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RESTORING SOLVENT FOR NUCLEAR SEPARATION PROCESSES

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ABSTRACT

Solvent extraction separation processes are used to recover usable nuclear materials from spent fuels. These processes involve the use of an extractant/diluent (solvent) for separation of the reusable actinides from unwanted fission products. The most widely used processes employ tributyl phosphate as an extractant diluted with a normal-paraffin hydrocarbon. During use, the solvent is altered due to hydrolysis and radiolysis, forming materials that influence product losses, product decontamination, and separation efficiencies. In most processes, the solvent is recycled after cleaning. Solvent cleaning generally involves scrubbing with a sodium carbonate solution. Studies at the Savannah River Laboratory have shown that carbonate washing, although removing residual solvent activity, does not remove more solvent-soluble binding ligands (formed by solvent degradation), which hold fission products in the solvent. Treatment of the solvent with a solid adsorbent after carbonate washing removes binding ligands and significantly improves recycled solvent performance. Laboratory work to establish the advantage of adsorbent cleaning and the development of a full-scale adsorption process will be described. The application of this process for cleaning the first cycle solvent of a Savannah River Plant production process will be discussed.

INTRODUCTION

Usable nuclear materials are recovered at the Savannah River Plant (SRP) by chemical processing of dissolved reactor fuels. The desired actinides are separated

from fission products and one another by a solvent extraction process using tributyl phosphate (TBP) as a complexant in an n-paraffin diluent.

The process solvent is composed of 7.5% TBP (HM Process) or 30% TBP (Purex Process) in a C_{12-14} normal paraffin diluent. Solvent is degraded during processing through radiolysis by contact with highly radioactive fission products and by hydrolysis through contact with nitric acid solutions. Degradation products are formed from both the extractant and the solvent diluent. The types of degradation products reported in the literature appear to depend on the process in use. For example, the British report nitro, nitrate compounds and hydroxamic acids,[1,2] and German workers find carboxylic acids, ketones, diketones, and phosphate oligimers.[3] No detailed analysis of HM process solvent has been made, but a C_{13} carboxylic acid has been tentatively identified as a solvent component. Since TBP degradation to dibutyl phosphate (DBP) and monobutyl phosphate (MBP) is common to all processes, the difference in impurities probably stems from the type and source of diluents in use. DBP and MBP are easily removed by carbonate washing. The paraffin-based degradation products tend to be more soluble in the solvent and are largely unaffected by carbonate scrubbing.

Two approaches were followed in a effort to improve the quality of first cycle solvent. First, an increase in carbonate wash contact time was examined since equipment to provide longer contact times could be easily retrofitted into existing plant equipment. In addition, based on some work at Oak Ridge National Laboratory (ORNL), an adsorption cleaning process was examined as an alternative method to restore solvent quality.

LABORATORY RESULTS

Laboratory studies were conducted with first cycle solvent from the SRP processes. Both uncleaned and plant-cleaned solvent were studied.

Solvent Quality Tests

Three tests were used to define solvent quality in the laboratory. The tests were (1) determination of gross gamma activity and the isotopes contributing the activity, (2) interfacial tension of the solvent in contact with 2.5 wt % sodium carbonate, and (3) zirconium pickup, the amount of zirconium-95 retained by the solvent after extraction, scrubbing, and stripping. The values for degraded solvent were compared to the values obtained for fresh solvent.

Residual gross gamma activity of the solvent showed whether the wash treatment effectively removed fission product activity from the solvent. Isotope analysis established whether or not the treatment favored the removal of a particular species.

The interfacial tension was used to determine if the phase disengaging behavior had been altered by the wash treatment. Interfacial tension has been shown to be inversely related to disengaging time. The drop-volume method[5] was used for determining interfacial tension. The higher the interfacial tension, the faster the solvent separates from the aqueous phase.

