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SOLVENT STABILITY IN NUCLEAR FUEL  
PROCESSING: EVALUATION OF THE LITERATURE,  
CALCULATION OF RADIATION DOSE, AND  
EFFECTS OF IODINE AND PLUTONIUM

Charles A. Blake, Jr.

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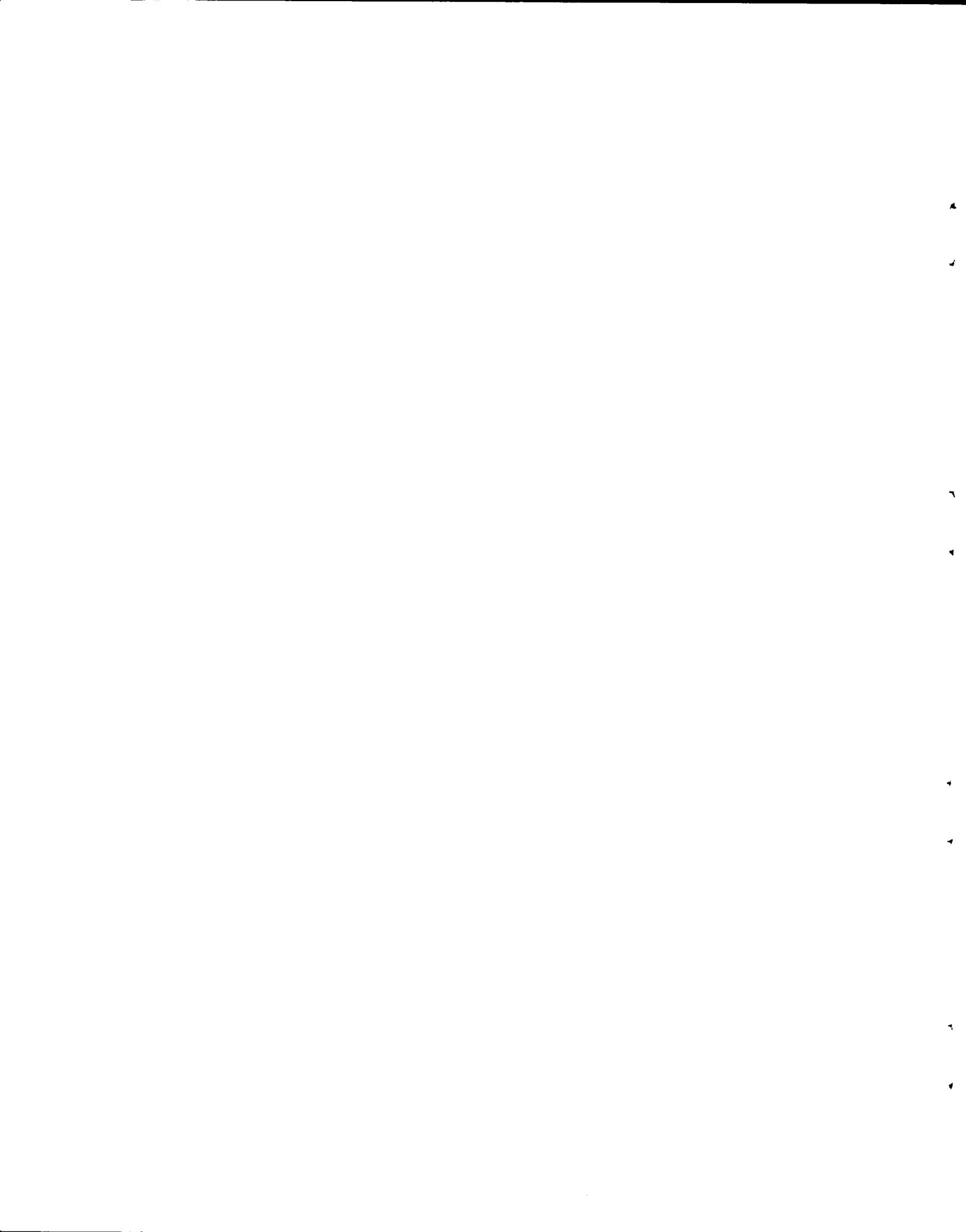
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CHEMICAL TECHNOLOGY DIVISION  
Chemical Development Section BSOLVENT STABILITY IN NUCLEAR FUEL PROCESSING:  
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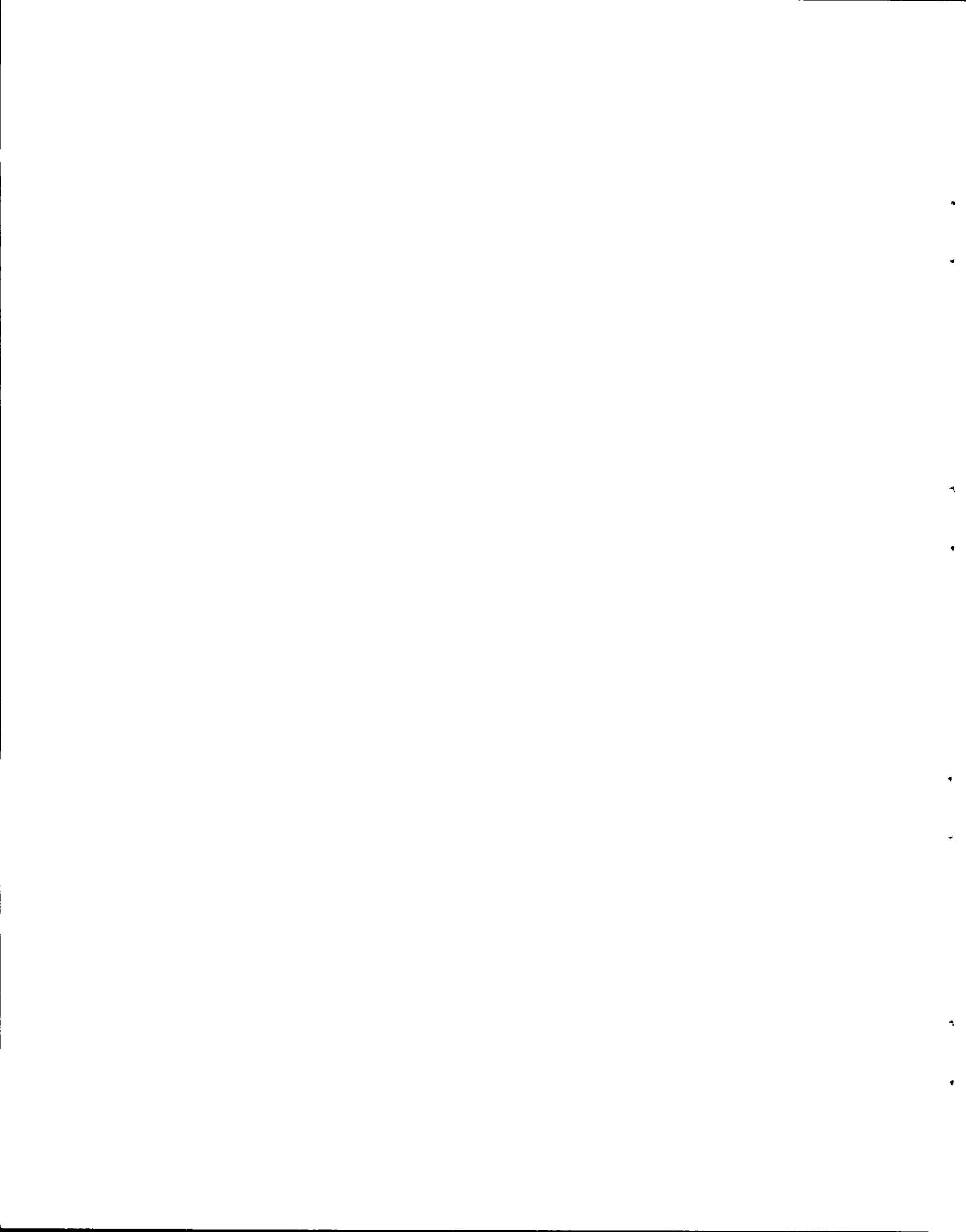
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CONTENTS

