

# **Gamma Ray Radiolysis of the FPEX Solvent**

**9th Information Exchange Meeting for  
Actinide and Fission Product  
Partitioning and Transmutation and  
Seminar at University of Manchester**

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September 2006

The INL is a  
U.S. Department of Energy  
National Laboratory  
operated by  
Battelle Energy Alliance



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## GAMMA RAY RADIOLYSIS OF THE FPEX SOLVENT

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### Abstract

FPEX contains a calixarene for Cs extraction, a crown ether for Sr extraction, Cs7SB modifier, and TOA to aid in stripping, in Isopar L diluent. The radiation stability FPEX must be evaluated prior to process use. Radiolytic degradation of species in solution are due to reaction with the direct radiolysis products of the diluent. In Isopar L, the reactive species produced include  $e^-$ ,  $\cdot H$  and alkane radicals, resulting in a reducing environment. However, in nitric acid, oxidizing hydroxyl ( $\cdot OH$ ) and nitro ( $\cdot NO_2$ ) radicals dominate system chemistry. Thus, the nature of diluent and the presence of radical scavengers affect the results of irradiation. We report the preliminary results of a new program to investigate the radiolysis of FPEX using the  $^{60}Co$  irradiation of FPEX neat solvent, acid pre-equilibrated solvent and mixed aerated phases. The Cs and Sr distribution ratios were used as metrics.

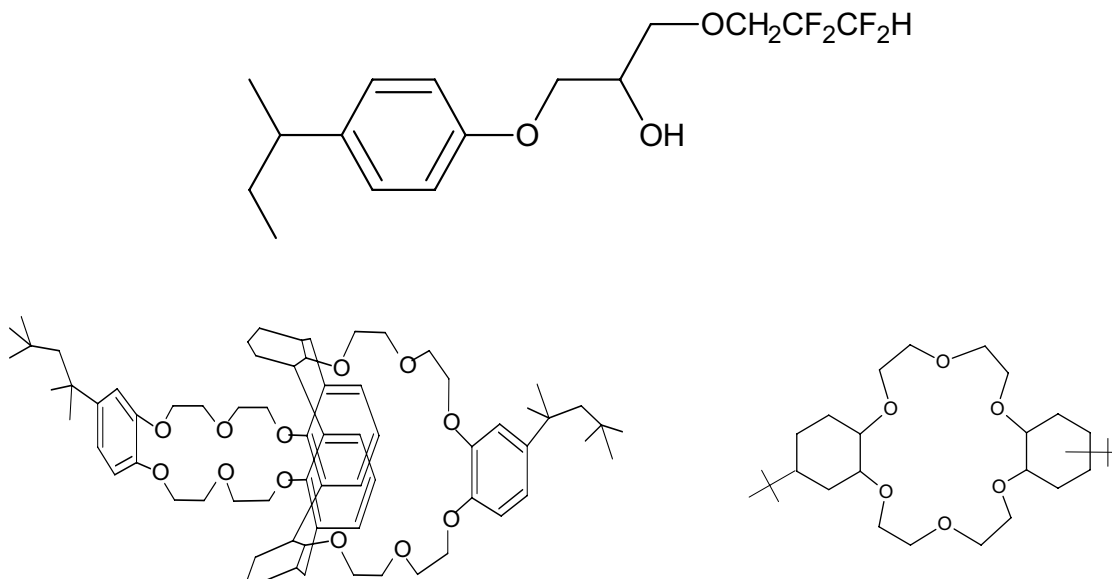
## Introduction

The solvent extraction formulation known as FPEX (Fission Product Extraction) contains the macrocyclic ether compounds calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) and 4,4', (5')-di-(t-butylidicyclohexano)-18-crown-6 (DtBuCH18C6) as Cs and Sr extractants, respectively. The solvent is Isopar L, an alkane diluent. While the solvent extraction performance of FPEX has been found favorable [1], the radiation stability of this formulation must be evaluated prior to implementation of a commercial process based on BOBCalixC6 and DtBuCH18C6.

The radiolytic decomposition of a compound in a diluent is primarily due to reaction with reactive species caused by radiolysis of the diluent. In an organic diluent such as Isopar L, the reactive species resulting from solvent radiolysis include electrons, hydrogen atoms ( $\cdot\text{H}$ ) and alkane radicals, resulting in an overall reducing environment [2]. By contrast, in aqueous nitric acid solution, electrons are scavenged by oxygen, nitrates and  $\text{H}^+$ , and the oxidizing hydroxyl radical ( $\cdot\text{OH}$ ) dominates system chemistry [2].

