Impact of Irradiation on Solvent used in SRS Waste Treatment Processes - 9122

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ABSTRACT

Savannah River Site (SRS) will use a Caustic Side Solvent Extraction (CSSX) process to selectively remove radioactive Cs-137 from the caustic High Level Waste (HLW) salt solutions stored in the large carbon steel waste tanks in the SRS Tank Farm. This HLW resulted from several decades of operations at SRS to produce nuclear materials for the United States Government. The removed Cs-137 will be sent to the Defense Waste Processing Facility (DWPF) where it will be immobilized along with the HLW sludges from the SRS Tank Farm into a borosilicate glass that will be put into permanent disposal. Currently the CSSX process is operating on an interim basis in the Modular Caustic Side Solvent Extraction Unit (MCU) facility. Eventually the process will occur in the full scale Salt Waste Processing Facility (SWPF) currently being built. The organic solvent developed for the process is primarily a mixture of the Isopar® L (a blend of C_{10}-C_{12} branched alkanes such as dodecane) and an alkyl aryl polyether added as a Modifier (commonly called Cs-7SB) to enhance the solubility of the extractant which is a calixarene-crown ether. The solvent also includes trioctylamine to mitigate the adverse impact of lipophilic agents on the stripping of the cesium into nitric acid. Since the mixture is primarily organic hydrocarbons, it is expected that radiolysis of the mixture with gamma rays and beta particles from the Cs-137 will produce the flammable gas H_2 and also eventually degrade the solvent. For example, much research has been performed on the radiolysis of the organic solvent used in the tributylphosphate (TPB) extraction process (PUREX process) that has been used at SRS and in many other countries for several decades to separate U and Pu from radioactive U-235 fission products such as Cs-137.[1]

The purpose of this study was to investigate the radiolysis of the organic solvent for the CSSX process. Researchers at Savannah River National Laboratory (SRNL) irradiated samples of solvent with Co-60 gamma rays. Prior to the irradiation, the solvent was contacted with the aqueous solutions that will be used in the MCU and SWPF facilities. These were the aqueous caustic salt feed, the scrub solution, and wash water. The rates of radiolytic H_2 production were measured both by determining the composition of the gases produced and by measuring pressures produced during radiolysis. The irradiated solvents were then analyzed by various analytical techniques to assess how much of the Isopar® L, the Modifier, and the extractant had decomposed.

Results indicated that the rates of H_2 production in terms of G values (molecules of H_2 produced per 100 eV of energy absorbed) were very similar to those measured for the organic solvent in the PUREX process.[1] The rates calculated in terms usable for plant operation were 5.9×10^{-6} Liter of H_2 (at 25 °C) per hour per liter of spent MCU solvent and 9.6×10^{-5} Liters of H_2 per hour (at 25 °C) per liter of solvent during SWPF operation. This study also determined that degradation of the solvent should not be significant. For example, solvent irradiated to a dose of 32×10^4 Grays, a conservative estimate of one year's dose in the SWPF, showed 14% decomposition of the crown ether extractant, and only ~1% of the Modifier and the Isopar® L.

INTRODUCTION

After many studies the CSSX process was identified as the preferred technology for removing Cs-137 from the HLW salt solutions stored in the Tank Farm at SRS.[2-6] As a result, the MCU facility was built in the SRS Tank Farm to process liquid waste for an interim period until the full scale SWPF could be built and begin operations. Both the MCU and SWPF use the CSSX technology, although the facilities differ in size and processing rate.

In the CSSX process, the solvent contacts aqueous HLW salt solution in centrifugal contactors. During the contact, cesium transfers from the aqueous phase (i.e., salt solution) to the organic solvent and the aqueous and organic phases are separated. The solvent is then contacted with a scrub solution (i.e., 0.05 M nitric acid) and then stripped of cesium by dilute nitric acid (0.001 M) in subsequent contactors. Following separation of the strip solution from the solvent, the strip solution is transported to the DWPF where the Cs-137 is immobilized into a borosilicate glass for safe final disposal. The decontaminated aqueous salt solution is transferred via a piping system for ultimate disposal as low level waste through the Saltstone Production Facility. The stripped solvent is washed with 0.01 M NaOH to prepare it for reuse in the process. During the solvent extraction process, the solvent degrades due to radiolysis and eventually has to be replaced. It has been estimated that after the solvent can no longer be used, it contains 0.08 Ci/liter of entrained Cs-137.[7]

The organic solvent for this process contains four components. The main component (69.14 wt %) is Isopar® L, a mixture of branched chained aliphatic hydrocarbons such as dodecane.[3,4,5,6] The extractant for Cs-137 is a calixarene-crown ether, calix[4]arene-*bis*(tert-octylbenzo-crown-6), called BOBCalixC6. It is only present at 0.94 wt %. The second main component is a Modifier (29.8 wt %), which is an alkyl aryl polyether. The Modifier is added to keep the extractant dissolved in the solvent and increase its ability to extract cesium in the process. The Modifier is 1-(2,2,3,3,-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, and is also called Cs-7SB. Finally the solvent contains 0.12 wt % of a suppressant, trioctylamine (TOA), which descreases the effects of anionic organic impurities and improves the extraction of cesium from the solvent by the dilute nitric acid in the stripping section.

