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CLEANUP OF 7.5% TRIBUTYL PHOSPHATE/N-PARAFFIN SOLVENT-EXTRACTION SOLVENT

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ABSTRACT

The HM process at the Savannah River Plant uses 7.5% tributyl phosphate in n-paraffin as an extraction solvent. During use, the solvent is altered due to hydrolysis and radiolysis, forming materials which influence product losses, product decontamination, and separation efficiencies. Laboratory studies to improve online solvent cleaning have shown that carbonate washing, although removing residual solvent activity, does not remove binding ligands which hold fission products in the solvent. Treatment of solvent by an alumina adsorption process removes binding ligands and significantly improves recycle solvent performance. Both laboratory work defining a full-scale alumina adsorption process and the use of the process to clean HM process first cycle solvent is discussed.

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INTRODUCTION

The Savannah River Plant (SRP) HM process for recovering uranium uses 7.5 volume % tributyl phosphate (TBP) in an n-paraffin diluent as an extraction solvent. To produce high quality product, solvent must exhibit good fission product rejection in the first cycle. Since late 1984, more frequent reprocessing of the HM process product stream has been necessary to meet product specifications because the standard carbonate solvent washing process is unable to produce and maintain solvent of required quality. A two-pronged program was conducted to correct current solvent behavior. First, within the framework of the current washing process, the benefit of extended carbonate/solvent contact was examined. Second, the potential of a new process using alternative reagents or methods was investigated.

SUMMARY

Treatment of H-Area solvent with alumina restored solvent properties to near fresh solvent levels. Extended carbonate washing removed residual radioactivity from the solvent, but did not improve the ability of the solvent to reject radioactivity. To characterize cleaned solvent, three quality tests were used: solvent total gamma activity, the interfacial tension between solvent and sodium carbonate solution (related inversely to solvent disengaging time), and zirconium pickup which evaluates the ability of the solvent to reject fission products. Extended carbonate washing removed residual solvent activity, but the interfacial tension and zirconium pickup of the extended-washed solvent remained essentially unchanged from current plant washed solvent. Longer contact allowed the carbonate solution to further strip radioactivity from solvent, but the binding ligands responsible for extracting the radioactive species were not removed by carbonate scrubbing. Treatment of washed solvent with alumina not only removed residual activity, but also increased interfacial tension and restored zirconium pickup to near fresh solvent levels.

A full-scale cleanup of the HM process first cycle solvent was successfully completed. The 16,500-gallon inventory of first cycle solvent was cleaned by an alumina adsorption process. The cleanup was carried out using a recirculating side stream process over an

18-day period. The column inlet and outlet streams were sampled frequently during the run to monitor column performance. The small adsorption column was replaced four times during the run period. The cleaning run proceeded smoothly without operating problems and without requiring first cycle production stoppage.

Solvent properties were significantly improved after alumina treatment. The solvent interfacial tension was increased from 11.2 to 13.9 dynes/cm (fresh solvent is 14.5 dynes/cm). The residual solvent activity was reduced to 1/3 of its pretreatment level and improved (lower) zirconium pickup was observed (about 1/3 that of the uncleaned solvent). H-Area first cycle process responded immediately to the cleaned solvent with first cycle fission product decontamination factors returning in one step to the higher pre-1984 levels. Attendant with using the cleaned solvent, the first carbonate wash use-life has increased from about two days to two weeks, which significantly reduced the H-Area salt waste burden.

Additional laboratory work is underway to established if other SRP solvents can be improved by cleaning with an adsorption process.

DISCUSSION

Background

Uranium fuels containing ^{235}U are processed and recovered, along with neptunium and plutonium byproducts, in the H-Area at the Savannah River Plant (SRP).[1] The fuels to be processed are dissolved in nitric acid. U, Np, and Pu are separated from fission products and from one another by multistage countercurrent solvent extraction, using mixer-settler contactors, with 7.5% tributyl phosphate (TBP) in n-paraffin. Nitric acid is used as a salting agent in addition to aluminum or other metal nitrates present in the feed solution. The enriched uranium is recovered as a dilute solution and shipped offsite for further processing.

The overall process consists of a first cycle for primary decontamination of U, Np, and Pu from fission products, followed by a second cycle for final purification of the actinides. Separate second cycles are used for uranium and for neptunium/plutonium. Each cycle involves extracting the actinides into an organic solvent, scrubbing the resulting product-bearing solvent to purify it, and stripping the product back into an aqueous stream. Separate solvent inventories are maintained for each cycle. The solvent is washed with sodium carbonate after each pass through the process and then reused.

During 1985, the zirconium-95 level in the product exceeded specifications, requiring the product to be recycled through the second cycle purification. In early 1986, the ruthenium-106 level increased to and sometimes exceeded product specifications. Examination of process parameters indicated that in mid-1984 a drastic reduction in the first cycle zirconium decontamination factor (DF) had occurred (Figure 1), and the process has remained at the lower DF thereafter. The extraction bank DF (Figure 1, 1A ZR DF) remained essentially constant while the scrub bank DF (Figure 1, 1B ZR DF) became lower, suggesting that the scrubbing operation had become less effective.

Laboratory work to improve first cycle DF showed that a higher DF was obtained when new solvent was used than with plant solvent. In addition, plant solvent was discolored and cloudy in appearance. In an independent study, solid silica particles were observed in the first cycle solvent. Gamma activity analysis of first cycle solvent after washing showed it contained a high residual activity, and during a production run the activity increased as the run progressed (Figure 2). These observations indicated that a poor solvent quality may have been partially responsible for poor first cycle performance.

Two approaches were followed in an 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),[2] and adsorption cleaning process was examined as an alternative method to restore solvent quality. This report discusses the laboratory work leading to a new SRP cleaning process and the scaleup of the process to clean the 16,500-gallon first cycle solvent inventory.

Solvent Degradation

HM process solvent is composed of 7.5 volume % TBP as an extractant in a C_{12}-C_{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 (Figure 3). 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, [3,4] German workers find carboxylic acids, ketones, diketones, and phosphate oligimers.[5] No detailed analysis of HM process solvent has been made, but a C_{13} carboxylic acid has been tentatively identified as