The structures of BOBCalixC6 and DtBuCH18C6 are shown in Figure 1. The calixarene and modifier aromatic groups are expected to be susceptible to oxidative attack by  $\cdot\text{OH}$  and  $\cdot\text{NO}_2$  radicals. The presence of oxygen greatly influences the extent of reaction of the resulting carbon centered radicals through the formation of peroxy radicals [2]. Therefore, irradiations were conducted under various conditions, including neat FPEX, acid-pre-equilibrated FPEX and mixed aerated phases. The Cs and Sr distribution ratios of post-irradiation extractions were used as a metric to quantify solvent performance.

**Figure 1. Structure of the Cs7SB modifier (top), BOBCalixC6 (left) and DtBuCH18C6 (right).**



## Experimental

The FPEX solvent composition used in this study was 0.007M-BOBCalixC6, 0.15M-DtBuCH18C6, 0.75M-Cs7SB and 0.003M trioctylamine (TOA) in Isopar L diluent, as described in Reference [1]. Irradiations were performed with an MDS Nordion (Ottawa, Canada) Gammacell 220E  $^{60}\text{Co}$  irradiator. The Gammacell contains  $8.9 \times 10^{14}$  Bq (24,000 Ci) of  $^{60}\text{Co}$ , with a sample cell, center-line dose rate of 20 kGy/h (2.0 MRad/h). The duration of irradiation was varied to achieve the required absorbed dose. Neat samples of FPEX, and FPEX that had been pre-equilibrated with 1.5M- $\text{HNO}_3$  were irradiated in triplicate in sealed, septum-capped vials. These irradiated solutions were then used to contact aqueous light water reactor fuel dissolution simulant solutions (Table 1), spiked with  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$ . Contacts were of equal volume, 1 minute in duration, and conducted at  $25 \pm 1^\circ\text{C}$ . Following extraction, the samples were centrifuged and the phases separated by pipet. Stripping of the loaded organic phases was conducted with 0.01M  $\text{HNO}_3$ .

One additional set of samples irradiated consisted of FPEX and 1.5M  $\text{HNO}_3$  being continuously mixed by air sparging. The sparging was achieved by inserting a syringe needle through the vial septum, deep into the aqueous phase and supplying air with an Ultra 5/20 diaphragm pump (Fritz Chemical Co., Texas, USA). A second syringe needle inserted into the sample headspace allowed sparged air to escape the vial. The temperature in the irradiation chamber was measured as  $48^\circ\text{C}$ , due to gamma heating. For comparison purposes, a blank set of mixed phases was air-sparged at  $50^\circ\text{C}$  in a laboratory oven in the absence of radiation for comparison. All sparged solutions were centrifuged, and the organic phase was removed and split into duplicate aliquots for contact with spiked simulant for extraction and stripping distribution ratio measurements.

The Sr and Cs distribution ratios were determined as the ratio of the appropriate specific activity in the organic and aqueous phases, as determined by gamma-ray counting. Counting time was selected to provide  $<1\%$  counting uncertainty. The reported distribution ratio values are the means of triplicate measurements (duplicates for air sparged samples). The average relative standard deviation of the triplicate measurements was  $\pm 5\%$ .