	<u>Page</u>
Abstract. . . . .	1
1. Introduction. . . . .	2
2. Difficulties in Extrapolating Solvent Stability Data Found in the Literature to Actual Fast-Reactor Fuel Processing Conditions. . . . .	6
3. Calculation of Radiation Exposures Received by the Solvent Phase . . . . .	12
3.1 Exposure During Mixing . . . . .	13
3.2 Exposure During Disengagement of Phases. . . . .	18
3.3 Compilation of Reported Values for Process Solvent Exposures. . . . .	20
4. Behavior of Iodine in the Processing of Short-Cooled Fuels by Solvent Extraction . . . . .	23
5. Irradiation of the Solvent by Plutonium . . . . .	26
6. Acknowledgment. . . . .	28
7. References. . . . .	29



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ABSTRACT

A survey of the literature was made to accumulate information concerning the stability of organic solvents during the processing of nuclear fuels. Many of the data, obtained in laboratory studies of solvent stability against radiation and chemical attack, require large extrapolations when they are used to predict results during actual fuel processing operations. In these laboratory studies, the radiation exposures were frequently massive, that is, up to 100 whr/liter compared with those expected (0.05 to 1.0 whr each cycle) during fast-reactor fuel processing. Many of the studies, which featured wide variations in organic- and aqueous-phase compositions and in irradiation conditions, were made with reagents that were degraded in the absence of an aqueous phase. It was concluded that: (1) the extrapolation of most of the reported data to predict process conditions would produce erroneous results, (2) the decrease in decontamination factors for fission products in the tributyl phosphate--hydrocarbon--heavy-metal systems will probably not be significant (perhaps up to a factor of 2) at a solvent radiation exposure of 0.5 whr per liter per cycle, and (3) adequate solvent wash systems will limit the cumulative effect of radiation. Good solvent performance has been observed in installations that employ continuous processing methods; here, accumulated doses have exceeded tens of watt-hours per liter.

Solvent exposure in pulsed columns is a function of processing conditions such as heavy-metal and tributyl phosphate (TBP) concentrations, extent of flooding, and contact time. For example, with 15% TBP in dodecane and a flow rate that is 75% of flooding, the calculated solvent exposure would be less than 0.1 whr per liter per cycle when 30-day-cooled fast reactor fuel having an average burnup of 38,500 Mwd/metric ton is processed. The solvent exposures would be higher in present mixer-settler contactors and lower in contactors having short residence times. The alpha radiation from plutonium does not contribute significantly to solvent exposure in the first cycle of extraction with thermal reactor fuels but can contribute approximately 10% of the total dose for fast-reactor fuels, in which 1% of the plutonium is present as  $^{238}\text{Pu}$ . Alpha radiation effects in the second plutonium cycle are more significant and are proportional to the plutonium concentration and the residence time of plutonium in the organic phase.

A standard method is proposed for the calculation of solvent exposure. Assuming that homogeneous phase mixing is a basic parameter, solvent exposure in the mixing chambers is found to be equal to the product of the radiation density of the aqueous feed (w/liter), the volume fraction of the aqueous feed in the mixing chamber, and the residence time of the organic phase in the mixing chamber (hr). The calculation of the additional exposure that is incurred in the settling chambers in various contactors requires special assumptions for each contactor.

Sufficient data are not found in the literature to allow a quantitative prediction of the distribution of iodine between the dissolver, the off-gas, and solvent extraction system under varying conditions.

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## 1. INTRODUCTION

The success of the fast-reactor program will depend upon the development of fuel cycles capable of handling reactor cores that have experienced high burnups of fissile materials, perhaps in excess of 100,000 Mwd per metric ton of contained metal. Economic considerations may require the fuel to be processed after a cooling period as short as 30 days. Under these conditions the aqueous feeds to the solvent extraction operation will have very high radiation power densities. Some authors<sup>1,2</sup> estimate that these may range from 6 to 120 ( $\beta + \gamma$ )-w/liter, depending on the heavy-metal concentration in the aqueous feed and the method of processing the core and the blanket (i.e., separately or in combination).

The stabilities of the customary extraction reagents and diluents have frequently been questioned when solvent extraction has been considered as a method for recovering uranium and plutonium from solutions that have high radiation power densities. Three aspects of this problem have caused concern:

- (1) The high radiation density could enhance the chemical degradation of the extractant and the diluent to give products that would impair phase separation and decrease decontamination.

- (2) When a significant concentration of radioiodine is present in a feed obtained by dissolving short-cooled fuel, the iodine may accumulate in the organic phase, giving it a high background activity level and, possibly, causing further degradation.

(3) A high concentration of plutonium, particularly  $^{238}\text{Pu}$ , in the organic extract may provide a continuing source of potential degradation after the extractant leaves the extraction column. we know  
0.06%  
Pu 238

The radiation-enhanced degradation of process solvents has been studied at many laboratories. Papers presented at the Solvent Extraction Chemistry Symposium in Gatlinburg, Tennessee, in 1962<sup>3</sup> and at the International Conference on the Solvent Extraction Chemistry of Metals at Harwell, Great Britain, in 1965<sup>4</sup> give good accounts of many of these studies and include extensive bibliographies. Many of these data have, in turn, been summarized by Solomon and Lopez-Mencheró.<sup>5</sup>

It is unfortunate that the conditions used in many laboratory tests require large extrapolations in order to simulate those that prevail during actual fuel processing. This is because, to obtain measurable effects, a laboratory exposure frequently consists of one massive dose, which is well in excess of that anticipated during each cycle of fast-reactor fuel processing. In addition to the possibility of causing secondary radiation effects, the "one-shot" exposures eliminate possible ameliorating effects that may result each time the solvent passes through the normal extraction-scrub-strip-cleanup cycle while accumulating the same total dose in a continuous process. Further, whereas it has been established clearly that degradation proceeds by the chemical reaction of organic and aqueous phase components and that the extent of reaction is enhanced by radiation, many of the laboratory studies of solvent irradiation have been made in the absence of any aqueous phase. Because of the relationship between radiation and chemical effects, the comparison and interpretation of results that have been obtained under these different conditions—including wide variations in organic- and aqueous-phase composition, different methods of irradiation, and wide temperature ranges—are extremely difficult.

Recognizing the difficulty of interpreting batch irradiation data, researchers at UKAEA, Windscale,<sup>3</sup> and CNEN, Rome,<sup>6</sup> set up recycle experiments in which a solvent phase was contacted with feed solution in a radiation field and then subjected to scrubbing, stripping, and cleanup. In the Windscale tests, 20% TBP in odorless kerosene continued to perform well, even after an accumulated exposure of 20 whr/liter (0.125 whr per liter per cycle). Some loss in decontamination efficiency was observed, and degradation products of both diluent and TBP were found in the recycle organic phase; however, it is difficult to assess these results in terms of the changes in operation during the run. In the CNEN test a tertiary amine in an aromatic diluent was exposed to a level of 45 whr/liter (2.8 whr per liter per cycle). "Degradation of the amine was insignificant and decontamination did not show important variation with number of cycles."<sup>6</sup> An external radiation field (<sup>90</sup>Sr at Windscale and <sup>60</sup>Co at CNEN) was used in each of these tests. Cyclic radiation tests are included in the planned ORNL fast-reactor fuels processing studies.

Small plants that closely approximate actual fuel processing plants are being constructed at Karlsruhe, Germany,<sup>7</sup> and at L'Hague, France.<sup>8</sup> These two plants are designed to process, daily, about 1 kg of fuel (10 to 25% plutonium) that has been irradiated to burnups as high as 100,000 and 50,000 Mwd/metric ton, respectively. A small test facility is also planned at Oak Ridge National Laboratory (ORNL).

Since information on the processing of fast-reactor fuels of the uranium oxide-plutonium oxide type is not available, it has been customary to cite the results obtained at ORNL during the processing of irradiated, short-decayed thorium fuel by the Thorex Process. The feed solutions in these runs had radiation densities of about 10 w/liter.<sup>9</sup> However, operational problems, not necessarily associated with solvent damage, were encountered in these tests; consequently, it is difficult to relate these data to the processing of fast-reactor fuel solutions.

Recently, based on work at Dounreay in which solutions (2 to 3 w/liter) of fast-reactor fuels (uranium-molybdenum alloy) are being processed by TBP extraction, the British<sup>10</sup> have decided to use TBP extraction to process plutonium-enriched fuels that have been irradiated to burnups of

8 to 10%, that is, approaching 100,000 Mwd/metric ton. Currently, the formation of precipitates, possibly insoluble inorganic molybdenum salts and metallic salts of the TBP degradation products, is causing difficulty in the operation of their mixer-settlers.

