Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Diluent Degradation Products in the Purex Solvent

J. C. Neace[a]
[a] Allied-General Nuclear Services Barnwell, South Carolina

To cite this Article Neace, J. C.(1983) 'Diluent Degradation Products in the Purex Solvent', Separation Science and Technology, 18: 14, 1581 — 1594
To link to this Article: DOI: 10.1080/01496398308056116
URL: http://dx.doi.org/10.1080/01496398308056116

SEPARATION SCIENCE AND TECHNOLOGY, 18(14&15), pp. 1581-1594, 1983

Diluent Degradation Products in the Purex Solvent

J. C. NEACE

ALLIED-GENERAL NUCLEAR SERVICES
BARNWELL, SOUTH CAROLINA 29812

ABSTRACT

A number of laboratory tests were conducted in which various impurities, known to be present in degraded Purex solvent, were injected into fresh solvent samples and the effects of these impurities tested in an operating miniature pulse column and in batch contactors. Common fission product elements which interfere in the Purex process were spiked with radiotracers and added to the aqueous phase samples with which the test solvents were contacted. Process controls and blanks were used to verify test data. Periodically, samples of the organic phase were withdrawn for analyses by radiochemical means. From the data obtained, a number of theories were postulated on the mechanisms by which diluent degradation products interfere in the Purex process.

INTRODUCTION

For thirty years Purex, a solvent extraction process, has been the prime method for reprocessing spent nuclear fuels. The Purex process has proven to be reliable and few unresolved problems remain. No alternate process is now being seriously considered. One of the principal unresolved problems that remain with the use of the Purex process relates to degradation products of the paraffin hydrocarbons (NPH) used to dilute the organic extractant,

 0149-6395/84/1814-1581$3.50/0

tri-butyl phosphate (TBP). These degradation products are introduced through irradiation and chemical attack on the diluent. Through secondary reactions, these unwanted by-products generate various surfactants, complexants, emulsifiers, and crud formers which tend to interfere in the process. Even today, there is no consensus of opinion concerning the mechanisms by which diluent degradation products interfere in the Purex process. Also, no practical means for removal of diluent degradation products from the Purex solvent has yet been demonstrated.

DISCUSSION

Diluent Degradation Products

A sample of the diluent Amsco-140 was degraded by boiling it for four hours in an 8M HNO_3 solution. A before and after infrared scan of the diluent is shown in Figure 1. Here the three principal peaks of diluent degradation products are shown. These are nitro alkanes, alkyl nitrates, and oxidation products containing carbonyl groups. The various diluent oxidation products consist of such compounds as alcohols, aldehydes, ketones, esters, and carboxylic acids. These primary diluent degradation products are largely innocuous in the Purex solvent but, through secondary reactions, they produce a whole spectrum of surfactants, complexants, emulsifiers, and crud formers which do interfere in the process.

Minicolumn

Through tests in a miniature pulse column, closely simulating full-scale Purex process runs, it was established that the fission products zirconium and niobium are fixed in the Purex solvent by complexants, while the fission product ruthenium is fixed in the Purex solvent by surfactants.