The radiation field existing in the MCU and SWPF processes will degrade the solvent, leading to the generation of hydrogen gas. Both facilities need to know the rate of solvent degradation and hydrogen generation. The storage of cesium contaminated MCU solvent in a drum also poses a hazard by the accumulation of radiolytically generated H_2 in the drum. Finally degradation of solvent in the SWPF process could reduce process efficiency or adversely impact process safety due to hydrogen generation.

In this study SRNL researchers contacted the solvent with aqueous liquids representing solvent washing for reuse in the process, the initial extraction step removing the cesium from the HLW salt solution, and the solvent scrubbing step of the process. They then irradiated the solvent samples with gamma rays at known dose rates to measure H_2 production and solvent degradation. The researchers analyzed the gases produced by radiolysis of some samples and measured the radiolytic pressures generated from others. They also analyzed the liquid solvent before and after irradiation to measure solvent decomposition.

EXPERIMENTAL APPROACH

The authors performed two sets of irradiation tests. The first set was directed toward measuring the radiolytic hydrogen generation and solvent degradation from spent MCU solvent being temporarily stored in drums. The Cs-137 concentration in the spent solvent is assumed in this study to be 0.08 Ci/L. The second set of tests was directed at measuring radiolytic hydrogen production during operation of the extraction and scrubbing steps in the SWPF process. These are the process steps where the dose to the solvent will be the largest.

SRNL researchers collected an approximately 100-mL sample of MCU solvent. They washed the solvent by contacting it with 0.01 M NaOH, and analyzed it by Gas Chromatography–Mass Spectroscopy Semi-volatile Organic Analysis (GCMS-SVOA), by High Performance Liquid Chromatography (HPLC), and by Fourier Transfer Infrared (FTIR) Spectroscopy. These methods measured the Isopar® L, Modifier, BOBCalixC6, and trioctylamine concentrations. The measured concentrations agreed with those given above so aliquots of this sample were used for the radiolysis tests.

Washed MCU Solvent Irradiation Testing

Prior to irradiation, aliquots of the organic solvent were contacted with the 0.01 M NaOH to simulate the processing the solvent would experience prior to storage and ensure that during the irradiation the solvent was saturated with the aqueous solution. The organic solvent was then separated from the aqueous solution and known amounts (~15 mL) placed into each of three stainless steel vessels. The vessels could be sealed with a screw cap that contained a valve. Each vessel contained ~30 mL of air in the void space between the sample and the valve on the cap. After the irradiation each vessel could be connected to a header containing a gas chromatograph (GC) for determination of the composition of the gas produced. A vacuum system was used to evacuate the connection to the GC. The total volume of this system including the void space above the sample was ~95 mL. A vessel containing 0.01 M NaOH was also irradiated as a control sample. All the vessels were irradiated with a 5-year equivalent dose (based on 0.08 Ci/L (0.3 Ci./gallon) of Cs-137 that was estimated to be in the spent solvent.[7] This dose was 7.1×10^4 Grays. Equation (1) shows the calculation.

$$\left(0.08\frac{\text{Ci}}{\text{L}}\right)\left(4.84\frac{\text{W}}{\text{kCi}}\right)\left(\frac{1\,\text{kCi}}{1000\,\text{Ci}}\right)\left(\frac{1\,\text{eV/s}}{1.6\times10^{-19}\ \text{W}}\right)\left(3.15\times10^{7}\ \frac{\text{s}}{\text{y}}\right)$$
$$\left(\frac{1\,\text{L}}{852\,\text{g}}\right)\left(\frac{1\,\text{Gray}}{6.24\times10^{15}\ \text{eV/g}}\right)\left(5.0\ \text{y}\right) = 7.2\times10^{4}\ \text{Gray} \qquad \text{(Eq 1)}$$

The irradiations occurred in SRNL’s Co-60 gamma ray source and were performed at 50 °C. The dose rate of the radiation was determined with the Fricke Dosimeter [8] and was 3.0×10^3 Grays/h. After the irradiation, the SRNL researchers placed the vessels individually into the sampling apparatus to measure the composition of the gases produced. They first connected a vessel to the vacuum system and the GC. While the valves to the solvent vessel and the GC were closed, the connecting lines were evacuated. After evacuating the line, they disconnected the vacuum line and opened the line to ambient air. They then opened the valve to the GC and sampled the air. When the air samples contained less than 10 ppm hydrogen as well as oxygen and nitrogen concentrations typical of air in the hood holding the GC, the system was deemed sufficiently purged. The line was again evacuated and then closed. The researchers then opened the valves to the GC and the irradiation vessel. The gas expanded into the GC and three samples of the gas were then analyzed by the GC. Excellent agreement was found between the second and third measurements and the third concentration was used as the composition of the gas from that irradiated sample. Following the analysis of gas sample from the first vessel, the vessel was disconnected from the sampling apparatus and the header was then evacuated using vacuum system in the hood. This step was followed by analyzing several air samples on the GC until the hydrogen in the lines was considered purged (measured concentration < 10 ppm). This process was repeated for the remaining three vessels. The three organic samples of the irradiated solvent were then analyzed by FTIR and HPLC spectroscopy.

