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APPLICATION OF AQUEOUS TECHNOLOGY TO LMFBR
SEPARATIONS PROCESSES. PROGRAM PLAN FOR
TASK T-1: SOLVENT PERFORMANCE

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CONTENTS

	Page
INTRODUCTION	1
OBJECTIVES	1
DESCRIPTION OF WORK	2
EQUIPMENT	4
FEED MATERIALS AND FLOWSHEETS	13
OPERATING PROCEDURES	17
DOSIMETRY MEASUREMENTS AND CALCULATIONS	21
TENTATIVE RUN SCHEDULE	24
PERFORMANCE CRITERIA	25
REFERENCES	37
APPENDIX A - CALCULATION OF ACCUMULATED SOLVENT DOSE	
APPENDIX B - CALCULATION OF SINGLE-PASS SOLVENT DOSE	
APPENDIX C - ESTIMATION OF BETA AND GAMMA ENERGY ABSORPTION IN IRRADIATION VESSELS	
APPENDIX D - URANIUM, PLUTONIUM AND FISSION PRODUCT ANALYTICAL METHODS	

APPLICATION OF AQUEOUS TECHNOLOGY TO LMFBR SEPARATIONS PROCESSES.

PROGRAM PLAN FOR TASK T-1: SOLVENT PERFORMANCE

G. L. Richardson

INTRODUCTION

The Purex process is currently the prime candidate for reprocessing LMFBR fuels. These fuels will be irradiated to very high burnups (100,000 MWd/MT or more) at high specific powers (1000 to 2000 kW/kg of fissile plutonium); consequently, the solvent radiation exposure will be many-fold higher than in current reprocessing plants, particularly if cooling times as short as 30 days are used to reduce the plutonium inventory.

Over the last 15 years or so, a tremendous amount of laboratory work has been performed world-wide to determine the effects of irradiation on TBP (tributyl phosphate) and various diluents.^(1,12) Such work, typically, has involved external irradiation of extractants (either alone or in contact with some aqueous phase) to a particular desired dose. Subsequent analyses and empirical solvent quality tests have been used to estimate solvent performance as a function of absorbed dose. Results of these tests have generally been quite encouraging and, as far as they go, indicate that TBP should be a suitable extractant for processing of LMFBR fuels.

Nevertheless, a system undergoing continuous irradiation at levels expected from processing LMFBR fuels may exhibit kinetic, emulsifying, and other inherent effects which could seriously impair the performance of a TBP extractant even in a single cycle of extraction. Furthermore, conventional solvent washing procedures may be inadequate to prevent accumulation of deleterious degradation products of TBP and diluent in the recycled solvent. Answers to these and similar questions about the performance of a TBP extractant in processing LMFBR fuels can best be provided by an evaluation of solvent performance under dynamic conditions. The purpose of this experimental task is to conduct such a study.

OBJECTIVES

Laboratory-scale investigation of TBP solvent performance will be conducted with the following objectives:

1. Determine TBP solvent performance using a dynamic system with radioactive feed solutions as near to those expected from LMFBR as

practicable. Specifically, the dynamic system will be operated to establish and evaluate the effects of irradiation dose rate and cumulative exposure on TBP solvent properties as they relate to process kinetics, plutonium and uranium losses in the 1B and 1C column stripping operations, and fission product decontamination in the product streams.

2. Note and resolve differences, if any, between solvent performance data established in the dynamic tests and either the data from present laboratory tests or actual solvent quality data from the Hanford Purex Plant.
3. Provide a reliable means of extrapolating solvent performance in the dynamic system to plant-scale performance in any of several kinds of contactors.
4. Determine the effectiveness of conventional solvent washing treatments in maintaining and restoring the quality of TBP solvent used to process LMFBF fuels and, if necessary, develop and test suitable washing procedures.

In fulfilling these objectives, we expect to maintain close liaison with ORNL personnel who are conducting similar studies on a batch basis.

DESCRIPTION OF WORK

The experimental apparatus will consist of a single-stage mixer for the irradiation (1A) contact, a miniature continuous centrifuge for rapid separation of the phases leaving the mixing stage, and three multi-stage banks of Savannah River Laboratory-type miniature centrifugal contactors in series performing the functions of a 1A column scrub section, a 1B column extraction section, and a 1C column. One or more single-stage mixers will be used to continuously wash the spent solvent for immediate recycle for those tests involving cumulative radiation dose effects. The system will be operated to demonstrate the performance of a Purex process first extraction cycle at varying solvent phase residence times and radiation exposure rates. The studies will be conducted in C-Cell of the WADCO 325A Building.

For such studies multi-stage, miniature centrifugal contactors are a convenient research tool. They have several desirable characteristics as

compared to other laboratory-scale contactors: steady state conditions are attained rapidly upon start-up because of the low holdup volumes per stage, high throughput rates minimize experimental running times, and, of special advantage, phase residence times per stage can be easily varied to correspond to contactors with both short and long (e.g., pulse column) residence times.

In the scheduled test runs, the feed solutions to the 1A and 1A scrub contactors will simulate, as far as possible, the chemical and radiochemical composition expected for actual LMFBR feed solutions. Such feed solutions will be prepared from irradiated fuel dissolver solution and a rare earth (Ce-144) concentrate prepared by the Hanford Waste Management Program. Local sources of plutonium, uranium, etc., will be used as required. The extractant for the runs will be a solution of TBP in a normal paraffin hydrocarbon diluent (primarily n-dodecane). Appropriate scrub, partition, and strip solutions will be introduced at the proper points in the system. The extractant will be washed after each pass through the system by contact with an appropriate wash (initially a Na_2CO_3 solution) and, for the recycle tests, returned to the extraction contactor. For each set of flowsheet conditions, appropriate end-stream samples will be taken from each of the contactors to establish how loss and decontamination patterns change with solvent exposure rate and cumulative dose.

A series of runs will also be made under Hanford Purex Plant flowsheet conditions to establish the reliability of extrapolating the results of the Laboratory tests to full-scale plant conditions. The range of operating conditions and dose rates will extend and complement the results obtained with the LMFBR feed solutions.

For each set of operating conditions, portions of the extractant will be removed from the system periodically, tested, and analyzed to evaluate solvent behavior further. Various standard solvent quality tests (e.g. distribution ratio measurements, dispersion-disengaging behavior, plutonium retention, physical properties) will be made. Such tests are sensitive indicators of changes in the chemical and physical behavior of TBP extractants; and, based on Hanford Purex Plant experience, they can be useful indices of the expected performance of a solvent during plant operation.

Knowledge of the rate at which the solvent receives irradiation in the various parts of the dynamic system is an essential prerequisite to

obtaining credible and usable data about actual and expected solvent stability and performance. Two approaches will be used to obtain reliable estimates of dose rates. One will involve calculation of dose rates using known contactor geometry, aqueous and organic phase compositions, etc. The other will involve the use of TBP as a dosimeter. G values for the formation of DBP (dibutyl phosphate) from TBP are well known,^(2,12) and refined analytical techniques for DBP have been recently developed.^(3,4,12,13) During initial dosimeter tests, it is planned to operate the system with radioactively simulated LMFBF feeds which do not contain uranium, plutonium, or other cations strongly complexed by DBP in order to simplify DBP analyses.

Results obtained in FY 1970 include the fabrication and shakedown testing of the experimental apparatus, comparison of different methods for determining DBP concentrations, and preliminary evaluation of the proposed dose rate calculation methods. The bulk of the high-level testing will be performed in FY 1971 with the completion of the tests with Purex and dilute LMFBF flowsheets expected. Work with more advanced flowsheets will be completed in FY 1972. Reports summarizing the experimental results will be prepared at the conclusion of specific flowsheet studies.

EQUIPMENT

A simplified layout of the experimental apparatus is shown in Figure 1. It consists of the following equipment arranged in series:

- Feed preparation tanks where stock solutions of uranium, plutonium, fission product concentrates, and "cold" chemicals are blended.
- In-cell feed tanks for recycled solvent (1AX) and radioactive feeds (Ce-144 irradiation solution and 1AF).
- A single-stage 1A irradiation contactor overflowing to a miniature centrifuge.
- An 8-stage bank of modified Savannah River Laboratory (SRL)-type centrifugal contactors serving as a 1A column for introduction of the full fission product spectrum and to demonstrate fission product scrubbing performance of the irradiated solvent leaving the 1A contactor.
- A 6-stage bank of centrifugal contactors serving as a 1BX column to demonstrate plutonium and fission product partitioning.

FIGURE 1. SCHEMATIC LMFBR SOLVENT EXTRACTION TEST STAND, C-CELL, 325 BLDG.

- A 6-stage bank of centrifugal contactors serving as a 1C column to demonstrate uranium stripping behavior and retention of uranium, plutonium, and fission products in the stripped solvent.
- A solvent washing facility consisting of a single stage mixer for washing the solvent with dilute sodium carbonate, a solvent decanter for phase separation, and a solvent storage vessel from which the washed solvent can be recycled to the irradiation (1A) contactor. Additional scrubbing vessels will be added if necessary to restore solvent quality.

The equipment will be installed on a stainless-steel table top in C-Cell of the 325A Building Hot Cell facility. Several large tanks are located below the work table for storage of the fission product stock solutions and for interim storage of high-level waste solutions. Solutions will be transferred between tanks by pressurization and/or vacuum transfer techniques. Feed, scrub, and strip solutions will be pumped to the test apparatus by positive displacement metering pumps (FMI Lab Pumps, Fluid Metering, Inc.). Further details of the contactors and the reason for their selection are described in the following sections.

Single-Stage Mixers

The single-stage contactors to be used for the irradiation contact and for solvent washing are made from the bottom sections of graduated glass cylinders. Vigorous agitation is supplied by 4-bladed stirrers turned by laboratory motors at about 2400 rpm. Baffles are installed in the larger vessels to minimize vortex formation and to assure complete, homogeneous mixing. The operating volume of each mixer is set by an overflow tube installed at the desired operating level. Currently we have 5 of these contactors built with overflows at 34, 59, 115, 160 and 320 ml, respectively; actual operating volumes will be slightly less than these because of the volume occupied by the agitator and by the vortex developed by the agitator. The three smaller vessels (nominally 30, 50 and 100 ml) were sized to provide extraction contact solvent residence times of 4 to 12 min., comparable to the residence time obtained in pulse columns, as discussed in Appendix B. Aqueous and organic feeds will be introduced near the bottom of the vessel to minimize short-circuiting of the feed to the overflow. The contactors

to be used in the cell are jacketed for hot water heating.

