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TRUEX PROCESS SOLVENT CLEANUP WITH SOLID SORBENTS

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ABSTRACT

Solid sorbents, alumina, silica gel, and Amberlyst A-26 have been tested for the cleanup of degraded TRUEX-NPH solvent. A sodium carbonate scrub alone does not completely remove acidic degradation products from highly degraded solvent and cannot restore the stripping performance of the solvent. By following the carbonate scrub with either neutral alumina or Amberlyst A-26 anion exchange resin, the performance of the TRUEX-NPH is substantially restored. The degraded TRUEX-NPH was characterized before and after treatment by supercritical fluid chromatography. Its performance was evaluated by americium distribution ratios, phase-separation times, and lauric acid distribution coefficients.

INTRODUCTION

The TRUEX process has been developed over the last decade (1-7) as a treatment for PUREX process raffinates and other acidic nitrate waste streams contaminated by transuranics (TRU). The key ingredients in the TRUEX solvent extraction process are octyl(phenyl)N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), a bifunctional extractant, and tri-n-butyl phosphate (TBP), which acts as a phase modifier and in some cases as a co-extractant. Both of these extractants are subject to degradation under processing conditions for nuclear waste, and their degradation products affect both the extraction and stripping effectiveness of the TRUEX process. A normal paraffinic hydrocarbon (NPH) is used as diluent.

The concentration of CMPO in the TRUEX-NPH solvent affects metal distribution ratios and, therefore, the success of the TRUEX process. Four studies of TRUEX solvent degradation have been

reported (7-10). In three studies (7-9), the amount of CMPO in the degraded TRUEX solvent was determined from americium distribution ratios between the degraded TRUEX solvent and 2M HNO_3, assuming a third-order extractant dependency for americium. In the other study (10), the amount of CMPO present in the degraded solvent was determined by gas chromatography (GC). Gas chromatography is a very powerful tool for qualitative and quantitative measurements of volatile organic compounds, but it is less suitable for analyzing thermally unstable compounds such as CMPO. CMPO decomposes at ~180°C, a temperature much lower than normal gas chromatographic conditions. Supercritical fluid chromatography has been found to be a useful tool for analyzing thermally unstable and non-volatile compounds such as CMPO (11).

The presence of acidic impurities and degradation products has a drastic effect on the stripping properties of the TRUEX solvent; their formation, therefore, is usually of greater concern than the loss of CMPO to successful processing using the TRUEX process. Measurements of the distribution ratios of americium between degraded TRUEX solvents and 0.01M and 0.05M HNO_3 solutions were the basis for measuring the effects of the formation of acidic degradation products in three studies (7-9). Measurements of concentrations of acidic degradation products by methylation and GC analysis were the basis of the fourth study (10).

Solvent cleanup methods used and proposed for use in the PUREX process include 1) washing the solvent with sodium carbonate solution; 2) washing the solvent with hydrazine carbonate (12); and 3) passing the solvent through a column of solid sorbents such as macroreticular resins (13), titanium dioxide (12), sodium silica gel (14), and alumina (15). The first two methods are subject to operational difficulties because of slow phase disengagement separation, gassing, and interfacial "crud" formation. Organic resins used as solid sorbents are susceptible to chemical and radiation damage and work well only with acid-free solvents. The titanium dioxide method has not been demonstrated on a large scale. The silica gel and alumina methods have shown promise for eliminating many of the problems encountered with organic resins.

The purpose of the present work is to develop a procedure for cleaning up degraded TRUEX-NPH process solvent, which initially contains 0.2M CMPO and 1.4M TBP in an NPH diluent. Development of the procedure has been based on 1) the effectiveness of a carbonate wash followed by treatment with a solid sorbent compared to a carbonate wash alone and 2) the relative effectiveness of the alumina, silica gel, and Amberlyst A-26 sorbents. Phase-separation times, distribution coefficients for lauric acid, and americium distribution ratios have been measured to determine the effectiveness of the solvent treatments. The solvent has also been characterized by supercritical fluid chromatography (SFC) before and after degradation and after each treatment.