Radiolysis of Solvent Simulating Processing in the SWPF

Personnel collected three samples of washed organic solvent containing all four components (Isopar® L, Modifier, Trioctyl amine, and BOBCalixC6). They contacted two solvent samples with a salt solution that was 1.9 M NaOH, 2.1 M $NaNO_3$, and 0.52 M $NaNO_2$ simulating the HLW feed to the SWPF. They also contacted a third sample with 0.05 M HNO_3 that simulated the scrub acid solution that will be used to treat the organic solvent prior to stripping the Cs-137 from the solvent. The scrub acid solution was selected rather than the 0.001 M HNO_3 strip solution so that testing bracketed the entire pH range the solvent will experience

Known amounts (~ 30 mL) of solvent were placed into stainless steel vessels, containing ~ 100 mL of air. They irradiated these samples in SRNL's Co-60 source at 50 °C to provide insight to H_2 generation at a temperature well exceeding the nominal processing and storage temperatures for the solvent. Each vessel was connected to a sensitive pressure transducer that measured the pressure in inches of H_2O above atmospheric. The data loggers were programmed to take pressure measurements every 5 to 10 minutes during the irradiation. The measurements were recorded by a computer. They irradiated the vessels with a dose of 32×10^4 Grays which is 107 hours of irradiation time. This dose was selected to a conservative maximum dose exceeding that the solvent would receive in one year of service in the SWPF and to match dose being used in a parallel study currently being performed at another national laboratory.

RESULTS AND DISCUSSION

Radiolysis of Washed MCU Solvent

Table I shows the composition of the gas measured by the GC after the samples of washed solvent and the 0.01 M NaOH wash solution had been exposed to a dose of 7.2×10^4 Grays in the Co-60 source. Table I also shows the concentrations in air measured in the hood containing the samples. In the last column in the table, the ratios of N_2 to O_2 measured in the gas samples are given.

Table I. Concentration of Gases (Mole Percent) Measured by Gas Chromatograph

Sample	H_2	O_2	N_2	CO_2	N_2/O_2 Ratio
Washed MCU Solvent, 1	3.92	10.0	75.6	0.29	7.56
Washed MCU Solvent, 2	4.16	9.9	75.8	0.33	7.7
Washed MCU Solvent, 3	4.31	9.8	76.1	0.32	7.8
0.01 M NaOH	1.98	16.4	72.0	0.00	4.39
Hood Air	0.00	19.5	73.0	0.00	3.74

Results in Table I show that the radiolysis of the organic solvent has produced H_2 along with some CO_2. The results also indicate that radiolysis of the solvent has caused O_2 to be depleted based on comparison of the N_2/O_2 ratios in the last column for the irradiated samples with the ratio measured for air.

There is extensive published data in the literature of radiation chemistry that indicate that H_2 is the main gaseous product in the radiolysis of aliphatic hydrocarbons.[9] In the radiolysis of commercial organic solvents used in the solvent extraction purification of U and Pu using TBP as an extractant, it has been shown that H_2 is the main gaseous product. (See Table 11 on page 254 in Reference 1) The chemical mechanism for H_2 production from radiolysis of aliphatic hydrocarbons primarily involves H atoms and organic radicals produced by the radiation.[9] The H atoms abstract an H atom from the aliphatic hydrocarbon and form H_2. This leaves an organic radical that can recombine with another organic radical or can react with the dissolved O_2 in the sample. These reactions with O_2 have been shown to be very efficient and fast.[10] This is a possible mechanism to explain the decreases observed for the O_2 in the air irradiated with the MCU solvent. The dissolved O_2 in the MCU solvent reacts with the organic free radicals to produce organic peroxides. As the dissolved O_2 concentration decreases in the solvent, O_2 from the air diffuses into the solvent and the O_2 partial pressure decreases. Note that the O_2 is only slightly depleted in the radiolysis of the wash solution 0.01 M NaOH that contains no added organics.

To compare the results with published radiation chemistry data, G values for the production of H_2 and CO_2 were calculated. These G values can also be used to calculate the rate of gas production if the dose rate of the radiation is known. The following equation was used to calculate the G values.

$$G_i = \left(\frac{\%X_i}{100}\right)\cdot\left(\frac{M\cdot N\cdot V}{D\cdot M_s\cdot C}\right)\cdot 100 \qquad \text{(Eq 2)}$$

In this equation

G_i = molecules of gas i produced per 100 eV of radiation absorbed
$\%X_i$ = mole percentage of gas i in the gas
M = the moles of gas in 1 Liter at ambient temperature of 25 ºC (0.0408 Mole/L)
N = Avogadro's number (6.02 x 10^{23} molecules/mole)
V = liters of gas being analyzed (0.095 L)
D = the absolved dose in Grays (7.2 x 10^4 Grays)
M_s = mass of MCU solvent irradiated (15 mL × its density of 0.85 g/mL)
C = the conversion of Grays to eV/g (6.24 x 10^3 eV/g per Gray)

The second factor of 100 converts the results from molecules per eV to molecules per 100 eV, the units of a radiation chemistry G value.

The decrease in the mole percentage of O_2 was calculated by assuming that N_2 is inert and if O_2 was not depleted by radiolysis then the ratio N_2/O_2 should not change from what it is in the air (3.74). The percent O_2 lost due to radiolysis was then calculated from the following equation

$$\%O_2(lost) = \frac{\%N_2}{3.74} - \%O_2(meas) \qquad \text{(Eq. 3)}$$

where

$\%O_2$(lost) = mole percentage of O_2 depleted by the radiolysis
$\%N_2$ = mole percentage of N_2 measured in the gas
$\%O_2$(meas) = mole percentage of O2 measured in the gas.