Confirmation that homogeneous mixing and a constant phase volume ratio will be attained in the contactors was obtained in special tests with a 30 ml mixing vessel. The solvent and aqueous feed streams were introduced to the initially-empty contactor at a constant rate. Periodic samples of the overflowing mixture were taken to determine if the flow rates of aqueous and organic phases from the mixer were the same as those into the mixer. At the end of the test, the agitator was shut off and the volume ratio of the two phases left in the mixer was measured. The results, presented in Table I, show that the aqueous/organic (A/O) ratio in each of the collected samples and in the solution remaining in the mixer at the end of the test was the same as the ratio of the streams into the mixer within $\pm 4\%$. Similar performance was observed in 20 min. tests with a 100 ml, baffled mixing vessel. Further confirmation of intimate mixing is shown in Figure 2, a high-speed photograph of dispersion obtained in a 50 ml contactor. The maximum dispersed drop size, scaled from this photograph, was about 0.6 mm.

TABLE I EFFLUENT VOLUME MEASUREMENTS

Test 1: Nominal A/O Flow Ratio = 1.0

<u>Sample</u>	<u>Time Period</u> <u>Min</u>	<u>Volume, ml</u>		<u>A/O</u>
		<u>Aqueous</u>	<u>Organic</u>	
1	5-10	19.8	19.0	1.042
2	15-20	19.3	19.6	0.985
3	30-35	19.0	19.1	0.995
4	60-65	19.6	19.8	0.990
Total Feed In	0-65	253	253	1.000
Volume Left In Mixer	End	13	13	1.000

Test 2: Nominal A/O Flow Ratio = 0.23

1	6-11	4.6	19.4	0.237
2	15-20	4.4	19.45	0.226
3	30-35	4.4	19.4	0.227
4	60-65	4.6	20.0	0.230
Total Feed In	0-65	58	253	0.229
Volume Left In Mixer	End	4.7	20.6	0.228

FIGURE 2. CLOSE UP OF UNJACKETED 50 ML MIXING VESSEL SHOWING TYPICAL DISPERSION OBTAINED IN 1A IRRADIATION CONTACTORS.

The single stage mixer design was chosen because of its simplicity of construction, operation, and geometry for dose rate calculations. Originally we planned to use a multi-stage contactor for this purpose, but each additional stage would add an uncertainty factor in the dose rate calculations because of the increased geometrical complexity. The only benefit of a multi-stage unit would be the detection of inextractable uranium or plutonium species that might be produced by solvent degradation. However, there is a strong probability that several added stages would still not give representative uranium-plutonium losses because our Ce-144 stock solution is contaminated with phosphoric acid from prior separations plant processing. We do not have a source of phosphate-free feed since all of the available high level fission products are contaminated to some extent by phosphate-based solvents.

Centrifugal Contactors

Multi-stage miniature centrifugal contactors based on an SRL design^(5,6) are used to provide the succeeding 1A contactor scrub section, 1BX, and 1C contactor functions; and a single miniature centrifuge of the same design is used to separate the mixed phases overflowing from the 1A single-stage mixer. The mixer and centrifuge sections of these contactors are virtually identical with the SRL design, but they are arranged in linear, rectangular blocks containing 6 or 8 complete stages rather than the 16-stage circular design used at SRL. Electrical strip heaters are mounted on the sides of the blocks to permit operation at elevated temperatures. Figure 3 is a photograph of a disassembled six-stage contactor; Figure 4 shows two of these contactors in series operation, and Figure 5 shows the three multi-stage centrifuge units as they will be installed in the cell.

The SRL stages reportedly have a holdup of 3 ml in the mixing section and 7 ml in the centrifuge section. Our own calculations, based on the SRL drawings, show that holdup volume in the centrifuge bowl is about 4.5 ml to the overflow weirs. The relative proportions of aqueous and organic phases in each stage depend on the respective flow rates and the ratio of phase densities. The organic holdup in the mixer section is determined primarily by the aqueous/organic flow ratio, while that in the centrifuge

FIGURE 3: EXPLODED VIEW OF 6-STAGE MINIATURE CENTRIFUGAL CONTACTOR.

FIGURE 4: "COLD" TEST STAND

FIGURE 5: TEST STAND MOCK UP IN C-CELL

section is determined primarily by the density ratio. Calculated total organic holdups in the experimental units under normal Purex flowsheet operating conditions are 33, 28, and 16 ml for the 1A, 1BX, and 1C contactors, respectively. The capacity of the SRL contactors is in excess of 100 ml/min, sum of flows. The total flow rates for the test units in the LMFBR study will be about 6 to 10 ml/min in order to obtain solvent residence times in the various contactors comparable to those in pulse columns.

The centrifugal contactors are particularly attractive for this study because of their wide range of operating flow rates and the small holdup volumes. A close approach to steady-state operation is usually achieved in a continuous, countercurrent operation after about 5 throughputs of feed solutions, or within about two to three hours in our apparatus at the planned flow rates.

FEED MATERIALS AND FLOWSHEETS

A rare-earth fission product stock solution will be used to obtain aqueous phase power densities in the 1A irradiation contactor comparable to LMFBR dissolver solutions. The rare earth concentrate is produced in Hanford's B-Plant as part of the ARHCO Waste Management Program and will have a power density of about 10 to 15 W/liter, mostly as CePr-144. It will be well aged at the time of use to assure complete destruction of residual solvent from the separations process. The rare earth feed solution will also contain uranium and nitric acid at concentrations prevailing in the upper mid-section of a 1A column extraction section; it will not contain plutonium or those fission products which might be precipitated as phosphates.

An irradiated Hanford N-reactor fuel element will be dissolved in the cell and used to provide a complete radio-fission product spectrum for fission product performance studies. Typical 1AF solutions will be prepared by blending this solution (containing about 0.5 W/liter) with solvent-free uranium and plutonium stock solutions and appropriate amounts of other chemicals as needed. The power density of the 1AF will be adjusted to <10% of the cerium feed power density. Feed compositions will simulate the current Hanford Purex Plant 1AF and the ORNL-proposed LMFBR 1AF compositions. Uranium and plutonium concentrations will be adjusted to

provide the desired IAP solvent product loading. To avoid criticality problems in the hot cell and its auxiliaries, the plutonium concentration in the LMFBR feed will be kept below 4 g/g for most of the runs. The IAF will be fed to the second stage of the 8-stage 1A contactor, leaving 6 stages available for the scrub section.

Conceptual flowsheets to be used in the test apparatus for processing the two feeds are shown in Figures 6 and 7. The LMFBR flowsheet is based on suggested ORNL flowsheets^(9,10) and differs from the Purex flowsheet primarily in the use of 15% TBP rather than 30% TBP and the use of a greater reductant flow in the IBX column. Other flows are adjusted as necessary to match the requirements of the different solvent concentration. No final decision on the normal operating temperature has been made, but provisions have been made for heating the contactors to 50°C. Operating performance and extraction kinetics are improved by operation at higher temperatures; but chemical degradation of the solvent is also increased, and it may prove more important to operate at ambient temperatures to be able to distinguish better between chemical and radiolytic degradation of the solvent. The ambient cell temperature is expected to be 30 to 35°C.

The solvent flow rate shown in the flowsheets was set to provide a solvent residence time in the scrub portion of the 1A contactor comparable to that in a Purex Plant pulse column, a factor believed to be important because of the slow scrubbing kinetics for certain zirconium species.⁽⁷⁾ Most of the Hanford Purex Plant pulse columns have the design capability of operating at superficial organic volume velocities of 500 to 1500 gal/hr-ft². The 1A column is operated with the organic phase continuous and occupying about 85% of the column volume in the contacting section.* This translates

*

Over many years of operation with glass pulse columns, we have observed that pulsing conditions must be set to give at least 15% average dispersed phase holdup in order to obtain maximum mass transfer efficiency. Higher holdups are frequently obtainable and are often desirable with certain cartridges or flowsheets to obtain increased efficiency. The 15% holdup used in example calculations here and in Appendix B is believed to represent the minimum acceptable dispersed phase holdup in the contacting section of a 1A pulse column. This number agrees with that obtained using a correlation relating holdup to flooding;⁽²⁴⁾ however, such correlations provide only rough approximations at best and should be supplemented by actual column data wherever possible. Such data can conveniently be obtained in installed columns by static or differential pressure measurements, which in effect measure the average density of the column contents.

FIGURE 6. HANFORD PUREX FLOWSHEET ADAPTED FOR SOLVENT IRRADIATION TEST

FIGURE 7. ORNL LMFBR FLOWSHEET ADAPTED FOR SOLVENT IRRADIATION TEST

to actual linear organic velocities of about 80 to 230 ft/hr. Solvent residence times in the 20-ft-tall Plant 1A column scrub section would thus range from 0.25 to 0.085 hours. The specified solvent flow of 4 ml/min, together with the calculated 26 ml solvent holdup in the 1A scrub contactor, will provide a solvent residence time of 6.5 min, equivalent to that obtained with an organic volume velocity of 1180 gal/hr-ft² in the Purex Plant column. Higher solvent rates can and will be tested in the test apparatus to see how much the scrub residence time does limit fission product scrubbing.

The IAF flow rate in the flowsheets was set to equal the solvent flow rate. This will provide equal holdup volumes of solvent and aqueous phases in the single-stage 1A contactor and should improve the reliability of absorbed dose calculations, as described in Appendix B. Other flow ratios can and will be used to test the assumption that the radiation dose is absorbed equally by both phases.

OPERATING PROCEDURES

This section summarizes the normal operating procedures as they are visualized at this time.