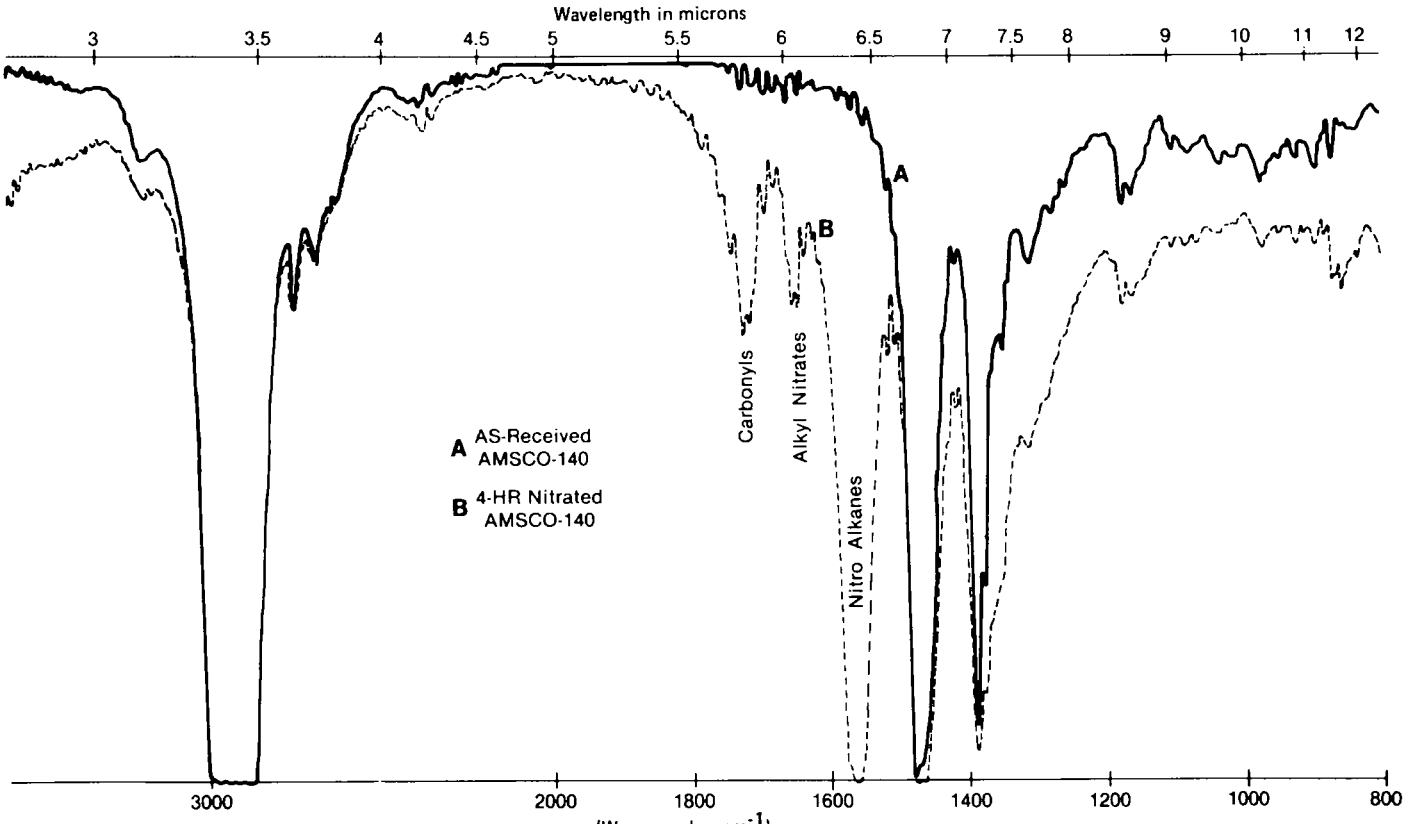


FIGURE 1. IR Scans, Nitration Products of AMSCO 140.

This led to a number of tests in small contactors involving added amounts of various commerically available chemicals representing impurities previously identified as degradation products of the Purex solvent, together with added radiotraced fission product elements.