Very little information is available about the solubility of the salts of TBP degradation products in the solutions that are used in fuel processing systems. In 1961, Davis<sup>11</sup> reported the solubilities of uranyl and iron(III) dibutyl- and monobutylphosphates in TBP-diluent systems. Other studies in the iron dibutylphosphate--TBP system have been reported by workers at Dounreay<sup>12</sup> and at Fontenay-Aux-Roses.<sup>13</sup> Studies with iron dibutylphosphate and other metal salts are currently being made at ORNL.

Large cumulative doses have been received by process solvents in the Purex processing plants at Savannah River and at Hanford. The Savannah River Plant utilizes a TBP--n-paraffin solvent phase that has been sufficiently recycled to accumulate doses of tens of watt-hours per liter; yet the uranium-fission product decontamination factors remain high. This is significant from two standpoints: (1) degradation products of TBP are being removed in the washing cycle to a low concentration level, and (2) degradation products of the diluent not expected to be removed in the solvent washes have not accumulated to levels that seriously impair decontamination.

The results just described are encouraging from the standpoint of the processing of short-cooled fast-reactor fuels, but are in contradiction with often-quoted laboratory data. One purpose of this report is to survey these laboratory data and to interpret them in terms of their process significance. In making the survey, it became obvious that several methods have been used to calculate actual or expected solvent exposures, and depending upon process conditions, the methods give widely divergent values for the dose received in a particular process. A second purpose of this report, therefore, is to propose that a uniform method be used to calculate solvent exposure levels. These methods of calculation will be discussed relative to exposures in actual or proposed flow-sheets.

Surveys of the literature describing diluent stability studies and solvent cleanup procedures, including distillation, have been reported previously.<sup>3,4</sup>

The report concludes with discussions of the behavior of radioiodine in processing by solvent extraction and of the small, but significant, contribution that the alpha radiation from plutonium can make to the degradation of the pregnant organic extract. Additional studies are needed in each of these areas.

## 2. DIFFICULTIES IN EXTRAPOLATING SOLVENT STABILITY DATA FOUND IN THE LITERATURE TO ACTUAL FAST-REACTOR FUEL PROCESSING CONDITIONS

It is difficult, and frequently misleading, to use some of the existing solvent stability data to predict solvent performance in fast-reactor fuel processing. This statement is best justified by a discussion of the numbers most often quoted. Many of these appear in a summary paper that was presented by Cooper and Walling<sup>14</sup> at the Second Geneva Conference. Data in one of the tables appearing in a section of the paper, which was entitled "Process Implications of Solvent Radiolysis," are reproduced in Table 1. A column has been added to identify the individual entries.

Table 1. Some Often-Cited Solvent Irradiation Data<sup>a</sup>

Entry	Solvent Exposure ( $\beta$ -whr/liter)	Observed Effect
1	0.01	None
2	0.5	Twofold decrease in Ru decontamination factor (Thorex)
3	4.3	Twofold decrease in TBP-25 process decontamination factor; significant Pu loss
4	5-10	Severe emulsions in Thorex
5	18	Significant U loss
6	24	25-fold decrease in TBP-25 process decontamination factor

<sup>a</sup>See ref. 14.

This table, which was prepared at ORNL for inclusion in the paper by Cooper and Walling (discussed above), is based exclusively on ORNL data. Since the necessary qualifying data could not be included in the paper, because of its brevity, one must study the original references in order to fit the data into the present study with proper perspective. With the exception of entry 4, all entries were the results of laboratory tests, and all exposures, except those in entries 1 and 4, were obtained by irradiation by a  $^{60}\text{Co}$  gamma-ray source. The exposures were, therefore, achieved by the absorption of gamma energy or beta- and gamma-ray energy (as in entry 4), and were not due to beta energy alone as indicated in the table. It should also be emphasized that, while the table implies that radiation was the only variable in the degradation of the solvent, changes also occurred in other variables in the system; these changes contributed to the chemical degradation of TBP and the diluents.

Entry 1. This is probably not the result of a specific test; instead it is based on numerous observations made in the laboratory with TBP-Purex systems.

Entry 2. A 1.5 M TBP--naphtha\* solution was irradiated by a  $^{60}\text{Co}$  source while being stirred with a simulated Thorex dissolver solution.<sup>15</sup> The irradiated solvent was then used without additional treatment in a countercurrent test of extraction of uranium from a simulated Thorex feed. The decontamination of uranium from ruthenium was decreased to one-half that obtained with virgin solvent, but the zirconium-niobium decontamination factor was unimpaired. Poor decontamination from ruthenium has been related to the chemistry of TBP

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\* A term used to describe a refined petroleum product. The composition varies with the geographic source and with the vendor, but is usually high in branched chain and cyclic paraffins and low in aromatic and unsaturated hydrocarbons. In early testing the diluents used were not well characterized. Products associated with the tests are generally termed mineral spirits, odorless kerosene, and white oils. The trade names of typical commercial products are: Amsco 125-82 and 125-15 (American Mineral Spirits Co.), Ultrascene (Atlantic Refining Co.), and Shell E-2342 (Shell Oil Co.).

degradation products,<sup>3,4</sup> and if the exposed solvent had been washed with an alkaline solution prior to the test, the decontamination probably would have been improved. In addition, the ruthenium in this test may not have been typical of that in an actual Thorex feed. This test, however, more closely approximates conditions that could exist during fast-reactor fuel processing than the other tests listed.

Entry 3. In this test,<sup>16</sup> a 1.5 M TBP--naphtha solution was equilibrated with 2 to 3 M HNO<sub>3</sub>, and then the organic phase was irradiated in a <sup>60</sup>Co source. After being irradiated, the solvent was used in a countercurrent test to extract uranium from a UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>-HNO<sub>3</sub> feed solution that had been "spiked" with plutonium and fission product radionuclides. The overall factor for the decontamination of uranium from fission products was only one-half that obtained with virgin solvent, and 0.3% of the extracted plutonium (and 0.02% of the uranium) remained in the solvent after stripping with water. Additional laboratory studies, which are mentioned in the text of the paper, describe the <sup>60</sup>Co irradiation of the TBP-diluent system to an exposure level of greater than 300 whr/liter while the system was in contact, but not stirred, with Thorex dissolver solution. The irradiated solvent, after alkaline and acid washes, was indistinguishable from fresh solvent in subsequent extraction and stripping tests.

Entry 4. Entry 4 represents the only actual process data included in the table. The results were obtained at ORNL during the recovery of thorium and uranium in the short-cooled Thorex runs. The calculations were based on assumptions that were intended to give maximum credible exposure, and the calculated doses are now considered to be much higher than those actually received. A more-precise calculation was later made by Davis,<sup>9</sup> who showed that the organic phase (1.5 M TBP--Amsco 125-82) received an exposure of ~ 0.12 whr/liter on each pass through the extraction column and an accumulated dose of only 0.2 to 0.3 whr/liter during each run. The reason for the severe emulsion and precipitate formation is not known. This test serves as an excellent demonstration of the necessity of correlating radiation and

and chemical effects in order to accurately interpret the results. Operational difficulties, which were, at first, unrelated to solvent stability, caused intermittent process shutdowns that allowed contact of the aqueous and organic phases (at one time for 5.5 hr). Although the radiation dose was increased during these periods, the opportunity also existed for chemical attack; thus the relative effects cannot be assessed. Additionally, some organic phase that was entrained in the aqueous first-cycle raffinate was known to have been degraded in the intercycle evaporator used to prepare feed for the second cycle. Consequently, degradation products could have been acquired by the second-cycle solvent phase, which was recycled without treatment to the first-cycle extraction column. All of these factors greatly increased the degree of degradation, and the resulting emulsions impaired phase separation and increased the deposition of solids. The Thorex runs, although significant as the first successful demonstration of very-high-level radiochemical processing by solvent extraction, were not adequate for determining processing exposure limits for the solvent phase.

Entry 5. In this test, dry 0.7 M TBP--Amsco 125-82 solution was irradiated by a  $^{60}\text{Co}$  source.<sup>17</sup> The irradiated solvent was equilibrated with an equal volume of 3 M  $\text{HNO}_3$  containing 0.17 M  $\text{UO}_2(\text{NO}_3)_2$ . The extract was stripped several times with water. Uranium (0.2%) was retained by the organic phase. However, in a similar test when dry solvent, which had been irradiated to 35 whr/liter, was scrubbed with sodium carbonate solution, essentially no uranium retention was observed.