Feed Preparation

The cerium and IAF feed solutions will be prepared by careful blending of well-analyzed stock solutions of fission products, uranium, plutonium, nitric acid, and cold chemicals simulating major fission products not adequately represented in the actual fission product stock solutions. The radioactivity for solvent irradiation will be supplied by the CePr-144 stock solution. A separate feed (IAF), derived from a dissolved fuel element, will be added to the 8-stage 1A contactor to provide sufficient ZrNb-95 and RuRh-106 activity for decontamination performance measurements. The IAF will contain at least 100 μ Ci/ml of each of these fission products so that normal product DF's on the order of 10^4 - 10^5 can be measured accurately.

The smaller feed batches will be made up in a graduated glass blend tank located on the work table for accuracy in measuring the volumes of fission product solutions added. Larger feed batches, for the longer solvent

recycle tests, will be made up in a 150 liter storage tank located below the table top. This tank will be fitted with a weight factor instrument for monitoring solution volumes. Solution volumes added to the makeup tank will be measured and added via graduated vessels located on the work table or external to the cell. Feed from this storage tank will be transferred to the feed tank on the work table as required during the run.

Startup

The experimental apparatus will normally contain "cold" solutions left from the previous shut-down procedure. Startup will involve turning on the heaters to heat the various contactors to the desired operating temperature. Agitator motors are then turned on, and "cold" scrub and strip flows are started and adjusted to the desired operating rates. After an operational check to assure the operability of the apparatus, the "hot" cerium and IAF feeds and the solvent will be introduced. Optionally, the solvent and the cerium feed may be started ahead of time to fill the irradiation contactor. Flow rates and heating rates will be adjusted as necessary during this startup period to attain the desired operating conditions. Occasionally, a new run will be started by changing the feed composition, flow rates, or other variables without shutting down between runs.

Normal Operation

Two modes of operation will be investigated in this program. The first mode will involve determining the effect of increasing dose rates, solvent residence time, etc. on the solvent performance parameters on a once-through basis for the solvent. In this type of run, the apparatus would be operated just long enough under the given run conditions to assure that steady-state profiles had been obtained. Steady-state gamma profiles will be confirmed by analyzing successive grab samples of solutions leaving each contactor with a shielded and collimated gamma spectrometer detector installed in the cell. Steady-state plutonium and uranium profiles will be confirmed by conventional analyses of successive grab samples of the effluent phases. The number of samples required to confirm steady state

should decrease with operating experience. Total run lengths should not exceed 5 hours per test, and considerably less time should be required for runs involving the change of a single variable without a shutdown between runs (essentially a continuation of the preceding run).

The other mode of operation will involve recycling the solvent continuously throughout the run. In these tests, a minimum inventory of 200-250 ml of solvent would be placed in the system at the beginning of the run and be recycled continuously by pumping the solvent from the solvent decanter (or washed solvent receiver) to the 1A mixer stage. Fresh solvent would be added in batches of about 25 ml each to replace losses and samples removed for analyses or testing. Operated in this mode, the solvent will approach a steady-state cumulative absorbed dose after about 10-15 days of operation. Most runs, however, will be terminated before this time if there are no significant changes in solvent properties with time. Alternatively, we can start with a larger inventory of solvent and let it decrease throughout the test without replacement. Radiation levels and solvent residence time in the 1A mixer will be adjusted so that the steady-state cumulative dose in the test apparatus approaches or exceeds that that would be attained in an LMFBR processing plant (assuming that the solvent inventory and solvent loss rates are comparable to those in the Hanford Purex Plant). A detailed analysis of the calculations involved is presented in Appendix A.

Sampling

Effluent samples from each contactor, particularly of the solvent phase, will be taken frequently to determine changes in the gamma spectrum caused by approach to steady-state or cumulative solvent exposure. These will be placed in a cell-holder of fixed geometry and counted in the cell by a gamma spectrometer detector installed in the rear door of the cell and a 400-channel analyzer located outside the cell. More precise analyses for gamma emitters, as well as for uranium and plutonium, will be performed on selected samples removed from the cell. Analytical methods and expected precisions are described in Appendix D.

Bulk samples of solvent will also be removed from the cell for measurement of physical properties (density, viscosity, etc.), standard distribution

ratio tests, and for the development of improved solvent washing techniques. We expect to be able to remove liter quantities of used, carbonate-washed solvent from the cell with little or no protective shielding required.

The optimum frequency of sampling will be determined in early tests.

Shutdown

At the conclusion of a test run, the feed streams to the 1A mixer stage and the agitator will be shut off momentarily to measure phase disengaging times at the steady-state solvent dose and to confirm that the steady-state phase volume ratio in the mixer was the same as the flow ratio. If no further runs are planned for that day, the "hot" feed will be displaced by running a "cold" feed (plutonium-free) for about an hour under otherwise normal operating conditions. The apparatus would then be shut down with the uranium and nitric acid profiles still at steady state. In some cases, the mixer stage will be emptied and replaced by a different-sized mixer before the next run.

Waste Disposal

High-level aqueous waste from the 1A contactor will be collected in a storage tank below the work table. Periodically this waste will be transferred to another storage tank in a vault below the cell and, eventually, to a shielded cask for disposal. The spent aqueous solution from the multistage 1A contactor and the spent carbonate solution from solvent washing will be combined with this waste. Other aqueous effluent streams containing uranium and plutonium will be removed from the cell and returned to the Hanford Purex Plant or disposed of as separate waste streams, depending on the product value. All solvent wastes will be removed from the cell for further testing or for disposal via a separate waste system. The only effluent stream to be reused throughout this study will be the solvent stream; all aqueous effluent streams will be discarded to avoid the possibility of recycling an unknown amount of degraded solvent that might be entrained or dissolved in the aqueous effluents.

DOSIMETRY MEASUREMENTS AND CALCULATIONS

The solvent radiation exposure will be calculated by the method described by Blake.⁽¹⁾ The procedure involves calculating the radiation power density in the mixer and multiplying it by the time that the organic phase remains in the extraction zone. The steps outlined by Blake are as follows:

1. Obtain the average beta and gamma power densities in the blended IAF solution. In our case, this will be obtained by careful laboratory analysis of the radioactive fission products in the high-level waste stock solutions.
2. Calculate the beta and gamma power densities in the mixing section of the extraction apparatus by multiplying the power density of the aqueous feed by the aqueous feed fraction of the combined feed, scrub (if present), and organic-phase volumes in the mixer. Thus, if the actual volume ratios of feed, scrub, and organic streams present in the mixer are 1:1:2, the power density in the mixer is one-fourth that of the feed. It is assumed that droplets of the dispersed phase are infinitely small and, therefore, that each molecule in the mixed solution exists in a field having this power density, regardless of whether the molecule is from the organic or aqueous phase. Implicit in this assumption is the necessity for the size of each dispersed aqueous droplet to be considerably less than the path length of the beta particle. Our system should meet this criteria since the average beta energy of CePr-144 is about 1.1 MeV, the estimated average beta energy of our feed will be about 1 MeV, and the maximum range of a 1 MeV beta particle is about 4 mm,⁽¹¹⁾ about 7 times the maximum drop diameter measured in one of our test mixers.
3. Calculate an effective radiation power density to account for the escape of some of the radiation energy from the system. It is customary to assume that the mixed phases absorb all (or nearly all) of the beta energy. On the other hand, only a portion of the gamma energy is absorbed, the fraction depending upon the geometry of the system. In our case, with mixer diameters under 2 inches, we expect most of the gamma energy to escape from the system. However, over

90% of the total radiation power density of our feed will be supplied by CePr-144, and over 95% of its radiation power is due to its beta energy; thus, neglecting the gamma energy in our calculations should have little or no effect on the calculation accuracy. A more detailed discussion of the factors we will consider in evaluating the effective radiation power density is presented in Appendix C.

4. Calculate the radiation dose in watt-hours per liter by multiplying the effective power density by the residence time of the organic phase in the mixing section.

The equation for this radiation dose follows:

$$E = t_m (G_\beta D_\beta + G_\gamma D_\gamma) P = t_m D_e P \quad (1)$$

where E = exposure of organic phase during mixing (W-hr/liter)

t_m = residence time of the organic phase in mixer (hr)

D_β = beta power density in aqueous feed (watts/liter)

D_γ = gamma power density in aqueous feed (watts/liter)

D_e = effective total power density in aqueous feed (watts/liter)

G = fraction of beta or gamma radiation absorbed in mixer

P = aqueous feed volume fraction in mixer.

Radiation doses calculated by using this equation will still be approximate values because of inaccuracies both in the equation and in the quantities used in the equation. This equation, however, is the best available method for pulse column solvent dose calculations, and relative errors will be minimized by using the same calculation method for our test stand dose calculations.

Appropriate corrections to the above equation are usually supplied to account for exposure during phase disengagement. The use of a miniature centrifuge in our apparatus to separate the mixed phases immediately after leaving the mixer will minimize this exposure time. We will attempt to estimate the incremental dose received by the solvent in the centrifuge; however, the residence time (≤ 20 sec) is so short that the incremental dose should be negligible. The incremental dose from the separate IAF stream will also be estimated (should be $< 5\%$ of the total dose).

Solvent radiation exposure in succeeding contactors due to extracted and entrained radioactivity and that due to plutonium is small and usually ignored. In our case, it should amount to less than 1% of the total exposure per pass.

Calculations of this type were made to estimate solvent exposures obtained in Hanford-type pulse columns when operated under current Purex process conditions and that would be obtained with a typical LMFBF flow-sheet. The results are summarized in Appendix B. The results show that solvent dose rates per pass would be about 0.005 and 0.1 W-hr/liter for the two respective flowsheets ($\pm$ a factor of two, depending on the assumed feed activity and processing rates). These results agree with the results of similar calculations made at ORNL.⁽⁸⁾

A series of special dosimetry runs is planned at the start of the "hot"-cell operations to try to confirm the calculated absorbed solvent radiation dose. This will be done by measuring the amount of DBP and MBP (di- and mono-butyl phosphates) formed as a function of the calculated average radiation power density in the mixer and the solvent residence time. The results will be compared with published G-values for radiation decomposition of TBP. (Laboratory determination of TBP G-values may be included in this study to minimize any bias that might be introduced by DBP-MBP analytical methods used by the various researchers.) As currently visualized, the dosimetry runs would involve operation of the 1A mixer and scrub contactors only, using fresh solvent and various dilutions of the CePr-144 fission product stock solution. Uranium, plutonium, and other fission products would be omitted to simplify analyses. At least two different volumetric flow ratios will be used to check the assumption that the radiation dose is absorbed equally in both phases.