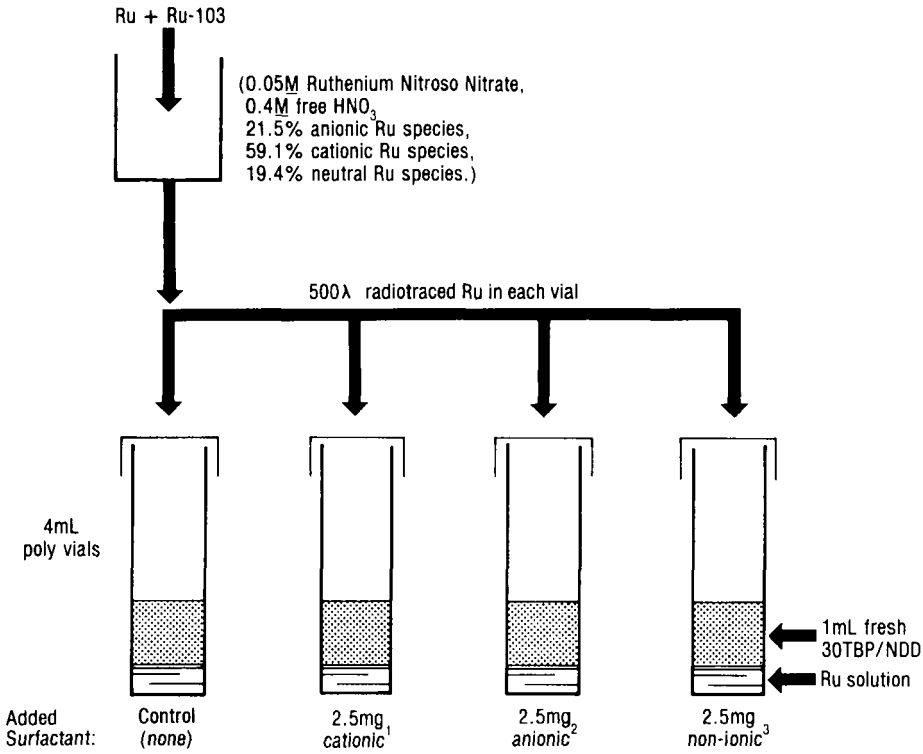
Batch Contactor

The use of batch contactors is illustrated in Figure 2. Here 2.5 mg samples of various surfactants, listed on the figure, were shaken in 4-mL poly vials with 1-mL portions of fresh 30% TBP/70% normal dodecane (30TBP/NDD) along with a radiotraced ruthenium solution. The species of ruthenium present in the test solution (cationic, anionic, or neutral) were determined by means of ion-exchange separations followed by gamma-counting. After shaking, a centrifuge was used (required in the case of crud formation) to separate the phases, then the organic phase was sampled for gamma-counting. All gamma counts were normalized to a value of 100 for the control containing no added surfactants. Test data from Figure 2 are shown as Test 1 in Table 1 along with the data from three other tests identical to Test 1 except for ruthenium species present and the condition of the solvent used.

Test 1 indicates the results are about what might be expected if the cationic CTAH selectively fixes the anionic Ru species (~20% abundant) in the solvent, and the anionic ABS selectively fixes the cationic Ru species (~60% abundant) in the solvent. The non-ionic surfactant appears to be suppressing Ru fixation to a slight extent in this experiment.

The results for Test 2 tend to confirm that anionic ABS fixes cationic Ru species in the solvent, and that cationic CTAH attracts only anionic Ru.

In Test 3 the anionic Ru species are shown to be selective toward cationic CTAH. An important property of surfactants was evident in Tests 3 and 4 in which carbonate-cleaned, used (partially-degraded) organic phase was tested. In the sample



Shake 60 seconds, centrifuge, pipet out 500λ organic phase for γ-counting.

γ-counts (norm)	100.0	108.6	161.2	95.8

[1]CTAH: Cetyl Trimethyl Ammonium Hydroxide ($CH_3(CH_2)_{15}N(CH_3)_3OH$) (Eastman #9719), a cationic surfactant.

[2]ABS: Sodium Alkyl Benzene Sulfonate (Allied Chemical "Nacconol"), an anionic surfactant.

[3]POSM: Polyoxyethylene(20) Sorbitan Monolaurate (Tween-20), a nonionic surfactant (E. H. Sargent Co.)

FIGURE 2. Ruthenium Fixation in Solvent by Surfactants.

Table 1: Ruthenium Fixation in the Solvent

Test	Species Pres.	Org. Phase	Normalized Gamma Counts Ctrl.	CTAH*	ABS**	POSM***
1	All	Fresh	100.0	108.6	161.2	95.8
2	Cationic & Neutral	Fresh	100.0	69.7	258.1	90.3
3	Anionic	Used	100.0	204.4	145.4	20654 (Crud)
4	Neutral	Used	100.0	78.1	129.7	374.5 (Crud)

*CTAH: Cetyl trimethyl ammonium hydroxide, a cationic surfactant.
**ABS: Sodium alkyl benzene sulfonate, an anionic surfactant.
***POSM: Polyoxyethylene (20) sorbitan monolaurate, a non-ionic surfactant (TWEEN-20).

containing the non-ionic surfactant, an abundance of interfacial crud, highly retentive for Ru, was formed. No similar crud was observed in Tests 1 and 2 where fresh organic phase was used. Subsequent tests indicated that this interfacial crud breaks down during stripping with dilute acid and deposits any radionuclides it may contain in the aqueous product stream.