EXPERIMENTAL

Materials

Extraction-grade CMPO with a purity of approximately 98% was purchased from M&T Chemical Company, Rahway, NJ. The material used for the experiments was further purified by a modified MIX procedure (16). The modification included reducing the reaction temperature to room temperature and increasing the reaction time to two hours for treatment with each ion exchange resin. Finally, CMPO was recrystallized from heptane. The resulting white crystalline material was analyzed by supercritical fluid chromatography and found to be >99% pure. Gold-labeled TBP was obtained from Aldrich Chemical Company. Conoco C_{12}-C_{14} was obtained from Vista Chemical Company, Westlake, LA.

Solid sorbents tested included alumina, sodium silica gel, and Amberlyst A-26. Activated neutral alumina was obtained from Aldrich Chemical Co. as the Brockman 1, 150 mesh. Davisil silica gel (grade 634, 100-200 mesh) from Aldrich Chemical Co. was treated with NaOH, water washed, and air dried before use. Amberlyst A-26 anion exchange resin (chloride-form) was obtained from American Scientific and was converted to the hydroxide-form by treating the resin with 1M NaOH. All other chemicals used were reagent grade or better.

Solvent Degradation

One liter of TRUEX-NPH solvent was degraded by stirring and heating it for four hours under refluxing conditions with an equal volume of 8M HNO_3. The phases were then separated, and the organic phase was washed with water to remove nitric acid.

Supercritical Fluid Chromatography

Analyses of the solvent were performed on a Lee Scientific Model 622 supercritical fluid chromatograph/gas chromatograph (SFC/GC) with flame ionization detector (FID). The properties of SFC have been discussed in detail elsewhere (11). Experimental conditions used were:

1) Carrier fluid: SFC grade CO_2 from Scott Specialty Gas (linear flow rate was controlled by the length of the frit restrictor and was usually set at 10 times the minimum linear velocity),
2) Injection temperature: room temperature,
3) Density (pressure) program: initially 0.25 g/mL held for 10 min; ramp 0.02 g/mL/min to 0.6 g/mL; held for 2 min,
4) Oven temperature: 100°C,
5) Detector temperature: 325°C, and
6) Column: 50 μm i.d. x 10 m SB-Methyl-100 (Lee Scientific)

The samples for SFC analysis were prepared by dissolving 150 μL (~0.12 g) of the analyte in 10 mL of dichloromethane (B&J GC/MS grade). Concentrations of CMPO, TBP, NPH, and their degradation products were calculated by comparison with an external standard, the undegraded TRUEX-NPH.

Phase-Separation Times

Phase-separation times were used to estimate the ability of contacting equipment to mix and separate the two phases in a process. The phase-separation times were determined by the Mailen et al. method (14). Accordingly, 2 mL of the organic solution and 2 mL of 0.25M Na_2CO_3 were placed in a 13 x 100 mm culture tube and mixed by slow inversion for 15 sec. The separation time was taken to be the time for the emulsion to collapse to one layer of drops at the interface of the two phases.

Distribution Measurements

Distribution measurements for americium between TRUEX-NPH and HNO_3 and for lauric acid between TRUEX-NPH and solid sorbents were performed at 25°C. Americium distribution ratios (D_{Am}) were determined by contacting aliquots of washed and nitric-acid-preequilibrated TRUEX-NPH with 0.01, 0.05, and 2M HNO_3 containing trace amounts of Am-241. Lauric acid distribution coefficients (K_d) were measured by adding a trace amount of [1-^{14}C]lauric acid to the washed TRUEX-NPH and contacting it with a fixed amount of solid sorbent, which had been pre-equilibrated with heptane and dried under nitrogen. For D_{Am}, two aliquots from each phase were analyzed by gamma counting (MINAXI, United Technologies, Parkard). The initial and final activities of lauric acid in the organic phase were counted with a Parkard Tri-Carb 2000 Liquid Scintillation Analyzer. Distribution measurements were reproducible within ±5%.

RESULTS AND DISCUSSION

Characterization of Degraded TRUEX-NPH

The extent of degradation in the hydrolyzed TRUEX-NPH solvent was characterized by SFC and D_{Am} measurements. Supercritical fluid chromatograms of undegraded and degraded TRUEX-NPH are shown in Figs. 1 and 2, respectively. The concentrations of CMPO and TBP in the degraded solvent were determined by SFC analysis to be 0.055M and 1.14M, 28% and 82% of their initial values. The former compares well with a CMPO concentration of 0.057M calculated by a third-order dependence on the D_{Am} value for 2M HNO_3 (see Table 1). Based on the decrease in peak areas, the NPH concentration in the degraded solvent was 80% of that in the undegraded solvent.

