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Batch-Equilibrium Hot-Cell Tests of Caustic-Side Solvent Extraction (CSSX) with SRS Simulant Waste and Internal ^{137}Cs Irradiation

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ORNL/TM-2001/49

Chemical Technology Division

BATCH-EQUILIBRIUM HOT-CELL TESTS OF CAUSTIC-SIDE SOLVENT EXTRACTION (CSSX) WITH SRS SIMULANT WASTE AND INTERNAL ^{137}Cs IRRADIATION

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BATCH-EQUILIBRIUM HOT-CELL TESTS OF CAUSTIC-SIDE SOLVENT EXTRACTION (CSSX) WITH SRS SIMULANT WASTE AND INTERNAL ^{137}Cs IRRADIATIQN

ABSTRACT

The solvent was loaded with ^{137}Cs and subsamples were stored on a shaker table while in contact with the extract, scrub, or strip aqueous phases. Evidence of solvent degradation was evaluated at exposure times of 0, 20, 54, and 83 days. This resulted in estimated solvent doses ranging up to 1.24 Mrad, equivalent to the dose expected to be received during 16.5 years of operation at the plant proposed for the Savannah River Site. The break times and distribution of cesium of the batch samples remained constant within experimental error; in addition, no third-phase formation was observed. The solvent concentrations of calix[4]arene-bis-(*tert*-octylbenzo-crown-6) and 1-(2,2,3,3-tetra-fluoroproproxy)-3-(4-*sec*-butylphenoxy)-2-propanol remained constant within experimental error. Solvent degradation with irradiation was evidenced by a decrease in the trioctylamine (TOA) concentration in the solvent and an increase in the solvent concentration of the degradation product 4-*sec*-butylphenol. No decline in extraction or scrubbing performance of the irradiated solvents was observed. The stripping performance of the solvent was seriously impaired with irradiation; however, a mild caustic wash and replenishment of the ,TOA concentration restored the ability to strip the irradiated solvent.

1. INTRODUCTION

Removal of cesium from high-level tank waste, such as that stored at the U.S. Department of Energy (DOE) Savannah River Site (SRS), continues to be a challenging problem. Difficulties with the decomposition of cesium tetraphenylborate precipitate have led to an intensive search for alternative technologies to accomplish the cesium separation. Prior research at the Oak Ridge National Laboratory (ORNL) was directed toward the development of a solvent extraction process that would meet or exceed the process requirements for removal of cesium from SRS high-level waste. The caustic-side solvent extraction (CSSX) process was the result of this research.[1,2]

Before the CSSX process can be used to treat SRS waste, considerable applied development work must be accomplished. Specific requirements for the process include

1. the ability to accept at the rate of -20 gal/min, a feed solution that is
   (a) 5.6 *M* in Na^+ and
   (b) has an average ^{137}Cs activity of 1.42 Ci/gal;
2. the ability to generate a low-level waste stream suitable for solidifying into saltstone that
   (a) contains no more than 45 nCi/g (215 μCi/gal) of ^{137}Cs,
   (b) exhibits a decontamination factor (DF) of -7,000 for the average feed, and
   (c) exhibits a DF of 240,000 for the maximum ^{137}Cs concentration observed in the tanks; and

3. yields a strip effluent containing the separated cesium that is volumetrically concentrated by a factor of approximately 15.

General issues that must be addressed as part of the applied development program include:

1. acquisition of solvent matrix physical data,
2. an understanding of the chemical and radiological stability of the solvent matrix,
3. bench-scale testing of the proposed process flow sheet,
4. commercialization of the supply of the solvent components, and
5. testing of the process flow sheet with actual SRS high-level waste.

The stability of the solvent under the chemical and radiological operating conditions at SRS is not completely understood. Either the degradation of the solvent itself or the buildup of decomposition products could impact the extraction capabilities of the solvent matrix. These degradation products must be identified and may need to be removed from the solvent matrix in order for the process to continue to operate efficiently.

This report presents the results of a study of the effect of internal irradiation on the solvent. A batch of solvent was loaded with ^{137}Cs from a SRS simulant. This loaded solvent was subsequently scrubbed and stripped by single-batch contacting. Subsamples from each process step-Extract, Scrub, and Strip—were stored on a shaker table for an extended period. A set of samples was removed from the shaker table at three different time intervals and evaluated for signs of deterioration or decrease in performance in the solvent. This task was closely linked to another batch test of self-irradiation of the solvent to be conducted at SRS (Work-Scope Matrix element 4.1.1). In the latter task, the solvent will be loaded with ^{137}Cs from samples of actual waste. The data from these two tasks are to be directly comparable, so the two experimental tests were similarly designed. The batch size was larger for the test described in the present report, as the quantity of real-waste sample was limited.

2. BACKGROUND

Cesium-selective solvents are created by combining lipophilic calixarene-crown ethers with alkylphenoxy alcohol-based modifiers in iso-paraffinic diluents.[1–4] According to Bonnesen et al.,[2]

> "The modifiers serve as necessary solvating components and function synergistically with the calixarene-crown ether extractant to greatly increase the extraction strength for cesium. They also enhance the solubility of the extractant and extraction complexes, increasing resistance to third-phase fonnation."

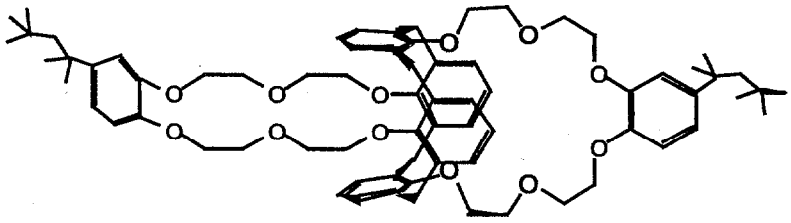
The robust solvent developed for the CSSX process uses the crown ether calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (BOBCalixC6) with the modifier 1-(2,2,3,3-tetrafluoroproproxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB) in the diluent ISOPAR® L. Stripping performance of the solvent was improved by the addition of a lipophilic trialkylamine, making it more tolerant of lipophilic anion impurities in the feed and allowing stripping by dilute nitric acid solutions.[2] Trioctylamine (TOA) was the amine used in the solvent adopted as the standard for the current studies. TOA may also suppress dissociation of nitrate from the loaded solvent, an effect that becomes more important as the cesium is stripped from the solvent by sequential contacts.

Thus, the solvent used in the study reported here consisted of 0.01 A4 BOBCalixC6, 0.5 A4 Cs-7SB, and 0.001 A4 TOA in ISOPAR® L. Figure 1 illustrates the structures of the constituent organic molecules. Table 1 lists the baseline organic/aqueous (O/A) ratios used for this study; included are the volumes used for the irradiation batches. These batch sizes were dictated by the analytical and evaluation needs at the conclusion of the irradiation program.

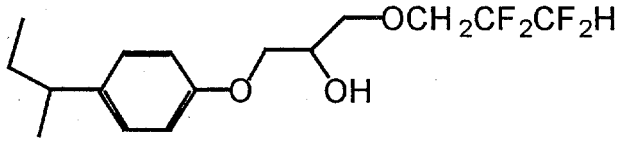
3. EXPERIMENTAL METHODS

3.1 SIMULANT

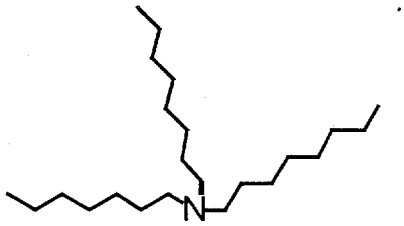
About 125 L of the SRS supemate simulant was prepared in a clean 55-gal stainless steel (SS) drum using the SRS recipe, minus cesium.[5] This recipe targets the average SRS waste diluted to 5.6 *M* sodium as feed for solvent extraction centrifugal contactors. Tables 2 and 3 list the target compositions for this simulant. The 55-gal drum supplied simulant for most of the CSSX tasks at ORNL. The measured density and concentrations of the major constituents of the recipe simulant indicated that it was slightly more concentrated than preferred. Thus, the solution in the drum was diluted to a level closer to the desired values before use. Each volume withdrawn for testing was filtered through 0.5-μm-pore sintered SS. The concentrations in the simulant were measured after filtering. Table 4 lists the concentrations measured for the quantities withdrawn and filtered for the self-irradiation test. Note that no cesium had been added to the simulant at this point and <0.1 mg/L of cesium was measured in the simulant. The filtered simulant, whose composition is listed in Table 4, will be referred to simply as "simulant" throughout the remainder of this document.



Calix[4]arene-bis-(*tert*-octylbenzo-crown-6)
"*BOBCalixC6*"



1-(2,2,3,3-tetrafluoropropoxy)-3-
(4-*sec*-butylphenoxy)-2-propanol
"*Cs-7SB*"



Trioctylamine
"*TOA*"

Fig. 1. Components of CSSX solvent.

Table 1. Baseline O/A ratios and batch volumes for self-irradiation samples

Sample	O/A ratio	Batch volume (mL)		
		Organic	Aqueous	Total
Extract	1/3	35	105	140
Scrub	5	75	15	90
strip	5	75	15	90

Table 2. Target salt composition of the simulated waste solution (simulant)

Component	Concentration (*M*)
Na^+	5.6
K^+	0.015
Cs^+	0.00014
OH^-	2.06
NO_3^-	2.03
NO_2^-	0.5
AlO_2^-	0.28
CO_3^{2-}	0.15
SO_4^{2-}	0.14
Cl^-	0.024
F^-	0.028
PO_4^{3-}	0.007
$C_2O_4^{2-}$	0.008
SiO_3^{2-}	0.03
MoO_4^{2-}	0.000078
NH_3	0.001

Table 3. Target simulant concentrations of potential catalytic metals and trace organics

Component	Concentration (mg/L)
Copper	1.44
Chromium	75
Ruthenium	0.82
Palladium	0.41
Rhodium	0.21
Iron	1.44
Zinc	8
Tin	2.4
Mercury	0.05
Lead	2.1
Silver	0.01
Tri-n-butyl phosphate (TBP)	0.5
Di-n-butyl phosphate (DBP)	25
Mono-n-butyl phosphate (MBP)	25
n-Butanol	2
Formate	1500
Trimethylamine	10

During the preparation of the large batch of recipe simulant, a volume of -10 L was withdrawn and stored after addition of the salts (Table 2) and also after addition of the catalytic metals (Table 3). The first subsample consisted of only the salts specified in the recipe and was designated as the "salts only" (S) simulant. The second subsample consisted of only the salts and metals (lacking only the organic compounds) and was designated as the "salts & metals" (S&M) simulant. Just as with the "full" simulant, each of these simulants required a small dilution (same factor as that for the full simulant) and filtration before use. One extraction batch of each of the two simulants was prepared for both the control and irradiation samples. These four samples were included in the final set of batches at the conclusion of the irradiation program.

Table 4. Concentrations measured in filtered simulant used to prepare irradiation and control samples

	Measured concentration	Target concentration
Major components, A4		
Al(III)	0.25	0.28
K^+	0.021	0.015
Na^+	5.35	5.60
Br^-	< 0.006	0.024
Cl^-	0.019	0.024
F^-	0.029	0.028
NO_3^-	0.6	0.5
NO_3^-	2.23	2.03
PO_4^{3-}	0.008	0.007
SO_4^{2-}	0.15	0.14
Trace metals and organics, mg/L		
Cs	0.076	
Mo	7.9	7.5
Pb	2.4	2.1
Pd	0.14	0.41
Rh	0.16	0.21
Ru	0.64	0.82
Sn	0.6	2.4
Ag	< 0.10	0.01
Ba	0.044	
Be	< 0.002	
Ca	< 0.030	
Cd	< 0.182	
co	< 0.068	
Cr	54	75
cu	1.20	1.44
Fe	2.73	1.44
Mg	0,386	
Mn	0.134	
Ni	< 0.120	
Sb	< 1.86	
Sr	0.016	
Th	0.642	
U	< 0.206	
V	< 0.032	
Zn	7	8
Hg	< 0.05	0.05
Total carbon	3760	2094
Total inorganic carbon	2700	1800
Total organic carbon	1060	294
Density, kg/L	1.264	1.258

3.2 SOURCE OF MATERIALS

The source of the materials used in this study is listed in Table A.1 in Appendix A. The CSST prewashed solvent which consisted of BOBCalixC6, Cs-7SB, TOA, and ISOPAR® L, was supplied by the Chemical and Analytical Sciences Division of ORNL. The prewashing removed traces of 4-*sec*-butylphenol and possibly other impurities. The quality assurance report for the lot of solvent used in this experiment is given in Appendix B.

3.3 TRIPLE-RINSE PROCEDURE

The 55-gal stainless steel (SS) drum was rinsed and cleaned with water, 1 *M* HNO_3, 1 A4 NaOH, deionized water, and pure grain alcohol (PGA). After drying, the recipe amount of deionized water for preparing the large batch of simulant was added. This water was tested to verify its purity and to ensure that it was free of organic contamination after being added to the drum.

Prior to use, all other containers, except the large carboy, were triple rinsed with (1) house distilled water, (2) deionized water, and (3) PGA or acetone (acetone was only used if PGA was unavailable). After this triple-rinsing procedure, the containers were drained and allowed to air dry. The simulant for control batch preparation was added to the large carboy before the triple-rinse procedure was adopted as "standard operating procedure." This carboy was rinsed with distilled and deionized water and allowed to air dry prior to use.

4. PREPARATION OF CONTROL BATCH

The equipment and procedures were designed for batch preparation inside the hot cell. The entire process was validated outside the hot cell during preparation of the control batch, but in exactly the same manner as that intended for the hot cell. A photograph of all the equipment, minus the centrifuge, is illustrated in Fig. 2. Separate vessels were used for extraction, scrubbing, and stripping throughout the project to minimize possible cross-contamination of the aqueous phase.

The control batch was prepared and stored outside the hot cell at room temperature until the equipment was moved into the hot cell and the irradiation samples were prepared. The full simulant was processed in one large batch and then subdivided into individual small lots for storage during irradiation. Before processing the large batch of full simulant, one small extraction batch each of the S and S&M simulants was prepared. To mimic the hot cell preparation as closely as possible, a solution of cold

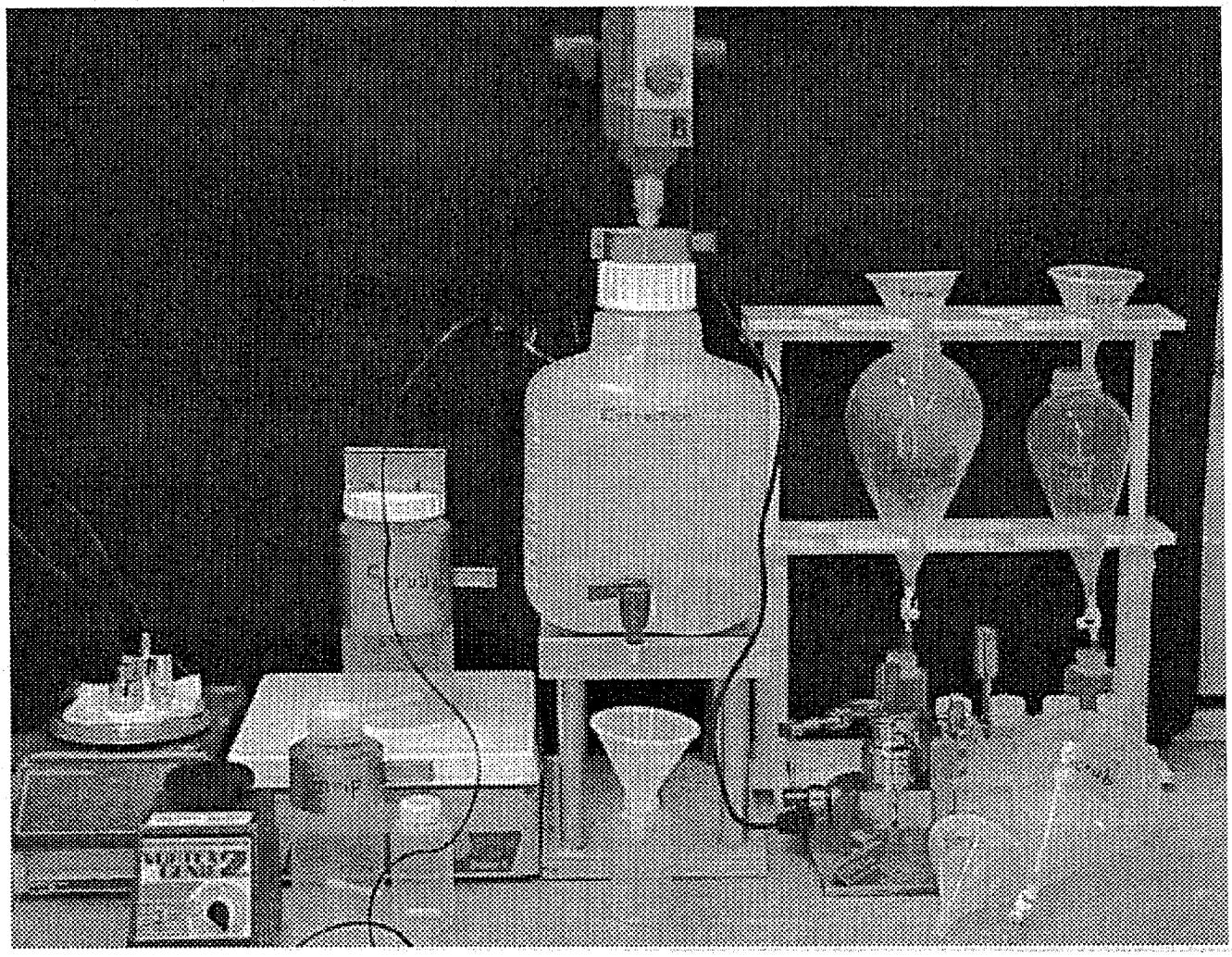


Fig. 2. Photograph of equipment (except the centrifuge) for solvent extraction, scrubbing, and stripping of large batch of simulant.

reagent-grade CsCl was prepared to make simulant concentrations of 0.00014 *M* and a total . mass matching that of the ^{137}CsCl source solution. The small extraction batches were prepared by weighing out the mass needed for one batch size of each simulant, spiking each with the amount needed for 0.00014 *M* cesium and then adding the mass of solvent calculated to result in the desired O/A ratio of 1/3 for extraction. Both batches were dispersed at room temperature to distribute the cesium, sealed inside the SS bottles, and stored in the cold laboratory. The shaker tables were later moved with the control samples to the irradiation hot cell when the processing equipment was moved into the processing hot cell for preparing the irradiation samples. The shaker tables were not started until the irradiation, samples had been prepared and stored on the tables.

Enough simulant was weighed into a large polypropylene carboy to use all of the remaining spike solution and achieve the target cesium solution. The carboy was set on a ring stand with an overhead stirrer for dispersion of the carboy contents. The impeller of the stirrer was inserted through a hole drilled into the carboy lid for this purpose. The carboy was essentially inaccessible for adding the cesium spike once the overhead stirrer had been installed and the carboy lid tightened. Thus, a hole was drilled at the top of the vessel body for insertion of a funnel. Figure 3 is a photograph of the carboy, stirrer, and ring stand on the support platform to raise the spigot level for draining . The spike solution was added through the funnel while stirring the simulant. A small amount of simulant was withheld from the carboy in order to dilute the spike solution prior to pouring through the funnel and to rinse the spike solution container and the funnel in order to minimize any cesium losses (from splashing, wall wetting, etc.).' Table 5 'lists the cesium concentrations after spiking with cold cesium outside the hot cell and with ^{137}Cs inside the hot cell. Solvent was added through the same fimnel. Mixing at high speed dispersed the solvent into the simulant. Dispersing for 45 min ensured that equilibrium distribution of the cesium between the phases was achieved. The break time was measured after the stirrer had been turned off. After the dispersion broke, the organic phase appeared clear and free of the aqueous phase. However, backlighting revealed a fine cloud of microdrops still dispersed throughout the aqueous phase. Both phases appeared clear after standing overnight. The aqueous portion of the batch Extract samples was weighed directly from the carboy through its bottom spigot into the SS bottles used to store the batch samples on the shaker tables. Figure 4 is a photograph of one of these bottles with its Viton® beaded gasket, the sealing clamp, and the special tool fabricated to open and close these bottles inside the hot cell.

After the extracted simulant needed for the Extract batch samples had been subdivided, the remainder of the simulant was removed from the loaded solvent and archived. After as much clean aqueous phase as possible had been drained through the carboy spigot, the remainder was dumped with the organic phase into the Teflon@ FEP Extract separatory funnel (see Fig. 2). After the material in the separatory funnel had been allowed to settle for 15 to 30 min, the last remaining aqueous phase was drained off, the organic phase needed for the batch Extract samples was subdivided, and the remaining organic phase was recovered in the Extract Teflon@ FEP centrifuge bottles. The organic phase was then centrifuged for 5 min at 3000 rpm. Only a few hundredths of a milliliter of aqueous solution was evident in the organic phase after centrifuging. The organic phase was then poured into the Teflon@ bottle used for scrubbing; only a small volume of solvent was retained along with the tiny amount of aqueous solution on the inside shoulder of the centrifuge bottles.