Assuming for the moment that surfactants are present in degraded solvent, the results from the above experiments appear to relate to some questions concerning Purex plant operation such as: (1) the mechanism for interfacial crud formation, (2) why there is an induction period before ruthenium begins to grossly contaminate a fresh solvent, (3) why Ru does not follow the usual mechanisms of solvent extraction, (4) why different reprocessing plants (using different diluents of different degrees of degradation) report significant differences in the behavior of ruthenium in their process streams, and (5) why "weak ligands" (i.e., interfacial crud) retain certain fission products in the organic phase then, during stripping, deposit these fission products in the product stream.

For the final experiment with Ru, radiotraced Zr and radiotraced Nb were also added to the feed solution, so that the effects of interfacial crud, produced by a non-ionic surfactant, on Zr and

Nb could be studied. In the test solution, Zr and Nb were each ~0.025M in concentration and the spikant for these elements was Zr-Nb-95. The free HNO_3 concentration in the aqueous solution of radiotraced elements was 0.5M. Fresh 30TBP/NPH was used as organic phase. Results are expressed as percent of radionuclides reporting to the organic phase. Two counts were made, one when the samples were first prepared and one after a one-day stand. The results are shown in Table 2.

In the above experiment, neither Zr nor Nb was initially fixed, to any significant extent, by any of the surfactants tested. Also, the crud, which formed later, acted as a collector of Ru, Zr, and Nb. When the aqueous phase was replaced by 0.01M HNO_3, all interfacial crud disappeared after three contacts and the Ru, Zr, and Nb present passed into the aqueous phase.

Analytical Procedures

Among the analytical procedures used during the course of this study were: (1) Z-test,[1] where the solvent is shaken in a vial with radiotraced zirconium, and after centrifuging, a sample of the organic phase is gamma- counted. (Results are expressed in ppm DBP equivalent.); (2) C-test[2] in which the solvent is shaken in a vial with dry lime, $Ca(OH)_2$, centrifuged, and a Z-test run; (3) MB-test, an adaptation of a qualitative test for anionic surfactants[3] where the blue color is measured spectrophoto-

Table 2: Solvent Retention of Fission Product Nuclides

Additive	Ru-103,%		Zr-95,%		Nb-95,%	
	10 min.	1 day	10 min.	1 day	10 min.	1 day
Control	13.1	19.2	0.3	0.2	0.0	0.1
CTAH	15.2	23.5	0.2	0.4	0.1	0.1
ABS	14.8	20.4	<0.3	0.4	<0.1	0.6
POSM*	13.3	37.5	<0.1	26.5	0.0	27.5

*No interfacial crud formed when this sample was first prepared, but a copious quantity of interfacial crud was present after a one-day stand.

metrically: and (4) D&M-test where the solvent is shaken in a glass vial with 0.20M sodium carbonate then the time for phase separation measured and the shape of the meniscus at the interface observed. A flat meniscus indicates the presence of excessive cationic surfactants. A fully concave meniscus indicates a good quality solvent.

The D&M-test has proven to be a quick and reliable means for determining the suitability of a solvent for use in the Purex Process. The theory behind the meniscus-test is that the glass carries a negative charge and the positively charged colloidal ions of cationic surfactants plate out on the glass surface by electrostatic attraction. This renders the glass surface non-wettable by the water, hence the absence of a meniscus at the water-organic interface.

Complexants

The first indication that surfactants may be involved in complexant formation came rather unexpectedly. A factorial design experiment was run in which various impurities were injected into a solvent to study their effects on solvent properties. A small quantity of the anionic surfactant ABS was used as one of the variables.

