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RICHLAND
02 R&D PROGRAM

ANNUAL REPORT

SUMMARY

June 30, 1970

RICHLAND OPERATIONS OFFICE

ATLANTIC RICHFIELD HANFORD COMPANY

DOUGLAS UNITED NUCLEAR, INC.

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coordinated by

CHEMICAL PROCESSING DIVISION

and

PRODUCTION REACTOR DIVISION

Classification Cancelled and Changed To

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RICHLAND 02 R&D PROGRAMANNUAL REPORTSUMMARYINTRODUCTION

The complete annual R&D report consists of this summary and two companion reports, one from DUN which covers reactors and another from ARHCO which covers separations. These companion reports are listed in the set of references in the back of this summary.

This annual report covers progress in R&D during the second half of FY 1970 and is based on plans outlined in the June 30, 1969 annual report and the forms 189 for FY 1970. The financial status is shown in the table following this introduction. The programs for FY 1971 and 1972 are consistent with the forms 189 shown in BUD-700 (Estimates of Appropriation for the Fiscal Year Ending June 30, 1972 - Operating Expenses). Overall expenditures for FY 1970 are consistent with the \$3.5 million R&D budget for the year. Expenditures under major program headings were in the same order as the original budget figures, that is, in the order of descending magnitude as follows:

Waste Management

Environmental and Regulatory Technology

Basic Production

Product Flexibility

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Development work on the Basic Production and Product Flexibility Programs has been consistent with funding levels. Increased emphasis has been placed on N reactor operational problems as well as on assessing the K reactor inlet cooling piping integrity and zirconium hydriding problems. Work has been in progress to improve the Purex plant extraction performance by in-plant testing of the "Zirflex Tonic" effect.

On the Product Flexibility Program, developmental work was conducted to establish either enriched uranium or nondefense plutonium (or both) as a reactor fuel and to provide further technology for the production of high-purity plutonium-238. With the further curtailment associated with the shutdown of KW reactor, this program is being phased out.

Activities on the Environmental and Regulatory Technology Program were pointed toward developing technology to assure safe operation of the Hanford project facilities. Major emphasis was placed on the study of metal-water (irradiated N fuels) reactions to simulate loss of coolant conditions, and with attention to the related safety assurance features. Work is under way to develop accurate predictive capabilities for determining the consequences of accidental release of radioactive

materials. This work will be continued in future years.

Increased emphasis has been placed on the Waste Management Program with intent to develop technology for a substantial reduction in releases of low- and intermediate-level radioactive waste to the environment. The salt waste processing and the waste solidification in-tank subprograms have both been reduced in level of R&D effort for the reason that B Plant and the in-tank solidification units are now operating successfully and do not need further R&D support. Emphasis has been maintained on the development program for purifying and encapsulating fission-product strontium and cesium. Efforts to reduce the salt content of Purex wastes have been increased because of the projected waste management cost savings and concomitant improved strontium recovery. For the reactors, Waste Management always has been closely associated with the Environmental Program. This type of work for reactors has been incorporated in the Environmental & Regulatory Technology Program so that no reactor funds are shown for FY 1971 and 1972. No large Columbia River program is covered as in past years, since this work is being carried on under Process Technology and the Plant Assessment Pool.

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02 PROCESS DEVELOPMENT PROGRAM COSTS

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	<u>FY 1970 (Est. Cost)</u>			<u>FY 1971 (Est. Cost)</u>			<u>FY 1972 (Est. Cost)</u>		
	<u>DUN</u>	<u>ARHCO</u>	<u>TOTAL</u>	<u>DUN</u>	<u>ARHCO</u>	<u>TOTAL</u>	<u>DUN</u>	<u>ARHCO</u>	<u>TOTAL</u>
BASIC PRODUCTION	<u>579.0</u>	<u>288.0</u>	<u>867.0</u>	<u>250.0</u>	<u>125.0</u>	<u>375.0</u>	<u>250.0</u>	<u>100.0</u>	<u>350.0</u>
PRODUCT FLEXIBILITY	<u>178.0</u>	<u>83.0</u>	<u>261.0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>
ENVIRONMENTAL & REGULATORY TECHNOLOGY	<u>725.0</u>	<u>343.0</u>	<u>1,068.0</u>	<u>675.0</u>	<u>350.0</u>	<u>1,025.0</u>	<u>675.0</u>	<u>450.0</u>	<u>1,125.0</u>
WASTE MANAGEMENT	<u>43.0</u>	<u>1,254.0</u>	<u>1,297.0</u>	<u>0[#]</u>	<u>975.0</u>	<u>975.0</u>	<u>0[#]</u>	<u>1,050.0</u>	<u>1,050.0</u>
TOTAL	<u>1,525.0</u>	<u>1,968.0</u>	<u>3,493.0</u>	<u>925.0</u>	<u>1,450.0</u>	<u>2,375.0</u>	<u>925.0</u>	<u>1,600.0</u>	<u>2,525.0</u>

#Work of this nature will be handled under Environmental & Regulatory Program

[REDACTED]

BASIC PRODUCTION PROGRAM

This program is aimed at providing advanced production reactor and separations technology, applicable to improved plutonium production efficiency and capability, and consistent with reduced operating levels of the plant. The work involves activity in a wide variety of disciplines, such as chemistry, physics, thermal hydraulics, materials technology and fuels technology. The program spans the range from basic research to in-plant development.

Objectives and Incentives

Efforts have been and in the future will be directed toward development of new reactor and separations production technology to:

- Improve product quality
- Reduce costs
- Improve maintenance
- Increase plant utilization
- Extend plant life
- Improve plant performance
- Reduce product losses

In this way, the Richland complex can continue to perform consistent with or in excess of its commitments.

Reactors

K Reactor Zircaloy Hydride

Major Accomplishments to Date

Zircaloy process tubes in low pressure reactors become hydrided in the warm water spacer section behind the active charge due to a galvanic couple between the aluminum spacers and the tube. Permeation of hydride into the base metal causes embrittlement of the tube. Anodized spacers prevent the reaction in new tubes or tubes cleaned of hydride. A practical technique for removal of hydride already formed has been demonstrated on the KE reactor.

Progress During Report Period

The objective of this activity was to determine the causes and mechanisms contributing to the hydriding of K reactor Zircaloy process tubes, promote measures to minimize additional hydriding, and develop methods and techniques for hydride case layer removal to prevent subsequent diffusion of hydrogen into the base metal.

The study of hydriding mechanisms was terminated with the shutdown of KW reactor. Analysis of coupons that had been exposed in the outlet sections of KW reactor tubes for up to 14 months has been completed. An alternate case hydride removal process involving an anodic stripping operation followed by an electrolytic etch was developed and demonstrated to supplant the grit blasting process developed earlier. A 10-tube reactor test of the process was demonstrated with no problems, and full-scale adaptation should be readily possible.

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Downstream sections of 25 C reactor Zircaloy tubes were removed for examination and use in development of the electrochemical cleaning process. C reactor tubes were found to be hydrided more erratically than K reactor tubes.

Future Plans

Of the ten tubes cleaned in KE reactor, two have been removed for examination. The other eight will be removed in pairs at 18-month intervals to determine if any bad effects have resulted from the cleaning and whether hydriding has resumed.

Reactor Plant Life

Major Accomplishments to Date

Irradiation of N and K reactor graphite through higher flux of the ETR (Engineering Test Reactor, Idaho Operations Office) to exposures well beyond that which is in the reactors has provided basis for coping with future problems, particularly those posed by contraction.

Progress During Report Period

This activity's objective is to assure that the ability of the Hanford reactors to produce irradiation products economically does not become constrained by irreplaceable facilities. Irreplaceable facilities are defined as those which cannot be replaced without essentially rebuilding the entire complex (the graphite stack or reactor shields, for example) or those which are so expensive to replace that economic considerations suggest reactor decommissioning as the more palatable alternative (external piping complex or water treatment system, for example).

Irradiation of 18 graphite samples removed from KW reactor in 1966 was completed in the ETR. Based on results, turnaround of K reactor graphite growth is predicted to occur in 1973-74.

The irradiation of large blocks and small samples of graphite in N reactor to determine the effects of size and stress on dimensional changes continued, with latest results indicating the contraction rate of large blocks to be approximately 30 percent greater than the small samples.

Laboratory development of a process to apply oxidation-resistant coatings to graphite moderators using organosilanes in the gas atmosphere was completed. Coated graphite showed improved oxidation resistance by a factor of seven compared to standard graphite. It was concluded that the probability of success in applying oxidation-resistant coatings to Hanford reactor moderators was good, provided adequate application techniques could be developed.

Future Work

ETR irradiation data on KW reactor graphite samples will be analyzed to determine value of technique for predicting long-range behavior of graphite. If results are positive, N reactor samples will be irradiated in the ETR to establish long-range distortion behavior of N Reactor Moderator.

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Plant Cost ReductionMajor Accomplishments to Date

Studies have shown that adapting process computer technology to the N reactor is both feasible and economically attractive. A system study was completed showing systems and components for application of automatic surveillance.

Progress During Report Period

Adapting existing technology or developing new technology, which when implemented, will result in a direct reduction in plant operating cost, or avoidance of costs, was the objective of this activity.

There was no progress during the report period. The completed systems study, including selection of systems or components for application of automatic surveillance with principal emphasis on Process Standards, systems critical to nuclear safety, prestartup checks, and consolidation of control in the 105-N Control Room, was submitted to the Atomic Energy Commission for approval and adoption. No further action on this program was taken as the result of curtailment of funds.

Future Plans

There are no plans to continue this program.

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Chemical Separations

Extraction-Zirflex Tonic Effect

Major Accomplishments to Date

Prior work showed that addition of fluoride-to-feed solutions derived from aluminum-clad fuels improved the solvent extraction behavior of Zr (Nb was not affected). It was determined that the Nb:Zr ratio in Purex feed solutions is normally low so that significant improvement in Zr decontamination would result in a significant increase in Zr-Nb decontamination.

Two plant tests were run; in one, the extraction column feed (HAF) was adjusted to approximately 0.065M Al and 0.005M F during processing of aluminum-clad fuel. At this high aluminum-to-fluoride ratio of approximately 13, a factor of two improvement was noted in the Zr-Nb decontamination. In the second extraction column feed test, aluminum was added to two HAF batches during coproduct processing where excellent Zr-Nb decontamination was being obtained. As the aluminum concentration was increased by factors of 2 and 2.5 above normal, the extraction column Zr-Nb decontamination decreased by factors of approximately 1.5 and 3.0 from previous values.

