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Potential Signatures of Semi-volatile Compounds Associated With Nuclear Processing

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June 2002

Prepared for the U.S. Department of Energy
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**Potential Signatures of Semi-Volatile Compounds
Associated With Nuclear Processing**

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Abstract

Semi-volatile chemicals are associated with nuclear processes and can provide sticky residues or signatures that will attach to piping, ducting, soil, water, or other surface media. Volatile compounds that are more suitable for electro-optical sensing have been well studied. However, the semi-volatile compounds have not been well documented or studied. A majority of these semi-volatile chemicals are more robust than typical gaseous or liquid chemicals and can have lifetimes of several weeks, months, or years in the environment. However, large data gaps exist concerning these potential signature compounds, and more research is needed to fill these data gaps so important signature information is not overlooked or discarded. This technical report investigates key semi-volatile compounds associated with nuclear separations, identifies available chemical and physical properties, and discusses the degradation products that would result from hydrolysis, radiolysis, and oxidation reactions on these compounds.

Summary

Semi-volatile chemicals are associated with nuclear processes (e.g., the reprocessing of uranium to produce plutonium for nuclear weapons, or the separation of actinides from processing waste streams), and can provide residues (signatures) that will attach to piping, ducting, soil, water, or other surface media. Semi-volatile compounds are compounds that have low volatility (i.e., have measurable but low vapor pressure (<0.1 torr @ 20° C) and are compounds that under ambient conditions are present in detectable concentrations in the atmosphere, either in vapor phase or absorbed on particulates. A majority of these semi-volatile chemicals are more robust than typical gaseous or liquid chemicals and can have lifetimes of several weeks, months, or typically years in the environment.

As large data gaps exist concerning these potential signature compounds and their physical properties, this document provides 1) preliminary lists of key compounds related to actinide separations and their chemical and physical properties, 2) a list of the key semi-volatile organophosphorus compounds and their suspected main byproducts formed from breakdown processes (e.g., hydrolysis, radiolysis, and oxidation), and 3) the chemical lifetime (environmental stability) information for these compounds. In addition, a rough estimation of some the potential emissions that could result from a hypothetical batch separation process were included. This estimation was included to understand the potential amounts of precursor semi-volatile compounds that could be released to the environment.

Chemical separation technologies, and related methods, for nuclear production are still being studied by various countries to find more efficient methods for removing long-lived actinides and increase the recovery yields of uranium and plutonium from irradiated fuel and waste streams. These technologies are of interest for not only radioactive waste reduction but also for the non-proliferation of nuclear weapons. Many of the older processing techniques are still in use and are well documented. However, there is now a shift to new chemical separations methods that are water-based instead of solvent-based, have increased separation efficiencies, use less process materials, and provide less obvious waste products. These processing methods use very strong semi-volatile molecules, which are highly resistant to radiolytic reactions, and have a higher selectivity and separation efficiency for the nuclides under consideration.

Many of these processing methods use various semi-volatile organophosphorus compounds that are considered “sticky” and will typically plate out on nearby surfaces. As a result of the separations process, these complex chemicals will produce numerous degradation products that may also provide robust signatures, when released to the environment. This report builds on the unique chemical properties of these semi-volatile compounds that will have a significant effect on their fate (where they will go) when they are released into the environment. As large data gaps exist concerning these issues, this report introduces a limited list of semi-volatile compounds and provides estimations of their chemical and physical properties and key degradation products. It should be noted that this list is not yet comprehensive, and further work is needed to prioritize these chemicals, understand the stability of the byproducts that could form, and obtain critical data gaps.

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1.0 Introduction

Nuclear separation techniques can incorporate the use of tried and true methods such as the plutonium extraction (PUREX) process to reprocess spent fuel to recover uranium (U) and plutonium (Pu) metals. However, newer techniques such as the transuranic extraction (TRUEX) process and other processes using bidentate extractions or combinations of separation techniques are also being utilized for defense waste separations, which could play a role in proliferation activities. The newer processes use complex organic molecules that have higher efficiencies for the nuclides being separated, are highly resistant to radiolysis and hydrolysis, reduce much of the waste "tails" that are normally contaminated by the nuclides, and allow separations to be carried out routinely and safely even by poorer industrial nations or groups.

The majority of degradation products formed during the separations processes are from hydrolysis and radiolysis. Radiolysis and photo-oxidation will form basically the same products via virtually the same mechanisms. However, photo-oxidation reactions will be much slower, and products will be formed after the reagents are released to the environment. That is because photo-oxidation involves radiation coming from sun energy (typically ultraviolet radiation) and radiolysis involves higher energy radiation coming from radionuclides (typically gamma and beta radiation).

Our experience in the laboratory with these organophosphorus compounds has shed new light on the degradation products that may develop when these chemicals are released to the environment. In addition to the organophosphorus compounds, there are amines and solvents that, when mixed with the organophosphorus compounds, form unique byproducts that will also degrade into sticky signatures. The understanding of these products can provide new insights for detection methodologies. For example, alkyl carbamoyl phosphine oxide-tributyl phosphate formulations used for actinide separations tend to form degradation products from radiolysis and hydrolysis. Some of these compounds formed are acidic (phosphinic acids), and some are neutral oxides (phosphine oxides). These compounds are often unique and provide good signatures of ongoing or historical separations processes.

The finding deduced from the information researched for this document is that significant fingerprints from combinations of degradation products would be formed from all of the actinide separation/extraction procedures and almost all of the degradation products would likely contain some of the same products (i.e., tributyl, dibutyl, and monobutyl phosphates; butanol, phosphoric acids, and hydrocarbon (C10-C16) chains. If secondary or tertiary separations are performed with these procedures that utilize crown ethers or alkylamines, the original compounds used (i.e., dibenzo-15-crown-5 and/or tridecylamine) and long polyoxyethylene (oligomeric) chains would be mixed in with the compounds mentioned above. These compounds are all robust, not very volatile, and could remain on surfaces or in soils for extended periods of time.

1.1 Background

It is well understood that with sufficient resources, available open source information (e.g., on the Internet), recently unclassified nuclear-sensitive information, and some specialist help, the ability exists to build a nuclear weapon of mass destruction. The September 11 terrorist attacks revealed that there were critical weaknesses in international nuclear inspection routines, export controls, and intelligence gathering. It has now been established that there are clandestine, very well funded nuclear weapons programs that have the capability of building nuclear weapons from diverted reactor fuel during waste separation techniques (www.idsa-india.org).

In 1991, International Atomic Energy Agency (IAEA) inspectors, through the United Nations Special Commission (UNSCOM), learned that important nuclear documents were stored in downtown Baghdad. These documents disclosed that Iraq had been in the midst of a full-blown program designed to produce highly enriched U (HEU) (and possibly Pu) and turn it into a deliverable, implosion-type nuclear weapon. Iraq had no option but to hand over to the IAEA half a million pages of secret documents, 20 tons of high-strength steel, and stocks of fiber for more than 1000 gas centrifuges (www.fas.org/nuke/guide/iraq/nuclear/iaea.htm).

In addition to Iraq, the North Korean peninsula is viewed as an accurate barometer of the security environment in Northeast Asia, and it remains a very volatile arena and a most destabilizing factor with respect not only to nuclear, but also chemical, and biological weapons (Report to Congress on the Korean Peninsula 2001).

With regard to semi-volatile chemicals associated with nuclear separation processes, most of the key precursors and waste products contain organophosphorus compounds. Many of these compounds are trialkyl phosphates, alkyl phosphonates, di- and tri- alkyl phosphine oxides, or di-alkyl carbamoyl phosphine oxides, or di-alkyl carbamoyl phosphonates. These compounds all have very low vapor pressures, and tend to stick to metal surfaces and ducting, even when heated. For example, various studies performed on the Hanford Tank Waste head gasses indicated that the headspace gases appeared as diffuse electro-optical spectra as a result of the strong surface interactions on the windows of the absorption cells. Nearly identical electro-optical spectral shapes were observed with organophosphoryl analogs, like tributyl phosphate, that contain the O=P bond (Kelly 2001).

2.0 Nuclear Separation Processes

Nuclear separations are processes that divide the desired isotopes from the undesirable isotopes. While not every process is designed for weapon's production purposes, several of the separations processes use semi-volatile compounds that, if released to the environment, will degrade into sticky signatures.