Nineteen additional peaks are found in the chromatogram of the degraded solvent (Fig. 2). These degradation products appear predominantly at retention times between 15 and 20 min. When a

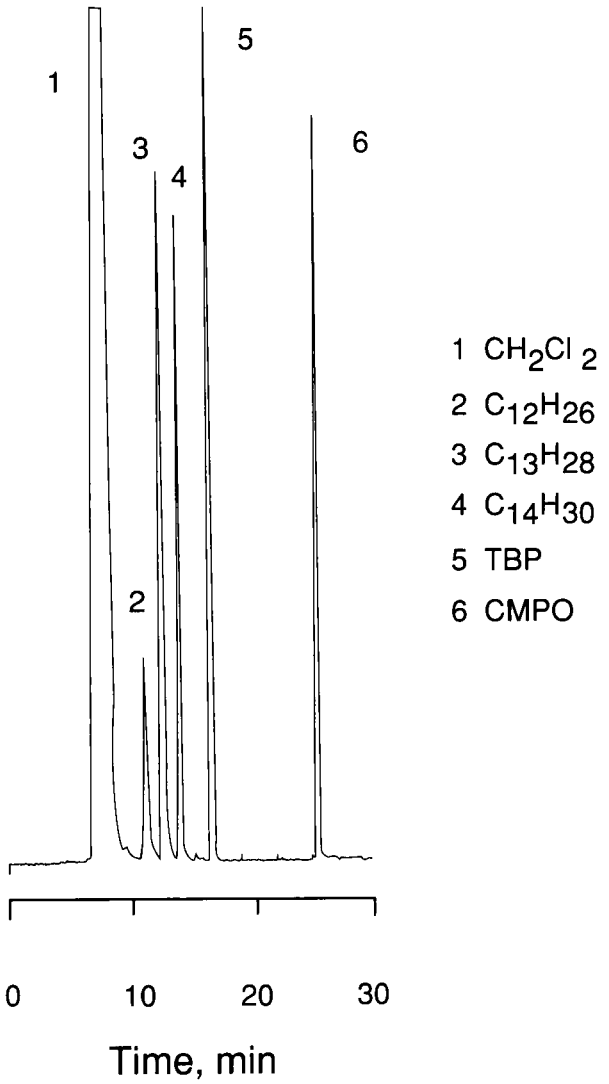

Fig. 1. Supercritical Fluid Chromatogram of Undegraded TRUEX-NPH Solvent

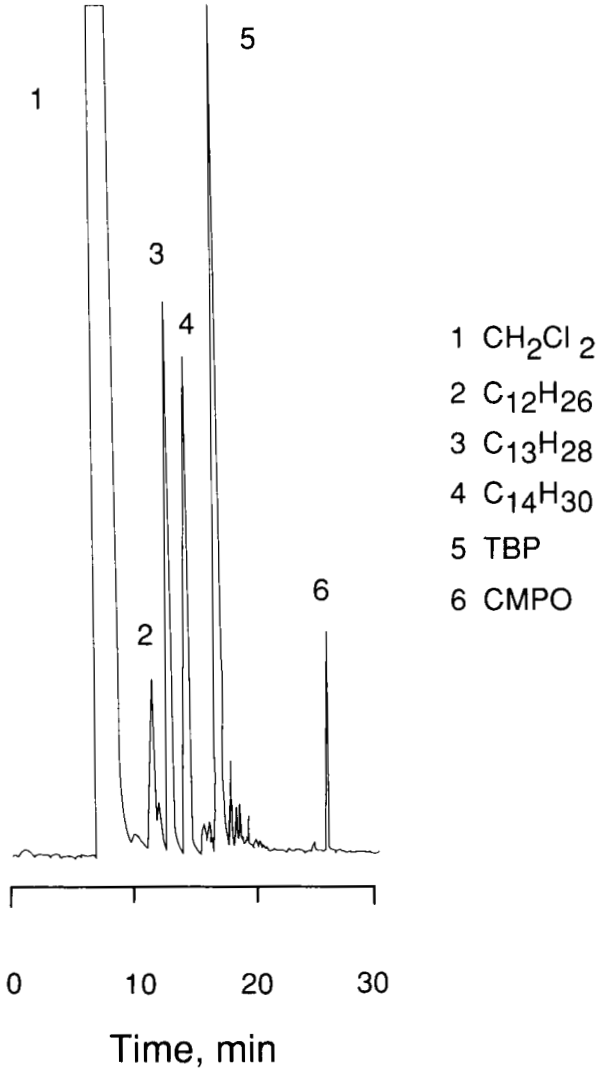

Fig. 2. Supercritical Fluid Chromatogram of Degraded TRUEX-NPH Solvent

sample of degraded solvent was derivatized with diazomethane to convert acidic compounds into methyl esters, an additional peak appeared at a retention time of 21.6 min. A comparison of the SFC and GC results reported by Nash et al. (10) suggests that this acidic compound may be octyl(phenyl)phosphorylacetic acid.

The relatively large increase in D_{Am} between undegraded and degraded TRUEX-NPH shown in Table 1 for 0.01 and 0.05M HNO_3 may be explained by the presence of acidic compounds, which extract Am at low HNO_3 concentrations. The D_{Am} value at 2.0M HNO_3 reflects the amount of CMPO present in the TRUEX-NPH, assuming that all acidic compounds are protonated and do not extract Am as neutral extractants.

Phase-Separation Times

The phase-separation time is an important factor in the choice of processing parameters and contacting equipment. Slow phase disengagement can cause process upset. Degradation products that are interfacially active affect the interfacial tension and, therefore, phase disengagement. Table 2 shows the separation times for undegraded and degraded TRUEX-NPH and the effects of treatment by carbonate wash alone or in combination with silica gel, Amberlyst A-26, or alumina. Dispersion numbers used in designing equipment have been calculated based