the same value (93%) as Section A. This indicates that the presence of material H in column I had little effect on the iodine retention of the iodine sorbent. This is further confirmed by comparing iodine loading in 10 cm of the silver sorbent at 1% breakthrough. A total of 5.8 g of iodine was metered to column I compared to 5.9 g metered to column II, before a 1% breakthrough was measured. The data also indicated that the presence of airborne TBP did not have a deleterious effect on the iodine retention capacity, since the retention of iodine was at the stoichiometric maximum for this iodine sorbent.

Because TBP seemed to be having no effect on the iodine sorbent, an investigation was carried out to determine the airborne concentration of TBP in the feed stream to the columns. In the past, airborne TBP concentrations were calculated by estimating the volume of TBP/NPH liquid lost during a run and assuming TBP was 30% of that volume. Using this method the airborne TBP concentration was calculated to be 80 mg/m³. However, in this investigation the PA460-2 analyzer was used. The analyzer was used to measure TBP in the feed stream to the column at conditions identical to those in the experiments. An airborne TBP concentration of ~10 mg/m³ was measured. This concentration was about 80 times less than that estimated from volume loss calculations.

FIGURE 2. Breakthrough History for Methyl Iodide Retention in Column I

FIGURE 3. Breakthrough History for Methyl Iodide Retention of 14 wt% Ag Material in Column II.

TABLE 1. Analysis of Iodine Retention of 14% Ag Impregnated Iodine Sorbent^(a)

Sample	Measured % CH ₃ I Breakthrough (C/C ₀ ×10)	Calculated CH ₃ I Retention from Breakthrough Curves ^(b) gI/g Ag ^(d)	Theoretical Maximum ^(c) gI/g Ag
Column I			
Section A	100 (material H)	(1.3) ^(e)	
Section B	90 (material H)	(1.8) ^(e)	
Section C	84	1.1	1.2
Section D	61	0.4	
Section E	38	0.1	
Column II			
Section A	93	1.6	1.2
Section B	17	1.1	

(a) Calculated retention at 1% breakthrough in two 10-cm sections of iodine sorbent (from raw data); 5.8 g of I was metered to column I (protection) and 5.9 g of I was metered to column II (no protection); uncertainty is $\pm 25\%$ at the 95% confidence level.

(b) Uncertainty is $\pm 25\%$ at the 95% confidence level.

(c) Based on the reaction $\text{Ag} + \text{I} \rightarrow \text{AgI}$.

(d) Based on 7 wt% Ag.

(e) Grams of Iodine.

It was decided that a higher airborne TBP concentration was necessary for experimentation. A review of the literature indicated that a concentration of $\sim 1000 \text{ mg/m}^3$ is assumed in a typical off-gas stream. Therefore, modifications were made to the TBP generator apparatus. An analysis after the modifications were made showed a TBP concentration of 500 mg/m^3 , which was considered adequate for experimentation.

The second demonstration experiment this quarter was run using the modified TBP generation method. In this experiment, column I contained two 5-cm sections (Sections A and B) of material H followed by three 5-cm segments (Sections C, D, and E) of an 18% Ag substituted mordenite sorbent; column II contained four 5-cm segments (Sections A through D) of the 18% Ag sorbent. The columns were conditioned with air at 2% relative humidity for 20 h and air plus TBP/NPH vapor for 1 h before metering methyl iodide to the air stream. During the experiment, the average airflow was 2 L/min and the average methyl iodide concentration was 160 mg/m^3 .

When the experiment was terminated, the total methyl iodide metered to column I was 6.75 g and to column II was 6.11 g. Breakthrough was followed by gas chromatographic analysis. Figure 4 shows the breakthrough curve for column I; Figure 5 shows the breakthrough curve for Sections A and C of

column II, and Figure 6 shows the breakthrough curve for Sections B and D of column II.

To determine the effectiveness of the TBP sorbent to protect the iodine sorbent, a comparison of breakthrough curves was made between Section C in column I and Section A in column II, and between section D in column I and Section B in Column II. Table 2 summarizes the breakthrough data.

The iodine retention at a 1% breakthrough in 10 cm of column I (Sections C and D) was 30 times greater than the iodine retention in 10 cm of column II (Sections A and B). This experiment showed the deleterious effect of TBP on this iodine sorbent. Material H protected the iodine sorbent, increasing the iodine retention capacity. The iodine retention capacity of the iodine sorbent in column I is significantly less than the theoretical capacity. If breakthrough for column I is extrapolated to $C/C_0 = 100\%$, the iodine retention would be $\sim 0.7 \text{ g}$, which is 60% of the theoretical capacity.

The effect of NO_2 on iodine retention was assessed using the bench-scale demonstration unit. No TBP sorbent was used to protect the iodine sorbent in this experiment. The TBP sorbent was to be included in future studies using NO_2 in the feed stream.

FIGURE 4. Breakthrough History for Methyl Iodide Retention in Column I

FIGURE 5. Breakthrough History for Methyl Iodide Retention of 18 wt% Ag Substituted Mordenite in Column II, Sections A and C

FIGURE 6. Breakthrough History for Methyl Iodide Retention of 18 wt% Ag Substituted Mordenite in Column II, Sections B and D

TABLE 2. Analysis of Iodine Retention of 18% Ag Substituted Mordenite Iodine Sorbent(a)

Sample	Measured % CH ₃ I Breakthrough (C/C ₀ ×100)	Calculated CH ₃ I Retention from Breakthrough Curves(b) gI/g Ag	Theoretical Maximum(c) gI/g Ag
Column I			
Section A	90	(1.3)(d)	
Section B	82	(1.25)(d)	
Section C	55	0.4	1.2
Section D	7	0.2	
Section E	None	0.1	
Column II			
Section A	65	0.4	1.2
Section B	60	0.2	
Section C	45	0.2	
Section D	30	0.1	

(a) Calculated iodine retention at 1% breakthrough in two sections of silver sorbent (from raw data); 4.4 g of I metered to column I (protection) and 0.14 g of I metered to column II (no protection); uncertainty is +25% at a 95% confidence level.

