Consolidated Fuel Reprocessing Program

Solvent Degradation and Cleanup: A Survey and Recent ORNL Studies*

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ABSTRACT

This paper surveys the mechanisms for degradation of the
tributyl phosphate and diluent components of Purex solvent by
acid and radiation, reviews the problems encountered in plant
operations resulting from the presence of these degradation
products, and discusses methods for minimizing the formation
of degradation products and accomplishing their removal.
Scrubbing solutions containing sodium carbonate or hydroxyla-
mine salts and secondary cleanup of solvents using solid
sorbents are evaluated. Finally, recommendations for improved
solvent cleanup are presented.

INTRODUCTION

All existing and planned reactor fuel reprocessing plants use the
Purex solvent extraction process for recovery of the fissionable materials
from the spent fuel elements. The process consists of dissolution of the
oxide fuel in nitric acid to yield a solution containing ~200 g/L of
heavy metals in 3 to 4 $\underline{M}$ HNO_3. This solution is then extracted using a 6
to 30 vol % solution of tri-n-butylphosphate (TBP) in a mixture of nor-
mal, saturated hydrocarbon, commonly called normal paraffin hydrocarbon
(NPH). The uranium and plutonium are preferentially extracted into the
organic phase, leaving the bulk of the fission products in the aqueous
raffinate. The extract is scrubbed with nitric acid to increase the
separation from fission products, and the heavy metals are then stripped
from the solvent with dilute nitric acid or reductive stripping tech-
niques. The Purex process for LWR fuel has been reviewed in a recent
book.[1] The TBP-NPH used in these processes is degraded by radiation
damage and by hydrolytic and dealkylation reactions with the nitric acid.
A variety of methods have been proposed for cleanup of the used solvent in
the Purex process to minimize the various problems encountered when the
degradation products accumulate in the recycled solvent.

This paper contains two parts; first, a survey of solvent degrada-
tion and cleanup and, second, a report of recent studies of primary and
secondary solvent cleanup methods conducted at Oak Ridge National Labora-
tory (ORNL). The survey section examines the source of the degradation
products in the Purex process, the identity of the degradation products,

the problems associated with the accumulation of various degradation prod-
ucts in the recycle solvent, methods for prevention of the formation of
degradation products, and methods for their removal. The recent ORNL
studies include a comparison of the effectiveness of sodium carbonate and
hydroxylamine salt solutions as scrubbing solutions, conducted in a
system containing three mixer-settlers, and a study of the use of solid
sorbents for secondary cleanup, using Savannah River Plant (SRP) solvent.

SURVEY OF SOLVENT CLEANUP TECHNOLOGY

Source of Degradation Products

Tri-n-butylphosphate is degraded by hydrolysis or dealkylation reac-
tions when contacted with nitric acid; the degradation rate increases
with both the concentration of the nitric acid and the temperature.[2,3]
If the degradation is by hydrolysis, the primary products will be butyl
alcohol and dibutylphosphoric acid (HDBP); if the primary reaction is
dealkylation, the initial products will be butyl nitrate and HDBP. The
butyl nitrate would subsequently slowly hydrolyze to form butyl alcohol.
Butyl alcohol and butyl nitrate are volatile and would enter the off-gas
system and probably be vented safely to the stack. Butyl nitrate could
accumulate in some low-temperature region of the off-gas system, but the
quantities are likely too small to be of consequence. The HDBP can be
hydrolyzed (or dealkylated) to form, successively, monobutylphosphoric
acid (H_2MBP) and phosphoric acid. The solvent also contains extracted
metal ions which can accelerate the degradation of TBP by nitric acid;
zirconium greatly accelerates the degradation of TBP to HDBP until the
ratio of HDBP to zirconium is ~1:1.[3] Thereafter, the presence of zir-
conium has no effect on the degradation of TBP by nitric acid, probably
through inactivation of the zirconium after complexing with DBP.

Radiation degradation of the TBP-diluent-HNO_3 system depends on many
factors, including the presence of uranium and of oxygen.[4-7] The best
tests of the combined degradation by nitric acid and radiation in the
mixed system containing nitric acid and the cations of interest, at the
process temperature, conclude that the DBP:MBP ratio is likely to be <10,
the values for the formation of DBP and MBP are quite variable, depending
on the conditions, and a major increase in the G values is seen in the
presence of uranium.[4-6] The significance of radiation degradation rela-
tive to that by nitric acid depends on many factors peculiar to each
Purex plant design.[8]

The NPH diluent degrades significantly on exposure to >4M HNO_3 at
elevated temperature. The TBP-NPH solvent, which has been in use for
many years at SRP, has been found to contain ~1% diluent degradation
products.[9] The degraded solvent contains many surface active mate ials
whose presence leads to serious emulsions if the solvent is vigorously
agitated in sodium carbonate scrubbers. The recycle solvent also con-
tains pH-sensitive chromaphores that, upon contact with a base, give the
solvent a distinct yellow color similar to that of uranyl ion. The
mechanism for the degradation of the diluent by nitric acid involves
radical-like NO_2 molecules that react to form a free hydrocarbon
radical:[10,11]

$$RCH_3 + \cdot NO_2 \longrightarrow \cdot RCH_2 + HNO_2 \quad . \tag{1}$$

The hydrocarbon radical ($\cdot RCH_2$) then reacts with a molecule of NO_2 to give a nitro or nitrite compound. Further reactions and interactions of these compounds lead to a large variety of organic compounds, alcohols, and various unsaturated compounds.[9] Many compounds have molecular weights greater than the parent compounds, as would be expected from a free radical reaction. Stored solvent containing nitric acid is particularly vulnerable to this type of degradation. In the Purex plant, the diluent is degraded by a combination of radiation and nitric acid; both free radical and ion-molecule reactions are probably important. The diluent degradation products under these conditions are not well-defined but are probably consistent with those identified in the studies of degradation by nitric acid.

When both TBP and the diluent are present, the primary degradation products interact to form secondary degradation products. These materials may include long-chain organic compounds that are not removed by the standard scrubbing techniques using basic solutions. One example is the formation of long-chain acidic organophosphates that are capable of retaining tetravalent ions, such as Zr^{4+} and Pu^{4+}.[12] While their sodium salts, formed during sodium carbonate scrubbing, are soluble in the solvent, they can be removed by a subsequent scrubbing with water or a solution that is low in sodium.[13] Many of the other secondary degradation products, including those that decrease interfacial tension and lead to increased phase separation times, are not completely removed by standard treatments; additionally, their identities and chemical properties are unknown. Thus, the secondary degradation products present a combination of problems that are difficult to completely eliminate.

