AEC Research and Development Report

PACIFIC NORTHWEST LABORATORY
MONTHLY ACTIVITIES REPORT
DECEMBER 1971

DIVISION OF PRODUCTION AND
HANFORD PLANT ASSISTANCE
PROGRAMS

January 1972
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PACIFIC NORTHWEST LABORATORY

MONTHLY ACTIVITIES REPORT

DECEMBER 1971

Division of Production

and

Hanford Plant Assistance

Programs

by the

Staff of Battelle-Northwest

R. S. Paul, Director

January 1972
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PACIFIC NORTHWEST LABORATORY
MONTHLY ACTIVITIES REPORT
DIVISION OF PRODUCTION AND HANFORD PLANT ASSISTANCE PROGRAMS
W. D. Richmond

ASSISTANCE TO ATLANTIC RICHFIELD HANFORD COMPANY

Summary

Program III

In radionuclide transport model studies an executive monitor program was developed which allows user keyboard control of all iterative sequence program functions.

Two additional pump test analysis models were selected for use and are presently under evaluation.

The tank leak simulation continued with emphasis on decreasing the time for convergence.

Refilling of the two lysimeters south of 200 East Area was completed during the report period.

To continue the verification of sorption and transport models for the prediction of the movement of radionuclides in Hanford soils, the movement of $^{137}$Cs was measured through a saturated tank farm sandy loam soil.

A study to determine a depth series of soil chemical parameters for a group of 12 Hanford wells was continued.

Program IV

Laboratory studies were initiated on the use of N, N' methylene bisacrylamide for crosslinking sodium acrylate to form a stable ion exchange resin for possible use as a grout to stabilize contaminated soils.

Further ion exchange column runs to define operating conditions for the ion exchange purification of B-Plant cesium showed that cesium purity was not greatly affected by the length of the columns used. At the flow rates used in these studies, the length of the advancing band of cesium during load-on was constant for a column length greater than about 50 cm.
Mild steel corrosion test coupons exposed at 60-90 °C to "solidified" alkaline waste corroded during 3 months' exposure at about 2 mils/yr. This is about ten-fold faster corrosion than found with unconcentrated waste. The rates are expected to decrease with further exposure time.

Thermal conductivity measurements were made on four samples of simulated waste tank sludge. The samples contained an average of 52.45% water. Thermal conductivities ranged from 0.447 to 0.557 Btu/(hr)(ft²)(°F/ft) respectively.

In a 10-cycle test, 1000 grams of mixed combustible material were processed through 1000 grams of fused alkali metal carbonates in the fused salt incinerator. After the final cycle the salt contained 0.0014 gram of carbon per gram of salt. A 3-cycle test with NaOH-NaNO₃ as the fused medium gave poorer results than with the carbonate system.

In studies on the conversion of NaNO₃ to NaCl, partial chlorination at 600 °C and final chlorination at 860 °C gave a suitable product. Conversion of sodium sulfate and phosphate requires a higher temperature. The system is highly corrosive at the higher temperatures; neither fused silica nor Vycor appears suitable as a container material but magnesia appears to be.

Process Technology

Four optimized alpha monitoring crystal photo tube assemblies were delivered to the Purex plant for installation.

A review of literature pertinent to instrumentation as applicable to safeguards, criticality and fissile isotope analysis was conducted.

Instrumentation studies in support of the Plutonium Reclamation Facility related to electrodeless conductivity, Pu valence control and visual rotameters.

Efforts to strip Pu from simulated Plutonium Reclamation Facility strip column (CC) organic effluent containing dibutylphosphate have been unsuccessful.

Separation of Am from Pu in the Plutonium Reclamation Facility waste treatment system S-1 column was demonstrated in a mixer-settler using 0.1M HNO₃ for the S-1 extractant. High Pu waste losses were encountered in a series of S-2 column demonstration runs.

Americium distribution ratios E₉ of from 15 to 30 were obtained using 5-6M NaNO₃ at pH 0-1 as aqueous and dibutyl butylphosphonate (DBBP) in CCl₄ as extractant. The Am can be stripped easily from the extractant with water and concentrated by precipitation as the
oxalate. The DBBP-CCl₄ system appears superior to the HDEHP-TBP-NPH system in distribution coefficient, pH range and compatibility with other Plutonium Reclamation Facility systems.

General corrosion was slight (< 1 mil/yr) and there was no evidence of preferential attack in weld areas during three weeks' exposure of 304L stainless steel and E-Brite 26-1 alloy coupons to 1.7M Al(NO₃)₃ - 1.7 to 4.4M HF solutions at 25 and 40 °C. The environment is of interest in a Plutonium Reclamation Facility application.

Studies were initiated to find suitable techniques for the chemical destruction of ARC-359 ion exchange resin. Heating the resin in air to 350 °C blackened it but did not decompose it. The resin reacts vigorously with molten alkali metal nitrate salts and mixtures of these salts with NaOH.

The Environmental Research Laboratory seismograph station and the hydroseismic system were maintained in continuous operation for the report period.

Analytical results from samples taken during earlier experiments indicate that a lesser quantity of active material is airborne from the combustion of flammable materials containing uranium nitrate solid residues or solutions than from similar materials containing uranium dioxide. The maximum airborne concentrations detected under these circumstances was in the order of 10⁻⁶ g of uranium per cubic foot with as much as one-half percent of the uranium in the source potentially airborne.