Results for the G value calculations are shown in Table II.

Table II. G Values (molecules/100 eV) Calculated for Gases from Radiolysis of Washed MCU Solvent Contacted with 0.01 M NaOH Wash Solution

Sample	$G(H_2)$	$G(CO_2)$	$G(-O_2)$
Washed MCU Solvent, 1	1.6	0.12	-4.2
Washed MCU Solvent, 2	1.7	0.14	-4.3
Washed MCU Solvent, 3	1.7	0.13	-4.3
0.01 M NaOH	0.82	0.00	-1.2

The calculated G values for H_2 production for the three tests of the radiolysis of the MCU solvent are in very good agreement and are within the range of $G(H_2)$ values (0.82 to 1.9 molecules/100eV) measured for radiolysis of solutions of the organic diluent used in the solvent in the PUREX process (see Table 11 on page 254 of Reference 1). There is no available data on the production of CO_2 from radiolysis of the organic diluent and the TBP used in the solvent extraction process for purifying U and Pu. The G values for O_2 depletion are larger than H_2 production suggesting that the yield of organic radicals in the radiolysis is higher than that for H atoms. Part of this is due to the mechanism for the production of H_2 which is H atom formation following by reaction of the H atom with the organic to produce H_2 along with formation of another organic radical.[9] In this case G(-O_2) would equal twice G(H_2). The slightly larger G(-O_2) than twice G(H_2) suggests that some additional radiolytically produced species may be reacting with O_2.

The slight O_2 depletion (G = -1.2 molecules/100eV) in radiolysis of the 0.01 M NaOH that did not contain any added organic could be due to dissolved O_2 reacting with aqueous electrons formed by the radiolysis of the water. The value for G(H_2) from radiolysis of that solution is larger than the published value of 0.45 molecules/100 eV for molecular H_2 production but lower than 2.1 molecules/100eV, the highest yield that could be produced from radiolysis of pure 0.01 M NaOH.[11] Based on the above discussion it is concluded that the results for gas generation are consistent with published radiation chemistry data.

The results for FTIR analyses of the three irradiated samples of MCU solvent along with a sample of the unirradiated solvent that had been contacted with 0.01 M NaOH are shown Table III.

Table III. Isopar® L and Modifier Concentrations (wt %) Measured by FTIR[a]

Sample	Isopar® L	Modifier
Unirrad. Solvent	69.1	29.8
Irrad. Solvent,1	69.3	29.8
Irrad. Solvent,2	69.6	29.9
Irrad. Solvent,3	69.9	29.9

[a]Target values in the solvent are 69.1 wt % Isopar® L and 29.8 wt % Modifier

The control sample (unirradiated, washed solvent) yielded the expected result of 69.1 wt % Isopar® L and 29.8 wt % Modifier (by FTIR). Clearly no significant degradation of Isopar® L or Modifier is observed. Table IV shows the results of the HPLC analysis.

Table IV. Modifier and BOBCalixC6 Concentrations (wt %) Measured by HPLC

Sample	Modifier	BOBCalixC6
Unirrad. Solvent	30.3	0.92
Irrad. Solvent,1	30.1	0.85
Irrad. Solvent,2	28.6	0.85
Irrad. Solvent,3	29.8	0.82

[a]Target values in the solvent are 29.8 wt % Modifier and 0.94 wt % BOBCalixC6

The modifier concentration for all samples is within 2% of the target. The BOBCalixC6 concentration is within 8% to 11% of the target for all the irradiated samples suggesting some depletion due to radiolysis. This radiolytically induced depletion has been observed before.[12, 13] Finally, neither of the above analytical methods detected any radiolytic degradation products in the solvent.

Tests Simulating Radiolysis of Solvent in the SWPF

These tests were performed to estimate radiolytic gas formation from the solvent while it is being used in the SWPF. Figure 1 shows the pressure changes produced by the simultaneous irradiation for ~100 hours of two samples of the solvent after contacting each with simulated caustic salt feed solution that would contain the Cs-137. This solution is primarily 1.9 M NaOH, 2.1 M $NaNO_3$, and 0.52 M $NaNO_2$. For both tests a slight amount of the aqueous solution was left in contact with the organic to ensure that it was always saturated with the aqueous solution during the testing. These tests were identical except a slightly larger amount of solvent was irradiated in Test 2 (32 mL instead of 30 mL). In these tests pressures were measured every 10 minutes during the irradiation at 50 ºC.