Some of the separation processes that were investigated for this report include:

- The Bismuth Phosphate Process
- The REDOX (Reduction-Oxidation) Process
- The PUREX Process
- The TRUEX Process
- The SREX (Strontium Extraction) Process
- The TALSPEAK Process
- The TRAMEX Process
- The DIAMEX Process
- Bidentate Extractions
- Dicarbollide Extractions

Actinide separation processes primarily use two phase systems (aqueous/organic) and employ a large range of complexation reagents, including phosphine oxides, phosphonates, alkyl phosphates, alkyl amines, crown ethers, and others, dissolved in a suitable organic solvent typically kerosene. The processes of interest for this report were primarily PUREX, TRUEX, SREX and TRAMEX. The PUREX process would most often be used to separate large volumes of U and Pu from spent fuel for weapons production. The other processes would typically be used for additional actinide separations on waste tails or for recycling solvents. Uranium enrichment separations were not considered for this report as the semi-volatile compounds are primarily used for the separation processes listed above. Table 2.1 summarizes the compounds that are used and the major groups of degradation products that could be available for signatures from each process.

The Bismuth Phosphate Process was the first large-scale radiochemical separation process. Purification of Pu was accomplished by alternately oxidizing Pu to PuO_2^{2+} and reducing it to Pu(III) and/or Pu(IV) (to cause it to precipitate again). The disadvantages of this process was that it is very complex, uses large amounts of reagents, requires several batch operations, and recovers Pu only after irradiation (Choppin et al. 1999). Solvent extractions eventually replaced this process, and the REDOX or Hexone process was found to be suitable for large-scale operations and could isolate both U and Pu from the fission products. The Redox process used methyl isobutyl ketone (MIBK) or hexone. The major disadvantage of the REDOX process is that the reagents are highly flammable and dangerously explosive, and the hexone will decompose in the strong nitric acid used for the aqueous phase (Choppin et al. 1999).

Table 2.1. Summary of Compounds Associated with Key Nuclear Separation Processes

Process	Starting Chemicals Used in the Process.	Chemical compounds that may be present as source reagents or degradation products.
REDOX	Hexone, kerosene, ¹ MIBK. ²	Ketones, kerosene (decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, aromatics), decanal, undecanal..., decanoic acids, undecanoic acids..., nitrodecane, nitroundecane...
Bismuth Phosphate	Na ₂ CrO ₄ , NaBiO ₄ , BiPO ₄ , FeNH ₄ SO ₄ , nitric acid, phosphoric acid, and water.	Chromate, nitrate, bismuthate, sulfate, and phosphate salts.
PUREX	TBP, ² kerosene, ¹ nitric acid, water.	TBP, DBP, MDP, H ₃ PO ₄ , kerosene (decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, aromatics), decanal, undecanal..., decanoic acids, undecanoic acids..., nitrodecane, nitroundecane...
TRUEX	CMPO, TBP, ² nitric acid, dodecane.	CMPO, MOOPO, DiIBAN, OOPA, TBP, DBP, MDP, ² H ₃ PO ₄ , oxalic acid, dodecane, dodecanol, decanal, dodecanoic acid, nitrododecane.
SREX	TBP, kerosene, ¹ nitric acid, water, crown ethers (18-crown-6, benzo-15-crown-5...).	TBP, DBP, MDP, ² H ₃ PO ₄ , kerosene (decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, aromatics), decanal, undecanal..., decanoic acids, undecanoic acids..., nitrodecane, nitroundecane..., 18-crown-6, benzo-15-crown-5, dicyclohexyl-18-crown-6, dibenzo-18-crown-6.
TRAMEX	TBP, ² kerosene, ¹ nitric acid, water, DEHPA, ² trialkyl amines, and tetraalkyl ammonium salts (trioctyl amine, trilauryl amine).	TBP, DBP, MDP, ¹ H ₃ PO ₄ , kerosene (decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, aromatics), decanal, undecanal..., decanoic acids, undecanoic acids..., nitrodecane, nitroundecane, DEHPA, ² trioctylamine, trilaurylamine, mixed alkyl ammonium salts.
<p>Note: Kerosene is a mixture composed of branched and linear alkanes ranging from C₁₀H₂₂ (decane) to C₁₆H₃₄ (hexadecane). (C₁₁ - undecane, C₁₂ - dodecane, C₁₃ - tridecane, C₁₄ - tetradecane) It also contains a variety of substituted aromatic compounds (i.e. alkylated benzenes, naphthalenes, etc.). There are a staggering number of possible isomers in kerosene. For example, pentadecane (C₁₅H₃₂) has 4,347 isomers. Kerosene could possibly consist of over 50,000 isomers. However, the majority of kerosene most likely consists of a few hundred different compounds. Each batch of kerosene produced will have slightly different compositions. The degradation products would be alcohols, aldehydes, ketones, acids, nitrated alkanes, nitrated aromatics, dimers, trimers, and oligomers of all of these isomers.</p> <p>¹Researchers use dodecane to simplify results, but commercial processes use kerosene for lower costs. ²MIBK = methylisobutylketone, TBP = tributylphosphate, DBP = dibutylphosphate, MBP = monobutylphosphate, CMPO = carbamoyl methylene phosphine oxides, MOOPO = methyl (octyl-phenyl) phosphine oxide, DiIBAN = di-isobutyl ammonium nitrate, OOPA = Octyl phenyl phosphinic acid, DEHPA = di-2-ethylhexyl phosphoric acid.</p>		

The PUREX process was the first to use tributyl phosphate (TBP), a durable semi-volatile compound, to isolate both U and Pu from the fission products. The advantage of using TBP was that nitric acid could be used as the salting agent, and TBP was available in large quantities at a reasonable cost. With the previous bismuth phosphate and redox processes, aluminum or magnesium salts had to be used. Other

advantages were that the solvent and aqueous reagent streams could be recycled in the process, which was more economical for large-scale productions and reduced the volume of the waste streams (Choppin et al. 1999). This process is also well documented in literature. It is used throughout the world, and is the most efficient for spent fuel-processing purposes.

The TRUEX, SREX, TALSPEAK, and TRAMEX processes are being used to treat defense wastes as are the DIAMEX, Dicarbollide (ChCoDiC) processes and some other bidentate extractions. Ion exchange and partitioning and transmutation (P/T) processes are also being used for specific separation processes. However, these processes are not practical for separating the large volumes of Pu or U needed for weapons production purposes.

The TRUEX process is a solvent extraction process that uses octyl(phenyl)-N,N-dibutylcarbamoylmethylphosphine oxide (CMPO) as the extracting agent – that is dissolved in a liquid alkane (dodecane or similar chemical). This process is effective for treating waste streams from the PUREX process and actively reduces the volumes of U and Pu in the wastes by a factor of 10^2 or 10^3 . However, TRUEX does not separate the tri and tetravalent actinides from the lanthanide fission products (Choppin et al. 1999).

The SREX process is used to isolate ^{90}Sr from defense wastes. This process uses crown ethers, which have a strong affinity for extracting strontium. The disadvantages of this process are the cost of the reagents and solubility of crown ethers in the aqueous phase. Crown ethers are also very subject to radiolytic degradation (Choppin et al. 1999).

The TALSPEAK process separates lanthanide fission products from trivalent actinides and uses di (2-ethylhexyl) phosphoric acid (HDEHP) and diethylenetriamine pentaacetate (DTPA). The TRAMEX process used trialkylamines or tetraalkylammonium salts dissolved in organic solvents to separate tri- and tetravalent actinides from lanthanides and other fission products. It can be used to treat wastes from the PUREX process. However, it involves special processing equipment and several additional processing steps to treat the waste before separation (Choppin et al. 1999).

The DIAMEX process is a French solvent extraction process that uses dimethyl dibutyltetradecylmethyl amide (DMDBTDMA) dissolved in alkanes for the extraction of TRU elements from nitric acid solutions. Advantages to this process include low solubility of the extractants in nitric acid solutions and good thermal and radiolytic stability (Choppin et al. 1999).