on the phase-separation times (17) and are also given in Table 2. Since the dispersion number for the degraded solvent is ~1/7 of that for the undegraded solvent, the residence time in the contacting equipment would need to be about seven times longer for the degraded solvent. A carbonate wash alone decreases the phase-separation time of the degraded solvent but does not restore it to its original value. A follow-up treatment with sodium silica gel or Amberlyst A-26 further decreases the phase-separation time. When alumina is used as the sorbent, the phase-separation time is restored to its original value. Thus, most of surfactants are removed by a carbonate wash followed by treatment with an alumina sorbent.

Removal of Carboxylic Acids from Degraded TRUEX-NPH

During the degradation of TRUEX-NPH by acidic hydrolysis, not only will CMPO and TBP be degraded, but also the normal paraffinic hydrocarbons (C_{12}-C_{14}) may be hydrolyzed to their acidic form, carboxylic acids (15). Because organic-soluble carboxylic acids are, in general, interfacially active and act as acidic extractants, they can 1) increase phase-separation times and 2) cause inferior stripping performance of the TRUEX solvent. Lauric acid (C-12) was selected to evaluate the removal of organic-soluble carboxylic acids from degraded TRUEX-NPH solvent by solid sorbents.

Lauric acid distribution coefficients are shown in Table 3 for Amberlyst A-26 and alumina. Both sorbents remove lauric acid from

Table 1. Americium Distribution Ratios for Undegraded and Degraded Solvent

$[HNO_3]$ (M)	D_{Am}	
	Undegraded	Degraded[a]
0.01	1.2×10^{-2}	1.3×10^{2}
0.05	2.3×10^{-1}	4.3×10^{0}
2.0	2.9×10^{1}	6.6×10^{-1}

[a]Water washed.