(b) Uncertainty is +25% at a 95% confidence level.

(c) Based on reaction $\text{Ag} + \text{I} \rightarrow \text{AgI}$.

(d) Grams of Iodine.

Two stainless steel columns were prepared. Both columns contained five 5-cm segments of 7 wt% Ag silica gel iodine sorbent. The columns were placed in the oven and preconditioned for 24 h with air at 2% relative humidity and air plus TBP/NPH vapor for 1 h before metering methyl iodide to the air stream. The columns were kept at 130° to 135°C throughout the experiment.

Methyl iodide was metered along with the TBP/NPH vapor laden air at 1.95 L/min until a total of 6.66 g of iodide were loaded onto each column. The approximate methyl iodide concentration was 200 mg/m³ and the approximate airborne TBP vapor concentration was 500 mg/m³.

Breakthrough curves for each column were derived from the data. Figure 7 shows the breakthrough curve for column I and Figure 8 shows the breakthrough curve for column II. The iodine retention calculations are given in Table 3. The data indicate that TBP had no effect on the total loading of iodine in the 7% Ag silica gel sorbent; the calculated loading was greater than the stoichiometric maximum in both columns.

The material from column I was removed, examined and photographed to note the

changes that occurred. Originally, the iodine sorbent was white and beaded. At the end of the iodine loading, the sorbent in the first two 5-cm segments of column I was a light yellow mixed with a few black beads. The third 5-cm segment was about an equal mixture of yellow and grey-black beads and the last two segments were entirely black. This pattern was expected since the first two sections were saturated with iodine and the yellow is a characteristic color of AgI. The mixture of yellow and black beads in the middle section confirmed that the middle section was only partially loaded with iodine. The last two sections had not "seen" any iodine and were black. The black color is characteristic of silver oxide, which is formed by the sorbent reacting with the air and/or the TBP/NPH vapor.

Column II was left in the oven at 130° to 135°C. Dry air containing ~2% NO₂ was then metered to the column at 1.9 L/min for 45 h. This was done to determine the effect the NO₂ had on the iodine sorbent after the sorbent had been loaded with iodine in the presence of TBP/NPH. It was assumed that column II looked the same as column I before introducing the NO₂.

FIGURE 7. Breakthrough History for Methyl Iodide Retention of 7 wt% Ag Sorbent in Column I

FIGURE 8. Breakthrough History for Methyl Iodide Retention of 7 wt% Ag Sorbent in Column II

TABLE 3. Analysis of Iodine Retention of 7% Ag Iodine Sorbent Prior to Introducing NO₂

Sample	Measured % CH ₃ I Breakthrough (C/C ₀ ×100)	Calculated CH ₃ I Retention from Breakthrough Curves ^(a) gI/g Ag ^(c)	Theoretical Maximum ^(b) gI/g Ag
Column I			1.2
Section A	100	1.8	
Section B	100	1.8	
Section C		0.7	
Section D	0	--	
Section E	0	--	
Column II			1.2
Section A	100	1.8	
Section B	100	1.8	
Section C		1.2	
Section D	0	--	
Section E	0	--	

(a) Uncertainty is +25% at the 95% confidence level.

(b) Based on the reaction Ag+I AgI.

(c) Based on 7 wt% Ag.

At the end of 45 h, the material in column II was examined and photographed. The first two 5-cm segments were all white, resembling the virgin sorbent. The third 5-cm segment was nearly all white with a thin layer of yellow near the bottom (downstream) of the segment. The last two segments were a pure light yellow; this, as noted earlier, is characteristic of silver iodide. It appears that the iodine loaded onto the first two segments of column II was "washed" onto the last two segments of the column by the NO₂, leaving the iodine sorbent in the first two sections in its original white state (regenerated). It was thought that

the first two segments of column II would remain loaded with iodine and thus would be the characteristic yellow color. It was also expected that any of the sorbent not loaded with iodine (the sorbent that was dark) would be regenerated to the white color of the virgin material, because the silver on the silica gel would be reduced to the ionic (original) AgNO₃ state from the oxide (black) state by the NO₂. Confirmation that the iodine was washed onto the last two segments would require analysis of the last two column sections to determine the iodine content.

PROJECT TITLE: STUDY OF IODINE CHEMISTRY IN PROCESS SOLUTIONS

PROJECT MANAGER: H. H. Van Tuyl, Applied Chemistry Section,
Chemical Technology Department

PRINCIPAL INVESTIGATORS: J. L. Swanson and R. D. Scheele, Applied Chemistry Section,
Chemical Technology Department

OBJECTIVE

The objectives of this project are to study the behavior of iodine species that are not volatilized from the dissolver solution, and to develop means of managing iodine in the various plant streams to minimize its release to the environment.

SUMMARY

During this quarter we continued to investigate several different methods of sorbing iodine from 0.01M HNO_3 (the expected composition of the excess water stream from a fuel reprocessing plant). Very promising results continued to be obtained with adsorbents that are prepared by loading polyiodide ions (I_3^- or I_5^-) onto an anion exchange resin. Valuable data were also obtained on an alternative procedure for preparing MnO_2 -impregnated polymeric adsorbents and on the effectiveness of iodine-pretreated polymeric adsorbents. Data were also obtained on reducing the volatility of iodine during the vaporization of excess water; Ce(IV) , Pb(II) and Cu(II) were found to be relatively ineffective for this purpose.

This report completes the reporting on this program, which was terminated unexpectedly near the end of this quarter. A comparison of the major results obtained with various sorption processes is presented in Table 4. Table 4 includes data obtained this quarter as well as data obtained earlier; the progress through February 1978 was summarized in an interim progress report (Swanson 1978a) and later work was described in quarterly reports (Swanson 1978b and c). While the choice of a sorption process

depends on a variety of factors, it appears to us that the polyiodide ion-loaded anion exchange resin adsorbent shows the most promise for being used to remove iodine from an excess water stream, and that a pre-treated polymeric adsorbent shows the most promise for being used to remove iodine from plant streams that are to be recycled.