The dicarbollide processes are very efficient for extracting cesium and strontium from nitric acid solutions using bisdicarbollycobaltate. This process has been used effectively on PUREX wastes. In addition, rather simple anionic exchange-column processes that use dilute nitric acid will also enrich plutonium. However, these will most likely not produce semi-volatile effluent signatures.

2.1 Semi-Volatile Chemicals of Interest

The processes that use complex organic compounds were of primary interest, especially processes that use complex semi-volatile chemicals that have low vapor pressures (typically <0.1 torr) and contain the strong phosphorus – oxygen bonds. To understand the potential fingerprint or combination of signatures that may be present, it was important to understand the key chemicals used for each process. Each of the key chemicals could go through the process unchanged or break down into other chemical compounds.

To catalog these compounds, it is useful to know that in nearly every process a high separation factor means a low yield, a fact that calls for continual compromise. If a certain quantity of raw material is fed into a separation process, some of the material will be enriched, some will be depleted and some will remain unchanged. Parts of these three fractions will be lost and parts will be recovered. Separation processes that strive to extract actinide ions from complex ions can be accomplished with many organic substances. Actinide separations are challenging because the elements and their compounds are chemically very similar. Their extractability by these substances varies from element to element and depends on their oxidation states (Kolarik and Schuler 1994).

The compound categories of interest included:

- Alkylphosphonates
- Alkylphosphine oxides
- Trifunctional carbamoylphosphonates
- Carbamoyl(alkyl)phosphine oxides
- Mixtures of phosphorus-based acids and phosphates.
- In addition to the organophosphorus compounds, other semi-volatile compounds associated with actinide separations were reviewed. These compounds are used in some of the newer separation methods that minimize the use of organic solvents and include crown ethers, beta-diketonates, trialkylamines, and carbollides. However, the focus of this report is to obtain essential physical and chemical properties of the phosphate-oxygen bond-containing complexants and investigate the potential degradation products that could be formed from the separation of actinides.

The alkylphosphinates and alkylphosphine oxides are effective in the recovery of actinides and technetium because of their high solubility in organic solvents (diluent). These compounds are generally used in combination with TBP in separations. For example, in the TRUEX process, phenyloctyl-isobutyl-carbamoylphosphine oxide is diluted in dodecane and TBP is added as a solubilizer for extraction (Ozawa et al. 1998).

The use of bidentate organophosphorus extractants, such as n-octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), dihexylheptyl phosphine oxide (TRPO), tri-n-octylphosphine oxide (TOPO), and dihexyl N, N-diethyl carbamoyl methylene phosphonate (DHDECMP), all have strong extractive properties towards the tri, tetra, and hexavalent actinides from highly acidic waste solutions. These processes were commercialized in the eighties in the United States. The trialkyl phosphine oxide, TRPO, is now produced in China on a large scale. When these bidentates

are mixed with TBP, the transfer kinetics are improved and higher product-yields are achieved (Choppin et al. 1999; Zhu and Jiao 1994; Casarci et al. 1989).

Chemicals used in the older technologies continue to be used in the newer processes. Older technologies (1950s through 1980s) relied on organic solvents, such as kerosene, and produced large amounts of waste, causing expensive disposal issues. Newer methods, at least for those countries striving for environmental responsibility, are investigating the use of aqueous-based separations that will avoid the current waste-disposal problems found at the Hanford Site^(a) and elsewhere.

2.2 Semi-Volatile Chemicals Used in Nuclear Separations

Table 2.2 provides a list of semi-volatile organophosphorus compounds and their chemical and physical properties, used in various nuclear separations processes. As most of the vapor pressures and boiling points are not experimentally available, estimation methods that rely on structural-functional group analyses were applied.

2.3 Volatile Chemicals Used in Nuclear Separations

As volatile chemicals are also used in nuclear separations and will, in many cases, be mixed or combined with the semi-volatile chemicals, a list of the major volatile chemicals is provided in Table 2.3

(a) The 586-square-mile Hanford Site, located in eastern Washington State, is one of the largest nuclear waste sites in the United States.

Table 2.2. Chemical and Physical Properties of Chemicals Related to Actinide Separations

Compound Class	Chemical Name	Chemical Formula	Cas No.	F.W. (g/mol)	m.p. (°C)	VP @ 25°C (torr)	b.p. (°C)
phosphine oxides				*Values estimated using EPA's EPISuite program.			
D [∞] P	diphenyl phosphinic acid	(C ₆ H ₅) ₂ PO(OH)	1707-03-5	218.19	194	*3e-7	*373
O [∞] P	n-octyl(phenyl) phosphinic acid	(C ₆ H ₅)(C ₈ H ₁₇)PO(OH)	31066-81-6	254.31	43	*4e-7	*382
DOP	di-n-octyl phosphinic acid	(C ₈ H ₁₇) ₂ PO(OH)	683-19-2	290.43	83	*2e-7	*390
D [∞] PO	diphenyl phosphine oxide	(C ₆ H ₅) ₂ PO(H)	4559-70-0	202.19	57	*5e-4	*320
DOPO	di-n-octyl phosphine oxide	(C ₈ H ₁₇) ₂ PO(H)	3011-82-3	274.43	86	*2e-4	*339
TRPO	dihexyl heptyl phosphine oxide	(C ₆ H ₁₃) ₂ (C ₇ H ₁₅)PO		316.51	*74	*3e-5	*373
TRPO	hexyl diheptyl phosphine oxide	(C ₆ H ₁₃)(C ₇ H ₁₅) ₂ PO		330.53	*84	*1e-5	*385
TRPO	dihexyl octyl phosphine oxide	(C ₆ H ₁₃) ₂ (C ₈ H ₁₇)PO		330.53	*84	*1e-5	*385
TRPO	triheptyl phosphine oxide	(C ₇ H ₁₅) ₃ PO	17262-51-0	344.56	38 (*84)	*7e-6	200/2 mm Hg (*396)
TRPO	diheptyl octyl phosphine oxide	(C ₇ H ₁₅) ₂ (C ₈ H ₁₇)PO		358.59	*87	*4e-6	*408
TRPO	heptyl dioctyl phosphine oxide	(C ₇ H ₁₅)(C ₈ H ₁₇) ₂ PO		372.61	*84	*2e-6	*420
TOPO	tri-n-octyl phosphine oxide	(C ₈ H ₁₇) ₃ PO	78-50-0	386.64	52 (*85)	*1e-6	202/2 mm Hg (*431)
[O [∞] PO]	n-octyl(phenyl) phosphine oxide	(C ₈ H ₁₇)(C ₆ H ₅)PO(H)	107694-27-9	238.31	*65	*3e-4	*330
[M(O)([∞] PO)]	methyl-n-octyl phenyl phosphine oxide	(CH ₃)(C ₈ H ₁₇)(C ₆ H ₅)PO	107694-26-8	252.34	*56	*1e-4	*341
TEHPO	tris-2-ethyl hexyl phosphine oxide	((C ₄ H ₉)CH(C ₂ H ₅)CH ₂) ₃ PO	2785-32-2	386.64	*83	*3e-6	210/2 mm Hg (*410)
[D [∞] D(iB)CMPO]	diphenyl-N,N-diisobutyl carbamoyl methylene phosphine oxide	(C ₆ H ₅) ₂ P(O)CH ₂ C(O)N(CH ₂ CH(CH ₃)) ₂		371.46	*90	*6e-8	*479

Table 2.2. (contd)