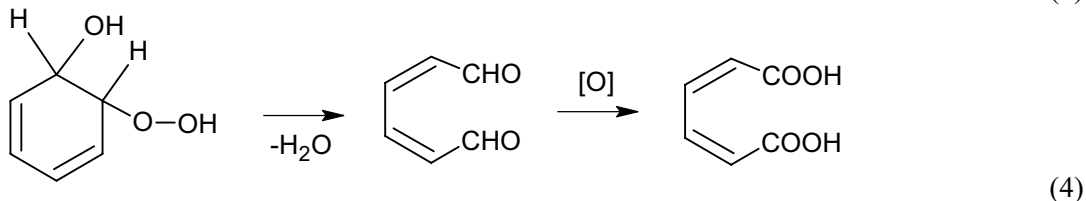
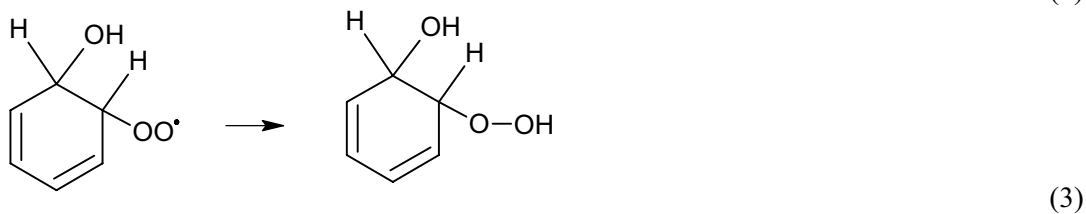
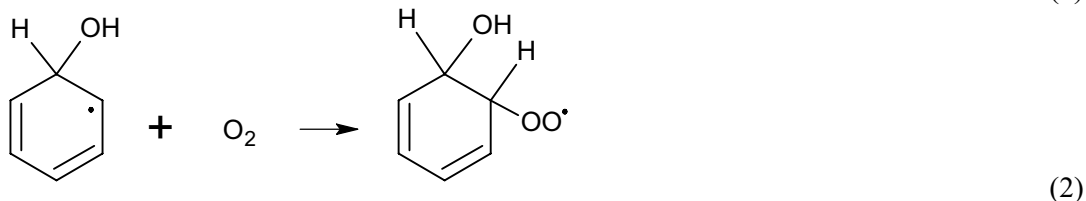
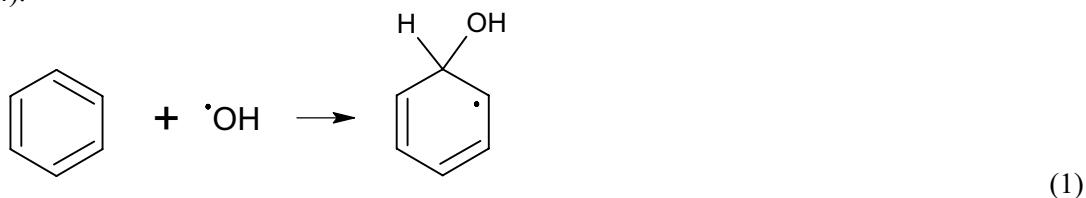
**Table 1. Composition of the simulant used as aqueous phase in FPEX extractions.**

Component	Conc. (M)	Component	Conc. (M)
H+	1.5	Sr	$2.0 \times 10^{-3}$
Cs	$4.1 \times 10^{-3}$	Zr	$1.1 \times 10^{-2}$
Ba	$3.7 \times 10^{-3}$	La	$2.2 \times 10^{-3}$
Ce	$4.3 \times 10^{-3}$	Nd	$7.2 \times 10^{-3}$
Sm	$5.0 \times 10^{-3}$	Gd	$2.6 \times 10^{-4}$
Eu	$1.4 \times 10^{-4}$	Y	$1.4 \times 10^{-3}$
Rb	$1.0 \times 10^{-3}$		

## Results and Discussion

A plot of Sr and Cs extraction and strip distribution ratios versus absorbed radiation dose is shown in Figure 2, for FPEX pre-equilibrated with 1.5M HNO<sub>3</sub>. Irradiation had little effect on the stripping ratios. For the forward extraction, there is an exponential decrease in distribution ratios for both Sr and Cs in the early stages of irradiation. The overall decrease in Sr and Cs distribution ratios is about 20% and 40%, respectively, which occurs by 40 kGy (4 MRad), with little change thereafter. The exponential decrease in distribution ratios is reminiscent of the pseudo-first order decrease in concentration often seen for analytes undergoing radical reaction with continuous irradiation [3]. However, the species responsible is apparently consumed by 40 kGy, after which decomposition appears to be suppressed. This suggests that this species is present in limited concentration, and introduced by the act of pre-equilibration.