These tests, of course, do not provide an opportunity for chemical reaction of the organic phase with the aqueous acid feeds and, therefore, should not be compared without qualification with entries 1-4.

Entry 6. Again, a dry TBP-naphtha solution was irradiated by a  $^{60}\text{Co}$  source.<sup>14</sup> The irradiated material was used in a countercurrent extraction test identical to that used for testing the solvent discussed in entry 3. Interestingly, in another test in this same series,<sup>14</sup> a solvent that contained water and nitric acid and had been irradiated

to 30 whr/liter gave a uranium-fission product decontamination factor that was only one-ninth of that obtained with virgin solvent.

The descriptions given above emphasize that the data of Table 1 are of limited value for estimating the effect of solvent radiation damage on process performance. Nevertheless, it can be concluded that, at solvent exposures on the order of 0.5 whr per liter per pass, some loss in decontamination from fission products can be expected; there is evidence, however, that adequate solvent wash systems in the cycle will limit the cumulative effect. In addition, a severalfold decrease in the decontamination factor should not be considered a serious disadvantage in fast-reactor fuel reprocessing, assuming that fuel refabrication will be done largely by remote means.

The data just discussed have been quoted widely. The entire table was included in a report issued by workers at Karlsruhe.<sup>18</sup> Entry 2 and associated tests were discussed by Bruce,<sup>19</sup> by Nicholson,<sup>1</sup> and by Levensen, Tvie, and Mecham.<sup>20</sup> The data have also appeared in publications by Goode<sup>21,22</sup> and Cathers.<sup>16</sup> Workers at the Japanese Atomic Energy Research Institute have cited<sup>23</sup> many of these tests.

Additional laboratory studies have been made by Rigg and Wild<sup>24-26</sup> at Windscale and by Isihara, Tsujino, and Yamamoto at JAERI.<sup>23</sup> In the Windscale tests, 0.75 M TBP--kerosene was equilibrated with 0.25 volume of 3 M HNO<sub>3</sub>, and samples of the separated organic phase were irradiated with fast electrons. The irradiated samples were then contacted with an equal volume of either 0.002 M U(VI) or 0.0014 M Pu(IV) in 3 M HNO<sub>3</sub>. Fission product radionuclides were added to the uranium solution in one test series. Each extract was stripped several times with two volumes of 0.001 M HNO<sub>3</sub>. No retention of uranium in the organic phase was observed at radiation levels below about 7 whr/liter. A plutonium retention of about 10 ppm was evident at an exposure level of 0.7 whr/liter, and the retention increased to 275 ppm at 18 whr/liter. The report describes the precipitation of plutonium at exposure levels higher than 18 whr/liter, but it is not clear whether the precipitation occurred during the extraction or the stripping step. When the solvent dose was 0.7 whr/liter, the retention of fission products by the stripped solvent was higher, by a

factor of 3, than that by virgin solvent. Each of these effects was duplicated by adding dibutyl phosphate and monobutyl phosphate (DBP:MBP mole ratio = 12) to unirradiated solvent, the amount added being in accordance with a radiation yield of  $1.8 \times 10^{-4}$  mole of DBP per liter (40 ppm) for each whr/liter ( $G_{\text{DBP}} = 0.5$ ). As indicated earlier in the present report, if the irradiated solvent had been washed with an alkaline solution prior to use in extraction tests, the levels of retention of heavy metals by the organic phase would undoubtedly have been much lower. These tests are particularly pertinent to process application since the retention of plutonium was small at radiation dose levels that exceed those anticipated for each cycle of the organic phase in fast-reactor fuel reprocessing schemes (see next section) and since the plant would be equipped with efficient alkaline wash systems.

In the JAERI tests, dry 1.1 M TBP--kerosene solutions were irradiated by a  $^{60}\text{Co}$  source. Exposure levels<sup>23</sup> reportedly ranged from 0.05 to 500 whr/liter. The irradiated solvents were then shaken with equal volumes of aqueous phases containing fission products. Extraction coefficients were calculated for fission product extraction, and correlations were made with DBP and MBP concentrations. Because of the absence of water and nitric acid during the degradation, the results are of limited use for predicting effects of solvent irradiation on process performance.

In summary, the irradiated organic phases used in the laboratory tests described in this section were prepared by three different methods:

1. Irradiation of dry solvent.
2. Irradiation of solvent that had been prescrubbed with nitric acid. Typically, if 1 M TBP--Amsco 125-82 solution is scrubbed with 2 M  $\text{HNO}_3$ , the nitric acid concentration in the organic phase is 0.4 M.
3. Irradiation of a two-phase system that was representative of an actual process, but without a high radionuclide concentration.

The radiation fields were provided by either  $^{60}\text{Co}$  or fast-electron sources. The irradiated organic phases were used in batch and countercurrent extraction tests. The poor performance in extraction tests (retention, precipitation, emulsion formation) has been ascribed to the accumulation of TBP degradation products (the degraded phases were never washed to remove

these degradation products). Since most of the exposures received by the organic phase were larger than those expected in a single cycle of fast-reactor fuel processing, the data are not useful for predicting solvent irradiation damage effects in an actual system. In addition to the possibility of causing secondary radiation effects, a "one-shot" exposure eliminates possible ameliorating effects, which may occur each time the solvent passes through the normal extraction-scrub-strip-cleanup cycle while accumulating the same dose in a continuous process. Only one actual process result, that for the short-cooled Thorex run at ORNL, is included. In this case, the particular conditions of the test make the interpretation of the solvent behavior difficult.

Finally, none of the studies described in this section considers the stability of the diluent and the effects of degradation products of the diluent upon the extraction process. In all the tests, kerosenes and "naphthas," as typified by Amsco 125-82 and "odorless" kerosene, were used. These diluents, relatively extensively branched and cyclic paraffins, were considered to be essentially inert during most of these experiments. The fallacy of this opinion has now been established, and the more-stable normal paraffins are favored for process use. It appears likely that some of the test results with acidified organic phases, particularly those obtained at the high irradiation dose levels, were appreciably influenced by the presence of degradation products of the diluent as well as by degradation products of TBP. Thus the extrapolation of test results, obtained by using these diluents, to the much more stable TBP--n-dodecane system, which will probably be used in processing fast-reactor fuel solutions, is complicated by an additional difficulty.

### 3. CALCULATION OF RADIATION EXPOSURES RECEIVED BY THE SOLVENT PHASE

Estimates of process solvent exposures have frequently been made by calculating the power density (watts/liter) of an aqueous feed solution and multiplying this value by the time (in hours) that the organic phase remains in the high-radiation-level extraction equipment. Several authors<sup>1,2,26</sup> have realized the necessity for refining the calculations

in order to evaluate the solvent exposures properly. In particular, Davis made a detailed calculation<sup>9</sup> of the exposure received by the solvent phase during the short-decay Thorex runs at ORNL. A composite of the features of several of the calculation methods is presented below as a recommended procedure for estimating solvent exposure, first, in the portion of the equipment where the active feed and the organic phase are mixed and, second, in the regions where the two phases disengage.

### 3.1 Exposure During Mixing

The procedure involves calculating the radiation power density in the mixer (or extraction column) and multiplying it by the time that the organic phase remains in the extraction zone. The steps are as follows:

1. Obtain the average beta and gamma power densities in the discharged reactor core and blanket (in watts per kilogram of initial heavy element). Accurate fission product yields from fast fission have not been established; however, several methods of approximating them are cited by Jones.<sup>2</sup> Nicholson<sup>1</sup> used calculations resulting from a computer code that had been prepared previously by Arnold<sup>27</sup> for use in calculating  $^{235}\text{U}$  fission yields.\* Tables 2 and 3 show the fission product activities as functions of burnup, specific power, and decay time for the core and the blanket. Alpha irradiation is not included in these calculations since the effect in the extraction system is small, compared with that from beta and gamma irradiation. Alpha irradiation is discussed further in Sect. 5.
2. Calculate the beta and gamma power densities in the aqueous feed solution. These depend upon the densities calculated above, the burnup of the heavy metals originally present, the proportion of

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\*The code was adjusted to compensate for some of the differences in uranium and plutonium fission yields. It is estimated that the data in Tables 1 and 2 are very nearly correct for fast-reactor fuels after a short cooling period and that the error in the data for long-term cooling is less than 10%.