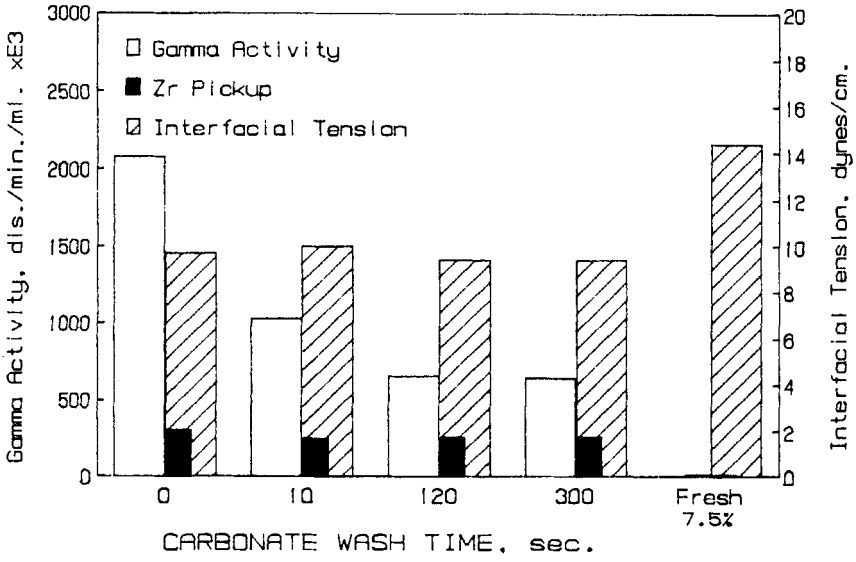

FIGURE 1. Effect of Wash Time on 7.5% TBP Solvent Properties

The zirconium pickup test involved contacting the solvent sample with a simulated feed containing a spike of actual process feed, scrubbing the extract with 2.8M or 4.5M HNO_3, and then stripping the scrubbed solvent with 0.01M HNO_3. The pickup test used single-stage contacts at room temperature mixed in a centrifuge tube on a Vortex mixer and separated by centrifugation. The resulting stripped solvent was then analyzed by gamma spectrometry. Low activity indicated that fission product binding ligands had been removed.

Carbonate Washing

Extended carbonate washing studies were conducted on the HM process 7.5% TBP solvent. This solvent has the shortest carbonate contact time (approximately 10 seconds) in the SRP process. A sample of unwashed HM solvent was washed with 2.5 wt % sodium carbonate for various contact times. After phase separation by centrifugation, the washed solvent properties were measured. Solvent properties as a function of contact time are shown in Figure 1. Much of the Zr-95 is removed quickly in a short contact, followed by a slower removal as contact time increases. The zirconium pickup of the extended-washed solvent was found to be unchanged, even though the activity level on washing was reduced. The interfacial tension was also not improved (increased) with extended washing. These results indicate that longer carbonate washing removes the radioactive species from the solvent, but the more organic-soluble binding ligands are not removed and remain in the solvent to again complex fission products when the solvent is recycled. Overall, these results show that increasing two-phase contact time in the HM carbonate washers would not be cost effective.