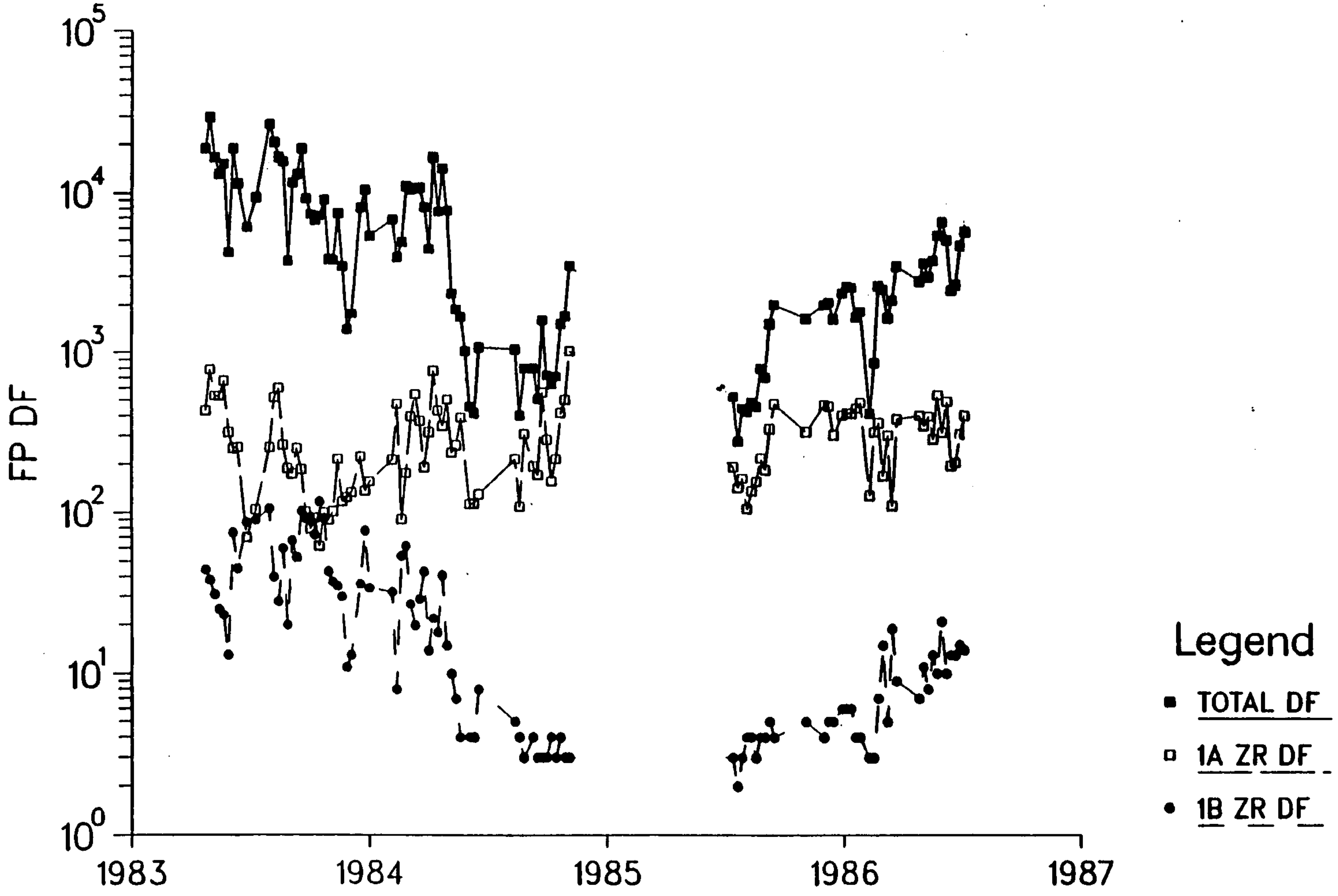


Figure 1. Zr Fission Product DF

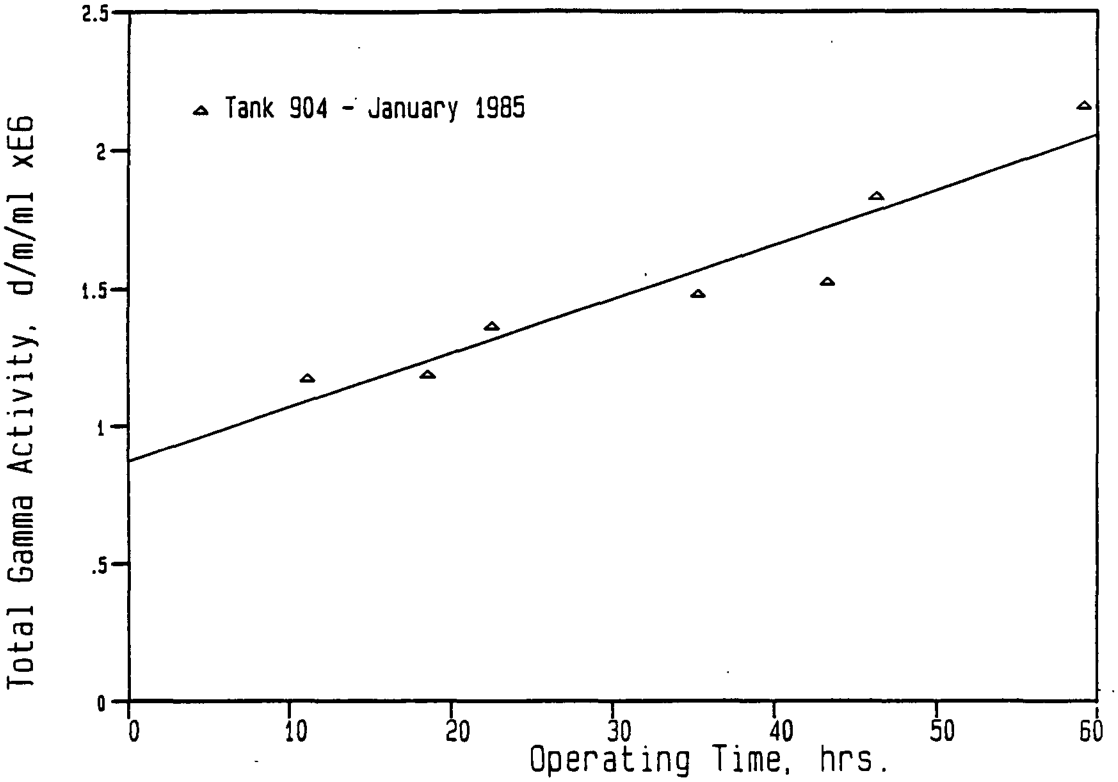


Figure 2. **Solvent Properties during Operating Cycle**

- TRIBUTYLPHOSPHATE EXTRACTANT
  - DIBUTYLPHOSPHATE
  - MONOBUTYLPHOSPHATE

- n—PARAFFIN DILUENT
  - LONG—CHAIN CARBOXYLIC ACIDS
  - KETONES AND DIKETONES
  - NITRO & NITRATE COMPOUNDS
  - HYDROXAMIC ACIDS
  - PHOSPHATE OLIGOMERS
  - ALCOHOLS

Figure 3. **Typical Solvent Degradation Products**

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.

Laboratory Studies

Laboratory studies were conducted with first cycle solvent from the SRP HM process. 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 gross gamma activity showed whether the wash treatment effectively removed fission product activity from the solvent. The 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 (Figure 4). The drop-volume method[6] was used for determining interfacial tension. The higher the interfacial tension, the faster the solvent separates from the aqueous phase. The zirconium pickup test involved contacting the solvent sample with a simulated feed containing a spike of actual H-Area 1AF, scrubbing the extract with 2.8M HNO_3, and then stripping the scrubbed solvent with 0.01M HNO_3. The pickup test used single-stage contacts at room temperature. The resulting stripped solvent was then analyzed by gamma spectrometry. Low activity indicated that fission product binding ligands had been removed.

Carbonate Washing Studies

A sample of unwashed solvent (tank 15.1 was washed with 2.5 wt % sodium carbonate for various contact times in the laboratory. The organic phase was checked for Zr-95 content after phase separation in a centrifuge. The removal of Zr-95 as a function of contact time is shown in Figure 5. Most of the Zr-95 is removed quickly in a short contact, followed by a slower removal as contact time increases. This behavior is typical of all laboratory wash experiments. The zirconium pickup of the extended-washed solvent (Figure 6) was found to be unchanged, even though the activity level on washing was reduced. The interfacial tension (Table 1) 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 ligand is not removed and remains in the solvent to again complex fission products when the solvent is recycled.

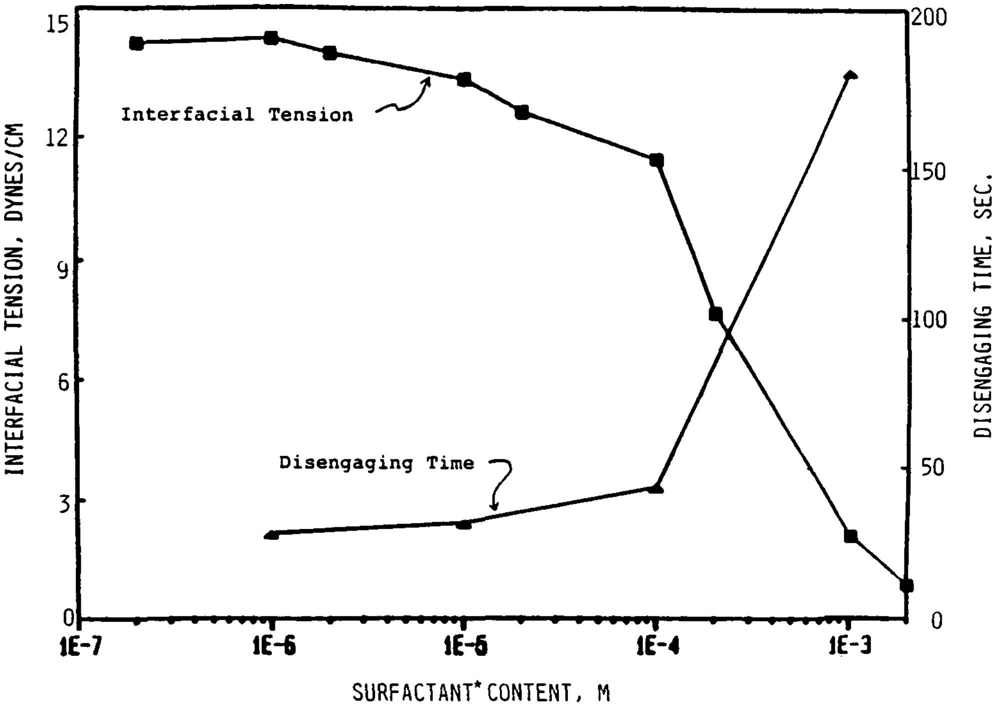
TABLE 1

Solvent Properties after Extended Washing

Carbonate Wash Time	Total Gamma Activity d/m/ml x 10^3	Interfacial Tension, Dynes/cm	Zirconium Pickup, d/m/ml x 10^3
10 seconds	805	10.5	230
120 seconds	421	10.1	204
300 seconds	342	10.1	207
Fresh 7.5% TBP	0	14.5	0

To experimentally estimate two-phase contact time in carbonate washer 12.6, samples were taken from tank 15.1 and the organic phase of washer 12.6. The 15.1 sample was laboratory-washed with carbonate for various contact times. The Zr-95 activity of the 12.6 sample was interpolated on a plot of activity versus wash time to determine the equivalent two-phase contact time in the washer. The results of two such measurements (Figures 7 and 8) indicate that the two-phase contact time in washer 12.6 is 9 to 11 seconds. This compares favorably to the calculated 5-second time from an engineering analysis of the washer.

Examination of the plant wash system, shown schematically in Figure 9, showed that a significant lag time exists between wash contacts in the plant equipment. To established if "aging" between washes affected Zr-95 removal, a laboratory wash was conducted which represented two passes through the plant system. In one case, the six-contact sequence (carbonate, carbonate, acid, carbonate, carbonate, and acid) was conducted as rapidly as practical. In all cases, disengagement was accomplished by centrifugation. In the second case, the six-contact sequence was conducted using calculated waiting periods between wash contacts.