Compound Class	Chemical Name	Chemical Formula	Cas No.	F.W. (g/mol)	m.p. (°C)	VP @ 25°C (torr)	b.p. (°C)
[OΦD(iB)CMPO]	n-octyl(phenyl)-N,N-disobutyl carbamoyl methylene phosphine oxide	$(C_8H_{17})(C_6H_5)P(O)CH_2C(O)N(CH_2CH(CH_3)_2)_2$		407.57	*90	*6e-8	*480
[DOD(iB)CMPO]	di-n-octyl-N,N-disobutyl carbamoyl methylene phosphine oxide	$(C_8H_{17})_2P(O)CH_2C(O)N(CH_2CH(CH_3)_2)_2$		443.69	*90	*6e-8	*480
phosphates/ phosphonates				*Values estimated using EPA's EPISuite program.			
DHDECMP	dihexyl N,N-diethyl carbamoyl methylene phosphonate	$(C_6H_{13}O)_2P(O)CH_2C(O)N(C_2H_5)_2$	7369-66-6	363.48	*87	*6e-7	*441
TBP	tri-n-butyl phosphate	$(C_4H_9O)_3PO$	126-73-8	266.32	-79	7e-3	182/22 mm Hg (*329)
DBP (HDDBP)	di-n-butyl phosphate	$(C_4H_9O)_2PO(OH)$	107-66-4	210.21	-13	*2e-5	125/0.01 mm Hg
MBP (H ₂ MBP)	mono-n-butyl phosphate	$(C_4H_9O)PO(OH)_2$	1623-15-0	154.10	150	*2e-5	*312
TEP	triethylphosphate	$(C_2H_5O)_3PO$	78-40-0	182.16	-52	0.39 mm Hg	215
DIDPA	disodecylphosphoric acid	$(C_{11}H_{23}O)_2P(O)CH_2C(O)N(CH_3)_2$		378.53		*8e-10	*458
DABP	di-n-amyyl-t-butyl phosphonate	$(C_8H_{17}O)_2((CH_3)_3C)PO$		278.37		*2e-4	*326
DAAP	di-n-amyyl-n-amyyl phosphonate	$(C_8H_{17}O)_2(C_8H_{17})PO$	6418-56-0	292.40		*4e-5	150/2 mm Hg (*351)
DNBNDP	di-n-butyl-n-butyl phosphonate	$(C_4H_9O)_2(C_4H_9)PO$	78-46-6	250.32		*7e-4	100/0.1 mm Hg (*313)
DNBPP	di-n-butyl phenylphosphonate	$(C_4H_9O)_2(C_6H_5)PO$	1024-34-6	270.31		*3e-5	96/0.01 mm Hg (*354)
DTBPP	di-t-butyl phenylphosphonate	$((CH_3)_3CO)_2(C_6H_5)PO$	143490-04-4	270.31		*1e-4	180/0.01 mm Hg (*330)
DNHPP	di-n-hexyl phenylphosphonate	$(C_6H_{13}O)_2(C_6H_5)PO$	6924-93-2	326.41		*2e-6	180/0.01 mm Hg (*400)

Table 2.2. (contd)

Compound Class	Chemical Name	Chemical Formula	Cas No.	F.W. (g/mol)	m.p. (°C)	VP @ 25 C (torr)	b.p. (°C)
D2EHPA	bis(2-ethylhexyl) hydrogen phosphate	$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}]_2\text{P}(\text{O})\text{OH}$	298-07-7	322.42	-60	*2e-7	*400
Trialkylamines				*Values estimated using EPA's EPISuite program.			
	2-dimethylamino ethanol	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$	108-01-0	89.14	-70		133
TOA	trioctyl amine	$(\text{C}_8\text{H}_{17})_3\text{N}$	1116-76-3	353.68		*7e-6	366
TLA	trilaurylamine	$(\text{C}_{12}\text{H}_{25})_3\text{N}$	102-87-4	522.00	16	*5e-11	200/0.1 - 0.01 mm Hg
TLMA	trilaurylmethylamine						
	dilaurylamine	$(\text{C}_{12}\text{H}_{25})_2\text{NH}$	3007-31-6	353.67	41	*6e-7	249/10 mm Hg
	di-n-decylamine	$(\text{C}_{10}\text{H}_{21})_2\text{NH}$	1120-49-6	297.57	39	*2e-5	180/2 mm Hg
crown ethers		Crown ether structures: double dash (--) on each end of the structure indicates a cyclic structure.					
18C6	18-crown-6 ether	$(-\text{CH}_2\text{CH}_2\text{O}-)_6$	17455-13-9	264.32	40	*7e-5	116/0.2 mm Hg
B15C5	benzo-15-crown-5 ether	$(-\text{OC}_6\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_3(\text{CH}_2\text{CH}_2-))$	14098-44-3	268.31	79		
DCH18C6	dicyclohexyl-18-crown-6 ether	$(-\text{OC}_6\text{H}_{10}\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_{10}\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)$	16069-36-6	372.50	55	*8e-8	342
DB18C6	dibenzo-18-crown-6 ether	$(-\text{OC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)$	14187-32-7	360.41	165	*7e-9	380
DB21C7	dibenzo-21-crown-7 ether	$(-\text{OC}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_{10}\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)$	14098-41-0	404.46	107		
DB24C8	dibenzo-24-crown-8 ether	$(-\text{OC}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{C}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_3-)$	14174-09-5	448.52	104		
DB27C9	dibenzo-27-crown-9 ether	$(-\text{OC}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{C}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_3-)$	61260-08-0	492.56	70		
DB30C10	dibenzo-30-crown-10 ether	$(-\text{OC}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{C}_6\text{H}_{10}\text{O}(\text{CH}_2\text{CH}_2\text{O})_4-)$	17455-25-3	536.63	107		

Chemical Name	Chemical Formula	Cas No.	F.W. (g/mol)	m.p. (°C)	VP @ 25°C (torr)	b.p. (°C)	density (g/cm ³)	Fp (°C)
dodecane	C ₁₂ H ₂₆	112-40-3	170.34	-12	1 mm Hg @ 70°C	216	0.75	71
undecane	C ₁₁ H ₂₂	1120-21-4	156.31	-26	0.9 mm Hg @ 35°C	196	0.74	60
cyclohexane	C ₆ H ₁₂	110-82-7	84.18	6.5	96.9 mm Hg	81	0.779	-18
n-hexane	C ₆ H ₁₄	110-54-3	86.18	-95	150 mm Hg	69	0.659	-23
kerosene	C ₁₀ H ₂₂ through C ₁₆ H ₃₄	8008-20-6	142 - 226		0.480 mm Hg	175-325	0.8	81
trichloroethylene	C ₂ HCl ₃	79-01-6	131.39	-85	69 mm Hg	87	1.46	none
chloroethane	CH ₃ Cl	74-87-3	50.49	-97	4300 mm Hg	-24	0.915(lig)	
iodomethane	CH ₃ I	74-88-4	141.94	-64	405 mm Hg	42	2.28	none
n-butyl alcohol	CH ₃ CH ₂ CH ₂ CH ₂ OH	71-36-3	74.12	-90	5.5 mm Hg	118	0.81	35
n-butyl nitrate	CH ₃ CH ₂ CH ₂ CH ₂ ONO ₂	*	119.12	*	*	*	*	*
n-butyl nitrite	C ₄ H ₉ NO ₂	544-16-1	103.12	*	*	78	0.882	-18
dibutyl carbitol	C ₈ H ₁₇ OC ₂ H ₄ OC ₂ H ₄ OC ₄ H ₉	112-72-3	218.38	*	*	256/760	*	*
dibutyl ether	C ₈ H ₁₇ OC ₂ H ₅	142-96-1	130.23	-98	6.01 mm Hg	142	0.764	25
phenyl hydrazine	C ₆ H ₅ NHNH ₂	100-63-0	108.14	19	0.026 mm Hg	240	1.1	88
nitric acid	HNO ₃	7697-37-2	63.01	-41.6	63.1 mm Hg	83/760	1.503	none
hydroxylamine nitrate	HONH ₂ ·HNO ₃	13465-08-2	96.04	*	*	*	*	*
carbon tetrachloride	CCl ₄	56-23-5	153.82	-23	115 mm Hg	77	1.594	none
t-butyl benzene	C ₆ H ₅ C(CH ₃) ₂	98-06-6	134.22	-58	2.20 mm Hg	169	0.867	34
oxalic acid	HOOC ₂ COOH	144-62-7	90.40	190 decompose	0.54 mm Hg @ 105 C	sublimes at 157	1.9	none
formic acid	HCOOH	64-18-6	46.03	8.3	42.59 mm Hg	100.5	1.22	68
acetylhydroxamic acid	CH ₃ CONHOH	546-88-3	75.07	90	*	*	*	*