The Scrub bottle was weighed to determine the net mass of solvent recovered. Subsequently, the appropriate amount of Scrub solution was added to the loaded solvent in the Scrub bottle, the bottle was sealed, and the Scrub solution was dispersed in the solvent for 45 min using a Teflon@-coated magnetic

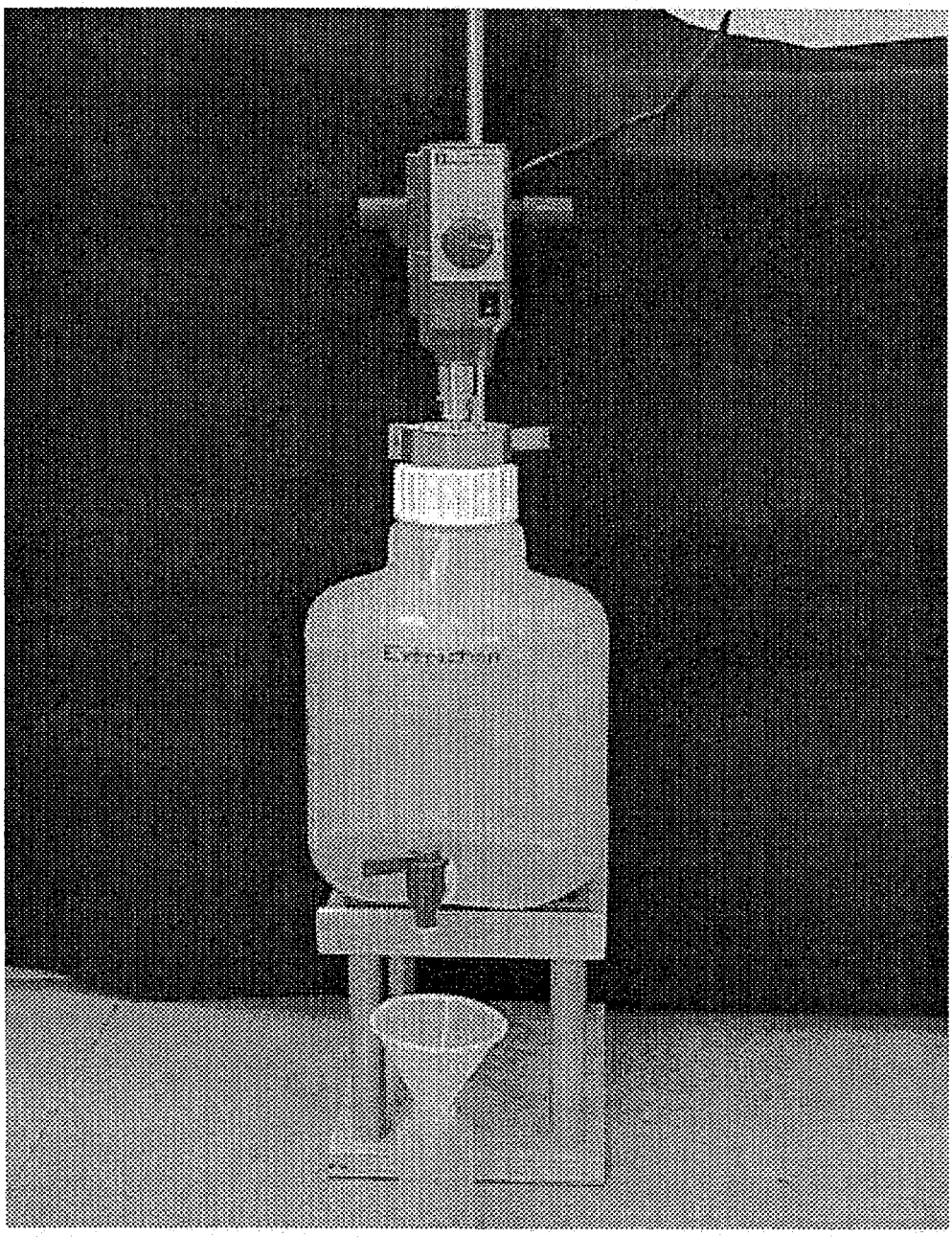


Fig. 3. Photograph of large carboy with overhead stirrer for large batch extraction. The hole that was drilled in the top left shoulder for insertion of a funnel to spike the simulant and add solvent is not visible.

Table 5. Measured cesium concentrations in spiked simulants

Isotope	mg/L	mol/L
ICP-MS results		
Control simulant		
^{133}Cs	17.7	0.00013
Irradiation simulant		
^{133}Cs	13.7	0.00010
^{135}Cs	9.4	0.00007
^{137}Cs	5.2	0.00004
Total cesium	28.3	0.00021
^{137}Cs assay, wt %	18.4[a]	
Calculated activity, Ci/L	0.454	
Gamma spectrometry results		
^{137}Cs activity, Ci/L	0.35 1	
ICP/gamma ratio, %	129	
Calculated ^{137}Cs concentration	4.0	0.00003
Total cesium from assay	21.9	0.00016

[a] ^{137}Cs content of the average waste was 22.6%.

stir bar and magnetic stirrer. The break time was measured after the stirrer had been turned off. Both phases were dumped into the Scrub separatory funnel and allowed to settle overnight. The aqueous portion for each batch of Scrub sample was drained directly from the separatory funnel. The remaining aqueous solution was then separated from the organic phase, the solvent needed for the batch Scrub samples was subdivided, and the remaining solvent was drained into the Scrub centrifuge bottles. The solvent was subsequently centrifuged and recovered using the same procedure described above for extraction. The loaded, scrubbed solvent was recovered in the Teflon@ bottle used for stripping.

The Strip bottle was weighed to determine the net mass of solvent recovered. Subsequently, the appropriate amount of Strip solution was added to the loaded solvent in the Strip bottle, the bottle was sealed, and the Strip solution was dispersed in the solvent for 45 min using a Teflon@-coated magnetic stir bar (a different stir bar from the Scrub) and magnetic stirrer. The break time was measured after the stirrer had been turned off. Both phases were dumped into the Strip separatory funnel and allowed to settle overnight. The aqueous portion for each batch Strip sample was drained directly from the

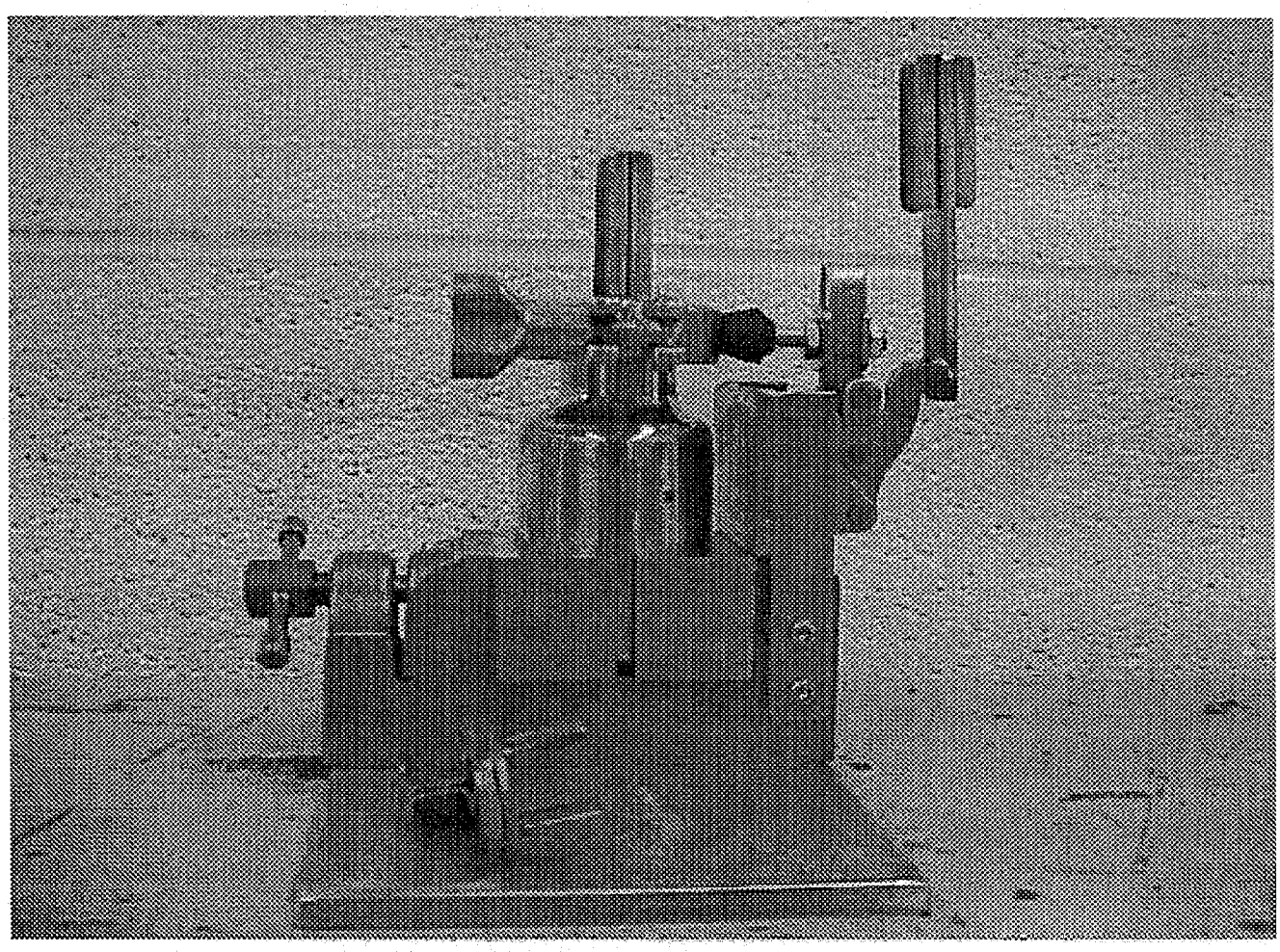


Fig. 4. Photograph of sample stainless steel bottle sealed with its Viton® gasket and clamp held in the special tool modified for opening and closing these bottles in the hot cell. The tool in front is a special wrench that fits the clamp if extra leverage is needed. The sealing gasket is not visible, but is beaded to fit within matching grooves on the sealing surface of the bottle and lid.

separator-y funnel. The remaining aqueous solution was then separated from the organic phase, and the solvent needed for the batch Strip samples was subdivided. The remaining stripped solvent was archived.

Preparation of the control batches is summarized in Table 6. The distribution ratios are consistent with previously measured values for the solvent at room temperature. Note that the estimated outgoing cesium for each process step was within 6% of the estimated incoming cesium-which is well within the reported measurement error of 10%.

Table 6. Preparation of large batch of simulant for subdividing into small control batches

	Cesium conc. (mg/L)	*D*	Temp. (°C)	Mass (g)	Volume[a] (L)	O/A	Total cesium (mg)	Mass balance out/in (%)[b]
				After spiking				
Simulant	17.70			6111	4.942		87.48	
				After extraction				
Simulant	2.53			6108	4.940		12.50	
Solvent	50.12	19.81	23.5	1327	1.602	0.3	80.28	106.1
Small Extraction batches for T_0–T_3 prepared from both phases and remaining solvent used in large batch Scrub.								
				After scrubbing				
Aqueous	29.40			265	0.264		7.76	
Solvent	45.23	1.54	25.3	1094	1.321	5.0	59.74	102.0
Small Scrub batches for T_0–T_3 prepared from both phases and remaining solvent used in large batch Strip.								
				After stripping				
Aqueous	132.00			140	0.140		18.43	
Solvent	18.97	0.14	25.0	580	0.701	5.0	13.29	100.1
Small Strip batches for T_0–T_3 prepared from both phases.								

[a]Calculated from the mass and density corrected for temperature.
[b]Calculated from the measured phase concentrations and the phase quantities.

5. PREPARATION OF IRRADIATION BATCH

The equipment was moved into the hot cell and used to prepare the batch irradiation samples. The same method as described above for the control samples was used except that a ^{137}CsCl source solution rather than a cold CsCl solution was added to spike the simulant. The ^{137}Cs assay for the source was measured at 18.4 wt % by inductively coupled plasma mass spectroscopy (ICP-MS) (see Table 5). The activity level of the simulant was measured to be 0.35 1 Ci/L by gamma spectroscopy (GS). This activity and the assay of 18.4 wt % translate to a cesium concentration of 0.00016 *M*. The control simulant was found to be 0.00013 Min cesium. Table 7 summarizes the data for preparation of the irradiation samples.

About 40% of the loaded solvent was lost when one bottle of loaded solvent was dropped during transfer from the carboy to the Extract separatory funnel. (Teflon® I-L cylindrical bottles were used for this transfer. These bottles were slippery, especially as the manipulator grips became wetted with a little solvent.) When the bottle was held aloft for dumping into the separatory funnel, it just "popped out" of

Table 7. Preparation of large batch of simulant for subdividing into small self-irradiation batches

	^{137}Cs conc. (Ci/L)	*D*	Temp. (°C)	Mass (g)	Volume[a] (L)	O/A	Total activity (Ci)	Mass balance out/in (%)[b]
				After spiking				
Simulant	0.351			6193	4.89		1.72	
				After extracting				
				Before organic loss				
Simulant	0.108			6193	4.887		0.53	
Solvent				1298	0.105	0.324		
				After organic loss				
Simulant	0.097							
Solvent	0.908	9.3	34	770	0.940		0.854	111[c]
Small Extraction batches for T_0–T_3 prepared from both phases and remaining solvent used in large batch Scrub.								
				After scrubbing				
Aqueous	1.189			149.1	0.150		0.178	
Solvent	0.620	0.52	34.3	609.3	0.743	5.0	0.461	95
Small Scrub batches for T_0–T_3 prepared from both phases and remaining solvent used in large batch Strip.								
				After stripping				
Aqueous	2.378			83.4	0.084		0.199	
Solvent	0.104	0.04	34.8	343.4	0.419	5.0	0.044	94
Small Strip batches for T_0–T_3 prepared from both phases.								

[a]Calculated from the mass and density, corrected for temperature.
[b]Calculated from the activity in each of the phases of the large batch before and after processing.
[c]Calculated from the measured phase activities after loss of about 40% of the loaded solvent and from the phase quantities before loss of this solvent.

the manipulators onto its side on the floor, dumping most of the contents. After this loss, transfers were achieved by using rectangular high-density polyethylene (HDPE) bottles. These bottles are handled with much greater ease by the manipulators and are less likely to slip out of the manipulator grips. The solvent remaining in the dropped bottle and the carboy was recovered and weighed. The number of originally planned time intervals was decreased by three to accommodate this loss, with little negative impact since the total maximum irradiation time remained unchanged. The loss compromised our ability to balance the cesium for extraction; however, the outgoing cesium was estimated to be within 11% of that ingoing, using the phase concentrations after the loss, the phase quantities before the loss, and the spiked simulant concentration before extraction. The cesium balance values for the Scrub and Strip were within 6% (well

within the reported measurement error of 10%). The distribution ratios were well below those measured for the control preparation; however, they were consistent with previous values after correction to 25°C.

The SS bottles containing the batch irradiation samples were added to those already on the shaker table located inside the irradiation hot cell. Orbital shaker tables with an orbit of 1 in. were used with a rotation rate of 100 rpm. Prior testing with orbital shaking indicated that adequate dispersion occurred only at about 800 rpm, higher than that achievable by the robust model required for the heavy SS bottles. Although this model is capable of 500 rpm, it was feared that the shaker would not survive very long using a high rotation rate with the heavy load of these SS bottles and samples. Thus, the modest rate of 100 rpm was used to provide some mixing during the self-irradiation period. The dose received by the solvent during irradiation was conservatively estimated for quiescent separation of the two phases in the SS bottles using the volumes listed in Table 1.[6] At 100 rpm, some phase intermixing occurs-albeit not much.

Preparation in the hot cell was slow, and the solvent that had been loaded with ^{137}Cs underwent self-irradiation for some time before all of the SS bottles were finally loaded, sealed, and moved to the shaker tables. Estimates of this dose are listed in Appendix C as 0.18-0.24 Mrad. Nevertheless, the nominal irradiation time started at the time all of the bottles were loaded onto the table and concluded when a given bottle was removed from the table. The annual dose received during plant operation was estimated to be only 0.0917 Mrad.[6] However, significant self-irradiation also occurred between the time of removal of the bottles from the shaker table, when nominal irradiation ceased, and the point when the solvent could be separated from the aqueous solution and stripped of most of its activity for organic analysis and performance evaluation (extra dose of 0.01-0.08 Mrad estimated in Appendix C during sample preparation). Thus, the conservative self-irradiation times used with the estimated dose rates listed in Table 8 resulted in the conservative estimated doses listed in Table 9. Figure 5 summarizes these estimated doses with time for the sample sets. According to the estimates provided in Appendix C, these doses are offset by 0.18-0.24 Mrad to account for the dose received before initiation of the nominal dose. The T_0 samples received a dose of 0.23-0.29 Mrad before they were stripped of most activity. A further dose of 0.01-0.08 Mrad was received before most of the activity was stripped foi the samples in the other time intervals.

6. EVALUATION OF EACH SET OF TIME-INTERVAL SAMPLES

Sets of samples were removed from the shaker table and transferred from the irradiation cell to the processing hot cell after 20, 54, and 83 days. Both irradiation and control samples were processed inside

Table 8. Estimated dose rates to solvent in the stainless steel bottles

Extraction			Scrub			strip		
Organic phase	Aqueous phase	Total	Organic phase	Aqueous phase	Total	Organic phase	Aqueous phase	Total
			Concentration, mCi/L					
908	97		620	1,189		104	2,378	
			Activity, mCi					
32	10		47	18		8	36	
			Dose rate to the organic phase, rad/h					
620	4	624	446	14	460	75	320	395

Table 9. Exposure times and doses for self-irradiation samples

Time interval	Date removed from shaker table[a]	Exposure time (d)	Dose (Mrad)			Number of annual doses		
			Extraction	Scrub	Strip	Extraction	Scrub	Strip
T_0	10/5/00, 11:15 a.m.	0	0	0	0	0.0	0.0	0.0
T_1	10/25/00, 9:24 a.m.	19.92	0.30	0.22	0.19	3.3	2.4	2.1
T_2	11/28/00, 2:30 p.m.	54.14	0.81	0.60	0.51	8.8	6.5	5.6
T_3	12/27/00, 8:20 a.m.	82.88	1.24	0.92	0.79	13.5	10.0	8.6

[a]For T_0, this is the time the bottles were placed on the shaker table. The T_0 samples were never placed on the shaker table.

this hot cell. The irradiation cell in the Radioactive Materials Analytical Laboratory is located behind the bank of hot cells in a less insulated part of the building. Consequently, the temperatures of the shaker table were consistently lower than those of the hot cell and fell below 20°C during part of the irradiation period. This meant that the cesium redistributed in favor of the organic phase upon removal from the' hot cell and while stored on the shaker tables. However, the cesium redistributed in favor of the aqueous phase when transferred into the hot cells, which were typically at 35°C. The T_0 irradiation samples never left the processing hot cell, of course. After the other batch of irradiation'samples had been moved to the shaker tables with their batch control samples, the T_0 control samples were brought into the hot cell and the T_0 set was evaluated. Typically, a time-interval set consisted of six batch samples-both control and

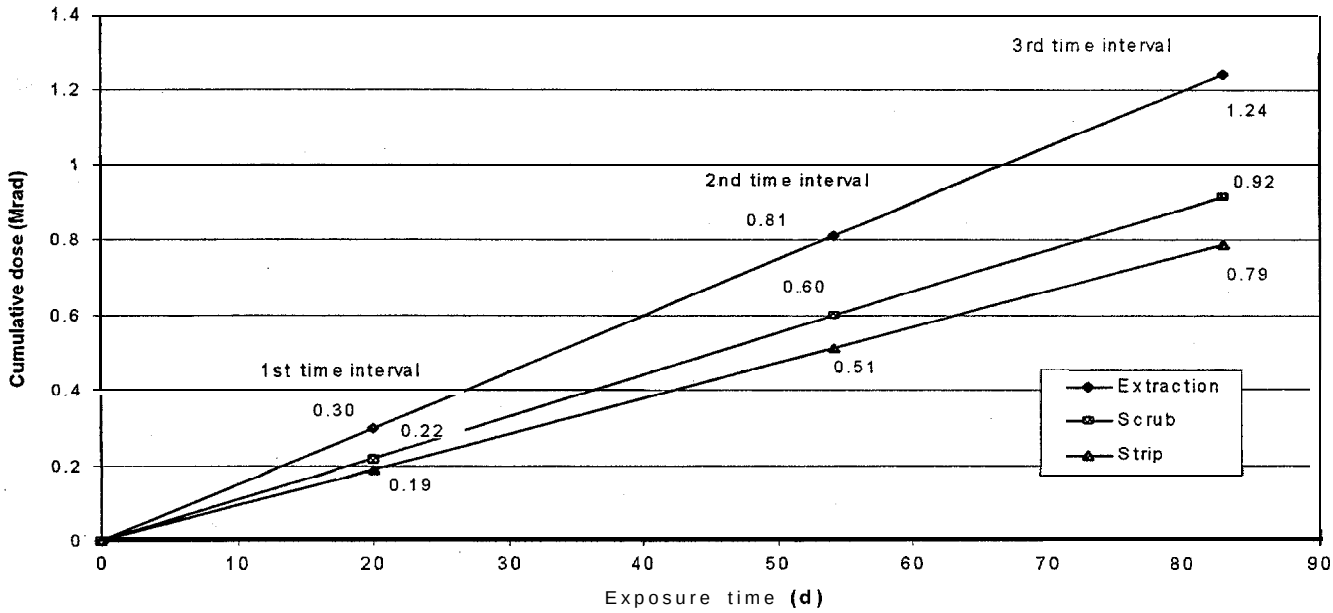


Fig. 5. Calculated dose received by batch self-irradiation samples while on shaker table.

irradiation batches for Extract, Scrub, and Strip (ESS). The last time interval had two sets of extra Extract samples for the S and S&M simulants (a total of four extra batches since both also had controls, giving a total of ten batch samples for the final time interval). In general, the control samples were processed before their corresponding irradiation samples in order to minimize contamination of the control samples. Processing of each time-interval set consisted of the following general procedure:

1. Each SS bottle was opened, and its contents were dumped into its corresponding centrifuge bottle. Six centrifuge bottles were used: one for each of the three processes (Extract, Scrub, and Strip) and two activity levels (control and irradiation).
2. The phase material was dispersed in each centrifuge bottle, in turn, and the break time was measured.
3. Each bottle was centrifuged for 5 min at -3000 rpm and evaluated for third-phase formation.
4. The clean centrifuged phases of the irradiated batches were subsampled for analysis. The technique of subsampling after centrifugation, but before phase separation, led to some sampling errors because the aqueous phase was sampled through the organic phase. In one case, an “aqueous” sample was actually organic phase.
5. The temperature of the liquid was measured using a Teflon PFA-coated Type J thermocouple.