Table 2. Fission Product Activities<sup>a</sup> in Reactor Cores as a Function of Decay Time, Specific Power Density, and Burnup

Decay Time (days)	10	20	30	60	90	120	180
<b>Activities</b>							
<u>(watts/kg fuel)</u>							
		100 kw/kg;	50,000 Mwd/metric ton		FBR Core		
Gamma	124.8	90.51	70.88	43.46	31.22	23.67	14.53
Beta	89.12	71.15	61.32	45.46	36.92	31.19	23.62
Total	214.0	161.7	132.2	88.92	68.15	54.86	38.15
		200 kw/kg;	50,000 Mwd/metric ton		FBR Core		
Gamma	236.6	168.9	130.4	77.68	54.81	40.94	24.37
Beta	154.2	119.2	100.4	70.99	55.90	46.16	33.78
Total	390.8	288.1	230.8	148.7	110.7	87.11	58.15
		400 kw/kg;	50,000 Mwd/metric ton		FBR Core		
Gamma	420.1	289.3	216.5	121.3	83.06	61.05	35.57
Beta	253.3	186.5	151.7	100.2	75.68	60.75	42.85
Total	673.4	475.7	368.3	221.5	158.7	121.8	78.41
		100 kw/kg;	100,000 Mwd/metric ton		FBR Core		
Gamma	127.4	92.98	73.28	45.67	33.27	25.57	16.19
Beta	97.58	79.42	69.39	53.00	43.99	37.83	29.50
Total	225.0	172.4	142.7	98.68	77.26	63.40	45.70
		200 kw/kg;	100,000 Mwd/metric ton		FBR Core		
Gamma	249.7	181.0	141.8	86.92	62.45	47.34	29.06
Beta	178.2	142.3	122.6	90.92	73.84	62.39	47.23
Total	427.9	323.3	264.4	177.8	136.3	109.7	76.29
		400 kw/kg;	100,000 Mwd/metric ton		FBR Core		
Gamma	473.2	337.7	260.9	155.4	109.6	81.89	48.74
Beta	308.5	238.4	200.8	142.0	111.8	92.33	67.56
Total	781.7	576.1	461.7	297.3	221.4	174.2	116.3
		15.45 kw/kg;	20,000 Mwd/metric ton		LWR Core		
Gamma	19.78	14.46	11.42	7.151	5.232	4.039	2.585
Beta	15.43	12.62	11.07	8.520	7.115	6.151	4.844
Total	35.21	27.09	22.49	15.67	12.35	10.19	7.429

<sup>a</sup> Calculated by PHOEBE Code (ref. 27).

Table 3. Fission Product Activities<sup>a</sup> in Fast Breeder Reactor Blankets as a Function of Decay Time, Burnup, and Irradiation Time

Decay Time (days)	10	20	30	60	90	120	180
Activities (watts/kg fuel)							
		2000 Mwd/metric ton		250-day Irradiation			
Gamma	9.464	6.754	5.217	3.107	2.192	1.638	0.975
Beta	6.169	4.768	4.016	2.840	2.236	1.847	1.351
Total	15.63	11.52	9.233	5.947	4.428	3.484	2.326
		2000 Mwd/metric ton		500-day Irradiation			
Gamma	4.994	3.620	2.835	1.738	1.249	0.947	0.581
Beta	3.565	2.846	2.453	1.818	1.477	1.248	0.945
Total	8.558	6.466	5.288	3.557	2.726	2.195	1.526
		6600 Mwd/metric ton		250-day Irradiation			
Gamma	31.23	22.29	17.22	10.25	7.235	5.405	3.217
Beta	20.36	15.74	13.25	9.371	7.378	6.094	4.459
Total	51.59	38.03	30.47	19.62	14.61	11.50	7.676
		6600 Mwd/metric ton		500-day Irradiation			
Gamma	16.48	11.95	9.356	5.737	4.122	3.124	1.918
Beta	11.76	9.392	8.094	6.001	4.874	4.118	3.117
Total	28.24	21.34	17.45	11.74	8.995	7.242	5.035

<sup>a</sup>Calculated by PHOEBE Code (ref. 27).

core and blanket in the solution, and the concentration of heavy metals in the solution.

3. 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, and organic-phase volumes in the mixer. Thus, if the ratios 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 the 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.\*
4. 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 completely absorb the beta energy. On the other hand, only a portion of the gamma energy is absorbed; the fraction depends upon the geometry of the

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\*The range of a 0.3-Mev (estimated average energy of beta particles derived from short-cooled fast-reactor fuels) beta particle in water is about 0.75 mm. Very little information has been found to permit a judgment of the aqueous droplet size distribution in any of the mixer types. However, some information is known about the sizes of organic droplets in aqueous continuous systems. Groenier and Ryon<sup>28</sup> established that, in a 2-in.-diam. pulsed column, they ranged from 0.49 to 0.79 mm when the aqueous:organic phase ratio was 50, with pulses at frequencies of from 70 to 50 counts/min and a 1-in. amplitude. The column plates had 23% free area and were spaced at 2-in. intervals. The aqueous feed was 4 M in NaNO<sub>3</sub> and 0.004 M in uranium; the organic phase was 30% TBP in Amsco 125-82. Vanderveen<sup>29</sup> measured the diameters of organic droplets in several systems within a mixer as a function of the distance from the impeller tip. Under some of the experimental conditions, these diameters were less than 0.5 mm in diisobutylcarbinol-water, cyclohexanone-water, and methylisobutyl-ketone-water systems; however, larger droplets were found when mixing was only slightly less efficient. Woods<sup>30</sup> reports that the droplet diameter is less than 0.1 mm in the stacked-clone contactor<sup>31</sup> that is being developed at ORNL for fast contact and quick separation of aqueous and organic phases.

system. For example, Nicholson<sup>1</sup> assumed 40% absorption in a 10-in.-diam pulsed column.

5. 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:

$$E_m = T_m \left( D_\beta + GD_\gamma \right) P ,$$

where  $E_m$  = exposure of organic phase during mixing (whr/liter)

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

$D_\beta$  = beta power density in aqueous feed (watts/liter)

$D_\gamma$  = gamma power density in aqueous feed (watts/liter)

$G$  = fraction of gamma radiation absorbed in mixer .4

$P$  = 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. Some of the sources of difficulty are listed below:

1. Some drop sizes are larger, particularly in pulsed columns, than the size which permits the assumption of a uniform beta field to be a good approximation.
2. Coalescence at plates in the column is not considered.
3. No correction is made for differences in the coefficients for absorption of radiation energy by the organic and aqueous phases.
4. Beta and gamma power densities in the discharged fuel, as listed in Tables 1 and 2, are approximations since the fission yields are not known precisely and since no corrections have been made for the loss of rare gases or iodine from short-cooled fuel either prior to, or during, dissolution, or for possible incomplete dissolution of the fission products.
5. Values for the factor  $G$  in the equation are difficult to determine. It should be pointed out that corrections for items 1-4 will tend to give smaller values for the calculated radiation doses. Refinements can, and probably will, be made to incorporate these effects, but the actual exposures will still be subject to the

effects of periods of atypical operation of the extraction equipment.

6. The radiation density in the extractor will be higher than that calculated should reflux of radionuclides, e.g., rare earth fission products, occur during the extraction.

The calculation method just described is essentially that used by Jones,<sup>2</sup> Davis,<sup>9</sup> and Nicholson.<sup>1</sup> A variation used by Rigg<sup>26</sup> determines the power density in step 3 by multiplying the power density of the feed by the organic-phase volume fraction in the mixer (rather than by the feed volume fraction); however, this operation is not justified. There is also a tendency to obtain the power density in the mixer by multiplying the power density of the feed by the feed:organic volume ratio. While this does, indeed, give watts per liter of organic phase, the result is meaningless because it completely neglects the concept of power density.