Table 5 contains highlights of the results we obtained earlier on the suppression of the volatilization of iodine during the vaporization of excess water. Adding an appropriate amount of mercuric nitrate to the acidic vaporizer bottoms solution and adding sodium hydroxide in an amount equal to 1.1 times that required to neutralize the acid in the excess water stream were both found to be effective in suppressing iodine volatilization. These processes could be used either instead of, or in addition to, the sorption processes described above. Some of the potential adverse interactions between certain sorption processes and these volatilization suppression processes were discussed in a previous paper (Swanson 1978a).

TECHNICAL PROGRESS

We continued our efforts in the development of methods for sorbing iodine species from 0.01M HNO_3 , which is the expected composition of the excess water stream from a nuclear fuel reprocessing plant. We also obtained more data on suppressing iodine volatilization during water vaporization.

Polyiodide Ion-Loaded Anion Exchange Resin

The two long-term tests begun last quarter (Swanson 1978c) using I_3^- -loaded resin were continued and a test was begun using an

TABLE 4. Comparison of Iodine Sorption Processes Studied

Experimental Values for 0.01M HNO ₃					
Adsorbent	Maximum DF at 100 CV ^(a,b,c)	Maximum CV Achieved Before DF = 10	Potential Advantages	Potential Disadvantages	
				When used for excess water stream	When used for other plant stream
<u>Polymeric Adsorbent</u>					
• Untreated	~20 ^(d)	(e)	• Relatively insensitive to HNO ₃ concentration.	• H ₂ O ₂ addition required. DF is highly dependent on flow rate, H ₂ O ₂ concentration and iodine concentration. Regeneration procedures not established.	• Excess H ₂ O ₂ remains in plant stream.
• I ₂ -Pretreated	~100 ^(f)	2,500 ^(f)	• Less H ₂ O ₂ required than above	• Same as above.	• Same as above.
• I ₂ -Loaded	~100 ^(g)	2,000 ^(g)	• No feed additive required. Little effect of flow rate.	• Regeneration procedures not established.	• Inactive I is added to stream.
• MnO ₂ -Impregnated ^(h)	~100 ⁽ⁱ⁾	8,500 ^(j)	• No feed additive required. Little effect of flow rate.	• Adsorbent preparation conditions are critical. Regeneration procedures not established.	• Mn is added to stream. Higher acidity decreases throughput capacity.
<u>Anion Exchange Resin</u>					
• Untreated					
I ⁻ feed	~100	400	• Little effect of flow rate.	• Reductant addition required. Frequent regeneration is required (1M HNO ₃ + 0.1M HAN works well).	• Higher nitrate concentration decreases throughput capacity.
I ₂ feed	~100 ^(k)	1,000 ^(k)	• Little effect of flow rate.	• Frequent regeneration is required. Regeneration adds Na to waste.	
• Polyiodide Ion Loaded	~50 ^(l)	14,000 ^(m)	• No feed additive required. High throughput capacity.	• Regeneration procedures not established.	• Inactive I added to stream. Higher nitrate concentration will likely decrease throughput capacity

(a) DF = (concentration of iodine in feed)/(concentration of iodine in effluent at that time)

(b) Obtained at a flow rate of about 10 column volumes/h

(c) CV = column volumes of feed processed

(d) Obtained with 0.3M H₂O₂ present in the feed (which contained 10⁻⁵M I₂).

(e) Not determined directly, but it appears to be in the thousands

(f) Obtained with 0.03M H₂O₂ present in the feed (which contained 2 x 10⁻⁶M I₂)(g) With 10⁻⁵M I₂ in the feed

(h) Best results achieved when a small bed of non-impregnated polymeric adsorbent preceded the impregnated material

(i) With 10⁻⁵M I₂ in the feed; the throughput capacity was about 3000 CV(j) With 10⁻⁷M I₂ in the feed; the DF was about 20 through most of the run(k) Obtained with 10⁻⁵M I₂ in the feed

(l) Achieved with a pentaiodide-loaded adsorbent which gave DF ~40 until run was stopped at termination of program (~10,000 CV)

(m) Achieved with a triiodide-loaded adsorbent which gave DF ~30 through most of the run

TABLE 5. Comparison of the Use of Mercuric Nitrate and Sodium Hydroxide to Suppress Iodine Volatilization during Vaporization of Excess Water(a)

I_2 in feed, M	Bottoms Solution Composition, M				DF(b)
	Hg	HNO ₃	NaOH	NaNO ₃	
10^{-6}	0.01	0.5	-	-	80
10^{-5}	0.01	0.5	-	-	10
10^{-5}	0.06	0.5	-	-	60
10^{-6}	-	-	0.05	0.5	160
10^{-5}	-	-	0.05	0.5	50

(a) Vaporization conditions simulated a continuous vaporizing operation with a feed solution (0.01M HNO₃) to bottoms solution flow ratio of 50

(b) DF = (Concentration of iodine in feed)/(concentration of iodine in distillate)

I₅-loaded resin. The I₃ test that used a glass column and a resin preloading of 0.17 mmol total I/ml resin was terminated after about 14,000 column volumes (CV) of feed had been processed; the decontamination factor (DF) at this point had dropped to 10 (from the value of 20 to 30 obtained during most of the run). The concentration of radioiodine in the effluent at the end of the run was the same whether or not iodine was present in the feed solution; thus, it was demonstrated that the radioiodine DF was controlled by washing off previously sorbed material.

The results of the I₃ test that used a stainless steel column and a resin preloading of 0.69 mmol total I/ml resin were similar to the results of the first I₃ test. This second test was terminated after 13,000 CV of feed had been processed (the DF was still about 20 at that time).