Table 2.3. Volatile Chemicals Associated with Separation Processes

3.0 Nuclear Separation Chemistry

Typically, separation processes are carried out under harsh conditions (i.e., low aqueous phase pH, greater than ambient temperatures, oxygen atmosphere, and in the presence of highly ionizing radiation). Under such conditions, high or moderate rates of chemical degradation via acid catalyzed hydrolysis, radiolysis (radiation induced decomposition via radical mechanisms), thermolysis, and chemical oxidation is expected. Thermolysis reactivity in this scenario refers to the increase in reaction rates of hydrolysis, radiolysis, and oxidation at elevated temperatures. Oxidation is one of the several reaction pathways that species will follow after initial bond cleavage due to radiation (radiolysis). However, the chelating reagents (organophosphates) used in these separation processes are quite robust and fairly resistant to these degradation reactions, which is one of the main reasons for using these reagents. Measurable degradation does occur during the separations, however. In addition to pH and temperature, contact time greatly affects the amount of degradation. If mixing or contact time is minimal in a particular procedure, perhaps less than 10 percent degradation may occur. This infers that the solvent system could be reused multiple times, and quite often this is the case. Each time the solvent system is recycled it degrades further, and eventually the performance does not meet specifications. At this point, degradation products may still be the minority species present (<50 percent) but they are present in high enough concentrations to reduce the efficiency of the solvent system to below specifications. The solvent is now either discarded or put through a rigorous purification procedure. Limited kinetic data on the degradation rates of some of the reagents listed in Table 3.1 are available. The degradation rates are highly dependent on experimental conditions; for example, relatively small changes in pH and/or temperature can change hydrolysis or radiolysis degradation rates by several orders of magnitude.

Separations procedures that involve high temperatures in conjunction with high acidity result in relatively high rates of degradation via hydrolysis. Table 3.1 identifies which species are susceptible to hydrolysis and lists the products formed if they undergo hydrolysis. For most of the reagents that will undergo hydrolysis multiple mechanisms are proposed or suggested, but in general, the hydrolysis reactions are acid catalyzed or enhanced by high protic concentrations, and the kinetics increase with temperature. Acid concentrations of the actinide solutions being extracted by the organic-phase complexing reagents can range from 0.5 to 6 M or higher, depending on what separations process is being employed and what stage the process is in. At ambient temperatures, hydrolysis of alkyl phosphates and phosphonates is slow even in 1 M acid. However, significant increases in hydrolysis rates are observed with acid concentrations of 3 to 6 M at high temperatures (from 50°C to 100°C). At 100°C, rates are dramatically increased. For example, the half-life of tri-n-butyl phosphate (TBP) is decreased to less than ten hours if heated to 100°C in 5 M perchloric acid (HClO₄). Under such harsh conditions, contact times between the extractant solution and the acid phase will be minimized to reduce total hydrolysis. However, complete extraction is also required. During these stages of the process the greatest amount of degradation occurs.

Radiolysis rates tend to be slower than hydrolysis rates, although high temperatures will have dramatic effects on the kinetics, increasing rates substantially. Since more than half of the reagents listed in Table 2.2 are inert to hydrolysis, radiolysis is the primary degradation pathway. Some of the most prominent radiolysis degradation products are listed in Table 3.1. Many more possible products are not listed. The ionizing radiation promotes the formation of radicals; however, radical chain mechanisms do

Table 3.1. Degradation Process and Key Byproducts of Chemicals Related to Actinide Separations

Chemical Name ¹	Separations process	Breakdown Process	Key Byproducts ²	Stability (time)
diphenyl phosphinic acid	PUREX TRUEX	radiolysis oxidation	Phenyl phosphonic acid, biphenyl, phenol, other.	2,3,8
n-octyl(phenyl) phosphinic acid	PUREX TRUEX	radiolysis oxidation	Phenyl phosphonic acid, n-octyl phosphonic acid, n-octylbenzene, biphenyl, hexadecane, phenol, 1-octanol, octanal, octanoic acid, other.	2,3,8
di-n-octyl phosphinic acid	PUREX TRUEX	radiolysis oxidation	N-octyl phosphonic acid, hexadecane, 1-octanol, octanal, octanoic acid, other.	2,3,8
diphenyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Diphenyl phosphinic acid, phenyl phosphonic acid, phenyl phosphonic acid, biphenyl, phenol, other.	2,3,8
di-n-octyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Di-n-octyl phosphinic acid, n-octyl phosphonic acid, n-octyl phosphonic acid, hexadecane, 1-octanol, octanal, octanoic acid, other.	2,3,8
dihexyl heptyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Dihexyl phosphinic acid, hexyl heptyl phosphinic acid, 1-hexanol, hexanal, hexanoic acid, 1-heptanol, heptanal, heptanoic acid, dodecane, tridecane, tetradecane, other.	2,3,8
hexyl diheptyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Diheptyl phosphinic acid, hexyl heptyl phosphinic acid, 1-hexanol, hexanal, hexanoic acid, 1-heptanol, heptanal, heptanoic acid, dodecane, tridecane, tetradecane, other.	2,3,8
dihexyl octyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Dihexyl phosphinic acid, hexyl octyl phosphinic acid, 1-hexanol, hexanal, hexanoic acid, 1-octanol, octanal, octanoic acid, dodecane, tetradecane, hexadecane, other.	2,3,8
triheptyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Diheptyl phosphinic acid, heptyl phosphonic acid, 1-heptanol, heptanal, heptanoic acid, tetradecane, other.	2,3,8
diheptyl octyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Diheptyl phosphinic acid, heptyl octyl phosphinic acid, 1-heptanol, heptanal, heptanoic acid, 1-octanol, octanal, octanoic acid, tetradecane, pentadecane, hexadecane, other.	2,3,8
heptyl dioctyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Dioctyl phosphinic acid, heptyl octyl phosphinic acid, 1-heptanol, heptanal, heptanoic acid, 1-octanol, octanal, octanoic acid, tetradecane, pentadecane, hexadecane, other.	2,3,8
tri-n-octyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Dioctyl phosphinic acid, octyl phosphonic acid, 1-octanol, octanal, octanoic acid, hexadecane, other.	2,3,8
n-octyl(phenyl) phosphine oxide	PUREX TRUEX	radiolysis oxidation	Phenyl-n-octyl phosphinic acid, phenyl phosphonic acid, n-octyl phosphonic acid, phenyl phosphonic acid, n-octyl phosphonic acid, n-octylbenzene, phenol, 1-octanol, octanal, octanoic acid, other.	2,3,8
methyl-n-octyl phenyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Phenyl-n-octyl phosphinic acid, methyl phenyl phosphinic acid, methyl n-octyl phosphinic acid, phenyl phosphonic acid, n-octyl phosphonic acid, methyl phosphonic acid, methanol, formaldehyde, formic acid, 1-octanol, octanal, octanoic acid, phenol, n-octylbenzene, toluene, nonane, other.	2,3,8
tris-2-ethylhexyl phosphine oxide	PUREX TRUEX	radiolysis oxidation	Bis-2-ethylhexyl phosphinic acid, 2-ethylhexylphosphonic acid, 2-ethyl-1-hexanol, 2-ethylhexanal, 2-ethylhexanoic acid, hexadecanes, other.	2,3,8