Several high-volume air sampling filter systems are being prepared for measuring particle resuspension from swamp disposal areas.
ASSISTANCE TO ATLANTIC RICHFIELD HANFORD COMPANY

Program III - Environmental and Regulatory Technology

Radionuclide Transport Model
(D. B. Gearlock, Water Resources Systems Section)

The PDP-9 version of the iterative sequence was incorporated into a single package under the control of an executive monitor program. This means that all of the current capabilities of the system may be exercised by merely pressing keys on the display console. To the user this means immediate switching between all of the system functions. As future options are added they too will be placed under control of the executive monitor.

Two models have been selected from a literature review for use in analysis of Hanford pump test data. These will be compared to the normally used Theis model which has some limiting assumptions. The first, Boulton's model, is for a totally penetrating well in an unconfined aquifer and is only slightly more complicated than the Theis model. The second model selected is that developed by Dagan for partially penetrating wells. Actually Boulton's model is a special case of Dagan's.

Clay content analyses are being run on selected drilling samples from the 23 pump-tested wells in order to determine aquifer thickness before the test, identify confined aquifer areas and determine the degree of partial penetration of the wells. These data will be used for testing the above-mentioned models used in the latter task.

Data from potential measurements around Gable Mountain and the driller's logs are still under review. The water levels in the vicinity of the mountain show three areas of inconsistency. In the areas of wells 56-43, 66-39, and 54-34 large variations in potential appear between closely spaced wells. These could be the result of confined aquifer penetration, errors in well casing elevations, or non-equilibrium water levels. Each of these possible explanations is under investigation.

Progress on the tank leak problem has been somewhat limited by the heavy vacation schedule during the report period and slow convergence of the unequally spaced grid version of the Partially Saturated Transport program. However, in the time-planes completed no "data holes" have occurred in the moisture content as had been the case with equally spaced grid. A means of iterating on the currently changing part of the matrix is being tested to provide faster convergence.

Refilling of the two lysimeters south of 200 East Area was
completed. The soil used for refilling came from 15 mixed soil
batches, each consisting of 30 cubic yards of soil. Four soil samples
were taken from each batch for moisture content determinations.

Lysimeter soils are being prepared for calibration of the neutron
probe and psychrometers. Six 55-gallon drums are to be filled with
soils of various water content. A 1.66 in. diameter aluminum tube
will be installed in the center of the drums. The soil psychrometer
cables will then be installed about a foot from the aluminum tubes.
After equilibrium is attained, the soils will be sampled with an
auger for water content measurements thus permitting calibration of
the neutron probe and soil psychrometers.

Soil-Waste Interactions
(R. C. Routson and R. J. Serne, Water and Waste Management Section)

To continue the verification of sorption and transport models for
the prediction of the movement of radionuclides in Hanford soils, the
movement of $^{134}$Cs was measured through a 24 cm column of saturated tank
farm sandy loam soil (TF soil).

To develop the sorption parameters, two two-level factorial design
experiments were run to develop linear sorption equations to predict
the KdCs as a function of equilibrium macroion solution concentration.
In the first high-level sorption experiment, the levels of (K), (Na),
and (Ca) used in the experiment were 0.01-0.15M, 0.05-0.20M, and 0.01-
0.15M, respectively. The calculated linear regression equation for pre-
dicting KdCs is:

$$
\text{KdCs} = 44.7 - 7.89X\text{Ca} - 33.0 \text{XK} + 7.36 \text{XCaXXK} \\
-2.09 \text{XNa} + 2.61 \text{XCaXNa} + 1.66 \text{XXXNa} \\
-2.64 \text{XCaXXXNa} \\
(1)
$$

where

$$
\text{XX} = \frac{\text{CK} - 0.08}{0.07} \\
\text{CK} = \text{(K)} \\
\text{XNa} = \frac{\text{CNa} - 0.125}{0.075} \\
\text{CNa} = \text{(Na)} \\
\text{XCa} = \frac{\text{CCa} - 0.08}{0.07} \\
\text{CCa} = \text{(Ca)}
$$
In the second low-level sorption experiment, the levels of (K), (Na), and (Ca) used in the experiment were 0.001-0.01M, 0.03-0.20M, and 0.01-0.15M, respectively. The calculated linear regression equation for predicting the KdCs is:

\[
KdCs = 174 - 32.1 \times Ca - 96.4 \times K + 16.9 \times XXXCa
-24.9 \times Na + 7.88 \times XCaXNa + 21.1 \times XXXNa
\]

where

\[
XX = \frac{CK-0.0055}{0.0045} \quad (9)
\]

\[
CK = (K) \quad (10)
\]

\[
XNa = \frac{CNa-0.125}{0.075} \quad (11)
\]

\[
CNa = (Na) \quad (11) \quad (12)
\]

\[
XCa = \frac{Ca-0.08}{0.07} \quad (13)
\]

\[
CCa = (Ca) \quad (14)
\]

Equations 1 and 8 are valid only for -1 ≤ XCa, XNa, XK ≤ 1, i.e., the levels used in the experiment. The large dependence of KdCs on (K) is in good agreement with Cs sorption on a Burbank sand, and is due to the known competition of K⁺ and Cs⁺ for selective exchange sites.

The model-predicted and the measured normalized movement of \(^{134}\text{Cs}\) (C/Co) through the TF soil as a function of the column volumes of solution were in good agreement.

A study to determine a depth series of soil chemical parameters for a group of 12 Hanford wells was continued. Parameters being measured include: (1) moisture content-moisture potential relationships at 15, 1.5, and 0.33 bars of tension; (2) pH in a saturated paste and 0.01M CaCl₂; (3) cation exchange capacity; (4) mechanical analysis; (5) CaCO₃ content; (6) field moisture content; and (7) porosity.