*Lauric Acid

Figure 4. Effect of Surfactant

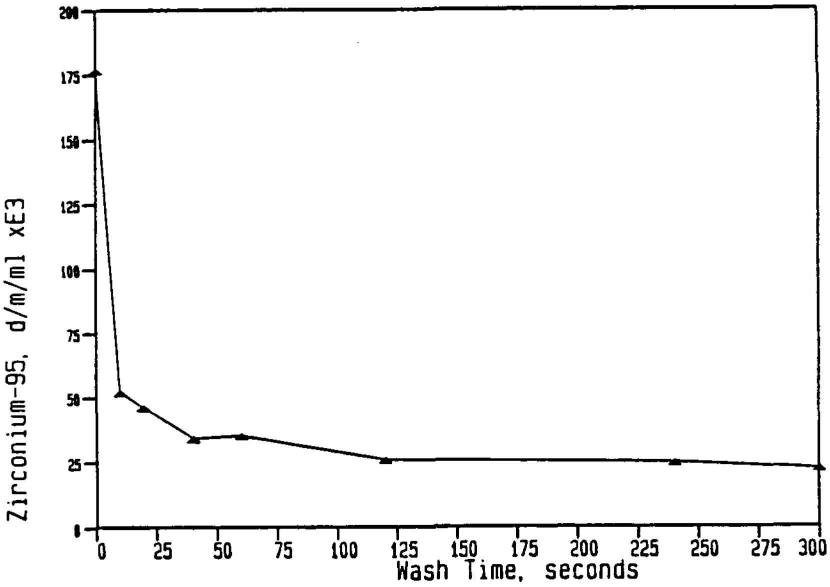


Figure 5. Effect of Carbonate Washing on Zr-95 Content

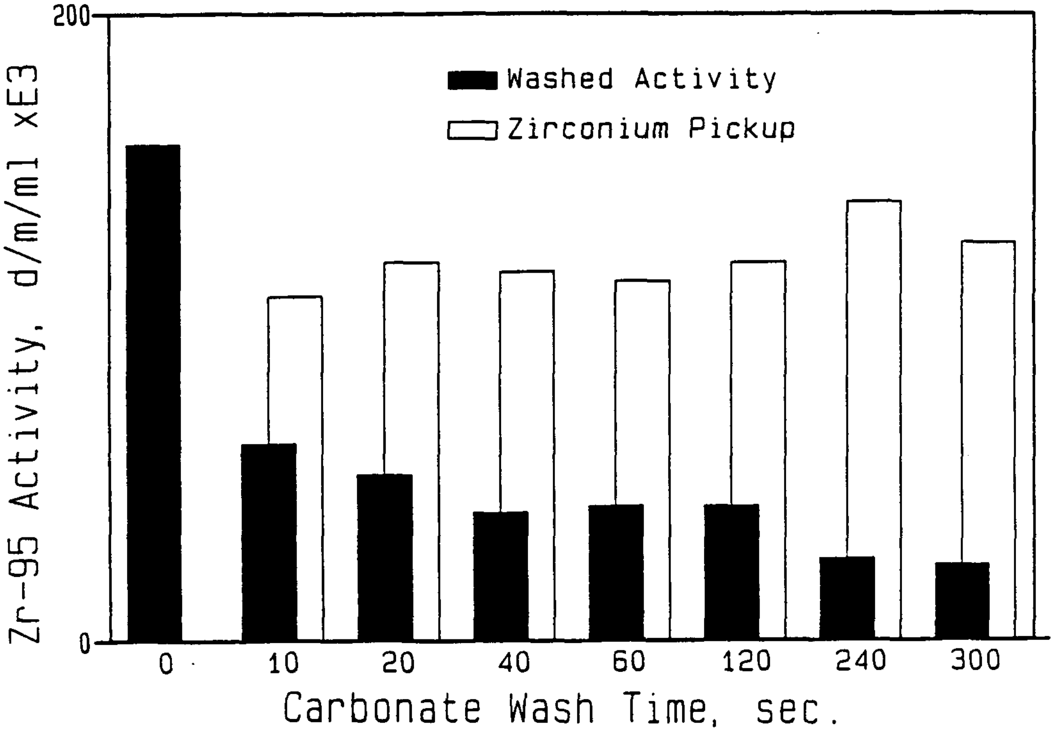


Figure 6. Effect of Wash Time on Solvent Properties

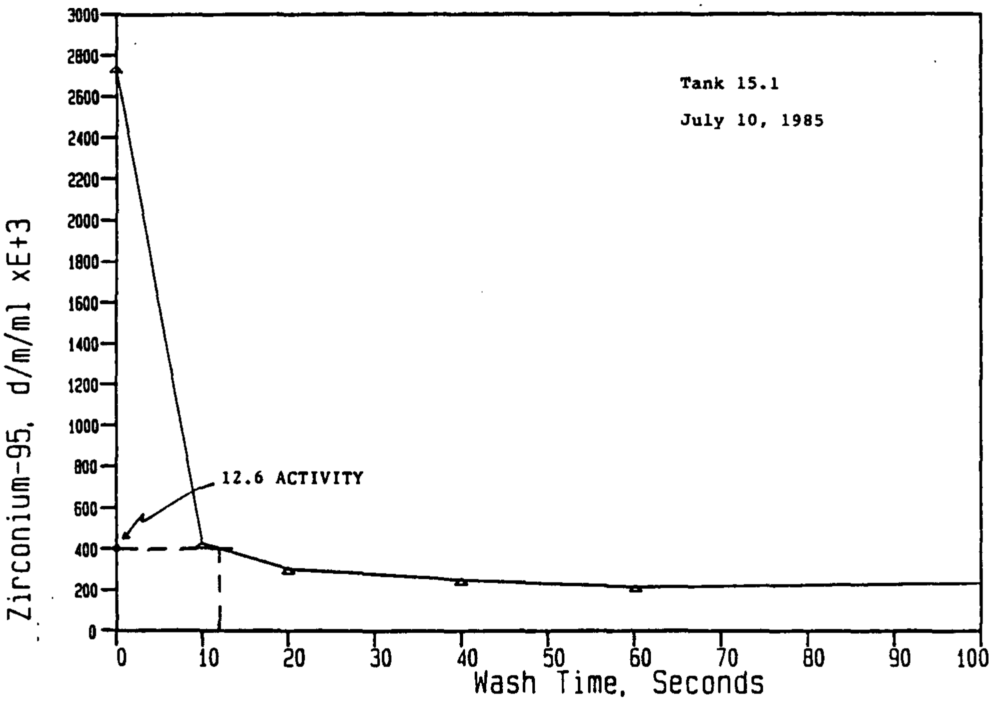


Figure 7. Estimation of Washer 12.6 Contact Time - I

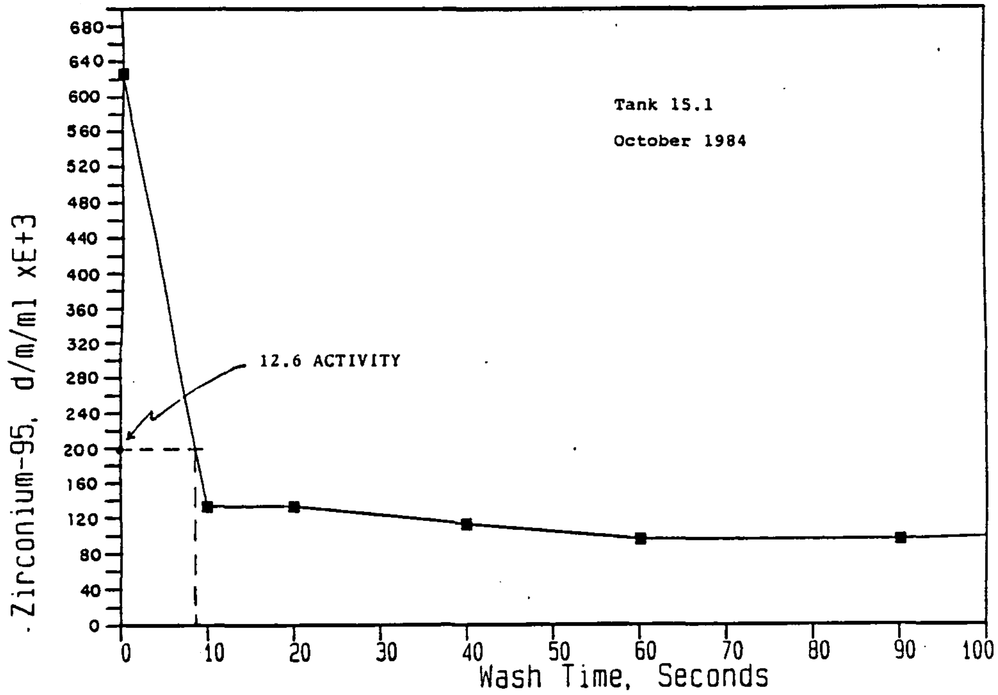


Figure 8. Estimation of Washer 12.6 Contact Time - II

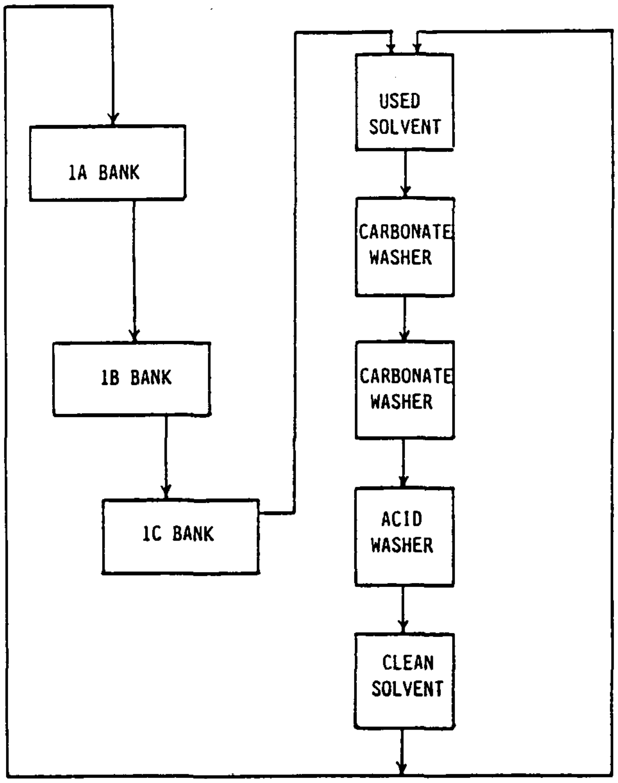


Figure 9. H-Area First Cycle Solvent System

The waiting periods between contacts were 2.7 hours (washer 12.6), 2.7 hours (washer 12.8), and 11.5 hours (combined time of washer 903, solvent tank 904, and tank 15.1). As shown in Table 2 and Figure 10, a larger amount of Zr-95 was removed when a waiting period was used between the two-phase contacts. This suggests that a more strippable species is formed during the waiting period.

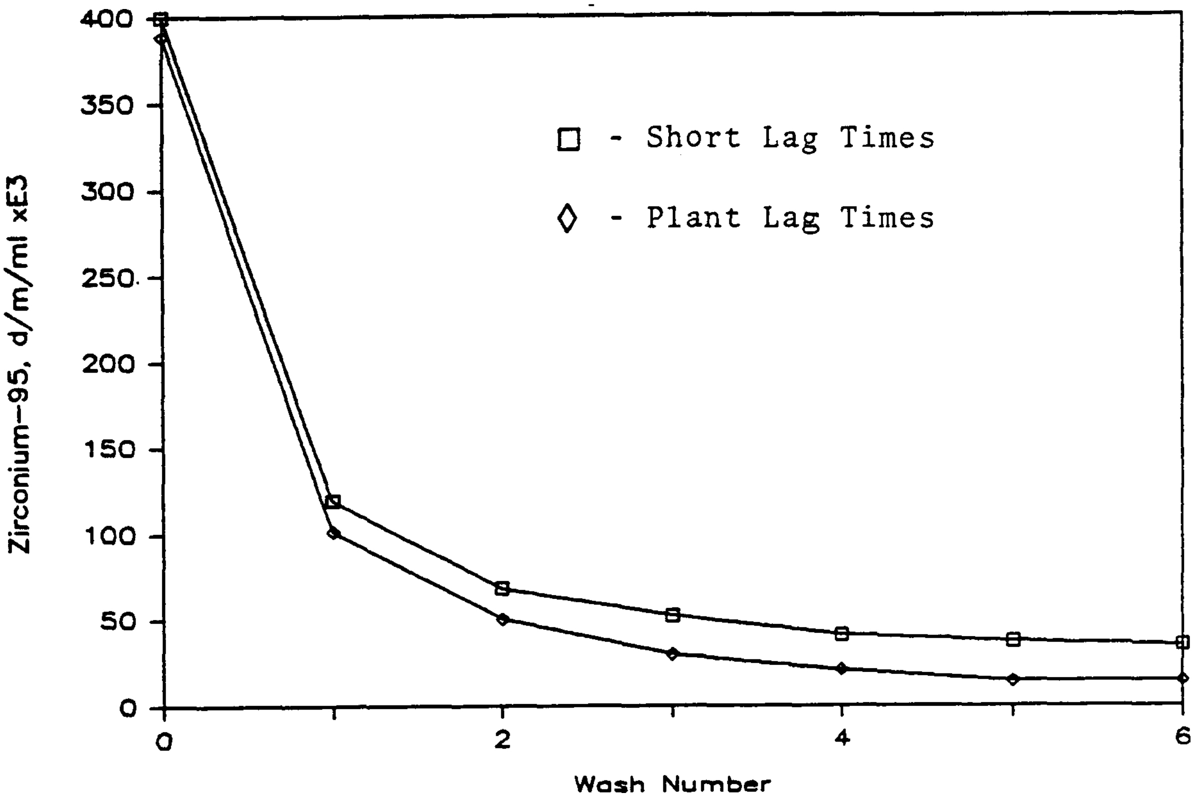
TABLE 2

Effect of Lag Time on Zirconium Removal

		Zr-95 Decontamination Factors			
Wash		No Lag		Plant Lag Times	
Carbonate		3.4		3.8	
Carbonate		1.7		2.0	
Acid		1.3		1.7	
	1st pass		7.7		13.2
Carbonate		1.3		1.4	
Carbonate		1.1		1.4	
Acid		1.1		1.0	
	2nd pass		1.5		2.1
	Overall		11.4		27.2

The order of washing was examined to determine if the second carbonate wash would be more effective if solvent were reacidified before carbonate washing. The results obtained for washing solvent with carbonate, then acid, and finally with carbonate (Figure 11) showed no significantly different activity removal than that obtained from the normal H-Area carbonate, carbonate, acid wash sequence.