The I₅-loaded resin was prepared by loading 10 mmol of total I (from a "KI₅" solution prepared from KI and I₂) onto a 5-ml bed of Amberlite IRA-900 anion exchange resin and then washing the bed with 2000 CV of 0.01M HNO₃. The wash removed about 19% of the I, giving a preloading of 1.6 mmol total I/ml resin. Before the program was terminated, 10,000 CV of 0.01M HNO₃ + 10^{-6} M I₂ was passed through this bed. The iodine DF ranged from 30 to 50 (at a flow rate of about 9 CV/h) during the course

of this run. Flow rate effects were measured near the end of the run; doubling the flow rate decreased the DF approximately two-fold.

MnO₂-Impregnated Polymeric Adsorbent

Previous work with MnO₂-impregnated polymeric adsorbents emphasized impregnated adsorbent preparation techniques that involve the reaction of KMnO₄ solution with a bed of the polymeric adsorbent. This quarter we began to examine batch methods of preparing impregnated adsorbent. Batch methods may be more suitable for preparing adsorbent for use in large-scale tests. The first batch was prepared by soaking 10 ml of the polymeric adsorbent (XAD-4) two times in 30 ml of 0.02M KMnO₄, each time for 1 h; this batch contained about 0.051 mmol MnO₂/ml adsorbent (which corresponds to impregnation of about 40% of the added manganese). The second batch was prepared by soaking 10 ml of XAD-4 in 30 ml of 0.01M KMnO₄ for 1 h; this batch contained about 0.027 mmol MnO₂/ml adsorbent (which corresponds to impregnation of about 90% of the added manganese). The iodine DF was higher with a column of material from the second batch than from the first. No handling problems were encountered with either batch.

Iodine-Pretreated Polymeric Adsorbent

The experiment began last quarter with an iodine-pretreated adsorbent, a flow rate of ~9 CV/h, and a feed composition of $2 \times 10^{-6} \text{M}$ I_2 in 0.01M HNO_3 + 0.03M H_2O_2 was continued until the iodine DF dropped to ten. The DF dropped to 10 after processing about 2500 CV of feed. Only about half of the loaded iodine was eluted by passing (upflow) 500 CV of 0.05M to 0.1M NaOH through the adsorbent.

Suppression of Iodine Volatilization During Water Vaporization

Several additives were evaluated as iodine volatilization suppressors during water vaporization, using the equipment and procedures described by Swanson (1978b). The presence of 0.5M Ce(IV) resulted in a significant suppression of iodine volatilization, with all of the nonvolatilized iodine being present in a solid phase. However, decreasing the Ce(IV) concentration to a more reasonable value of 0.01M resulted in very little suppression of iodine volatilization.

In another series of experiments, elemental iodine in the feed was reduced with

hydroxylamine nitrate (HAN) to iodide ion, and HAN as well as Pb(II) or Cu(II) was present in the bottoms solution. Little if any suppression of iodine volatilization was observed in these experiments.

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PROJECT TITLE: HIGH-LEVEL WASTE TREATMENT

PROJECT MANAGER: J. H. Jarrett, Nuclear Process Technology and Analysis Section,
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Chemical Technology Department

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OBJECTIVE

The objective of this project is to develop process design information for the calcination and vitrification of high-level liquid waste from the reprocessing of irradiated thorium fuel.

September 8, 1978 - O. F. Hill visited SRL to discuss thorium fuel reprocessing and the composition of Thorex high-level waste.

SUMMARY

- A simulated Thorex feed (TW-2) was successfully processed in the pilot-scale spray calciner/in-can melter system. Fluoride losses were not more than 2%. Corrosion rates of test coupons were negligible.
- A simulated Thorex feed (TW-3) with higher fluoride and little aluminum content was processed in the remote laboratory-scale spray calciner. Fluoride volatility and corrosion were also low in this run.
- A waste glass composition was developed for the Thorex TW-3 calcine.

TECHNICAL PROGRESS

We completed runs with Thorex feed in the pilot-scale spray calciner/in-can melter system and in the remote laboratory-scale spray calciner. Work continued on glass formulation investigations.

Spray Calciner/In-Can Melter Tests

The pilot-scale spray calciner was operated coupled directly to the pilot-scale in-can melter. The feed was simulated TW-2. The composition of the TW-2 feed (Hill 1978a) is based on the use of aluminum nitrate in the dissolver to control fluoride corrosion in the dissolver. The average feed rate was 20 L/h for 7.5 h. The in-can melter was held at a melt temperature of about 1050°C for 11 h. The calcine-to-frit ratio was expected to be 1:4, but due to a problem with controlling the frit feeder the ratio was actually 1:7.6.

TRIPS AND VISITORS

September 7, 1978 - O. F. Hill visited the Oak Ridge National Laboratory to discuss alternative fuel technology, with specific interest in information on high-level waste from thorium fuel reprocessing.

Analyses of samples of glass from the top, middle, and bottom of the canister showed 0.12, 0.18, and 0.60 wt% fluoride, respectively. The higher fluoride content in the bottom of the canister was expected since the high calcine-to-frit ratio in the early portion of the run caused the

formation of a slag (a second phase other than glass). An overall fluoride balance for the run gave the expected fluoride concentration of 0.16 wt%, which is similar to the top and middle fluoride concentrations. The analysis of fluoride in condensate samples indicated a loss of only 2%. This compares favorably with previous laboratory-scale spray calciner and simulated melter fluoride losses (Hill 1978a).

Corrosion coupons were used during the pilot-scale test. The materials were 304, 304L, 310 and 316L stainless steel, and Inconel 601 and 690. These coupons were placed in the sintered-metal filter, the plenum condenser (vapor phase), the condensate tank, and in the piping above the in-can melter. Corrosion rates were negligible; in fact, most coupons gained about 1 mg in weight. Optical examination of the coupons revealed no unusual effects.

Samples of one of the eight cooling fins and of the bottom of the canister wall were inspected for corrosion. These were chosen since they contacted the hot glass for the longest period. In addition, corrosion here would be expected to be a maximum because of the higher fluoride concentrations. However, negligible corrosion is shown in Figures 9 and 10, which are photomicrographs of the 304L stainless steel materials.