Problems with Degradation Products

The degradation products of TBP and NPH cause a variety of problems in the solvent extraction process. Assuming the solvent is cleaned in each cycle using an alkaline scrub, the major degradation products that remain are those that originate with the diluent or are formed by interactions between the TBP and the diluent degradation products. Neither of these classes of degradation products are removed effectively by standard scrubbing methods, and they will build up to a level controlled, largely, by their rate of formation and the rate of solvent loss from the plant, unless special operations are used to remove them. The interfacially active constituents contribute to emulsion difficulties, and certain components will complex metal ions to different degrees than does TBP and may lead to contamination of product streams. A separate problem, partially linked to solvent degradation and partially due to strong complexing by TBP, is the retention of ruthenium in the solvent.[14] The retention of ruthenium by the solvent was substantially reduced by the switch from diluents derived from kerosene fractions to linear hydrocarbon diluents.[15] Significant amounts of ruthenium are still retained through both acid and alkaline scrubbing steps; the increased background radiation produced by the retained ruthenium creates problems in equipment maintenance and contributes to the radiolytic degradation of the solvent.[16]

The primary degradation products of TBP, HDBP, and H_2MBP are better understood than the diluent degradation products and secondary degradation products, and removal methods have been well-demonstrated in Purex plants. The HDBP and H_2MBP retain fission products and actinides in the solvent and may result in the precipitation of some complexes, particularly those of zirconium with MBP.[17] Precipitation should be avoided, since it will lead to interfacial cruds, emulsions, and undesirable coatings on the equipment walls. The interfacial cruds contribute to emulsion problems and can lead to plutonium losses to the aqueous waste streams. Coatings on vessel walls limit decontamination factors to the level represented by the solubility of the precipitated material.

Prevention of Formation of Degradation Products

One method for decreasing the problems associated with extractant degradation is to use extractants that are more resistant to chemical and radiolytic degradation. For example, it has been proposed that tri-2-ethylhexylphosphate (TEHP) be used as a substitute for TBP, since it has much greater resistance to degradation by nitric acid and because it and di-2-ethylhexylphosphate, the primary degradation product, form complexes with metal ions that are more soluble in the organic phase.[18] Unfortunately, the TEHP is not more resistant to radiation than is TBP, and its primary degradation product, di-2-ethylhexylphosphate, is more difficult to remove by sodium carbonate solutions. It is possible that superior extractants can be developed; however, this development would require a significant effort and the new extractants would be expensive.

The known catalysis of the diluent degradation by NO_2 suggests that sparging of the solvent with an inert gas will reduce the degradation rate.[10,11] Diluent degradation by nitric acid was reduced by about a factor of 10 in laboratory experiments, by sparging with argon, as compared with sparging with a 50-50 mixture of air with NO_x.[9] Experiments have also shown that the degradation by nitric acid depends strongly on the concentration of the acid and on the temperature. The effect of increasing the HNO_3 concentration is probably to increase the formation of HNO_2 and NO_2 and to increase the extraction of HNO_2. The degradation increases by a factor of 10 when the acid concentration is increased from 4 $\underline{M}$ to 8.2 $\underline{M}$.[9] With a nitric acid concentration of 4 $\underline{M}$, the degradation at 25°C was almost undetectable. Both degradation by nitric acid and degradation by radiation are time dependent and can be minimized by using centrifugal contactors or other fast contactor systems and by rapid removal of the extracted acid and radioactive species from the solvent. The worst problems occur when a process upset causes unstripped solvent or an acid-solvent mixture to remain untreated for a long period of time.

Removal of Degradation Products

Vacuum distillation: A common method for purifying organics is distillation; considerable effort has been devoted to development of this method for solvent purification.[19-25] A prescrub with sodium carbonate is beneficial.[19] The instability of TBP at elevated temperature requires either steam or vacuum distillation; flash vaporization to limit the time at elevated temperature is also beneficial.[20-25] Studies with plant

solvents showed that steam flash distillation removed the contaminants that complex zirconium and did not lead to significant decomposition of TBP.[22,23] Addition of complexing agents to lower the volatility of degradation products has been demonstrated.[21]

Even though a significant amount of effort has been expended on the development of distillation techniques for purification of contaminated solvent, their use has not been favored for operating Purex plants. This is partly due to the extensive instrumentation required for safe operation and control and the necessity of handling the residue from the distillation. Distillation is also a major change in technique and would require different components and cell layout. The necessity for a prior sodium carbonate scrub relegates distillation to use for secondary cleanup; the use of solid sorbents gives a more compact and simpler process.[19]

Sodium carbonate scrubbing: Virtually all solvent cleanup operations in Purex plants have relied on scrubbing with sodium carbonate solutions; these solutions are effective since the majority of the degradation products are acidic in nature. The solution has usually been 0.1 to 0.5 $\underline{M}$ Na_2CO_3; sodium hydroxide has been used, but the carbonate is preferable since it complexes many metal cations and minimizes precipitates and interfacial cruds. The advantages of sodium carbonate for solvent scrubbing are its low cost, its effectiveness, its lack of chemical or biological hazards, and the relative ease of incorporating it into subsequent waste disposal systems. The perceived disadvantages of sodium carbonate scrub solutions are that they generate large quantities of permanent salts (largely sodium nitrate), and they do not remove all contaminants from degraded solvents. In addition, Purex plants have reported occasional failure of a solvent scrubbing unit due to formation of emulsions.[26] The complexants which are not removed by sodium carbonate scrubbing, or by any other basic scrub system, are degradation products which have long organic chains. The emulsion problem in carbonate scrubbers is usually controlled by inserting an acid scrub between two basic scrubbers, which breaks the emulsion. The sodium carbonate scrub solutions decrease in effectiveness as they accumulate degradation products, due to a combination of effects. As the sodium carbonate is reacted, the pH and the carbonate concentration of the solution decrease. At lower pH values, the effectiveness of the scrub solution for the removal of slightly acidic degradation products is decreased. The decrease in the carbonate concentration decreases the stability of the carbonate complexes and may lead to increased precipitation of insolubles such as zirconium; insolubles will cause problems in phase separation in the scrubbers (note that zirconium may not be completely soluble, even in fresh scrub solutions). The rate of transfer of uranium–DBP complexes from the organic to the aqueous phase has been shown to depend on the second power of the sodium carbonate concentration.[27] Thus, if the scrubber reactions are controlled by kinetics, the performance will decline as the sodium carbonate concentration decreases. The effectiveness of sodium carbonate scrub solutions will also decline with use since the sodium salts of the acidic complexers are somewhat soluble in the organic phase.[28] Thus, the concentration of the sodium salt of the