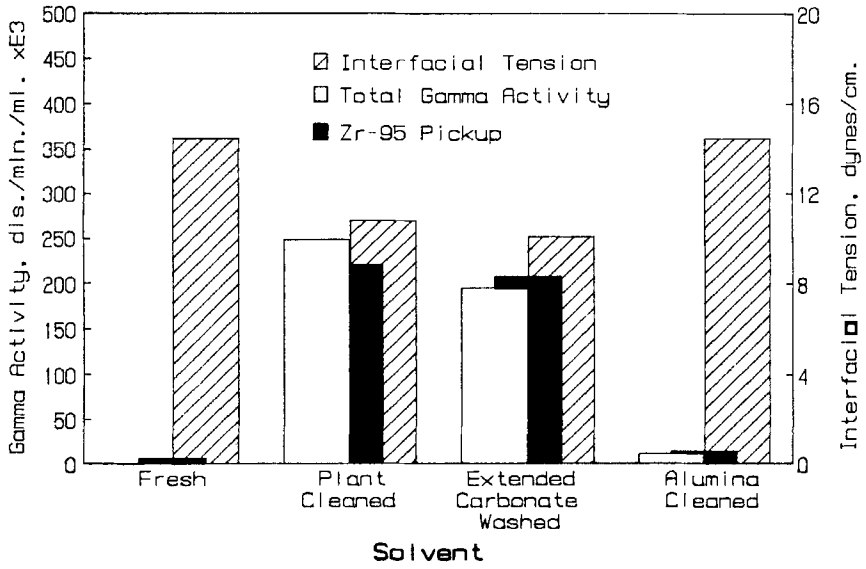

FIGURE 2. Effect of Cleaning Process on 7.5% TBP Solvent Properties

Adsorbent Cleaning

The use of solid sorbents for cleaning solvents used in nuclear processing has been reported in the literature.[4,5,6] Based on the work of Mailen and Tallent[4] with SRP Purex solvent, activated alumina was selected for cleanup of first cycle solvent. Laboratory work was done using plant-washed first cycle solvent and Kaiser commercial-grade activated alumina. Columns were prepared using 1-inch ID glass tubes and fed using Fluid Metering, Inc. piston pumps with flow entering the bottom of the column.

Alumina adsorbs TBP initially, which increases the solvent interfacial tension. After about 1-2 column volumes are processed, the interfacial tension falls to a constant level. The steady-state interfacial tension was 14.7 for 7.5% TBP and 10.3 dynes/cm for 30% TBP solvents whose values are equal to that obtained for their respective freshly prepared solvents.

The 7.5% TBP solvent cleaned with alumina was found to contain significantly lower gamma activity and near fresh solvent Zr pickup. A comparison of solvent properties cleaned by extended carbonate washing and alumina is presented in Figure 2. This graph compares the properties of freshly prepared 7.5% TBP (Fresh) and solvent washed by the normal plant process (Plant) with the properties