Relatively high dose rates will be used in the dosimetry runs to improve the accuracy of G(DBP) measurements. We expect to generate about 200-300 mg DBP/W-hr in our dosimetry tests.⁽¹²⁾ At our proposed dose rates, we should find about 20 to 600 mg DBP/l in the irradiated solvent. We plan to use a modification of the methylation procedure developed by Kibbey and Davis⁽⁴⁾ to analyze DBP. The precision of our method hasn't been determined yet but should equal or exceed the published value (± 0.95 mg over the range 6.5 to 32.5 mg of DBP).

TENTATIVE RUN SCHEDULE

The following list is a rather broad outline of the number and types of runs that are currently planned for the initial testing program. Additional runs will be planned where warranted (including replicate runs to establish the amount of random variation in decontamination and losses) to study such variables as diluent composition, temperature effects, etc.

TBP Dosimetry

<u>Type of Run</u>	<u>Approximate Number</u>	<u>Variables Tested</u>
Single-Pass	6	Average radiation power level: 0.5 to 5W/l. Solvent residence time: 4 to 40 min. A/O volume ratio: 0.5 and 1.

Current Purex Process Flowsheet (30% TBP)

Single-Pass	5-10	Average radiation power level: 0.05 to 1 W/l. Solvent residence time: 1 to 12 min. Solvent flow rate: 4 to 20 ml/min. Range of absorbed solvent dose to overlap that for LMFBR tests: 0.003 to 0.1 W-hr/l.
Recycle	1	Cumulative solvent exposure to about 4 W-hr/l. (Additional runs may be planned to cover higher cumulative exposure at higher radiation power levels.)

LMFBR Flowsheet (15% TBP)

Single-Pass	10-15	Average radiation power level: 0.25 to 5W/l. Solvent residence time: 1 to 25 min. Solvent flow rate: 2 to 16 ml/min. Total absorbed dose: 0.02 to 2 W-hr/l.
Single-Pass Recycle	5	Solvent washing technique (involves single-pass recycle of once-used solvent after being washed by various techniques).
Recycle	3- 5	Cumulative solvent exposure to about 80 W-hr/liter at two or more radiation power levels and 2 or more solvent residence times.

Several combinations of solvent residence time and average power levels giving the same calculated absorbed solvent dose will be tested to determine whether the effect of radiation depends only on the absorbed dose/pass or also on the rate the dose was received. A conceptual list of run conditions is presented in Tables II and III. These tables were prepared as a guide for planning and scheduling purposes and may not be representative in detail of the final list of runs.

PERFORMANCE CRITERIA

The effect of radiation on solvent performance will be measured by the effect of a progressively increasing dose (both single-pass and cumulative during recycle) on the following parameters:

1. The zirconium, niobium, and ruthenium decontamination factors in the 1AP and the uranium and plutonium product streams (1CU and 1BXP).
2. The plutonium loss to the uranium product stream (1CU).
3. The uranium (and plutonium) loss to the 1C column stripped solvent (1CW).
4. The accumulation of activity in the stripped solvent (1CW) before and after carbonate washing.
5. The density and viscosity of the washed solvent.
6. The phase disengaging times in the 1A contactor.

In addition, we will withdraw macro samples of solvent at various times for additional dispersion-disengagement time tests, batch distribution ratio tests, solvent washing (fission-product retention) tests, plutonium retention tests, and other tests as warranted.

The goal of our program is to demonstrate, on a continuous, miniature scale, how the performance of the first cycle of a Purex process is affected by increasing solvent radiation exposure, both instantaneous and on a long-term, cumulative basis. The parameters we have chosen to observe are those we consider most important to a fuel reprocessor; namely, the decontamination and product recovery performance and those factors (disengaging times, viscosity, density) most likely to affect the operating (flooding) capacity of the plant columns. The performance of the miniature system will be

TABLE II
TENTATIVE RUN CONDITIONS - SINGLE PASS TESTS

Aqueous/Organic flow ratio = 1 in mixer; temperature = 30°C, except as noted.

Run No.	V _m , Mixer, Size, M ₂	F, Solv. Flow, m ² /hr	t _m , Solv. Resid., Time, Min.	D _e , IAF Activity, Watts/liter	E, Solv. Dose, W-hr/liter	Remarks
<u>TBP Dosimetry (30% TBP):</u> ~1 month required						
1	100	120	25	1	0.21	
2	50	120	13	1	0.10	
3	50	120	13	2	0.21	
4	30	240	3.7	2	0.062	
5	100	120	25	10	2.1	
6	100	106	38	10	2.1	A/O = 0.5
<u>Purex Flowsheet (30% TBP):</u> ~2 months required (50°C)						
7	30	240	3.7	0.1	0.0031	
8	50	240	6.2	0.1	0.0052	Typical Purex dose
9	100	240	12.5	0.1	0.0104	
10	30	240	3.7	0.2	0.0062	
11	50	240	6.2	0.2	0.0104	
12	50	480	3.1	0.2	0.0052	
13	50	240	6.2	0.5	0.026	
14	50	1200	1.2	0.5	0.0052	
15	50	240	6.2	2	0.104	
16	30	240	3.7	2	0.062	
<u>LMFBR Flowsheet (15% TBP):</u> ~3 months required						
17	30	240	3.7	0.5	0.016	
18	50	240	6.2	0.5	0.026	
19	50	240	6.2	1	0.052	
20	50	240	6.2	2	0.10	Typical LMFBR dose
21	30	240	3.7	2	0.062	
22	30	960	0.9	2	0.16	
23	100	240	12.5	2	0.21	
24	100	480	6.2	2	0.10	Solv. collected for wash tests below
25	50	240	6.2	5	0.26	
26	30	240	3.7	5	0.16	Same as (24)
27	30	240	3.7	10	0.31	
28	30	960	0.9	10	0.078	Same as (24)
29	50	240	6.2	10	0.52	
30	100	240	12.5	10	1.0	
31	100	120	25	10	2.1	
32	50	240	6.2	2	0.104	Replicate and wash test control run. Demonstration of effect of various solvent wash procedures on performance of recycled solvent.
33	50	240	6.2	2	0.104	
34	50	240	6.2	2	0.104	Same as (33)
35	50	240	6.2	2	0.104	Same as (33)
36	50	240	6.2	2	0.104	Same as (33)

TABLE III
RECYCLED TESTS

<u>Run No.</u>	<u>V_m, Mixer Size, ml</u>	<u>F, Solvent Flow, ml/hr</u>	<u>t_m, Solvent Residence Time, min</u>	<u>D_e, 1AF Activity, Watts/liter</u>	<u>Solvent Dose, W-hr/liter</u>	
					<u>Per Pass</u>	<u>Cumulative</u>
<u>Purex Flowsheet (30% TBP): ~1 month required</u>						
1	50	240	6.2	0.6	0.031	4
<u>LMFBR Flowsheet (15% TBP): ~3 months required</u>						
2	50	120	12.5	8	0.83	80
3	100	240	12.5	6	0.62	80
4	100	240	12.5	4	0.42	80
5	100	120	25	4	0.83	80
6	100	120	25	2	0.42	50

compared with that of the Hanford Purex plant at similar solvent exposures to provide a reference scale as to the validity of the results. A sufficient range of radiation exposures will be studied to permit extrapolation of the results to zero activity levels so that the chemical degradation effects can be distinguished from the radiolytic degradation effects. The following discussion summarizes the significance of the chosen performance criteria and some of the measurement uncertainties.

General Discussion

The major effect of radiation on the solvent is expected to be the radiolytic decomposition of the TBP to DBP, MBP, phosphoric acid, and butanol. Of these, only DBP is expected to be present in sufficient quantity to seriously affect separations performance. Some diluent attack can also be expected but will be minimized by the use of a normal paraffin diluent (n-dodecane or a mixture of C-10 to C-14 paraffin hydrocarbons). DBP affects separations performance in several ways:

- It forms strong complexes with zirconium, plutonium, and uranium (strength decreasing in approximately that order).
- The complexes are strongly organic-favoring and result in the retention of these three constituents in the solvent.
- This in turn leads to decreased Zr-95 DF's and increased uranium and plutonium loss to the solvent wash system.
- A number of metal-DBP complexes are only sparingly soluble in the solvent, forming waxy, surface-favoring precipitates.
- The surfactant properties of some DBP complexes can lead to pulse column flooding through forming stable emulsions (notably the Zr-DBP complex).
- The formation of fission product-DBP precipitates can lead to occasional bursts of activity in the products through physical entrainment of surfactant, interface-seeking films.

DBP is one of a series of organic phosphoric acids that have received considerable study recently. The most widely studied and used analog is HDEHP (di-2-ethylhexyl phosphoric acid).⁽¹⁶⁾ These acids are typically dimeric

in hydrocarbon diluents, they form strong complexes with most metal ions with the strength increasing generally with increasing metal ion valence, and they react with basic solutions to form aqueous-soluble sodium salts. Equilibrium data for the extraction of metal ions into organic phases containing these organic phosphoric acids are usually correlated by mass action constants based on the two-phase chemical reaction:

where the underlined compounds represent organic phase compositions, M is the metal ion, and R is the organic phosphate radical. In molar concentration units, the corresponding mass action constant is

$$K'_{eq} = \frac{(M(HR_2)_a)(H^+)^a}{(M^{+a})((HR)_2)^a} = D_m [(H^+)/((HR)_2)]^a$$

where D_m is the organic/aqueous distribution ratio of the metal ion.

The degree of extraction of most metal ions forming DBP complexes is highly dependent on the acidity of the aqueous solution and the concentration of free, uncomplexed H-DBP in the organic phase. This latter term is dependent on the amount of total DBP in the system as well as on the amount of DBP complexed by competing metal ions. The presence of a large amount of uranium or plutonium in the system, for example, will depress the formation and extraction of Zr-DBP.