Program IV - Waste Management

Fixation of Radionuclides in Soil and Salt Cakes with Chemical Grout
(B. W. Mercer, Water and Waste Management Section)

Laboratory studies were started on the use of N, N' methylene bisacrylamide for crosslinking sodium acrylate to form a stable ion
exchange resin. The N, N' methylene bisacrylamide is a water soluble crosslinking agent that is used to crosslink acrylamide in AM-9 chemical grout. Since both the crosslinking agent and sodium acrylate are soluble in water, the need for an organic solvent, such as ethanol, in the grout formulation is eliminated. The ion exchange capacity of sodium acrylate -10% N, N' methylene bisacrylamide resin was found to be 8.0 meq per gram of dry resin. For comparison, Amberlite IRC-50, a commercial weak base acrylic resin, is reported to have an ion exchange capacity of 9.5 meq per gram.

Experiments are being conducted to determine gel time as a function of initiator, catalyst, and inhibitor concentrations. Preliminary results indicate that the inhibitor, potassium ferricyanide, can be used to control gel time much in the same manner as in the case of AM-9 grout. The sodium acrylate grout appears to gel satisfactorily in Hanford soil.

Cesium Purification Flowsheet Studies
(J. A. Partridge, Chemical Development Section)

Studies were continued toward optimizing the ion exchange flow-sheet for purifying B-Plant cesium. Ion exchange column runs with Zeolon 900 exchanger were made using a simulated feed solution having the composition 0.10M Cs - 0.65M Na - 0.45M K - 0.0016M Rb - 0.15M HCO₃⁻. Columns of three different bed lengths, 35, 53, and 83 cm were used. The exchanger beds were all preconditioned and converted to the ammonium ion form prior to the runs reported here.

A 0.14M ammonium carbonate solution was used to elute sodium and potassium from the ion exchange column after the feed load-on. This was followed by a 2M ammonium carbonate solution for elution of the cesium. At the end of the cesium elution the columns were in the ammonium ion form and ready for the next run.

The six runs in this series all resulted in cesium products ranging from 96 to 99 wt% cesium.

No real trend was observed in product purity as a function of exchanger bed length. The main effect of increasing the bed length (assuming the bed diameter is constant) is that more cesium can be processed per run. The amount of sodium and potassium scrub solution used is the important factor in product purity.

In those runs in which cesium was loaded to breakthrough, about 12% of the loaded cesium was lost to the ammonium carbonate scrub used to remove the sodium and potassium.

The cesium breakthrough history and the amount of cesium eluted from the exchanger bed were used to calculate the length of the band in a column which is only partially loaded to the equilibrium cesium
capacity as the feed solution flows through the column. The calculation of the length of this partially-loaded band was made corresponding to the point in time in the loading cycle for each run when the initial cesium breakthrough occurred. The calculated lengths were 12 and 13 cm in the 35 cm column (flow rate 0.43 gal/ft²/min), 17 cm in the 53 cm column (flow rate 0.43 gal/ft²/min), and 17 and 14 cm in the 83 cm column (flow rates 0.43 and 0.64 gal/ft²/min, respectively). It appears from the data that, at the flow rate used in these tests, the leading band of cesium has established a somewhat steady state length in the 53 cm column and does not increase in length as the total column length is increased.

Batch contacts with sodium solutions containing trace concentrations of barium showed that barium would load on the Duolite ARC-359 resin and can be eluted with ammonium ion. A column test with simulated feed containing 0.01M barium also demonstrated that barium loads on Duolite ARC-359 and can be eluted with ammonium ion.

Waste Management Corrosion Studies
(R. F. Maness, Corrosion Research and Engineering Section)

An exploratory study is in progress to determine the corrosiveness of "solidified" alkaline high-level waste and to determine the ability of the waste to produce stress corrosion cracking in pre-cracked mild steel C-ring specimens. Corrosion specimens are being exposed at 60, 80, and 90 °C to simulated waste containing 2, 5, and 10 percent excess water. Results to date (three months' exposure) indicate a corrosion rate of about two mils/year for all exposure conditions, about ten-fold higher than that found with unconcentrated waste solution. Corrosion rates are expected to decrease with increased exposure time. No stress corrosion cracking has been noted. However, only three specimens have been inspected to date.

Pre-cracked 1020 mild steel C-ring specimens are being used to evaluate the propensity for stress corrosion cracking in nitrate solutions. Variables include pH, temperature, nitrate concentration, presence of oxidants, presence of reductants, and the presence of neutral salts. Results to date indicate pH is probably the most important variable. No cracking has been observed in 5 to 10M NaN0₃ solutions at pH > 11. Cracking occurred in boiling 2 to 10M NaN0₃ solutions with pH values of 7 to 10 in a matter of a few hours to days. The effect of the presence of 0.001 to 0.01M CrO₃ and 0.01 to 0.1M NaN0₂ appeared to be nil (perhaps some reduction in time to crack). Cracking also occurred in 5 to 10M NaN0₃ solutions at 90 and at 80 °C but not at 60 °C. Strangely, the presence of 1M acetate ion prevented stress corrosion cracking in nitrate solutions at pH > 9. These studies are continuing and will be expanded to include caustic solutions.
Thermal Conductivity of Waste Sludge
(D. G. Bouse, Applied Chemistry Section)

Four samples of simulated waste tank sludge were obtained for thermal conductivity (TC) measurements. The samples were received as grayish-white slurries identified only by number. The water content of the samples was determined by drying weighed portions of each sample in a vacuum oven for 24 hours at 100 °C and reweighing the dry sample. Each sample was thoroughly mixed and 4 to 5 TC measurements were made on the "as received" material at varying heat level inputs. The average TC values obtained are tabulated below.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thermal Conductivity, Btu/(hr)(ft²)(°F/ft)</th>
<th>Sample Water Content, Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>0.447</td>
<td>52.86</td>
</tr>
<tr>
<td>1B</td>
<td>0.449</td>
<td>48.33</td>
</tr>
<tr>
<td>2A</td>
<td>0.475</td>
<td>54.87</td>
</tr>
<tr>
<td>2B</td>
<td>0.557</td>
<td>53.74</td>
</tr>
</tbody>
</table>

Cesium-Strontium Packaging Studies
A. Flowsheet Development Studies
(H. T. Fullam, Chemical Development Section)

A report on cesium chloride flowsheet development studies was issued: BNWL-B-142, H. T. Fullam and L. A. Bray, Cesium Chloride Flowsheet Development Studies for the Waste Packaging Program, November 1971.