Progress During Report Period

Laboratory and plant testing have confirmed the fact that the "Zirflex Tonic Effect" (improved plutonium decontamination) is due to fluoride. Laboratory data indicate that the same effect can be achieved with less fluoride by addition to the codecontamination column (HA) scrub stream rather than to the feed stream. Oxalate and EDTA (ethylenediaminetetraacetic acid) were found to be effective complexants only when present at the time of extraction.

Future Plans

The plans are to determine the effectiveness of adding fluoride to the extraction column scrub stream in a plant test, to continue evaluating other possible complexants, and to study the mechanism of the effect of fluoride on Zr behavior.

Computer Simulation of TBP Extraction System

Major Accomplishments to Date

A computer program was developed at Oak Ridge National Laboratory in support of their LMFBR program. This code, named SEPHIS, is based on an earlier computer code developed by J. T. Lowe of Savannah River Laboratory.

Progress During Report Period

The solvent extraction simulation computer program SEPHIS was obtained from

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Oak Ridge National Laboratory, and it is currently being debugged on local computers. Preliminary test runs have duplicated the hand calculations. The program will provide transient response information after a perturbation of operating conditions.

Future Plans

The original program was based on a correlation of laboratory equilibrium data obtained at 25°C with 15 percent TBP. Refinements are necessary to improve the data fit at 30 percent TBP and at elevated temperature. The program also needs to be modified to correct for volume changes caused by uranium and nitric acid mass transfer. Further refinements may include addition of other transferring components, such as thorium, uranium (IV) and certain fission products.

Neptunium Chemistry-Rate Accelerating Material (RAM)

Major Accomplishments to Date

Prior accomplishments include design and development of a reactor system, including controls to produce the "RAM" in pilot plant quantities. The program was discontinued shortly after the beginning of the report period in response to changing Purex Plant requirements.

Progress During Report Period

Design of equipment to produce the neptunium oxidation rate accelerating material (RAM) for a plant test was firmed up. However, work was discontinued pending determination of the effect of proposed flowsheet changes in neptunium recovery.

Future Plans

No further work is planned. A topical report will be issued.

Effect of Water on Burning Plutonium

Major Accomplishments to Date

None. This is a new program.

Progress During Report Period

Work to determine the effect of water on burning plutonium metal was planned.

Future Plans

The reaction of water with burning plutonium will be studied with respect to both chemical and physical effects. The possibility of formation of combustible gases, i.e., hydrogen, by the reaction will be investigated. Initial studies will be with small quantities of plutonium. Burning masses will be expanded to production quantities as information is developed.

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Monitoring Np and Pu Losses in Purex HAW

Major Accomplishments to Date

Analytical methods have been tested, improved and used for certain elements from each group in the Periodic Table which must be separated from Np and Pu. These methods include x-ray fluorescence, atomic absorption spectroscopy, spectrophotometry and radioactive counting. These methods were applied to evaluate experimental results with synthetic Np and Purex waste solutions.

Progress During Report Period

X-ray fluorescence was found to be the best practical method for in-line analysis of neptunium and plutonium in the Purex first cycle extraction column waste (HAW) since it is highly selective and only a few interfering elements require pre-analysis separation. The use of an isotopic x-ray source and a solid state detector should result in an installation requiring a minimum of maintenance.

Future Plans

Work will be done to:

1. Find the optimum technique for the most quantitative collection of Np and Pu from extremely dilute solutions by liquid-liquid extraction.
2. Make a final choice of reagents and separation procedures for removing most of the highly radioactive and interfering elements.
3. Select the measuring instrumentation which has the greatest possibility for sustained operation.
4. Test the whole procedure on Purex waste.
5. Work out the equipment problems and modifications necessary for automating the procedure and for remote installation and maintenance.
6. Determine the effect of Np and Pu carried on solids in HAW.

Measurements of Nitric Acid in S&C Dissolvers

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Major Accomplishments to Date

Methods to measure and control the nitric acid strength in slag and crucible dissolvers are required to control the hydrogen explosion potential and to enhance rates of dissolution. A method is needed to measure the H^+ concentration continuously in the slag and crucible dissolvers to an accuracy of $\pm 0.5M$ over the range of 1 to 5M (or higher).

Tests conducted with conductivity measurements demonstrated the expected double valued behavior and showed the measurement effects of the addition of various salts. As the salt concentration increased, an increase in the conductivity (as a function of acid molarity) became evident, resulting in an apparent 2.5 molar variation of nitric acid when the salts varied from the minimum expected concentration to the maximum. A theoretical study indicated the possibility of a frequency dependence which could lead to the discrimination between H^+ ions and other. Conductivity tests performed in the range of 25 to 70 MHz showed some effect of frequency on the measured parameter, but did not demonstrate an ability

to separate those effects due to the acid from those due to the salt. Further testing indicated that H^+ could likely be indicated by comparison of measurements of conductivity and specific gravity and effort was directed to develop sensors and equipment for these measurements.

Progress During Report Period

Efforts were centered on a final preparation of a prototype assembly. The prototype assembly contains acid-resistant piping and supports for in-line installation on a simulated process line. Laboratory calibration and testing on the combined sensor assembly showed capability of measuring the specific gravity from 1.0 to 1.36 and the conductivity from 0.03 to 0.9 mhos/cm over the expected acidity range of 0.1M to 6.0M. When final laboratory tests are completed, the unit will be installed in the test continuous dissolver in the 300 Area.

Future Plans

The prototype acid monitor will be installed and tested with glass test dissolver in the engineering laboratory.

Nondestructive Plutonium Assay by Gamma Energy Analysis

Major Accomplishments to Date

Nondestructive plutonium assay is a portion of a broad mission to account for all source and special materials without sampling, regardless of the matrix in which it is found.

Neutron counting to determine Pu-239 content has been used routinely. Precision and accuracy is poor, however, and neutron emission rates are dependent upon isotopic composition, the weight of fissile material (k_{eff}) and impurity content (α, n). More recently the NaI(Tl) gamma energy detector was used to supplement the neutron data. The use of the lithium-drifted, germanium detectors, however, permits direct gamma energy analysis of Pu-239. With its improved resolutions, individual Pu-239 peaks can be distinguished from the U-237 peak and the general Compton interference experienced with NaI(Tl). A rotating package assembly was set up to analyze pulses from the Ge(Li) detector with a 4096 channel pulse height analyzer, both with and without a Cs-137 source to measure self-absorption. Subsequently it was determined that Ba-133 offered advantages over Cs-137 for measurement of self-absorption and was adopted for use in the package measurement assembly.

Progress During Report Period

Analysis of the counting system has indicated that in packages containing an unknown distribution of emission and absorption locations, it is important that the ratio of observed Ba-133 emissions to the unabsorbed value be obtained from the volume maximum absorption cross-section as the package is rotated. The absorption correction is proportional to the cube root of the ratio in packages of low density relative to plutonium. In packages with densities approaching plutonium (i.e., plutonium oxide and plutonium metal scrap), the absorption correction is proportional to the sixth root.

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Future Plans

A system is being designed to measure Pu-239 in waste cartons (18 x 18 x 36 in.) and smaller receptacles. The detector will be a vertical line array of four closed-end, coaxial Ge(Li) detectors in one cryostat. The sample will be rotated and oscillated vertically between the detector assembly and the Ba-133 self-absorption source. Data will be pulse height-analyzed and reduced to gram weight Pu-239 in one automated operation.

Instrumentation - General Applications

Major Accomplishments to Date

In April 1969, a new capacitance probe interrogator was installed in the Purex N cell and is working satisfactorily. Since that time, efforts have continued to improve this instrument for use with the Bowling Ball Cask Capacitance Probe. The instrument response is nonlinear which is satisfactory for N cell where a relative measurement is made, but not suitable for the casks where a quantitative measurement must be made. In October 1969, a new circuit concept was developed to achieve a linear response. A circuit employing this principle has been built and has been successfully tested.

A new design for an in-line sampling valve was fabricated and cold tested.

Progress During Report Period

Performance tests were conducted on the pulse frequency controller (Third Plutonium Cycle) with satisfactory results. The design was changed slightly to place the solid state switches in the power line between the 115 VAC and the Hannifin valve coils. A similar design for the continuous solvent extraction project was requested using a timed pulse counter, but problems have arisen due to the fact that two induction coils in the timed counter are being switched causing transients that mistriggered the Hannifin valve. A new circuit has been designed and a printed circuit board built and tested. The results appear favorable.

Future Plans

Investigations will be continued on the following items of development work: -

1. Applications of digital circuitry for improvement of instruments.
2. Applications of the benefits of size and price of integrated circuitry in the design of new or improved instruments.
3. Following progress of other laboratories in the development of the "neutron interrogation" method of monitoring or assaying of materials for their enrichment.
4. Improvement of equipment wherever new or better concepts can be conceived.

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PRODUCT FLEXIBILITY PROGRAM

The purpose of this program was to develop production capabilities other than that of weapons-grade plutonium.

Objectives and Incentives

The initial objective was to develop the full production potential of the Richland site. The individual R&D items included were tritium, transplutonium, plutonium-238, other isotopes, and enriched fuel. Efforts within the reporting period have been directed toward the development of highly-enriched (oralloy) fuels to be used as the sole fuel or in conjunction with slightly enriched uranium fuel elements (spike-concept) to produce a desired product mix in the reactors. Development of the technology for the production of medical-grade plutonium-238 includes the advantage of the reactors favorable thermal neutron spectrum. The incentives were, for example, improved production capability, reduction of product unit costs, and beneficial safety analyses. Since this program was composite, each subitem has a unique objective.

Reactors

Enriched Fuel Program

Major Accomplishments to Date

This program was to demonstrate the use of oralloy and plutonium bearing fuels for production in Hanford reactors. Calculations were completed for a small scale K reactor test involving fuel with less than 5 percent oralloy. Parameters were developed for production of the oralloy fuel. Analyses were completed with respect to maximum throughput and core fraction that can be tolerated in using plutonium bearing fuel in a K reactor.

Progress During Report Period

The objective of this program was to develop and demonstrate technology to permit use of oralloy or nondefense plutonium as reactor fuel, and perform nuclear safety evaluations required for use of enriched fuels.

The program progressed satisfactorily up to the time it was canceled subsequent to KW reactor shutdown. Fuel fabrication efforts were terminated immediately prior to beginning fabrication of fuel for a small test loading. The 20 kg of oralloy obtained from Oak Ridge was never used and was returned as received. The program status has been documented to minimize effort required in the event of future program reactivation.

Future Plans

There are no future plans for an Enriched Fuel Program.

Pu-238 - Reactors-Fuels

Major Accomplishments to Date

Production rates of N_p -237 over a wide range of exposures and uranium fuel have been determined. Pu-238 production rates from irradiation of neptunium have been established.