There are exceptions to these rules. Zirconium extraction by DBP was reported by Hardy and Scargill⁽¹⁷⁾ to be independent of the hydrogen ion concentration, probably because of its prevalence as hydrolyzed species at low acidities. The observed extraction behavior was interpreted to follow the reaction:

Some metals (notably uranium) also form solvation complexes with acid phosphates at high nitric acid normalities comparable to the TBP solvation complexes.⁽¹⁴⁾ This effect is probably not of great importance at the acidities we will use in our tests.

MBP forms metal complexes similar to those with DBP, but it has been considerably less studied. It is formed in minor amounts, (generally <20% of the amount of DBP),⁽²⁾ and its effects on process performance are not usually considered separately from the effects of DBP.

Although we will be using a very stable diluent, prolonged degradation studies and Purex plant experience indicate that a small amount of fission product zirconium, niobium, and ruthenium become "fixed" in the solvent. Unlike DBP, the ligands causing this effect are incompletely removed by washing the solvent with carbonate or hydroxide solutions. We expect to distinguish the growth of any such ligands in our solvent by measuring fission product retention after extensive alkaline solvent washing. Although the fission product-ligand complexes are strongly solvent favoring, they do have finite distribution ratios between the two phases and can be one of the major factors limiting the overall fission product DF's to the aqueous product of a solvent extraction cycle.

With the above discussion as background, it may be appropriate now to discuss the individual performance criteria specified in the Program Plan. These were chosen specifically because we consider them to be of most importance to a potential fuel reprocessor:

- The individual fission product DF's because they may determine whether the desired overall decontamination can be accomplished in the normal two or three solvent extraction cycles;
- the plutonium loss to the 1CU stream because this may affect plutonium contamination in the final uranium product or, in a worst case, cause criticality problems in the uranium cleanup system;
- the uranium and plutonium loss to the 1CW because this will normally represent a process loss to the solvent treatment waste;
- the accumulation of activity in the stripped solvent before and after washing with alkaline solutions as an indirect measure of the relative amounts of DBP-MBP and diluent degradation ligands;
- the density and viscosity of the washed solvent as a measure of physical changes in the solvent that may affect flooding or capacity of the Plant solvent extraction contactors; and

- the phase disengaging times in the 1A contactor as a measure of the formation of surfactants that might affect emulsification tendencies or mass transfer rates.

Fission Product Decontamination Factors (DF's)

Formation of DBP should have a major effect on the Zr-95 DF, a lesser effect on the Nb-95 DF, and probably little or no effect on the Ru-103,106 DF.^(14,15) DF's from all other fission products, including the CePr-144 used to provide the majority of the radioactivity in the tests, should be very high (greater than 10^5) and virtually unaffected by solvent degradation. With all of the metal constituents of the feed held constant, the Zr DF to the 1AP should decrease proportionately to the increase in the solvent dose. We have six scrub stages available to assure that all of the normal zirconium and other fission product species are removed before making this first retention test. Laboratory and pilot plant experience has shown that very little DF improvement is obtained by increasing the number of effective stages beyond 6; thus an increase in fission product retention should be a direct measure of an increase in complexing ligands in the solvent. We intend to confirm this by batch scrubbing selected samples of the 1AP and measuring the fission product distribution ratios.

A summary of the expected analytical precision of gamma analyses is presented in Appendix D. We foresee no difficulties in analyzing any of the organic streams or aqueous product streams due to interference from the macro amounts of CePr-144 in the feed. The mixed-fission product fraction will be obtained from a fuel element of known irradiation history, and the fission product activities will be calculated and compared with the analytical values.

The total amount of fission product elements in the feed will be supplemented with cold chemicals to the levels expected in LMFBR fuels. Ruthenium and zirconium will be added during the dissolution step to promote isotopic interchange. A major limitation of the measurement technique may lie in how well these simulated fission products (as well as those obtained from the uranium metal fuel element) simulate actual LMFBR dissolver solutions. It is well known that the dissolution technique,

digestion, acidity, etc. can have a pronounced effect on Zr, Nb, and Ru performance.^(14,15) In the case of zirconium and niobium, the effect may be due to the formation of a variety of hydrolytic species. Ruthenium chemistry is more complex; a wide variety of nitro, nitroso, nitrato, etc. species have been identified; and several are quite extractable in TBP. Ideally, the final feed mixture should be digested at elevated temperature for several hours to assure an isotopic interchange between the "hot" and simulated fission product species, but we are not sure yet whether this will be feasible to do on a routine basis or necessary. The actual simulation of the fission product species present in an LMFB reactor dissolver solution is not as important as maintaining a constant ratio of such species so that variations in DF due to different species behavior do not mask the effect of solvent degradation.

Behavior of extracted hydrolytic species of zirconium and especially niobium are believed to be responsible for much of the apparent random variation of ZrNb-95 DF's in years past. One possible interpretation of the data is that these species have a very small distribution ratio into the organic phase but once there are difficult to remove because of their polymeric size and low diffusivities. The efficiency of removal would depend on the degree of agitation or phase dispersion and on contact time. Very possibly some of these species extract normally but hydrolyze or polymerize in the organic phase before they can be scrubbed. We hope to minimize trouble in this respect by using uniform contacting conditions. Residence time effects will be studied by operating the scrub and strip contactors at different flow rates for a limited number of tests. Residence or contact times may also affect ruthenium behavior through a slow equilibrium interchange between species.

Another explanation of erratic ZrNb-95 behavior lies in the affinity of these fission products for interfacial solids and in their formation of precipitates or surface-forming compounds with solvent degradation ligands. At high dose rates, we may expect to see increasing random variations in ZrNb-95 activities in solvent raffinate streams due to precipitation or adsorption on contactor surfaces. Entrainment of interfacial solids or precipitates in the solvent or aqueous product samples would result in

erratic fission product activities in successive samples and should be detectable for that reason.

A steady-state level of such solids should tend to accumulate in the contactors at a given dose rate. Activity would tend to leach from these solids at a fairly constant rate, adding another measure of uncertainty to the results, particularly if a low-dose run follows a high-dose run. We hope to minimize this effect by frequent replacement of the irradiation vessel, by periodically decontaminating the contactors, and by running low dose-rate runs first.

Fission product decontamination in the subsequent 1BX and 1C contactors will help indicate how tightly the fission products were held in the solvent by the degradation products. In the Purex Plant at Hanford, about half of the fission products in the scrubbed solvent follow the partitioned plutonium stream and perhaps half of that remaining in the solvent is stripped with the uranium in the 1C contactor. Even with high distribution ratios, some of the "fixed" fission products will be stripped; the relative concentrations in the organic and aqueous effluent streams being approximately equal to the organic/aqueous distribution ratio.

Plutonium Loss to the Uranium Product

DBP should not affect the ability to partition plutonium from uranium. Laboratory studies have shown that DBP does not interfere with the reduction of plutonium in the presence of macro uranium and that Pu(III) is not appreciably complexed by DBP in the U-HNO₃ system.^(12,18) In the absence of competing metal ions, however, it is very difficult to reduce and strip the plutonium from DBP-contaminated solvent. It seems advisable, therefore, to investigate the ability to strip the plutonium from the irradiated solvent in a 1BX contactor to assure ourselves that DBP or other solvent degradation products do not interfere with Pu(IV) to Pu(III) reduction. Six stages should be sufficient to remove all of the readily reduced and strippable plutonium so that an increase in plutonium concentration in the uranium product (1CU) and in the 1CW streams above some to-be-determined flowsheet level should be a measure of this effect. Batch equilibrations of effluent streams will be made periodically to establish whether plutonium losses were due to solvent impurities or to malfunction of the contactors.

Plutonium retention may also depend on the plutonium/uranium concentration ratio because of the competition between them for DBP or other solvent ligands. We plan to run one or more runs at the full LMFBF plutonium concentration to determine the magnitude of this effect.

Uranium and Plutonium Loss to the 1C Contactor

The presence of DBP will increase the uranium loss to the 1CW stream. A number of studies have been made showing the effect of various concentrations of uranium, DBP and TBP on the uranium distribution ratio under 1C column conditions.^(19,20) The results of these studies will be used to interpret the analyzed uranium retention values. A preliminary evaluation indicates that our maximum anticipated DBP concentration of about 600 mg/l should increase the uranium loss from <0.02 g/l to about 0.3 g/l in the 1CW.⁽²¹⁾ Uranium retention in degraded solvent is not necessarily linear with increased radiation dose or DBP concentration. DBP and uranium-DBP complexes have a small but definite distribution ratio to the aqueous phase that increases with decreased HNO₃, DBP, and TBP concentrations.⁽¹⁹⁾ Also, published studies⁽²³⁾ indicate that a "phosphate radiation polymer" which also complexes and holds uranium in the solvent may be formed. Apparently this is not acidic and could build up in recycled solvent.

As indicated with other retention tests, we will periodically make distribution ratio measurements of stripped solvent to see if high uranium concentrations are caused by abnormal distribution ratios or by poor contactor performance.

Plutonium retention in the 1CW will be measured to help determine the mechanism by which plutonium was not stripped in the 1BX column.

Accumulation of Activity in 1CW and Carbonate-Washed Solvent (100)

As indicated earlier, the ability to wash fission products from the solvent by Na₂CO₃ solutions should serve to distinguish between DBP and diluent complexing ligands. This test will be especially important in recycle tests to determine if such ligands continue to build up with cumulative dose rate or reach an equilibrium level determined either by solvent replenishment rate or by the complete degradation of an easily degraded trace impurity in the TBP or diluent. Increasing solvent activity with recycle would be a major consideration in the ability of a plant to maintain a consistently high DF.

A special plutonium retention test, similar to that used as a process control index of solvent quality in the Hanford Purex plant, will also be made on selected IOO samples. The test involves contacting the washed solvent with a standard aqueous plutonium solution and measuring the amount of plutonium remaining in the solvent after a specified series of stripping contacts. This test should be especially helpful in determining the relative effectiveness of various solvent washing or other solvent cleanup procedures. It is currently being used by Schulz⁽²⁷⁾ to demonstrate the excellent cleanup of used solvent that can be obtained with macroreticular anion exchange resins.