B. Compatibility Studies
(H. T. Fullam, Chemical Development Section)

Photomicrographs of test capsules maintained at temperature for 36 months were received and reviewed. In no case is excessive attack of the containment materials evident; the results are in agreement with those from shorter test periods. With all of the compatibility tests completed and the results available, a final report summarizing the entire compatibility program can be prepared.

Size Reduction of Contaminated Equipment
(J. D. Kaser, Chemical Development Section)

Shaped-charge explosives have been ordered for a demonstration of explosive cutting as a means for dismantling large scale, contaminated chemical process equipment. A non-contaminated L-cell package has been selected for the demonstration of explosive cutting. The demonstration is scheduled for January 1972.
Equipment Meltdown Studies
(H. T. Fullam, Chemical Development Section)

Tests with a variety of fused salts continue to show that it is possible to decontaminate metal equipment using fused salts. However, the large volumes of waste salt generated appear to make the process impractical. Even when the salt was reused to the maximum degree, a waste salt to metal ratio of at least 3:1 was required for adequate decontamination. Of the fused salts tested, fused nitrates continue to be the most effective medium for decontamination.

Fused Salt Incineration of Combustible Waste
(E. J. Wheelwright, Applied Chemistry Section)

A multi-cycle test of fused salt incineration employing a molten salt of composition 27 mole % K$_2$CO$_3$ - 42 mole % Li$_2$CO$_3$ - 31 mole % Na$_2$CO$_3$ was completed this month. In this 10-cycle test, 1000 grams of mixed combustible material were incinerated in 1000 grams of molten salt. Each cycle included the following steps:

1. Combustible material was added over a 3-hour period. The salt was held at 600 °C and sparged with nitrogen.

2. The salt temperature was increased incrementally to 800 °C over a period of 3 hours. The salt was sparged with air during this period.

3. The salt was held at 800 °C for one hour; it was sparged with air during this period.

4. The temperature was decreased to 600 °C and the salt was sampled.

The salt samples were cooled, weighed and dissolved in dilute acid; the insoluble carbon was recovered, dried and weighed. The carbon residues ranged from a high of 0.015 gram per gram of salt to a low of 0.0005 gram per gram of salt. There was no increase in residue with increasing number of cycles. After the first cycle the salt contained 0.0037 gram of residue per gram of salt and after the 10th cycle it contained 0.0014 gram of residue per gram of salt. There was no visual indication of corrosion of the nickel metal salt loop.

In a 3-cycle experiment similar to the 10-cycle test just described, 300 grams of mixed combustible scrap were incinerated in a molten mixture of 921 grams of NaOH and 184 grams of NaN0$_3$. The performance of this system was inferior to that of the carbonate system. There was a definite increase in the carbon residue per cycle and the dark green color of the salt, when discharged from the loop, indicated some corrosion of the nickel loop.
Salt Cake Volume Reduction
(J. L. Ryan, Applied Chemistry Section)

A proposed approach to reducing the volume of radioactive salt cake wastes is to reduce the sodium (a major constituent) to sodium metal and purify the metal by distillation. For electrolytic reduction of the sodium it is necessary to convert the sodium salts in the cake [predominantly sodium nitrate (and nitrite) with some sodium carbonate, sodium phosphate and sodium sulfate] to sodium chloride. Chlorination of the salt at elevated temperature has been proposed; no experimental data for the reaction are available. Although elevated temperature thermodynamic data (principally heat capacity data) for NaNO₃ are not available, the data for the reaction

\[ \text{NaNO}_3 + \frac{1}{2} \text{Cl}_2 \rightarrow \text{NaCl} + \text{NO}_2 + \frac{1}{2} \text{O}_2 \]

can be fairly closely approximated. The reaction is endothermic. At 25 °C \( \Delta H \approx 21 \text{ kcal/mole} \) and at 825 °C \( \Delta H \approx 22 \text{ kcal/mole} \) (the data at 825 °C are of particular interest since NaCl melts at 801 °C). The free energy is definitely positive at room temperature (\( \Delta G \) at 25 °C = 7.95 kcal/mole) and becomes negative near or slightly below the NaNO₃ melting point (307 °C). At 825 °C, \( \Delta G \approx -22 \text{ kcal/mole} \) and the reaction will actually be driven slightly further to the right at elevated temperatures than indicated due to the endothermic reaction \( \text{NO}_2 \rightarrow \text{NO} + \frac{1}{2} \text{O}_2 \).

In a small scale experiment 1.5 g of NaNO₃ was heated gradually in a quartz tube to \( \sim 900 \) °C. Chlorine gas was passed through the tube during this period. Brown fumes (presumably NO₂) were evolved and >99.98% of the nitrate was converted to neutral NaCl. In larger scale experiments (10-25 g NaNO₃) severe corrosion of the fused SiO₂ or Vycor equipment occurred at the higher temperatures and prevented obtaining quantitative results. Crucibles of MgO were not appreciably attacked in the environment and MgO tubes have been ordered for future work. Little or no reaction of Cl₂ with molten NaNO₃ occurred at 450 °C. Reaction (evolution of brown fumes) became apparent at 500-550 °C. At 600 °C the melt solidified in 1 1/2 hours and NO₂ evolution ceased. Crushing and heating this solid to 800 °C in a stream of Cl₂ produced a neutral product containing < 0.002% NO₃⁻ + NO₂⁻. Further work at high temperatures will be done in MgO equipment.