Table 3.1. contd

Chemical Name	Separations process	Breakdown Process	Key Byproducts ²	Stability (time)
di-phenyl-N,N-diisobutyl carbamoyl methylene phosphine oxide	TRUEX	radiolysis oxidation hydrolysis	(Diphenyl phosphine oxide) acetic acid, diisobutyl ammonium nitrate, phenyl-N,N-diisobutyl carbamoyl methylene phosphinic acid, biphenyl, phenol, other.	2,3,4,8
n-octyl(phenyl)-N,N-diisobutyl carbamoyl methylene phosphine oxide	TRUEX	radiolysis oxidation hydrolysis	(n-octyl phenyl phosphine oxide) acetic acid, diisobutyl ammonium nitrate, n-octyl-N,N-diisobutyl carbamoyl methylene phosphinic acid, phenyl-N,N-diisobutyl carbamoyl methylene phosphinic acid, n-octylbenzene, phenol, 1-octanol, octanal, octanoic acid, other.	2,3,4,8
di-n-octyl-N,N-diisobutyl carbamoyl methylene phosphine oxide	TRUEX	radiolysis oxidation hydrolysis	(Di-n-octyl phosphine oxide) acetic acid, diisobutyl ammonium nitrate, n-octyl-N,N-diisobutyl carbamoyl methylene phosphinic acid, hexadecane, 1-octanol, octanal, octanoic acid, other.	2,3,4,8
dihexyl N,N-diethyl carbamoyl methylene phosphonate	TRUEX	radiolysis oxidation hydrolysis	(Dihexyl phosphine oxide) acetic acid, diethyl ammonium nitrate, hexyl-N,N-diisobutyl carbamoyl methylene phosphinic acid, dodecane, 1-hexanol, hexanal, hexanoic acid, other.	2,3,4,8
tri-n-butyl phosphate	PUREX TRUEX SREX TRAMEX	radiolysis oxidation hydrolysis	Di-n-butyl phosphate, n-butyl phosphate, phosphoric acid, 1-butanol, butanal, butanoic acid, octane, other.	2,5,8
triethylphosphate	PUREX TRUEX	radiolysis oxidation hydrolysis	Diethyl phosphate, ethyl phosphate, phosphoric acid, ethanol, acetaldehyde, acetic acid, butane, other.	2,5,8
bis(2-ethylhexyl) phosphoric acid	TRUEX TALSPEAK	radiolysis oxidation hydrolysis	2-ethylhexyldihydrogen phosphate, phosphoric acid, 2-ethylhexanol, 2-ethylhexanal, 2-ethylhexanoic acid, other.	2,5,8
diisodecylphosphoric acid	TRUEX TALSPEAK	radiolysis oxidation hydrolysis	isodecyl phosphoric acid, phosphoric acid, isodecanol, isodecanal, isodecanoic acid, other.	2,5,8
di-n-amyl-t-butyl phosphonate	PUREX TRUEX	radiolysis oxidation hydrolysis	N-amyl-t-butyl phosphonic acid, t-butylphosphonic acid, phosphoric acid, 1-pentanol, pentanal, pentanoic acid, t-butanol, other.	2,5,8
di-n-amyl-n-amyl phosphonate	PUREX TRUEX	radiolysis oxidation hydrolysis	N-amyl-n-amyl phosphonic acid, n-amylphosphonic acid, phosphoric acid, 1-pentanol, pentanal, pentanoic acid, other.	2,5,8
di-n-butyl-n-butyl phosphonate	PUREX TRUEX	radiolysis oxidation hydrolysis	N-butyl-n-butyl phosphonic acid, n-butylphosphonic acid, phosphoric acid, 1-butanol, butanal, butanoic acid, other.	2,5,8
di-n-butyl phenylphosphonate	PUREX TRUEX	radiolysis oxidation hydrolysis	N-butyl-phenyl phosphonic acid, phenyl phosphonic acid, phosphoric acid, 1-butanol, butanal, butanoic acid, phenol, other.	2,5,8
di-t-butyl phenylphosphonate	PUREX TRUEX	radiolysis oxidation hydrolysis	T-butyl-phenyl phosphonic acid, phenyl phosphonic acid, phosphoric acid, t-butanol, 2,2,3,3-tetramethylbutane, phenol, other.	2,5,8
di-n-hexyl phenylphosphonate	PUREX TRUEX	radiolysis oxidation hydrolysis	N-hexyl-phenyl phosphonic acid, phenyl phosphonic acid, phosphoric acid, 1-hexanol, hexanal, hexanoic acid, phenol, other.	2,5,8

Table 3.1. contd

Chemical Name	Separations process	Breakdown Process	Key Byproducts ⁹	Stability (time)
2-dimethylamino ethanol	TRAMEX	radiolysis/oxidation	Dimethyl amine, methyl amine, ethanol, methanol, formaldehyde, acetaldehyde, formic acid, acetic acid, other.	6,8
trioctyl amine	TRAMEX	radiolysis/oxidation	Diocetyl amine, octyl amine, hydroxyl amines, octanol, octanal, octanoic acid, other.	6,8
trilaurylamine	TRAMEX	radiolysis/oxidation	Dilauryl amine, lauryl amine, hydroxyl amines, dodecanol, dodecanal, dodecanoic acid, other.	6,8
di-n-decylamine	TRAMEX	radiolysis/oxidation	Decyl amine, hydroxyl amines, decanol, decanal, decanoic acid, other.	6,8
18-crown-6 ether	SREX	radiolysis/oxidation	7	7,8
benzo-15-crown-5 ether	SREX	radiolysis/oxidation	7	7,8
dicyclohexyl-18-crown-6 ether	SREX	radiolysis/oxidation	7	7,8
dibenzo-18-crown-6 ether	SREX	radiolysis/oxidation	7	7,8
dibenzo-21-crown-7 ether	SREX	radiolysis/oxidation	7	7,8
dibenzo-24-crown-8 ether	SREX	radiolysis/oxidation	7	7,8
dibenzo-27-crown-9 ether	SREX	radiolysis/oxidation	7	7,8
dibenzo-30-crown-10 ether	SREX	radiolysis/oxidation	7	7,8
¹ Chemicals in bold print are primary precursors and are key signature chemicals.				
² All phosphorous based compounds are good sources of phosphorous for many biological organisms. Therefore their biodegradable half-lives may be less than chemical degradation half-lives if conditions exist which would promote biological growth. The EPA based EPISuite program estimates many phosphorous based compounds to have half-lives on the order of weeks or months via a biodegradation pathway.				
³ Phosphine oxides are inert to hydrolysis and relatively robust toward radiolysis under separation/extraction conditions. Reaction pathways via radiolysis (radical mechanisms) would form dimerization or oligomerization products, and oxidized products such as alcohols, aldehydes, and acids.				
⁴ Alkyl substituted carbamoyl phosphine oxides are relatively robust to radiolysis. As with phosphine oxides, radiolysis will produce dimerization products, alcohols, aldehydes, ketones, and acids. They are susceptible to hydrolysis in acidic media producing the carboxylic acid phosphine oxide derivative and the dialkylammonium salt (i.e., $R_2P(O)CH_2COOH + R'_2NH_2^+$).				
⁵ Phosphates and phosphonates will undergo hydrolysis slowly in acidic media, as acidity and temperature increase, rates of hydrolysis increase. They are relatively robust toward radiolysis but will undergo radiolysis degradation under separations conditions.				
⁶ Trialkylamines are inert to hydrolysis. In strong acidic media all amines will be cationic (protonated). At low reaction rates radiolysis will break down the amines via radical pathways forming the corresponding amines and oxidation products.				
⁷ Crown ethers are inert to hydrolysis. At slow rates radiolysis will break the cyclic structure, via a radical mechanism, forming open oxyethylene chains which can react with a second crown ether and dimerize. Over long periods of time, poly oxyethylene chains will form (i.e., $-O-CH_2-CH_2-O-CH_2-CH_2-O-\dots$). During these radical processes the open chains are subject to further oxidation.				
⁸ Stability times are greatly dependent on laboratory and environmental conditions. For separation/extraction procedures, the organic phases are exposed to highly acidic solutions at varying temperatures and varying times. Rates of hydrolysis are highest during these periods. If exposed to strong acid (5 M) and high temperatures (> 50°C), half-lives can be reduced to days. At moderate acidities and temperatures, rates of hydrolysis and radiolysis are much slower. Depending on acidity levels, temperature, and surrounding media, half-lives can vary from weeks to years.				
⁹ The number of possible byproducts is extremely large. For example, the table does not list any nitrification byproducts, yet many would be produced in varying amounts.				

not occur. Radical formation can result in P-O, P-C, and C-C bond cleavage followed by termination reactions producing dimers or oligomers, or by oxidation reactions that produce alcohols, aldehydes, or acids.

3.1 Degradation Products

As stated above, the vast majority of degradation products formed during the separations processes are from hydrolysis and radiolysis reactions. Radiolysis and photo-oxidation will form virtually the same products via virtually the same mechanisms although photo-oxidation will proceed much more slowly. Photo-oxidation products will be formed only after the reagents are exposed to sunlight. With photo-oxidation the radiation source is the sun (typically ultraviolet radiation), and with radiolysis the radiation source is radionuclides (typically gamma and beta radiation).