The most significant carbonate wash variable studied was wash temperature (Figure 12). Significantly more gamma activity was removed at 50°C than at 23°C. The SRP wash system is normally run at 45°C to 50°C. These results show that increasing two-phase contact time in carbonate washers 12.6 and 12.8 is not cost effective. Longer carbonate washing will remove additional radioactivity from the solvent, but does not remove the ligands which complex radioactive fission products (Figure 13). The ligands, solvent degradation products, are more soluble in the solvent and remain to complex and retain fission products when solvent is recycled after carbonate washing, as indicated by the lower interfacial tension and the high zirconium pickup of the washed solvent compared to new solvent behavior.



Wash No.	Composition
1	2.5 Wt % Sodium Carbonate
2	2.5 Wt % Sodium Carbonate
3	0.1M Nitric Acid
4	2.5 Wt % Sodium Carbonate
5	2.5 Wt % Sodium Carbonate
6	0.1M Nitric Acid

Figure 10. Effect of Lag Time Between Washes

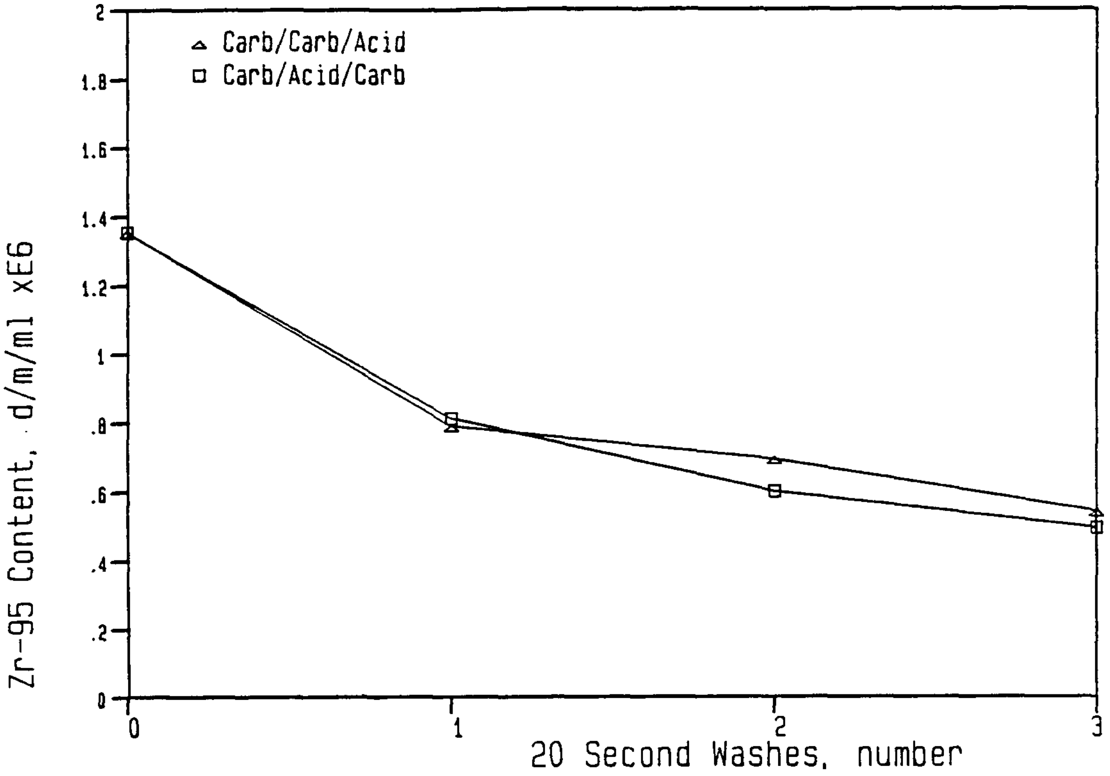


Figure 11. Effect of Wash Order

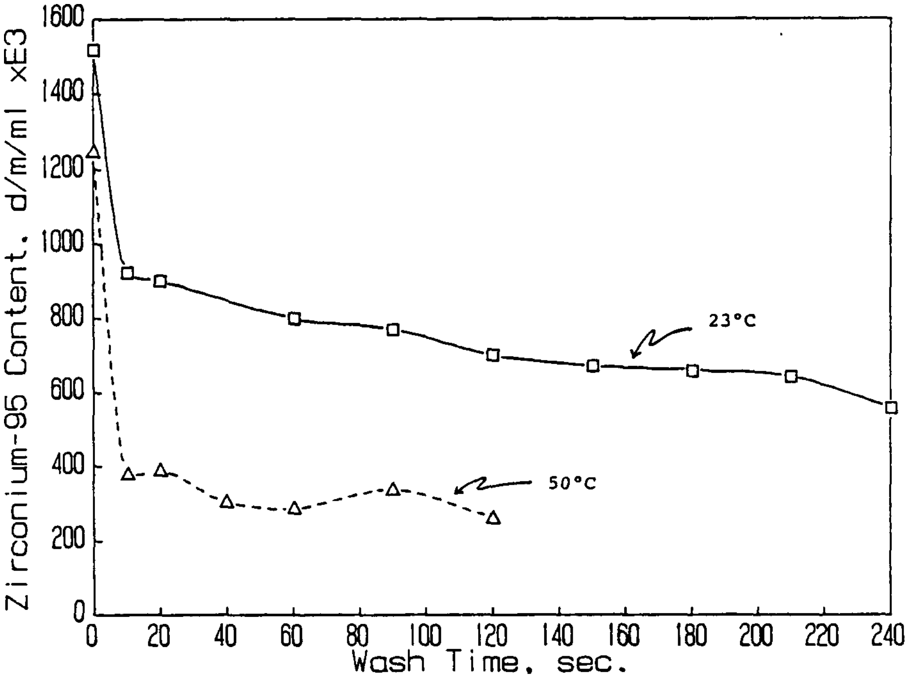


Figure 12. Effect of Temperature on Zr-95 Removal

Adsorption Process Studies

The use of solid sorbents for cleaning solvents used in nuclear reprocessing has been reported in the literature.[2,6,7] Based on the work of Mailen and Tallent with SRP Purex solvent,[2] activated alumina was selected for cleanup of HM first cycle solvent. Laboratory work was done using plant-washed first cycle solvent (tank 904) and Kaiser commercial grade activated alumina. Columns were prepared using 1-inch-ID glass tubes with end diameters reduced to allow flexible tubing connections. The column was fed using Fluid Metering Inc. piston pumps with flow entering the bottom of the column. Fractions were collected, by gravity, from the top of the column.

A typical curve showing the change in solvent interfacial tension with volume processed through an alumina column is shown in Figure 14. The alumina adsorbs TBP until saturated, about 1 to 2 column volumes, which causes the high interfacial tension at the beginning. The interfacial tension then becomes constant until column breakthrough occurs (not reached in this example). In this experiment, the steady-state interfacial tension was 14.5 dynes/cm, which is equal to that obtained for freshly prepared 7.5 volume % TBP. The 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 15. This graph compares the properties of freshly prepared 7.5% TBP (Fresh) and solvent washed by the normal plant process (Plant) with the properties of plant solvent after extended carbonate washing (Extended) and after treatment with activated alumina (Alumina). Treatment with alumina nearly restores plant 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.

Alumina Process Definition

Laboratory studies were conducted to establish whether or not solvent cleaning would be practical on a full-scale basis. Commercial grade alumina from Kaiser Chemicals was used for this work. 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/fraction for quality tests. The effect of column residence time and alumina particle size was tested.

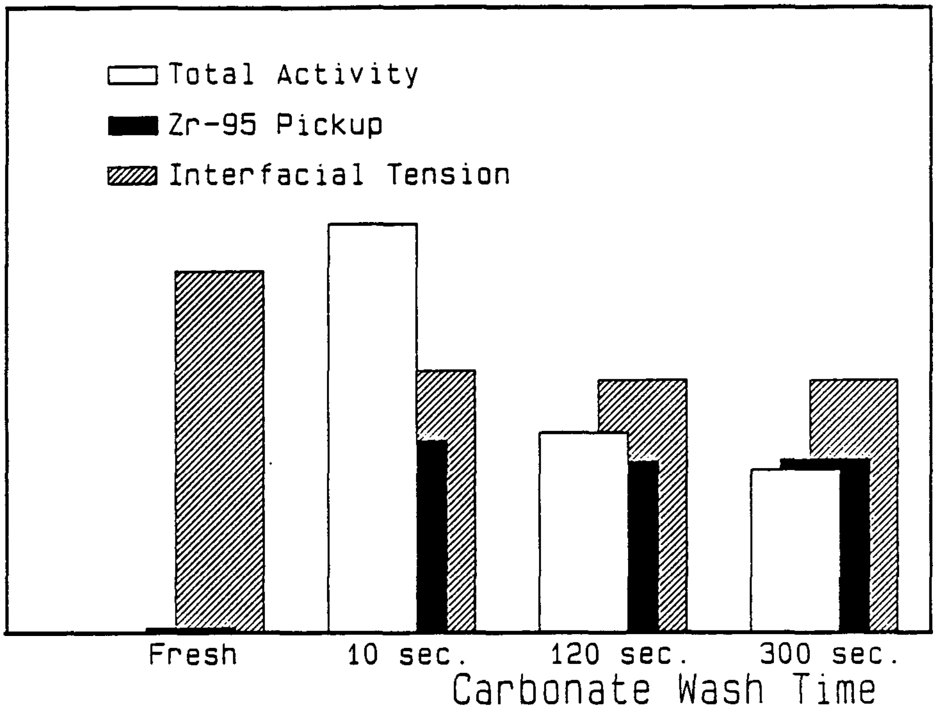


Figure 13. Effect of Wash Time on Solvent Properties

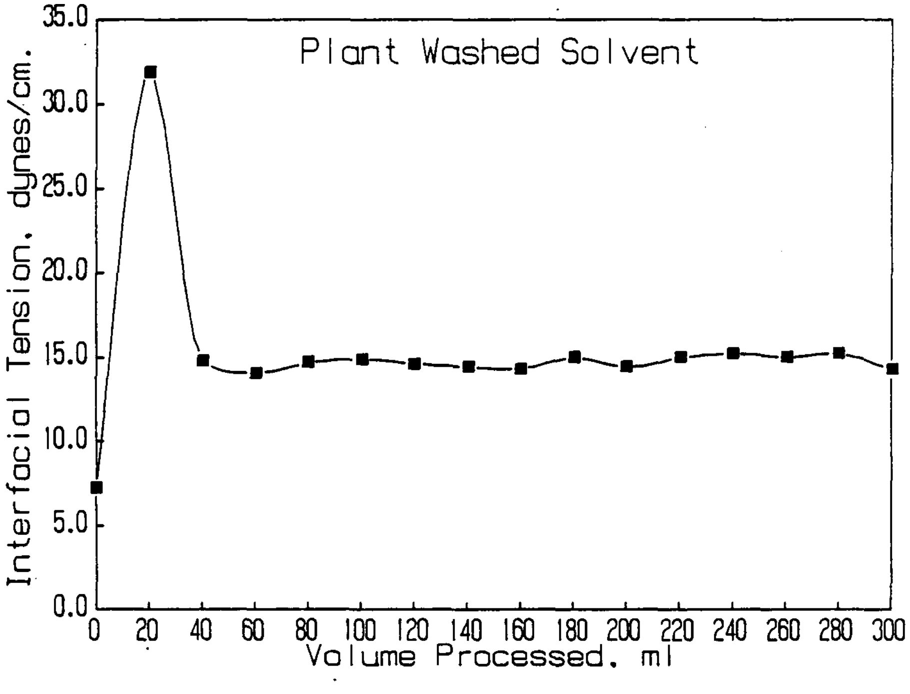


Figure 14. Alumina Cleaned Solvent Properties

Alumina Particle Size

Two types of alumina were examined, a small spherical shaped particle about 1.68 mm in diameter and a crushed sphere variety with a nominal 1.41 mm particle size. Column residence time was held at 5.5 minutes. The interfacial tension and total gamma activity profiles, presented in Figures 16 and 17, show that solvent is more effectively cleaned using smaller particle size adsorbent. Based on these results, further studies of process parameters were done using the crushed alumina (Kaiser Chemical A-2 8 x 14).