6. Each phase was dumped into the corresponding separatory funnel for the sample and allowed to settle for 15–30 min.
7. Clean aqueous phase was drained into a polypropylene (PP) sample bottle.
8. The interface was purged through the valve and discarded.
9. Clean organic phase was drained into a PP sample bottle for the control sample and into a rectangular 250-mL HDPE bottle for the irradiated sample.
10. The irradiated solvent was stripped of most of its activity in the HDPE bottle by sequential scrub and or strips. Excess aqueous solution was used for this stripping by filling the HDPE bottle containing the irradiated solvent with Scrub or Strip solution. For the Extract samples, one Scrub contact was followed by one Strip contact. For the Scrub and Strip samples, two sequential Strip contacts were performed. For T_3, one extra Strip contact was performed for each of the five irradiated solvents. Sometimes a stable emulsion was formed at the interface during the stripping operation. No stable emulsion was observed during this test for samples at the baseline O/A ratios listed in Table 1, while the activity was stripped from irradiated solvents with a large excess of aqueous solution using a reversed continuous phase.
11. The irradiated subsamples, stripped irradiated organic samples, and both phase samples of the controls were removed from the hot cell and submitted for analysis. The irradiated aqueous-phase samples were archived inside the hot cell. The ^{137}Cs concentration of each phase in the irradiated subsamples was measured by gamma spectroscopy. Sample dilutions (with deionized water for aqueous samples and with ISOPAR® L for organic samples) were performed after removal from the hot cell and prior to counting. In addition, the potassium and sodium concentrations of the aqueous phase were measured by ICP-atomic emission spectroscopy (ICP-AES). A check for aqueous cross-contamination was made by measuring the aqueous pH using the paper-strip m&hod. The control sample phases were subsampled in the analytical laboratory, their cesium concentrations measured by ICP-MS, and the aqueous potassium and sodium concentrations measured by ICP-AES. Staff members further stripped, subsampled, and measured the concentrations of BOBCalixC6 (Calix), Cs-7SB (modifier), TOA, and 4-*sec*-butylphenol in the stripped, irradiated organic samples. The Extract-Scrub-Strip (ESS) performance protocol[7] of the irradiated solvents was also completed.

7. RESULTS

Tables 10–14 list the results measured for the batch self-irradiation samples. Tables 10 and 11 summarize the cesium distribution values, aqueous concentrations of potassium and sodium, and aqueous pH values for the irradiated and control samples, respectively, including subsamples taken during the large-scale processing. Table 12 lists the break times and evaluates the third-phase formation. Tables 13 and 14 list the organic analytical results and the ESS evaluation results, respectively.

Tables 10 and 11 not only list the cesium distribution coefficient (D) values measured at the cell temperature, but also include the D values corrected to 25°C using the temperature parameter from the temperature model. The current model uses an Arrhenius temperature dependence for D, as shown in Eq. (1):

$$D(T) = Ae^{(m/T)}, \tag{1}$$

where

D = cesium distribution ratio;

A = preexponential term;

m = temperature parameter, K;

T = temperature, K.

Assuming that the preexponential term is independent of temperature, the relationship between D at two temperatures is readily obtained from Eq. (1), and is given in Eq. (2) for the case of correcting a measured D to 25°C:

$$D_{298\,\mathrm{K}} = D_{\mathrm{T}} e^{k(3.354 - 1000/T)} \tag{2}$$

The parameter k ($k = m/1\,000$) for the three segments of the CSSX process are as follows:

Process	k (K)
Extract	7.48
First Scrub	7.55
First Strip	9.26

Table 10. Summary of concentrations for irradiated samples during exposure period

Process	Aqueous phase K (mg/L)	Aqueous phase Na (mg/L)	Aqueous phase pH	Aqueous phase ^{137}Cs (Ci/L)	Organic phase ^{137}Cs (Ci/L)	Cesium distribution ratio D	Cesium distribution ratio Temp. (°C)	Cesium distribution ratio Corrected to 25°C[a]
Large batch preparation								
Extract				0.108[b]		8.41[c]	34.0	17.5
				0.097	0.909	9.34	34.0	19.5
Scrub				1.19	0.620	0.52	34.3	1.12
Strip				2.38	0.104	0.04	34.8	0.12
Baseline samples (T_0)								
Extract	979	125,000	14.0	0.095	1.09	11.5	34.9	25.7
			14.0	0.111[d]		9.79[d]	34.9	21.9
Scrub	227	57	1.0	1.24	0.598	0.48	34.6	1.06
Strip			3.0	2.97	0.124	0.04	34.0	0.10
First time interval (T_1)								
Extract	1,150	124,000	14.0	0.095	0.819	8.66	35.4	20.2
Scrub	229	53	2.0	1.32	0.575	0.43	35.4	1.01
Strip	<5	7	2.5	2.30	0.122	0.05	35.4	0.15
Second time interval (T_2)								
Extract	767	140,000	14.0	0.070	0.864	12.3	34.6	26.9
Scrub	284	57	2.0	1.22	0.598	0.49	34.7	1.09
Strip	26	19	3.0	2.24	0.133	0.06	34.8	0.16
Third time interval (T_3)								
Extract	734	135,000	14.0	0.078	0.996	12.7	35.1	28.9
Scrub	271	60	2.0	1.16	0.842	0.72	34.4	
					0.576[e]	0.50	34.4	1.08
Strip	29	14	3.0	2.16	0.709	0.33	34.3	
					0.487[e]	0.23	34.3	
					0.178[f]	0.08[f]	34.3	0.21
Extract-S[g]	760	132,000	14.0	0.070	0.144	2.05	35.3	
					0.146[e]	2.08	35.3	
					0.824[f]	11.7[f]	35.3	27.1
Extract-S&M[h]	745	132,000	14.0	0.076	2.21	29.3	35.0	
					0.908[e]	12.0	35.0	27.1

[a]Distribution ratio measured at cell temperature and then corrected to 25°C using the model temperature parameter.
[b]Aqueous phase separated from organic phase before loss.
[c]Distribution ratio calculated from aqueous phase before loss and organic phase after loss.
[d]Remeasured archived aqueous stored in cell.
[e]Sample activity recounted as cesium distribution ratio was not self-consistent.
[f]Calculated from aqueous-phase activity and batch total activity.
[g]Extract batch using a "salts only" simulant.
[h]Extract batch using a "salts & metals" simulant.

Table 11. Summary of concentrations for control samples during exposure period

Process	Aqueous phase K (mg/L)	Aqueous phase Na (mg/L)	Aqueous phase pH	Aqueous phase Cs (mg/L)	Organic phase Cs (mg/L)	Cesium distribution ratio *D*	Cesium distribution ratio Temp. (°C)	Cesium distribution ratio Corrected to 25°C[a]
Large batch preparation								
Extract				2.5	50.2	19.8	23.5	17.5
Scrub				29.4	45.2	1.54	25.3	1.58
Strip				132	19	0.14	25.0	0.14
Baseline samples (T_0)								
Extract	1,020	122,000	14	5.5	50.2	9.06	34.6	19.8
Scrub	518	377	2	76.5	43.2	0.56	34.6	1.25
Strip	18	<1	2.5	171	11.8	0.07	34.2	0.17
First time interval (T_1)								
Extract	1,130	120,000	14	5.9	49.4	8.43	35.5	19.8
Scrub	530	385	2	72.4	42.7	0.59	35.5	1.40
Strip	15	<1	2.5	167	12.0	0.07	35.5	0.21
Second time interval (T_2)								
Extract	716	131,000	14	5.1	50.6	9.90	33.5	19.8
Scrub	550	401	2	67.0	42.4	0.63	33.5	1.28
Strip	42	7	3	169	11.8	0.07	33.5	0.17
Third time interval (T_3)								
Extract	752	133,000	14	5.8	52.0	8.92	34.3	19.1
Scrub	538	392	2	74.2	43.9	0.59	35.2	1.37
Strip	50	6	3	175	11.8	0.07	35.3	0.19
Extract-S[b]	784	134,000	14	5.7	49.0	8.67	35.5	20.4
Extract-S&M[c]	745	131,000	14	5.8	50.5	8.65	35.4	20.2

[a]Distribution ratio measured at cell temperature and then corrected to 25°C using the model temperature parameter.
[b]Extract batch using a "salts only" simulant.
[c]Extract batch using a "salts & metals" simulant.

Table 12. Break-time and third-phase results

Process	Break time (s)		Presence of third phase	
	Irradiated	Control	Irradiated	Control
		Processing		
Extract	90	180	No	No
Scrub	65	120	No	No
Strip	90	110	No	No
		Baseline samples (T_0)		
Extract	90	105	No	No
Scrub	115	120	No	No
Strip	115	115	No	No
		First time interval (T_1)		
Extract	60	90	No	No
Scrub	60	90	No	No
Strip	75	75	No	No
		Second time interval (T_2)		
Extract	120	105	No	No
Scrub	120	60	No	No
Strip	60	60	No	No
		Third time interval (T_3)		
Extract	100	80	No	No
Scrub	120	60	No	No
Strip	60	60	No	No
Extract-S[a]	100	100	No	No
Extract-S&M[b]	120	105	No	No
	Mean[c]	**Mean**		
Extract	94 ± 21	109 ± 33		
Scrub	96 ± 31	90 ± 30		
Strip	80 ± 23	84 ± 27		

[a]Extract batch using a "salts only" simulant.
[b]Extract batch using a "salts & metals" simulant.
[c]The variation is one standard deviation about the mean.

Table 13. Concentrations of organic constituents in irradiated solvents

Time interval	Dose (Mrad)	TOA[a] (ppm)	Modifier (*M*)	Calixarene (*M*)	4-*sec*-butylphenol (ppm)
			Nominal standard		
		350	0.5	0.01	
			Extraction		
T_0	0	285	0.51	0.0096	<5
T_1	0.30	244	0.51	0.0093	<5
T_2	0.81	246	0.51	0.0096	27
T_3	1.24	176	0.5	0.0096	27
T_3-S[b]	1.24	146	0.62	0.0099	30
T_3-S&M[c]	1.24	160	0.5	0.0094	25
			Scrub		
T_0	0	281	0.48	0.0093	<5
T_1	0.22	321	0.48	0.0094	6.3
T_2	0.60	260	0.48	0.0096	5.6
T_3	0.92	307	0.48	0.0094	11.8
			Strip		
T_0	0	276	0.48	0.0094	11.1
T_1	0.19	357	0.46	0.0094	7.9
T_2	0.51	284	0.47	0.0096	6.2
T_3	0.79	288	0.47	0.0097	7

[a]Trioctylamine.
[b]Extract batch using a "salts only" simulant.
[c]Extract batch using a "salts & metals" simulant.

Table 14. Cesium distribution ratios of irradiated solvents at room temperature from ESS testing

Extraction test of solvent samples

	T_0	T_1	T_2	T_3	T_3 (controls)	T_3 (S)	T_3 (S&M)
Pristine[a]	18.16	18.40	18.23	2 cycles[b]	17.62		
Extract[c]	22.44	21.29	21.11	23.01	19.33	21.26	21.51
Scrub[d]	22.76	21.17	21.34	22.42	17.96		
Strip[e]	22.25	20.91	21.55	20.70	20.29		

Scrub test of solvent samples

	T_0	T_1	T_2	T_3	T_3 (controls)	T_3 (S)	T_3 (S&M)
Pristine	1.59	1.60	1.59	2 cycles	1.81		
Extract	2.33	2.18	2.10	2.33	1.76	1.85	1.91
Scrub	2.13	1.95	1.94	2.08	1.76		
Strip	2.17	2.03	1.99	2.05	1.79		

Strip test No. 1 of solvent samples

	T_0	T_1	T_2	T_3	T_3 (controls)	T_3 (S)	T_3 (S&M)
Pristine	0.142	0.148	0.152	2 cycles	0.170		
Extract	0.250	0.248	0.282	0.326	0.183	0.245	0.242
Scrub	0.229	0.221	0.217	0.258	0.196		
Strip	0.234	0.233	0.224	0.240	0.186		

Strip test No. 2 of solvent samples

	T_0	T_1	T_2	T_3	T_3 (controls)	T_3 (S)	T_3 (S&M)
Pristine	0.082	0.091	0.089	2 cycles	0.103		
Extract	0.149	0.154	0.200	0.261	0.106	0.153	0.168
Scrub	0.134	0.130	0.140	0.166	0.118		
Strip	0.138	0.127	0.134	0.153	0.120		

Strip test No. 3 of solvent samples

	T_0	T_1	T_2	T_3	T_3 (controls)	T_3 (S)	T_3 (S&M)
Pristine	0.059	0.077	0.074	2 cycles	0.083		
Extract	0.128	0.130	0.208	0.288	0.085	0.143	0.157
Scrub	0.104	0.103	0.116	0.139	0.095		
Strip	0.107	0.099	0.111	0.139	0.092		

Strip test No. 4 of solvent samples

	T_0	T_1	T_2	T_3	T_3 (controls)	T_3 (S)	T_3 (S&M)
Pristine	0.053	0.056	0.056	2 cycles	0.070		
Extract	0.127	0.127	0.221	0.300	0.072	0.142	0.153
Scrub	0.093	0.093	0.107	0.133	0.080		
Strip	0.093	0.089	0.108	0.119	0.079		

[a]Pristine solvent.
[b]After cycling pristine solvent through ESS twice.
[c]Solvent sample stored in contact with simulant during the time of irradiation.
[d]Solvent sample stored in contact with Scrub solution during the time of irradiation.
[e]Solvent sample stored in contact with Strip solution during the time of irradiation.

Inconsistencies were noted in some of the data for the irradiated solvents in Table 10. The cesium activity for the baseline solvent was significantly higher than that measured, either during processing, or for the other time intervals (see Table 10 and Fig. 6). The volume of the sample was quite small, which may have contributed to this discrepancy; however, a recount of this sample was not possible. *No* archive existed for the organic samples (the organic samples were stripped of activity and removed from the cell for analyses of their organic concentrations and performance testing), but the archived aqueous counterpart of this sample was resampled in order to remeasure its activity. The aqueous recount was higher, leading to a lower *D* value, but a higher aqueous count makes the cesium mass even higher. Although the *D* value is high compared with that measured during processing, it is not high compared with the values measured during later time intervals. Larger volumes were taken for all later high-activity samples to allow for recounts in the event of future self-inconsistencies.

On the other hand, the "aqueous" sample from the baseline strip solution appeared to be solvent and was proven to be organic phase via total carbon analysis. Thus, the aqueous concentrations are not listed in Table 10 for this sample. Consequently, the archived aqueous solution was remeasured, resulting in a more reasonable strip *D* value of 0.04. The first and second time-interval sample sets did not appear to have these self-consistency problems. However, the gamma count for four out of the five irradiated solvents in the final time interval (T_3) appeared to be self-inconsistent (aqueous counts were in line with the measurements of the prior time intervals, but the organic counts were not). All four organic samples were recounted, which appeared to correct the inconsistency for the Scrub and Extract-S&M samples; however, this was not true for the Strip and Extract-S samples. Thus, the organic count calculated by mass balance using the aqueous counts is also listed in Table 10 and is used in the figures presented later.

Determining the break times was subjective; however, reproducible measurement was difficult inside the hot cell. At best, one could say a break time of a few minutes was consistently observed. If the break time had increased significantly, to 5-10 min for example, then one could conclude that irradiation was interfering with phase separation, which could have had serious implications for plant operation. Thus, no evidence of solvent degradation was observed in the measurements of break time, and no third phases were observed throughout the self-irradiation period (see Table 12).

Figure 6 illustrates the relatively constant phase concentrations of ^{137}Cs for the Extract samples throughout the self-irradiation period. Experimental error is believed to be responsible for the higher concentration in the T_0 solvent, as explained above, especially since the concentration observed during processing agrees (within the counting error) with the later time intervals. Figure 7 illustrates the constant phase concentrations of cesium for the Extract control samples over the same period. Figure 8 illustrates the relatively constant extraction *D* values for both the irradiated and the control Extract samples. Figures 9-l 1 illustrate the same point for the Scrub samples. Figures 12-14 are the equivalent plots for the Strip

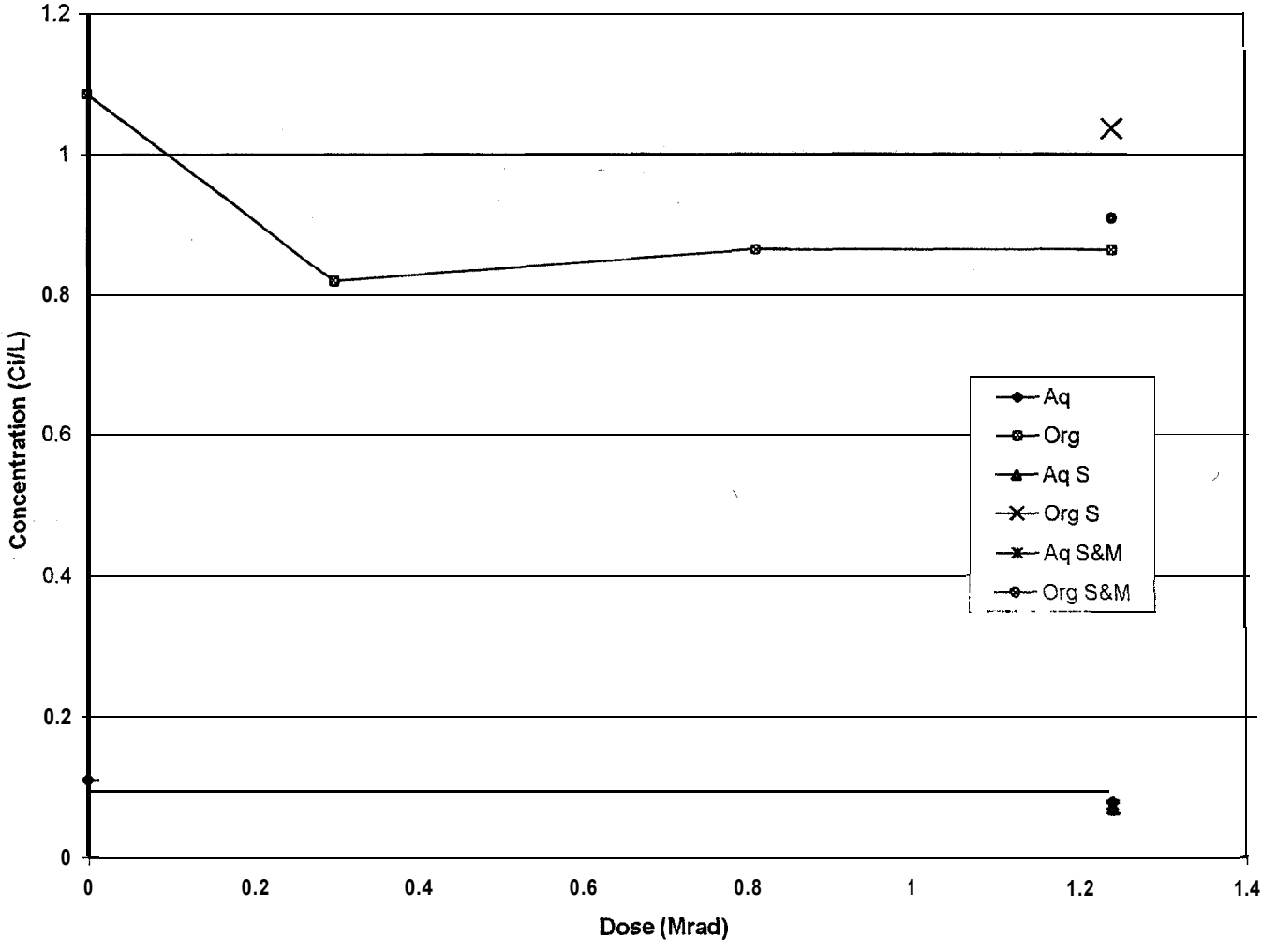


Fig. 6. Cesium-137 concentrations in Extraction phase during self-irradiation.