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An improved method for irradiating neptunium using higher flux and operational charge-discharge has been demonstrated.

Production of Pu-238 containing 0.3 ppm Pu-236 was demonstrated.

An advanced thin-annulus neptunium target has been charged in KE reactor.

Progress During Report Period

Work on this activity was intended to demonstrate continued capability to produce medical-grade Pu-238, develop improved technology for medical-grade Pu-238 production, and evaluate alternative methods for Pu-238 production.

An irradiation test was conducted to determine the effects of fabrication techniques on wafer behavior in a reactor environment. Test results indicate that inadequate provision for graphite growth during irradiation and not fabrication parameters contributed to the failure of matrix targets in an earlier test.

Fabrication techniques and procedures were developed for advanced thin-annulus target elements containing a series of thin-walled hollow cylinders of pressed and sintered NpO_2 -aluminum cermet. Twenty elements, ten with graphite cores and ten with water cores, were charged in KE reactor for three months of irradiation.

The irradiation of the 150 grams of americium oxide charged into KE reactor during May 1969 is continuing with discharge planned in the first quarter of FY 1971. A two to three year cooling time is planned to allow Pu-238 to build up through decay of curium 242.

Future Plans

Arrangements have been made for processing of thin-annulus targets at completion of the irradiation. It is believed the product will have less than 0.2 ppm Pu-236. No provision has been made for processing or analyzing the americium targets now in reactor. It is planned to let these elements cool for two to three years for Cm-242 decay.

Other Isotopes

Major Accomplishments to Date

1. Economical tritium production has been successfully demonstrated in the K and N reactors.

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2. Buildup of higher plutonium isotopes and transplutonium up to Cm-244 has been predicted from small scale irradiations and production; cost models for Cm-244 have been completed.
3. A Pu-Al fuel model capable of 100 kw/ft has been designed and fabricated.
4. A cobalt-bearing process tube has been irradiated in KW reactor.
5. Cobalt-60 and thulium-170 production has been demonstrated in the N reactor.
6. A plutonium deep burn program has continued successfully for six months.

Progress During Report Period

This activity was intended to enhance capability of the Hanford reactors to produce various isotopes, and determine the cost and capability of production for those isotopes not included in other activities.

Cobalt-60

Studies related to the cobalt base alloy tube (Haynes alloy 25, nominally 51 percent cobalt) were continued until the shutdown of KW reactor at which time the tube had been irradiated for eight months. Monitoring of reactor effluent showed a slow buildup of cobalt-60 release for six months until after the third charge-discharge when a ten-fold increase in activity was noted. The tube was not removed from the reactor following shutdown.

Thulium-170

Extrapolation of final calorimetric results received on the 176 grams of thulium-169 charged into N reactor in the fall of 1967 indicated that an average of 126 curies per gram of thulium-170 was realized.

Plutonium Burning

The 13 PuAl columns in the single-column width slab in KE reactor continued to operate at design levels. An initial monitor column was discharged in June 1970. Future discharges will be timed according to the level of interest in higher isotopes of plutonium, americium, and curium.

Lithium Bearing Spline Development

On the basis of results of spline samples which contained three different forms of lithium and which were irradiated for three months in KE reactor, it was concluded that tritium production in supplemental control splines was not-feasible.

Future Plans

Irradiation of 10 kilograms of plutonium in KE reactor is to be continued three more years with discharge of tubes every six months. There are no plans for chemical processing and analysis.

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Chemical SeparationsClean Pu-238 StudiesMajor Accomplishments to Date

Neptunium oxide has been produced for target fabrication as required by way of calcination, both continuous and batch. Neptunium irradiated in both an aluminum and a graphite matrix has been processed in the 325-A Building Hot Cell Facility by ion exchange processes. Solvent extraction flowsheets for Purex Plant processing for either coextraction or consecutive extraction of Np-237 and Pu-238 from nitric acid solution of the irradiated Np-Al targets have been devised and demonstrated. Operating schemes for processing up to 8000 kg of neptunium per year through Purex, with oxide production in the 234-5 Building, have been costed.

Progress During Report Period

The hot-cell equipment used for separation of plutonium-238 from irradiated neptunium-237 R&D targets is being readied for processing both the aluminum and graphite targets which were recently irradiated. Laboratory investigations on the effect of solvent degradation indicated that neptunium (IV) forms a strong complex with dibutylphosphate (DBP), a radiolysis product of tributylphosphate (TBP). Under stripping conditions, 0.01M nitric acid with solvent containing DBP, distribution coefficients as high as 3.2×10^3 were measured. With solvent containing no DBP, distribution coefficients were about 1×10^{-3} . Plutonium was shown to be retained by 33 percent TBP solvent to the extent of approximately 22 mg of Pu per watt-hour of absorbed dose.

Future Plans

Both aluminum and graphite targets, irradiated in the current development campaign, will be processed to the oxide and shipped. The thin-walled aluminum targets, expected to be charged into the reactors during May 1970, will be processed after the proper irradiation and cooling times (about the end of CY 1970). Work on the development of solvent extraction processes will be continued to the end of the fiscal year and phased out due to program redirection and allocation of funds. Additional processing will be supported with process technology funds.

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ENVIRONMENTAL AND REGULATORY TECHNOLOGY PROGRAM

The Environmental and Regulatory Technology program contains the following research and development items: Nuclear safety, radionuclides in soils, and making the reactors equivalent to power reactors from a licensability standpoint. The activities under these items are being conducted to assure that the Hanford production reactors and separation plants are maintained and operated safely, to minimize the heat and isotope loading of the Columbia River, and to determine those parameters by means of which the consequences of accidental releases (including those caused by earthquakes) of radioactive and chemically toxic materials to the atmosphere or groundwater can be predicted.

Objectives and Incentives

Effort is under way to model the consequences of reactor loss of cooling accidents including temperature transients, reactions in the overheated core, and fission product release from overheated fuel. Development of this technology will permit a quantitative assessment of the basic risk of facility operation. Methods for controlling the fission gas released following reactor accidents are being developed. This will reduce the most acute consequences of reactor accidents. The characteristics of aerosol formation from nuclear material are being determined in support of shipping hazards analyses. A transport model is being developed to predict the rate and direction of travel of fission product materials from accidental release to the soil.

Reactors

Metal Water Reactions

Major Accomplishments to Date

Seventeen metal-water reaction tests and three clad expansion tests have been completed. Measured hydrogen evolution from the zircaloy-steam reaction on unirradiated fuel and process tubes agrees within ten percent of the Baker-Just parabolic rate law being used by the nuclear industry. Results from tests with irradiated fuel above the clad failure temperature indicate the hydrogen generation varies with the physical characteristics of the failed fuel. Measured hydrogen evolution has been less than predicted by current analytical models.

Progress During Report Period

The metal-water reaction test program proceeded at a rapid pace until early February, including tests at temperatures above clad failure but below uranium melting temperature, above uranium melting temperature, and involving special clad expansion. Since February, no tests have been performed due to fund limitations, but plans include resumption of testing in FY 1971.

Future Work

Metal-water reaction tests with molten fuel will be completed. Fission product releases from molten fuel will be measured and the analytical determination of releases will be resolved. Detailed planning for fuel quench tests will be started to simulate core performance during transition from normal to emergency cooling for N reactor fuels.

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Meteorological Studies

Major Accomplishments to Date

A meteorological data acquisition system has been installed and put into operation at N reactor. Five remote portable wind stations are in operation. From recorded data, 159 streamline analyses have been made.

Progress During Report Period

A report issued by Battelle-Northwest summarized tetroon (constant elevation balloon) releases, streamline studies and wind direction correlations for the various meteorological stations involved. A major conclusion reached is that the wind regime around 100-N Area is of a complex nature such that a release of material at N reactor would pass over the Wahluke Slope 43 percent of the time.

Future Plans

Collection of data will be continued. N meteorological software will be completed. The field station network will be revised to optimize knowledge of airflow. Balloon releases, aircraft soundings, and smoke and zinc sulphite tracer studies will be started.

Soil Studies

Major Accomplishments to Date

Minimum travel time for I-131 from the 1301-N crib to the river has been evaluated by various methods. The I-131 concentration in springs from the crib has been found to be approximately three times the 10 CFR 20 limits for uncontrolled areas.

Progress During Report Period

The minimum travel time from the 1301-N crib to the river bank springs was found to be 9 ± 1 days.

Future Plans

The second phase of digital modeling of hydrological factors related to the emergency waste disposal (EWD) basin will be started. This study will involve effects on ground water of discharge of liquid into the EWD basin. The effect of the 1301-N crib also will be evaluated. Ground infiltration rate and decontamination factors of water entering EWD basin will be determined.

Lattice Heating Transients and Confinement System Analysis

Major Accomplishments to Date

Experimental apparatus for fuel heat transfer experiments has been completed.

Progress During Report Period

Computerized models were developed for primary cooling system blowdown calculations and confinement system pressurization studies. Experimental work was started to

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simulate N reactor loss of coolant accidents to verify calculations of post-accident fuel temperature transients and metal-water reaction effects.

Future Plans

Blowdown and confinement pressurization studies will continue with enough pipe break cases to determine effects of key pipe breaks. Data will be developed to provide calculations of offsite radiation dosage consequences so that needs for modification to the confinement system can be identified. Heat transfer experiments simulating loss-of-coolant accidents will be conducted and used to refine studies.

K Reactor Metal-Metal Studies

Major Accomplishments to Date

Offsite experimental results on heat formation of uranium-aluminum compounds have been utilized to study effects of a fuel meltdown. It appears that the reactions are slow in relation to the timing of temperature excursions from loss of coolant.

Progress During Report Period

There was no progress on this program during the reporting period due to de-emphasis of K reactor related R&D effort following the shutdown of KW reactor.

Future Plans

There are no plans to continue this work.

K Seismic Studies

Major Accomplishments to Date

A preliminary report has been prepared on part of the primary piping system. Analysis on the stack and shields, piping and 105 Building has been largely completed.

Progress During Report Period

Work on this program was terminated in February due to lack of funding and no significant progress was made.

Future Plans

No future work is planned.

Noble Gas Partition Studies

Major Accomplishments to Date

Data have been gathered on dissolution of krypton in water in a closed vessel, release of krypton from water to air, and transport of krypton through turbulent water pools.

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Progress During Report Period

Information was obtained on the dissolution of krypton in water in a closed vessel, the release of krypton from water to air after dumping water to an open vessel, and transport of krypton through water pools having varying degrees of turbulence.