organic complexers in the cleaned organic from a scrubber will be proportional to the concentration of the organic complexer in the aqueous scrub solution. Most of these problems will be greatly improved by using two scrubbers in series, where the second scrubber will remove most of the materials not removed by the first scrubber. The use of two scrubbers in series allows better utilization of the sodium carbonate without sacrificing scrubbing effectiveness. In cases where the carbonate scrub is ineffective in regenerating degraded solvent, permanganate has been added with some success; its efficiency varies little with the degree of solvent degradation.[29] The use of permanganate, however, results in copious precipitation of manganese oxide. In tests at the Windscale Works, appreciable quantities of manganese oxide were carried in the solvent phase (20 mg/L), and this solid was only slowly removed by subsequent nitric acid washes. The problems in isolating the manganese oxide precipitate are about as bad as the degraded solvent problems that were alleviated. Purex plant scrubbers have normally used simple sodium carbonate scrub solutions with replacement of the scrub solutions when the effectiveness declines; sometimes the solvent is continuously circulated through the solvent cleanup during plant shutdown periods to improve the solvent quality.[14]

Hydrazine and hydroxylamine salts: Concern about the large amount of sodium nitrate waste generated by sodium carbonate scrubbing (as much as 100 kg of sodium nitrate per ton of fuel processed) has led to studies of basic scrub solutions in which the components can be decomposed into gases.[30] The use of hydrazine hydrate/carbonate was patented in the Federal Republic of Germany (FRG).[30] Major disadvantages of the hydrazine hydrate/carbonate method are that the reagent wash solutions are unstable and difficult to prepare and store.[28] Tallent demonstrated the use of hydrazine hydrate/oxalate solutions that are easier to prepare and are more stable than hydrazine hydrate/oxalate solutions.[28] Also, the operational behavior of the solvent cleanup system was significantly improved with precipitation, gassing, interfacial crud formation, and slow phase separations being either eliminated or reduced. With either hydrazine salt scrubbing solution, the procedure and equipment are similar to those required for present wash methods, with little disruption of present fuel recycle flow sheets. Hydrazine possesses potential hazards, including the potential for reaction with nitric acid; however, the proposed solvent cleanup processes would use only dilute aqueous solutions in which the danger of oxidation-reduction reactions would be significantly reduced.[31] Nevertheless, contact of the hydrazine salt solutions with concentrated or hot nitric acid must be avoided. Hydrazine reacts with nitrous acid to yield hydrazoic acid, a volatile, explosive compound (Eq. 2); further reaction of hydrazoic acid with nitrous acid yields the innocuous gases, N_2 and N_2O (Eq. 3):[33]

$$N_2H_4 + HNO_2 \longrightarrow HN_3 + 2H_2O \, , \tag{2}$$

$$HN_3 + HNO_2 \longrightarrow N_2O + N_2 + H_2O \, . \tag{3}$$

The destruction of hydrazine by nitrous acid in a Purex plant requires rapid reaction of hydrazine with a large excess of nitrous acid to avoid

accumulation of hydrazoic acid. Hydrazine can also be decomposed electrochemically.[34] Hydrazine is toxic and is a suspected carcinogen.[31] Dilute aqueous solutions have a low hydrazine overpressure, but they should be used only in well-ventilated areas and preferably in an effective fume hood. Hydrazine salt solutions are at least as effective for solvent cleanup as are sodium carbonate solutions. The major difficulty with their use is the remote possibility that the formation of hydrazoic acid could lead to an explosion. While it is easy to show that the probability is remote, it is difficult to show that it is impossible, as may be required for licensing a U.S. facility. Thus, to my knowledge, all consideration of hydrazine salt scrub solutions has ceased in the U.S., although they are still under consideration in the FRG. Another organic base that may have some merit is hydroxylamine.[35] This weak base has been tested, and its performance vs sodium carbonate scrub solutions will be summarized later in this paper.

Solid sorbents: A variety of solid sorbents have been proposed for primary cleanup and others for secondary cleanup following a primary cleanup using a basic scrub solution. Among the solids proposed are macroreticular resins, base-treated silica gel, inorganic on exchangers, lead dioxide on silica gel, and hydrous titanium dioxide.[36-40] Except for the lead dioxide solid and the inorganic ion exchangers, all the solid sorbents mentioned act as bases to effect removal of the acidic degradation products and are thus similar, in principle, to the aqueous scrubbing systems. All these materials have the potential advantage of the simplicity of packed column operations. The solid sorbents must be strong enough to stand transfer operations without generating significant amounts of dust, must be compatible with the range of possible solutions they may contact, and must not react to form hazardous materials or to degrade physically. To be useful as the primary cleanup agent for the solvent, a solid sorbent should have a large capacity for use in a once-through mode. Alternatively, it must be easily regenerated and the regeneration must not result in waste solutions that are difficult to handle. The spent sorbent must also be easily handled as a separate waste stream or must be incorporated into the normal waste handling system. These many requirements severely limit the commercially available materials that can be used. Specially designed and fabricated materials are possible, but the small demand may make them prohibitively expensive when in competition with more standard solvent cleanup methods.

The hydroxyl form of strongly basic anion exchange resins (Rohm and Haas A-26) is effective in removing complexants formed in degraded solvents along with their complexed cations.[36-37] One drawback of the macroreticular resins is that regeneration requires hydrogen fluoride solutions. Additionally, it was found that organic materials were leached from the resins; while it is not known that these would degrade the performance of the treated solvent, their presence is a potential disadvantage.[41] If the resins are inadvertently exposed to solvent which contains as much as $0.03 \underline{M} \ HNO_3$, severe physical damage (crumbling) occurs.[41] Although this would not normally occur, it is possible that a process upset could allow acidified solvent to enter the treatment system. The resins were developed as a primary cleanup method, but it is possible that they would be more suitable for secondary cleanup: here