A fingerprint (a unique combination of reagent and degradation chemicals) would be formed from all of the actinide separation/extraction procedures, and virtually all the fingerprints formed would likely contain many of the same components (i.e., tributyl, dibutyl, and monobutyl phosphates; butanol, phosphoric acids, and hydrocarbon (C₁₀-C₁₆) chains). If secondary or tertiary separations that utilize crown ethers and/or alkyl amines are also performed, these added components will be found in the fingerprint (i.e., one or more crown ethers and trialkyl amines). The fingerprint would also contain the degradation products of these compounds (oligomeric oxyethylene chains, alkyl ammonium salts). These compounds are all robust, only slightly volatile, and could remain on surfaces or in soils for extended periods of time.

It is reasonable to estimate that the majority of chelating reagents listed in Table 2.2 and the majority of the degradation products listed in Table 3.1, have half-lives of months or years. It is important to note, however, that the phosphorous-based reagents are also an excellent source of phosphorous for many biological organisms and are therefore susceptible to biochemical degradation. Biochemical degradation is of concern only after disposal of separations solutions as laboratory conditions are much too harsh for the existence of any biological organisms. Following the separation processes and after disposal of separation solutions, under ideal conditions (i.e., aqueous media, moderate temperatures, abundant algae life or other biological organisms) half-lives for these compounds could possibly be reduced to weeks or even days via a biochemical degradation pathway.

Below are listed possible reaction pathways for selected chemical degradation reactions.

3.2 Acid Catalyzed Hydrolysis Products

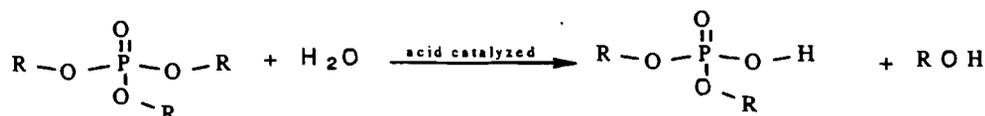
Hydrolysis of phosphoric acid alkyl ethers (and phosphonates), alkyl carbamoyl phosphine oxides, and alkyl carbamoyl phosphonates:

In weak to moderately strong acid solutions (low pHs) at ambient conditions, the hydrolysis of trialkyl esters of phosphoric acid is very slow. The reactions most likely proceed via nucleophilic substitution (although other mechanisms are possible) producing the dialkyl ester and alcohol. Further hydrolysis of the dialkyl ester can occur producing the monoalkyl ester and another equivalent of alcohol.

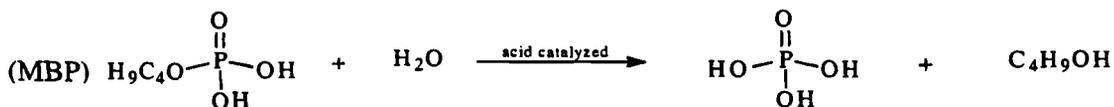
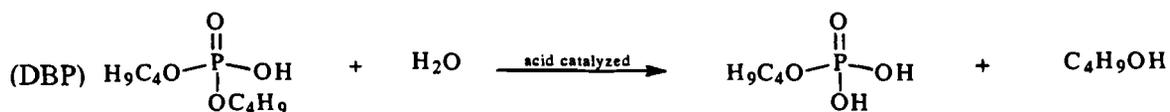
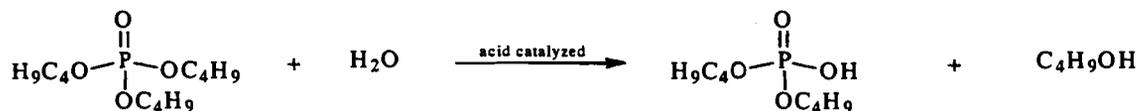
The monoalkyl ester can undergo a third hydrolysis reaction producing phosphoric acid and a third equivalent of alcohol. The second and third hydrolysis steps occur at much slower rates than the first step. The rate of hydrolysis of phosphoric acid alkyl esters can be enhanced if extremely high concentrations (5 M or greater) of strongly protic acids (HClO₄) are used in conjunction with high temperatures (100°C or greater). Under such extreme reaction conditions, half-lives of phosphoric acid alkyl esters can be reduced to 5 to 10 hours (Katz and Bond 1979).

- a. Hydrolysis of phosphoric acid alkyl ethers. (The general reaction given below demonstrates phosphonate hydrolysis as well. The P-C bond in phosphonates is not susceptible to hydrolysis.)

General reaction.

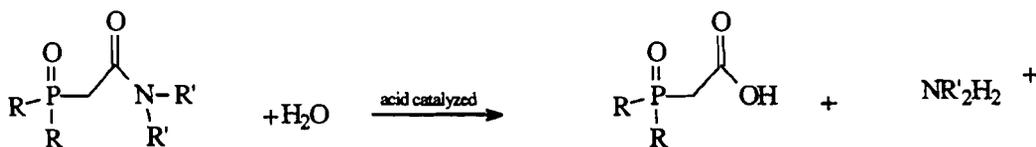


Example, phosphoric acid tributyl ester (TBP).

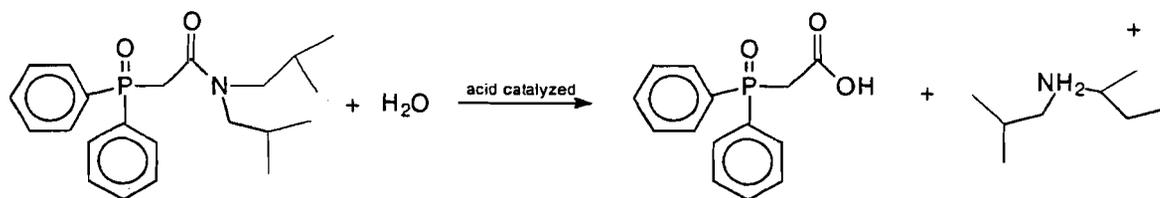


- b. Carbamoyl phosphine oxides.

General reaction. The alkyl phosphine groups (P-R) are not susceptible to hydrolysis.



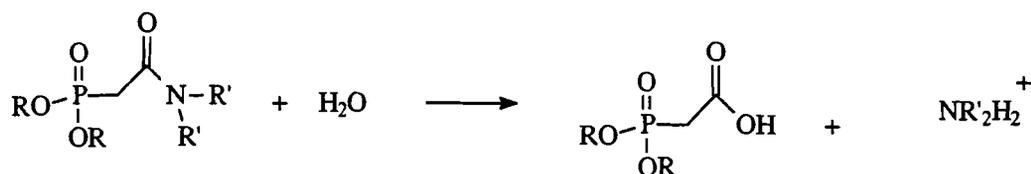
Diphenyl-N,N-diisobutyl carbamoyl methylene phosphine oxide.



c. Carbamoyl phosphonates.

General reaction.

Carbamate hydrolysis.

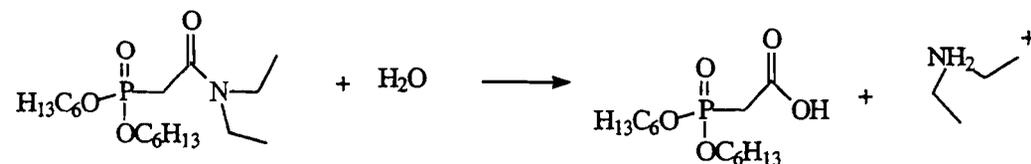


Phosponate hydrolysis.

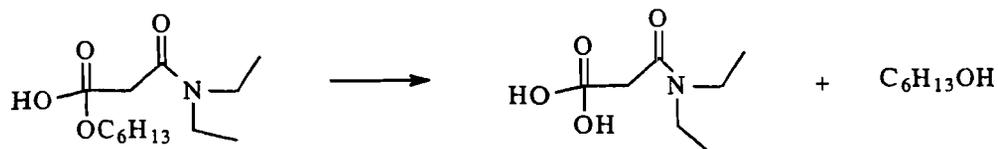
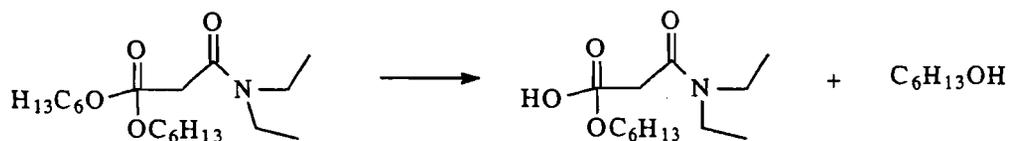


Dihexyl-N,N-diethyl carbamoyl methylene phosphonate.