Future Plans

Variation of krypton transport with pool depth as well as partition coefficients of radio-krypton introduced into water by a carrier gas will be studied. Possibility of large scale tests at N reactor will be investigated.

Confinement Charcoal Filters

Major Accomplishments to Date

Procedures for receipt and complete freon testing of charcoal filters have been successfully demonstrated for both K and N reactor charcoal filter banks. Permanent in-place testing facilities have been installed in operating reactors for future quarterly testing.

Progress During Report Period

Progress was excellent, including:

1. All cells at a level of 99.95+ for iodine removal capability.
2. Permanent in-place test lines installed with significant savings in manpower.
3. Incorporation of test procedures in the KE reactor Process Standards.

Future Plans

Future work will be of an operational nature. All development is completed.

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Chemical Separations

Nuclear Safety

Atmospheric Dispersion of Radioactive Particles

Major Accomplishments to Date

This study has progressed through a sequence of tasks which have yielded significant information regarding the airborne release of plutonium and its compounds during overheating. The first experiments were designed around plutonium systems because of the urgent need to establish preventative and recovery measures in plutonium handling facilities. The parameters of time, ignition temperature, air velocity and source material characteristics were typified, but not fully explored. The data obtained from these first experiments provided order-of-magnitude estimates of the quantities which could be airborne and transported.

Progress During Report Period

Design of experiments to study the release of uranium (a stand-in for plutonium) in petroleum product fires was completed. These experiments will be conducted in the large-scale Radioactive Aerosol Release Laboratory (242-B Building).

Future Plans

Analysis of specimens from RFP will be completed. Evaluation of the data will be made and the information integrated into this study.

The large Radioactive Aerosol Release Laboratory will be completed and the parameters associated with the airborne release of uranium and its compounds (stand-in for plutonium) will be characterized.

A study will be made to characterize radioactive particles emitted from processing plants to allow prediction of their areal distribution as a function of airborne concentration.

Seismic Investigations

Major Accomplishments to Date

In 1966 Jones and Deacon made a study of the geology and tectonic history of the Hanford area. In their report they stated that photogeologic mapping revealed two areas of recent and historic faulting. They recommended that a more detailed geologic investigation involving trenching and drilling in these areas of inferred faulting be made. On the basis of this recommendation, a more detailed geologic study was initiated. A portion of this investigation was made by the U. S. Geological Survey (USGS) and sponsored by the Division of Reactor Development and Technology. The USGS study included the establishment of an array of highly sensitive geophones around the periphery of the Hanford Reservation. This network has been in continuous operation since March 23, 1969.

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Several studies were made to estimate the magnitude and location of the maximum potential earthquake for the Hanford area based on the assumption that the faults inferred by Jones and Deacon are real. Significant conclusions reached in these studies are:

1. The probability of earthquakes occurring in southeast Washington with accelerations of 0.1g, 0.15g and 0.2g are once in 1850, 4000, and 16,700 years respectively.
2. The maximum possible earthquake might never have occurred within the period of recorded history.
3. The best estimate of the magnitude of the maximum potential earthquake for the Hanford area is 5.8. This estimate is based on the Milton-Freewater shock of 1936.
4. An earthquake similar to the Milton-Freewater shock could occur anywhere along the fault system.
5. The nearest credible location of an earthquake similar to the Milton-Freewater shock is the Rattlesnake Hills along the southwestern boundary of the Hanford Reservation.
6. Since a shock of magnitude greater than 5.8 or intensity greater than MM VI has never been recorded in the Hanford Reservation area in the last one hundred years, there is no reason to believe there will be any shocks of this magnitude during the next 50 to 100 years.

A strong motion recording seismograph was installed on Gable Mountain to record ground response data over a range of accelerations from 1.0 to $10^{-4}g$. Measurements of ground motion resulting from quarry blasting were made at a number of locations on the Hanford Reservation including the strong motion station on Gable Mountain. The results of these measurements showed vertical accelerations up to 0.48g at 800 feet from the shot site to $10^{-4}g$ at distances of 24,000 feet. The dominant frequencies were found to be in the band between 2.5 cps to 10 cps.

A portable continuously recording hydroseismic system was fabricated to extend the capability for detecting earthquakes occurring in the vicinity of the Hanford Reservation. This system is comparable to a combined conventional long-period and short-period inertial seismograph and can detect frequencies from 1/6 second to about 150 seconds.

In support of the USGS investigation of possible young faulting on Gable Mountain and Gable Butte, approximately 2000 feet of trenches were excavated. Those trenches that contained the most complete exposure of features relative to determining the presence or absence of faulting at these sites were mapped and logged and the data documented.

Progress During Report Period

In recognition of the rapid advances now being made in the field of earthquake engineering and related sciences, the Seismic Investigations program was

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revised. New program elements and significant changes are:

1. A Planning and Review Committee composed of working representatives of each of the involved Hanford contractors, the USGS, the US Coast and Geodetic Survey, and expert consultants in the pertinent disciplines of geology, hydrology, seismology, earthquake engineering, and structural analysis was recommended.
2. The scope of the geological and geophysical studies was enlarged to include the tectonics of the entire northwestern portion of the United States. This is consonant with the evolution of plate tectonic theory.
3. Recommendations were made to expand the geophone array to determine precise locations and focal depths of microearthquakes over a broader area surrounding the Hanford Reservation.
4. Structural analyses data for evaluating critical structures with respect to predicted ground motions from earthquakes was added to the program.
5. An expenditure pattern for the Seismic Investigations program of \$1,000,000 over the next five years was recommended.

Future Plans

The Planning and Review Committee will be activated as soon as practicable. Geological and geophysical studies will be resumed in the areas of inferred and mapped faults surrounding the Hanford Reservation.

Regional studies will be made to relate local structures to regional and western tectonics.

Identification and evaluation of microearthquakes in the Hanford region will continue. Additional geophones will be incorporated into the current array as needed.

Physical constants of Hanford-type rocks will be determined as needed for incorporation into a response spectra model for the Hanford Reservation.

An analysis of the capability of critical structures to retain their integrity during the most intense ground motions predicted for Hanford will be made.

Radionuclides in Soils

Major Accomplishments to Date

A theory was developed and documented showing how ground water travel paths and travel times could be obtained in large heterogeneous flow systems from a knowledge of ground water potential distribution and a select number of permeability measurements. It was shown that from these data the permeability

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distribution for the entire flow system could be calculated. To calculate travel times the porosity was assumed to be constant over the entire region. Application of this theory only extended to steady-state flow system.

Assuming quasi-steady-state flow conditions beneath the Hanford Reservation, this theory was tested by determining the flow paths and travel times for that portion of the Hanford flow system between the 200 Areas and the Columbia River.

A transport simulation model to solve radionuclide and toxic chemical transport in either saturated or partially saturated and in either transient or steady-state ground water flow system was developed. Two general sets of equations describing ground water transport have been formulated; one, a set of simultaneous equations and the other, a set of independent equations. An algorithm for the solution of the simultaneous equations was developed which gives the time dependent concentration distribution of macro-ions in solids. A knowledge of the macro-ion concentration distribution as a function of time and space and soil characteristics then permits the calculation of the trace ion concentration distribution using the independent equations. Input data for this program are obtained from laboratory determinations of the chemical properties of the Hanford sediments. These properties include solution ions, solid-phase carbonates, cation exchange capacity, ion exchange constants, and all soluble components.

Studies were started to verify and evaluate the transport equations. Saturated soil columns, filled with Hanford sediment previously characterized, were prepared and solutions containing trace concentrations of cesium and strontium ions were introduced into the test flow system. Good agreement was observed between predicted distributions and those observed in the soil columns. Laboratory column studies were then initiated to evaluate the sorption routine in unsaturated systems.

Hydrological measurements have been made in the laboratory and in the field to determine hydrological characteristics of the Hanford sediments in both the saturated and partially saturated regions. These data have been incorporated into the several mathematical models which describe the Hanford ground water flow system. Soil psychrometers were also implanted in the partially saturated region to obtain data on the total water potential distribution in these sediments as a function of time.

Concurrently with the theoretical development of the steady-state saturated flow model, other flow models were developed and documented for predicting water flow paths and travel times in saturated and partially saturated transient flow systems. As part of this development, error and sensitivity analyses were made on the input parameters.

One error and sensitivity analysis of the steady-state saturated flow model showed that slight changes in water potential could cause nearly an order of magnitude change in the calculated permeability values. As a consequence the predicted water flow paths and travel times obtained by this flow model were less accurate than previously thought. To obtain the accuracy required for future predictive capability, a new method for determining water flow paths and travel times was developed and documented. This method is based on continuity of flow in a stream tube which relates ground water potential with transmissibility. The sensitivity of water potentials to transmissibilities is within the accuracy of field measurements.

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For solution of steady-state saturated flow problems, a two dimensional model was assumed to be adequate on the basis of the ratio of the thickness of the Hanford ground water flow system to its lateral extent, 1:100. With the subsequent development of the transient saturated flow model, the capability for changing aquifer thickness was incorporated. This model is called the Variable Thickness Transient flow model (VTT). The partially saturated transient flow model (PST), while developed independent of the VTT, was designed to interface with the VTT and to provide modeling capability for transient flow in the entire system without the need to handle each model separately. Work on developing computer routines for predicting water flow paths and travel times by the VTT and PST flow model was initiated.

A computer controlled data display system was developed to provide a three-dimensional view simulating the Hanford ground water flow system. Within hours following input of data into this system visual observations can be made of the predicted water flow paths from any given site on the Hanford Reservation. The relative rate at which pollutants would travel down these flow paths with respect to ground water travel times can also be observed on this display system.

A detailed critical path analysis and planning program of the research for development of a transport model for the Hanford ground water flow system was documented. A revision of this document was made to incorporate the knowledge gained from the first year's research effort and recommendations of the ARHCO consultants in hydrology and soil chemistry. The revised program was directed toward providing analytical tools compatible with either field data presently available or field data that can be obtained reasonably.

Progress During Report Period

Work continued on developing and evaluating ground water flow models and their associated computer routines. Results of this effort are summarized as follows:

1. A literature review was conducted to determine recent advances in the theoretical description of moisture movement in partially saturated soils. The results of this review suggests that irreversible thermodynamics (which includes all flow from any measurable driving force) be used for modeling purposes.
2. Efforts to develop a numerically stable algorithm for computer solution of the PST flow model have been unsuccessful. The problem is nonconvergence of the solution after an initial number of time steps are taken.
3. The computer routine for the VTT flow model has been debugged, tested, and is ready for use.
4. Transmissibility calculations were made for the saturated ground water flow system. These data have been input to the VTT flow model to determine how accurate it will predict the current and pre-Hanford water table potential pattern.
5. A number of transmissibility measurements were made from pump drawdown tests in wells that penetrate the unconfined ground water system. These measurements were made in areas where no accurate data were available. These data were input into the VTT flow model.