The 304L fins showed some intergranular corrosion. The average depth of penetration was 0.002 in. The canister wall also showed corrosion, but not as severe as the fins. The average depth of the canister wall was 0.001 in. Corrosion on the exterior of the canister was similar to that on the interior.

Remote Laboratory-Scale Spray Calciner Tests

The remote laboratory-scale spray calciner was tested with simulated TW-3 feed (Hill 1978b). This feed is based on the use of zirconyl nitrate in the dissolvent to control fluoride corrosion in the dissolver. The principal difference between TW-3 and TW-2 is that TW-3 has a higher fluoride concentration and little aluminum content. The off-gas system consisted of a condenser and a packed scrubber. Scrubber flow was recycled to build up fluoride concentrations in the scrubber stream and thereby to permit a more accurate fluoride analysis.

Two 8-h runs were made with TW-3 feed. The feed rates averaged 0.75 and 1.5 L/h. Analyses of the calcine and the feed indicated that fluoride losses were 3% to 7%. However, based on fluoride analyses of the condensate and scrubber solution, only 0.2% and 0.06%, respectively, of the fluoride in the feed collected in these streams. Thus, zirconium is apparently at least as effective as aluminum in reducing fluoride volatility during high-temperature calcination. The concern about ZrF_4 volatilizing was unwarranted, since competing solution equilibria between ZrF_4 and fluozirconate complexes apparently exist. A comparison of aluminum (TW-2) and zirconium (TW-3) as fluoride volatility suppressants indicates that they are both effective in reducing fluoride losses to less than 10%, and losses are typically less than 3%.

Coupons were also used in operations of the remote laboratory-scale spray calciner. The materials tested were identical to those in the pilot-scale run: 304, 304L, 310, and 316L stainless steel, and Inconel 609 and 690. The coupons were placed in the calciner filter housing, the off-gas condenser (vapor phase), and the condenser condensate tank. The weight changes found on the various coupons are shown in Table 6. The Inconel coupons showed the most effects of the corrosion, while the 304L stainless steel showed the least.

Glass Formulation

A glass composition, shown in Table 7, was developed for use with TW-3 calcine. This glass has a higher waste loading than previous glasses (24 versus 20 wt%). Its viscosity is 250 P at 1050°C. Weight loss was 0.76 wt% in 24-h Soxhlet leaching tests (99°C, deionized water).

The characteristics of this glass are sensitive to the chemical substitution of cerium for thorium. Cerium may be substituted for thorium in simulated feed for engineering-scale demonstrations to avoid potential radioactive contamination problems. If the calcine resulting from the simulated feed and the glass additive are not mixed well, CeO_2 crystals may be present in the final glass.

6 3X

A

250X

A

100X B

100X

B

250X

A

250X

A

100X B

100X

B

250X

#1

FIGURE 9. 304L Fin

#2

FIGURE 10. 304L Canister Wall

TABLE 6. Remote Laboratory-Scale Spray Calciner Coupon Weight Changes

Location	Material Weight Change, mg					
	304	304L	310	316L	INC 601	INC 690
Filter Housing	-0.4	-0.3	-0.3	+0.2	-0.4	-0.4
Upper Condenser	-0.4	-0.1	-0.5	-0.2	-0.9	-0.6
Condensate Tank	-0.13	-0.1	-0.4	--	-0.6	-1.2

TABLE 7. Glass Composition for Thorex Waste Studies

Constituent	wt% in Glass
calcine (TW-3)	24.0
SiO ₂	41.7
B ₂ O ₃	14.4
Na ₂ O	8.6
CaO	3.3
BaO	3.3
ZnO	2.4
K ₂ O	2.4

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PROJECT TITLE: ELECTROPOLISHING TO DECONTAMINATE METALLIC WASTE
FROM ALTERNATE AND THORIUM CONVERTER FUEL CYCLES

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PRINCIPAL INVESTIGATORS: R. P. Allen, H. W. Arrowsmith, Metallurgy Research Section,
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OBJECTIVE

The objective of this work is to develop and provide the concepts, information, and engineering data needed by the AFCT and TFCT programs to design and operate electropolishing facilities that will decontaminate surface-contaminated solid metallic waste. Major program tasks include:

- the identification and transfer of compatible technology from the commercial electropolishing and related surface-finishing industries;
- the development of solution treatment procedures to extend electrolyte life and minimize secondary waste volume;
- the development of techniques to minimize or remove contamination entrained in cut edges by component sectioning operations;
- the adaptation and optimization of electrochemical decontamination techniques and secondary waste minimization approaches for thorium converter fuel cycle metallic waste, with thorium and ^{233}U as the principal contaminants.
- A special barrel electropolishing system that will permit the use of titanium, tantalum, and other passivating metals as the anode contact has been obtained for evaluation studies.
- An automatic height-control system based on voltage-distance variations is being designed for the plasma-arc-torch cutting system. This will ensure more uniform cuts, and thus reduce entrained contamination.
- Reciprocating acid-adsorption purification tests for phosphoric acid electrolytes containing dissolved stainless steel show that the iron and chromium can be removed as a metal-phosphate precipitate.
- Purification/recycling studies of the rinse and pretreatment solutions are in progress using a dual-effect evaporator system, which is capable of processing up to 60 gal of water/h.
- A direct caustic-neutralization procedure has been developed to convert spent phosphoric acid waste into a neutralized solid that is suitable for onsite disposal.

SUMMARY

- Prepolishing studies are in progress to quantitatively evaluate the relationship between various commercially finished stainless steel samples and the effectiveness of standard decontamination techniques.

TRIPS AND VISITORS

August 2, 1978 - M. D. Boersma and L. Dworjanyn of SRL visited PNL to discuss the progress and plans of the program.