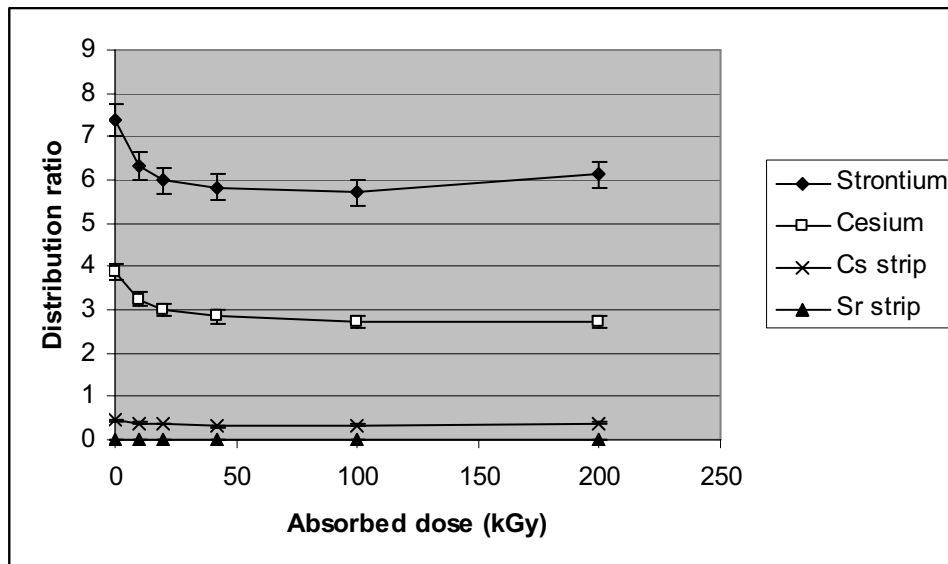
The reactive species that may be present due to pre-equilibration include hydroxyl radicals ( $\cdot\text{OH}$ ), a major product of water radiolysis; and nitrite radicals ( $\cdot\text{NO}_2$ ) from HNO<sub>3</sub> radiolysis; both oxidizing species. Data from our laboratory (not shown) indicates that FPEX does not extract significant amounts of acid, therefore, water is expected to be present in greater amounts than HNO<sub>3</sub> in the pre-equilibrated solvent. The exponential decrease in distribution ratios may be due to action of  $\cdot\text{OH}$ , which is known to undergo addition reactions with aromatic rings [4], as shown in Equation 1. In the presence of O<sub>2</sub>, aromatic rings are subsequently decomposed to organic acids via a peroxy radical intermediate, as shown in Equation 2. The peroxy radical undergoes hydrolysis and dehydration to form acidic products (Equations 3 and 4).



The effect of radiolysis on Sr and Cs extraction was identical, however the only functional group in common between DtBuCH18C6 and BOBCalixC6 is the macrocyclic ether ring, which is relatively stable [5]. Hydroxyl radical reaction would be expected to occur at the BOBCalixC6 phenyl rings, but not to occur on the saturated cyclohexano rings of DtBuCH18C6. Based on these considerations, it is therefore postulated that the effect of radiolysis on Sr and Cs

distribution ratios for pre-equilibrated FPEX is actually due to  $\cdot\text{OH}$  radical attack on the phenyl ring of the Cs7SB modifier. The modifier is present at a concentration 5 times that of DtBuCH18C6 and 100 times that of BOBCalixC6, and thus is most likely to react with species produced by radiolysis. Its modification would also be expected to affect distribution ratios for both metals [1].

**Figure 2. Cesium and strontium extraction and strip distribution ratios versus absorbed dose for irradiated FPEX that was pre-equilibrated with 1.5M- $\text{HNO}_3$ .**