When the effects of the variables were calculated, the ABS had a highly significant effect on the C-test, which correlated with diluent nitration, but no effect whatever on the Z-test. Thus in the presence of diluent degradation products, dry lime appeared to cause ABS (a non- complexant for Zr) to produce a strong complexant for Zr. In an attempt to find some explanation for this observation, a number of tests were run as follows.

Solvent samples, consisting of 10-mL lots of fresh 30TBP/NDD, were stirred in beakers with five milligram test lots of CTAH, ABS, and POSM, respectively, at room temperature. After a five-minute stir, C-tests were run. The results were 0.0 for all samples including the control which contained no added surfactants. In

other words, dry lime failed to produce complexants in fresh solvent from any of the three surfactants tested.

Purified DBP was added to each of the above samples to produce a DBP concentration of 350 ppm. Each sample was stirred for one hour at room temperature then given another C-test. The results were 0.0 (control), 109.0 (CTAH), 0.9 (ABS), and 0.0 (POSM).

The first item of interest in these data is the 0.0 ppm complexants found by the C-test in the control sample even though 350 ppm DBP had just been injected into the control sample. It appears that the lime used in the C-test removed the DBP from the test solvent. Thus DBP is called a "Z-type" complexant -- it shows up on Z-tests but in low concentrations it is completely removed by the lime in C-tests. Of even more interest is the 109.0 ppm of "C-type" complexant (i.e., a complexant enhanced by dry lime) that is produced by the CTAH in this experiment when no "C-type" complexant was produced by any of the other surfactants. This suggests that C-type complexants, not removable by lime or carbonate, are produced by a direct union of CTAH and DBP with a splitting off of water.

In the next test, a comparison is made between two cationic surfactants, one organic-soluble and one water-soluble, in the production of complexants by reaction with TBP. Two organic phase samples, consisting of 20-mL portions of fresh 30TBP/NPH, were stirred for two hours at room temperature with 1/2 gram of the organic-soluble CTAH and 1 mL of an aqueous-soluble surfactant (Downy), respectively. (Downy is a fabric softener containing a water-soluble cationic surfactant and is a proprietary product of Proctor and Gamble.) A Z-test indicated 320 ppm DBP equivalent complexant for the sample containing CTAH and 0.0 for the sample containing the aqueous soluble surfactant.

Evidently, the aqueous soluble cationic surfactant remains in the aqueous phase where it cannot react with the TBP while the CTAH goes directly to the organic phase where it reacts with TBP to form complexants. In follow-up experiments, the sample containing the aqueous soluble surfactant produced C-type complexants when treated

with dry lime after (but not before) a carbonate wash. Apparently, it became organic-soluble after the carbonate wash, picked up OH^- groups from the dry lime, then reacted with TBP.

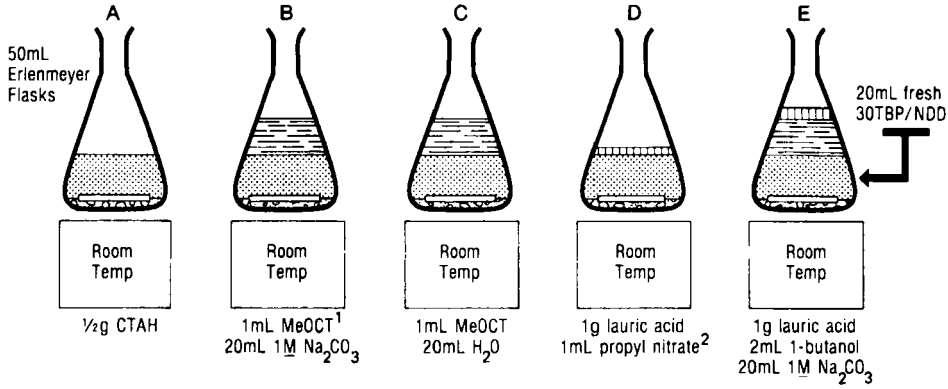
Up to this point, all surfactants used for testing have been purchased off the shelf, ready made. The next experiment demonstrates an attempt to produce surfactants, using only chemical species known to be present in degraded solvent. The reactions to be tested are: (1) carboxylic acid plus alcohol to produce ester plus water and (2) ester alkaline hydrolysis to produce a surfactant.