September 11, 1978 - R. P. Allen and H. W. Arrowsmith visited Hydrite Chemical Company, Milwaukee, WI to discuss solution processing and handling equipment and technology with program consultants L. S. Winter and D. Skvara.

September 12, 1978 - R. P. Allen, H. W. Arrowsmith and M. W. McCoy visited the International Machine and Tool Show at Chicago, IL to view and compare various types of shears, nibblers, punches, and other metal-working and sectioning equipment.

September 15, 1978 - R. P. Allen and H. W. Arrowsmith visited G. Wellman of WELCO company, Chicago, IL to discuss high-impact spray cleaning equipment and compounds for removal of paint and other surface material.

TECHNICAL PROGRESS

The following sections describe the progress made during the past quarter toward meeting our program objectives in the areas of technology transfer, solution treatment and entrained contamination removal studies.

Technology Transfer

This quarter we are continuing to assess the value of prepolishing for decontamination applications. Commercially available stainless steel samples with different surface finishes were contaminated to a level of approximately 700,000 dis/min·100 cm², by either (1) swabbing the surface with contaminated solution or (2) scrubbing the surface with plutonium oxide. The samples were then washed for 1 min using a high-pressure (500 psi) spray nozzle. This treatment reduced the contamination level to 12,000 dis/min·100 cm² for the as-received surface, 14,000 dis/min·100 cm² for the mechanically ground surface, and 7,000 dis/min·100 cm² for the electropolished surface.

Discussions with the vibratory finishing industry suggested the possibility of using vibratory finishing to decontaminate selected non-metallic items. This was investigated by processing a ball-channel inspection tool, constructed of stainless steel with rubber tubing covering about two-thirds of its length, in our 4-f³ vibratory finisher. Radiation levels on the tool were reduced from 1.5 rad/h to 70 mrad/h, with a 300-mrad/h hot spot on the tubing. This was

our first example of decontaminating a non-metallic item by vibratory finishing.

The investigation of barrel electropolishing techniques is continuing. A special barrel system, shown in Figure 11, has been obtained. This barrel system will permit the use of titanium, tantalum, and other passivating metals as the anode contact. This system will be cold-tested at Hydrite Chemical Co. in preparation for our studies with radioactively contaminated objects.

As a result of our visit to the International Machine and Tool Show at Chicago, IL, we identified several types of shears, nibblers, and other types of metal-working machines capable of sectioning stainless steel with a minimum of waste and a low probability of entraining surface contamination. A heavy-duty nibbler that can cut 0.25-in.-thick stainless steel at 6 f/min has been acquired and is being evaluated.

Solution Treatment Studies

As part of our efforts to develop solution treatment procedures to minimize process wastes, the major emphasis has been on identifying and developing safe, effective techniques for removing dissolved metal and contamination from the phosphoric acid electrolytes. The most promising of the ten approaches we have evaluated is an acid-adsorption purification process in which the spent electrolyte is forced through a column containing a suitable ion exchange resin. The phosphoric acid is selectively adsorbed (retarded), allowing the dissolved impurities to pass through the column. The purified acid is then recovered using water as the eluant.

We have acquired and tested a commercial acid-purification system to determine whether reciprocating acid-adsorption techniques can be used to remove dissolved metals, while producing a waste with a high metal-to-phosphorus ratio to maximize acid recovery and minimize waste volume. The three main parts of the acid-purification system are:

- the ion exchange bed
- the acid and water metering tanks
- the control system for the unit.

Phosphoric acid electrolytes containing electrolytically dissolved stainless steel have been used to evaluate the effectiveness of acid adsorption as an electrolyte

FEATURES.

- RACKING OF INDIVIDUAL PARTS ELIMINATED
- REDUCES PROCESSING EXPENSES AND OPERATOR EXPOSURE

FIGURE 11. Barrel Electropolishing

purification method as a function of various operating conditions. The acid and metal content of the initial feed solution and the resulting product and waste streams have been determined using neutralization titration and x-ray fluorescence methods.

Although an adequately purified product was produced using normal operating procedures (alternate short flows of electrolyte and water in opposite directions), the metal-to-phosphorus ratio for the waste stream was substantially lower (0.10) than the target ratio of 1.0. Consequently, we modified the purification cycle to permit recycling of the waste stream in order to determine if the metal content of the waste stream could be increased to an acceptable level. However, recycling only yielded a metal-to-phosphorus ratio of 0.08, which was even lower than for normal system operation. Furthermore, recycling the waste stream resulted in excessive dilution of the process stream and also significantly increased the processing time.

Unidirectional operation with alternate flows of electrolyte and water in the same

direction was also evaluated. This procedure produced waste with a higher metal-to-phosphorus ratio (0.21), but the product-to-waste volume ratios were not adequate for a practical purification process.

Extending the duration of the reciprocal electrolyte and water flows, and extracting only that part of the waste stream with a high metal-to-phosphorus ratio yielded the best purification. The variation of waste stream composition with waste volume for this procedure is shown in Figure 12. The dissolved nickel emerged from the ion exchange bed first, followed by the iron and the chromium in the form of an amorphous precipitate, with a molar metal-to-phosphorus ratio of about 1:2. The total metal-to-phosphorus ratio for the waste stream increased from about 0.20 to a maximum of 0.28 and then dropped rapidly. The amount of metal removed and acid lost for this initial portion of the waste stream as compared with an equal volume of feed solution was 100% for the nickel, 70% for the iron, 60% for the chromium, and only 15% for the acid.

FIGURE 12. Metal/Phosphorus Concentration Ratio as a Function of Waste Volume for Passage of Phosphoric Acid Containing Dissolved Stainless Steel Through Acid-Adsorption Bed

The iron-chromium precipitate that was obtained in these tests would be an excellent waste form for disposal, if it could be reliably obtained in reasonable quantities. Although the precipitate forms in the resin bed, a substantial fraction is apparently flushed out by the low-acid solution. The remaining precipitate is redissolved and removed as the phosphoric acid concentration reaches ~150 g/L. These acid-adsorption studies will continue with the emphasis on determining the effect of various operating procedures on the production and recovery of the precipitate and on the total metal-to-phosphorus ratio of the waste stream.