the presence of the primary solvent cleanup system would protect the resin from exposure to acidified solvent and would extend its useful life to the point where regeneration would not be required. Disposal of the spent resin could be accomplished by incineration. Tallent proposed and tested the use of packed columns of base-treated (NaOH or LiOH) silica gel for primary cleanup of degraded solvent.[38] In the preferred treatment, 12- to 42-mesh silica gel was soaked in aqueous 1.0 $\underline{M}$ NaOH solution, with occasional stirring, for 24 h, filtered, washed with about one gel volume of water, and air dried. The volume of 1.0 $\underline{M}$ NaOH used was sufficient to provide ~100% excess of sodium over the amount adsorbed on the gel surfaces. Packed columns of base-treated silica gel have many effective stages and give better removals of most materials than a typical one- or two-stage sodium carbonate scrubber. Some of the complexants, other than DBP, that are not effectively removed by simple sodium carbonate scrubbing, are significantly removed by treatment with base-treated silica gel.[42] However, the sodium-DBP salt formed on the surface of the gel has a significant solubility in the solvent under these conditions and its removal might require scrubbing with a low-sodium solution in a subsequent step (stripping coefficient of 280 to 540). The treated silica gels adsorb HNO_3, DBP, UO_2^{2+}, Pu^{4+}, various metal-ion fission products, and other species from the solvent. Adsorption mechanisms include neutralization, hydrolysis, polymerization, and precipitation depending on the species adsorbed. Adsorption rates are diffusion controlled, giving small temperature effects. Recycle of the gels can be achieved with an acid elution followed by retreatment with base, but this operation generates acidic and basic aqueous waste streams plus a small amount of organic waste. It may be better to discard the spent bed and incorporate it in a solid waste such as glass.

Reported information on the other solid sorbents, hydrous titania and lead dioxide on silica gel and inorganic ion exchangers, is sparse.[30,39,40] The hydrous titania, as tested by British workers, is highly basic and was intended for primary solvent cleanup. It is not currently under study in the U.S. or the United Kingdom. Lead dioxide on silica gel is reported by FRG workers to be useful for secondary cleanup after primary treatment with sodium carbonate or hydrazine salts. Inorganic exchangers were shown to be effective, but slow, for removal of zirconium and ruthenium from contaminated solvent.

NEW SOLVENT SCRUBBING TESTS

The discussion on sodium carbonate scrubbing summarized the perceived problems with this method. Recent studies have examined a variety of scrubbing options in an experimental system using three mixer-settlers.[43] A portion of this work, comparing scrubbing with 0.25 $\underline{M}$ sodium carbonate/ 0.02 $\underline{M}$ sodium tartrate or 0.14 $\underline{M}$ free hydroxylamine hydrate/0.17 $\underline{M}$ hydroxylamine tartrate solutions, will be presented here. The complete report presents other scrubbing data for hydroxylamine citrate, hydrazine oxalate, and lithium hydroxide sucrose solutions, plus the details of the operations of the system.

Several approaches for improved scrubbing with sodium carbonate solutions are feasible. One possibility, tested in the experiments reported here, uses a counter-current flow of the contaminated organic and the aqueous scrub solution to improve the use of the sodium carbonate and decrease the quantity of permanent salts produced. The addition of tartrate may increase the solubility of zirconium and decrease any interfacial crud problems due to zirconium precipitation. Other methods for decreasing the formation of permanent salts are to use hydrazine or hydroxylamine salts in the scrub solutions; these are subsequently decomposed into gaseous products.[28,30,35]

The bank of three mixer-settlers (Fig. 1) was constructed of glass, stainless steel, and Teflon, except for sintered carbon liners in the pumps (FMI Metering, Inc., Oyster Bay, NY). This guaranteed that no impurities were leached from the structural materials into either the aqueous or organic streams. The mixers and settlers were baffled and jacketed for temperature control, having volumes, respectively, of 194 and 250 mL. Mixing was provided by glass rods with three rectangular glass paddles. The stirrers were rotated at 440 to 880 rpm by adjustable speed motors. The organic was pumped at ~75 mL/min by a FMI pump to the first mixer-settler and flowed by gravity through the remainder of the system. The aqueous solutions used in the first two mixer-settlers were used in a captive fashion and exited from the bottom of the settlers through a jack-leg to return to their respective pump pots. Their total solution volumes were 300 to 450 mL each. The water scrubber had a continuous water makeup and overflow of 10 mL/min and a total volume during a test of ~5.5 L. Each aqueous phase was recirculated to its respective mixer by an FMI pump at ~50 mL/min. Temperature control was by circulation of warm water through the jackets of the mixers and settlers. The temperature of the solutions in the first settler was ~37°C and the temperatures in the remainder of the equipment were ~40°C. The simulated contaminated organic contained ~0.1 m$\underline{M}$ Zr, 0.2 m$\underline{M}$ U, 0.4 m$\underline{M}$ DBP, and 0.3 m$\underline{M}$ HNO$_3$.
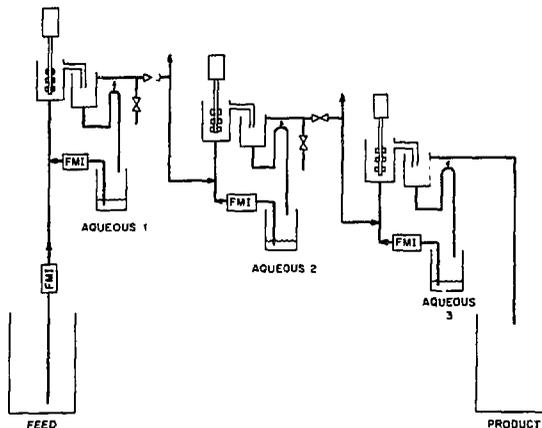
Fig. 1. Mixer-Settler Apparatus.

Samples of the feed taken at the beginning and end of each run and periodic samples of the organic effluents (gravity filtered through Whatman #40 paper and unfiltered) and aqueous scrub solutions were submitted to the ORNL Analytical Chemistry Division for uranium and zirconium analyses. Filtration through paper removes most of the particulate matter >8 μm in diam and most of any entrained aqueous drops. These filtered samples probably better represent the solvent that would result from high efficiency gravity settlers or centrifugal separators.

Analyses of the samples for zirconium was by inductively coupled plasma (ICP) and for uranium was by ultraviolet fluorescence. Nitric acid was essentially completely removed. The amount of DBP was too low for direct analysis and was estimated by extraction of plutonium, followed by three equal-volume water strips; each mol of DBP was assumed to retain one mol of plutonium.

Results of Mixer-Settler Tests

Interfacial crud problems: In both the sodium carbonate/tartrate and hydroxylamine hydrate/tartrate tests, interfacial crud was observed and appeared to consist of aqueous drops surrounded by a film-like skin. This skin is thought to be a hydrous zirconium-DBP material, since no such crud was observed in tests without zirconium and thin sheets or films were observed when these aqueous drops broke. The skin is likely similar to the layered structure compounds of zirconium previously described.[44,45] It was possible to operate with the entire aqueous space of the settler filled with this crud by allowing the crud to exit with the aqueous underflow from the mixer. Sometimes normal interfacial emulsions were observed as layers of droplets on the organic side of the interface; this problem is easily addressed by increasing the settling time or by decreasing the degree of mixing in the mixer. The interfacial crud was so slow in collapsing that increasing the settling time was not a practical approach.