Column Residence Time

The influence of column residence time was examined by changing volumetric throughput through the column or by changing column length. The results of these studies are shown in Figures 18 and 19. The improvement of solvent interfacial tension (Figure 18) 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. Using a short column at low throughput (5.2 min) or a longer column at higher throughput (5.5 min) made little difference in the interfacial tension response.

The response of gamma activity removal (Figures 19 and 20) showed that the longer the residence time, the more activity was removed. The initial low value of activity found for early fractions is the result of TBP removal. After column TBP saturation, the activity remains fairly constant.

The Zr pickup of solvent treated at various column residence times (Figure 21) was similar for 5 and 10 min and better than 2.6 min. 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.

Full-Scale Cleanup of SRP HM Process First Cycle Solvent

Process Details

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 22) through the alumina column, then through the normal wash train back to the clean solvent tank. The alumina column (Figure 23) was fabricated from a 30 gal stainless steel drum using a perforated pipe for the column inlet and outlet. The

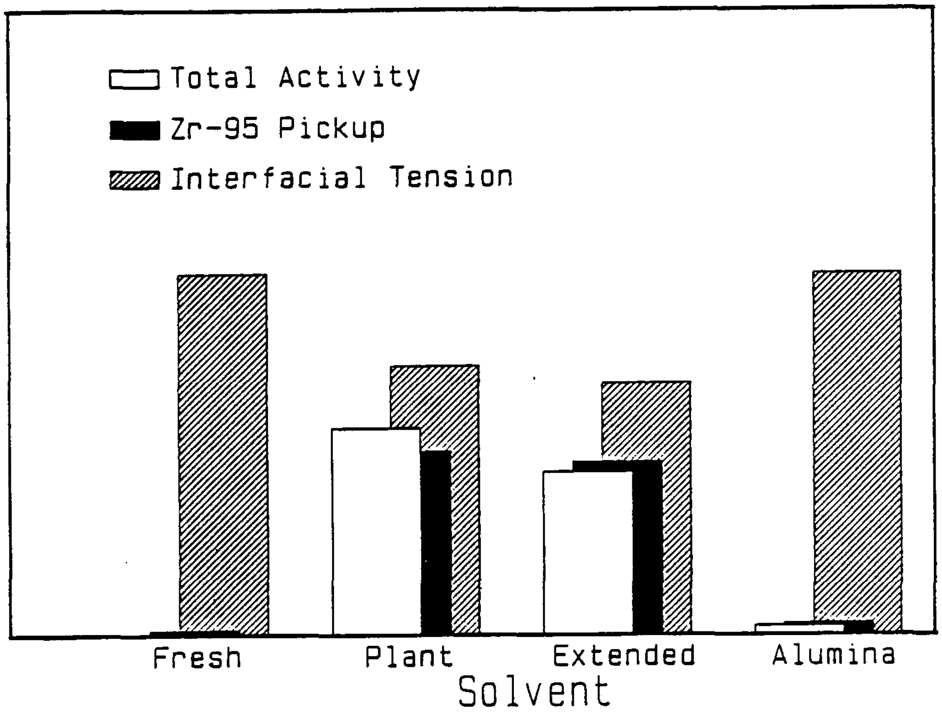


Figure 15. Effect of Cleaning Process on Solvent Properties

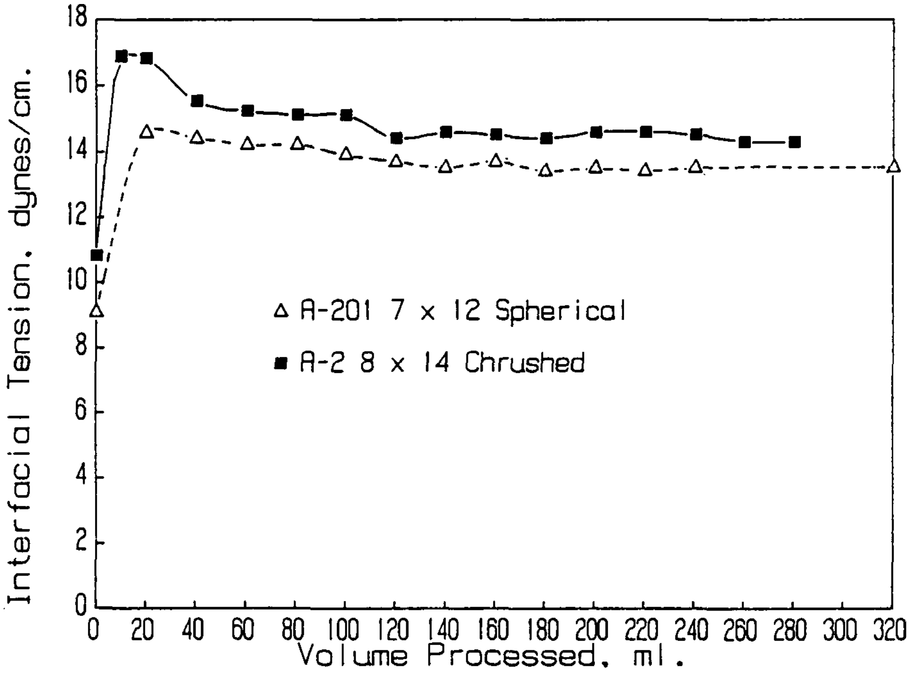


Figure 16. Effect of Alumina Type on Interfacial Tension Change

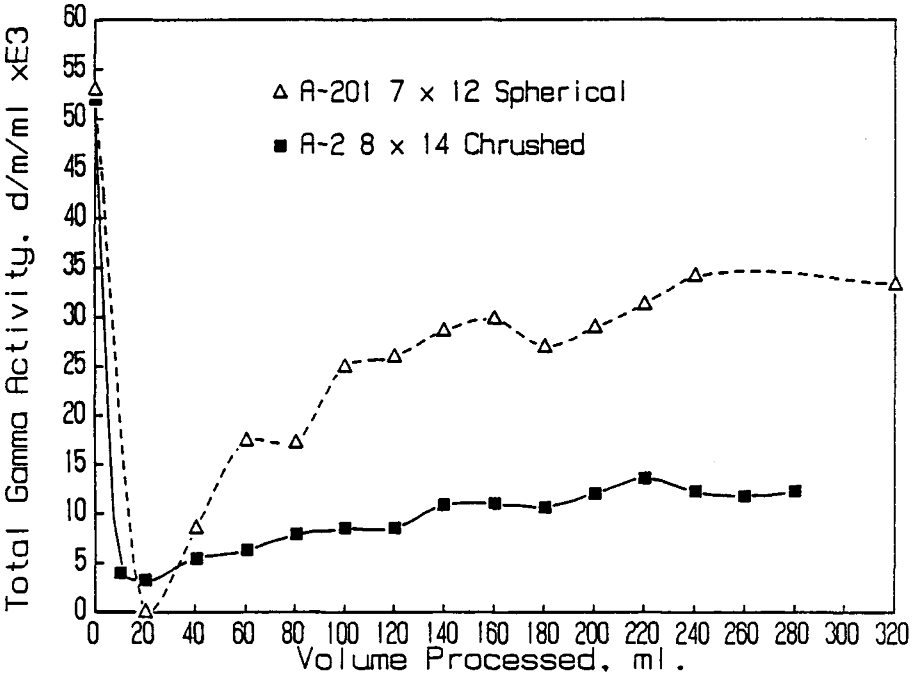


Figure 17. Effect of Alumina Type on Activity Removal

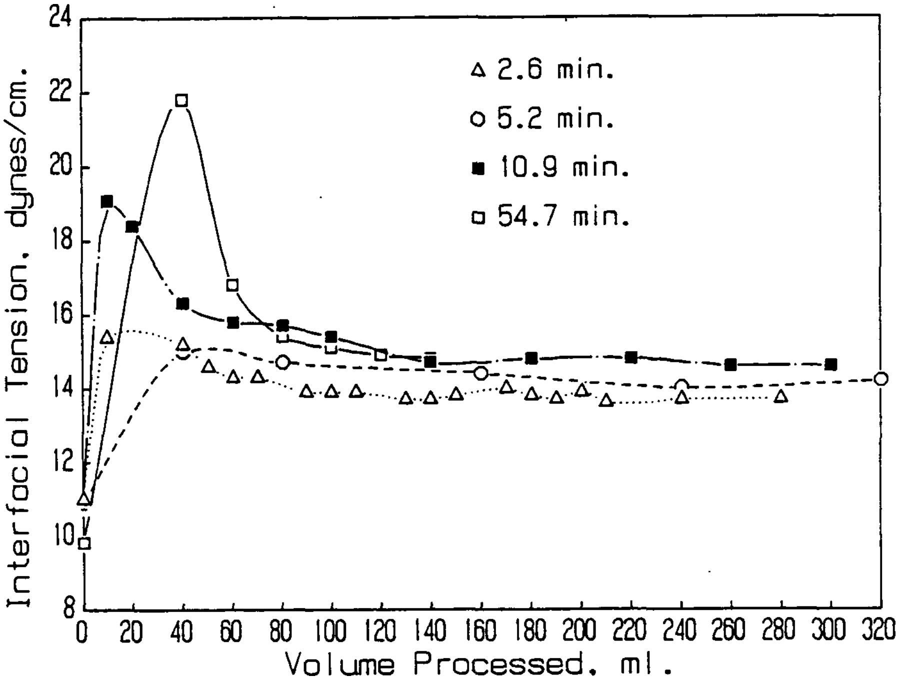