For future studies of the purification and recycling of pretreatment and electropolishing rinse solutions, a dual-effect evaporator system (Figure 13) has been installed. This system is comprised of two independent units and can run either one solution through two successive distillation cycles, or two separate solutions through the cycle simultaneously. Water from the rinse tanks and any aqueous process effluents from the pretreatment facility, such as vibratory-finishing liquids, will be piped

into feed tanks connected to the evaporator system. The evaporator will run this water through either one or two distillation cycles and into storage tanks where it will be monitored for residual contamination. If the liquid is still above release limits, the process will be repeated. The concentrated, highly contaminated "bottoms" resulting from this treatment will be removed and solidified for waste disposal.

Based on initial cold tests, this evaporator system can distill up to 60 gal/h. Feed and storage tanks are being installed, and criticality safety analyses are being completed. Testing of the system using contaminated liquids is expected to begin soon.

A direct caustic-neutralization process is being used to convert spent phosphoric acid electrolyte into a neutralized solid that is suitable for onsite disposal. In this process, 50% NaOH is added directly to the electrolyte. This causes a violent and instantaneous reaction, rapidly increasing the temperature from 25°C to 105°C. After the pH reaches 9 to 10, the addition of NaOH is stopped and the solution cools. By the time the mixture reaches ambient temperature, it has become a solid. This process produces about one barrel of neutralized solid per day and increases the volume of waste by a factor of 2.1.

Two alternative solidification processes were also investigated:

- adsorption of the electrolyte on an adsorbent clay followed by neutralization with 50% NaOH
- the use of urea-formaldehyde to form a solid matrix to contain the electrolyte.

There are two problems with the adsorption process: 1) the difficulty in mixing the electrolyte, caustic and adsorbent, and 2) the large increase in the volume of waste (by a factor of 3.8). The urea-formaldehyde process is simple, effective and produces one barrel of solidified spent electrolyte per hour. However, since the electrolyte is not neutralized prior to mixing, the acid could be easily leached away from the solid. In addition, since the matrix is organic, it could evolve radiolytic gases when containing an alpha producer.

Entrained Contamination

The development and testing of the plasma-arc-torch cutting system are continuing. Initial sectioning studies using this

FIGURE 13. Dual-Effect Vacuum Evaporation System Used for Purification and Recycling Studies of Pretreatment and Rinse Solutions

system have demonstrated the importance of an interactive height-control system to control the distance between the torch and the metal being sectioned. Controlling this distance is necessary to produce smoother, cleaner cuts and to counteract spacing changes due to distortion and warping of the work piece. Monitoring the voltage and the current reading while operating the plasma arc torch has shown that the voltage increases as the gap between the torch and work piece increases. Consequently, a servo-drive mechanism has been ordered for the torch and will be used in conjunction with a data acquisition/controller system to control the height of the torch.

FUTURE WORK

Although our work with the AFCT and TFCT programs monitored by SRL is terminating, the essential functions and goals are being continued as part of the Electropolishing for Surface Decontamination of Metals Program funded by the Department of Energy's Office of Nuclear Waste Management. The results of this work are formally published each quarter. In addition, a report on the solution treatment studies will summarize the results of these efforts.

PROJECT TITLE: U.S. SCALE TRANSPORT, DISPERSION,
AND REMOVAL MODEL COMPARISONS

PROJECT MANAGER: C. E. Elderkin, Manager
Atmospheric Sciences Department

PRINCIPAL INVESTIGATOR: W. E. Davis
Atmospheric Sciences Department

OBJECTIVE

The primary objective of this study is to provide documentation on a PNL U.S. scale assessment model. The documentation is to include theoretical background for equations used in the assessment as well as a user guide. Results from a short case-study using the model will also be sent to SRL.

SUMMARY

- A rough draft of the technical background and user-guide sections was completed.

TECHNICAL PROGRESS

Writing is continuing on the model with the technical section and user guide being completed in rough draft form. These are being sent to SRL for approval before a final draft is written.

PLANS FOR COMPLETION OF PROJECT

- Finish draft of PNL U.S. scale assessment model and send to SRL.
- Produce and send precipitation and wind tape for test run of model.

PROJECT TITLE: SAFETY CRITICALITY EXPERIMENTS

PROJECT MANAGER: E. D. Clayton, Criticality Analysis
Energy Systems Department

PRINCIPAL INVESTIGATOR: R. C. Lloyd, Criticality Analysis
Energy Systems Department

OBJECTIVE

The objectives of the criticality safety support task are to:

- utilize the PNL critical mass laboratory to provide the confirmatory criticality data required to support AFCT research and development
- establish benchmark data for code validation and safety assessment
- provide criticality safety parameters to support design concepts and equipment specifications.

SUMMARY

- Criticality experiments were completed on the series of latticed assemblies containing 4.3 wt% ^{235}U rods in uranyl nitrate and in uranyl nitrate containing Gd as a neutron absorber.

TECHNICAL PROGRESS

Experimental criticality data are needed for soluble neutron absorbers (poisons) to accurately determine their effectiveness in the prevention of criticalities and the control of solutions containing fissile material (Lloyd, Clayton and Hansen 1972; Lloyd and Clayton 1976; Lloyd and Clayton 1977; Lloyd, Durst and Clayton 1978). These data are needed to validate criticality-control calculational techniques that are used in the analysis of poisoned systems. The use of soluble absorbers can be a useful safety measure in the prevention of a nuclear criticality during the processing and storage of nuclear material.

Criticality data have been collected during a series of experiments in which lattices of fuel rods were immersed in uranyl nitrate. Three different lattice spacings were tested with a soluble neutron absorber. In particular, the effectiveness of Gd as a soluble neutron absorber for use in nuclear criticality preventions was tested. The data from these criticality experiments are presented, against which calculational techniques can be checked.