In the test using sodium carbonate/tartrate, the interfacial crud became substantial (>3.8 cm thick) in the first settler after ~1 h and remained substantial until ~4 h. During this time small amounts of crud exited with the aqueous underflow. The total crud layer in the settler then began to decrease until it was a layer only ~1.3 cm thick. Interfacial crud appeared at a later time in the second settler and remained substantial throughout the run; however, little exited in the aqueous underflow. Although some interfacial crud formed in the water settler, it was not a significant problem. Entrainment of aqueous drops was observed in all organic streams leaving all settlers.

In the test using hydroxylamine/tartaric acid, the interfacial crud in the first settler became substantial within ~1 h and remained substantial during the entire run. A small amount of crud exited with the aqueous underflow, but did not cause significant problems in the operation of the settler. Interfacial crud was never a problem in the second hydroxylamine/tartaric acid settler or in the water settler. Entrainment of small aqueous drops in the exit organic streams from all settlers was observed.

Comparison of tests: Table I gives a comparison of the percent removals of uranium and zirconium by each stage, based on the average cation contents of the filtered organic entering the stage.   The first stage of the sodium carbonate/tartrate test removed virtually all the uranium and zirconium fed to it.   The subsequent sodium carbonate/tartrate stage was apparently much less effective, although this may be an artifact, due to the small amount of material going into the second stage. The water scrubber apparently removed a small amount of uranium.   The hydroxylamine/tartaric acid scrub stages were much less effective, but a second stage did remove a significant additional amount of uranium and zirconium.   Water scrubbing was ineffective in additional removal.

Table I.   Removal effectiveness for uranium, zirconium, and DBP by test scrub solutions

Stage	U or Zr removed from stage feed		
	Sodium carbonate/tartrate		
	U (%)	Zr (%)	DBP (%)
1	99.8	97.5	----
2	6.3	----	----
3	33	----	----
Overall	99.99	>99.8	99.5
	Hydroxylamine/tartaric acid		
	U (%)	Zr (%)	DBP (%)
1	81.3	91.1	----
2	70	20	----
3	----	----	----
Overall	96.8	92.7	94.5

Estimates of DBP (by plutonium retention) were used to calculate the overall percent removals of DBP given in the last columns of Table I.   The overall removals of uranium, zirconium and DBP for each individual scrub solution are similar, indicating that the cations and DBP are removed to similar degrees.   The removals by the sodium carbonate/tartrate scrub solution were superior.

Table II gives the overall material balance for the metal ions in the tests.   In both tests complete accountability for uranium indicates uranium was not precipitated.   The low accountability for zirconium indicates a problem with zirconium solubility.   The percent and quantity of zirconium removed from product samples by filtration is shown in Table III.

Table II. Metal-ion material balances

Scrub solution	Amount found	
	U (%)	Zr (%)
Sodium carbonate/tartrate	107	52
Hydroxylamine/tartaric acid	114	81

Table III. Fraction of zirconium in product which is filterable

System	Zr removed by filtration (%)	Zr filtered (μg/mL)
Sodium carbonate/tartrate	>95.4	0.37
Hydroylamine/tartaric acid	4.9	0.04

These data indicate that the sodium carbonate/tartrate system is prone to generate particulate zirconium. The better behavior of the hydroxylamine hydrate/tartrate system may be due to its large concentration of complexing anion.

Recommendations for primary solvent scrubbing: The best solvent cleanup results were obtained using sodium carbonate/tartrate solutions; this system should be used if the quantity of sodium resulting from its use does not present a problem in waste management. Since the hydroxyla-mine hydrate/tartaric acid system showed a greater zirconium solubility, a tartrate concentration >0.02 $\underline{M}$ might be beneficial to the sodium carbonate/tartrate system. While the interfacial crud was present in the sodium carbonate/tartrate system, it did not present a serious problem. The use of a basic sodium system has the additional advantage of con-verting long-chain organic acids and some secondary complexants to sodium salts that can then be removed by a water scrub. The use of a water scrub with sodium carbonate/tartrate scrubbing did not cause any emulsion problems, but this may have been because a small amount of sodium car-bonate/tartrate (~0.001 $\underline{M}$) was present by entrainment. The effluent organic stream from scrubbing with sodium carbonate/tartrate should be filtered, since these tests indicated that this scrub solution is prone to generation of entrained solid material.

The only reason to consider use of any scrub system besides the sodium carbonate/tartrate (or similar ones) would be avoidance of sodium in the waste. If this is a consideration, the best alternative would be a hydroxylamine salt system followed by a sodium carbonate-type scrubber. The hydroxylamine system would remove the bulk of the contaminants and

greatly decrease the need for makeup sodium carbonate/tartrate. The use of a single sodium carbonate/tartrate scrubber would still retain the option of using a final water or dilute salt-containing scrubber to remove acidic long-chain organic contaminants.

NEW SECONDARY CLEANUP STUDIES

Primary solvent cleanup by sodium carbonate or equivalent methods is straightforward. The degradation products remaining after the primary cleanup, which cause phase separation problems and retention of cations, are less understood, as was discussed in the survey section. Since the identities and chemical properties of the important contaminants are unknown, secondary cleanup studies must use real recycle solvent.