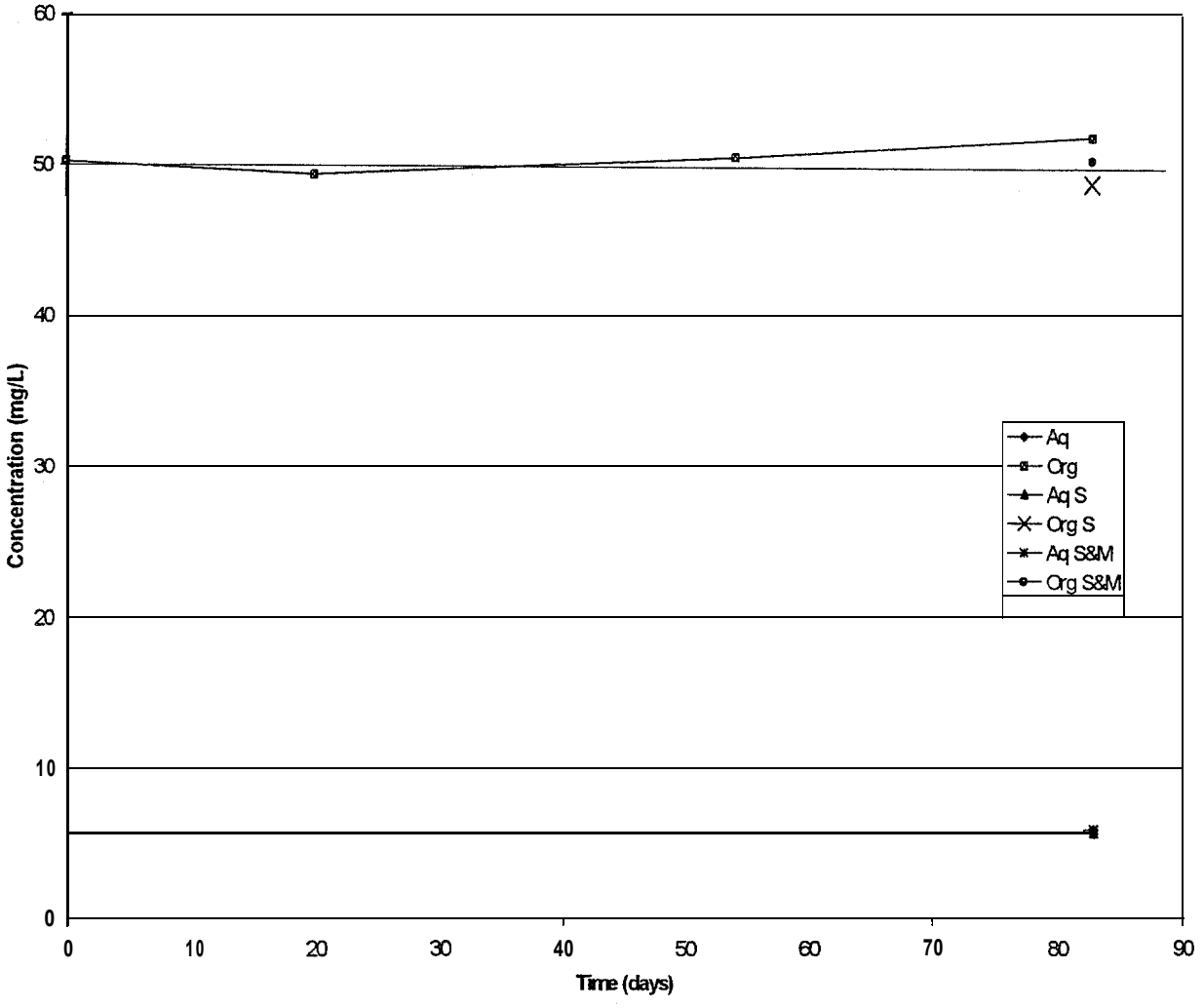


Fig. 7. Cesium concentrations in Extraction phase of controls during self-irradiation. Controls and irradiated samples were evaluated simultaneously, but the control samples received no dose. Hence, control-sample data are plotted vs time on shaker.

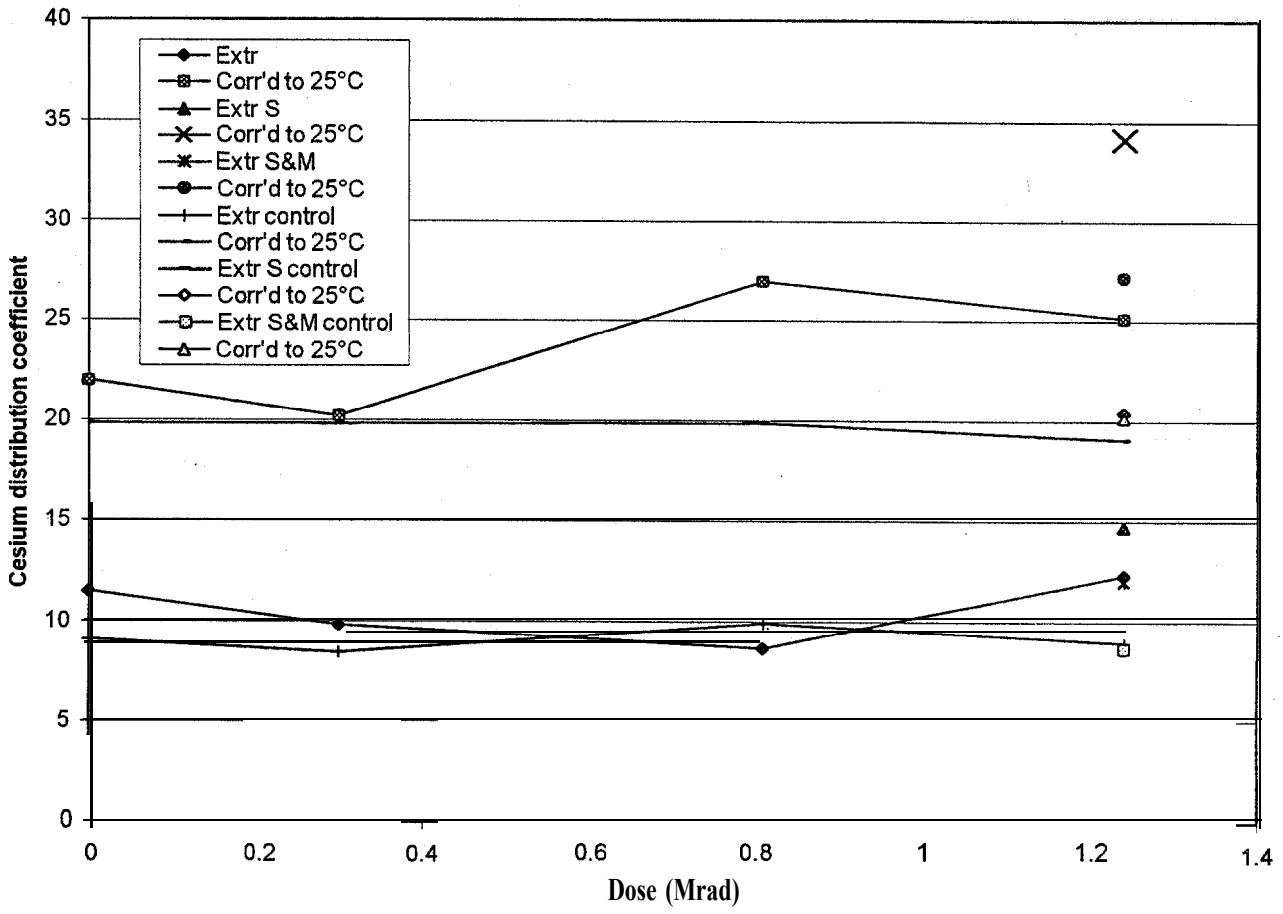


Fig. 8. Cesium distribution coefficient in Extraction phase during self-irradiation.

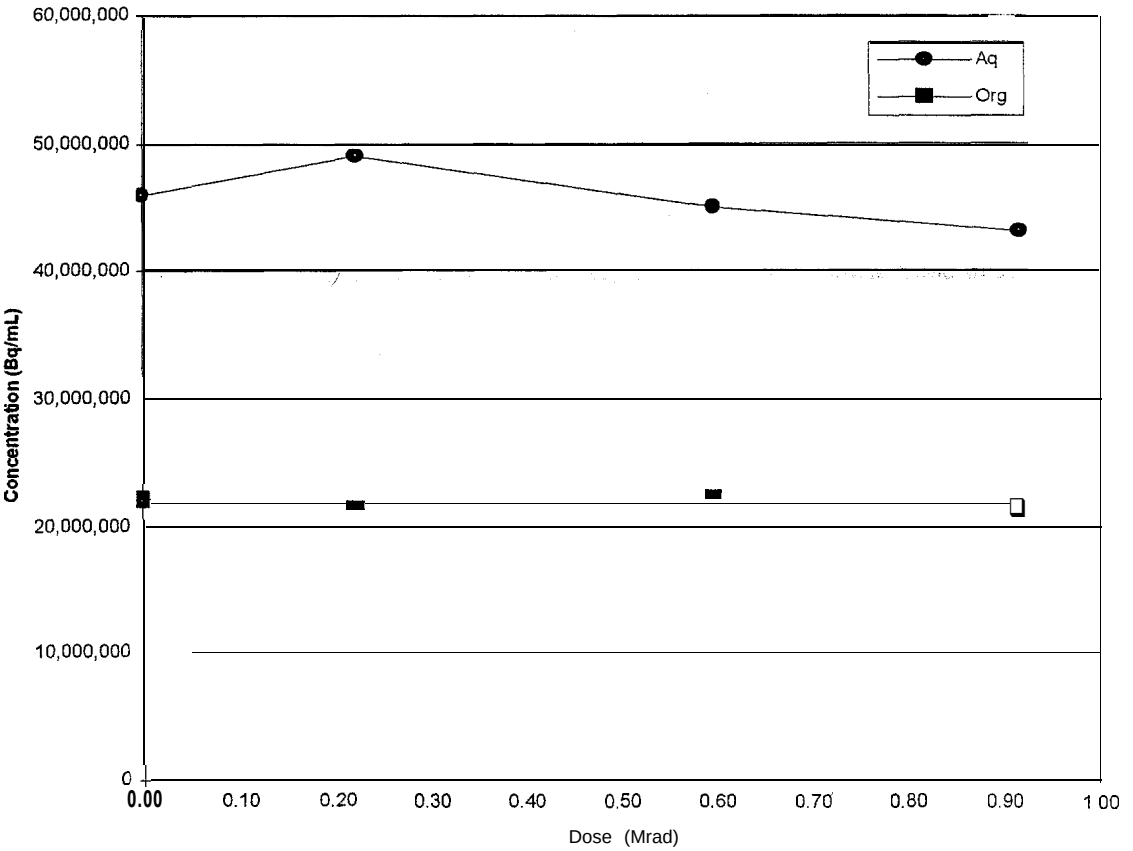


Fig. 9. Cesium-137 concentrations in Scrub phase during self-irradiation.

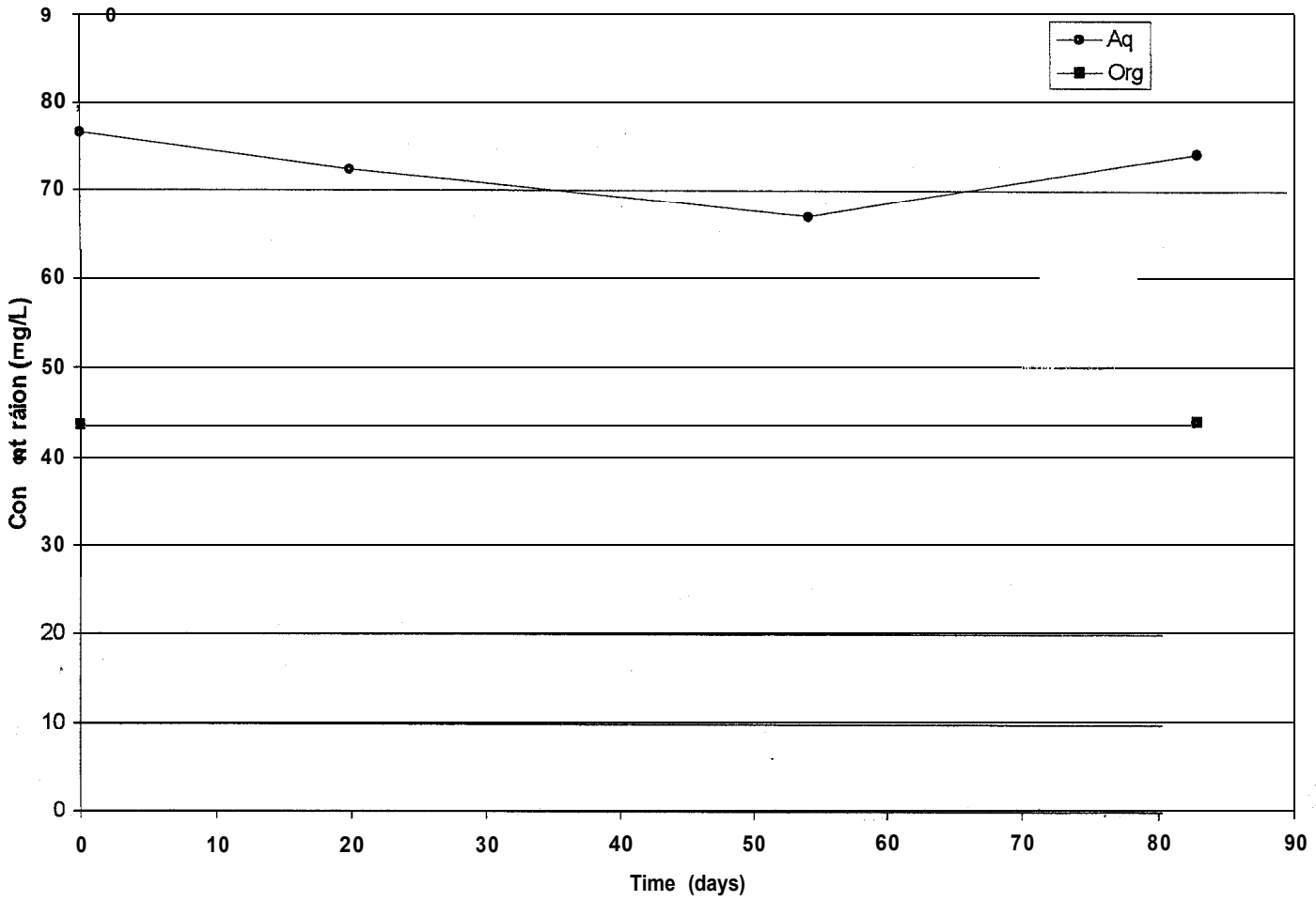


Fig. 10. Cesium concentrations in Scrub phase of controls during self-irradiation. Control and irradiated samples were evaluated simultaneously, but the control samples received no dose. Hence, control sample data are plotted vs time on shaker.

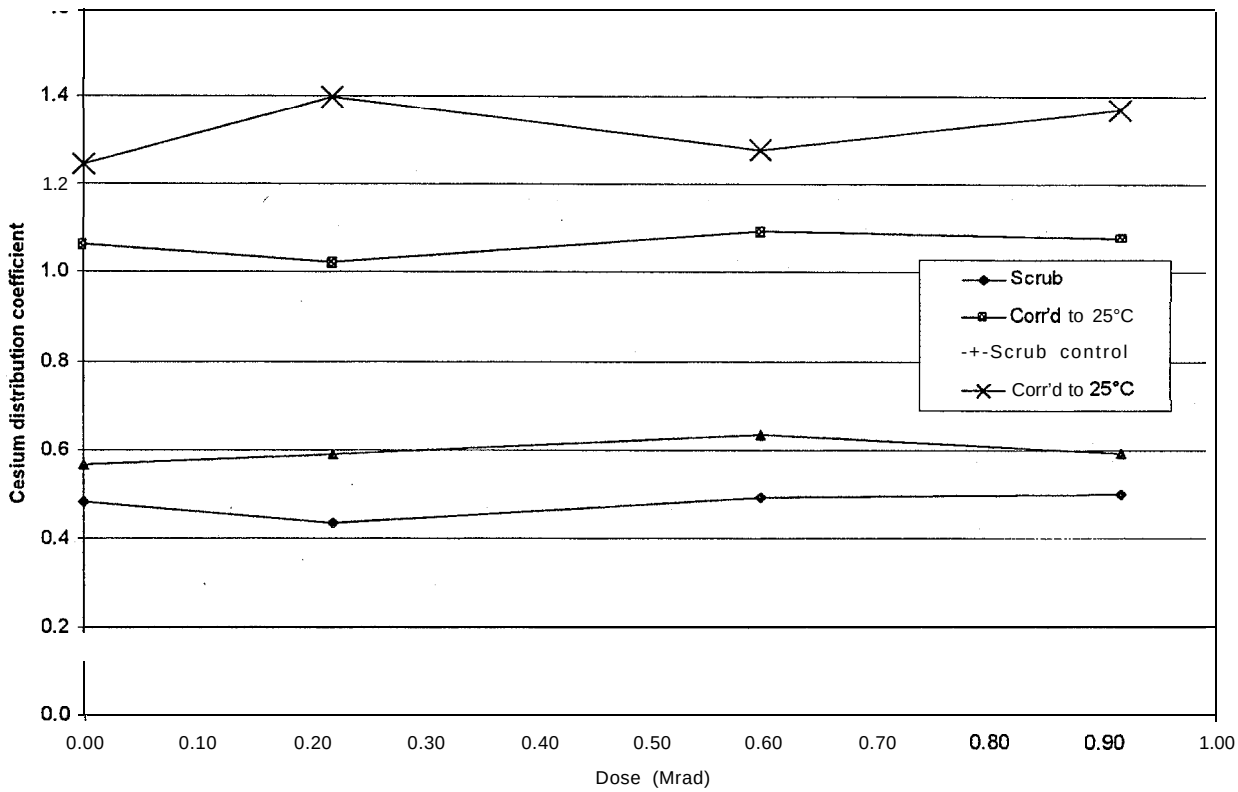


Fig. 11. Cesium distribution coefficient in Scrub phase during self-irradiation.