Figure 18. Effect of Residence Time on Interfacial Tension Change

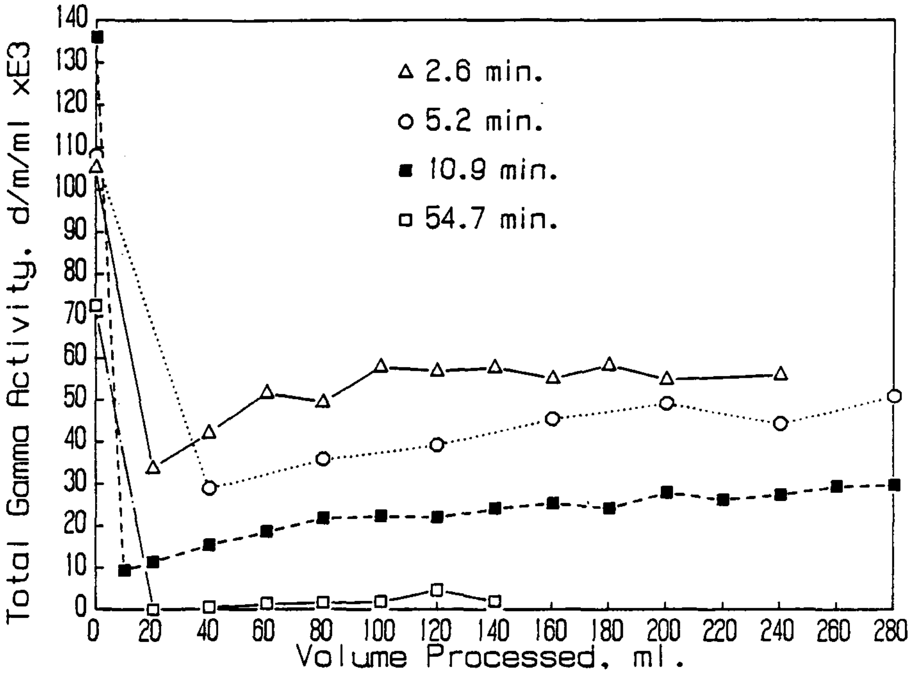


Figure 19. Effect of Column Residence Time on Gamma Activity Change

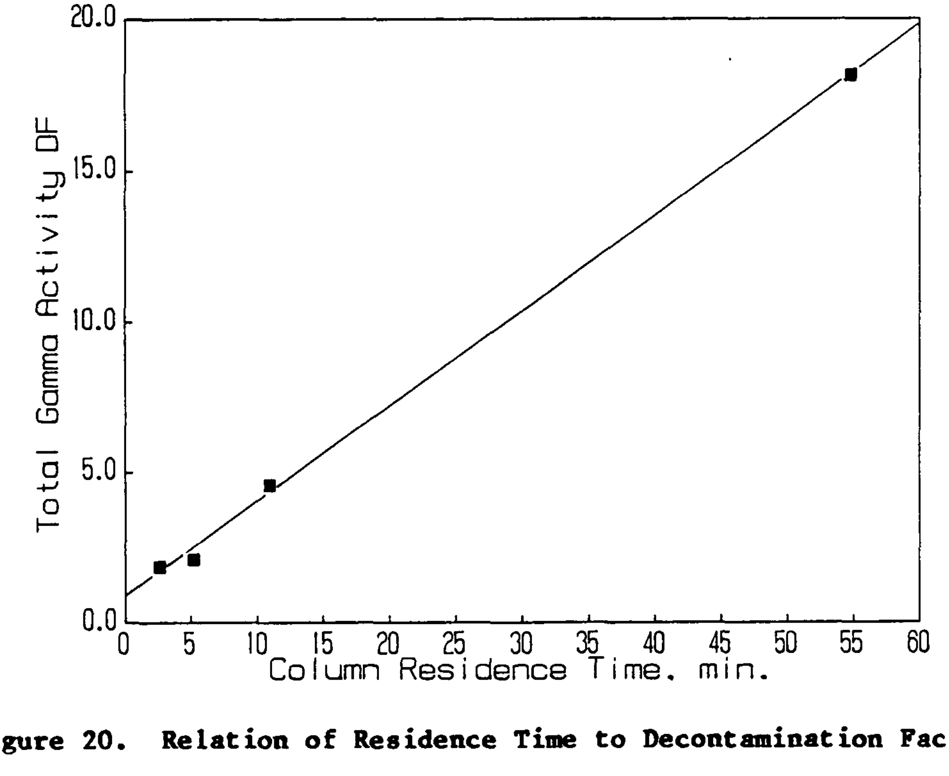


Figure 20. Relation of Residence Time to Decontamination Factor

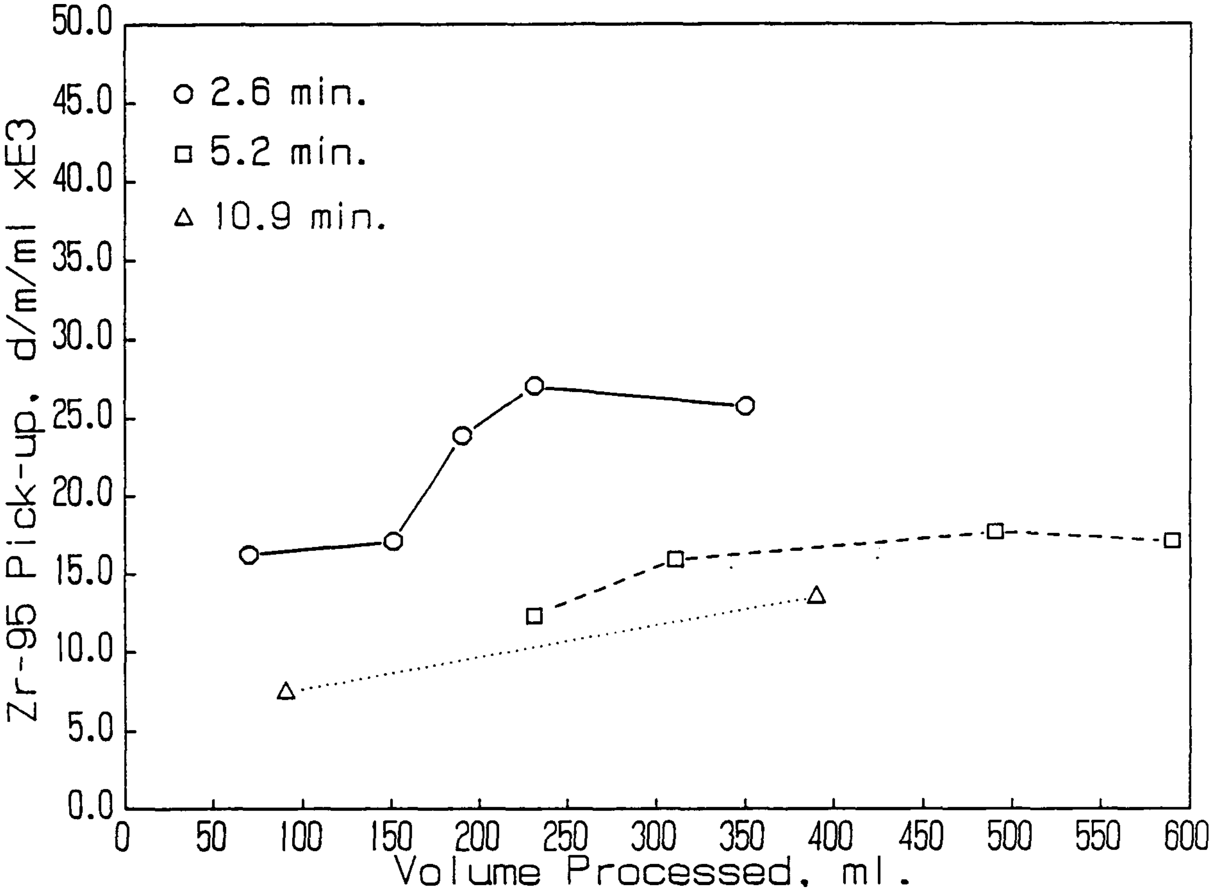


Figure 21. Effect of Residence Time on Pickup

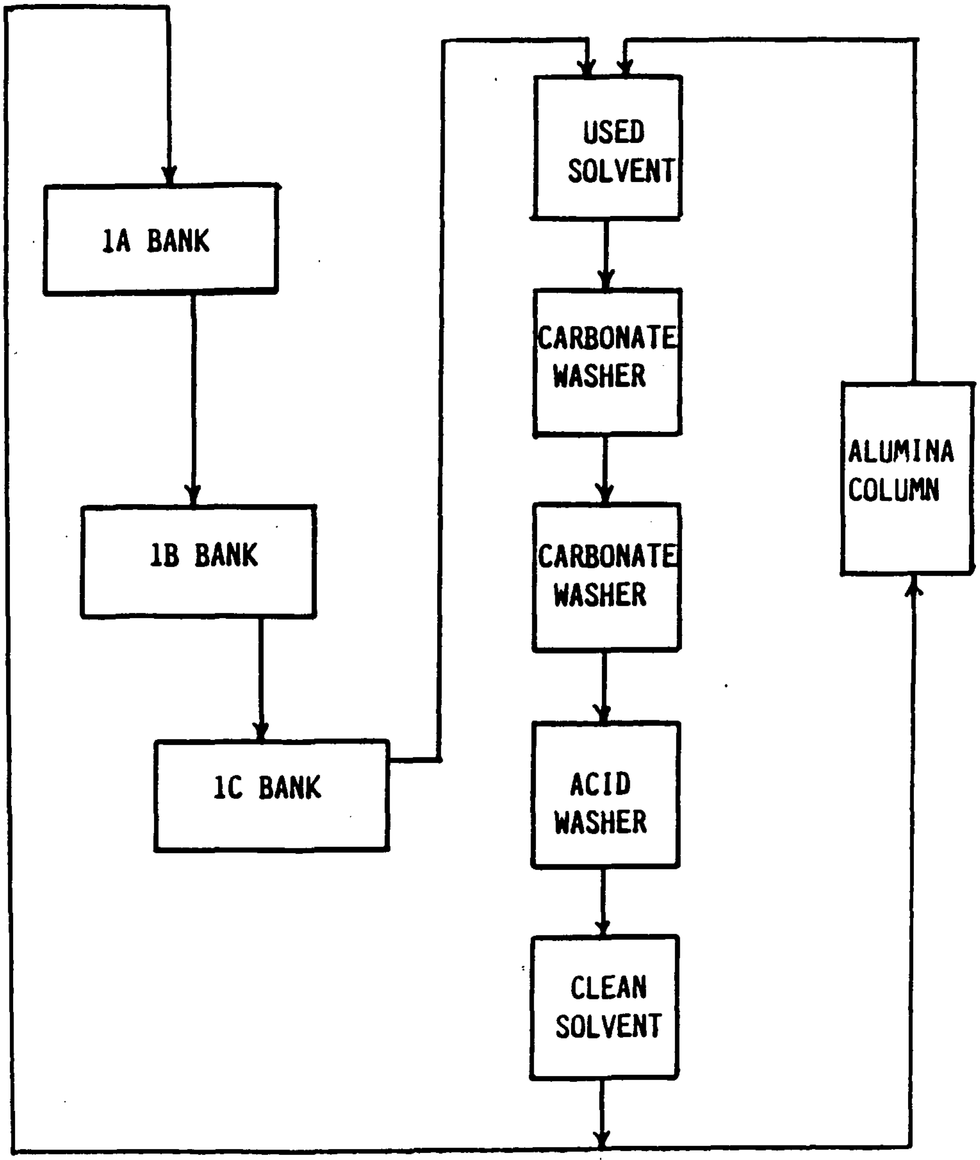


Figure 22. Canyon Solvent Cleaning Process

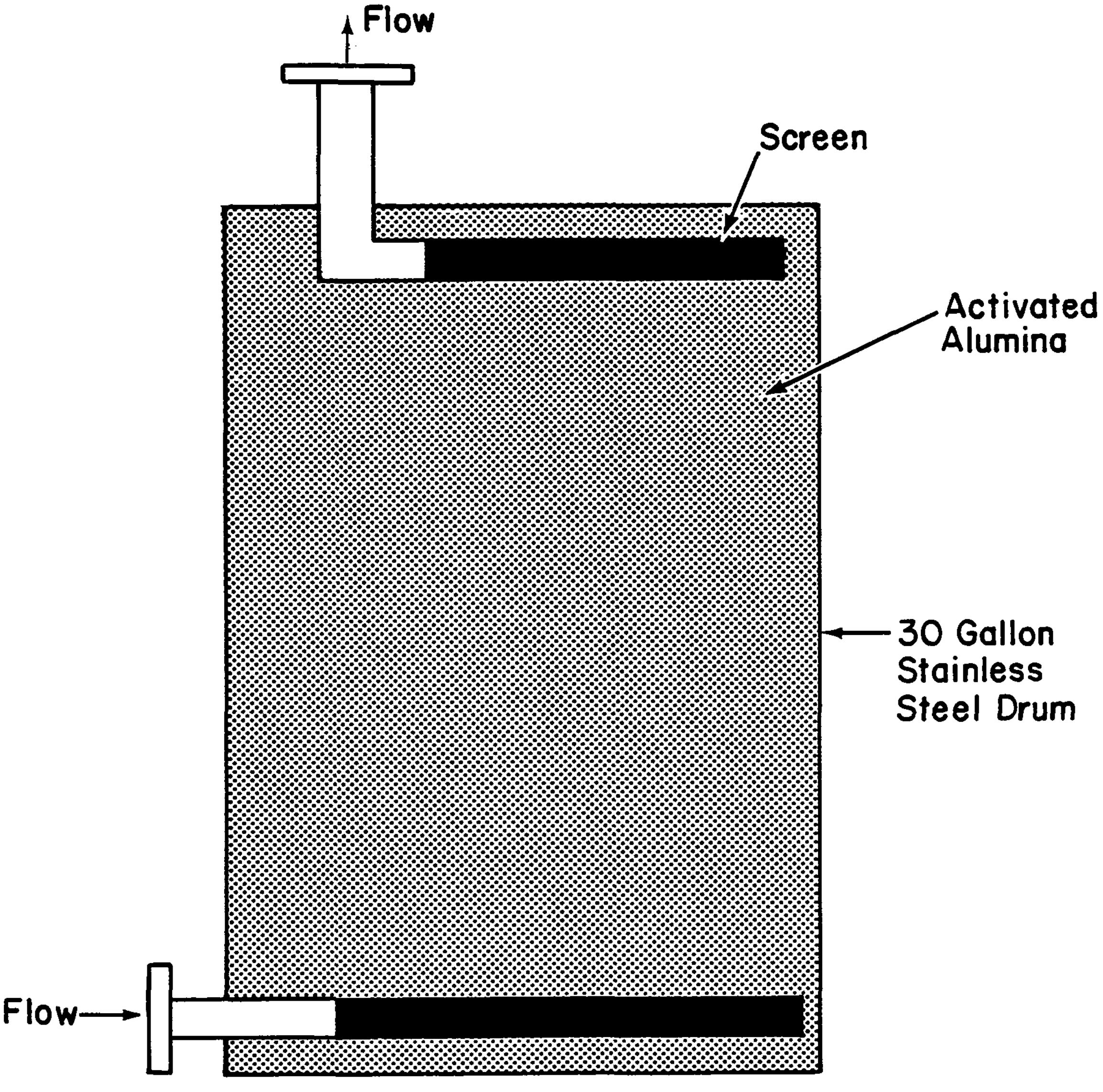


Figure 23. Cross Section of Column

perforated section was covered with stainless steel screen to keep alumina particles in the drum. The drum was filled with Kaiser Chemical Type A-2 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. The change in solvent properties during the cleaning period is shown in Figures 24 and 25. During the cleaning period, the HM first cycle was operated as needed.

Solvent Properties after Cleaning

The overall change in solvent properties is shown in Tables 3 and 4. The interfacial tension was increased to near fresh solvent levels. Total gamma activity was reduced about two-thirds, and the zirconium pickup was improved. The removal of activity was not equal for all isotopes (Table 4). About 90% of the Zr and Nb was

TABLE 3

Change in Canyon Solvent Properties

	Fresh 7.5% TBP	Before Cleaning	After Cleaning
Interfacial tension, dynes/cm	14.5	11.2	13.9
Total gamma activity, d/m/ml x E3	0	86.6	29.2
Zr-95	0	33.0	3.6
Ru-106	0	46.8	23.8
Zr pickup, d/m/ml x E3	0	23.4	7.8

TABLE 4

Activity Removal from Canyon Solvent

	Before d/m/ml x E3	After d/m/ml x E3	Df
Total gamma	86.7	29.2	3.0
Ru-103	2.7	1.0	2.7
Ru-106	46.8	23.8	2.0
Zr-95	33.0	3.6	9.2
Nb-95	4.2	0.8	5.2