Two samples consisting of 20-mL portions of fresh 30TBP/NDD (previously equilibrated with 2.5M HNO_3 to simulate actual plant operating conditions) were each combined with two grams lauric acid (representing long-chain carboxylic acids). To one sample (only), 20 mL 1-butanol were also added. Each sample was heated, with stirring, five minutes at 105°C (to remove water of reaction), and five minutes at 130°C (to drive off unreacted 1-butanol). At the end of the 10-minute test, analyses indicated for (a) the Z-test: 179 (no 1-butanol) and 4170 (1-butanol present) and (b) the C-test: 165 (no 1-butanol) and 5347 (1-butanol present). These data indicate that a C-type complexant is being formed at a significant rate in the sample containing 1-butanol, tending to confirm the reactions postulated above.

In the above tests, elevated temperatures, far beyond any temperature to which the solvent is normally subjected in a Purex Plant, were used. Another test, shown and described in Figure 3, in which surfactants and surfactant precursors were added to fresh 30TBP/NDD, was conducted at room temperature.

The results for the Z-test given in the figure, tend to indicate:

Experiment A: A time-related breakdown of pure 30TBP/NDD by the hydroxide form of a cationic surfactant to form a complexant. (The increase in complexants with time, shown in this test, may explain reported short-term rapid increases in the complexing action of post-irradiated solvent.)[4,5]



(A) Stir 2 hours at room temperature. Draw 1mL sample of organic phase for analysis.

Z-test (ppm)	1113	0.0	0.0	0.0	0.0

(B) Stir 18 hours additional time at room temperature for a total of 20 hours. Draw sample of organic phase for analysis.

Z-test (ppm)	7152	81	0.0	25	15

[1]MeOCT: Methyl Octanoate ($CH_3(CH_2)_6COOCH_3$), representing long chain esters.

[2]Propyl Nitrate ($CH_3CH_2CH_2NO_3$), representing alkyl nitrates.

FIGURE 3. Room Temperature Reactions Involving Solvent Degradation Products.

Experiment B: A conversion of a long-chain ester to a cationic surfactant by alkaline hydrolysis, then attack upon the TBP by the surfactants to form complexants. (This may explain reported non-linearity of complexant build-up at Purex facilities.)(5)

Experiment C: It appears that the hydrolysis reaction occuring in Experiment B will not take place in water, in the absence of an alkali.

Experiments D and E: Common solvent degradation products slowly reacting at room temperature to produce complexants.

Solid Sorbers

A number of solid sorbers were examined as possible polishing agents for the Purex solvent after washes with sodium carbonate or