Our studies have used solvent obtained from SRP for testing of solid sorbents, including activated charcoal, silica gel (as received and treated with NaOH), activated alumina, attapulgite clay, and macroreticular anion exchange resin. The SRP solvent is scrubbed, during each cycle, with sodium carbonate, dilute acid, and finally, with sodium carbonate. No treatment to remove the secondary degradation products is attempted. The activated alumina used in our tests (Alcoa F-1, 60-120 mesh; Aluminum Co. of America, Pittsburgh, PA) was by far the best material tested for secondary cleanup; this paper will summarize these results, while the complete paper will be available for additional details.[46]

The SRP solvent used was about a month old and was scrubbed with 1/5 volume of 0.25 $\underline{M}$ Na_2CO_3/0.02 $\underline{M}$ sodium tartrate (sodium carbonate/tartrate) and filtered through a Whatman #40 paper filter immediately before testing to eliminate any DBP or MBP which may have been present. The test columns were made of ~8-mm-OD, ~5-mm-ID glass tubing. A typical experimental setup is shown in Fig. 2. The test bed was first dried in place at ~300°C to obtain a completely dry bed. It was then treated in place with ~10 mL of fresh 30% TBP-NPH to presaturate the activated alumina with TBP. The solvent in the tests flowed down through the beds at 1 mL/min (bed residence time of ~30 s). The bed depth was ~5 cm and the solvent head required for the 1 mL/min flow rate was initially ~50 cm; by the end of the capacity test the required head was ~75 cm. All tests were at ~22°C. The effluent was saved in 5 mL increments and a number of these were examined for interfacial tension and phase separation time vs sodium carbonate/tartrate, anionic surfactant content by the methylene blue (MB) technique, plutonium retention, and ruthenium removal.[47] The zirconium retention of the solvent was so low (~1.5 × 10^{-7} $\underline{M}$) it was not considered to be of significance and was not routinely determined.[48]

Analysis Methods

Interfacial tension: The organic sample to be tested was first equilibrated with the sodium carbonate/tartrate solution. Drops of organic were slowly dispensed from a micrometer syringe equipped with a flat-ended stainless steel needle submerged under the aqueous phase. The interfacial tension was then calculated for each drop and the average determined for several drops.[49] The interfacial tension for 30% TBP-NPH,
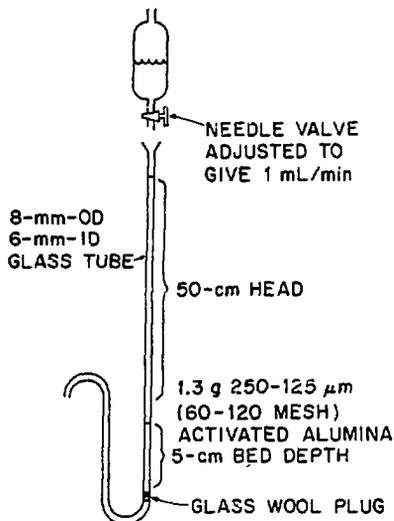
NEEDLE VALVE
ADJUSTED TO
GIVE 1 mL/min

8-mm-OD
6-mm-ID
GLASS TUBE

50-cm HEAD

1.3 g 250-125 μm
(60-120 MESH)
ACTIVATED ALUMINA
5-cm BED DEPTH

GLASS WOOL PLUG

Fig. 2.   Typical Column for Secondary Cleanup Tests

made from fresh ingredients, was ~10 to 11 dyn/cm. The interfacial
tension for initial SRP solvent, after scrubbing and filtering, was
7.0 dyn/cm.

Phase separation time: The phase separation time for the solvent
was determined by placing 2 mL of the organic and 2 mL of the sodium
carbonate/tartrate solution in a glass vial ~1.2 cm diam and mixing by
gentle inversion several times. The separation time was taken as the time
for the emulsion to collapse to one layer of drops at the interface. All
determinations were done by one individual to obtain the most consistent
results. Even so, this is an inexact measurement; it is a necessary
measurement, however, since phase separation from sodium carbonate solu-
tions is a known problem area. The phase separation time for clean 30%
TBP-NPH was found to be 20 to 25 s. The phase separation time for the
initial SRP solvent after scrubbing and filtering was ~105 s.

Plutonium retention: One drop (~0.05 mL) of 2.2 $\underline{M}$
HNO_3 containing ~40 mg/mL of plutonium was added to 2 to 5 mL of solvent.
The mixture was scrubbed three times with an equal volume of water. A
filtered organic sample was submitted for gross alpha determination.
Freshly prepared 30% TBP-NPH gave a plutonium retention of 2.8×10^{-6} $\underline{M}$;
the initial SRP solvent gave a plutonium retention of 2.9×10^{-5} $\underline{M}$.

MB test:[47]   Fifty mL of water, 10 mL of methylene blue reagent
(0.045 g of methylene blue in 1 L of 0.5 $\underline{M}$ acetic acids, pH adjusted to 5.0
with NaOH), 10 mL of chloroform, and 1 mL of the organic to be tested were
added to a 150 mL beaker and stirred vigorously for 60 S with a magnetic
stirrer. A sample of the chloroform layer was filtered through Whatman
#40 filter paper and its absorbance determined at 653 nm. This absorbance
was assumed to be proportional to the anionic surfactant content.

Results

The phase separation time is determined by several factors, including the interfacial tension between the two phases. When the SRP solvent was centrifuged at 1250 rpm for 1 min with a radius of 12.7 cm (222 × $\underline{g}$), the phase separation time from sodium carbonate/tartrate solution was decreased from 105 s to 50 s, indicating the presence of particulate matter, which affected phase separation. A packed bed of any material would probably act as a filter to improve phase separation time.

In earlier tests we concluded that the observed decrease with time in the effectiveness of the activated alumina beds was largely due to "poisoning" of the activated alumina by water dissolved in the solvent.[46] Drying the solvent in a plant requires a process that is simple and does not create waste problems; a likely approach is to contact the solvent with a dry gas stream at a modest temperature. In our test we sparged 200 mL of SRP solvent, which was saturated with water (6.85 g/L) for 6 h with 200 mL (STP) of dry air per min at 60°C. After 4 h and 6 h, the water contents were, respectively, 0.25 g/L and 0.21 g/L. Treatment at 60°C is safe since this is below the flash point of the solvent. Under these conditions only ~0.5% of the diluent would be volatilized and even this could be recovered by condensing the vapors and separating the diluent from the water. Interestingly, the phase separation time of the sparged solvent from sodium carbonate/tartrate was decreased to 75 s, indicating that some volatile components contribute to phase separation problems.

The solvent was then passed through the activated alumina column with the results given in Figs. 3 and 4. Up to the time when 250 column volumes were treated, the phase separation time (15 s) and the interfacial tension (>10.5 dyn/cm) were better than those measured for freshly prepared 30% TBP-NPH. The treatment capacity of the column was ~370 column volumes. Figure 4 shows the percent of the initial ruthenium and anionic surfactants in the feed remaining after passage through the column. The close agreement between the ruthenium and anonic surfactants removals supports the suggestion by Neace that retention of ruthenium is related to anionic surfactants.[50] The plutonium retention of the solvent was reduced to an average of 30% of the initial value. The lowest plutonium retentions were 2% after 200 column volumes and 9% after 400 column volumes, suggesting nearly complete removal of the plutonium complexers. The lack of any trend of the plutonium retention with volume of solvent treated suggests that the higher values measured may be due to entrainment.