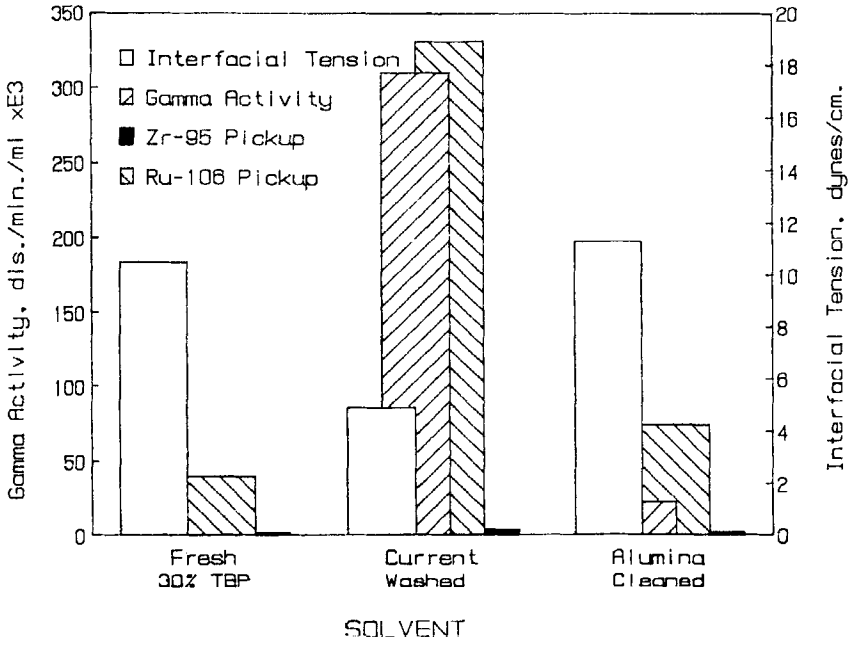

FIGURE 3. Effect of Cleaning Process on 30% TBP Solvent Properties

of plant solvent after extended carbonate washing (Extended) and after treatment with activated alumina (Alumina). Treatment with alumina nearly restores plant 7.5% TBP solvent to fresh solvent properties. The reduction in Zr pickup establishes that alumina is removing Zr binding ligands, compounds which complex and hold Zr in the solvent, as well as removing gamma activity. The 30% TBP solvent properties were also restored to near fresh solvent levels (Figure 3) by alumina cleaning. The residual Ru-106 and Zr-95 pickups were still higher than with fresh solvent, but considerably lower than with uncleaned solvent. Examination of the residual activity components (Table 1) shows that the Zr-95 was more effectively removed than Ru-106. These results indicate that alumina may not be the optimum adsorbent for removing Ru binding ligands.

Based on work by Neace[7] and Mailen,[4] 7.5% TBP solvent was cleaned using Florex LVM (an extruded attapulgite clay) to determine if it had a more appropriate cleaning capacity (Table 2). Florex-cleaned solvent had poorer Zr pickup properties (higher pickup) than activated alumina, while other cleaned solvent properties were similar. Thus activated alumina was selected for full-scale cleaning tests.

Table 1.

Effect of Alumina Cleaning on Solvent Gamma Activity Components, dis/min/ml

	7.5% TBP			30% TBP		
Isotope	Before	After	DF	Before	After	DF
Ru-103	1,630	160	10.2	3,300	200	16.5
Ru-106	19,760	3,130	6.3	301,000	22,200	13.6
Zr-95	2,420	160	15.1	3,100	0	–
Nb-95	1,210	80	15.1	2,400	40	60

Table 2.

Effectiveness of Adsorbent Type Used for Solvent Cleaning

	7.5% TBP After Treatment With:		
	Untreated 7.5% TBP	Activated Alumina	Attapulgite Clay
Interfacial Tension, dynes/cm	12.4	14.5	14.6
Total Gamma Activity, dis/min/ml	41,000	380	540
• Zr-95	3,000	0	0
• Ru-106	35,100	380	540
Zr Pickup, dis/min/ml	37,400	1,900	6,300
Ru Pickup, dis/min/ml	32,600	14,700	14,400

Laboratory studies were conducted to establish whether or not solvent cleaning would be practical on a full-scale basis for the HM 7.5% TBP process using commercial-grade alumina from Kaiser Chemicals. Glass columns 1 inch ID with varying lengths were fed solvent using Fluid Metering, Inc. piston pumps fitted with pulse dampeners. Generally, 20 ml fractions were collected which provided enough treated solvent for quality tests on each fraction. The effect of column residence time and alumina particle size was tested.

Two types of alumina were examined, a small spherical-shaped particle about 1.7 mm in diameter and crushed sphere varieties with nominal particle sizes of 1.2 and 0.5 mm diameter. Column residence time was held at 5.5 minutes (Table 3). The interfacial tension was independent of particle size. The gamma activity and Zr pickup results show that solvent is more effectively cleaned by smaller particle size alumina.

Table 3.

Dependence of Cleaned Solvent Properties on Alumina Particle Size

Particle Size, mm	Interfacial Tension dynes/cm	Total Gamma Activity dis/min/ml	Zr-95 Pickup dis/min/ml
0.5	14.4	8.6×10^3	2.0×10^3
1.2	14.5	13.9×10^3	3.1×10^3
1.7	14.8	17.4×10^3	5.5×10^3
Untreated	12.4	41.0×10^3	37.4×10^3

Table 4.