At temperatures above 800 °C all experiments so far have yielded strongly alkaline products and apparent incomplete destruction of NO₃⁻ and/or NO₂⁻. Whether this is due to lower solubility of Cl₂ in the melt or just to physical mixing problems caused by the viscous melts produced by dissolution of SiO₂ from the apparatus cannot be determined until complete MgO apparatus is available.

Analysis of the gaseous products has not yet been performed, but it certainly appears that NO₂ is the principal product. The decomposition of NO₂ to NO at elevated temperatures and the possible reaction
of NO with Cl₂ to form NOCl indicate that some NO and NOCl should be possible.

To be a suitable feed for electrolysis, the NaCl must have a low concentration of oxygenated anions. The salt waste contains sulfate, phosphate, and carbonate, but the latter is easily removed by neutralizing the solution with HCl. It has been proposed that sulfate and phosphate be removed by precipitation. An alternate after the conversion of the nitrate and nitrite content to NaCl might be to chlorinate in the presence of carbon to yield NaCl and volatile sulfur and phosphorous compounds. Preliminary experiments indicate that both can be chlorinated at about 900 °C in the presence of carbon. Chlorination of sodium pyrophosphate with carbon was tried only briefly on a small (~ 1 g) scale but appears to proceed at least reasonably close to completion. The chlorination of Na₂SO₄ + C appears to be a moderately vigorous exothermic reaction at 900 °C, yielding flammable gases (possibly CO and S). In the brief experiments tried so far (MgO crucible in a quartz tube) complete destruction of sulfate was not achieved, but here again extreme corrosion of the SiO₂ sparge tube produced complications. One drawback to such a method for removing sulfate and phosphate is in the difficulty of removing excess carbon from the NaCl product.

Process Technology

Purex Plant Instrumentation Assistance
(O. H. Koski, Chemical Development Section)

Four optimized alpha sensor photomultiplier tube assemblies were delivered to the plant.

A review of literature pertinent to instrumentation applicable to safeguards, nuclear safety and fissile materials assay was conducted. The purpose of the study is to determine the instrumentation methodology and devices which would be applicable to a broad range of plant problems and specifically to in-tank or in-line analysis of fissile material content.

The two methods in present use are active interrogation and passive. In both passive and active assay methods, the use of neutron spectroscopy and high resolution gamma analysis would be desirable.

A laboratory development effort directed toward better neutron energy analysis, practical (room temperature) high resolution solid state gamma energy analysis as well as a long life neutron pulse generation method is anticipated.

Laboratory effort toward the development of a neutron spectrometer using powdered neutron-active glass suspended in an optically
transparent plastic has been successful in only relatively thin shapes. Another method using an array of paralleled conventional BF$_3$ tubes located at varying moderator thicknesses so as to measure epicadmium neutrons entering each region appeared to have some process value. By requiring that each tube in the array have a distinctive gain as might be achieved with varying fill gas composition and pressure, the location of the tube and its count rate is determined from a multi-channel analyzer scan.

Plutonium Reclamation Facility Instrumentation Support
(O. H. Koski, Chemical Development Section)

The effort during the reported period consisted of work related to electrolytic conductivity, Pu valence ratio instrumentation, and visual rotameters.

An electrodeless conductivity system for the extraction column feed (CAF) stream was given its final calibration and delivered to the plant. Two additional systems are at present under construction with one to be used on fractional molar nitric acid and the other on nominal two-molar nitric acid.

Two cells were constructed in the development effort toward in-line plutonium valence ratio control. They consist of platinum electrodes separated by an electrically conducting low diffusion barrier with one electrode exposed to the process solution and the other to a chosen reference. In the initial cell the electrodes are subject to weeping and therefore will not be suitable for process use. The use of the diffusion barrier as a substitute for a salt bridge worked well for the short term of the test.

Six visual rotameters, three for ranges up to 25 l/hr and three for ranges up to 120 l/hr, were delivered to the plant. The 120 liter-per-hour rotameters were of a range not previously provided.

Plutonium Reclamation Facility Pulse Column Studies
(J. Dunn, Chemical Development Section)

A series of engineering-scale pulse column runs is in progress with the objective of defining operating conditions and cartridge designs which will result in increased capacity and improved operation of the PRF CA and CC columns.

A series of familiarization runs was completed with operation of the CA and CC columns approximating that at the Plutonium Reclamation Facility. Characterization of the extraction profiles of the columns has been started at various flow ratios and at various pulse amplitudes and frequencies to establish flooding characteristics and extraction
efficiencies. Determination of Htu's is next on the program plan. To date, several demonstration runs have been made to illustrate to ARHCO personnel the appearance of both local and total floods.

A separator has been designed and installed at the -36 in. level of the CC column to permit product withdrawal at the most highly concentrated point in the column and to effectively remove entrainment of organic from the aqueous CAIS. This small device is expected to replace a disengagement tank currently employed in the production plant.

Plutonium Reclamation Facility Equipment Development Studies
(J. Dunn, Chemical Development Section)

A Barrett Clarifuge being evaluated for removing solids from the PRF dissolver effluent has been modified using stainless steel to replace mild steel parts in the centrifuge as supplied by the vendor. The modified centrifuge will be evaluated after current dissolution runs in the glass mockup of the PRF dissolver are complete.