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Studies to verify and evaluate the transport equations continued. Modifications were made in the simultaneous equations that describe the time dependent movement and concentration of the macro-ions. The algorithm for solution of these equations was modified accordingly and debugged. Laboratory soil column tests are now being made to verify the improved predictive capability of the modified transport equations.

Future Plans

A numerically stable algorithm for computer solution will be developed for analysis of flow problems with the PST flow model.

Integration of the PST and VTT flow models such that the entire ground water flow system can be treated as a single boundary value problem will be evaluated.

Verification and evaluation of the transport simulation model capabilities will continue. The completed transport model for describing and predicting the movement of radionuclides and toxic chemicals through Hanford soils will be completed in FY 1972. As error and sensitivity analysis indicate need, refinement or extension of this model will be determined as needed.

Methods for controlling the rate and direction of ground water movement beneath the Hanford Reservation will be developed.

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WASTE MANAGEMENT PROGRAM

Waste Management

The research and development work under this program is to provide technology whereby the wastes (gaseous, liquid, solid) generated in the chemical processing of irradiated fuels and targets may, at low cost, be solidified and confined for long-term surveillance and control, or safely dispersed in the environment. Also, limited effort has been expended to develop technology to minimize radioactivity from reactor effluents, gaseous and liquid.

Objectives and Incentives

The purpose of this activity is to provide long-term high-integrity confinement and control of hazardous nuclear waste and to reduce the amount of radioactivity released to the environment to the lowest practical value.

The incentive for removing radioactive material from reactor effluent is to reduce activity in the Columbia River to the smallest possible amount consistent with need for plutonium and effect on the population.

The incentives for solidifying the bulk salt waste as opposed to continued in-tank storage are both safety (immobilization of fission products) and economics (estimated savings have a present worth of \$60 million as compared with continued storage in tanks having a 20-year life).

The incentive for improved treatment of low-level wastes is safety in keeping with the AEC anti-pollution campaign aimed at reducing significantly the amounts of radioactivity released to the environment.

The incentive for removing the long-lived heat emitters for separate high-integrity storage is near-term safety. The long-lived heat emitting isotopes, strontium-90 and cesium-137, are to be removed by solvent extraction and ion exchange, respectively, and packaged in high-integrity containers. The residual bulk wastes will be solidified in underground storage tanks in a few years instead of in several decades.

Reactors

Major Accomplishments to Date

This is a new program with all accomplishments shown under Progress During Report Period.

Progress During Report Period

Pilot plant facilities to obtain information for the design of equipment to reduce the release of radioactive material to the environment were scoped for KE and N reactors.

Future Plans

Two areas of work are planned, but these will be handled under the Environmental and Regulatory Program, or under Process Technology. The program will cover treatment of the coolant contamination at N reactor by use of ion exchange and monitoring of radioactive releases from both KE and N reactors.

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Chemical Separations

Low-Level Waste Stream Monitor

Major Accomplishments to Date

A standardized low-level radiation monitor and proportional sampling system was developed, fabricated and installed on a plant waste stream. The system collects a proportional sample, records total stream flow and radiation intensity, and provides an alarm at a pre-set level. Improved beta sensitivity is required to detect beta-emitting radionuclides at concentrations near 0.1 MPC_w .

Progress During Report Period

Evaluation of the above system has continued in the laboratory and in a field installation. An effort is being made to gain improved beta sensitivity. Work has been started to determine techniques for reducing background buildup. Various beta-gamma detector designs are being tested for sensitivity to isotopes normally found in process waste streams.

Proportional samplers of either a peristaltic tubing pump type or a plug valve type, can give satisfactory operation. Field tests are continuing.

As a result of the prototype evaluation, design is in progress for a similar monitor to be used on another waste stream.

Future Plans

The prototype system will continue to be tested and evaluated. The design of a detector with improved beta sensitivity for in-line use is planned.

Evaluation of alternate proportional samplers will be continued to obtain the most reliable and maintenance free type.

Gamma Monitor Cell Development

Major Accomplishments to Date

An improved technique for fabricating the brass cores used in the manufacture of plastic gamma monitor cells was developed. Several sample cells molded from the plastic Kynar were inspected and tested. Surface characteristics and absence of contamination retention appeared favorable in laboratory tests. Splitting and leaking molded-in fittings indicated a need for improvement in the molding technique and fitting design.

Progress During Report Period

A Kynar (trade name--Pennwalt Corp.) sample cell installed in the Purex Plant for field evaluation of gamma monitoring developed high background activity in less

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than one day. Electropolishing techniques for stainless steel cells show promise for minimizing the buildup of radioactivity.

Future Plans

The cathode design and current density value for electropolishing the internal surface of "U" shaped stainless steel sample cells, compatible with present gamma monitor installations will be optimized. A suitable prototype cell for field evaluation in the Purex Plant will be prepared.

The cathode design and current density value for electropolishing the internal surface of a large volume, low-level gamma monitor cell will be optimized. A modified low-level sample cell will be fabricated for field evaluation.

In-Line Alpha Monitoring

Major Accomplishments to Date

The relationship of cerium activated zone geometry to beta discrimination was defined. Specification of sensors to the manufacturer results in a variation of diffusion depth not likely to be acceptable as received. In-plant optimization appears as the alternative.

A mockup of a plant alpha cell was made and tested with plant electronics. Comparison of the performance of plant and laboratory electronics was made using plant stream samples. Investigation into the use of fiber optics to produce a virtual optimum active domain 2 mils in diameter 5 mils apart and 1 mil deep was made. The use of chemical milling of sensors using concentrated potassium hydroxide was also conducted. Cobalt irradiation of sensor and epoxy optical cement was made and evaluated. A mathematical correlation was developed which relates the thickness of the activated region with the beta count rate using a strontium gamma source. Comparison with a sensor of known thickness will give the thickness of sensor being analyzed.

Progress During Report Period

Variation between plant and laboratory performance of in-line alpha monitors appears to be due, at least in part, to differences in phototube sensor coupling, to light leakage, and to differences in the electronics.

Future Plans

Actual plant solutions and plant electronics are to be used in the laboratory to simulate plant condition. It is anticipated that comparison to plant conditions and operation will clarify the sources of difficulty. Built in system gain measurement will be evaluated, plant systems could then be readily adjusted to optimum performance.

Definition of Impurities in Purex Condensate

Major Accomplishments to Date

The presence of all the common organic materials used in the Purex process have been isolated from the recycle condensate. A gallon sample of a Purex process

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condensate stream (1UD) contained the following:

1.15 g NPH
1.97 g TBP
0.08 g DBP

The presence of DBP was determined by titrimetry assuming that all the acidic material found was DBP. It was important that a new analytical technique be developed to identify this material with greater certainty.

Progress During Report Period

Analytical techniques have been developed for determining normal paraffin hydrocarbon (NPH), tributylphosphate (TBP), and dibutylphosphate (DBP) in Purex condensates. DBP and TBP are extracted separately from aqueous solution by pH changes. DBP is methylated in carbon tetrachloride with diazomethane and determined by gas chromatography.

Future Plans

The acquisition of a combination gas chromatograph-mass spectrometer will now permit identification of organic substances at very small concentrations.

Condensate Recycle and Treatment

Major Accomplishment to Date

Development of an AW500 zeolite ion exchange process for removal of cesium-137 from AX tank farm condensate was completed. A prototype column has been installed and is operated routinely. Cesium-137 concentration meets discharge limits.

Studies with either a hollow nylon fiber reverse osmosis unit, or a cellulose acetate membrane unit showed that reverse osmosis can be used to reject radioactivity from at least some specific condensate streams. On the other hand, organic (TBP) removal was not complete and appeared to decrease as the unit was operated, possibly due to sorption on the surface of the membranes, followed by diffusion through the membrane with cleaned water. However, the TBP did not appear to interfere with ionic removal.

Progress During Report Period

High decontamination of B Plant process condensate was obtained in laboratory columns using Dowex-50 (trade name--Dow Chemical Company) and Dowex-1 ion exchanges. It was necessary to remove ammonia by steam stripping.

Reverse osmosis does not appear to provide the desired decontamination.

Future Plans

Column studies will be conducted to determine the breakthrough capacity and long-term decontamination ability of the resin beds.

The reverse osmosis studies will concentrate on methods of increasing process efficiency. Recycle and staging will be investigated in order to evaluate the

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feasibility of application of the process to certain waste streams. Cellulose acetate membranes will be evaluated.

Absorption and Oxidation of Nitrogen Oxides in TBP

Major Accomplishments to Date

It was determined that Dowex-50 with 0.1M HNO_3 does not effectively catalyze the oxidation of nitrous acid with air, contrary to the claims of the patents. Ozone at 55°C was found to be a reasonably effective oxidizer for nitrous acid at room temperature. The effect of hydrogen peroxide on TBP and NPH at 50°C was tested. No effect on TBP was observed. An unidentified impurity in NPH, not included in raffinate and not removed by silica gel, reacts at 50°C with hydrogen peroxide to produce a solid product. Approximate composition of the product is (mole %) C-17, O-17, Na-11, P-16, K-6, Ca-3, Cr-5, Fe-16, Ni-3, and Ca-4.

Some inexpensive systems and processes were checked for oxidation effectiveness in the absence of the resin "catalyst," again at 0.1M HNO_3 . Air and oxygen will oxidize the nitrous acid but only at elevated temperatures, 85° to 100°, and even then not sufficiently rapid to be practical. Similarly, disproportionation of nitrous acid by heat alone occurs but not rapidly.

Progress During Report Period

Studies are being performed on absorption of nitrogen oxides by scrubbing in TBP. It has been reported that Dowex-50 catalyzes oxidation of nitrous acid. Laboratory data show that the role of the Dowex-50 is to suppress an undesirable side reaction. Oxidation of nitrous acid is catalyzed by nitric acid.

Future Plans

Further experiments will include direct addition of nitrogen oxides (NO_2 and NO) to the TBP/NPH system rather than introduction of nitrous acid. Under these conditions the importance of reaction $\text{HNO}_3 + \text{HNO}_2 = 2\text{NO}_2 + \text{H}_2\text{O}$ may be minimized, even in the absence of resin; the effect of oxygen or air pressure on the oxidation rate will then be determined and the importance of TBP in the conversion of the nitrogen oxides to nitric acid can be determined.