Dependence of Cleaned Solvent Properties on Alumina Column Residence Time

Column Residence Time, min	Interfacial Tension dynes/cm	Total Gamma Activity dis/min/ml	Zr-95 Pickup dis/min/ml
Untreated	12.4	41.0×10^3	37.4×10^3
2.6	13.6	56.7×10^3	27.0×10^3
5.2	14.3	39.1×10^3	12.3×10^3
10.9	14.6	22.1×10^3	7.4×10^3
54.7	14.6	45×10^3	—
Fresh	14.6	—	0.2×10^3

The influence of column residence time was examined by changing volumetric throughput through the column or by changing column length (Table 4). The improvement of solvent interfacial tension requires about 10 minutes residence time to increase the interfacial tension to fresh solvent levels. Longer column residence times (54.7 min) were of no advantage. The response of gamma activity removal showed that the longer the residence time, the more activity was removed. The Zr pickup of solvent treated at various column residence times was similar for 5 and 10 minutes and better than 2.6 minutes. The pickup response was similar to the interfacial tension response, indicating that column residence times should be greater than 5 minutes, but times greater than 10 minutes were of marginal benefit.

These studies show that the solvent impurities which reduce interfacial tension were more readily removed than the impurities which complex and retain fission

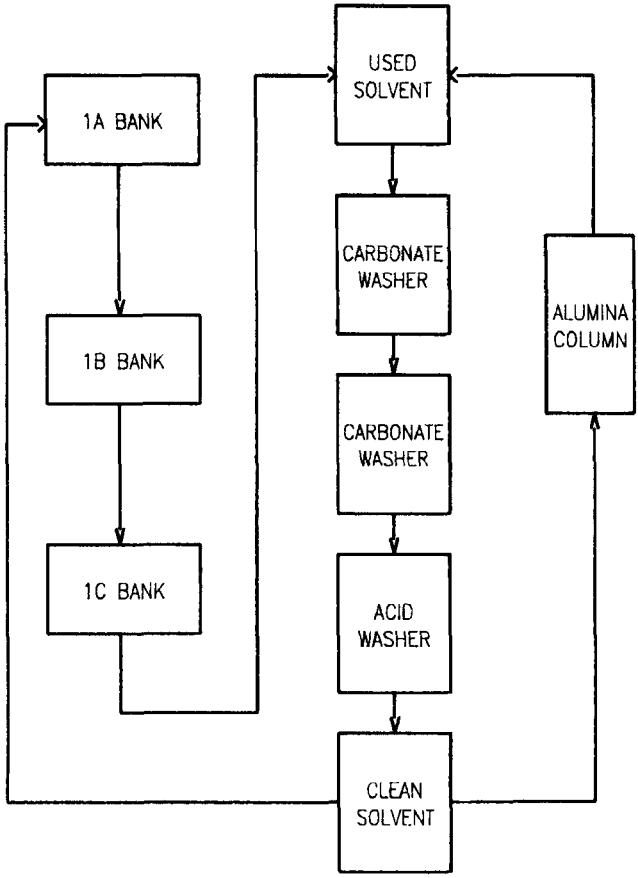

FIGURE 4. Canyon Solvent Cleaning Process

products. Fission product binding ligand removal is favored by having large adsorbent surface area and long adsorb times.

Full-Scale Cleanup

The entire HM process first cycle solvent inventory (~ 16,500 gal) was cleaned with activated alumina using a side stream process. Solvent was circulated from the clean solvent storage tank (Figure 4) through the alumina column, then through the normal wash train back to the clean solvent tank. The alumina column was fabricated from a 30-gallon stainless steel drum using a perforated pipe for the column inlet and outlet. The perforated section was covered with stainless steel

Table 5.

Change in Canyon Solvent Properties with Cleaning

	Fresh 7.5% TBP	Before Cleaning	After Cleaning
Interfacial Tension, dynes/cm	14.7	11.2	13.9
Total Gamma Activity, dis/min/ml	0	86.7×10^3	29.2×10^3
• Zr-95	0	33.0×10^3	3.6×10^3
• Ru-106	0	46.8×10^3	23.8×10^3
Zr Pickup, dis/min/ml	0.2×10^3	23.4×10^3	7.8×10^3

Table 6.