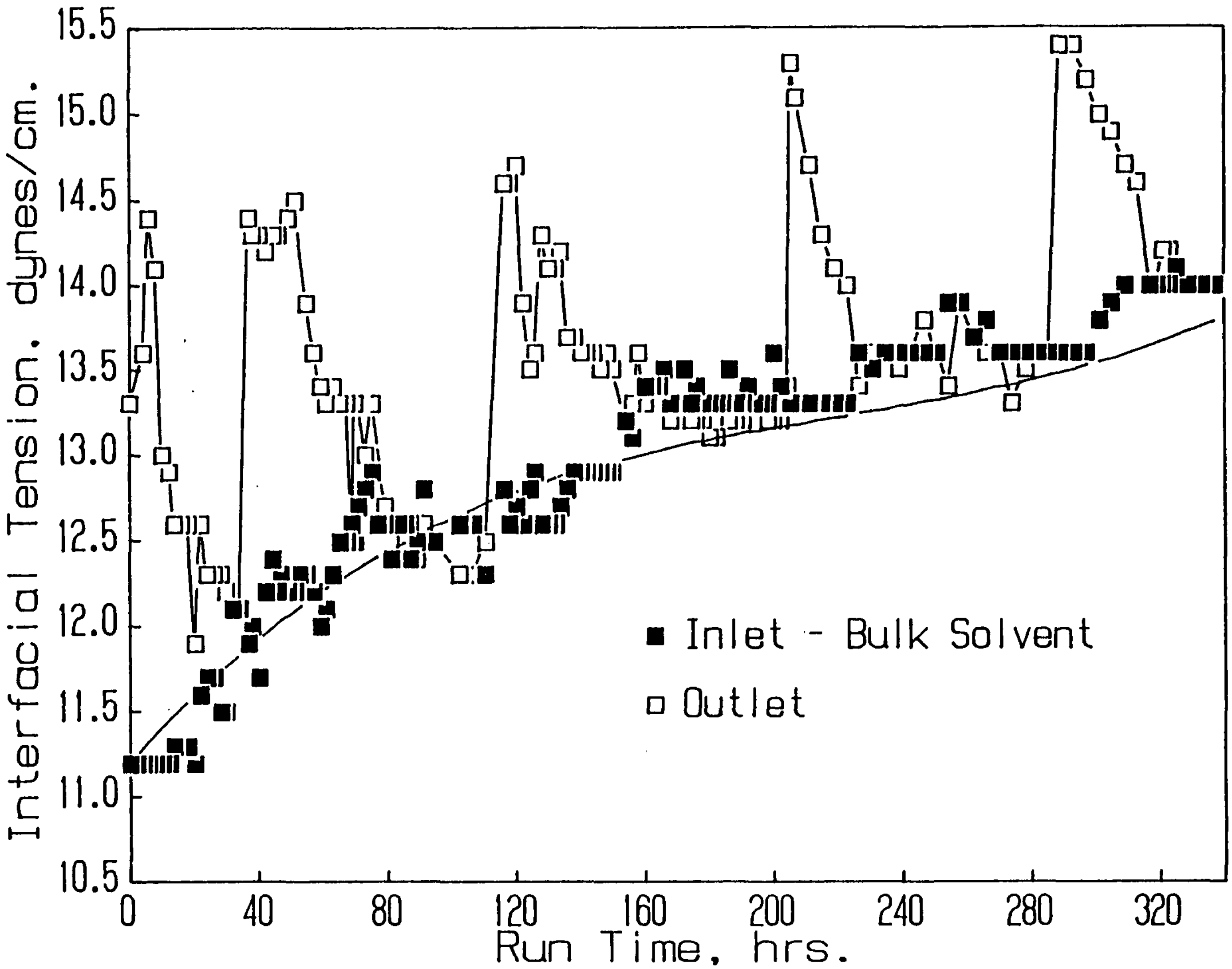


Figure 24. Canyon Solvent Cleaning - Interfacial Tension

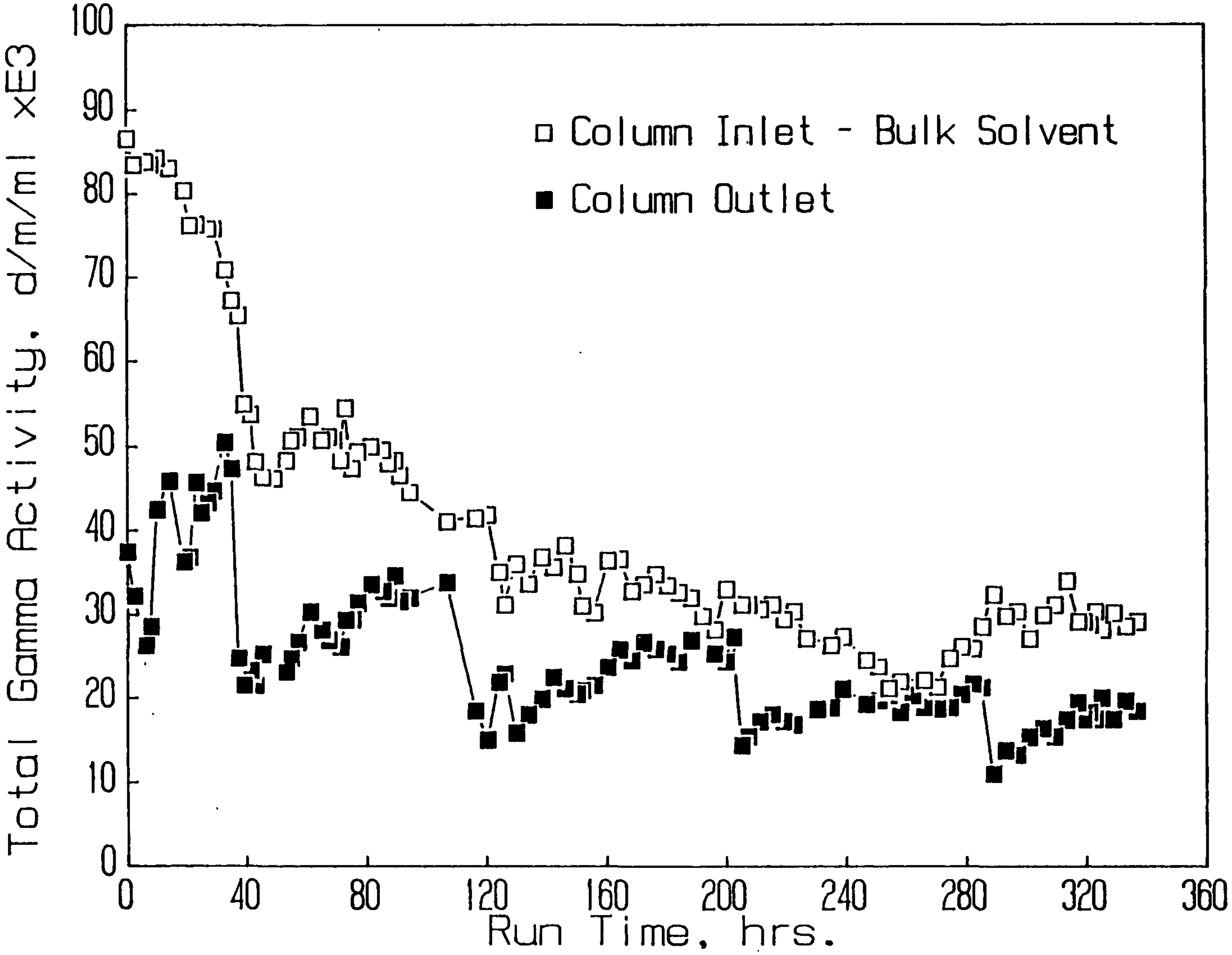


Figure 25. Canyon Solvent Cleaning - Total Gamma Activity

removed, but only 50% of the Ru-106 and 67% of the Ru-103 were eliminated. This suggests that alumina may not be the optium adsorbent for Ru binding ligands.

Postcleaning Process Behavior

The HM first cycle process showed an immediate response to cleaned solvent. The overall zirconium DF (Figure 26) 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 (Figure 27) over a 60-day period 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 14-day limit is an arbitrary limit and it is expected that the wash use-life can be extended further when solvent quality specifications are developed to establish when a wash change is needed.