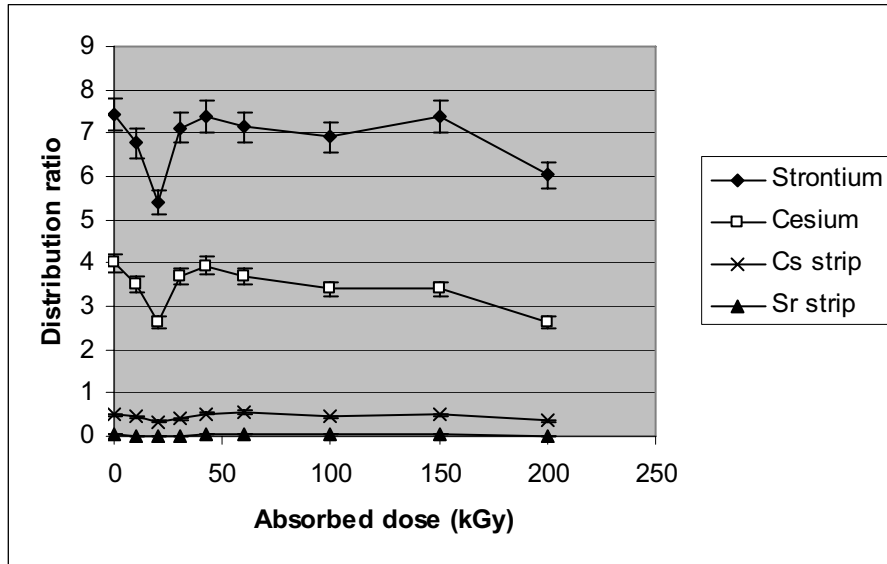


Irradiated neat FPEX exhibited different behavior than the pre-equilibrated FPEX. Although stripping distribution ratios were once again unaffected, it can be seen in Figure 3 that Sr and Cs forward extraction distribution ratios substantially decrease early in the irradiation, reaching a minimum at about 20 kGy (2.0 MRad) but then recovering. At the maximum absorbed dose of 200 kGy (20 MRad) the overall decrease was about 20% for Sr and 40% for Cs. The unusual trend shown in Figure 3 has been observed by others [6, 7].

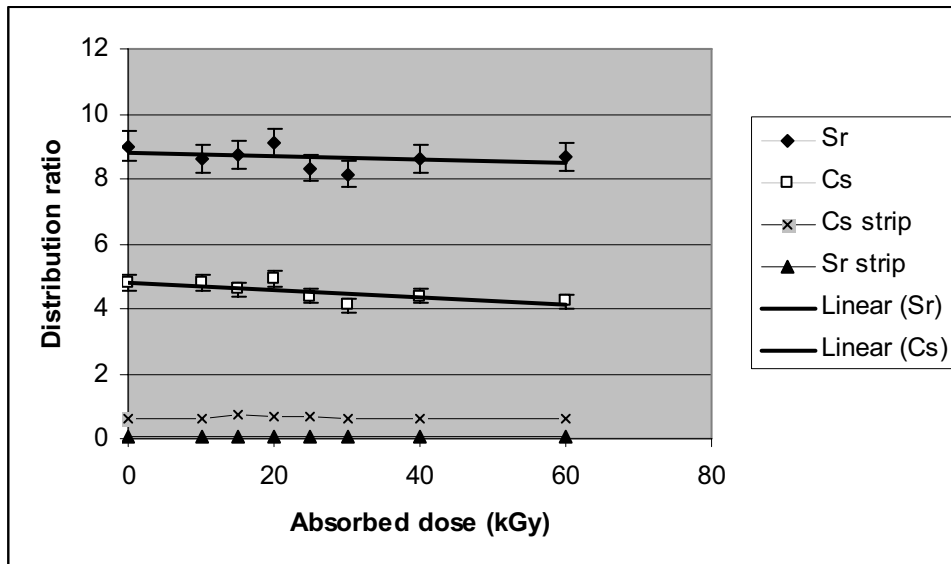
This unusual behavior is consistent with a mechanism dependant on dissolved oxygen. In the sealed vials used to irradiate these samples, oxygen would be quickly depleted by radiolytically generated electrons [2] and reactions dependent on it would then be suppressed. For example, when FPEX was irradiated following Ar-sparging to remove dissolved oxygen, the temporary decrease in distribution ratios was eliminated, confirming that the radiation-induced decrease is an oxygen-dependent mechanism. This is shown in Figure 4. The FPEX solvent is comparatively stable toward ionizing radiation in a reducing environment.

In the case of neat FPEX irradiation, as for pre-equilibrated FPEX, the behavior of Sr and Cs distribution ratios is analogous. This again suggests that the mechanism affects the modifier rather than the ligands themselves. The mechanism may involve a byproduct of radiolysis that interferes with metal binding in the macrocycle rings, which is decomposed by continued irradiation resulting in the recovery in distribution ratios shown in Figure 3. Alternatively, radical/radical addition reactions may actually repair the modifier with continued irradiation. Further research is needed.

**Figure 3. Cesium and strontium extraction and strip distribution ratios versus absorbed dose for neat, irradiated FPEX solvent.**