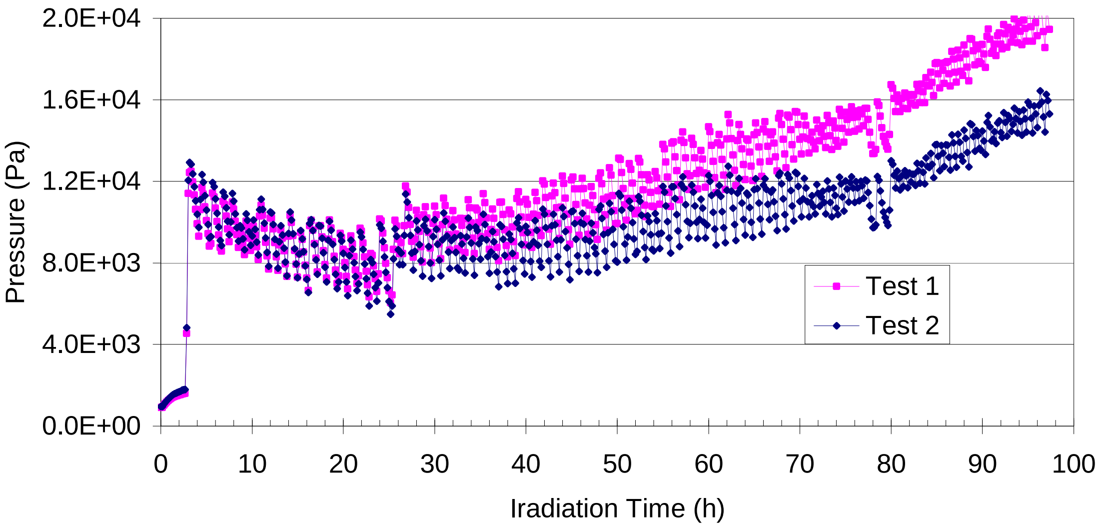

Figure 1. Pressures from two simultaneous radiolysis tests at 50 ºC of two samples of solvent contacted with simulated SWPF feed solution (1.9 M NaOH, 2.1 M $NaNO_3$, and 0.52 M $NaNO_2$).

Figure 2 shows the pressure changes produced by radiolysis at 50 ºC of a sample of solvent contacted with the 0.05M HNO_3. This solution simulates the solution that will be used in SWPF to scrub the organic solvent containing the Cs-137 prior to stripping it with 0.001 M HNO_3. Again a slight amount of the aqueous solution was left in contact with the organic during the irradiation. In this test exactly 30 mL of solvent were irradiated. Pressures were measured every 5 minutes during the 100 hours.

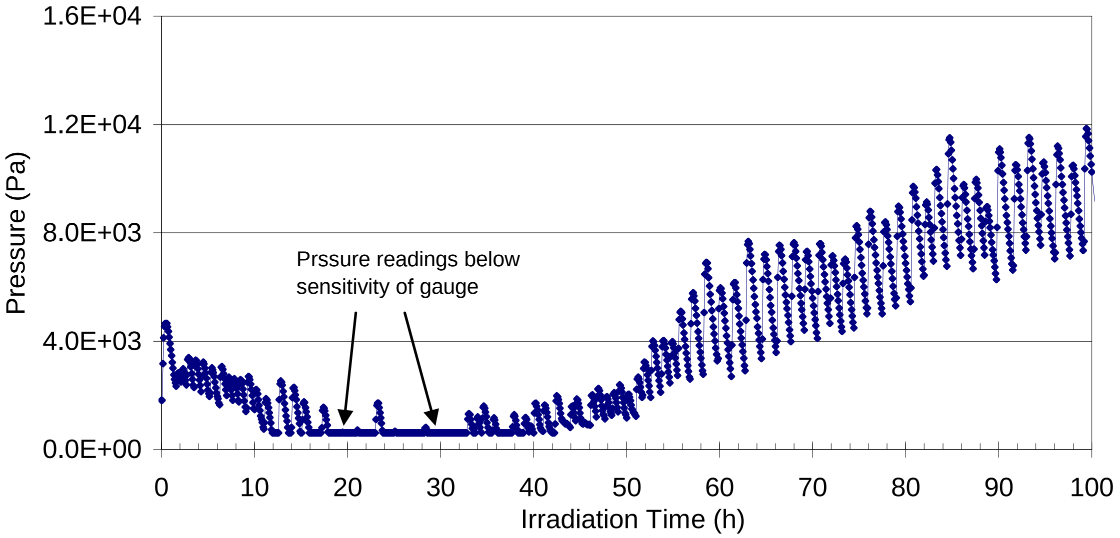

Figure 2. Pressure from a radiolysis test at 50 ºC of a sample of solvent contacted with simulated SWPF scrub solution (~0.05 M HNO_3).

In all three tests the pressure changes were automatically recorded by a computer. The initial rapid increase in pressure in each test is due to the temperature rise after the temperature controller was activated to achieve 50 ºC. After this initial rise the pressures initially decreased and then at approximately 40 hours began to increase. Even though the pressure data are very scattered, the initial decreases and increases of the pressure generated by radiolysis of each sample are clearly apparent. This type of behavior likely results from O_2 depletion and H_2 production as observed in the earlier tests where the compositions of the final gases were measured after the irradiation. Exact reasons for the large fluctuations of the pressure readings are not known, but the patterns of the fluctuations are identical in each test in Figure 1. In both irradiations the fluctuations are too cyclical and sharp (containing a period of nominally 1 hour) to be associated with any chemical changes in the radiolytic mechanism. This suggests that they may be due to variance in temperature control of the Al heating block holding both the samples or coupled with some periodic electronic oscillations of the pressure recording methods.

To perform a meaningful evaluation of the data from the three tests, a linear regression was applied to the pressure decreases and the pressure increases. G values for the gas depletion and production were calculated from the slopes of these linear regressions. Visual inspection of the periodic pressure fluctuations were performed to estimate when the periodic pressures fluctuations were decreasing or increasing in a linear fashion. All the data points were considered. The data for the pressure decreases did not fit well to a linear regression. For the pressure decreases, the R^2 correlation values for the regression ranged only from 0.36 to 0.58. This low correlation is due to the large number of pressure fluctuations compared to the short durations of the measured pressure decreases (~25 hours for Tests 1 and 2 and 15 hours for Test 3). For the pressure increases the linear regressions were better. The R^2 values ranged from 0.72 to 0.88. These regressions and the data are shown in Figures 3 and 4. For Tests 1 and 2 (see Figure 3) all pressure data taken from 38 to 96 hours in the irradiation were included. This is 366 pressure readings for each test. For Test 3 (see Figure 4) all pressure data taken from 50.3 to 100.8 hours in the irradiation were included. This is 594 individual pressure readings.