Seven cans of MgO (500 g each) were dissolved in the glass mockup of the PRF dissolver. The material is expected to introduce more heat into the dissolver when blended with first or reburned ash and thereby improve the dissolver efficiency. Leaks which have developed in the dissolver system have delayed operation of the dissolver. These have been repaired and dissolver operation can resume. A Pemberthy 62A jet being considered for dissolver cleanout will be evaluated at the end of the next complete dissolver run.

Corrosion Studies - Plutonium Reclamation Facility
(R. F. Maness, Corrosion Research and Engineering Section)

A change from "once through" to "closed" cycle operation of a scrubber, used in PRF plant operations to remove HF from a gas stream, has been proposed. The initial scrub solution will contain about 1.7M Al(NO₃)₃ solution, whereas the equilibrium solution will contain 1.7M Al(III) and 2.9M fluoride. Corrosion tests are being made with as-welded 304L stainless steel weldments and with sections of welded E-Brite 26-1 tubing exposed to 1.7M Al(NO₃)₃ solution containing 1.7, 2.9, and 4.4M HF at 25 and at 40 °C. To date (three weeks' exposure) metal wastage under all exposure conditions has been slight, ≤ one mil/year, with no evidence of preferential attack.

Americium Purification by Dibutyl Butylphosphonate (DBBP) Solvent Extraction
(L. A. Bray, Applied Chemistry Section)

A study was made of the possibility of purifying Americium by using DBBP solvent extraction with NaNO₃ or NH₄NO₃ salting. The feed
solution contained Al, Ca, and Fe at 10 to 20 times the Am concentration, and other cations at lower concentrations. The results of this brief study, using 30 v/o DBBP - CCl₄ as the extractant and 0.3M di-ethyltriamine pentacetic acid (DTPA) in the aqueous phase, indicate that americium distribution ratios of 15 to 30 can be obtained with the aqueous phase containing 5-6M NaNO₃ or NH₄NO₃ and at a pH in the range 0-1. The americium can then be easily stripped from the organic with H₂O and directly precipitated with oxalic acid. The DBBP-CCl₄ solvent extraction for the purification of americium should be considered as a replacement for the HDEHP-TBP-NPH system. The useful range of pH range (0-1) is wider, the Am Eₗ is larger (15-30 vs. 3-15), and the extractant is more compatible with existing plant organics. Even better extraction at high pH can be achieved by eliminating the DTPA from the aqueous.

Plutonium Reclamation Facility Flowsheet Development
(D. G. Bouse, Applied Chemistry Section)

Mixer-settler runs were continued to test various Plutonium Reclamation Facility flowsheets. The flowsheets for waste treatment system columns S-1 and S-2 were tested with various candidate stripping compositions and flow ratios. In a series of S-1 column runs designed to strip Am into an aqueous stream (S-1-P) and back extract the Pu into the organic stream (S-1-W), the following extractants (S-1-X) were tested: (a) 1.0M hydroxylamine nitrate (HN) with aqueous to organic flow ratios (L/V) of 0.2 and 0.083; (b) 1.0M HNO₃ with L/V = 0.1, L/V = 0.5 and L/V = 0.12; (c) 0.8M HNO₃ with L/V = 0.12 and (d) 0.1M HNO₃ with L/V = 0.27. The best results were obtained with the 0.1M HNO₃ wherein 97% of the Am went to the S-1-P and 92% of the Pu remained in the S-1-W. One run was designed to co-strip Pu and Am by using 0.1M HN - 0.03M HNO₃ for the S-1-X; however, the Pu did not strip in this run. The S-2 column, where the Pu is stripped from the S-1-W, was demonstrated in the mixer-settler with three different extractant (S-2-X) compositions: (a) 0.1M ferrous sulfamate - 0.1M HF, (b) 0.1M HF - 0.1M HNO₃ and (c) 0.2M ferrous sulfamate - 0.2M HF. The L/V was constant for these runs at 0.167. Pu was not completely stripped from the S-1-W in any of these runs. A different approach to the waste treatment system flowsheet is being considered.

A series of six CO column demonstration runs were made to test various extractants (COX) for stripping small amounts of Pu from the CC column waste organic (CCW). The synthetic CCW used for these runs was spiked to 0.02M with dibutylphosphate (DBP) to simulate organic degradation products common to the CCW. None of the COX solutions tested was effective in stripping Pu from a feed containing DBP.
Disposal of ARC-359 Ion-Exchange Resin
(E. C. Martin and F. P. Roberts, Applied Chemistry Section)

Efforts to find literature references to suitable techniques for the safe chemical degradation of ARC-359 resin were not successful. Primary sources reviewed were the recent environmental literature and Nuclear Science Abstracts.

The reaction of dry ARC-359 resin with air at elevated temperatures was studied. Dry resin was placed on a hot stage microscope and heated from ambient temperature to 355 °C. The following observations were made:

1. There was no evidence of vigorous oxidation - i.e., no smoke, no fire.
2. There was no evidence of a volatile component being vigorously expelled from the resin particle - i.e., no movement of the particles was observed.
3. There was no evidence of softening or flowing of the resin material - i.e., the sharp edges and striation marks on the resin were not disturbed.
4. There was evidence that oxidation had occurred. Thin layers of ARC-359 appear red under the microscope, although thick layers are black. As the heating process continued, the red coloration darkened and gradually disappeared. Particles of resin that had been heated to 355 °C were crushed and re-examined with a microscope. All fragments appeared black in contrast to the orange-red coloration of resin that had not been heated.
5. The oxidized resin still had mechanical strength. The material was quite brittle but an appreciable amount of force was required to crush the material.