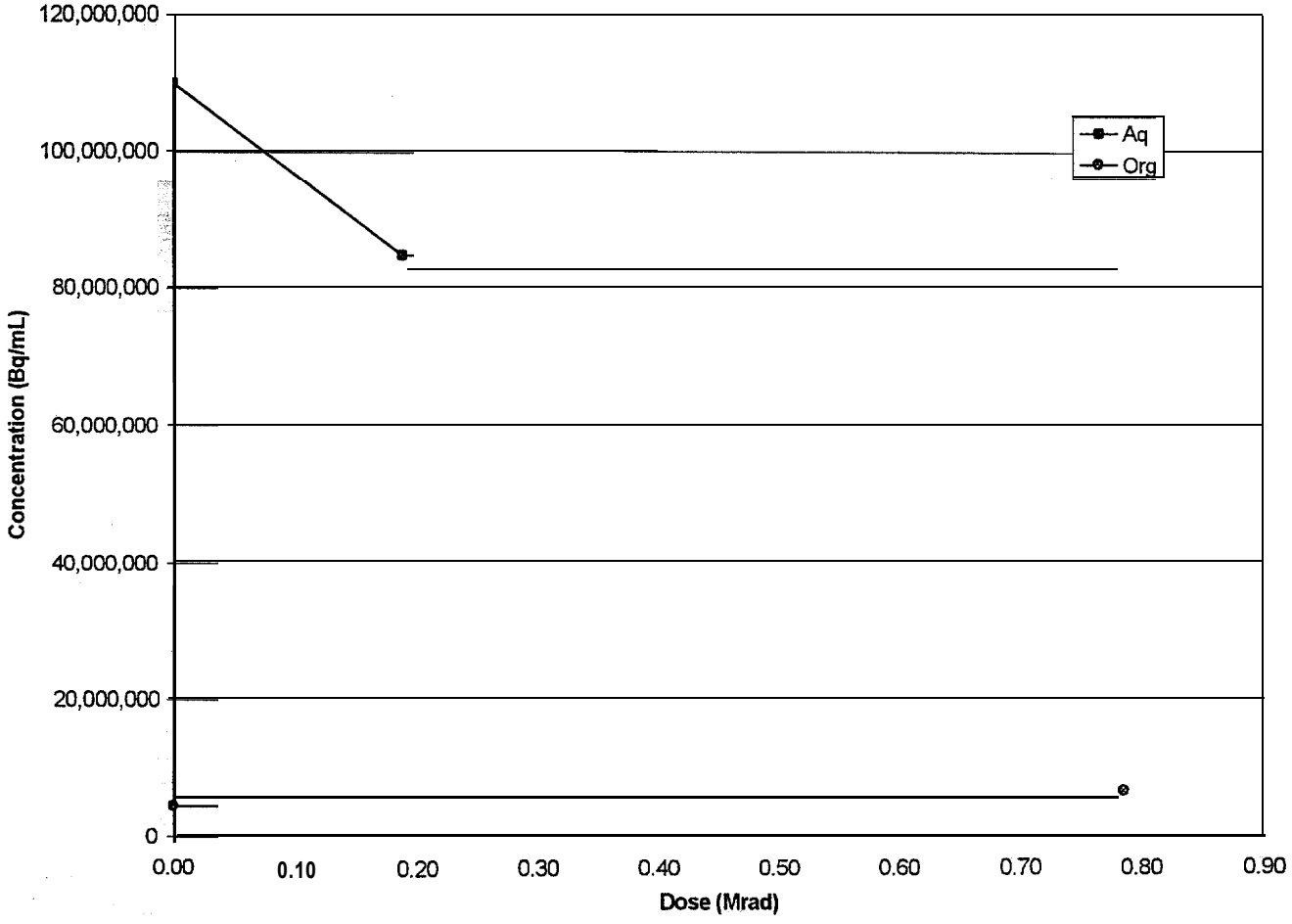


Fig. 12. Cesium-137 concentrations in Strip phase during self-irradiation.

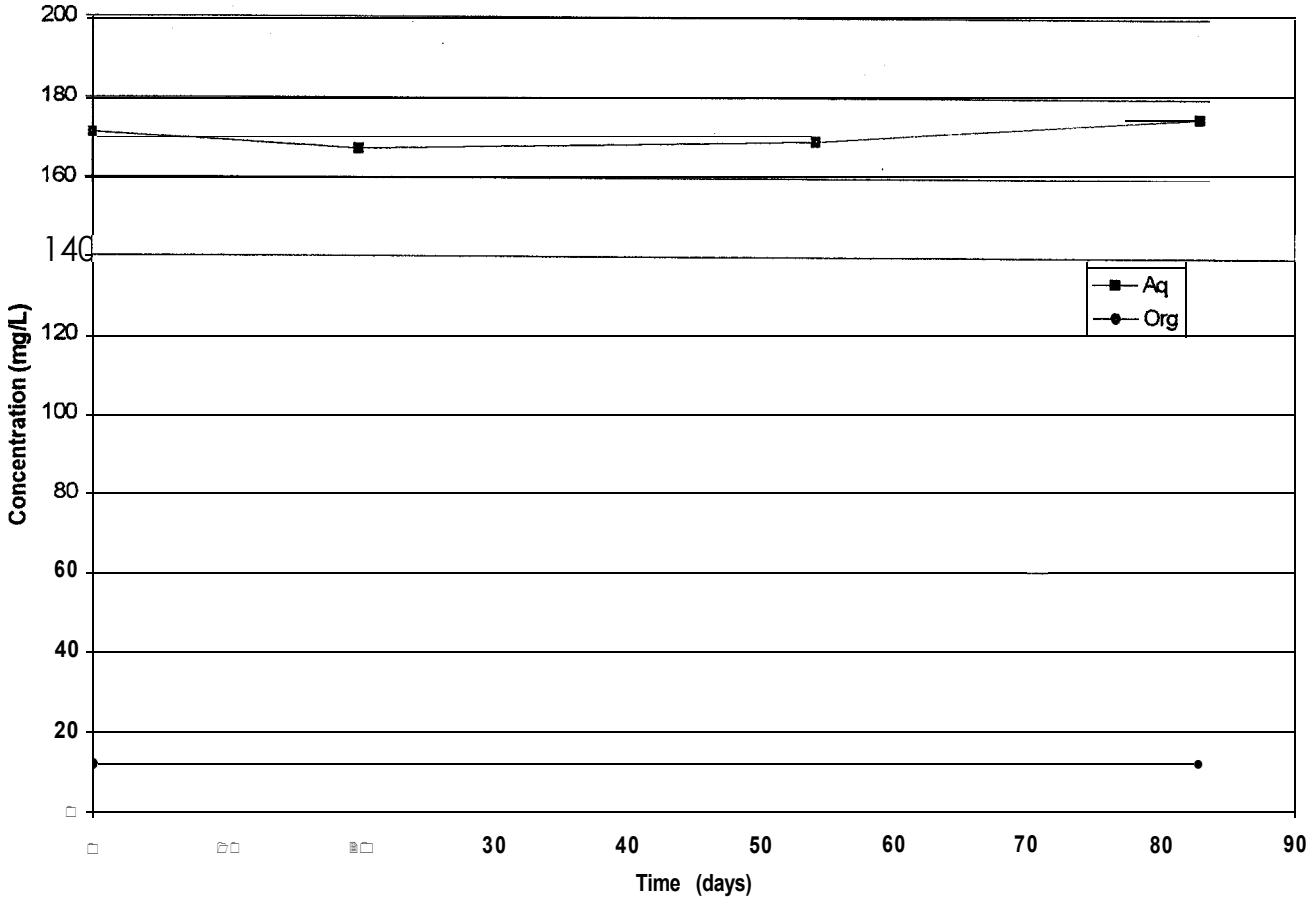


Fig. 13. Cesium concentrations in Strip phase of controls during self-irradiation. Control and irradiated samples were evaluated simultaneously, but the control samples received no dose. Hence; control sample data are plotted vs time on shaker.

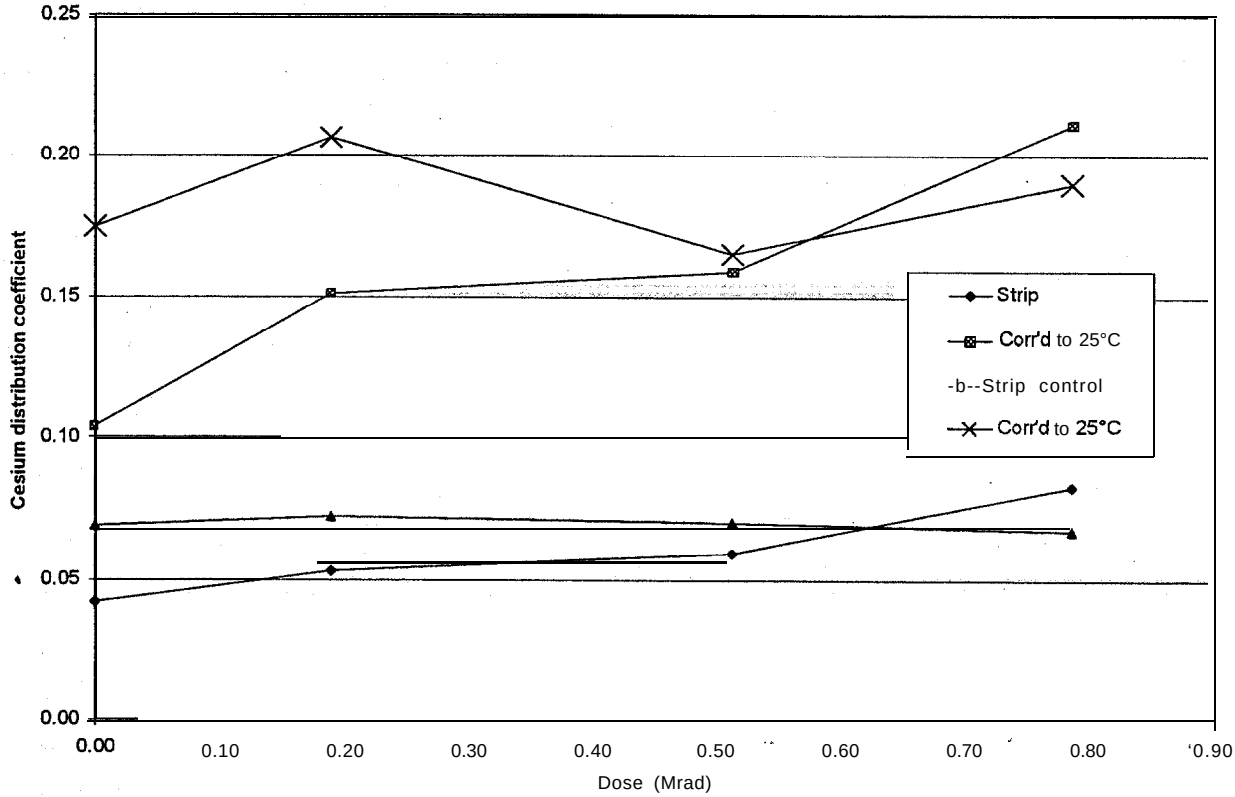


Fig. 14. Cesium distribution coefficient in Strip phase during self-irradiation.

samples. The baseline aqueous value in Fig. 12 is higher than either that measured during processing or that for subsequent time intervals, so this difference does not appear to be real. Although the remaining concentrations appear to be relatively constant, the strip D value in Fig. 14 appears to trend upward with dose, as compared with the controls.

The values listed in Tables 10 and 11 confirm that all the batches are in the expected pH range, indicating little or no cross-aqueous contamination during processing.

Figures 15-17 illustrate the aqueous potassium and sodium concentrations for the Extract, Scrub, and Strip samples, respectively. Note that Fig. 15 is a semilogarithmic plot, because of the large concentration difference between sodium and potassium in the simulant. Differences are noted in these measured Extract concentrations, but the controls mimic the differences observed in the irradiated samples, indicating that this is not an effect of irradiation. Although the solvent has a high specificity for cesium, these other two alkali metals are present at much higher concentrations than cesium and will be extracted. One of the purposes of the Scrub phase in the centrifugal contactor operation is to remove these noncesium cations and recycle them back into the extraction stages with the feed. Consequently, a modest concentration of each was expected in the Scrub and Strip solutions (as compared with the simulant concentration and despite the concentrating power from the different O/A ratios going from Extraction to Scrubbing or Stripping). With one exception at about 0.19 Mrad for the Strip samples (see Fig. 17), the potassium concentration was higher than the sodium concentration for both the Scrub and Strip samples (see Figs. 16 and 17), despite the fact that the sodium concentration of the simulant was about two orders of magnitude higher than that of potassium. This was expected, as potassium is the main competitor for the solvent. The Scrub solution concentrations were relatively "flat" during irradiation; the irradiated samples contained significantly less than the control samples (about 250 mg/L compared with about 525 mg/L for potassium and about 50 mg/L compared with about 400 mg/L for sodium. These differences are more likely a result of the large difference in temperature between the control (about 25°C) and the irradiated large batches (about 35°C), resulting in more potassium and sodium being extracted from the simulant at the lower temperature of control preparation and then being released into the aqueous solution at the higher temperatures inside the hot cell. The baseline potassium concentration for the irradiated aqueous strip sample seems high as compared with the other samples. Both alkali metal concentrations decline for the first time interval, but then increase. However, since this situation occurs for both control and irradiated samples, it appears unrelated to self-irradiation.

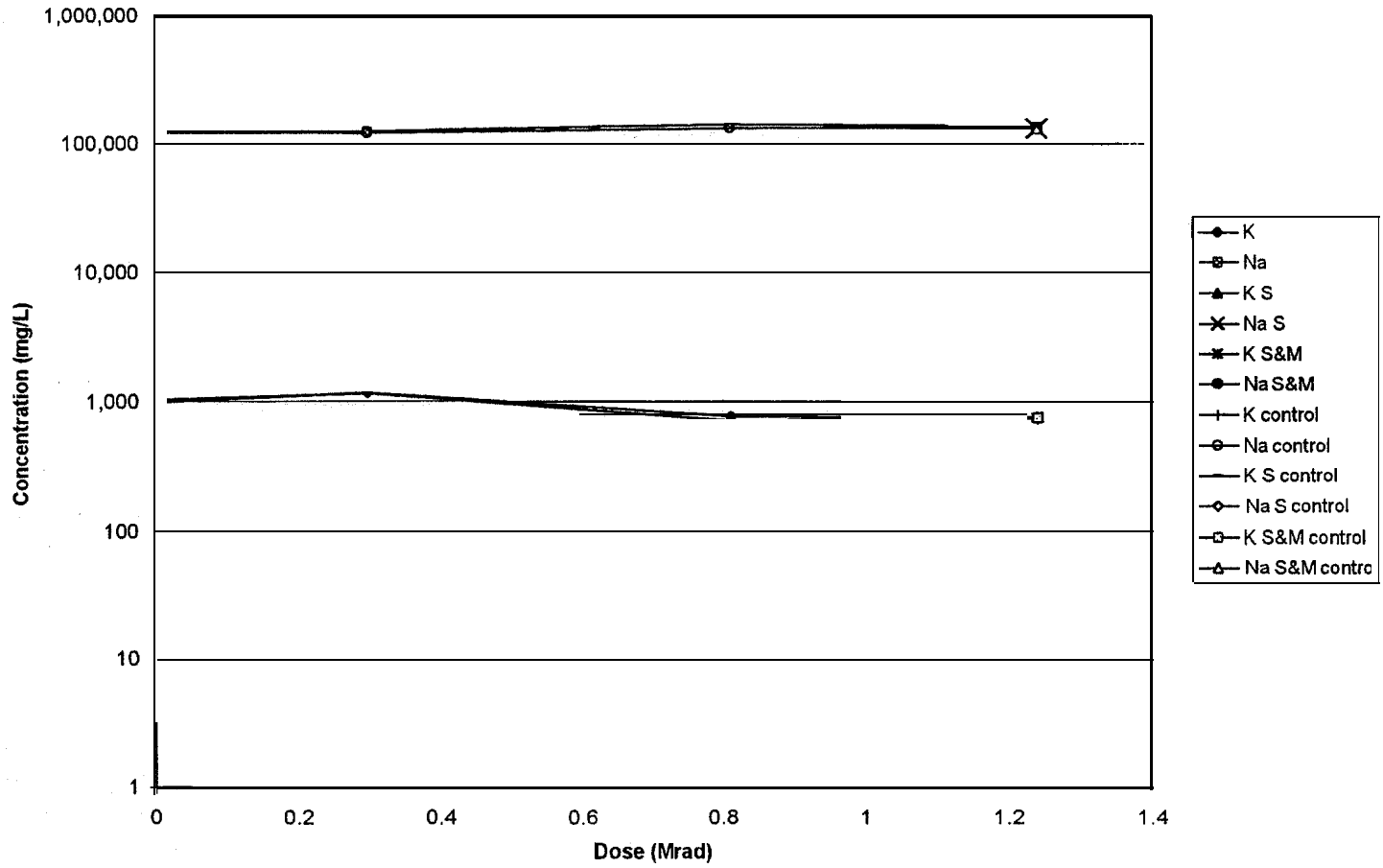


Fig. 15. Aqueous potassium and sodium concentrations in Extraction phase during self-irradiation.

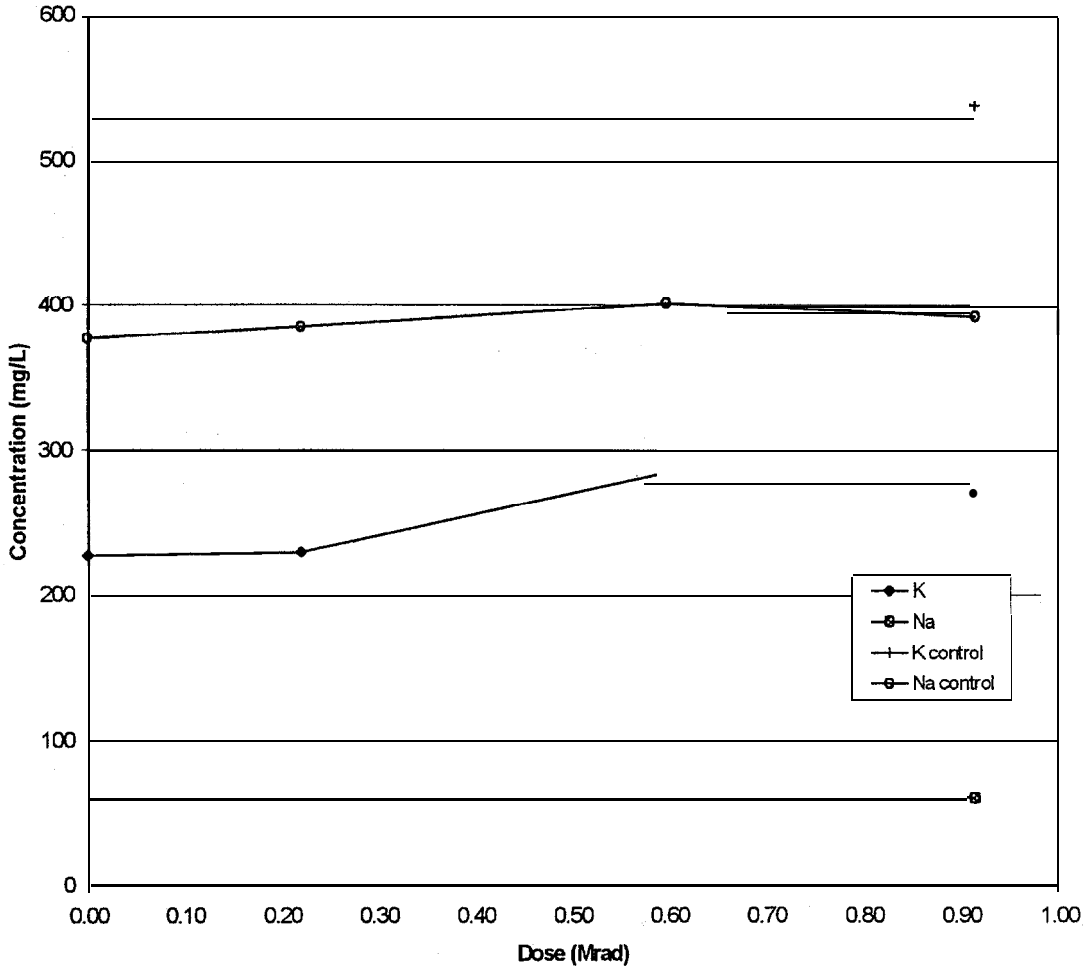


Fig. 16. Aqueous potassium and sodium concentrations in Scrub phase during self-irradiation.