The three different center-to-center fuel rod spacings were 22.9 mm, 27.9 mm and 33.0 mm, respectively. UO_2 pellets of 4.3 wt% ^{235}U enrichment were contained in stainless steel tubes with a clad OD of 14.4 mm (clad thickness of 0.813 mm). A detailed description of the fuel rods is given in Figure 14. The fuel rods were loaded into the three lattice templates, which were mounted in cylindrical 304L stainless steel vessels. A schematic of the experimental assembly is shown in Figure 15. The stainless steel vessels were reflected with water on the sides and bottom. The uranyl nitrate solution was remotely pumped into the stainless steel vessels containing the lattice templates. Critical approach measurements were made on increments in the height of the uranyl nitrate solution as a function of Gd concentration.

The effect of adding Gd to the three uranium rod latticed assemblies can be seen in Figure 16, where the critical heights are plotted against the Gd concentration. The assembly with the 22.9 mm lattice spacing contained 451 fuel rods in a vessel with a 557.5-mm ID. The critical height was determined to be 373 mm when the uranyl nitrate did not contain Gd and 752 mm when the solution contained 0.184 g/L of Gd. The

FUEL TUBE CANNED LENGTH*	(34.421 in.)	874.29 mm
FUEL ROD CORE LENGTH	(32.394 in.)	822.81 mm
FUEL PELLET LENGTH	(0.625 in.)	15.88 mm
CLAD - OD	(0.567 in.)	14.40 mm
CLAD THICKNESS (304L SS)	(0.032 in.)	0.813 mm
FUEL COLUMN DIAMETER	(0.498 in.)	12.649 mm
UO ₂ DENSITY (% THEORETICAL)	94.9 ± 0.6	
ENRICHMENT	4.29 w/o ²³⁵ U	

* MEASURED FROM BOTTOM OF END SPADE TO BOTTOM OF TOP SPADE

FIGURE 14. Description of 4.3 wt% ²³⁵U Enriched Fuel Rods

FIGURE 15. Schematic of the Experimental Assembly

assembly with the 27.9 mm lattice spacing contained 433 fuel rods in a vessel with a 658.0-mm ID. The critical height of the uranyl nitrate solution without Gd was 309 mm. Added Gd of 0.125 g/L increased the critical height to 565 mm. The vessel with the 33.0 mm lattice spacing had an ID of 761.6 mm and contained 421 fuel rods. The system was determined to be critical with an uranyl nitrate height of 333 mm without Gd and a height of 577 mm when the solution contained 0.075 g/L of Gd.

As a result of these experiments, criticality data now exist for low-enriched uranium rod systems immersed in uranyl nitrate solution containing Gd. These experimental data can be used to benchmark commonly used calculational methods of analyzing poisoned systems.

FIGURE 16. Effect of Gd in Uranyl Nitrate Solution on Latticed Assemblies

PLANS FOR COMPLETION OF PROJECT

- Complete comparisons between calculational techniques and results from the criticality experiments.
- Formalize report for submission to journal for publication.

REFERENCES

- Lloyd, R. C., E. D. Clayton, and L. E. Hansen. 1972. "Criticality of Plutonium Nitrate Solution Containing Soluble Gadolinium." Nuclear Science and Engineering 48:300-304.
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- Lloyd, R. C., B. M. Durst and E. D. Clayton. 1978. "The Effect of Soluble Neutron Absorbers in Latticed Assemblies." Trans. Am. Nucl. Soc. 30:260-261.

PROJECT TITLE: CRITICALITY RESEARCH IN SUPPORT OF THORIUM
FUEL CYCLE TECHNOLOGY PROGRAM

PROJECT MANAGER: S. R. Bierman, Criticality Analysis
Energy Systems Department

PRINCIPAL INVESTIGATORS: S. R. Bierman, W. E. Converse, D. E. Friar,
B. F. Gore and R. A. Libby, Criticality Analysis,
Energy Systems Department

OBJECTIVE

The criticality research program is directed toward providing reliable technology for safe and economical criticality controls in chemical processing. The primary goal in the fiscal year 1978 was to establish a program plan for obtaining the criticality data needed in the chemical reprocessing of fuels from the TFCT program.

SUMMARY

Three documents were issued. These documents delineate the criticality data needed for the TFCT program, including the data currently available and the data currently unavailable; the series of experiments required to obtain the unavailable data is also presented.

TECHNICAL PROGRESS

Two documents, Criticality Research in Support of Chemical Reprocessing in the Thorium Fuel Cycle Technology Program (Libby 1978) and Compilation of Criticality Data Involving Thorium or ^{233}U and Light Water Moderation (Gore 1978a), have been issued. These two documents identify the criticality data needed and the data currently available that is applicable to the TFCT program. A third document, A Proposed Plan for Critical Experiments Supporting Thorium Fuel Cycle Development (Gore 1978b), has also been issued. This third document presents a detailed program plan for providing the experimental criticality data still

needed for assuring safe and economical criticality controls in the chemical reprocessing of fuels from the TFCT program.

The generation of calculated families of criticality curves for Th-U systems is about 80% complete. These curves are for use in process and engineering design and experimental planning.

PLANS FOR COMPLETION OF PROJECT

The series of calculated criticality curves for use in process and engineering design and experimental planning will be finalized and documented.

REFERENCES

- Gore, B. F. 1978a. Compilation of Criticality Data Involving Thorium or ^{233}U and Light Water Moderation. PNL-2080-12, Pacific Northwest Laboratory, Richland, WA 99352.
- Gore, B. F. 1978b. Proposed Plant for Critical Experiments Supporting Thorium Fuel Cycle Development. PNL-2080-15, Pacific Northwest Laboratory, Richland, WA 99352.
- Libby, R. A. 1978. Criticality Research in Support of Chemical Reprocessing in the Thorium Fuel Cycle Technology Program - Basic Process Description. PNL-2080-11, Pacific Northwest Laboratory, Richland, WA 99352.

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