Several experiments were carried out to establish the temperatures at which nitrate reacts with the ARC-359 resin. Differential thermal analyzer measurements showed that mixtures of NaNO₃ and the resin react vigorously with a sudden release of thermal energy at 310-315 °C. A mixture of NaOH, NaNO₃ and the resin reacted similarly but the temperature at which the reaction started was much lower (250-270 °C). Because of the complexity of the thermal behavior of the resin, no attempt was made to measure quantitatively the amount of heat released.

A fused salt bath (40% KNO₃ - 40% NaNO₃ - 20% NaOH; mole %'s) was prepared to investigate the reaction with a molten salt mixture in the range of 300 °C. The mixture was heated to the melting point and swirled to insure homogeneity. Ten grams of "as received" ARC-359 resin (sodium
form) was added in one portion to the mixture; the equipment was
arranged to collect the off-gases by displacement of water. The
initial reaction proceeded smoothly with gas evolution at a relative-
ly slow rate. However, as the reaction continued, a vigorous reac-
tion took place. A liter of gas was collected before the tubing was
blown from the receiver. Resin was spread throughout the length of
the tubing. There was no evidence of fire or salt splattering. This
would indicate merely that the resin decomposed so rapidly that it
was forcibly ejected from the reaction mixture.

The trapped gas was examined mass spectroscopically and was found
to contain carbon dioxide and oxides of nitrogen and traces of methane.
There was no evidence of hydrogen, benzene, or phenolic fragments.

Viscosity of DBP-TBP-CCl₄ Mixtures
(E. C. Martin, Applied Chemistry Section)

The viscosity of tributylphosphate-CCl₄ solutions which were also
0.05, 0.1 and 0.2M in dibutylphosphate was determined. No significant
differences in viscosity among the solutions were found.

Seismic Studies
(D. D. Tillson, Water Resources Systems Section)

The three component short period seismograph system was maintained
in continuous operation. Arrival time data were reported to the Nation-
al Earthquake Information Center for 28 teleseismic events and 46 re-
gional seismic events. Local seismic activity, which had been running
below normal for the past few months, showed an increase during the re-
port period. This follows a similar trend in activity observed during
the same period last year. Most of the activity appears to be along
the Saddle Mountains, north of the project. None of the local events
detected appear to have been of sufficient magnitude to be felt on the
surface.

Three short period vertical seismometers (Geotech Model S-13),
amplifiers, VCO's, and FM telemeter systems have been received and
checked for proper operation. These systems will be installed at
distances of 50-75 kilometers from the project in order to improve
regional epicenter location capability for earthquakes in the 2-4
magnitude range. A second purpose of these units will be to supple-
ment the detailed investigations of seismic energy coupling in the
200 Areas.

The hydroseismic system was maintained in continuous operation
in Well 36-46 during the report period. No operational problems were
encountered from the abnormal moisture or cold weather. Signal to
noise ratio was lower than normal because of the many barometric
pressure changes associated with winter storms passing through the area. Surface waves from seven teleseismics were detected by micro-fluctuations in the confined aquifer. The most prominent event was detected at 0038 hours, PST, 12/15/71. A magnitude 7.2 (ERL) earthquake in the Kurile Islands produced oscillations in the confined aquifer system for over two hours.

Atmospheric Release of Radioactive Particles
(L. C. Schwendiman and J. Mishima, Atmospheric Analysis Section)

Two additional experiments were conducted to measure the fractional airborne release during the burning of flammable materials containing radioactive compounds.

Uranium as uranyl nitrate solution was incorporated in flammable waste held in a waste carton. The carton was placed in the Radioactive Aerosol Release Tank (R.A.R.T.) and ignited. Periodic filter and 8-stage cascade impactor samples of the airborne material were taken.

Uranium as finely-divided uranium dioxide powder was incorporated in flammable waste held in a waste carton. The material was burned in the R.A.R.T. Airborne material was monitored by periodic filter and 8-stage cascade impactor samples.

Gaseous Waste Assistance; Particulate Resuspension Studies
(C. E. Elderkin, G. A. Sehmel and J. V. Ramsdell, Atmospheric Physics Section)

Several high-volume air sampling filter systems are being prepared for measuring particle resuspension from swamp disposal areas. Total air volumes of over 300,000 ft\(^3\) will be sampled to determine if air activity near swamps is greater than that anticipated from global fall-out. Results from these resuspension experiments for winter water level, wind, and soil conditions will be compared to summer water level, wind, and soil conditions.
TECHNICAL ASSISTANCE TO THE HANFORD PLANT

Summary

Environmental Evaluations

No unusual radioactivity measurements attributed to plant sources were reported during the month.

Radiation Standards and Engineering

Standard R-meter sets were recalibrated during the month. Also, a radiological hazards survey was made of a large $^{60}$Co source that was recently installed in the 331 Building.

Radiation Protection

Efforts continue to implement the changeover from film dosimeters to multipurpose thermoluminescent dosimeters.

Thermoluminescent Teflon discs are being added to the criticality dosimeters in place of glass rods to provide area gamma dosimetry in the event of a criticality accident.

Beta doses reported by U. S. Testing for a group of personnel film dosimeters required adjustment when they were accidentally exposed during the x-ray coding operations.

Dosimetry Technology

Additional TDL's (Types 700 and 600), ordered for another 340 multipurpose cards, were received.