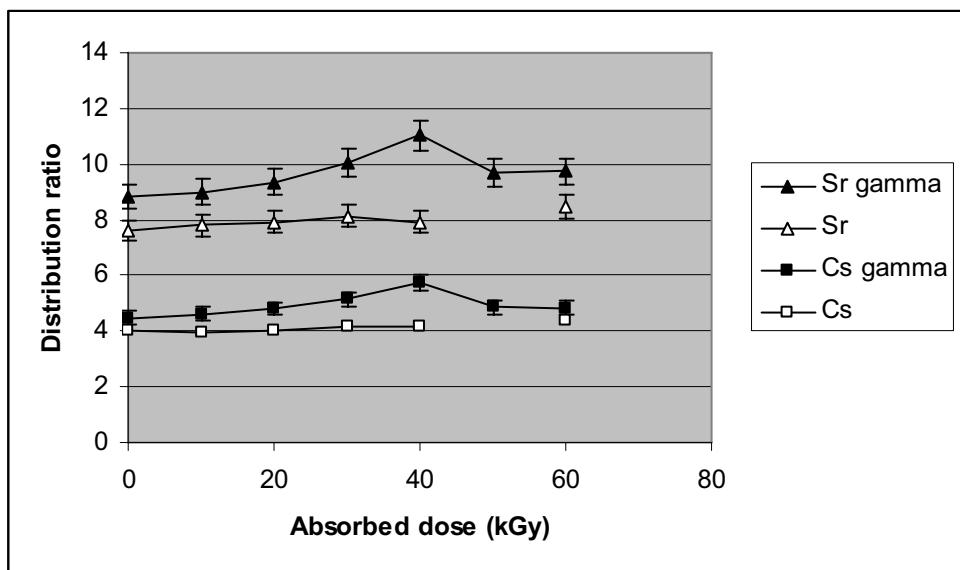
**Figure 4. Cesium and strontium extraction and strip distribution ratios versus absorbed dose for neat, argon-sparged, irradiated FPEX solvent.**



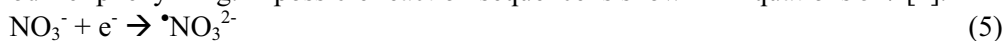
The susceptibility of the modifier to oxidative attack, and the corresponding decreases in Sr and Cs distribution ratios suggest that in a mixed phase irradiation, the continuous supply of  $O_2$  and  $\cdot OH$  would result in rapid loss of efficiency for metal extraction. However, when FPEX solvent was irradiated with continuous mixing of an equal volume of 1.5M- $HNO_3$  and organic phase using air sparging, an increase in forward distribution ratios was found, as shown in Figure 5. This continued until about 40 kGy (4 MRad), followed by a return to initial values at the maximum absorbed dose of 60 kGy (6 MRad). Once again, the behavior of Sr and Cs was analogous. Stripping (not shown) was not affected. Also shown in Figure 5 are the forward

extractions of Sr and Cs from mixed phase samples sparged at 50°C in the absence of radiation. These blank samples were sparged at irradiator temperature for the lengths of time used in the irradiations and are plotted against the dose corresponding to that time. It can be seen that there was either no change, or only a small increase in the distribution ratios for these non-irradiated samples. This confirms that the increase in distribution ratios is due to an irradiation effect.

**Figure 5. Cesium and strontium forward extraction distribution ratios versus absorbed dose for mixed FPEX/1.5M HNO<sub>3</sub> phases, with and without irradiation.**



However, increases in Sr and Cs distribution ratios have previously been observed when FPEX solvent was left in long-term contact with nitric acid, even in the absence of radiation. This may be due to nitration of the modifier. In the case of phase mixing with 1.5M nitric acid during irradiation, radiolytic production of nitrite radical in the aqueous phase may allow rapid nitration of the modifier phenyl ring. A possible reaction sequence is shown in Equations 5-7 [2].



## Conclusions

The effect of irradiation on Sr and Cs extraction using FPEX is highly dependent upon the conditions under which the irradiation was conducted. Batch irradiations in sealed vials did not reflect conditions experienced in a process because of the rapid depletion of dissolved oxygen by electron capture. The effect of oxygen and its depletion are evident when Sr and Cs distribution ratios are plotted versus absorbed dose for neat FPEX samples, as compared with Ar-sparged samples. Further, comparison of pre-equilibrated FPEX with mixed phase irradiations demonstrated that pre-equilibration did not represent the conditions seen by the solvent during the irradiation of the continuously mixed phases that would occur in a process. In the presence of continuous mixing, nitration of the FPEX increased distribution ratios, apparently counteracting  $\cdot\text{OH}$  radical attack, resulting in the FPEX solvent being stable to at least 60 kGy (6 MRad). The analogous behavior of the Sr and Cs distribution ratios under all conditions suggests that radiolysis affects a common component, likely the modifier due to its high concentration. Reaction of the modifier probably occurs by nitration and/or hydroxyl radical addition to the



phenyl ring. Additional experiments are underway to evaluate higher absorbed doses, and to better understand the reaction mechanisms discussed here.

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