The column was washed with hexane to remove TBP and any other loosely held species and then was redried at 290°C. A reloading test gave a capacity of only ~75 column volumes; regeneration does not appear to be simple and is not worthwhile unless a better regeneration procedure can be determined.

Recommendation for Secondary Cleanup

The procedure tested appears to be nearly ideal for plant application, but should be tested close-coupled with an operating Purex plant when optimum flow rates and operating temperatures have been determined.
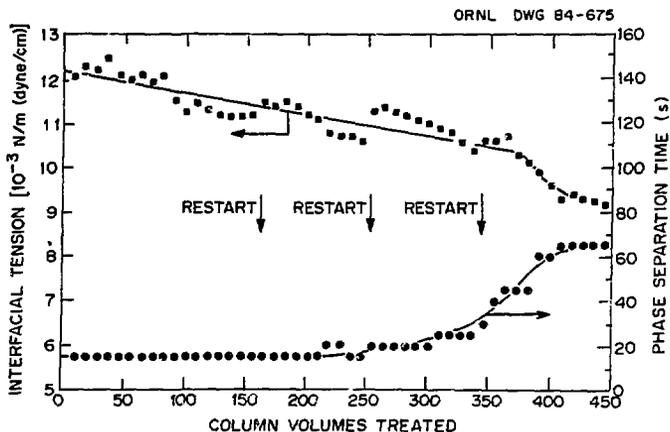
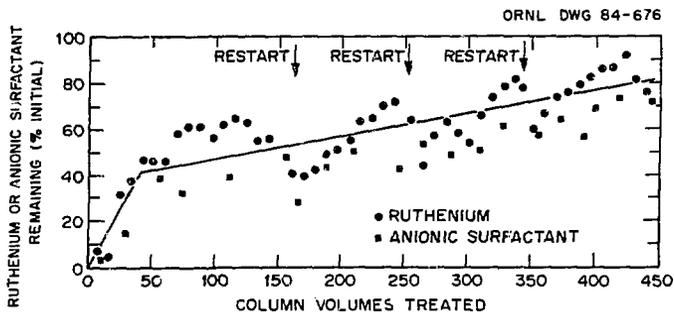Fig. 3. Interfacial tension and phase separation time of treated solvent.

Fig. 4. Ruthenium and anionic surfactants (by MB test) remaining in treated solvent. Line is for ruthenium data.

A primary cleanup using standard alkaline scrubbing should be used; the activated alumina bed would be used to treat a small side-stream or to perform occasional batch cleanup of the solvent.

REFERENCES

1. R. G. WYMER and B. L. VONDRA, ed., Light Water Reactor Nuclear Fuel
    Cycle, CRC Press, Boca Raton, Florida (1981).

2. L. L. BURGER, "The Chemistry of Tributyl Phosphate, A Review," USAEC
    Rep. HW-40920, Hanford Works (1955).

3. A. J. MOFFAT and R. D. THOMPSON, "Basic Studies of Chemical Stability
    in Extraction Systems I. The Effect of Zirconium Nitrate and Nitric
    Acid Upon the Stability of Tributyl Phosphate," IDO-14543, Idaho
    Chemical Processing Plant (1961).

4. Z. NOWAK, M. NOWAK, and A. SEYDEL, "The Radiolysis of TBP-Dodecane-
    HNO_3 Systems," Radiochem. Radioanal. Lett. 38, 343 (1979).

5. Z. NOVAK, M. NOVAK, and A. ZAYDEL, "Research on the Effect of Salts
    of Uranium, Zirconium and Ruthenium on Radiolysis of the Tributyl
    Phosphate-Dodecane-HNO_3 Systems," ORNL-tr-4879, translation of paper
    from 4th Symp. on Study into Irradiated Fuel Reprocessing, Karlovy
    Vary, Cz (1977).

6. I. A. KULIKOV, N. V. KERMONOVA, and M. V. VLADIMIROVA, "Radiolysis of
    TBP in the Presence of Plutonium and Uranium," Sov. Radiochem. 25,
    310 (1983).

7. L. STIEGLITZ, W. OCHSENFELD, and H. SCHMIEDER, "The Influence of the
    Radiolysis of Tributyl Phosphate on the Plutonium Yield in the Purex
    Process for High Plutonium Content," KfK 691, Karlsruhe Nuclear
    Research Center (1968).

8. W. SCHULZ and J. D. NAVRATIL, ed., Science and Technology of Tributyl
    Phosphate. Vol. 1: Synthesis, Properties, Reactions, Analysis, CRC
    Press, Boca Raton, Florida (1984).

9. O. K. TALLENT, J. C. MAILEN, and K. D. PANNELL, "Purex Diluent
    Degradation," USDOE Rep. ORNL/TM-8814, Oak Ridge National Laboratory
    (1984).

10. A. I. TITOV, "The Free Radical Mechanism of Nitration," Tetrahdron
    19, 557 (1963).

11. A. I. TITOV, "Theory of Nitration of Saturated Hydrocarbons and Their
    Derivatives. I. General Conclusions of the Study of the Primary
    Elementary Stage of the Reaction," Zh. Obsch. Khim. 16, 1896 (1946).

12. R. BECKER, F. BAUMGARTNER, and L. STIEGLITZ, "Identification of
    Complexing Radiolytic Products of the Purex Systems (20% TBP-
    Dodecane-HNO_3)," KfK-2304, Karlsruhe Nuclear Research Center (1977).

13. L. MAYA and C. D. BOPP, "Extraction of Zirconium from Nitric Acid Media by Butyl Lauryl Phosphoric Acid in Dodecane," *J. Inorg. Nucl. Chem.* **40**, 1147 (1978).

14. L. MAYA, "Chemistry of Extractable Nitrosyl Ruthenium Species in the System Nitric Acid-Tributyl Phosphate-Dodecane," *J. Inorg. Nucl. Chem.* **43**, 385 (1981).

15. M.M. BEARY, "Solvent Improvement Resulting from the Use of NPH in the Hanford Purex Plant," USAEC Rep. ARH-SA-73, Atlantic Richfield Hanford Company (1970).

16. J. T. BUCKNER, Savannah River Plant, Private Communication (1984).

17. L. MAYA, "Zirconium Behavior in the System HNO_3-30% Tributyl Phosphate-Dodecane in the Presence of Monobutylphosphoric Acid," *J. Inorg. Nucl. Chem.* **43**, 379 (1981).