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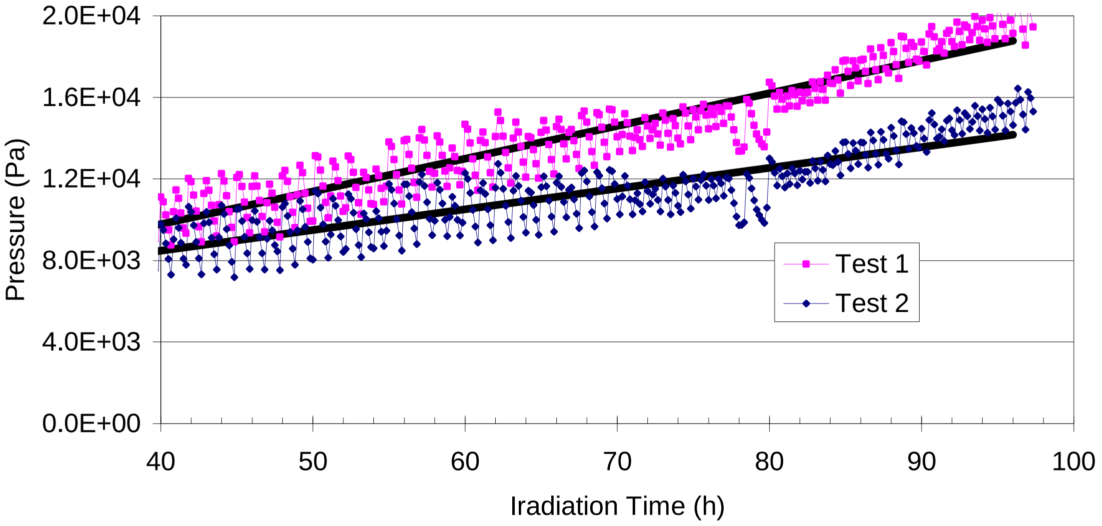

Figure 3. Results of the linear regression applied to data from Tests 1 and 2 simulating radiolysis of the SWPF organic solvent containing entrained caustic salt solution with Cs-137.

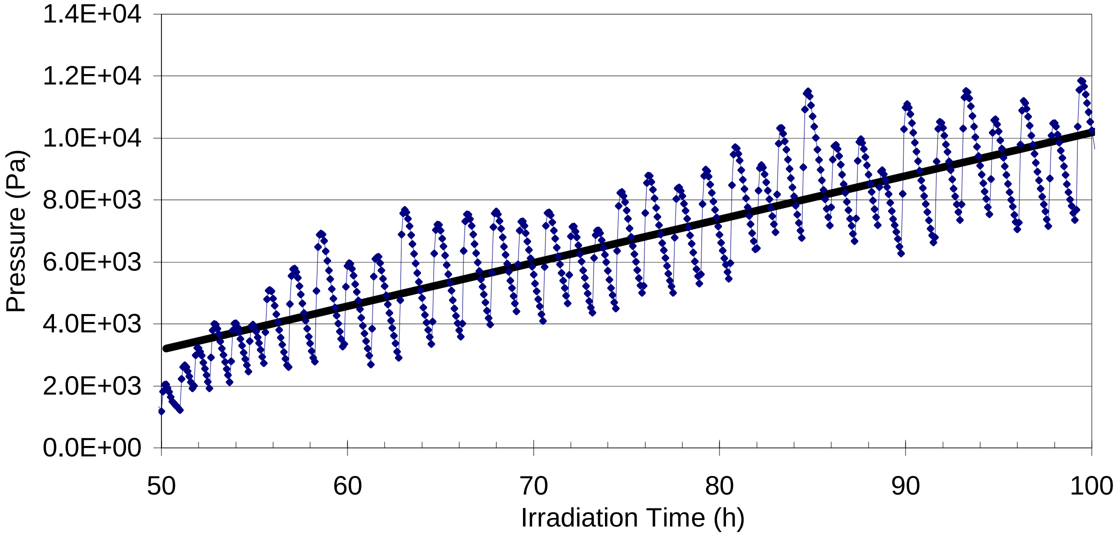

Figure 4. Results of the linear regression applied to data from Test 3 simulating radiolysis of the organic solvent containing entrained scrub solution with Cs-137.

The statically derived equations for the tests along with their R^2 value are given below.