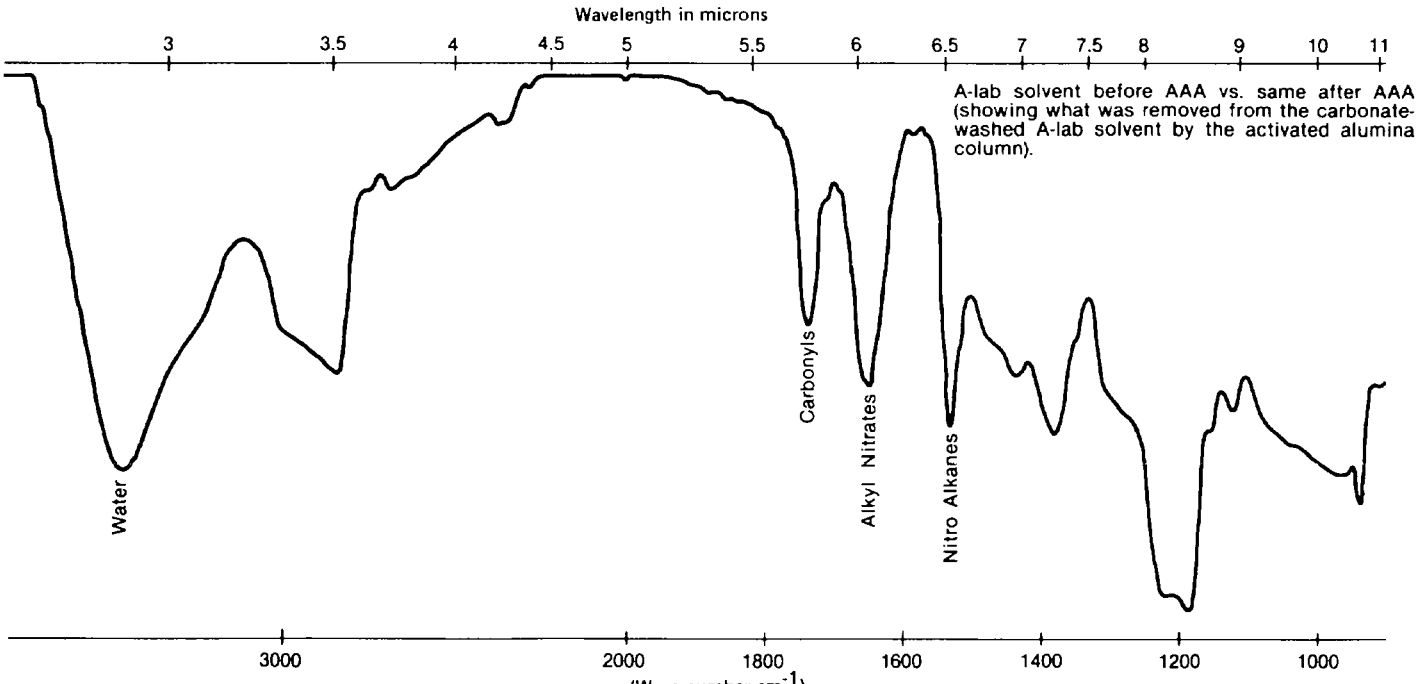


FIGURE 4. Differential IR Scans, Solvent Cleanup.

hydrazine oxalate. One solid sorber tried was activated alumina (Alcoa activated alumina Grade F-1). Differential infra-red scans of a carbonate-washed degraded solvent, before and after the activated alumina treatment, show excellent removal of nitro alkanes, alkyl nitrates, and carbonyls, all of which had remained after the prior cleaning with carbonate. (See Figure 4.)

CONCLUSIONS

The principal diluent degradation products are compounds containing carbonyls, alkyl nitrates, and nitro alkanes. These are not removable from the solvent by contact with common wash solutions. Surfactants produced by secondary reactions involving diluent degradation products cause formation of interfacial crud; react with TBP to form strong complexants; and are a fixant for non-strippable ruthenium species in the solvent. The interfacial crud is produced in partially degraded solvents by non-ionic surfactants and acts as a gathering agent for various radionuclides, causing localized high concentrations of these species. Radionuclides sorbed by interfacial crud are later discharged into the product stream during stripping operations. The interfacial crud also interferes with proper phase disengagement. Reactions involving TBP and organic-soluble cationic surfactants in the hydroxide form produce strong complexants for zirconium and niobium which, unlike DBP, are not removable by contact with dry lime or carbonate solutions. The presence or absence of surfactants in a given solvent is an index of the suitability of that solvent for Purex operation.

ACKNOWLEDGMENTS

The author is indebted to A. F. Cermak who designed the mini-column and to R. G. Spaunburgh who offered many helpful sugges-

tions. This work was performed under Contract DE-AC09-79ET35900 for the United States Department of Energy.

REFERENCES

(1) Garrett, T. P., Jr., "A Test for Solvent Quality," DP-237 (August 1957).

(2) Blake, C. A.; Davis, W.; and Schmitt, J. M., "Properties of Degraded TBP-Amsco Solutions," Nucl. Sci. Eng., 17, 626 (1963).

(3) Snell, F. D. and Ettre, L. S., editors, Encyclopedia of Industrial Chemical Analysis, 11 328, Wiley (1971).

(4) Nowak, Zofia, "The Radiolysis of the Tributylphosphate-Diluent - HNO_3 Systems. Part III. Dependence of Zr Number on the Dose and on the Post-Irradiation Effects," Nukleonika 18, 159 (1973).

(5) Geier, R. G., "Purex Process Solvent Literature Review," RHO-LD-74 (October 1979).