18. W. D. ARNOLD, Oak Ridge National Laboratory, Private Communication (1981).

19. F. SICILIO, T. H. GOODGAME, and B. WILKINS, JR., "Distillational Purification of Irradiated Tributyl Phosphate in Kerosene-Type Diluent," Final report, Project No. A-428, Engineering Experiment Station, Georgia Institute of Technology (1960).

20. S. IKEDA, et al., "Recovery Test of Dodecane from Degraded Solvent," in "Semi-Annual Progress Report of Power Reactor and Nuclear Fuel Development Corporation, Tokai Works," 146 (February 1979).

21. Y. KURODA and K. OGI, "Method of Recovering and Regenerating Organic Solvents Used for the Reprocessing of Radioactive Wastes," Japanese Patent 54-23,900/A (22 February 1979).

22. H. J. CLARK and G. S. NICHOLS, "Purification of Radioactive Solvent with a Flash Vaporizer," USAEC Rep. DP-849, Savannah River Laboratory (1965).

23. B. F. WARNER, United Kingdom Atomic Energy Authority, Windscale and Calder Works, Private Communication to R. H. Rainey, Oak Ridge National Laboratory (1963).

24. C. R. FORD and H. V. CHAMBERLAIN, "Steam Stripping TBP-Amsco Solutions from Non-Volatile Contaminants," USAEC Rep. IDO-14546 (1961).

25. P. R. AUCHAPT, et al., "Solvent Purification Using a Current of Water Vapor," ORNL-tr-244, translation of CEA-R 2404, Plutonium Production Center at Marcoule (1964).

26. D. A. ORTH and T. W. OLCOTT, "Purex Process Performance Versus Solvent Exposure and Treatment," *Nucl. Sci. Eng.* **17**, 593 (1963).

27. J. C. MAILEN, D. E. HORNER, S. M. ROBINSON, and S. E. DORRIS, "Scrubbing Kinetics of Uranium- and Zirconium-Dibutyl Phosphate Complexes," in Proceedings of Int. Solv. Extr. Conf. 1983, Denver, Colo., 80 (1983).

28. O. K. TALLENT and J. C. MAILEN, "An Alternative Solvent Cleanup Method Using a Hydrazine Oxalate Wash Reagent," Nucl. Technol. 59, 51 (1982).

29. A. J. HUGGARD and B. F. WARNER, "Investigations to Determine the Extent of Degradation of TBP/Odourless Kerosene Solvent in the New Separation Plant, Windscale," Nucl. Sci. Eng. 17, 638 (1963).

30. H. GOLDACKER, H. SCHIEDER, F. STEINGRUNN, and L. STIEGLITZ, "A Newly Developed Solvent Wash Process in Nuclear Fuel Reprocessing Decreasing the Waste Volume," Kerntechnik 18, 426 (1976).

31. N. I. SAX, Dangerous Properties of Industrial Materials, Van Nostrand Reinhold, New York, 727 (1979).

32. F. A. COTTEN and G. WILKINSON, Advanced Inorganic Chemistry, 3rd ed., Wiley Interscience, New York, 353 (1972).

33. J. L. SWANSON,, "The Destruction of Nitrous Acid and Hydrazoic Acid in Purex Systems," USAEC Rep. BNWL-B-121, Battelle-Pacific Northwest Laboratories (1971).

34. H. SCHMIEDER, F. BAUMGARTNER, H. GOLDACHER, and H. HAUSBERGER, "Electrolytic Techniques in the Purex Process, KfK-2082, Karlsruhe Nuclear Research Center (1974).

35. A. L. MILLS, Atomic Energy Research Establishment, Harwell, Private Communication (1982).

36. W. W. SCHULZ, "Macroreticular Ion-Exchange Resin Cleanup of Purex Process Tributyl Phosphate Solvent," in Solvent Extraction., Proc. Int. Solv. Extr. Conf. ISEC 71, The Hague 19-23 April 1971, Soc. of Chem. Industry, Vol. I, (1971), p. 174.

37. W. W. SCHULZ, "Macroreticular Anion Exchange Resin Clean-up of TBP Solvents," USAEC Rep. ARH-SA-129 (1972).

38. O. K. TALLENT, J. C. MAILEN, and K. D. PANNELL, "Solvent Cleanup Using Base (NaOH or LiOH) Treated Silica Gel Solid Adsorbent," USDOE Rep. ORNL/TM-8948 (1984).

39. C. N. TURCANU and D. RADU, "Sorption of ^{106}Ru and ^{95}Zr from Purex Solvent on Organic and Inorganic Ion Exchangers," Radiochem. Radioanal. Lett. 43, 245 (1980).

40. T. V. HEALEY, "Fuel Reprocessing Solvent Tributyl Phosphate," in _Management of Radioactive Wastes from the Nuclear Fuel Cycle, Proc. Symp. IAEA and NEA (OECD), Vienna, March 1976, Vol. I_, (1976), p. 201.

41. O. K. TALLENT, Oak Ridge National Laboratory, Private Communication (1978).

42. D. E. BENKER, Oak Ridge National Laboratory, Private Communication (1982).

43. J. C. MAILEN and O. K. TALLENT, "Assessment of Solvent Cleanup Methods Using a Mixer–Settler System," USDOE Rep. ORNL/TM–9118 (1984).

44. G. ABLERTI, U. COSTANTINO, S. ALLULLI, and N. TOMASSINI, "Crystalline $Zr(R-PO_3)_2$ and $Zr(R-OPO_3)_2$ Compounds (R = Organic Radical). A New Class of Materials Having Layered Structure of the Zirconium Phosphate Type," _J. Inorg. Nucl. Chem._ 40, 1113 (1978).

45. L. MAYA, "Structure and Chromatographic Applications of Crystalline $Zr(OPO_2R)_2$; R = Butyl, Lauryl and Octylphenyl," _Inorg. Nucl. Chem. Lett._ 15, 207 (1979).

46. J. C. MAILEN and O. K. TALLENT, "Cleanup of Savannah River Plant Solvent Using Solid Sorbents," USDOE Rep. ORNL/TM–9256 (1985).

47. J. C. NEACE, Allied–General Nuclear Services, Private Communication (1980).

48. T. P. GARRETT, "A Test for Solvent Quality," USAEC Rep. DP–237, Savannah River Laboratory (1957).

49. W. D. HARKINS and F. E. BROWN, "Determination of Surface Tension (Free Surface Energy) and the Weight of Falling Drops–Surface Tension of Water and Benzene by the Capillary Height Method," _J. Am. Chem. Soc._ 41, 499 (1919).

50. J. C. NEACE, "Diluent Degradation Products in the Purex System," _Sep. Sci. Technol._, in press.

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