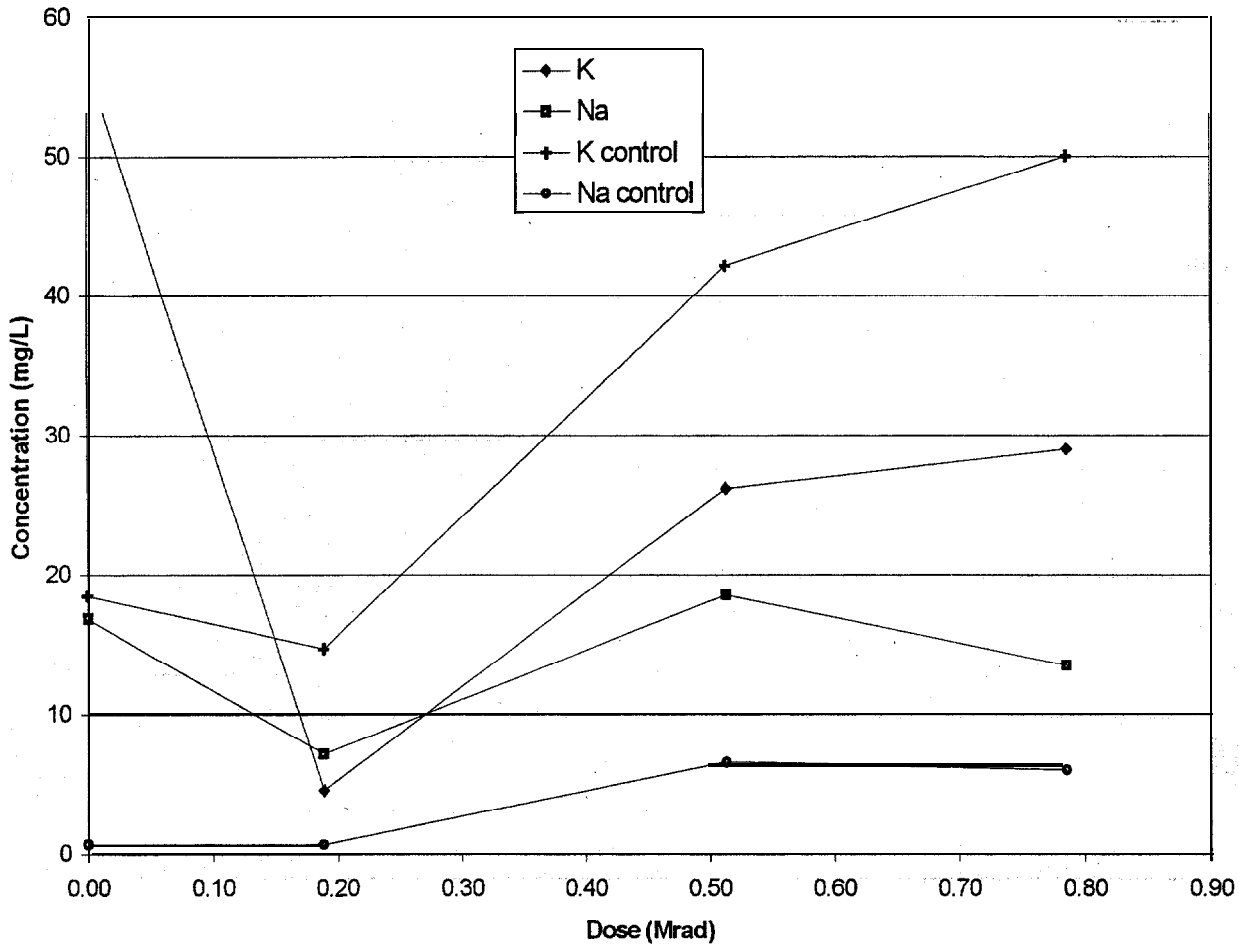


Fig. 17. Aqueous potassium and sodium concentrations in Strip phase during self-irradiation.

Figure 18 illustrates the measured TOA concentration in the irradiated solvents with dose. All of the concentrations at baseline are consistently about 280 ppm, but they differ significantly after that. The TOA concentrations remain in the range of 250-350 ppm, except for the samples with the maximum dose (third-time-interval Extract samples). Each sample with the maximum dose had only about half the content of the baseline concentration for pristine solvent. The external irradiation study had a similar sharp decline in TOA.[8] However, the doses reported for that study were much higher (20-50 Mrad) than for this self-irradiation study, and loss of half the TOA was not expected at doses <1.3 Mrad. The scatter in the data (shown in Fig. 18) is such that the functional form of the decline is unknown. Thus, TOA replacement had already been anticipated in the plans and development for the full-sized plant.

In addition, the external irradiation study predicted radiolytic cleavage of the modifier molecule, resulting in a buildup of the degradation product 4-*sec*-butylphenol.[8] This buildup interferes with the solvent extraction process, but caustic washes in other studies have proven effective in removing the phenol from the solvent.* As expected, Table 12 indicates there was no significant decline in either the modifier or the calix concentration over this range of doses. Also, no significant decline was observed in the external irradiation study at much higher doses.* Direct measurement of the phenol degradation product is the best way to check for modifier radiolysis.

Figures 19-24 illustrate the D values measured with dose for each step of the ESS evaluation in the performance testing of the irradiated solvents. Only the controls from the last time interval were evaluated and plotted in these figures. The D values are plotted against dose-not time. Although the controls were not irradiated, they are plotted as the dose equivalent to the exposure time and dose received for its corresponding irradiated sample, just as in other plots. Thus, the three control samples are plotted at the three different doses representative of the irradiated Extract, Scrub, and Strip samples for the third time interval.

No decline in Extraction or Scrub performance was observed with dose, as Figs. 19 and 20 illustrate. However, there was an obvious decline in ability to strip these irradiated solvents that became more obvious with sequential strip steps, as illustrated in Figs. 21-24. The decline in performance is apparent for the Extract solvent samples for even the first ESS strip (see Fig. 21). The decline for the Scrub and Strip solvent samples is not as obvious, but a trend in declining performance is also apparent for these samples through four ESS sequential strips (see Figs. 21-24). The increase of strip D values for the Extract samples is linear with increasing dose past the first time interval. This is especially apparent for the third and fourth strips (see Figs. 23 and 24). All of the ESS D values were measured at 25°C. At the process temperature of about 30°C, these values will be lower-sufficiently low that the solvent can still be stripped even for the values of 0.20-0.25 at 25°C measured in the first ESS strip (see Fig. 21).

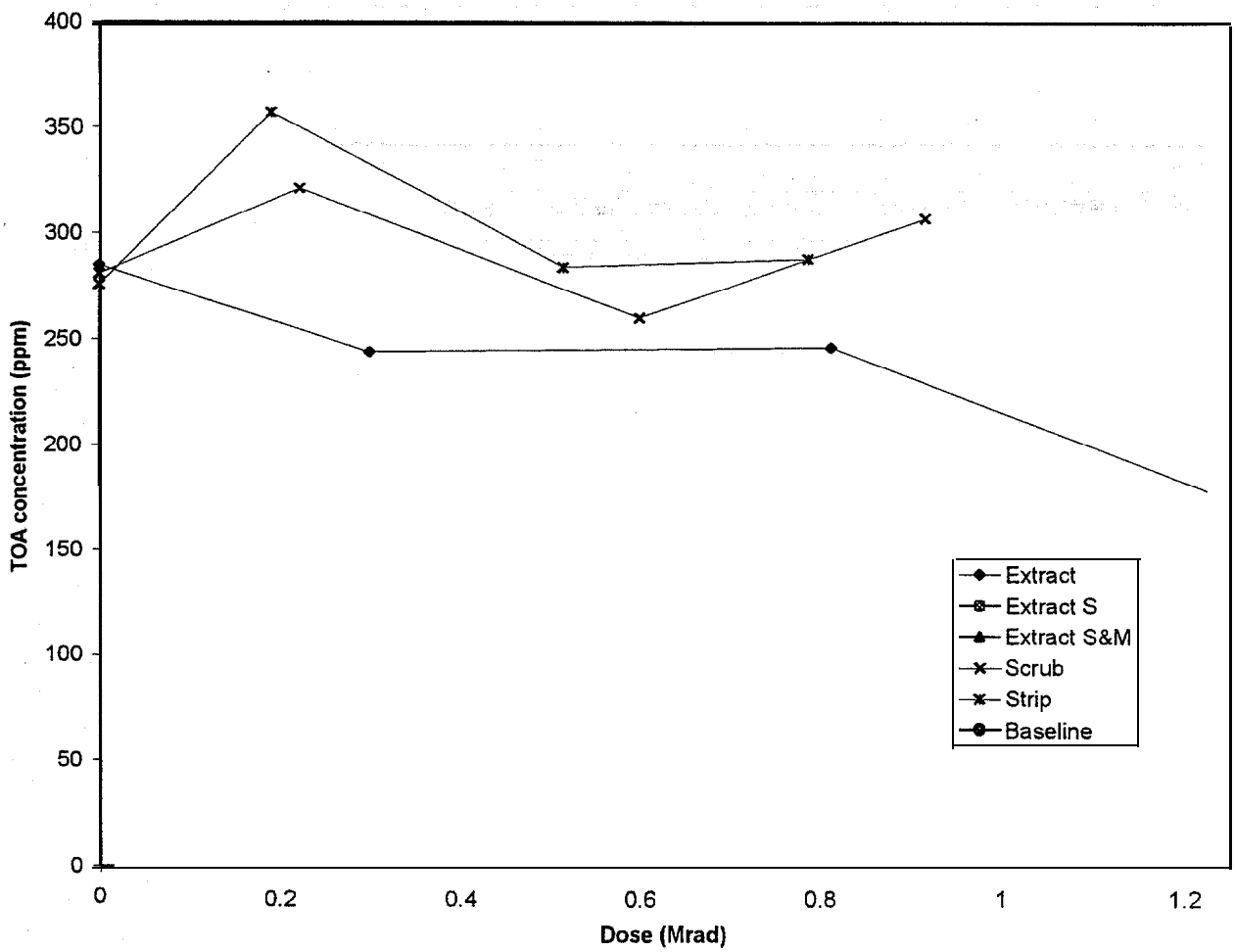


Fig. 18. Trioctylamine concentration in solvent as a function of self-irradiation.

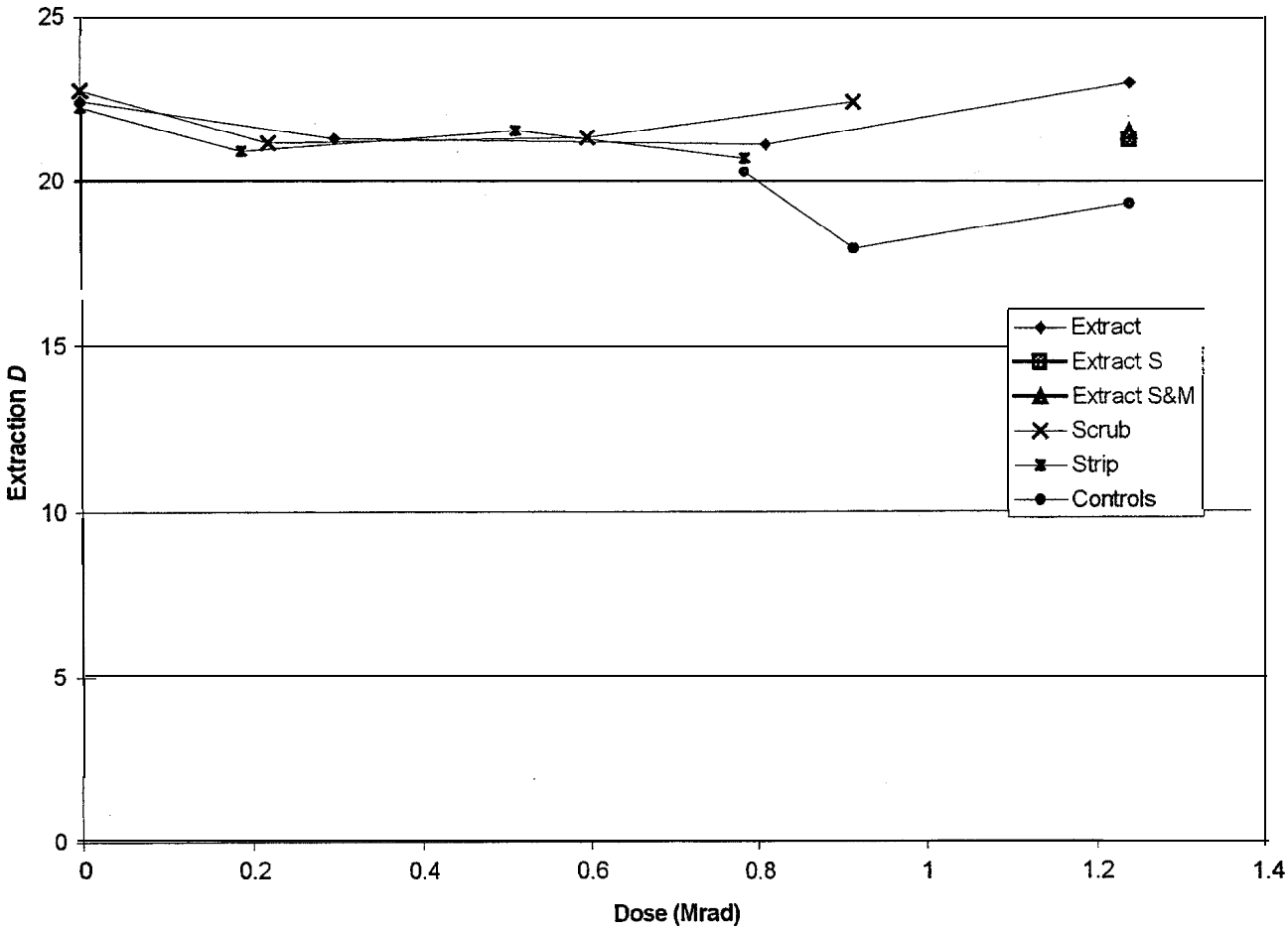


Fig. 19. Cesium distribution ratio (*D*) in Extraction phase for ESS testing of irradiated solvents at 25°C. Data for control samples from the final time interval are plotted to provide a reference point.

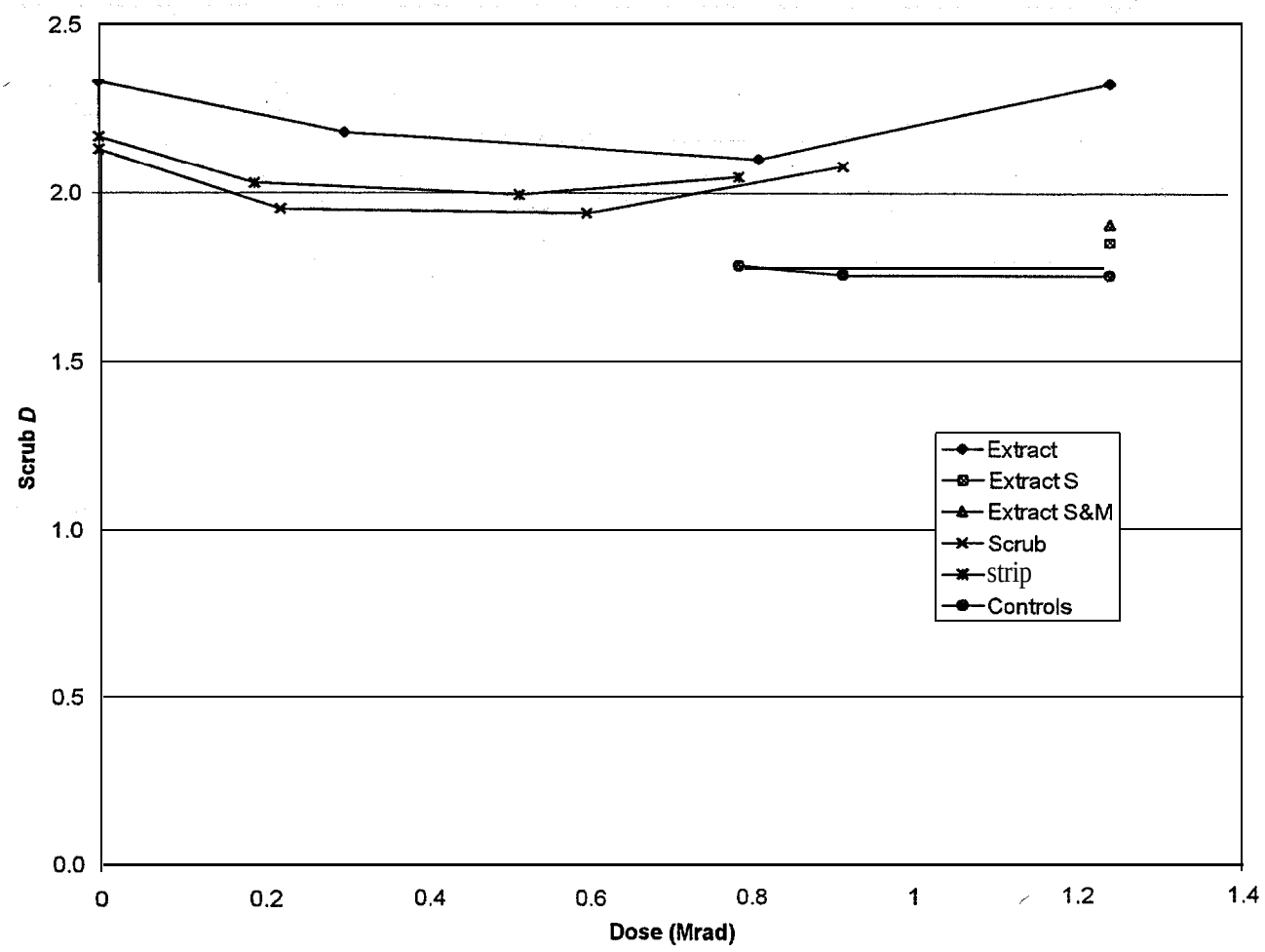


Fig. 20. Cesium distribution ratio (*D*) in Scrub phase for ESS testing of irradiated solvents at 25°C. Data for control samples from the final time interval are plotted to provide a reference point.

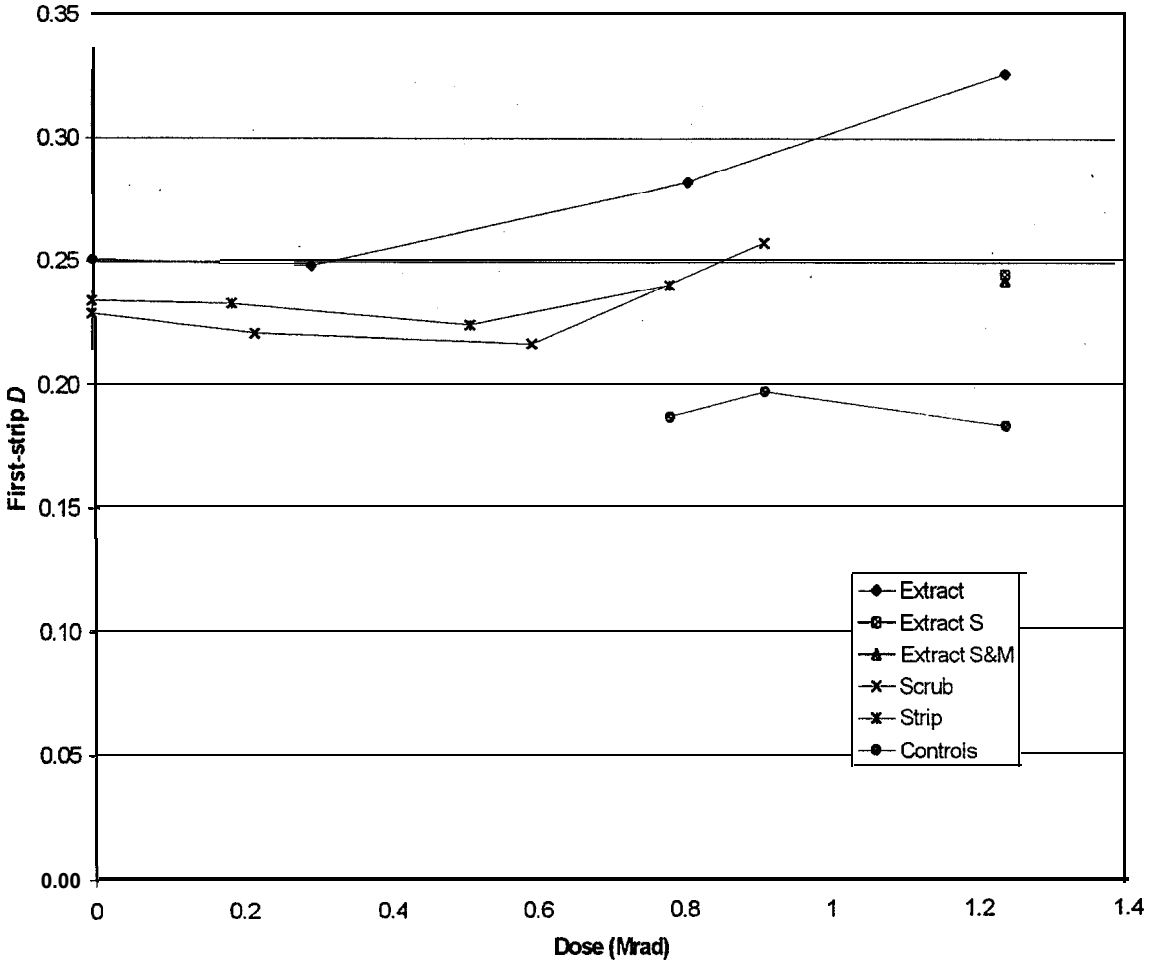


Fig. 21. Cesium distribution ratio (*D*) in the first-strip solution for ESS testing of irradiated solvents at 25°C. Data for control samples from the final time interval are plotted to provide a reference point.