Test 1 in Figure 3. Pressure (Pa) = 160 × time (hours) +3.4 x 10^3 $R^2 = 0.88$

Test 2 in Figure 3 . Pressure (Pa) = 102 × time (hours) +4.4 x 10^3 $R^2 = 0.73$

Test 3 in Figure 4. Pressure (Pa) = 140 × time (hours) – 3.9 x 10^3 $R^2 = 0.72$

Considering the large fluctuations of the pressure readings, the R^2 values are not unexpected. From the slopes of these regressions, G values can be calculated for the molecules of gas being produced. The G values for gas production were calculated from the following equation

$$G(P) = S_g \cdot \left(\frac{V \cdot N}{R \cdot T}\right) \cdot \left(\frac{1}{D_r \cdot M_s \cdot C}\right) \cdot 100 \qquad \text{(Eq 4)}$$

where

S_g = slope of the linear regression line (Pa/h)
V = Volume of gas whose pressure is being measured (0.165 L)
N = Avogadro's number (6.02 x 10^{23} molecules/mole)
R = ideal gas constant (8.31 x 10^3 L Pa/mole K
T = Temperature of the gas (50 ºC or 323 K
M_s = mass of MCU solvent irradiated
D_r = dose rate of absorbed radiation (3.0 x 10^3 Grays/h)
C = conversion from Grays to eV/g (6.24 x 10^{15} eV/g per Gray)

Again the factor of 100 converts the results from molecules per eV to molecules per 100 eV, the units of a radiation chemistry G value.

The G values for gas production in Tests 1 and 2 are 1.2 and 0.79 molecules/100 eV, respectively. For Test 3 the G value for gas production is 1.2 molecules/100eV in agreement with Test 1. These G values can be primarily attributed to H_2 production. All three values are within experimental error of the range of G values reported for gas production (0.82-2.1 molecules/100ev) from radiolysis of solutions of the organic diluent and the TBP extractant used in the PUREX process (see Table 11 on page 254 of Reference 1). They are also in reasonable agreement with the value of 1.2 molecules/100 eV reported for $G(H_2)$ in the radiolysis of TBP-diluent solutions equilibrated with 0.6M HNO_3 (see Table 14 on page 261 of Reference 1). Lastly we have no explanation why the G values for Tests 1 and 2 are not in agreement since it was attempted to perform duplicate tests. Also there is no apparent explanation of why the results for all three tests are lower than the results for the tests with solvent contacted with caustic salt or the acidic salt solution. Clearly more tests are needed to substantiate that the values are truly lower or whether this is due to experimental error.

In this portion of the study, three samples of the solvent were also irradiated to 32 x 10^4 Grays at 50 °C to measure radiolytic degradation of the solvent. The first had been contacted with water, the second with 0.05 M HNO_3 scrub solution and the third with the caustic salt solution that simulated feed to the SWPF. After the irradiation, the samples along with an unirradiated sample were analyzed by HPLC and thermogravimetric analysis (TGA). Results are shown in Tables V and VI, respectively.

Table V. Composition of Solvent (wt %) Following Irradiation at 32 × 10^4 Grays and 50 °C Measured by HPLC

Sample	Modifier	BOBCalixC6
Unirrad. Solvent	28.3	0.88
Solvent Contacted with Water	29.0	0.76
Solvent Contacted with Salt	29.1	0.76
Solvent Contacted with Scrub	29.2	0.76

[a]Target values in the solvent are 29.8 wt % Modifier and 0.94 wt % BOBCalixC6

The HPLC data shows no significant change in the Modifier concentration, but it does show a decrease (~14%) in the BOBCalixC6 concentration in the irradiated samples. This decrease was also observed with radiolysis of the MCU solvent samples (see Table IV) and has also been observed in other studies.[12, 13] Again, the HPLC analysis did not detect any radiolytic decomposition products.

Table VI. Composition of Solvent (wt %) Following Irradiation at 32 × 10^4 Grays at 50 °C Measured by TGA

Sample	Isopar®L	Modifier	BOBCalixC6	Unknown
Unirrad. Solvent	69.7	29.4	0.93	0.00
Solvent Contacted with Water	70.1	28.7	1.02	0.15
Solvent Contacted with Salt	70.1	28.7	1.06	0.31
Solvent Contacted with Scrub	69.9	29.0	1.02	0.19

[a]Target values in the solvent are 69.1 wt % Isopar® L, 29.8 wt % Modifier and 0.94 wt % BOBCalixC6

In agreement with the HPLC results, the TGA data showed no significant change in the concentration of Isopar® L. The TGA data indicated there could have been a slight decrease (1-2%) in the Modifier concentration from the irradiation but this is small enough to be attributed to analytical uncertainty in the results. The BOBCalixC6 results showed an increase in concentration in the irradiated samples which again is an indication of the uncertainty in the results. Finally, the TGA analysis did show the radiolytic formation of an unidentified compound with a concentration 0.15 to 0.31 wt % in the irradiated solvents.

Calculation of G Values for Depletion of the Extractant BOBCalixC6

To compare radiolytic depletion of BOBCalixC6 with that measured in a previous study [12], the G value for that depletion was calculated. In the present study G values were calculated from the HPLC data presented in Tables IV and V. To do this calculation the concentrations of the BOBCalixC6 had to be converted to moles/liter of solvent. This was done using the density of the solvent (850 g/L) and the molecular weight of BOBCalixC6 (1149.5 grams/mole). Results for the molarities and the G values are shown in Table VII.

Table VII. G Values Calculated for Radiolytic Depletion of BOBCalixC6 Measured by HPLC

Solvent	Dose, Grays	Initial Molarity	Final Molarity	G(-BOBCalixC6)
Contacted with 0.01 M NaOH.	7.1×10^4	0.0069	0.0063[a]	0.095 molecules per 100 eV
Contacted with water, salt or scrub solution.	32×10^4	0.0066	0.0057[b]	0.032 molecules per 100 eV

[a]Average molarity calculated from results of irradiating three replicate solvent samples (see Table IV).
[b]Calculated using the identical results of irradiating three solvent samples contacted with different aqueous solutions (see Table V).