### 3.2 Exposure During Disengagement of Phases

The settler in a mixer-settler unit contains separated organic and aqueous phases and, generally, a dispersion layer that contains both phases in approximately the same proportions that existed in the mixer. The exposure received by the solvent is calculated by multiplying the average power density of the radiation field in which the organic phase exists by the residence time in that field. It is assumed that the radiation exposure received by the emulsion results from both beta and gamma irradiation, but that the exposure received by the separated organic phase is almost entirely due to gamma irradiation from the underlying settled aqueous phase. The following equation incorporates these factors and can be used to give an approximation of the exposure:

$$E_s = T_s \left[ FM_e + D_\gamma RNH \left( \frac{O_s M_s}{V} + \frac{O_e M_e}{Q} \right) \right],$$

where

- $E_s$  = exposure of organic phase during disengagement (whr/liter)
- $T_s$  = residence time of organic phase in settler (hr)
- $F$  = effective power density in emulsion\* (w per liter of emulsion)

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\*The effective power density within the mixer,  $(D_\beta + GD_\gamma)$ , can be used as a first approximation here.  $G$  can be modified to fit the geometry of the emulsion phase.

$D_\gamma$  = gamma power density in aqueous feed (w per liter of feed)

R = flow ratio, aqueous feed: (aqueous feed + scrub)

H = fraction of gamma radiation not absorbed in the settled aqueous phase (like the G factor in the equation on page 17, this is a function of the geometry of the system and the radionuclides involved)

$$N = S_L : S_T$$

(here  $S_L$  = cross-sectional area of the settler and

$S_T$  = total surface area of the settled aqueous phase in the settler)

$O_s, O_e$  = fractions of gamma-ray energy, emerging through the interface, that are absorbed in the settled organic phase (s) and the emulsion (e), respectively. These quantities are obtained from the following expressions (assuming the average gamma-ray energy to be 0.5 Mev):

$$\log (1 - O_e) = - 0.0365 t_e$$

$$\log (1 - O_T) = - 0.0365 (t_e + t_o)$$

$$O_s = O_T - O_e$$

(here

$O_T$  = fraction absorbed by emulsion plus fraction absorbed by settled organic phase

$t_e, t_o$  = thickness (cm) of emulsion layer and organic layer, respectively)

$M_e, M_s$  = fraction of total organic phase (in settler) that is in the emulsion layer or in the settled organic layer

V = settled organic:settled aqueous phase ratio

Q = emulsion:settled aqueous phase ratio

The significance of each of the separate terms within the bracket of the above equation is as follows:

$FM_e$  = contribution to the power density by the beta and gamma radiation originating in the emulsion,

$\frac{D_{\gamma}RNHO_sM_s}{V}$  = contribution to the power density by that portion of the gamma radiation, originating in the aqueous phase, which is absorbed by the settled organic phase,

$\frac{D_{\gamma}RNHO_eMe}{Q}$  = contribution to the power density by that portion of the gamma radiation, originating in the aqueous phase, which is absorbed by the organic molecules within the emulsion.

It is apparent that the contributions from the first and third terms are dependent upon the amount of organic phase within the emulsion layer. If the layer is small with respect to the total volume of organic phase, then their contributions are small.

This equation, like that for calculating the exposure in the mixer, is useful but not exact. The calculation, for example, gives only an average radiation density for the combination of the dispersed and settled organic phases and does not consider the exact time that the individual organic phase molecules reside in either condition. Again, the sizes of the aqueous droplets within the emulsion tend to be larger than the size that permits the assumption of a uniform beta field to provide a good approximation.

Since there is no settled organic phase in the disengagement section of a pulsed column, the terms involving the settled phase will vanish from the equation when it is applied to pulsed-column calculations. It should be pointed out also that, in a pulsed column, some of the gamma radiation from the disengagement section can penetrate or "shine" into the mixing section and that no correction has been made for this in the equation that is used for calculating the radiation density in the mixer. The contribution to the power density of the mixer should be small since only a small fraction of the gamma radiation from the disengagement section is concerned and since the volume of the column in which the radiation is absorbed is much larger than the volume of aqueous phase in the disengagement section.

### 3.3 Compilation of Reported Values for Process Solvent Exposures

Some of the process solvent exposures that have been reported in the literature are shown in Table 4. As stated in the introduction to this

Table 4. Compilation of Reported Values for Process Solvent Exposures

Entry	Reference	Reactor Type	Burnup (Mwd/metric ton)	Cooling Time (days)	Aqueous Feed		Organic-Phase Residence Time (hr)	Reported Solvent Exposure (whr liter <sup>-1</sup> pass <sup>-1</sup> )	
					Metal	Conc. (g/liter)			Radiation Power Density (w/liter)
1	14	Thermal	588	90	U	320	0.0833	0.01 ( $\beta$ only)	
2	10	Fast	2322	83	U	135		1.5 <sup>a</sup>	
3	6	Thermal	3000	100-150	U			0.04	
4	14	Thermal	4000	30	Th	232	17	0.0833	1.3
5	9	Thermal	4000	30	Th	232	10	0.02	0.12
6	14	Thermal	10,000	10	U	320		0.0833	0.48 ( $\beta$ only)
7	14	Thermal	10,000	100	U	320		0.0833	0.27 ( $\beta$ only)
8	1	Fast	38,500 <sup>b</sup>	30	U	65	6	0.66	0.039 <sup>c</sup>
9	1	Fast	38,500 <sup>b</sup>	150	U	65	2	0.66	0.015 <sup>c</sup>
10	1	Fast	38,500 <sup>b</sup>	30	U	65	6	0.099	0.062 <sup>d</sup>
11	1	Fast	38,500 <sup>b</sup>	30	U	65	6	0.0091	0.070 <sup>e</sup>
12	14	Fast	(5% <sup>235</sup> U)	10	U	237		0.0833	1.9 ( $\beta$ only)
13	14	Fast	(5% <sup>235</sup> U)	50	U	237		0.0833	0.57 ( $\beta$ only)
14	2	Fast	85,000	30	U	262	120	0.061	1.7
15	26	Fast		30	U	200	17	1.24	1.1
16	26	Fast		120	U	200	4	1.24	0.29
17	20	Fast		120			4-7	~ 1	<5
18	18	Fast	100,000	100	U	200-300		0.167	3-4

<sup>a</sup>Apparently is the total exposure accumulated during campaign rather than for a single pass.

<sup>b</sup>Average burnup of combined core (110,000 Mwd/ton) and blanket (6000 Mwd/ton).

<sup>c</sup>10-in.-diam extraction column; 13% flooding; organic phase continuous.

<sup>d</sup>4.3-in.-diam extraction column; 75% flooding; organic phase continuous.

<sup>e</sup>4.9-in.-diam extraction column; 75% flooding; aqueous phase continuous.

section, estimates of exposures are frequently made by calculating the power density of the aqueous feed and multiplying it by the residence time of the organic phase in the mixer. Several of the entries in Table 4 are examples of this type of calculation (entries 1, 4, 6, 7, 12, 13, 17, 18). None of these considers either the reduced power density in the mixer (arising from occupation of part of the mixer volume by the organic phase) or the exposure that is incurred during the disengagement of phases. Only entries 2, 3, and 5 present actual process data (i.e., those from processing fuel in the Dounreay Fast Reactor, the Windscale New Separation Plants, and the ORNL short-cooled Thorex runs). Entries 8-11 and 14-16 are results of detailed calculations that consider exposures in both the mixing and the settling operations in proposed fast-reactor processing schemes.

The importance of making a detailed calculation is demonstrated by the data of entries 4 and 5, which represent two values for the same process. The second, more-detailed calculation by Davis<sup>9</sup> shows that the actual Thorex solvent exposure was only one-tenth of that indicated by the product of the power density of the feed and the residence time of the organic phase in the extraction column.

Nicholson<sup>1</sup> gives an interesting comparison of calculated exposures (entries 10 and 11) during organic-phase-continuous and aqueous-phase-continuous operations under comparable conditions. The calculation is part of a preliminary investigation of fast-reactor-fuel processing in the Nuclear Fuel Services Plant. The spent fuel consisted of uranium and plutonium oxides that had been irradiated to an average burnup of 38,500 Mwd/metric ton (110,000 Mwd/metric ton for the core, 6600 Mwd/ton for the blanket) and cooled for 30 days. The solvent extraction flowsheet was based on the use of 15% TBP and feeds of subcritical concentration (75 g of fuel per liter) in pulsed columns. The exposures of the solvent during organic-phase-continuous and aqueous-phase-continuous operations in the pulsed columns are nearly equal ( $\sim 0.07$  whr/liter) because, in the first case, although the effective power density is very low, the residence time of the organic phase is high. The situation is reversed when the aqueous phase is continuous. The exposures will increase if the concentration of

heavy metals in the feed is increased (higher by a factor of about 3 at a concentration of about 250 g/liter), and if the average burnup of the fuel is increased (higher by a factor of 2.9 when the burnup is 110,000 Mwd/ton), but will decrease if the cooling time is extended (by a factor of about 1.4 if the cooling period is 60 instead of 30 days.) The exposures could be further reduced if fast contactors<sup>31</sup> could be used; therefore, it may be possible to treat even more active feeds than those cited in Table 4.