Recovery of Plutonium from Z Plant Sump

Major Accomplishments to Date

Ion exchange loading of plutonium from sump solutions without pre-treatment to adjust the plutonium valence has been investigated. Solutions containing 100 g/liter Pu(IV) in 6M HNO_3 were diluted and neutralized to 0.3 g/liter Pu in 0.3M HNO_3 without localized polymerization. Loadings of 99.8 percent and elutions of 86 percent were obtained.

Progress During Report Period

Z Plant sump wastes were processed in a laboratory ion exchange column using Dowex-50. An unidentified species darkened the column and presumably caused the 50 percent plutonium breakthrough at 500 column volumes. Americium breakthrough was only 2 percent.

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Future Plans

The species responsible for column color change will be identified. Fluoride or nitrate complexants for selective ion exchange separation of plutonium from iron and aluminum wastes will be evaluated.

Treatment of Z Plant Organic Waste

Major Accomplishments to Date

Use of activated carbon to remove CCl_4 , TBP, DBBP, HDEHP, TOPO (trioctylphosphine oxide) from high salt aqueous waste streams was shown to be feasible. Removal of these materials was quantitative over a wide range of aqueous flow rates (10^2 - 10^3 gallons/hour/ft²) and feed conditions. Also, TBP and DBBP were found to be effective in extracting plutonium (but not americium) once the organic material had been absorbed onto the carbon. Recovery of the extracted plutonium and/or regeneration of the carbon bed, using low temperature steam or acetone, was only partially effective.

Progress During Report Period

Experiments were conducted which showed that activated carbon, used to remove organic solvents from high salt waste streams by absorption, can be regenerated to 92 percent capacity by gas purging at elevated temperatures. Alumina possesses potential as a sorbent for organics. If Z Plant high salt wastes are calcined, the alumina produced can sorb about one volume organic to four volumes of calcine.

Future Plans

Future work will consider the following:

1. Finish sorption loading and bed regeneration studies if ITS is selected.
2. Demonstrate the ability of the recently purchased, geometrically favorable centrifuge to accumulate solids while separating the organics from the salt wastes.

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Ion Exchange Removal of Cesium from Normal and Enriched Fuel Wastes

Major Accomplishments to Date

Synthetic and hot laboratory studies have indicated that ion exchange with "ABEDEM, Ti-A" inorganic resin, a product of the Belgain Company, Seria, may be an alternative process.

Progress During Report Period

ABEDEM ion exchange resin was tested in the laboratory for removing cesium from a synthetic current acid waste (Purex Acid Waste-Zirflex Acid Waste). Approximately 75 column volumes of feed was loaded before 50 percent cesium breakthrough. Strontium

was not retained. Cesium can be eluted with ammonium nitrate or ammonium acetate solution. Sodium-to-cesium ratios of 0.37 and 0.33 were obtained.

Future Plans

Flowsheets will be developed for 1) ion exchange processing of current acid waste (CAW) concurrently with stored waste, and 2) ion exchange processing of CAW alone.

Removal of Redox Supernate (RSN) by Ion Exchange

Major Accomplishments to Date

The characteristics of RSN are markedly different from Purex supernates (PSN). A process was developed for removing cesium from RSN using Duolite C-3 resin (Diamond Shamrock product). Advances in technology and new exchangers available on the market suggested that the process could be improved.

Progress During Report Period

Redox supernate (RSN) stored at or above 60°C must be diluted with an equal volume of water to form a stable solution for processing. Of several ion exchangers tested for removal of cesium from RSN, Zeolon (a product of Norton Company) was selected for this service. Since the sodium-to-cesium ratio is high (greater than 10) in the eluted product, a rework and purification cycle may be necessary.

Future Plans

Hot cell studies currently under way will be completed by FY 1971. Radiation stability experiments involving Duolite ARC-359 will be completed to fully evaluate this material as a backup for Zeolon.

Strontium Recovery from Current Acid Waste (CAW) and Purified Acid Sludge

Major Accomplishments to Date

New project.

Progress During Report Period

Conflicting results and observations have been obtained on examining the nature of solids and their role in the extraction of strontium from current acid wastes and Purex acidified sludge.

Future Plans

Additional studies will be performed on the scavenging of strontium from CAW solutions by the black compound layer solids. Additional determinations will be made on the composition of recent batches of plant solids. The susceptibility of these solids to metathesis and effects upon solvent extraction of strontium will be determined.

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Effect of Process Variables on Solvent Extractions

Major Accomplishments to Date

A steady-state pulse column model, including backmixing in both phases, was fitted to an existing set of measurements of internal C column compositions over a wide range of operating variables.

The behavior of selected metal ions as a function of complexing agents in the feed was investigated. Citric acid complexes iron and aluminum, but not lead. N-hydroxyethylethylenediaminetriacetic acid (HEDTA) complexes iron, aluminum and lead, but is about three times more costly on a mole-to-mole basis than citric acid. A mixture of citric acid and HEDTA can be used effectively to complex all three elements.

Progress During Report Period

The distribution ratio of cadmium, which may be present in B Plant feed because of its use in the Purex Plant for criticality control in some rework operation, was measured at 170, compared to a strontium ratio of 100 under the same conditions, when using citric acid as a complexant. Other complexants will reduce the cadmium extraction to satisfactory levels.

Future Plans

A statistically designed study is planned to derive empirical relationships for predicting $Sr E_a$ using known initial values of the various parameters which affect E_a . Some laboratory verification will be required to determine the range of validity of the expressions derived. If expressions can be derived which successfully predict strontium behavior, the study will be expanded to other elements of interest. The pulse column model will be expanded to accommodate multiple feed points.

Final Purification of Strontium

Major Accomplishments to Date

A sulfate precipitation process using lead carrier has been used previously at Hanford as a method for isolating strontium. Experience with this process, coupled with other laboratory experiments suggest this process without carrier addition may be adequate for strontium purification.

A study to purify strontium by ion exchange was initiated in August 1969. Nitrilotriacetic acid (NTA) was added to a synthetic B Plant strontium product solution to complex selected metal ions. The solution was then passed through a bed of zeolite 13X (trade name--Linde Division, Union Carbide Corp.) ion exchanger where strontium was selectively removed. Elution of the strontium was performed with ammonium carbonate-ammonium hydroxide solution. Through four loading and elution cycles, decontamination factors between feed influent and product effluent ranged from 6 to 30 for magnesium and manganese and 2 to 6 for calcium.

Progress During Report Period

Attempts to purify the strontium product from B Plant solvent extraction by hydroxide precipitation without additional purification prior to precipitation

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showed that additional purification is desirable. Both a multiple sulfate precipitation process and an ion exchange process are being studied to displace a second solvent extraction cycle for the purification (a citrate-kill step requiring a new specially designed concentrator would be required for the solvent extraction product). Both processes produce a product of satisfactory purity.

Future Plans

Hot cell demonstration of the multiple sulfate precipitation process is in progress using concentrated B Plant strontium solvent extraction product. Additional process optimization studies may be pursued, pending results of hot cell experiments.

Additional cold flowsheet studies of the ion exchange process will be performed to determine the feasibility of using more concentrated feeds. Hot cell tests of the process will be run. Optimization of the process will be studied. Effects of radiation on process solutions will be further investigated.

The hydroxide precipitation process will be tested on the product from hot cell studies of both the multiple sulfate process and the ion exchange process for product purification.

Corrosion Studies

Major Accomplishments to Date

Cathodic protection of 15-gallon tanks constructed of ASTM A-283, Grade C mild steel was successful for 49 weeks at ten milliamperes/square foot. Tanks failed at 5-8 weeks exposure with no protection or with only one milliamperes/square foot.

Progress During Report Period

Cathodic protection at ten milliamperes/square foot has been successful through 65 contact weeks for mild steel tanks containing high nitrate solutions. Mild steel weldments have not failed after 100 contact weeks in solutions containing 5M total nitrate plus nitrite, if the nitrate-to-nitrite ratios have been equal to or less than 1.5.

Future Plans

Monitoring of the model waste tank exposed to boiling simulated alkaline waste and cathodically protected with a current density of 10 milliamperes/square foot will continue.

Tests will continue with the mild steel weldments exposed to varying sodium nitrate and sodium nitrite concentrations. Also, a test to study the inhibiting effect of sulfate on the stress corrosion cracking of mild steel by alkaline nitrate-nitrite solutions will continue.

A study will continue to define the requisite Al/F mole ratio in Purex dissolver solutions and/or the replacement of aluminum with zirconium to give minimum corrosion rates of 304L.

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Waste Solidification in Tanks

Salt Cake Characterization

Major Accomplishments to Date

Differential thermal analysis of sludge from Tank 241-SX-108 showed several endotherms, but no exotherms at temperatures up to 930°F. Oxides of nitrogen evolved equivalent to about 3.5 percent of the sludge weight when sludge was heated to 1830°F in 360° increments. Volatilization of Cs-137 was 30 to 60 microcuries per gram of sludge.

The thermal conductivity of dry synthetic Redox sludge was determined with "line source" thermal conductivity equipment to be 0.121 Btu/(hr)(ft²)(°F/ft). Sludge from Tank 241-SX-108 was measured at 82°F to be 0.110 Btu/(hr)(ft²)(°F/ft).

Progress During Report Period

New data on thermal conductivity of sludges suggest that the in situ thermal conductivity of sludge in tanks may be appreciably higher than that measured for powdered materials. Thermal conductivity of loosely packed salt cake from Tank 116-TX increased on wetting and drying to a hard cake from 0.105 to 0.468 Btu/(hr)(ft²)(°F/ft).

Future Plans

Thermal conductivity measurements will be made on sludge from Tank 241-SX-108 at various temperatures and on other sludge samples as they are made available.

Waste Tank Thermal Analysis

Major Accomplishments to Date

Experiments were completed on the effect of moisture on soil thermal conductivity. A computer program was developed for one-dimensional transient heat transfer calculations.

Progress During Report Period

Computer calculations of maximum temperatures have been made for a wide variety of conditions for solidified wastes in underground tanks. Each specific set of experimental conditions requires separate evaluation.

Future Plans

Comparisons of the calculated results with tank operating conditions will be made for Tank 241-SX-108, which contains solidified air-cooled wastes. The effects of moisture in the soil will be included in the rapid calculation methods.

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Cesium-Strontium PackagingFlowsheet Development and Compatibility StudiesMajor Accomplishments to Date

A survey was made of strontium and cesium compounds, and SrF_2 and CsCl were selected as the optimum compounds for packaging. The various steps in the processes were checked out using both simulated and radioactive feed materials. Sufficient $^{90}\text{SrF}_2$ and $^{137}\text{CsCl}$ were prepared by the flowsheets to allow fabrication of the radioactive compatibility test capsules.