Table 2. Effect of Solvent Treatment on Phase-Separation Times between the Solvent and Carbonate Wash[a]

Solvent	Treatment[b]	Time (min)	Dispersion[c] Number
undegraded	none	1.0	11×10^{-4}
degraded	none	7.0	1.6×10^{-4}
degraded	carbonate wash	3.6	3.1×10^{-4}
degraded	carbonate + silica gel	3.2	3.4×10^{-4}
degraded	carbonate + Amberlyst A-26	1.5	7.4×10^{-4}
degraded	carbonate + alumina	1.0	11×10^{-4}

[a]Method of mixing phases was that used by Mailen and Tallent (14).
[b]Degraded solvent was water washed.
[c]Dispersion number = $1/t(z/g)^{1/2}$, where z is total height of two phases, t is the phase-separation time, and g = 9.81 m/s^2 (17).

undegraded TRUEX-NPH solvent with K_d values > 20. However, the K_d values were significantly lower for the degraded TRUEX-NPH solvent than for the undegraded solvent, an order of magnitude for the Amberlyst A-26 and three orders of magnitude for alumina. This suggests that the lauric acid is significantly complexed by some components in the degraded TRUEX-NPH. The treatment of the degraded TRUEX-NPH with sodium carbonate prior to the treatment with Amberlyst A-26 or alumina improves the performance of the solid sorbents. A carbonate wash followed by treatment with Amberlyst A-26 prior to the distribution measurement further improves the performance of the sorbents, although the K_d values are still lower than those for the undegraded TRUEX-NPH.

Table 3. Effect of Solvent Treatment on Adsorption of ^{14}C-Lauric Acid by Solid Sorbents

Solvent	Treatment	K_d (mL/g)[b] Amberlyst A-26	Alumina
undegraded	none	21	130
degraded	none[a]	0.72	0.12
degraded	carbonate wash	6.3	17
degraded	carbonate wash + Amberlyst A-26	11	67

[a]Degraded solvent was water washed.

[b] $$K_d = \frac{[\text{lauric acid}]_{\text{initial}} - [\text{lauric acid}]_{\text{final}}}{[\text{lauric acid}]_{\text{final}}} \cdot \frac{\text{mL of solvent}}{\text{g of sorbent}}$$

These results show that neither alumina nor Amberlyst A-26 alone can remove lauric acid from water-washed degraded TRUEX-NPH solvent. However, in combination with a carbonate wash, both sorbents can remove lauric acid, and presumably other high-molecular-weight acidic impurities, from degraded TRUEX-NPH.

Effect of Sorbent Treatment on Degraded TRUEX-NPH

Three solid sorbents were tested as possible follow-up treatments to the carbonate washes: Amberlyst A-26 anion exchange resin, neutral alumina, and sodium silica gel. Americium distribution ratios were measured between HNO_3 and degraded solvent before and after the sorbent treatment and are reported in Table 4. Pretreatment of the solvent before treatment with the sorbents consisted of washing four times (O/A = 0.5) with 0.25M Na_2CO_3, three times with 0.05M HNO_3, and finally with a small amount of water. The distribution results for 0.01 and 0.05M HNO_3 show that all treatments produce D_{Am} values lower than those for the degraded solvent (Table 1). Further, treatments with alumina and Amberlyst A-26 produce lower D_{Am} values than treatments with either no sorbent or sodium silica gel. Alumina and Amberlyst A-26 are, therefore, the best at removing the organic-soluble acidic species, which cause high D_{Am} at low HNO_3 concentrations and prevent stripping of TRU elements.

Table 4. Effect of Solid Sorbents on Am Distribution Ratios between Degraded Solvent[a] and HNO_3

	D_{Am}			
$[HNO_3]$ (M)	No Sorbent	Sodium Silica Gel[b]	Alumina[c]	Amberlyst A-26[d]
0.01	1.1×10^{-1}	3.1×10^{-1}	3.1×10^{-3}	4.0×10^{-3}
0.05	9.7×10^{-2}	1.4×10^{-1}	2.1×10^{-2}	1.3×10^{-2}
2.0	2.1×10^{0}	2.0×10^{0}	1.4×10^{0}	6.7×10^{-1}

[a]Four contacts with 0.25M Na_2CO_3 (O/A = 0.5, where O/A is the organic-to-aqueous ratio), three contacts with 0.05M HNO_3 (O/A = 0.5), and one contact with water.
[b]4 g silica gel + 10 mL washed solvent.
[c]4 g alumina + 10 mL washed solvent.
[d]5 g Amberlyst A-26 + 10 mL washed solvent.