#### 4. BEHAVIOR OF IODINE IN THE PROCESSING OF SHORT-COOLED FUELS BY SOLVENT EXTRACTION

The 8-day half-life of  $^{131}\text{I}$  is short enough to ensure nearly complete decay of this isotope in fuels that have been allowed to cool for more than 100 days before processing. At 120 days, for example, only 0.0033% of the  $^{131}\text{I}$  present in the fuel at discharge remains. Since most of the fuels processed to date have been cooled for at least this long, it is difficult to use the process data to predict, quantitatively, the role of iodine in processing short-cooled fuels by solvent extraction.

Significant concentrations of iodine did remain, however, in the short-decayed thorium fuel processed at ORNL in 1959<sup>32</sup> and in the 88-day-cooled fast-reactor fuel processed at Dounreay<sup>10</sup> in 1965. In the Thorex runs, from 30 to 60% of the iodine volatilized from the dissolver when aluminum-clad thorium metal fuel was dissolved in 11.7 M  $\text{HNO}_3$  that was 1.9 M in Al, 1.9 M in F, and 0.12 M in Hg. When 0.01 M KI was added continuously (1 liter for each 9 liters of dissolver solution) during the dissolution, 90 to 95% of the radioiodine volatilized. Sodium bisulfite was added to the solution that was fed to the solvent extraction column (0.005 mole for each liter of feed) to improve the ruthenium decontamination factor; in addition, it may have reduced some of the free iodine to iodide ion. Sodium bisulfite was also added to the scrub section of the extraction column. The decontamination factor for iodine through the extraction system was greater than  $10^7$ , and the iodine radioactivity of the organic phase was less than 10% of the total activity of that phase. Workers at Dounreay found that 95% of the iodine contained in their 88-day-cooled uranium-molybdenum alloy fuel volatilized during the uranium dissolution step. About one-half of

the remaining iodine was extracted by the solvent and was retained by the organic phase after scrubbing, stripping, and washing. Reportedly, the iodine in the organic phase was largely elemental (presumably dissolved in the solvent phase without actually forming iodides, etc.) and the level of iodine retention had little effect on the radiation dose received by the solvent or on the process as a whole. Although the iodine concentration was not specified, an average of less than 0.5 curie of  $^{131}\text{I}$  was extracted each day. When the solvent was saturated with stable iodine prior to use, the rate of buildup of active iodine was decreased. Although not stated, it is assumed that the iodine concentration eventually approached a level consistent with that in the previous tests.

A complete evaluation of the role of radioiodine in chemical processing would require further study of the following:

- (1) the identity, quantities, and distribution of the iodine species within the spent fuel,
- (2) methods for achieving volatilization of iodine from the dissolver solution and for removing the iodine from the off-gases,
- (3) methods for retaining the iodine species in the aqueous dissolver solution,
- (4) the identity and distribution of the iodine species in the solvent extraction feed,
- (5) the mechanism by which iodine is extracted, including the identification of organic iodine compounds, if found, and determination of their effects on the extraction process,
- (6) methods for removing extracted iodine from the organic phase.

A few comments that are pertinent to ORNL studies recently initiated in these areas are given below:

1. Arnold<sup>33</sup> has made a preliminary estimate of the activity due to  $^{131}\text{I}$  in discharged core--axial-blanket mixtures of fast-breeder oxide fuel. For a reactor whose midcycle power in the core is 167 kw/kg and whose specific power in the blanket region during the last 30 days (before discharge of the fuel) is twice its midcycle value (about 15 kw/kg), the average  $^{131}\text{I}$  activity of the core-blanket mixture on discharge, would be

about 3870 curies/kg. Cooling for 30 days reduces this activity level to about 300 curies, or 2.4 mg of  $^{131}\text{I}$  per kg of fuel (U + Pu + fission products). Assuming that no volatilization of iodine occurs during dissolution, a solvent extraction feed containing 100 g of heavy metals per liter could have an  $^{131}\text{I}$  concentration of  $2 \times 10^{-6}$  M. Other iodine isotopes (almost entirely  $1.7 \times 10^7$ -y  $^{129}\text{I}$ ) would bring the total iodine concentration in this solution to about  $7 \times 10^{-4}$  M.

2. The decay of fission product  $^{132}\text{Te}$  (half life, 3.3 d) also yields an active iodine isotope, 2.3-hr  $^{132}\text{I}$ . After 30 days the radioactivity contributed by the  $^{132}\text{Te}$  isotope is still 3 to 4% of that contributed by the  $^{131}\text{I}$  remaining in the fuel. Thus, even if all the  $^{131}\text{I}$  were volatilized during the dissolution, there would be about 10 curies of  $^{132}\text{I}$  per kg of fuel within 10 hr after the dissolution.

3. Iodide ion was oxidized readily to elemental iodine in 2 to 3 M  $\text{HNO}_3$ , particularly when no attempt was made to decrease the nitrous acid concentration. Sparging the solution with air, in effect, reduced the  $\text{HNO}_2$  content, and the rate of oxidation was decreased. When the aqueous phase was shaken with an extractant phase (e.g., 1 M TBP in *n*-dodecane), the oxidation took place very rapidly and all of the iodine was extracted. The ease of extraction of both iodine and nitrous acid by the TBP are probably important factors in this increased rate of oxidation. Addition of a holding reductant, sodium thiosulfate, prevented oxidation of the  $\text{I}^-$  to  $\text{I}_2$  in 3 M  $\text{HNO}_3$ , but no organic phase was present in the latter test.

4. No iodate or periodate ions were detected in the 2 to 3 M  $\text{HNO}_3$  solutions described above. Traces were found, however, in 12 M  $\text{HNO}_3$  that had been in contact with solid iodine for 16 hr at room temperature; the amount would probably have increased if the temperature had been increased. Depending upon the type of reactor fuel and the conditions of its dissolution, some  $\text{IO}_3^-$  and/or  $\text{IO}_4^-$  may be present in the dissolver solution. The ready reaction between  $\text{I}^-$  and  $\text{IO}_3^-$  (to give  $\text{I}_2$ ) precludes their simultaneous existence. (It is possible that the increase in iodine volatilization after the addition of KI during the dissolution of Thorex fuel, as mentioned above, was partly due to this reaction. If this is true, the

effectiveness of that treatment would vary with process conditions that affect the  $\text{IO}_3^-$  concentration).

5. Elemental iodine is extracted readily by the TBP-diluent phase. As stated previously, presaturation of the organic phase with nonradioactive iodine in tests at Dounreay delayed the buildup of  $^{131}\text{I}$  in the extract.

6. When a solution of 1  $\text{M}$  TBP in  $n$ -dodecane (which contained 0.3  $\text{M}$   $\text{I}_2$ ) was stirred with 3  $\text{M}$   $\text{HNO}_3$  in a  $^{60}\text{Co}$  gamma radiation field, about 30% of the iodine was combined with the organic molecules, presumably as an alkyl iodide, after a radiation dose of 100 whr/liter had been absorbed by the organic phase. Under these conditions the G value for iodide formation was, therefore, about 3.5. In 1954, Forsyth, Weber, and Schuler<sup>34</sup> reported that  $G = 7$  for the formation of alkyl iodide in  $n$ -heptane solutions containing  $10^{-4}$   $\text{M}$  iodine. Their system excluded oxygen and other reactive species that would decrease the yield. The results obtained at Dounreay<sup>10</sup> should be cited again (i.e., the iodine found in the organic phase was largely elemental).

7. Elemental iodine was readily stripped from the organic phase by scrubbing the solution with dilute aqueous sodium thiosulfate. No tests have been made to find methods for stripping the alkyl iodides; however, these compounds are known to have limited stability in alkaline systems, the stability varying with structure.