Compatibility testing of both radioactive and nonradioactive CsCl and SrF_2 with various materials of containment was initiated. The results of the six-month nonradioactive tests indicated that either 316L or Hastelloy-C can be used to contain CsCl ; and that either Hastelloy-C, Hastelloy-X or Haynes-25 can probably be used with SrF_2 .

Work was started on a program to evaluate methods for decontaminating $^{137}\text{CsCl}$ and $^{90}\text{SrF}_2$ from metal surfaces. Initial results indicated that washing with boiling water would remove most of the contamination from unwelded surfaces. However, a more effective procedure was needed to reduce the contamination to an acceptable level.

Progress During Report Period

Compatibility testing continued. None of the materials tested showed excessive attack. Currently, 316L stainless steel appears to be the best choice for cesium chloride (CsCl), and Haynes-25 appears to be a slightly better choice for strontium fluoride encapsulation (SrF_2). The three-month radioactive test capsules showed somewhat more attack than the equivalent nonradioactive capsules. However, the attack was nominal and not sufficient to raise doubt about the successful containment of either CsCl or SrF_2 . Welded surfaces exhibit essentially the same compatibility as nonwelded surfaces.

Removal of SrF_2 contamination from welded and unwelded surfaces is more difficult than removal of CsCl contamination. Procedures for removal of contamination are being developed.

Investigation of the cesium chloride (CsCl)-potassium chloride (KCl)-sodium chloride (NaCl) phase diagram is being conducted. The lowest phase transition measured was 310°C with a CsCl - KCl mixture containing 19 Wt% KCl . Preliminary evidence indicates that NaCl or KCl added to CsCl reduces the thermal expansion of CsCl on heating.

Future Plans

The compatibility testing will be continued as scheduled. An interim report summarizing results from the one-year nonradioactive and 6-month radioactive tests will be prepared.

The CsCl - KCl - NaCl phase diagram studies will be completed.

Efforts directed at optimizing the strontium purification flowsheet will continue as required.

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Engineering Scale Strontium Fluoride Flowsheet Development

Major Accomplishments to Date

Equipment was designed and assembled to demonstrate the conversion of strontium nitrate solution to solid strontium fluoride. The equipment was sized to produce about three pounds of SrF_2 per batch.

The parameters for purification of the nitrate feed solution to remove magnesium and iron impurities were determined. The decontamination factors for magnesium and iron were 37 and 150, respectively. Strontium losses to the solid magnesium and iron hydroxides that were removed by centrifuging were high (up to 8 percent) because no good method for washing the centrifuge cake was found. Losses could be reduced to less than 3 percent with adequate washing.

Parameters for the production of SrF_2 were determined. A temperature of $60^\circ - 80^\circ\text{C}$ for precipitation of SrF_2 and digestion of the SrF_2 slurry results in larger particles than are obtained at room temperature. Increasing the pH from 7 to 10 results in a decrease in SrF_2 particle size as determined by particle settling rate. Strontium losses as a function of the amount of excess NaF used and the volume of wash were determined from solubility data found in the literature.

A sintered stainless steel cylinder with a 5 micron mean pore diameter was tested for filtering the SrF_2 slurry. Complete separation of the solid SrF_2 was obtained and the filters have been reused twelve times without washing between runs. The sintered stainless steel filters have been recommended for the final process equipment.

The effect of sintering temperature on SrF_2 particle density and on moisture removal from SrF_2 was investigated. Sintering at $800 - 850^\circ\text{C}$ gave a higher particle density than sintering at $900 - 1100^\circ\text{C}$.

Powder handling techniques have been simplified by the use of large sintered agglomerates in the impact consolidation scheme for compaction. The dried SrF_2 can be dumped from the sintered metal filters into ceramic crucibles which are then placed in the sintering furnace. The sintered product can then be emptied into the feed mechanism for impact consolidation.

Progress During Report Period

Experimentally it was determined that an excess of 10 percent sodium fluoride (NaF) is required to reduce strontium losses to the supernate below one percent in the precipitation procedure. Apparently, with greater than five percent excess NaF, a small amount of fine SrF_2 passes through five micron pore diameter filters.

Future Plans

The equipment will remain operable to produce SrF_2 for capsule evaluation and compaction studies. Testing of components for the remote process equipment will be performed.

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Engineering Scale Cesium Chloride Flowsheet Development

Major Accomplishments to Date

The pan dryer process for production of CsCl powder was evaluated in tests conducted by the Bethlehem Corporation. Equipment design parameters were determined based on the results of the tests.

The melt-cast process for production of solid CsCl was evaluated.

An off-gas system for recovering CsCl entrained and volatilized during the evaporation and melting steps was evaluated.

Although some concern has been expressed on stress corrosion, prototype equipment for the melt-cast system was designed and built of 304L stainless steel.

Progress During Report Period

Modifications of the melt-cast prototype equipment were made to prevent overflow of the capsules. The 304L stainless steel dryer-melter does not show excessive corrosion after 150 hours at evaporation temperatures (100 to 200°C) and 30 hours at melter temperatures (600 to 720°C). There is still some concern, however, about stress corrosion with 304L stainless steel and other materials are being studied. Handling of the off-gas from the CsCl melter does not appear to present any difficult problems.

Future Plans

Corrosion of candidate materials for the dryer-melter will continue to be evaluated. Operating parameters for the melt-cast process will be determined. Alternative methods of sealing the capsules to the melt-transfer apparatus will be evaluated as necessary.

The computer program for calculating the ion exchange behavior of cesium, potassium, sodium, and ammonium ions during loading, scrubbing, and elution will be completed. Decontamination factors for potassium and sodium in plant scale columns will be estimated using parameters obtained from laboratory column experiments.

Encapsulation Development

Major Accomplishments to Date

Various methods of compacting SrF_2 were evaluated and impact consolidation was chosen for continued development.² A basic prototype unit was designed and fabricated. Several runs, including some thermally hot runs, were made with this equipment.

Progress During Report Period

Strontium fluoride was densified to 80 - 85 percent of theoretical in the impact consolidation prototype. The prototype will be used as a basis for final equipment design.

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Future Plans

Primary emphasis will be placed on the following:

1. Prototype refinement.
2. Establishment of operating parameters.
3. Loading of simulated cans for welding studies.
4. Evaluation of ceramic calcining boats.

Thermal and Economic Studies

Major Accomplishments to Date

The centerline and surface temperatures of the capsules were determined as functions of capsule surface emissivity, compaction density, capsule size, and gamma attenuation. Economic parameters affecting the compaction density were determined.

The thermal expansion of strontium fluoride and cesium chloride relative to the cladding materials was calculated in order to determine the allowable compaction densities. The allowable density was between 70 and 80 percent of theoretical for CsCl and was 96 percent of theoretical for SrF_2 .

A computer program, TIESOC, was written for the determination of the steady state temperature profiles in doubly encapsulated sources. The program can also be used for determination of temperatures of sources in various arrays.

The temperatures of the proposed SrF_2 and CsCl capsules in stagnant water were estimated. The temperature difference between the capsule walls and the water is between 15 and 20°C.

Progress During Report Period

Study of the thermal consequences of loss of coolant of a storage basin containing CsCl and SrF_2 capsules was begun using simulated 1 kilowatt capsules.

Future Plans

The temperatures around simulated capsules under typical flow conditions in the basin will be measured. The maximum temperatures attained under a series of potential nonstandard operating conditions will be estimated.

Thermal analyses of processing equipment will be performed as the equipment designs are developed.

Welding Development

Major Accomplishments to Date

Several weld joint designs for the strontium fluoride and cesium chloride capsules were examined. Test samples of the chosen design were delivered to NDT for development work. Preliminary welding of Hastelloy C containers loaded with inert SrF_2

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were successful in achieving seal welds (up to ca. 50 percent penetration) even at 500°C surface temperature on the capsules.

Progress During Report Period

Four actual size stainless steel capsules (two SrF_2 and two CsCl capsules) were welded using welding techniques developed suitable for remote operation.

Future Plans

Additional development work needed includes determination of a suitable helium leak detection test, determination of proper welding parameters at high surface temperatures, experimentation with planned containment materials, including destructive testing, and study of alternate joint designs which may offer improvements. Welding of actual capsules using the chosen materials will be performed for additional testing, for training production welders, and for providing bases for specifications.

Nondestructive Testing Support and Development

Major Accomplishments to Date

Ultrasonic test support on developmental weld samples was performed. An acoustic emission tester was fabricated for potential use as an ultrasonic test aid. Weld configurations which are compatible with remote ultrasonic test techniques were developed, and the ability to ultrasonically measure weld penetration was established. Weld penetration and interweld volume voids which exhibit areas as small as 0.010 inch in diameter parallel to the end cap are easily monitored with an ultrasonic beam aligned normal to the end cap. Flat bottoms of holes drilled into end caps provided references for developmental weld and test evaluation. The hole diameters ranged from 0.125 inches to 0.050 inches.

Future Plans

Support of the welding development and capsule integrity tasks will continue. Further refinement of electronic circuitry and ultrasonic test procedures is required. Scope designs of the mechanical and electronic portions of the remote ultrasonic test station will be completed.

Cell Mockup Facility

Major Accomplishments to Date

The initial fabrication and installation of all major pieces of equipment and associated piping for B cell has been completed with revisions to follow when additional data are supplied. An additional plywood structure was constructed to house D cell mockup equipment.

A purchase order was placed for a heavy-duty master-slave manipulator to be used in conjunction with one standard type. Initial development work was started on the A cell waste loadout technique.

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Progress During Report Period

The cell mockup facility is proving valuable as a tool in defining design bases. D cell was widened from eight feet to nine feet. Equipment and process lines were changed to take advantage of the added volume.

Future Plans

B cell will be altered to reflect the latest changes in the strontium process.

The A cell bag sealer will be evaluated. Other specific pieces of equipment will be mocked up as necessary to support detail design.

Equipment Design and Verification

Major Accomplishments to Date

Work was started on the design of a capsule calorimeter capable of handling both the SrF_2 and CsCl capsules. A program for testing the mechanical integrity of the capsules was outlined. Sampling techniques for hot-cell facilities were surveyed, and a design recommended for prototype testing.

Progress During Report Period

A conceptual design for a capsule calorimeter accommodating both CsCl and SrF_2 capsules was completed.

Future Plans

A prototype calorimeter will be fabricated and tested. Heaters will be made to simulate the capsules, and calibration runs will be made to determine the operating parameters of the device.

A prototype of a sampler for hot cell use will be built and tested.

Actual testing of complete and component sections of the capsules will be completed as capsules are fabricated. Modifications (or acceptance of the capsules as fabricated) will be based upon test results.