A previous study has published a G value for depletion of the BOBCalixC6 from Co-60 gamma radiolysis of 0.01 M BOBCalixC6 dissolved in 0.5 M Cs-3 Modifier and diluted with Isopar® L.[12] The sample was irradiated to 27×10^4 Grays and the depletion of the BOBCalixC6 measured by HPLC. The value for G(-BOBCalixC6) was 0.14 molecules/100 eV, which significantly higher than the results in Table VII. These G values may not be strictly comparable with that measured in the earlier study because the Modifier in the solvent in that study was a different organic compound than the Modifier currently being used in the CSSX process.

In this study the average G value for depletion of BOBCalixC6 in radiolysis of the three samples contacted with water, the salt feed or the scrub (0.032 molecules/100 eV) is lower than the G value of 0.095 for depletion in the MCU solvent contacted with 0.01 M NaOH. Again, the reason for this is not immediately apparent and more experiments are necessary to determine if this is actually the case or if it is due analytical uncertainty–especially since the G values are calculated from a small difference between two numbers that are significantly larger. Note however that both values for G(-BOBCalixC6) are lower than those for G(H_2). This is to be expected because the concentration of the BOBCalixC6 (0.94 wt %) is much lower than the concentrations of Isopar® L and the Modifer Cs-7SB (69.14 wt % and 29.8 wt %, respectively). On a mass basis, the BOBCalixC6 concentration is 105 times lower than the other two organic compounds. Consequently these two compounds are the primary source of H atoms produced by the radiolysis. These compounds can then react with the H atoms and produce H_2.

It is not known whether this decrease in BOBCalixC6 concentration of 14% at 32×10^4 Grays would decrease the extraction efficiency for Cs-137. However it has been shown by studies at Savannah River National Laboratory[13] and at Oak Ridge National Laboratory[14] that doses of 4×10^4 and 16×10^4 Grays do not decrease the extraction efficiency.

Calculation of H_2 Production Rates from G Values

This section discusses how G values can be used to calculate H_2 production rates applicable to plant operations. The rates of H_2 production can be calculated from G values if the dose rate of the radiation and the amount of solvent being irradiated are known. The following equation applies

$$R_{H_2} = \frac{G(H_2)}{100} \cdot \left(\frac{D_r \cdot M_s \cdot C}{N \cdot M} \right) \quad \text{(Eq. 5)}$$

where

R_{H_2} = liters of H_2 at 25 ºC being produced per hour per liter of solvent
$G(H_2)$= molecules of H_2 produced at 50 °C per 100 eV of absorbed radiation
D_r = dose rate of absorbed radiation in Grays per hour
M_s = mass of solvent irradiated (1 liter × its density of 850 g/L)
C = the conversion of Grays to eV/g (6.24 x 10^{15} eV/g per Gray)
N = Avogadro's number (6.02 x 10^{23} molecules/mole)
M = the moles of gas in 1 liter at ambient temperature of 25 ºC (0.0408 moles/L)

Two examples will be shown. One is for the spent MCU solvent where the dose rate is 16 Gray per hour calculated from Equation 1 and the value for $G(H_2)$ = 1.7 molecules/100eV, the average of the G values measured for the spent MCU solvent. In this example, 5.9 x 10^{-6} L of H_2 at 25 °C are produced per hour per liter of solvent. The second example is for H_2 being produced from radiolysis of the solvent in the extraction and scrub steps of the SWPF process. Based on the 3.2 x 10^4 Grays chosen to conservative for a one year's dose in the SWPF, the dose rate is 37 Gray per hour. For this example the value chosen for $G(H_2)$ was 1.2 molecules/100 eV. This value would be the conservative estimate since it the highest G value measured in the second series of tests. In this case the radiolytic production rate of H_2 is 9.6 x 10^{-5} liters of H_2 produced per hour per liter of solvent irradiated. These two rates can then be used to estimate H_2 production rates from spent MCU solvent and from the solvent during processing in the SWPF.

CONCLUSIONS

The following conclusions can be drawn from this study.

1. Radiolysis of the MCU or SWPF organic solvent will produce H_2 with G values ranging from 0.79 to 1.7 molecules/100eV.

2. Presence in the organic solvent of the dissolved aqueous streams that simulate the caustic HLW salt solutions containing radioactive Cs-137 or the scrub solution containing 0.05 M HNO_3 does not appear to have a significant affect the G values for H_2 production.

3. The estimated rate of radiolytic production of H_2 from the spent solvent containing entrained Cs-137 is 5.9 x 10^{-6} L of H_2 (at 25 ºC) per hour per liter of solvent.

4. The estimated rate of radiolytic production of H_2 from the solvent during processing in the SWPF is 9.6 x 10^{-5} L of H_2 per hour (at 25 ºC) per Liter of solvent.

5. There were no significant effects on the concentrations of major components of the solvent, the Isopar® L and the Modifier.

6. Some radiolytic degradation of the BOBCalixC6 was detected. At a dose of 7.1 x 10^4 Grays 8% was decomposed. At a higher dose of 3.2 x 10^5 Grays 14% was decomposed. Values for G(-BOBCalixC6) were 0.032 and 0.095 molecules/100 eV of radiation absorbed.

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