Future Work

Additional studies are underway at SRL to determine the effectiveness of alumina in improving properties of SRP solvents used in other HM cycles and in the Purex process cycles. Scouting work is planned to establish whether or not a more specific adsorbent for removal of Ru binding ligands is available and applicable. Finally, solvent quality tests are being sought which will provide a more sound procedure for SRP solvent management, i.e., establish when an adsorption cleaning cycle is needed and define the need for carbonate wash changeout.

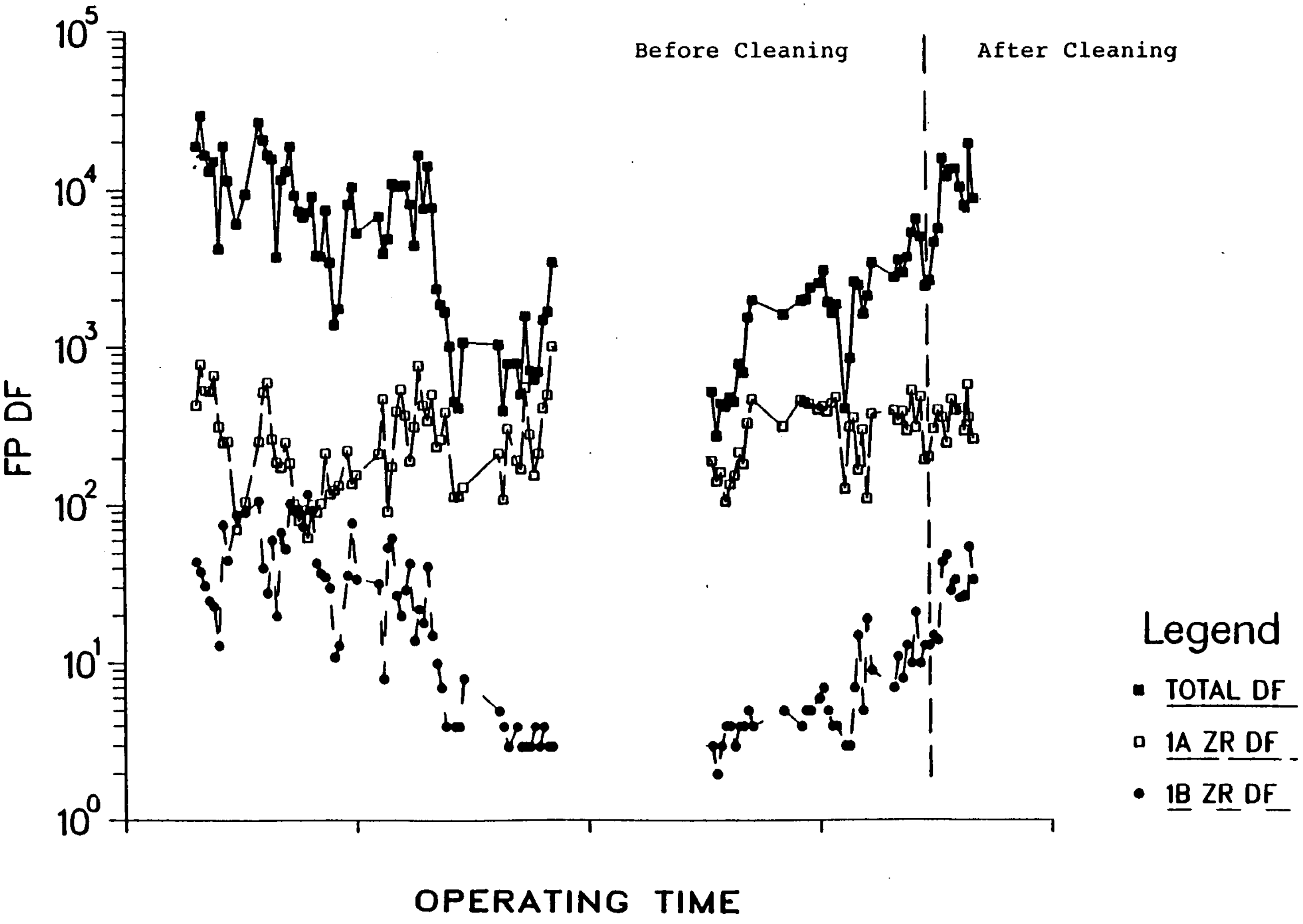


Figure 26. Zr Fission Product DF

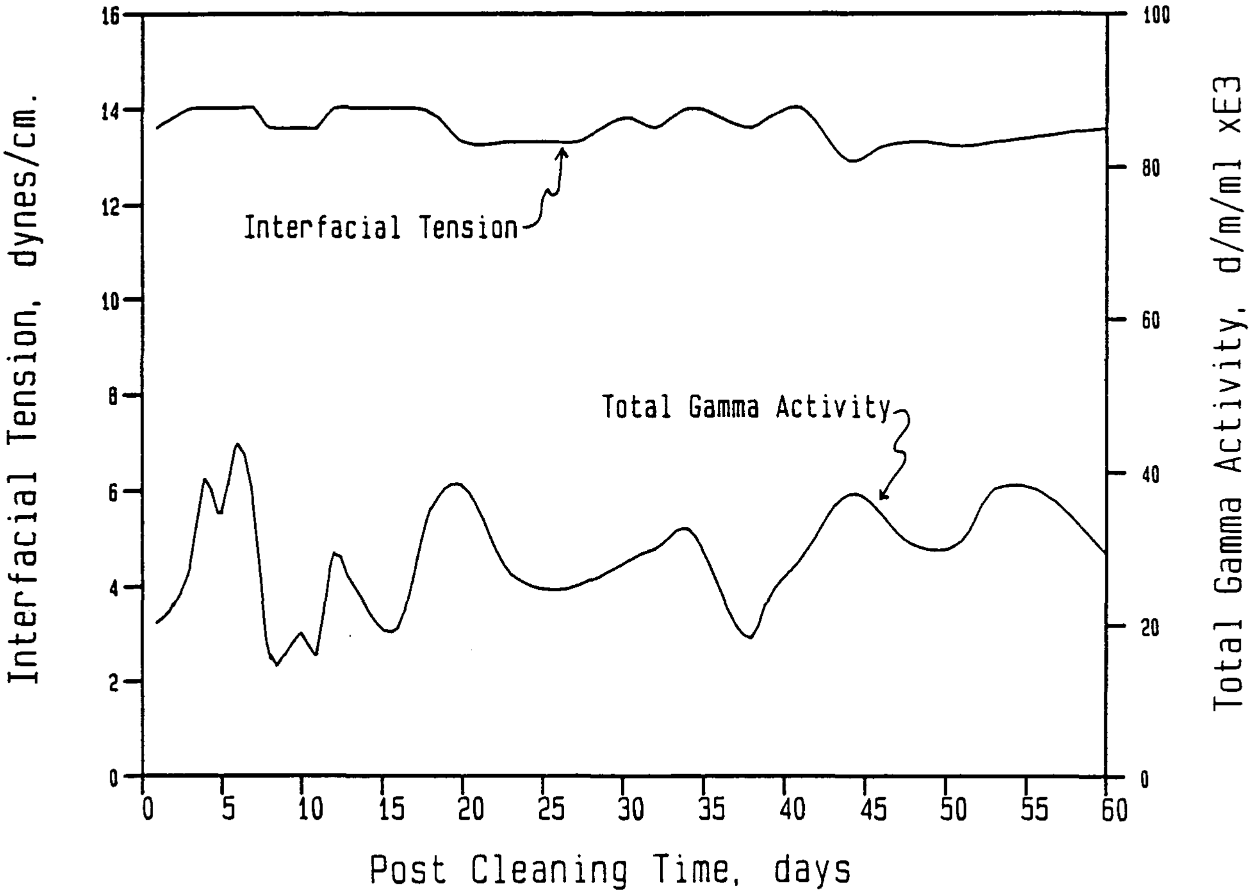


Figure 27. Canyon Solvent Properties.

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