The effect of sorbent treatment on D_{Am} at 2M HNO_3 is much smaller than that at 0.01 and 0.05M HNO_3. Treatments with alumina and Amberlyst A-26 produce lower D_{Am} than treatments with either no sorbent or sodium silica gel, as was observed for 0.01 and 0.05M HNO_3. However, the D_{Am} value for the degraded solvent is also lower than those for all treatments except with Amberlyst A-26. Analyses by SFC show that the concentration of CMPO in the degraded solvent is little changed after treatment of any kind (see Table 5). The reason for these differences in the D_{Am} values at 2M HNO_3 is not completely understood at this time. It is possible that some of the non-aqueous-soluble acidic species can act as neutral extractants for americium or be converted to neutral extractants by the alumina or silica gel.

These results show that sorbent treatment is a crucial step in the removal of the non-aqueous-soluble degradation products. Although alumina may be less effective than Amberlyst A-26 at removing degradation products, which extract americium at high HNO_3 concentrations, both alumina and Amberlyst A-26 effectively remove acidic degradation products, which prevent stripping of TRU elements and threaten the success of the TRUEX process.

SFC Analysis of Degraded TRUEX-NPH Solvent after Cleanup

The relative peak areas in Table 5 for the solvent components as a function of solvent treatment show that the CMPO concentration after the various treatments remains relatively constant, although the CMPO concentration was only 30% of its initial concentration in the TRUEX-NPH solvent. The TBP concentration also varied by less

Table 5. Relative SFC Peak Areas[a] of Components in Degraded TRUEX-NPH as a Function of Solvent Treatment

Component	Time (min)	Water Washed	Carbonate Washed	Carbonate wash followed by Amberlyst A-26	Carbonate wash followed by Alumina	Carbonate wash followed by Sodium Silica Gel
C-12	11	1.00	0.96	0.95	0.96	1.00
C-13	12	6.7[b]	7.4[b]	6.2[b]	8.2[b]	6.7[b]
C-14	14	0.98	0.96	0.97	0.97	0.98
TBP	16	0.99	0.97	0.92	0.86	0.97
CMPO	25	0.33	0.32	0.31	0.28	0.33
Other	15-20	30	23	15	26	29

[a]Relative peak area = {(area in sample)/(area in undegraded)} • {(C-13 area in undegraded)/(C-13 area in sample)}.
[b]Relative peak area = {(area in sample)/(g of sample)}•10^{-6}.

than 7%. Based on these relative peak areas, the effectiveness of the sorbents at removing degradation products with retention times between 15 and 20 min is:

Amberlyst A-26 > neutral alumina > sodium silica gel

Although more compounds with 15 to 20 min retention times appeared in the carbonate-washed degraded solvent after treatment by alumina and silica gel than with Amberlyst A-26, some care must be taken in viewing these data. Conversion of weak acids to sodium salts would greatly affect their retention times. This factor may explain some of the differences found in these peak areas after various treatments.

The chromatogram for alumina-treated degraded solvent shows an extra peak, which is not found in the degraded TRUEX-NPH chromatogram, at the shoulder of the TBP peak. This new peak may result from a compound that forms during the treatment with alumina and extracts Am at 2M HNO_3. This new peak is not observed after treatment with Amberlyst A-26 anion exchange resin.

CONCLUSION

The unchecked hydrolysis of TRUEX-NPH solvent by HNO_3 can present a significant problem for the TRUEX process. In addition to the destruction of the major extractant, CMPO, the acidic degradation products present in organic phase prevent the stripping of americium at low HNO_3 concentrations. A carbonate wash alone does not completely remove acidic degradation products and does not

restore the stripping performance of the degraded solvent. Solid sorbents alone do not restore the performance of the solvent either. However, solid sorbents in combination with a carbonate wash do remove acidic degradation products from the degraded TRUEX-NPH solvent and substantially restore stripping performance of the solvent. Based on D_{Am}, K_d for lauric acid, and phase-separation times, the performance of the sorbent-treated solvent follows the order:

Amberlyst A-26 ~ neutral alumina > sodium silica gel

After a two-step cleanup, SFC analysis shows that the degraded solvent still contains degradation products, but these compounds do not affect Am stripping. A two-step procedure, carbonate wash followed by treatment with either Amberlyst A-26 or alumina, is recommended for cleaning up degraded TRUEX solvent. The final choice of sorbent will depend, in part, on the method of sorbent disposal that will be used.

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