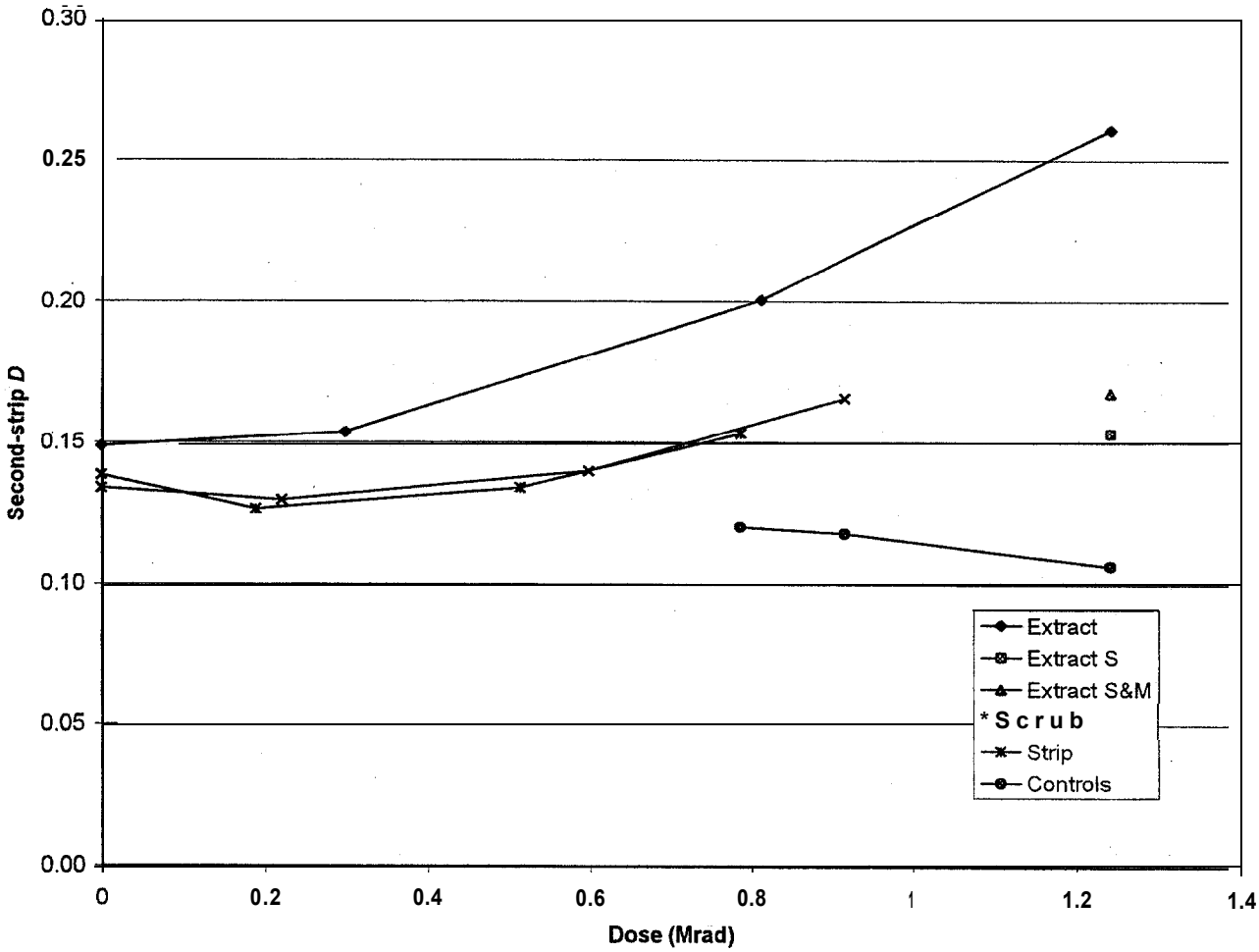


Fig. 22. Cesium distribution ratio (*D*) in the second-strip solution for ESS testing of irradiated solvents at 25°C. Data for control samples from the final time interval are plotted to provide a reference point.

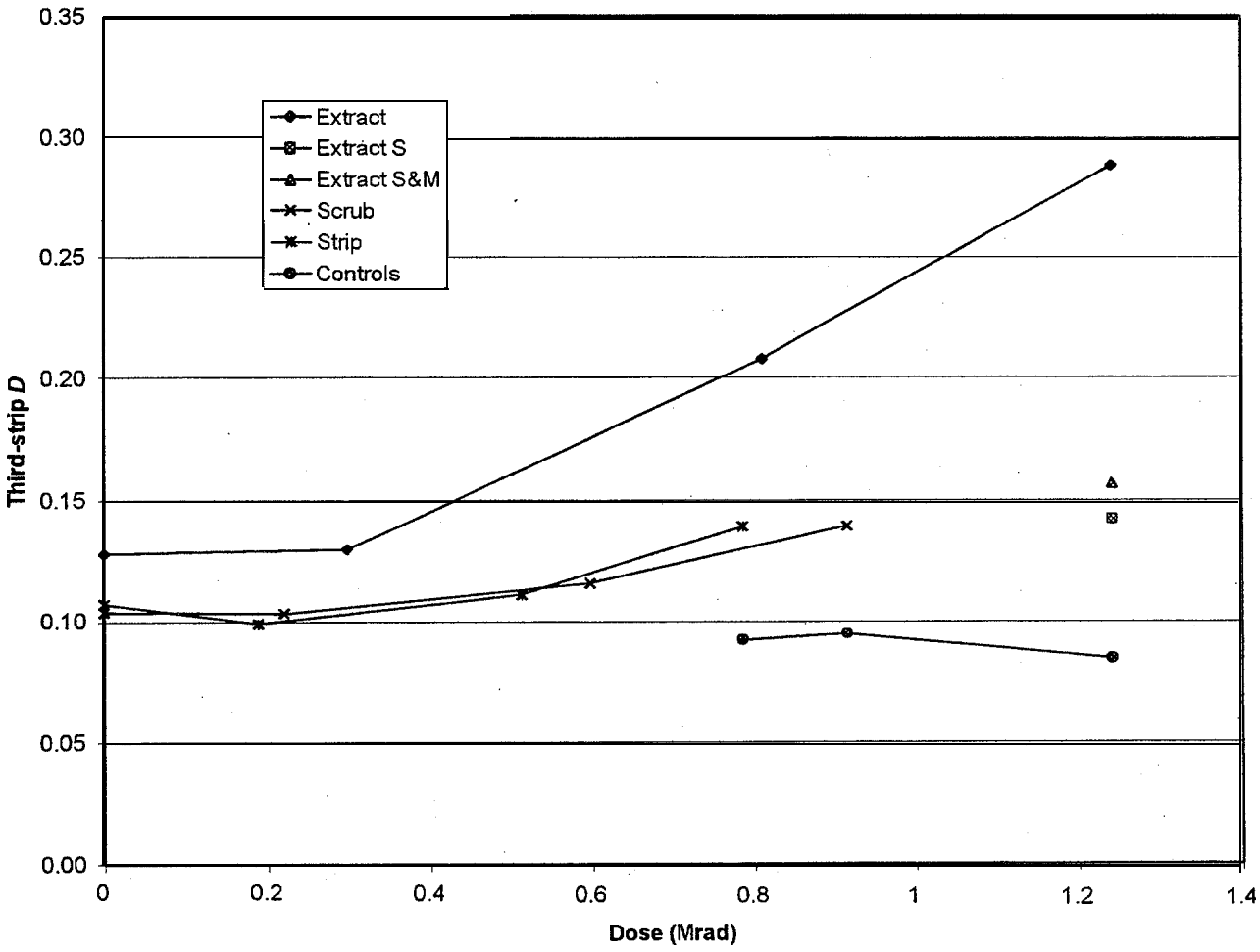


Fig. 23. Cesium distribution ratio (*D*) in the third-strip solution for ESS testing of irradiated solvents at 25°C. Data for control samples from the final time interval are plotted to provide a reference point.

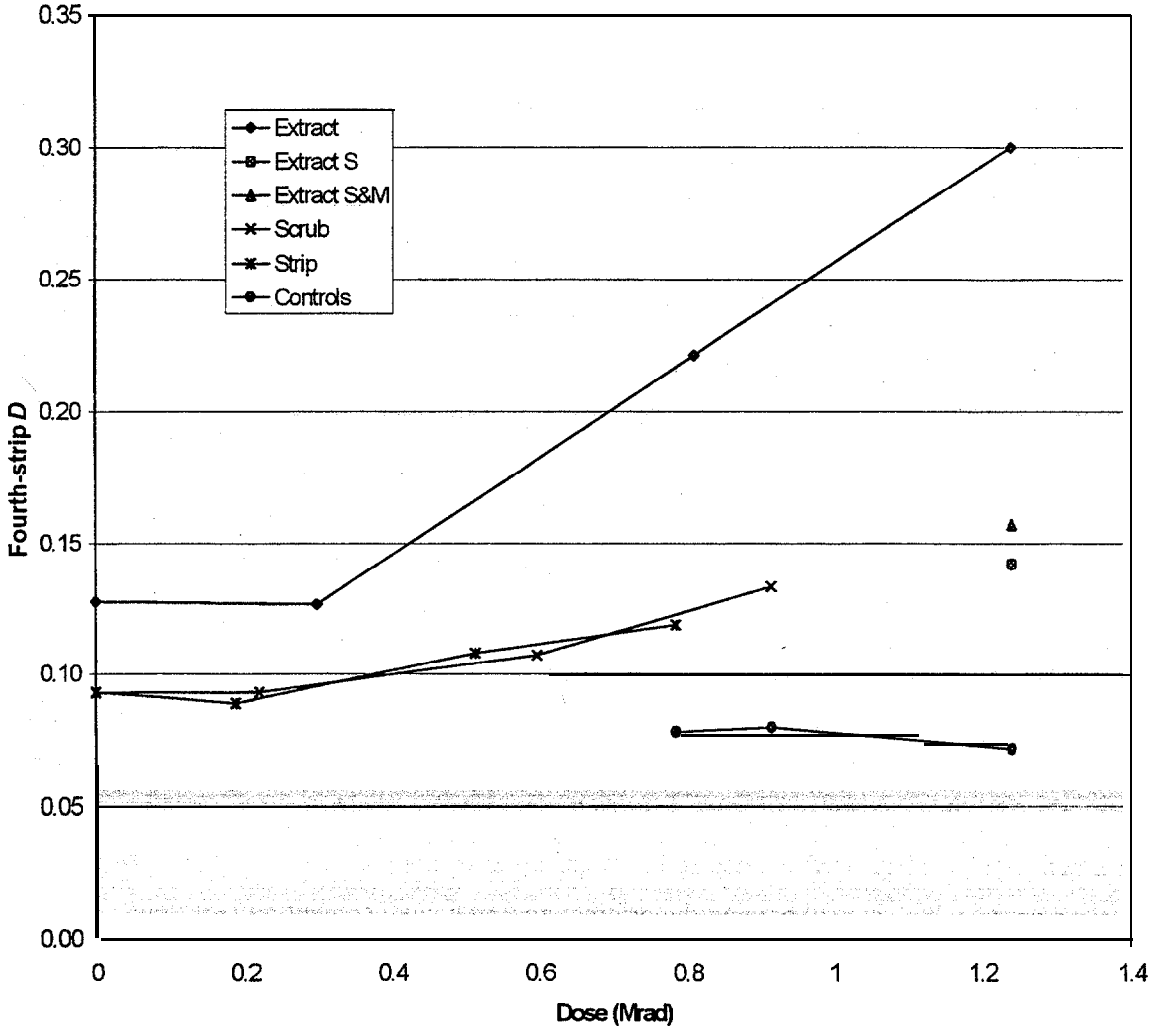


Fig. 24. Cesium distribution ratio (*D*) in the fourth-strip solution for ESS testing of irradiated solvents at 25°C. Data for control samples from the final time interval are plotted to provide a reference point.

The decline in TOA content was suspected of causing the decline in Strip performance. The ESS fourth-strip *D* values are plotted against the measured TOA concentrations for the irradiated solvents in Fig. 25. A general trend may exist; however the scatter in the data is too extensive to make an accurate determination. The most obvious trend appears to be for the Extract data set, which has a linear correlation coefficient of 0.76. It is interesting to note that the other two simulants did not exhibit the same increase in *D* value at the same decreased level of TOA content as did the full simulaut. Thus, there appears to be some evidence implicating the organic compounds contained in the full simulant-but not the other two simulants. Figure 26 replots the data (including the Scrub and Strip samples) in terms of the simulant used in preparation of the samples. In this case, a general trend seems to be evident for the full simulant, with the S and S&M simulants appearing as outliers. However, the large data scatter results in an even lower correlation coefficient of 0.63. The difference between the full sjmulant and the other two simulants involves the organic compounds added to the full simulant. Not enough information is available to conclude that these compounds are responsible in some way for part, or all, of the observed decline in stripping ability; however, it appears likely that this is the case. Figure 27 is a photograph of the irradiated solvents in contact with the full simulant during the extraction part of ESS. The color of some of the solvents was interpreted to indicate the presence of a phenol degradation product. A combination of decreasing TOA concentration and increasing phenol couceutration may be responsible for the observed decline in the ability of the irradiated solvents to strip. The highest 4-*sec*-butylphenol concentrations were measured in the Extract samples, including the Extract S and Extract S&M, but other ongoing studies have demonstrated no significant impact on stripping at the concentrations measured in these samples. Hence, other, as-yet-unidentified phenolic degradation products are possibly implicated, It should be noted that the strip performance did not appear to decline at doses up to 0.3 Mrad, or 3.3 annual equivalent doses, which is well beyond the original goal of annual solvent replacement.

Washing the solvent with mild caustic (0.01-0.50 A4 NaOH) and replenishing the solvent TOA concentration restored the strip performance. After this treatment, the ESS third-strip *D* values for the third time interval were 0.098, 0.105, 0.104, 0.094, and 0.085 for the Extract, Scrub, Strip, Extract S, and Extract S&M irradiated solvents, respectively. The third-strip *D* values for these same samples before restoration were 0.288, 0.139, 0.139, 0.142, and 0.153, respectively. The third-strip *D* values for pristine solvent were 0.070 and 0.083 after two cycles through ESS. However, the ESS third-strip *D* value for nonirradiated solvent that had been cycled through a centrifugal contactor for throughput and mass balance testing averaged 0.095. As noted above, the full simulant Extract sample suffered the most significant decline. Consequently, it exhibited the most dramatic recovery (from about 0.3 down to about 0.1), in line with baseline solvent previously processed with the simulant. There is an unexplained difference in the Strip *D* value between the T_0 irradiated solvents (about 0.1 for the ESS fourth strip) and the T_3 control solvents (about 0.08 for the ESS fourth strip). The samples, including T_0, received a significant dose beyond the nominal dose, calculated only for the time on the shaker table, which may help explain this discrepancy.

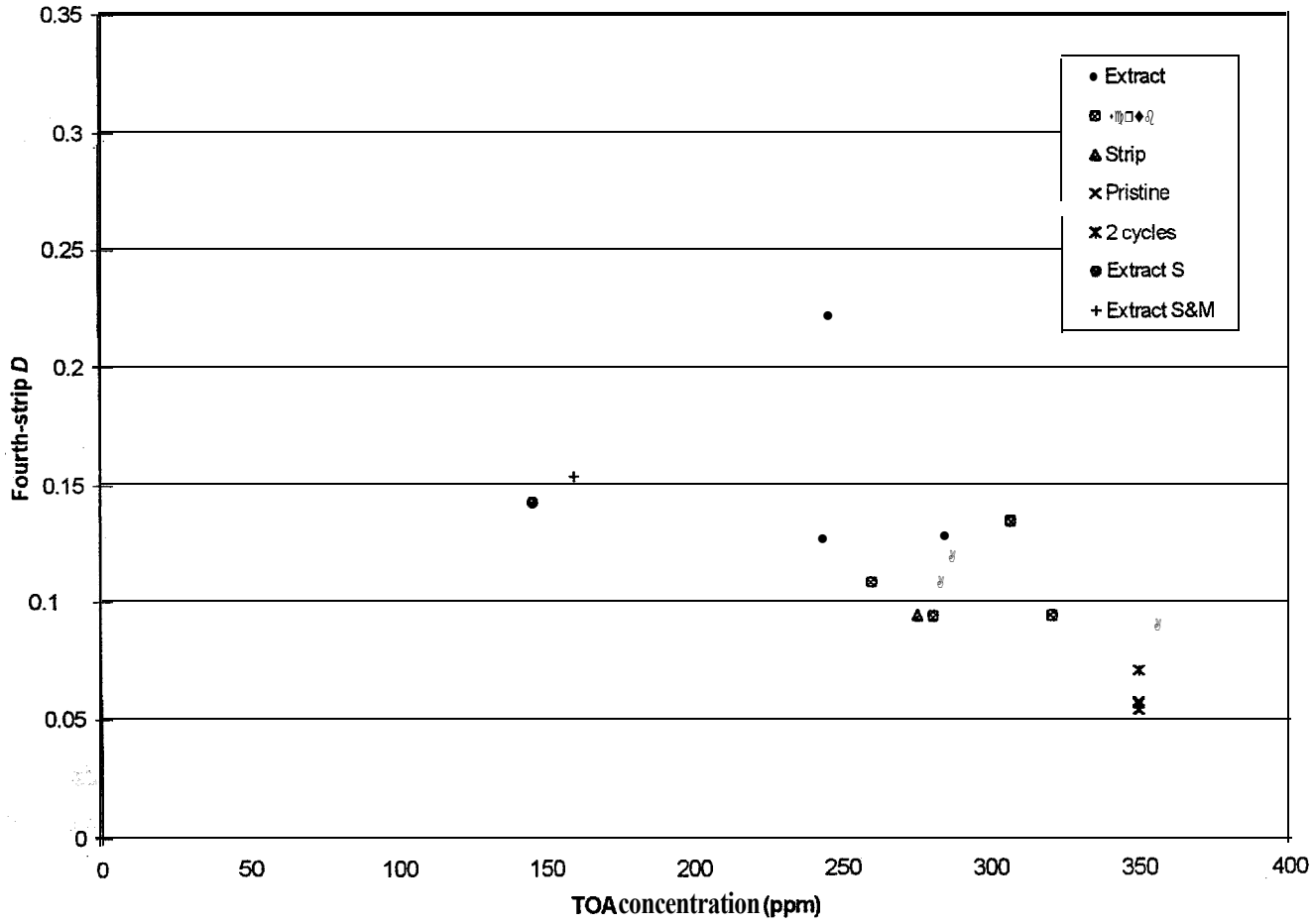


Fig. 25. ESS fourth-strip cesium distribution ratio (*D*) vs TOA concentration in solvent.

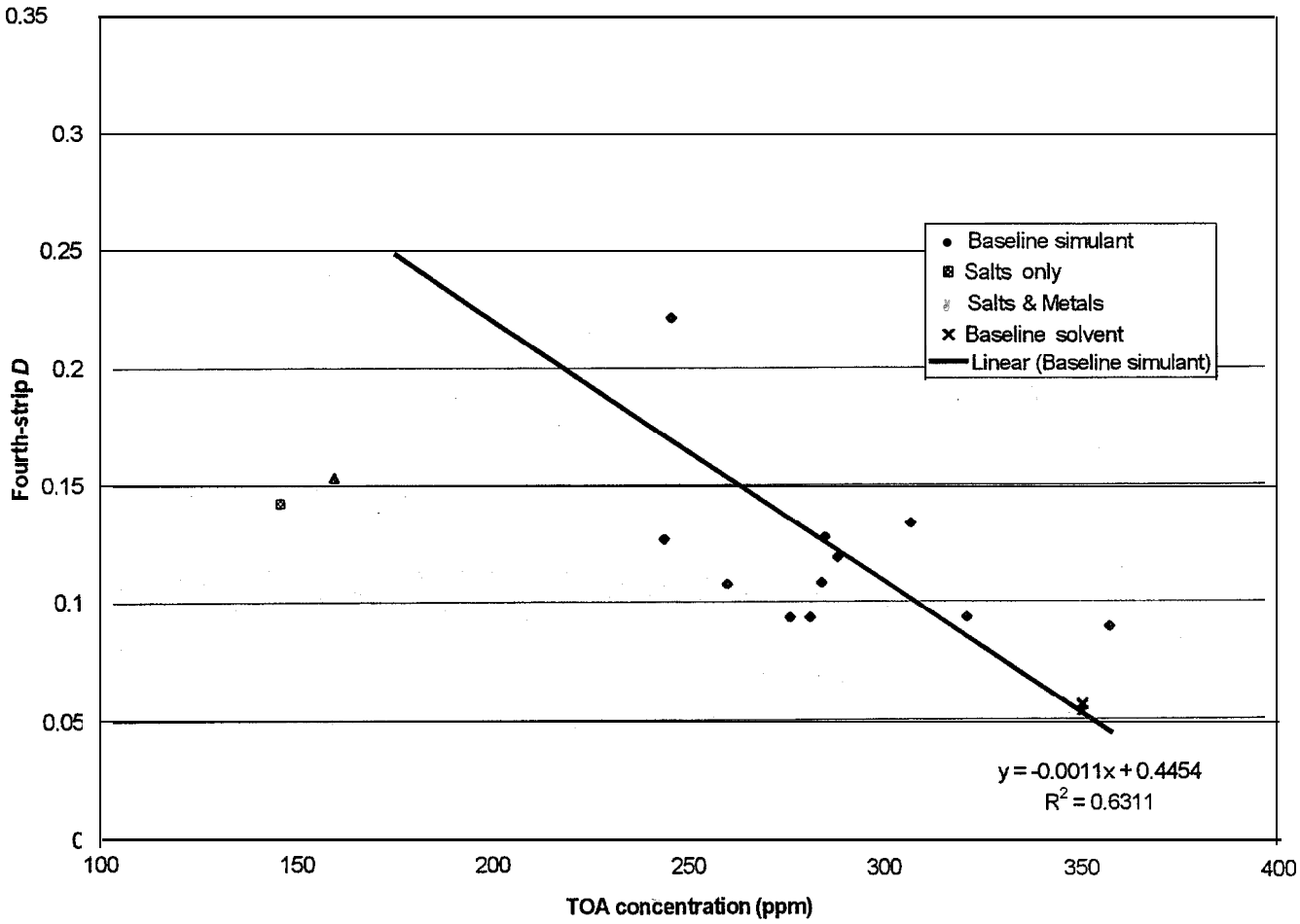


Fig. 26. ESS fourth-strip cesium distribution ratio (*D*) vs TOA concentration in solvent of irradiated samples.