Finally, Canva and Pages<sup>35</sup> made an interesting observation with respect to the effect of iodine on TBP degradation. They found that the yield of the acids DBP and MBP increased by a factor of 1.6 when an organic phase that was  $5 \times 10^{-4}$   $\text{M}$  in iodine was irradiated until it had received a dose of 9 whr/liter. The yield increased only slightly with increasing iodine concentrations and decreased at higher radiation dose levels.

## 5. IRRADIATION OF THE SOLVENT BY PLUTONIUM

Plutonium recovered from solutions generated in the processing of fast-reactor fuels will irradiate the extractant phase. The effect will be

more pronounced than that experienced during the processing of fuels from the present plutonium production reactors because fast reactors produce significant amounts of the relatively short-lived (89.6-y)  $^{238}\text{Pu}$ , which is 270 times as alpha-active as  $^{239}\text{Pu}$ . For example, the plutonium recovered from the reactor fuel considered by Nicholson<sup>1</sup> would have the following approximate isotopic power distribution:

<u>Plutonium Isotope</u>	<u>Half Life (y)</u>	<u>at. %</u>	<u>Radiation Density (<math>\alpha</math>-w/g total Pu)</u>
238	89.6	1	$4.9 \times 10^{-3}$
239	$2.44 \times 10^4$	60	$1.1 \times 10^{-3}$
240	$6.6 \times 10^3$	19	$1.3 \times 10^{-3}$
241	13.2	12	$0.01 \times 10^{-3}$
242	$3.8 \times 10^5$	8	<u><math>0.01 \times 10^{-3}</math></u>
Total			$7.3 \times 10^{-3}$

The radiation dose absorbed by the organic phase may be estimated by obtaining the product of the radiation density per gram, the organic-phase plutonium concentration (in g/liter), and the length of time (in hr) that the plutonium remains in the extractant phase. It is assumed that all the radiation is absorbed in the organic phase. In the flowsheet used by Nicholson,<sup>1</sup> the plutonium concentration in the first-cycle organic phase (4.4 g of plutonium per liter) and the estimated total residence time of the solvent (0.3 hr) in the extraction, scrub, and partitioning sections give the following estimated alpha irradiation dose per cycle:

$$(7.4 \times 10^{-3})(4.4)(0.3) = 0.0098 \text{ whr/liter.}$$

Since the plutonium concentration in the second-cycle organic phase is higher (30 g/liter), the alpha exposure will also be higher for an equivalent residence time.

The 0.02-Mev beta particles from  $^{241}\text{Pu}$  can also contribute to the radiation density of the organic phase. The beta radiation power density in the plutonium product described above is  $1.5 \times 10^{-3}$  w/g. Again, it may be assumed that all of this radiation will be absorbed in the organic phase.

The beta radiation dose received from this source, therefore, is equal to about one-fifth of the alpha dose.

The effects of the radiation from plutonium upon the extraction processes have not yet been assessed. Workers at Harwell<sup>10,36</sup> found that it was difficult to strip <sup>238</sup>Pu from TBP solutions when the extract was aged for 24 hr. Specifically, after repeated washes of the extract with 0.25 M HNO<sub>3</sub>, the retention of plutonium by 20% TBP in *n*-dodecane, Solvesso 100, or kerosene increased in the dose range 10<sup>-3</sup> to 100 whr/liter, according to the following expression:

$$\text{Residual Pu (M)} \sim 1.5 \times 10^{-4} \times \text{Dose (whr/liter)}.$$

Interestingly, the yield for the acid degradation products of TBP (i.e., MBP + DBP), follows the expression given below:

$$\text{Yield of (DBP + MBP) (M)} = 3.6 \times 10^{-4} G_{(\text{DBP + MBP})} \times \text{Dose (whr/liter)}.$$

The G value for the formation of DBP + MBP from acidified TBP solutions has been reported to be from 0.2 to 2.2.<sup>24</sup> It is apparent that plutonium retention can be related closely to the formation of DBP and MBP. This correlation was noted previously when the radiation was provided by an external source.<sup>15,24</sup> Further, the tests gave similar results with aromatic (Solvesso-100), or branched and unbranched aliphatic diluents; this indicates that plutonium retention is not dependent on the type or the structure of the diluent.

It is concluded that radiation effects from plutonium will be small compared with those from fission products in the first cycle of extraction from the fuel element solution. However, radiation effects in the second plutonium purification cycle can be significant if the organic phase has a high plutonium concentration and/or the plutonium remains in the organic phase for an appreciable time. Further study is needed in this area.

## 6. ACKNOWLEDGMENT

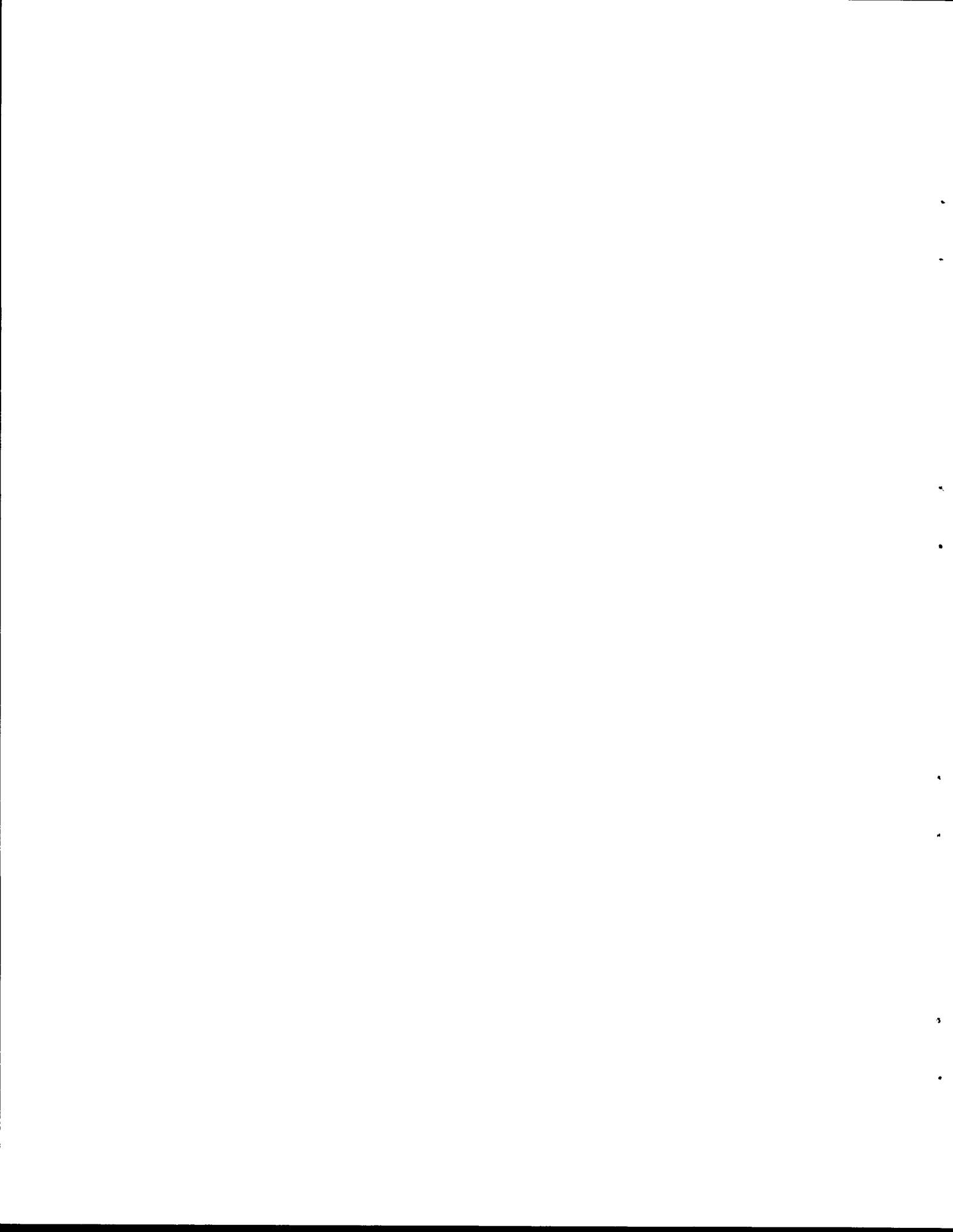
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