Salt Waste Volume Reduction

Alternate Purex Reductant - Uranium (IV)

Major Accomplishments to Date

Two single-stage and two six-stage Savannah River designed miniature centrifugal contactors were fabricated and tested for use in developing the technology supporting this task.

Pilot plant LBX pulse column runs demonstrated that a nearly flat uranium (IV) profile could be obtained by introducing uranium (IV) as a side stream near the bottom of the LBX cartridge.

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Progress During Report Period

The miniature centrifugal contactors are proving to be a useful tool in predicting the performance of the Purex partition column (1BX) using alternate reductants rather than ferrous sulfamate. Control runs, for example, have closely paralleled actual plant performance.

A plant test was run using uranium (IV) produced in PNL facilities by the aluminum powder reduction of uranyl nitrate in the presence of sulfamic acid. With adjustments in the flowsheet, the process performed successfully. However, under conditions of the test, the aluminum in the uranium (IV) stream was approximately equal to the iron in the normal (1BX) plutonium-uranium partitioning stream.

A high capacity cartridge was developed for the Purex partition column (1BX) for use if the present cartridge should prove inadequate to handle future production rates. The cartridge is a mixed-plate cartridge of stainless steel nozzle plates and fluorothene sieve plates.

Future Plans

Laboratory and pilot plant work will be continued on evaluation and demonstration of the use of a continuous platinum slurry reactor to prepare uranium (IV). Present plans are to scale-up the laboratory unit to approximately plant size.

A plant test of longer duration is planned for late third quarter or early fourth quarter of FY 1971. This test will use uranium (IV) solutions that do not contribute to the salt content of the waste. Tests will be conducted in the Separation Chemistry Laboratory's one-inch pulse columns prior to that time in an effort to develop an improved flowsheet for the plant test.

Other laboratory studies will be conducted prior to the plant test to evaluate the safety of using hydrazine in this application and/or the use of other holding reductants.

A plant test is scheduled for May 1970, in which the ferrous sulfamate presently added to the 2DF will be replaced by hydrazine in the 1CX and hydroxylamine nitrate in the 2DIS. If successful, this change will remove 30 percent of the added iron and sulfate from the Purex 1WW.

Alternative Purex Reductant - Platinum Catalyzed Hydrazine

Major Accomplishments to Date

The reductions of plutonium (IV) and uranium (IV) by hydrazine were found to be catalyzed by platinum. Catalyst pellets (platinum on a special alumina) suitable for long term use in nitric acid solutions were identified. Factors affecting the rate of reduction of uranium (IV) were investigated in beaker experiments.

Progress During Report Period

Preliminary tests showed that uranium (IV) can be continuously produced in a continuous platinum slurry reductor by catalytic reduction with hydrogen. These studies are continuing. Studies are also being performed on the catalytic production of uranium (IV) by hydrazine reduction.

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Future Plans

The plans are to continue studies aimed at identification of the catalyst poisons present in plant solutions, at removal of the poisons, and at finding ways to "live with" the poisons (if necessary).

Also, it will be determined whether or not the catalyst substrate is important to the poisoning mechanism.

Hydrazine Reaction Products

Major Accomplishments to Date

None

Progress During Report Period

Preparation of uranium (IV) solutions in the presence of hydrazine produces low concentration of hydrazoic acid. Methods are being sought to prevent formation or to destroy the hydrazoic acid in solution.

Future Plans

The study of reactions involving hydrazoic acid will be continued. Planned tests include determination of the volatility of hydrazoic acid in the organic phase and of the rate of the platinum-catalyzed decomposition of hydrazoic acid in the organic phase.

Plutonium (IV) - $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ Reaction: Kinetics and Stoichiometry

Major Accomplishments to Date

New project.

Progress During Report Period

The kinetics and stoichiometry of the reduction of plutonium (IV) with hydroxylamine nitrate is being studied under Purex partition column (LBX) conditions.

Future Plans

Future work will consider the following:

1. Apply the stopped-flow technique to some of the faster reactions.
2. Determine the effect of ionic strength on the reaction rate.
3. Temperature was controlled to $\pm 1^\circ\text{C}$. Better control to $\pm 0.1^\circ\text{C}$ will be possible with new equipment. More accurate results will be obtained.
4. Conduct additional studies with higher acid concentrations (1.5 to 2.5M).

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Dissolver Solids: Tests Involving Sodium GluconateMajor Accomplishments to Date

New Project

Progress During Report Period

Laboratory investigations showed that sodium gluconate prevents the formation of significant quantities of solids during the aluminum decladding step. There is no detrimental effect on the extraction of plutonium or uranium. Plant tests are being formulated and planned.

Future Plans

None planned.

Purex Process Solvent Treatment - Application of Macroreticular Ion Exchange ResinsMajor Accomplishments to Date

Initial investigations of macroreticular anion exchange resins showed that they had strong affinity for both DBP and fission product zirconium, niobium and ruthenium. Amberlyst 15, a cation exchange resin, was inferior to any of the anion resins for removing fission products. However, a mixture of Amberlyst 15 appeared to be more effective than either resin by itself.

Progress During Report Period

Macroreticular ion exchange resins continue to show promise as a means to displace current aqueous treatment methods for treating Purex process solvent. Fission product zirconium, niobium and ruthenium are strongly removed. Elution of the fission products by 3M nitric acid 0.05M hydrofluoric acid shows promise.

Future Plans

Future work will consider the following:

1. Column experiments to study loading of fission products from LCW solution as a function of flow rate will be started as soon as columns and feed material are available. Rate and degree of conversion of the chloride-form resin to hydroxide-form will also be studied.
2. Batch loading studies with laboratory-prepared 30 percent TBP-NPH spiked with DBP will be conducted to study uptake of this impurity by Amberlyst anion resins.
3. Batch elution studies to test new reagents for improved elution of ruthenium will be scouted.
4. Reuse of the resin after elution will be examined to estimate the life of the resin.

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Alternative Solidification Methods
Solidification of Purex High Heat Wastes

Major Accomplishments to Date

An undocumented study was made in June 1968 to scope estimated process development costs for various alternative solidification schemes. The results from the study were incorporated in report ARH-718. Bases and compositions of wastes to be studied were outlined preparatory to evaluating various solidification methods.

Progress During Report Period

Scope evaluations were made for six selected processes (and three additional adaptations of three of the processes) for solidifying three Purex high-heat flowsheets. It presently appears that the continuous fluidized-bed and spray calciner processes which produce loose calcines are the most favorable.

Future Plans

Detailed flowsheets and equipment needs will be determined for one or two selected solidification schemes, and areas requiring further research and development will be defined.

Solidification of Bulk Salt Waste

Major Accomplishments to Date

An engineering study investigating two alternative processes for solidifying low heating, high-salt wastes was completed in 1967. The two processes were solidification of the wastes by fluidized bed calcination and incorporation of the waste into an asphalt matrix. An outline of the proposed study was prepared and waste compositions defined.

Progress During Report Period

Alternative methods for processing and solidifying bulk salt wastes are being evaluated. Conversion of nitrate to sulfate should permit calcination of these wastes; however, fluoride volatility precludes immediate consideration of proven melt-solidification techniques. Candidate low-temperature processes range from evaporation-crystallization to incorporation into a second media, e.g., asphalt, plastic, or cement. Water solubility of the evaporation-crystallization process is high. Leachability of calcined products and cement fixation products are high. Recent recommendations have been made that oxidizing salts not be incorporated into asphalt.

Denitration, conversion to sulfate, and the use of plastic to incorporate the activity are candidates for possible methods.

Future Plans

One, and perhaps two, of what appear to be the most promising waste management schemes will be selected. Research and Development requirements will be established and a plan recommended.

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Fluidized Bed Calcination - Z Plant Wastes

Major Accomplishments to Date

1. Idaho Nuclear - Initial tests at the Idaho Nuclear Chemical Processing Plant showed that the Z Plant salt waste presently going to a crib could be successfully calcined in a 4-inch diameter experimental fluidized bed. Further tests in their experimental unit indicated that organic wastes could be processed simultaneously with the salt wastes to yield a dry granular solid with a mean particle diameter of 0.5 mm. The volume reduction with salt wastes and salt wastes plus organics was 6/1.
2. ARHCO 4-Inch Experimental Unit - Extensive study of existing fluidized beds was made. Flowsheets, flow diagrams, hood and equipment design were completed and fabrication and installation were initiated.
3. Plant Scale Unit - Preliminary cost estimates were prepared. The early work indicated that a full-scale budget study was warranted.

Progress During Report Period

Tests at the Idaho Nuclear Chemical Processing Plant show that Z Plant high-salt aqueous wastes can be calcined in a fluidized-bed while simultaneously burning organic wastes in the proper ratio. Low- or intermediate-level wastes from the Purex Plant require the addition of nitric acid and aluminum nitrate to produce a suitable calcine in fluidized-bed calcination.

Future Plans

Approximately twenty 14-hour runs are planned for processing synthetic high-salt aqueous waste stream material. Kerosene will be used as fuel for the first few runs and then replaced with a kerosene-synthetic liquid organic waste mixture. Once operational parameters are established, and any processing equipment malfunctions are remedied, actual high-salt aqueous wastes will be processed. The resulting granular product will contain plutonium oxide which should not be readily leachable with water or mildly acidic or basic solutions. This will be experimentally verified.

Dependent on the results from this series of runs, further tests may be conducted on a 12-inch diameter unit at Idaho Nuclear, and design will progress on a 3- to 4-foot diameter production scale unit.

The ARHCO experimental unit will then be used to calcine low- and intermediate-level Purex aqueous wastes. The principal effort will be to determine the minimum additions of nitric acid and aluminum nitrate required to calcine the waste.

Solid Waste Treatment

Major Accomplishments to Date

No prior work was performed.

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Progress During Report Period

A task force has been set up within ARHCO to examine current practices on management (mainly burial) of radioactive solid wastes and to recommend changes which will provide improvements in practices, leading to procedures which can meet new national standards which are anticipated to be more restrictive than those which have been applied. Minimum actions foreseen at this time include improved sorting, interim storage containers of increased integrity, installation of a waste incinerator and expansion of decontamination facilities for failed equipment to be stored/buried. Several innovative thoughts have been presented, but not yet developed nor demonstrated, for treatment of noncombustibles, including incinerator ashes. Suggestions include conversion of ceramic materials to building blocks for storage or limited use, and recycle of metals from failed equipment as contaminated stainless steels and/or structural materials for limited and controlled use.

Future Plans

During the next reporting period supporting R&D should be defined and initial experimental studies begun.

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