Gamma Activity Removal by Cleaning Canyon Solvent

	7.5% TBP Solvent		
	Before dis/min/ml	After dis/min/ml	DF
Total Gamma	86.7×10^3	29.2×10^3	3.0
Ru-103	2.7×10^3	1.0×10^3	2.7
Ru-106	46.8×10^3	23.8×10^3	2.0
Zr-95	33.0×10^3	3.6×10^3	9.2
Nb-95	4.2×10^3	0.8×10^3	5.2

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screen to keep alumina particles in the drum. The drum was filled with Kaiser Chemical Type A-2 (Size 8 x 14) alumina as received from the vendor. Solvent was fed to the bottom of the column at a nominal 4 gal/min throughput (8 min residence time). Solvent samples from the column inlet and outlet were taken frequently for interfacial tension and gamma activity analyses. The column was replaced when the inlet and outlet interfacial tensions were the same. Five columns were used over a 340-hour cleaning period. During the cleaning period, the HM first cycle was operated as needed.

The overall change in solvent properties is shown in Table 5. The interfacial tension was increased to near fresh solvent levels. Total gamma activity was reduced about two-thirds, and the zirconium pickup was improved. Similar to laboratory findings, the removal of activity was not equal for isotopes of different elements (Table 6). About 90% of the Zr and Nb was removed, but only 50% of the Ru was eliminated.

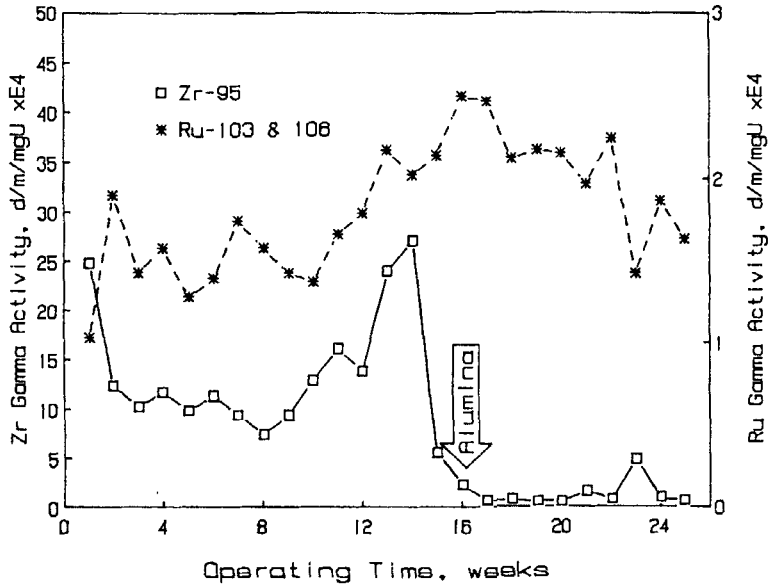

FIGURE 5. Product Stream Contents

Following the alumina cleaning (Figure 5), the HM first cycle process showed an immediate response to cleaned solvent. The overall zirconium DF made a step change upward to a previous acceptable level. The zirconium level of the first cycle product stream was reduced by a factor of 20. The solvent interfacial tension and gamma activity have remained essentially unchanged since the solvent was cleaned. This indicates that the degradation products which reduce interfacial tension and/or extract fission products (binding ligands) are not produced in significant concentrations quickly in the SRP HM first cycle process. The solvent properties will be routinely monitored to establish a frequency for alumina cleaning.

The improved rejection of fission products by the solvent has led to a large reduction in liquid or salt waste from the HM process. The lower gamma activity of the solvent entering the first carbonate washer has increased the use-life of the carbonate wash from 2 days before cleaning to 14 days since cleaning. The reduction in Zr content of the solvent has allowed process alteration to favor removal of Ru during scrubbing, which yields product meeting fission product specifications.

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