Physical Properties of Washed Solvent

Physical properties of irradiated solvent, such as density and viscosity, would be of interest to a reprocessor because of their effect on flooding capacity of the contactors. Pulse and packed column flooding correlations as a function of such variables have been published,⁽²²⁾ but we have found them of little value in applying them to plant performance: partly because of the gross effect of uranium and HNO_3 mass transfer on dispersion and disengaging properties and partly because trace impurities, surface wetting properties of the plate or packing material, etc., may have an overriding effect on the flooding capacity. A 1A extraction column, for example, has a much higher volumetric capacity than a 1C stripping column because of high uranium and nitric acid mass transfer rates in the 1A column. A 1B extraction column has a lower (and often much more variable) capacity than a 1C column because of low mass-transfer rates and an apparently greater sensitivity to the effects of trace impurities or plate wetting properties. We do not expect to be able to correlate the physical property data we will obtain with Hanford Purex Plant performance because of these limitations and the scarcity of actual plant performance data as a function of these variables.

In Situ Disengaging Times in the 1A Contactor

This test will be reported as an indication of the formation of a surfactant in the 1A contactor. Such a surfactant may leave the system via the aqueous raffinate and thus not be observed in similar laboratory tests mentioned below. This is a simple test, but we may not be able to relate the results quantitatively to 1A column dispersion performance. Certainly a two-fold or greater increase in the disengaging time would serve as a

warning that flooding trouble might occur in a plant contactor at the same solvent dose.

Special Tests

There are a number of other solvent properties we may look at from time to time as a function of cumulative absorbed dose. These might include interfacial tension, wetting characteristics (contact angle on stainless steel), standard U, Pu, and fission product distribution ratio tests, controlled dispersion-disengaging time tests, etc. Again, these would be supplied for the record together, where possible, with some indication of normal values obtained at the Hanford Purex Plant and the corresponding plant performance.

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APPENDIX ACALCULATION OF ACCUMULATED SOLVENT DOSEI. Derivation of Equations - J. D. Kaser NOMENCLATURE

C = Cumulative absorbed dose, W-hr/liter.

D_e = Effective power density in aqueous feed, watt/liter.

E = Solvent dose/pass = $t_m D_e P$, W-hr/liter.

F = Solvent flow rate, liters/hr.

L = Solvent loss rate, liters/hr = makeup solvent rate.

n = Number of solvent makeup batches added.

P = Aqueous feed volume fraction in mixer.

R = Radiation dose rate, watts.

t = Time, hours

t_m = Organic residence time in mixer, hours.

V = Total solvent volume in system, liters.

V_0 = Initial solvent volume in system, liters.

x = Fraction of initial solvent remaining just before solvent makeup batch is added $V/V_0 = (V_0 - L\theta)/V_0$

θ = Time between solvent makeup batch additions.

Case 1: Makeup solvent is added continuously to keep the solvent inventory $\underline{V}$ constant.

The absorbed energy balance is given by

$$V \frac{dC}{dt} = R - CL. \quad (2)$$

At time $\underline{t}$, the cumulative absorbed energy is given by

$$C = \frac{R}{L} (1 - e^{-Lt/V}). \quad (3)$$

The solvent dose/pass, $\underline{E}$, is related to $\underline{R}$ by

$$E = \frac{R}{F}, \quad (4)$$

$$\text{therefore, } C = \frac{EF}{L} (1 - e^{-Lt/V}). \quad (5)$$

Where Lt/V is small (i.e., very low solvent loss or short irradiation time), Equation (5) reduces to

$$C = \frac{EFt}{V} = \frac{Rt}{V} \quad (6)$$

Case 2: Makeup solvent is added batchwise at regular intervals to restore original solvent volume.

The absorbed radiation balance for this case is given by

$$(V_o - Lt) \frac{dC}{dt} = R. \quad (7)$$

Thus at time θ , just before makeup solvent is added for the first time,

$$C_1 = \frac{R}{L} \ln \left(\frac{V_o}{V_o - L\theta} \right) + C_o. \quad (8)$$

The absorbed dose just after the first batch of makeup solvent is added is

$$C_1' = \left[\frac{R}{L} \ln \left(\frac{V_o}{V_o - L\theta} \right) + C_o \right] \left(\frac{V_o - L\theta}{V_o} \right). \quad (9)$$

Substituting x for $\frac{V_o - L\theta}{V_o}$, EF for R, and letting $C_o = 0$,

$$C_1 = \frac{EF}{L} \ln \frac{1}{x} \quad (10)$$

$$\text{and } C_1' = \frac{xEF}{L} \ln \frac{1}{x}. \quad (11)$$

Continuing, just before the second makeup batch,

$$C_2 = (1 + x) \frac{EF}{L} \ln \frac{1}{x}, \quad (12)$$

and just after the second batch,

$$C_2' = (x+x^2) \frac{EF}{L} \ln \frac{1}{x} \quad (13)$$

Likewise, just before the nth batch of makeup solvent

$$C_n = \left(\frac{EF}{L} \ln \frac{1}{x} \right) \sum_{I=1}^n x^{n-I} \quad (14)$$

and just after the nth batch

$$C_n' = \left(\frac{EF}{L} \ln \frac{1}{x} \right) \sum_{I=1}^n x^n = x C_n \quad (15)$$

Since $x < 1$ and $\sum x^n$ is a geometric progression,

$$\sum_{I=1}^n x^n = x \frac{x^n - 1}{x - 1} \quad (16)$$

Thus,

$$C_n = \left(\frac{x^n - 1}{x - 1} \right) \frac{EF}{L} \ln \frac{1}{x} \quad \text{and} \quad (17)$$

$$C_n' = x \left(\frac{x^n - 1}{x - 1} \right) \frac{EF}{L} \ln \frac{1}{x} \quad (18)$$

At steady state, where $n \rightarrow \infty$, the maximum absorbed dose just before solvent is added is

$$C_\infty = \left(\frac{1}{1 - x} \right) \frac{EF}{L} \ln \frac{1}{x}, \quad \text{and} \quad (19)$$

$$C_{\infty} = \left(\frac{x}{1-x} \right) \frac{EF}{L} \ln \frac{1}{x}. \quad (20)$$

The degree of approach to the maximum steady state absorbed dose is

$$\frac{C_n}{C_{\infty}} = 1 - x^n. \quad (21)$$

II. Example Calculations

A. The Hanford Purex Plant has a solvent inventory in the No. 1 system of about 25,000 gal. The solvent loss rate is about 0.16% of the LAX solvent feed rate; and the loss is replaced when the inventory has decreased by about 25%, or when $x=0.75$. The maximum or steady state absorbed dose is given by equation (19) :

$$\begin{aligned} C_{\infty} &= \left(\frac{1}{1-0.75} \right) \left(\frac{EF}{0.0016F} \right) \ln \frac{1}{0.75} \\ &= 2500 E \ln 1.33 = 720 E. \end{aligned}$$

The number of batches of makeup solvent to reach 90% of the maximum dose is determined from Equation (21):

$$\frac{C_n}{C_{\infty}} = 0.9 = 1 - 0.75^n$$

$$\text{and } n = \frac{\ln 0.1}{\ln 0.75} = 8.0 \text{ batches.}$$

The Purex 1A column has a cross sectional area of about 3.7 ft^2 . At a 1A volumetric rate of 1000 gal/hr-ft^2 , the solvent rate is 3700 gal/hr and the loss rate is 5.9 gal/hr . The time between batch solvent additions is equal to the time required to lose 25% of the inventory:

$$\theta = \frac{(0.25)(25,000)}{5.9} = 1060 \text{ hrs,}$$

and the time to reach 90% of the steady-state dose is

$$(8)(1060) = 8480 \text{ hrs or } 353 \text{ days.}$$

- B. The solvent irradiation test stand will have a minimum solvent inventory during recycle testing of about 225 ml. The assumed solvent loss rate (due to sampling mostly) will be about 0.5% of the solvent feed rate, and the loss will be replaced by 25 ml additions of fresh solvent ($x = \frac{250 - 25}{250} = 0.9$). The cumulative solvent dose before makeup addition, from Equation (17), will be:

$$C_n = \left(\frac{0.9^n - 1}{0.9 - 1} \right) \left(\frac{EF}{0.005F} \right) \ln \frac{1}{0.9}$$

$$= 210.8 E (1 - 0.9^n).$$

But $n = Lt/L\theta = t/\theta$, and $\theta = 0.025/L = 0.025/0.005F$;
therefore, $n = 0.2 Ft$.

Also, $E = t_m D_e P$, (1)

where P = feed volume fraction in mixer,
 t_m = solvent residence time in mixer, hours.

After substitution of the relationships for E and n ,

$$\frac{C_n}{D_e} = 210.8 t_m P (1 - 0.9^{0.2 Ft}) = \frac{\text{cum. W-hr/l absorbed}}{\text{effective W/l in feed}}$$

The results of calculations for three laboratory mixer sizes are plotted in Figure A-1 for the case where the solvent and aqueous feed volumes in the mixer are equal. With this stipulation, $P = 0.5$ and

$$t_m = \frac{0.5 V_m}{F}$$

where V_m = volume of laboratory mixer, liters.

Therefore,

$$\frac{C_n}{D_e} = \frac{52.7 V_m}{F} (1 - 0.9^{0.2 Ft})$$

FIGURE A-1. CUMULATIVE ABSORBED RADIATION DOSE IN TEST-STAND SOLVENT

APPENDIX BCALCULATION OF SINGLE-PASS SOLVENT DOSEI. Pulse Column Solvent Residence Time

Pulse columns are designed to operate at superficial volume velocities up to about 2000 gal/hr-ft². In the Hanford Purex process, the solvent flow is about 70% of the total flow rate, so a reasonable range of solvent flow rates would be 500 to 1500 gal/hr-ft², which is equivalent to superficial linear velocities of 67 to 200 ft/hr. The solvent occupies about 85% of the column volume in the contacting section (organic phase continuous, pulse frequency set to about 80-90% of the flooding frequency); therefore, the actual linear solvent velocity is 79 to 236 ft/hr. The Hanford Purex 1A column has a 15-ft-tall extraction section and a 20-ft-tall scrub section; therefore the solvent residence times range from 4 to 11 min. in the extraction section and 5 to 15 min. in the scrub section. The calculations are summarized in Table B-1.