Mechanisms of Environmental Exposure

A resurvey of approximately 50 Riverview families was completed. Analyses of the data from this and a similar population group are under way. Final regression analyses of data for coastal residents are in progress.
Detectable concentrations of $^{131}$I were reported for milk samples from a West Richland supplier for two successive weeks, with a maximum concentration of 25 pCi/$\lambda$ of $^{131}$I on a sample obtained December 2. Two weeks later a sample from the same location was less than 2 pCi/$\lambda$. No detectable concentrations of radiiodine in milk were reported from any other location during the period, there was no indication of positive radiiodine concentrations in environmental air, nor was there any reported unusual radiiodine emission from plant sources. Airborne particulate activity through the first week of December continued generally at normal levels for this time of year.

A monitoring station was established in 100-H Area to provide dose estimates for personnel engaged in private commercial activities. Measurements include air and water concentrations and ambient dose-rate.

Routine audit surveys were made at several retired waste disposal sites and at the boundaries of selected active sites. Minor conditions requiring correction, such as missing signs and weed growth, were reported to the appropriate contractors.

No unusual radioactivity was detected on routine road and soil plot surveys.

Radiation Standards and Engineering
(H. V. Larson, Radiation Standards and Engineering Section)

Our standard (NBS calibrated) R-meter set was recalibrated by Victoreen on December 6. Data from this recent calibration check compare favorably with our free air ion chamber measurements (in the x-ray region). Thus, our reported exposures continue to be accurate to within a few percent. In addition to R-meter calibrations, we have remeasured the output from our $^{137}$Cs and $^{60}$Co sources.

The installation of the large $^{60}$Co source in the 331 Building was completed and a preliminary radiological hazards survey accomplished with Radiation Monitoring personnel. Shielding was adequate, with the exception of the door, which has a crack at the bottom permitting streaming. Recommendations regarding recessing the door or shielding the crack were made to Biology and RM personnel orally.

In conjunction with Personnel Dosimetry, a dosimetry study was made of a possible exposure at 231-Z Building to the hand of an x-ray
diffractionist. Based on a time-motion study, it was concluded that
the individual in question probably received no exposure, and that
even if the worst possible conditions were selected, the dosimetry in-
dicated an exposure of less than 2 R to the fingers. Cooperation with
operating personnel in both cases was excellent.

Radiation Protection
(K. R. Heid, Personnel Dosimetry Section)

The first draft of a procedure for processing multipurpose TL
dosimeters has been completed and routed for comments. This procedure
includes instructions for U. S. Testing regarding the annealing, calibra-
tion, control chart preparation, checks required, and reporting of re-
sults obtained for multipurpose TL dosimeters.

Precision specifications were developed and a quality control
audit program for the multipurpose TL dosimeters has been established.

Installation of the criticality dosimeter counting system in the
747-A Building has been completed. In the event of a critical radia-
tion event, the criticality dosimeters will now be processed at this
location. A revised procedure reflecting these changes has been com-
pleted.

Thermoluminescent Teflon discs have been issued to all contractor
radiation protection representatives with instructions to tape these
to the upper portion of the polyethylene rod of each criticality dose-
meter. These will replace the glass rods as the primary means of de-
termining the gamma dose associated with a criticality accident.

A smear from the container of a radioactive shipment received
from off site showed mostly $^{137}$Cs and $^{134}$Cs with a trace of $^{60}$Co when
subjected to qualitative gamma analysis.

A number of questionable beta doses were reported by U. S. Test-
ing for dosimeters worn during November. Follow-up investigation re-
vealed that this was due to partial exposure of the beta window during
the x-ray coding operations. Adjustments, based upon the density in
the unaffected portion of the beta window, were submitted by U. S.
Testing after this was called to their attention.

Readout of a basic TL dosimeter assigned to a visitor during Decem-
ber indicated a dose of 880 mrem; however, readout of the backup Teflon
disc indicated only 40 mrem and the dose was adjusted accordingly. A
reported dosimeter result of 1.85 rem for another visitor was confirmed
by the backup Teflon disc. In this case the contractor radiation pro-
tection follow-up revealed that the dosimeter was worn during the time
the person received radiation therapy.
A thorax burden of 0.5 nCi of $^{241}$Am which was detected during a routine in-vivo examination for a BNW employee was confirmed by follow-up examination. Additional evaluation of bioassay and in-vivo data will be required to determine the associated plutonium content, currently estimated at <50% of the sustained maximum permissible lung burden. Follow-up examinations are being requested for several other apparent thorax $^{241}$Am burdens detected by routine examination of contractor employees.

Changes in data processing programs required as a result of the changeover from film dosimeters to multipurpose TLD is progressing satisfactorily.

Several forms are being revised to reflect the change to thermoluminescent dosimeters. Two of these are also being revised to allow for better scheduling of in-vivo and bioassay examinations.

A new lens was received for the microfilm reader-stuffer. This will allow the stuffing of a three- to four-year accumulation of microfilm records in individual files.

Dosimetry Technology

(A. J. Haverfield, Radiological Physics Section, and K. R. Heid, Personnel Dosimetry Section)

Development of the Multipurpose Dosimeter

Additional TLD's (both Type 700 and Type 600), ordered for another 340 multipurpose cards, were received. The TLD's were counted, cleaned and annealed and then sent to the vendor for makeup into new dosimeter cards.

Columbia River Studies

Mechanisms of Environmental Exposure

(T. H. Essig, Radiological Physics Section)

A whole-body counter resurvey of approximately 50 Riverview (Pasco) residents was completed on December 8. Essentially all of these individuals represented recounts and are closely tied to the Mark Twain students counted in November, many of whom are also Riverview residents. Analyses of these data are under way.

Final least-squares regression analysis of the whole-body counting and dietary data for the coastal residents recently resurveyed is in progress.
Meteorological Services
(E. H. Phinney, Synoptic Meteorology Section)

Meteorological services, viz., weather forecasts and observations and climatological services were provided to plant operations and management on a routine basis.

DECEMBER, 1971

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