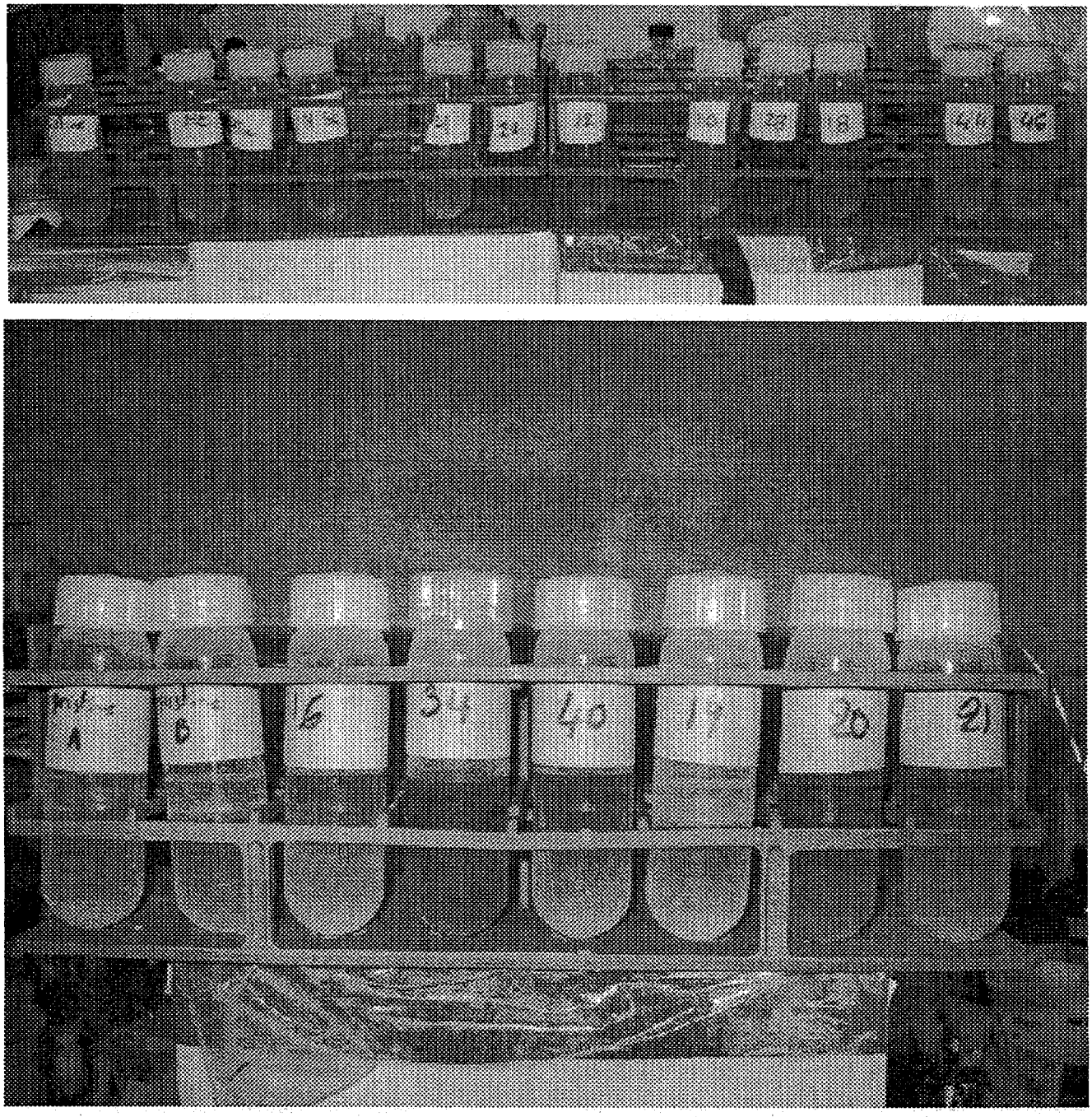


Fig. 27. Photographs of irradiated solvents in contact with simulant during ESS extraction. Top photograph—T_0: HE, HSb, HSp; T_1: 4, 22, 12; T_2: 10, 28, 18; T_3: Extract-S (44), T_3: Extract-S&M (46). Bottom photograph--?;: 16, 34, 40; T_3: Controls: 19, 20, 21.

8. SUMMARY AND CONCLUSIONS

The following effects were noted for the solvent as a result of self-irradiation while in contact with the aqueous solutions. of Extract, Scrub, or Strip for up to 13.5 (or 16.5, if the doses estimated in Appendix C are included) equivalent annual doses:

(1) color change,

(2) significant decline in TOA concentration,

(3) insignificant buildup of the degradation product 4-*sec*-butylphenol concentration, and

(4) significant decline in its ability to be stripped.

The sample phase distributions and break times remained about the same, and no third phase was evident. Solvent degradation was observed in the organic analysis and performance evaluation of the irradiated solvents. No significant decline in solvent concentration was noted for either the calixarene cesium extractant or the modifier, but the TOA concentration declined by up to one-half of the pristine solvent baseline value. In addition, a product from degradation of the modifier, 4-*sec*-butylphenol, was observed to increase with dose, although its concentration was never significant. No decline in extraction or scrubbing performance was observed in the solvent with irradiation, but the solvent did lose its ability to strip as the self-irradiation dose increased. TOA was added to improve stripping performance, so loss of TOA could be expected to affect stripping performance. The loss of stripping performance may also be related to unidentified degradation products and the organic compound(s) extracted from the simulated liquid waste. Other work indicates that the 4-*sec*-butylphenol concentration was not high enough to influence stripping. Unlike the operation expected for a full-sized plant, no washing or TOA replenishment was done during the self-irradiation of the batches during this study. Thus, cumulative solvent degradation at each dose was observed in this study, with no attempts at intermittent recovery during the period of self-irradiation. These results indicate that the solvent could be used for at least 3 years in the solvent extraction process proposed for SRS without significant degradation of solvent performance. In addition, the cumulative degradation of solvent stripping ability over the equivalent of 13.5 years of plant irradiation was overcome by mild caustic washing (0.01-0.50 *M* NaOH) and replacement of the lost TOA. These results imply that solvent replacement may occur an order of magnitude or more beyond the target time for annual replacement, if caustic washing and TOA replacement are part of the routine plant operation. Note that the estimates of equivalent annual doses cited in the report are conservative. These are estimates only of the dose received while on the shaker table and do not include the significant dose received during preparation and processing of the samples, which can add another three or more equivalent annual doses.

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Appendix A

SOURCE OF MATERIALS

Table A.1. Source of materials

Equipment or chemical	Source	ID or lot number
Equipment		**ID**
Stainless steel 55-gal drum	ORNL Stores	UN/1A2/X425/s/98 UN/1A2/X1.4/250/98 USA/M4492 LMES-6085
Deionized water	House distilled water, purified through Barnstead e-pure system (product water: 0.30 µmho/cm, <1 ppm TOC)	Barnstead Model # D4641
Mixer (for 55-gal drum of simulant)	Lightning direct drive, variable-speed mixer with 316 stainless steel propeller and shaft	Model No. EV1P25M
Balances	Mettler Mettler Ohaus	PM1200 AE200 B-5000
Pipettes	Kimax Type A	20 mL 100 mL
Volumetric flasks	Pyrex Type A	1 L
Stainless steel 2.2-L TCLP filtering apparatus	Associated Design and Manufacturing Company	
Porous sintered stainless steel filters, 0.5 µm	Associated Design and Manufacturing Company	
Teflon PFA coated Type J thermocouple	Calibrated by ORNL Instrumentation and Controls Division	M093384 (on calibration sheet)
Digital temperature display	Omega	
Plastic (Teflon, PP, HDPE) labware (beakers, bottles, separatory funnels)	VWR Scientific Products	
Stainless steel biological transfer bottles, 250 mL	Eagle Stainless Container	PS-6F
Innova® Gyrotory® orbital platform shakers	New Brunswick Scientific Co., Inc.	Model 2350
Vortex mixer	VWR Scientific Products	Genie 2
Magnetic stirrer	Thermodyne	Cimarec 3
Nonrefrigerated benchtop centrifuge	VWR Scientific Products	Allegra 21, Beckman Coulter
10-L HDPE carboy with molded bottom spigot	VWR Scientific Products	16101-404 (Nalgene 2319-0020)
Overhead mixer	Ikalabortechnik	RW16
Chemical		**Lot number**
NaOH flakes	Mallinckrodt	7712N06637 7712N37605
$CuSO_4 \cdot 5\ H_2O$	EM Science	8052
Na_2CrO_4	J. T. Baker	7350
0.1 *N* NaOH	J. T. Baker	H16531
$Zn(NO_3)_2 \cdot 6\ H_2O$	J. T. Baker	146086
$Pb(NO_3)_2$	J. T. Baker	21014
$Fe(NO_3)_3 \cdot 9\ H_2O$	J. T. Baker	763623
0.1 *M* HNO_3	J. T. Baker	J46530
$Al(NO_3)_3 \cdot 9\ H_2O$	J. T. Baker	N1154
$NaNO_3$	J. T. Baker	M14156

Table A.1 (continued)

Equipment or chemical	Source	ID or lot number
Chemical		**Lot number**
KNO_3	J. T. Baker	K19148
NaF	J. T. Baker	M44142
$Na_2HPO_4 \cdot 7\ H_2O$	J. T. Baker	M31146
$NaNO_2$	J. T. Baker	39341002
$Na_2CO_3 \cdot H_2O$	J. T. Baker	M05148
Na_2SO_4	EM Science	127273–122783
$Na_2MoO_4 \cdot 2\ H_2O$	J. T. Baker	N25623
NaCl	Fisher Scientific	745862
$SnCl_2 \cdot 2\ H_2O$	EM Science	38132918
NH_4NO_3	Fisher Scientific	765526
$Pd(NO_3)_2$ (10 wt % in 10 wt % HNO_3)	Aldrich	11519MU
$Rh(NO_3)_3$ (~10 wt % in >5 wt % HNO_3)	Aldrich	11506DU
Ruthenium chloride solution (40.19% Ru)	Matthey Bishop, Inc.	L0-B90-1
$AgNO_3$	Fisher Scientific	743846
CsCl	Mallinckrodt	7715KTKV
$^{137}CsCl$	J. L. Shepherd and Associates	
Washed solvent Cs-7SB/Isopar® L	ORNL (Peter Bonnesen)	PVB B000718-149W
$Na_2C_2O_4$	EM Science	38190834
$Na_2SiO_3 \cdot 9\ H_2O$	J. T. Baker	M16144
$Hg(NO_3)_2 \cdot H_2O$		
0.1 *N* HNO_3	J. T. Baker	N09508

Appendix B

QA DATA FOR THE SOLVENT LOT USED IN SELF-IRRADIATION TESTING (INCLUDING ESS TESTING OF THE PRISTINE SOLVENT)

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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Roger Spence
Chemical Technology Division
ORNL

July 18, 2000

Dear Roger:

Here are the QA data results for the 7 L of **Washed Solvent Cs-7SB / Isopar® L ORNL Lot No. PVB B000718-149W,** delivered in two 4 L Wheaton plastic coated glass bottles (pre-cleaned following the QA procedure). The solvent composition is 0.010 M BOBCalixC6 (IBC Advanced Technologies Lot No. 000711HMKC-0004), 0.500 M Cs-7SB Modifier (Lot No. B000718-48DM), 0.001 M Trioctylamine (Lot No. B000718-105L) in Isopar® L (Lot No. 03051700-5-2).

The performance of the solvent in batch contacting tests is as follows (1.0 mL each phase, 60 min contact at 25 °C via end-over-end rotation in 3.6 mL polypropylene Cryule® vials):

Results of Batch-Equilibrium Tests at 25 °C for Solvent B000718-149W with Various Aqueous Phases (average of three determinations).

Composition of Aqueous Phase	D_{Cs}, Cs-7SB/Isopar L, B000718-149W
Simple simulant (2 M NaOH, 3 M $NaNO_3$, 5.0E-04 M $CsNO_3$)	17.06 ± 0.38
0.05 M HNO_3	1.54 ± 0.03
0.001 M HNO_3	0.0279 ± 0.0004

The distribution values fall within the acceptable range for solvents for this procedure (see table below).

Acceptable Cesium Distribution ratios obtained from QA Procedure for Cs-7SB/Isopar L Solvents (95% confidence level)

Composition of Aqueous Phase	D_{Cs} range, Cs-7SB/Isopar L, 95% Confidence
Simple simulant (2 M NaOH, 3 M $NaNO_3$, 5.0E-04 M $CsNO_3$)	36.3 ± 1.1
0.05 M HNO_3	1.46 ± 0.12
0.001 M HNO_3	0.0280 ± 0.0047

Sincerely,

Peter Bonnesen

Tamara Keever

Appendix C

ESTIMATION OF SELF-IRRADIATION IN ADDITION TO THE NOMINAL VALUE

Appendix C. ESTIMATION OF SELF-IRRADIATION IN ADDITION TO THE NOMINAL VALUE

The nominal self-irradiation assumed in this report was only that received during the time the batch samples were on the shaker table. In fact, exposure to radiation occurred from the moment the solvent was added to the spiked simulant. The material included in this appendix contains estimates of the dose received by the solvent samples before the samples were placed on the shaker tables (including the dose received by the T_0 samples) and after the samples were removed from the shaker tables. The dose was estimated at times previous to the time that most of the activity was stripped from the solvent:' There is still residual activity in these stripped samples, but the exposure and rate of dose absorbed are far below the levels during the self-irradiation portion of this experiment. The ^{137}Cs activity levels during that portion correspond to the activity levels expected during actual plant operation, at SRS. The dose rates listed in Table 8 were used to make the estimated doses in this appendix. These dose rates are specific to the geometry, phase quantities, and activity concentrations of the batch samples stored in the SS bottles for this self-irradiation experiment. Thus, the doses reported here are simply rough estimates. These estimates should be reasonable, as the same liquids at about the same activity levels were involved. The main differences are the variations in vessel geometries and phase quantities during the large batch preparation at the beginning of the project and the sample evaluation, phase separation, and activity stripping at the end. At least for the large batch preparation, it is expected that the actual dose rate was higher, making this estimate conservative.

Table C. 1 lists the time lines for the preparation and subdividing of the batch samples used in this study, along with the estimated dose from the time the solvent was added to the spiked simulant until the batch samples were placed on the shaker table. Placement of the samples on the shaker table signaled the start of the nominal self-irradiation. The estimated doses received on the shaker table are listed in Table 9. These doses are used as reference doses for the various time intervals throughout the report. The values listed in Table C.l (0.18-0.24 Mrad) should be added to these doses to obtain values closer to the true doses received by the solvent samples.

Table C. 1 also lists the estimated doses for the T_0 samples. These samples were intended to represent the solvent at the beginning of self-irradiation and should have been practically indistinguishable from the control samples during evaluation. In actuality, they received doses ranging from 0.23 to 0.29 Mrad by the time all the samples had been prepared and the T_0 samples had been evaluated. These values represent equivalent annual doses of 2.5-3.1 years of plant operation and may explain some of the observed differences between these samples and the controls.

Table C.2 lists the additional doses estimated to be received by the later time-interval samples between the time when the samples were removed from the shaker table and most of the activity was stripped from them for organic analysis and performance testing. Note that the break times, third-phase assessments, and subsamples (for measurement of concentrations) were taken during this time period. Therefore, this extra dose does not apply to all the sample evaluations; it pertains only to the two more important evaluations of analysis of organic constituents and performance testing (ESS).

Table C.1. Time line estimating dose before start of nominal self-irradiation and dose received by the T_0 samples

		Extraction-S		Extraction-S&M		Extraction		Scrub		Strip	
Date, Time	Action	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)
Time line for batch preparation prior to nominal start of self-irradiation with placement of samples on shaker table (10/5/00, 11:15 a.m.)											
9/19/00, 10:43	Added solvent to spiked "salts only" simulant	0.0	0								
9/19/00, 13:59	Added solvent to spiked "salts & metals" simulant	3.3	0.00	0.0	0.00						
9/20/00, 9:15	Added solvent to large batch of spiked full simulant	22.5	0.01	19.3	0.01	0.0	0.00				
9/20/00, 15:17	Separated most of full simulant from large batch	28.6	0.02	25.3	0.02	6.0	0.00				
9/20/00, 16:10	Lost ~40% of loaded solvent from large batch	29.4	0.02	26.2	0.02	6.9	0.00				
9/22/00, 9:39	Consolidated remaining solvent and removed last aqueous phase	70.9	0.04	67.7	0.04	48.4	0.03				
9/26/00, 11:29	Subdivided Extraction batch samples into SS bottles	168.8	0.11	165.5	0.10	146.2	0.09				
9/26/00, 13:31	Added scrub solution to large batch of loaded solvent	170.8	0.11	167.5	0.10	148.3	0.09	0.0	0.09		
9/27/00, 14:13	Subdivided Scrub batch samples into SS bottles	195.5	0.12	192.2	0.12	173.0	0.11	24.7	0.10		
9/27/00, 14:16	Separated and centrifuged scrubbed solvent	195.6	0.12	192.3	0.12	173.0	0.11	24.8	0.10		0.10
9/28/00, 9:40	Added strip solution to large batch of scrubbed solvent	215.0	0.13	211.7	0.13	192.4	0.12	44.2	0.11	0.0	0.11
9/29/00, 10:30	Subdivided Strip batch samples into SS bottles	239.8	0.15	236.5	0.15	217.3	0.14	69.0	0.12	24.8	0.12
10/5/00, 11:15	Nominal start of self-irradiation; placed SS bottles on shaker	384.5	0.24	381.3	0.24	362.0	0.23	213.7	0.19	169.6	0.18
					Number of equivalent annual doses (y):						
			2.62		2.59		2.46		2.07		1.95
Evaluation of T_0 samples											
10/6/00, 9:44	Break-time and third-phase evaluations					384.5	0.24	236.2	0.20	192.1	0.19
10/9/00, 15:00	Separated and stripped Extract and Scrub solvents					461.8	0.29	313.5	0.24	269.3	0.22
10/10/00, 0:15	Separated and stripped Strip solvent									288.6	0.23
					Number of equivalent annual doses (y):						
							3.14		2.58		2.46

Table C.2. Additional doses received by solvents after conclusion of nominal irradiation

Date, Time	Action	Extraction-S		Extraction-S&M		Extraction		Scrub		Strip	
		Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)	Time (h)	Dose (Mrad)
					Evaluation of T_1 samples						
10/25/00, 9:24	Removed from shaker table, ending nominal irradiation					0.0	0.00	0.0	0.00	0.0	0.00
10/25/00, 4:48	Measured break times					5.4	0.00	5.4	0.00	5.4	0.00
10/30/00, 4:43	Separated and stripped solvent					125.3	0.08	125.3	0.06	125.3	0.05
					Number of equivalent annual doses (y):						
							0.85		0.63		0.54
					Evaluation of T_2 samples						
11/28/00, 4:30	Removed from shaker table, ending nominal irradiation					0.0	0.00	0.0	0.00	0.0	0.00
11/30/00, 6:18	Evaluated break times and third phase, and subsampled					49.8	0.03	49.8	0.02	49.8	0.02
12/1/00, 16:20	Separated and stripped solvents					73.8	0.05	73.8	0.03	73.8	0.03
					Number of equivalent annual doses (y):						
							0.50		0.37		0.32
					Evaluation of T_3 samples						
12/27/00, 8:20	Removed from shaker table, ending nominal irradiation	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
12/28/00, 5:13	Separated Scrub and Strip solvents	30.9	0.02	30.9	0.02	30.9	0.02	30.9	0.01	30.9	0.01
12/29/00, 5:25	Separated remaining solvents and stripped all	55.1	0.03	55.1	0.03	55.1	0.03	55.1	0.02	55.1	0.01
					Number of equivalent annual doses (y):						
			0.37		0.37		0.37		0.27		0.15

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