TABLE B-1Solvent Residence Times in the Purex 1A column

<u>Solvent Flow Rate</u>			<u>Solvent Residence Time^(b)</u>			
<u>Volume Velocity,</u>	<u>Superficial</u>	<u>Actual</u>	<u>Hours</u>		<u>Minutes</u>	
<u>GPH/Ft²</u>	<u>Ft/hr</u>	<u>Ft/hr^(a)</u>	<u>Extr.</u>	<u>Scrub</u>	<u>Extr.</u>	<u>Scrub</u>
500	67	79	0.191	0.254	11.4	15.3
1000	134	157	0.095	0.127	5.7	7.6
1500	201	236	0.064	0.085	3.8	5.1

(a) Solvent assumed to occupy 85% of column volume.

(b) Extraction section height = 15 ft; scrub height = 20 ft.

II. Solvent Dose Per Pass in Pulse Columns

The solvent dose in the extraction section of a 1A column can be approximated by the previously defined equation

$$E = t_m D_e P \quad (1)$$

where E = absorbed radiation dose in solvent, w-hr/liter.

t_m = solvent residence time in 1A extraction section, hr.

D_e = effective total power density in aqueous feed, w/liter.

P = aqueous feed volume fraction in 1A extraction section.

In the Hanford Purex process, the fraction of the feed activity in the aqueous phase throughout the extraction section = $\frac{1AF}{1AW} = 0.4$. The overall fraction of the extraction section occupied by the aqueous phase is 0.15. Therefore,

$$P = (0.15)(0.4) = 0.06.$$

Similarly, for the ORNL LMFBR flowsheet,

$$P = (0.15)(0.75) = 0.1125.$$

Single-pass and cumulative solvent doses were calculated for both Purex and LMFBR flowsheets as a function of feed activity and solvent flow rate. The results are presented in Table B-2. No corrections were applied for solvent irradiation in the disengaging section (calculated to be about 20% of that in the extraction section by Groenier⁽⁸⁾).

TABLE B-2

Calculated Absorbed Solvent Radiation Dose in a 1A Column

Solvent Volume Velocity GPH/Ft ²	E, Solvent Dose Per Pass, W-hr/liter			
	Purex (b)		LMFBR (c)	
	<u>D_e = 0.5 W/l</u>	<u>1 W/l</u>	<u>5 W/l</u>	<u>10 W/l</u>
500	0.0057	0.0115	0.107	0.215
1000	0.0028	0.0057	0.054	0.107
1500	0.0019	0.0038	0.036	0.072

	C, Cumulative Dose at Steady-State, W-hr/l ^(a)			
500	4.1	8.3	77	155
1000	2.0	4.1	39	77
1500	1.4	2.7	26	52

(a) Cumulative dose = 720 E (See Appendix A example calculation)

(b) Aqueous feed volume fraction = 0.06

(c) Aqueous feed volume fraction = 0.1125.

III. Test-Stand Mixer Sizing Calculations

The test-stand mixers were sized to provide solvent residence times comparable to those obtained in the extraction section of a typical 1A pulse column, or about 4 to 12 minutes. A further restraint, as discussed in the text, required that the solvent flow be set to provide solvent residence times in the scrub contactor comparable to those in a pulse column scrub section, or about 5 to 15 minutes as shown in Table B-1. The solvent holdup in the test-stand 1A scrub section is about 26 ml; therefore solvent flow rates of 2, 4, and 6 ml/min. will provide scrub residence times of 13, 6.5, and 4.3 min., corresponding to solvent volume velocities of 590, 1180 and 1770 gal/hr-ft² in the 1A pulse column.

The mixer vessel could be sized and operated to match both the solvent residence time and A/O volume rates obtained in the 1A extraction section. However, operation at aqueous/organic ratios differing significantly from 1.0 increases the percentage of error in dose rate calculations caused by small differences between actual and assumed values for P and t_m in Equation (1). This is illustrated in Figure B-1 where the absorbed dose for a given feed activity is plotted versus the aqueous/organic flow ratios for three mixer sizes. The maxima in these curves corresponds to an aqueous feed volume fraction of 0.5 ($A/O = 1.0$).

FIGURE B-1. EFFECT OF AQUEOUS/ORGANIC FLOW RATIO ON SINGLE-PASS SOLVENT RADIATION DOSE AND SOLVENT RESIDENCE TIME

The data in Figure B-1 for the 30, 50, and 100 ml mixers were calculated from the previously defined equation:

$$E = t_m D_e P. \quad (1)$$

Let V_m = volume of mixer, liters

V_s = volume occupied by solvent, liters

V_a = volume occupied by aqueous feed, liters

F = solvent flow rate, liters/hr.

t_m = solvent residence time in the mixer, hours.

$$P = \frac{V_a}{V_m} = \text{aqueous feed fraction in mixer.} \quad (22)$$

$$V_s = V_m - V_a = V_m (1-P), \quad (23)$$

$$t_m = \frac{V_s}{F} = \frac{V_m (1-P)}{F} \quad (24)$$

$$P = \frac{V_a}{V_a + V_s} = \frac{V_a/V_s}{1 + V_a/V_s} = \frac{A/O}{1 + A/O} \quad (25)$$

After substitution,

$$\frac{E}{D_e} = \frac{V_m (A/O)}{F (1 + A/O)^2} = \frac{\text{absorbed solvent dose, W-hr/liter}}{\text{Feed activity, watts/liter}} \quad (26)$$

$$\text{and } t_m = \frac{V_m}{F(1 + A/O)} \quad (27)$$

If we fix P at 0.5 ($\Lambda/O = 1$),

$$\frac{E}{D_e} = \frac{0.25 V_m}{F}, \quad (28)$$

which represents the maximum dose attainable in a given mixer.

APPENDIX CESTIMATION OF BETA AND GAMMA ENERGY ABSORPTION IN IRRADIATION VESSELS

J. C. Sheppard and G. L. Richardson

Beta Energy Absorption

An estimated 85 to 90% of the beta energy in the feed to our irradiation contactors will be absorbed by the two phases. The energy deposition will be distributed between the two phases in proportion to their volume ratio in the contactor with the intimate dispersion we obtain. These conclusions are based on the following analysis:

(1) Since the average atomic number of both the organic and the aqueous phase is about three (approximately equal electron densities), the stopping power of each phase should be similar. Thus, the two phases will look the same to CePr-144 beta particles passing through them.

(2) The average energy of CePr-144 beta particles will be about 1.0 MeV. The range of a beta particle in either phase will be the same, about 4mm. If the average diameter of a solvent drop is 0.6mm or less, as measured, statistically the beta will pass through about six drops as it loses its energy. Furthermore, the isotropic emission of the betas, the random motion of drops, and the uniform distribution of the beta emitters in the aqueous phase also contribute a uniform distribution of beta energy between the two phases.

(3) A beta particle can escape from the surface of an object only if the emitting nucleus lies within the range R of the surface, and only one half of those emitted at the surface will escape absorption. Of the betas emitted at an intermediate distance X from the surface, the fraction that escapes absorption is

$$F = \frac{2\pi R(R-X)}{4\pi R^2} = \frac{R-X}{2R}$$

This represents the fractional area of a sphere of radius R subtended by a plane (the surface of the object) passing through the sphere at a distance $R-X$ from the center. The average overall value of F as X varies from 0 to R gives the fraction of the betas emitted in this volume element which are not absorbed:

$$F = \frac{1}{R} \int_0^R \frac{R-X}{2R} dX = \frac{1}{4}.$$

Therefore, $3/4$ of the betas emitted in this volume element will be absorbed.

Now consider a spherical object having a radius ρ which is greater than the range of beta particles, R . This sphere can be divided into an inner core with radius $(\rho-R)$ in which all the betas are absorbed and an outer annular sphere in which only $3/4$ of the betas are absorbed, as in the analysis above. The fraction of all the betas emitted which are absorbed is given by

$$\begin{aligned} F_{\text{abs}} &= F_{\text{inner}} + F_{\text{outer}} \\ &= \frac{(4\pi/3)(\rho-R)^3}{(4\pi/3)\rho^3} + 3/4 \cdot \frac{(4\pi/3)\rho^3 - (4\pi/3)(\rho-R)^3}{(4\pi/3)\rho^3} \\ &= 3/4 + (1/4)\left(\frac{\rho-R}{\rho}\right)^3. \end{aligned}$$

When $\rho \gg R$, all of the beta energy is absorbed in the spherical object; when $\rho = R$, three-fourths of the energy will be absorbed. The table below shows the effect of various R/ρ ratios on the fractional beta absorption.

R/ρ	F_{abs}
0	1.00
0.01	0.99
0.03	0.978
0.05	0.964
0.10	0.932
0.15	0.914
0.20	0.878
0.25	0.829
0.50	0.781

A similar analysis can be made for other geometrical shapes. For example, the beta absorption in cylindrical vessels such as our irradiation contactors is given by

$$F_{abs} = 3/4 + (1/4) \left(\frac{D-2R}{D} \right)^2 \left(\frac{h-2R}{h} \right)$$

where D is the internal diameter of the vessel and h is the height of the solution in the vessel. For our small scale CePr-144 dosimetry experiments, the calculated value of F_{abs} is 0.85 for the 30 ml vessel, 0.88 for the 50 ml vessel, and 0.90 for the 100 ml vessel. Radioisotopes with lower energies will, of course, be absorbed more efficiently.

Gamma Energy Absorption

For our dosimetry tests, the gamma power density will be only about 1% of the beta power density and its fractional absorption can be ignored. For higher gamma/beta ratios and a spherical geometry, the fraction of the gamma energy escaping, q_s , can be approximated by

$$q_s = \frac{1}{R} \int_0^R e^{-\mu R} dR = \frac{1}{\mu R} (1 - e^{-\mu R}) ,$$

where μ - the linear absorption coefficient for the system, and

R = the radius of the sphere.

This equation is commonly used to correct for self absorption of gammas in spherical sources.