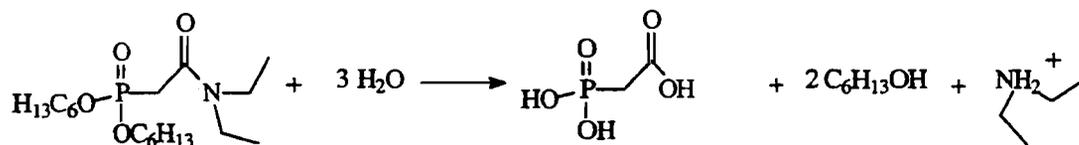
Carbamate hydrolysis prior to phosphonate hydrolysis.



Phosphonate hydrolysis prior to carbamate hydrolysis. (note: phosphonate hydrolysis can occur following carbamate hydrolysis.)



Complete hydrolysis of the carbamoyl phosphonate produces the acetic acid derivative of phosphoric acid:

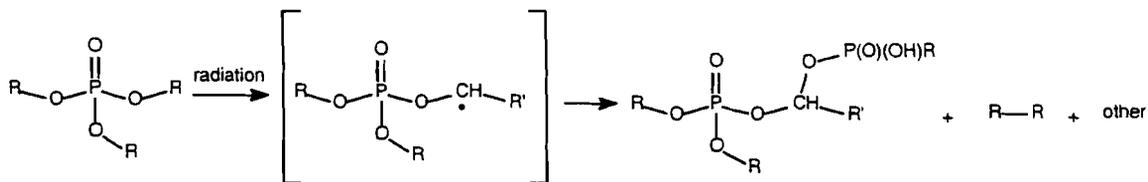


3.3 Radiolysis Reactions and Oxidation

Reaction mechanisms involved in radiolysis reactions are radical-based. The number of possible reaction pathways and resulting products is quite large. Therefore, only a limited number of the more prominent radiolysis reactions are given below as examples. Table 3.1 contains a much more extensive list of possible products generated when the complexing reagents listed undergo radiolysis reactions.

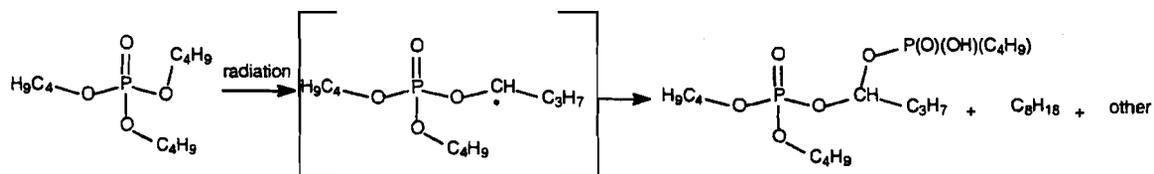
a. Radiolysis of phosphoric acid alkyl esters.

General reaction



other = oxidized alkyl products and other phosphoryl based dimers

b. Radiolysis of TBP.



other = CH₃CH₂CH₂CH₂OH, CH₃CH₂CH₂CHO, CH₃CH₂CH₂COOH, [(H₉C₄O)₂P(O)]₂, many other possible products.

4.0 Precursor Chemicals Used and Potential Release Amounts

Semi-volatile chemicals associated with nuclear processes can be released during normal production as emissions and from evaporation from spills or leaks from valves, transfer lines, and pumps. It was useful to investigate these potential emissions via a hypothetical scenario. While this report does not go into quantitative detail, an attempt was made to devise a batch process and estimate some of the potential emissions that could be released. For the scenario, the PUREX process was used as it is the basis for most worldwide enrichment facilities and the details of the process are well known. For the hypothetical scenario, it is assumed that a batch process, lacking many refinements and solvent recovery, is used to produce ~10 kg of Pu. Disassembly of fuel rods, via caustic, acid, or mechanical treatments, would be an essential preliminary treatment and a commercial junkyard shredder would be used to cut hulls into small pieces. After the pieces are cut, they are transferred to a dissolver where they are boiled in ammonium fluoride, ammonium nitrate, and nitric acid. Gaseous emissions (hydrogen, ammonia, iodine, and oxides of nitrogen) are produced. However, these gases are not semi-volatile.

Semi-volatile chemicals are emitted during the partitioning-extraction cycles. The organic solvents (30 percent of tributylphosphate in kerosene solution) and nitric acid and hydroxylamine nitrate or ferrous sulfamate are used to separate the fission products from U and Pu under counter-current flow, high-mixing conditions to enhance product recoveries. Unless correct adjustments of temperature, phase dispersion, and solvent saturation are made during the startup of separations, process upsets would likely occur. Solvent and product losses occur during these upset conditions.

In this scenario, some separations are carried out at temperatures up to 60°C. The hydrolysis of TBP is normally minimized at established production facilities by steam-stripping to heat-eliminate organics from the aqueous phase. However, this batch operation scenario eliminates these steam-stripping steps so dibutylphosphate (DBP) and monobutyl phosphate (MBP) species will be found at higher concentrations. Reactions to concentrate and enrich plutonium in the aqueous phase are applied in batch steps to concentrate the Pu product; evaporation steps are applied to drive off extraneous organics that promote the additional loss of key semi-volatile chemicals.

The amounts of semi-volatile organic chemical effluents released from this hypothetical scenario batch process are estimated for TBP, DBP, and kerosene. The initial amount of kerosene used is 12,000 gallons (~200, 55-gal drums), and the initial amount of TBP is 4,800 gallons (~88, 55-gal drums). To calculate emission concentrations, the losses are estimated using appropriate vapor pressures, feed volumes, solution temperatures, and molecular weights. Evaporative losses from tanks are estimated using the U.S. Environmental Protection Agency Version 4.09b Tanks Code. In addition to these normal process losses, there are typically leaks in valves, transfer lines, and pumps. The amounts of chemicals used for the scenario and the estimated emissions from production losses are listed in Table 4.1. Normal production emissions are estimated to be ~ 20 percent of the total emissions that could be released. As upsets occur during startup and unscheduled break-downs, the emissions typically triple, bringing the total estimated emissions to 27 kg of kerosene and 9 kg of TBP (PUREX Process Control Manual 1983; Choppin and Rydberg 1980).

Table 4.1. Hypothetical Batch Process Scenario Releases (PUREX Process Control Manual 1983)

Chemicals Used	Amount Used	Normal Production Emissions	Emissions From Leaks and Losses	Total Estimated Emissions	Estimated Release Rates
Kerosene	12,000 gallons	5.4 kg	21.6 kg	27 kg	0.0625 g/s
TBP	4,800 gallons	1.8 kg	7.2 kg	9 kg	0.0208 g/s

Assuming that the chemicals, including spills, are collected and vented without loss to surfaces or ducting from a single 0.25-meter diameter vent, which has a velocity of 0.1 m/s, the overall release concentrations are estimated for a continuous five-day production cycle. The estimated release rates of kerosene and TBP are 0.0625 g/s and 0.0208 g/s, respectively. When arbitrarily collected at a point-source, the releases are concentrations in ppm (by mass), shown in Table 4.2. These 5-day total release amounts occur at irregular rates over the time period and are quickly dispersed by winds from the source (Maughan 2001).

The number of extractions performed, the washing stages, and the type of extractor used are important for this separation process. The scenario used above to estimate release concentrations does not include this level of detail. In addition, the volumes of organic reagents and subsequently the release volumes of semi-volatiles are highly dependent on the equipment used. For example, a settling chamber, the simplest extraction device, would require large volumes of organic solvents but a highly efficient centrifugal extractor would not.

Table 4.2. Estimated Total Release Amounts From Hypothetical Batch Production Scenario

Chemical	Estimated Total Release Amount Over Production Cycle (ppm by mass)
Kerosene	10,000
TBP	3,300
DBP	600
Note: It is assumed that about 20% of TBP converts to DBP during this batch run scenario (Nowak et al. 1973).	

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