Mayneord⁽²⁸⁾ has calculated the escape probability or fraction of the gammas escaping, q_c , from an infinitely long cylinder of radius R from the equation

$$q_c = \int_0^1 e^{-\mu R / \sqrt{1-x^2}} dx.$$

This equation has not been reduced to a readily integrable form, but a table of q_c values as a function of μR is provided in the reference.

Values of μ to use in these equations were estimated from the average mass absorption coefficients for our system. These were calculated for several gamma-energies from the equation

$$\mu/\rho = \sum_i w_i (\mu_i/\rho_i),$$

where w_i = the weight fraction and μ_i/ρ_i = the mass absorption coefficient of the i -th element. The composition of the system to be irradiated was assumed to be an average of typical equilibrium aqueous and organic phase compositions present in the contactor at an organic/aqueous volume ratio of 1. Carbon, nitrogen, oxygen, and phosphorous have approximately equal mass absorption coefficients, so these elements were all taken as oxygen. Uranium, hydrogen and "oxygen" will have average weight fractions of 0.0365, 0.111, and 0.867, respectively; thus the equation for the mass absorption coefficient of the mixture is

$$(\mu/\rho)_{\text{mixture}} = 0.0365 (\mu/\rho)_U + 0.111 (\mu/\rho)_H + 0.867 (\mu/\rho)_O.$$

Since the density, ρ , of the mixture is nearly one, the mass absorption coefficient for the mixture is also approximately equal to the linear absorption coefficient, μ . The table below lists the mass absorption coefficients for the elements and mixture for gamma energies of 0.2, 0.5, and 1.0 MeV:

	Mass Absorption Coefficients, μ/ρ		
	0.2 MeV	0.5 MeV	1.0 MeV
Uranium	1.15	0.140	0.0479
Hydrogen	0.0525	0.0590	0.0555
Oxygen	0.0268	0.0298	0.0280
Mixture	0.0710	0.0375	0.0322

The following table lists values of gamma energy escaping factors, q_s and q_c , for several radii, using the average mass absorption coefficients tabulated above for our experimental system as μ .

Energy Escaping Factors for Spheres and Infinitely Long Cylinders

Radius, cm	0.2 MeV		0.5 MeV		1.0 MeV	
	q_s	q_c	q_s	q_c	q_s	q_c
1	0.965	0.881	0.981	0.920	0.984	0.926
2	0.932	0.805	0.963	0.875	0.968	0.887
3	0.901	0.743	0.946	0.832	0.953	0.851
4	0.871	0.657	0.928	0.743	0.938	0.815
5	0.842	0.612	0.912	0.755	0.923	0.782
10	0.716	0.391	0.834	0.595	0.855	0.639

The radiolysis vessels used in our experiments will approximate cylinders having height-to-diameter ratios between one and two. Parker⁽²⁹⁾ has shown that the absorbed radiation doses for cylinders with height-to-diameter ratios of one and two were only 1.5 and 4.5% greater, respectively, than for spheres of the same volume. Thus, the tabulated figures for q_s should closely correspond to the energy escaping factors from our irradiation

contactors. The radii of the radiolysis vessels will range between one and three centimeters. For typical gamma energies between 0.5 and 1 MeV, two to five percent of the gamma energy will be absorbed in the vessels. For all practical purposes, the contribution of gamma energy to the total solvent dose can be neglected.

The values of q_c cannot be applied to our radiolysis vessels, but they can be used to estimate the gamma energy absorbed in pulse columns. Thus, about 40% of the gamma energy in a typical LMFB reactor dissolver solution would be absorbed in a 20-cm diameter column.

APPENDIX DURANIUM, PLUTONIUM AND FISSION PRODUCT ANALYTICAL METHODS

Uranium, plutonium, and fission products will be analyzed by standard analytical methods in use many years at Hanford. Most of these are described in References 25 and 26. A brief description of some of the methods we will use is given below:

URANIUM METHODS1) Coulometric Method

Coulometric methods are based on the exact measurement of the quantity of electricity passed through a solution during the occurrence of a reaction involving the substance being determined. The quantity of reactant is computed directly from Faraday's law. The prime requisite is that only a single reaction take place, and conditions must be derived so that the current efficiency is 100 percent.

For uranium analyses, U^{6+} is titrated to U^{4+} according to the following reaction:

General Information

Sample size: 0.2 to 10 mg U

Sample volume: 10 λ to 1500 λ , depending on acidity

Sample size required for 5% accuracy: 200 μ g

Sample size required for 1% accuracy: 1 mg

2) X-Ray Fluorescence Method

When an electron is ejected from the K or L shell of an element by an X-ray photon, electrons from outer orbits of the electron may return to the vacant orbit and characteristic X rays will be produced.

These X rays are called fluorescent radiation. The fluorescent X rays are in all respects like the characteristic X rays of that element except in the manner of excitation. The emitted radiation passes through a collimating slit onto the crystal spectrometer and then into a detector (usually a Geiger-Müller, proportional, or scintillation counter).

In quantitative applications the intensity from a given element is affected mainly by the amount of that element present (and in an almost linear manner). Consequently, standards need not be especially close to the unknown in composition.

General Information

Concentration range:	0.1 g/l to 25 g/l
Sample acidity:	mix standards in same range
Sample volume:	1 ml
Precision:	±2% if sample is in a consistent matrix
Sample concentration required for 5% accuracy:*	0.1 g/l
Sample concentration required for 2% accuracy:	0.2 g/l
Sample concentration required for 1/2% accuracy:	10 g/l

* If an internal standard is used.

3) Fluorimetry Method

Many compounds will emit radiant energy after they have first absorbed radiant energy of some particular frequency. If there is no measurable time delay, usually less than 10^{-9} second, between the absorption and re-emission of the energy, the effect is called fluorescence. Measurement of the intensity of fluorescence is a convenient and rapid method for the determination of a large number of specific substances.

Uranium compounds fluoresce with a brilliant yellow color, and uranium is often determined by measuring the fluorescence of a sodium

fluoride bead containing the uranium sample. The fluorescence of uranium fluoride is measured in a sodium fluoride matrix.

General Information

Concentration range: 0.001 g/l to 25 g/l

Sample acidity: $\sim 1M$ HNO_3

Sample volume: depends on concentration

Precision: $\pm 20\%$ over the full range of concentration*

* The precision of a given determination can be increased by increasing the number of replicate measurements:

$$\sigma_{avg} = \sqrt{\sigma^2/n}$$

where σ = analytical relative random error

and n = number of replicate measurements.

PLUTONIUM METHODS

1) Alpha Counting Methods

The number of alpha particles emitted by a given plutonium nuclide in a given period of time is directly proportional to the amount of that nuclide present. The weight of nuclide on the counting disc is determined by a proportionality factor, which is a function of two variables: the specific activity of the alpha emitter and the counting efficiency of the counting instrument. Normally a mixture of plutonium nuclides is present, and an experimental specific activity factor must be determined by an independent analytical method such as mass spectrometry or X-ray fluorescence. The analytical precision is affected by solids absorption, backscattering, coincidence counting loss, beta discrimination, and counting efficiency. The first two of these can be controlled in many instances by extracting the plutonium away from high salt or highly radioactive solutions with specific solvents such as hexone or TTA.

General Information

Sample size: 100-10,000 d/m

Precision: $\pm 5\%$ for organic samples, $\pm 3\%$ for aqueous samples

2) X-Ray Fluorescence Method

See discussion under uranium methods.

FISSION PRODUCT METHODS

Most fission products will be analyzed by radiochemical methods. A brief description of the methods and estimated precision is presented below.

- 1) Gamma Emitters: Radionuclides for which gamma ray emission is a significant factor in radioactive decay are determined by counting a sample aliquot on a high resolution gamma spectrometer using a Ge(Li) detector. Radionuclides determined include: Nb-95, Zr-95, Cs-137, Cs-134, RuRh-106, Ru-103, Ce-141, and CePr-144. The accuracy and precision of reported concentrations depend on the relative concentrations present. Major constituents are determined to an accuracy of about $\pm 5\%$. The uncertainty in the determination of minor constituents may be as high as $\pm 50\%$.

We expect to obtain the following precision for the major radionuclides in our fuels:

<u>Radionuclide</u>	<u>CePr-144/Radionuclide Curie Ratio</u>	<u>Estimated Precision,* %</u>
CePr-144	1	± 2 (feed)
RuRh-106	≤ 200	± 10 (feed)
	< 1	± 3
Nb-95	≤ 400	± 10 (feed)
	< 1	± 5
Zr-95	≤ 800	± 20 (feed)
	< 1	± 10

* Detection limit will be about 10^{-3} $\mu\text{Ci/ml}$ at indicated precisions.
Sample sizes will be 10^{-2} to 100 μCi (10 ml maximum volume).

- 2) Beta Emitters: "Total beta" activity is determined by counting a sample aliquot with a thin window, gas flow, proportional counter. A counting efficiency of 50% is used to convert counts per minute to disintegrations per minute. Although this counting efficiency is estimated to be close to the actual counting efficiency for the mixture of beta emitters present in normal high-level waste samples, a large uncertainty exists because of the possible variations in sample composition. This method, if used, will provide only a rough check of the total beta activity as determined by analysis of individual beta emitters. The accuracy is $\pm 25\%$ with a precision of $\pm 5\%$. The detection limit is $10^{-3} \mu\text{Ci/ml}$.
- 3) Strontium-90: Strontium-90 is determined by separating the total strontium by chromatographic elution from a cation exchange column and measuring the yttrium-90 buildup with a proportional beta counter. The estimated accuracy is $\pm 10\%$ with a precision of $\pm 5\%$. The detection limit is $10^{-3} \mu\text{Ci/ml}$.
- 4) Rare Earths (Total): The total rare earths are determined gravimetrically after precipitation as the oxalates and ignition to the oxide. If the rare earths present are known to consist primarily of cerium, results are calculated assuming the dioxide is formed. If cerium is not the primary constituent, the results are calculated assuming that sesquioxide is formed. Elements forming acid insoluble oxalates interfere. The estimated accuracy is $\pm 15\%$, precision is $\pm 7\%$, and the detection limit is 2000 ppm.

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