**Assessment of Concentration Mechanisms for
Organic Wastes in Underground Storage Tanks
at Hanford**

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Summary

Pacific Northwest Laboratory (PNL) has conducted an initial conservative evaluation of physical and chemical processes that could lead to significant localized concentrations of organic waste constituents in the Hanford underground storage tanks (USTs). This evaluation was part of ongoing studies at Hanford to assess potential safety risks associated with USTs containing organics. Organics in the tanks could pose a potential problem if localized concentrations are high enough to propagate combustion and are in sufficient quantity to produce a large heat and/or gas release if in contact with a suitable oxidant. The major sources of oxidants are oxygen in the overhead gas space of the tanks and sodium nitrate and nitrite either as salt cake solids or dissolved in the supernatant and interstitial liquids.

The PNL evaluation covered the chemicals and concentration mechanisms for the three major phases: liquid, solid, and gas. The study was conducted in two parts: 1) a preliminary review of available information on potentially significant sources of organics added to the tanks, as well as their major chemical and radiolytic degradation products, and 2) an in-depth review of concentration mechanisms. Probable organic constituents were assigned to the liquid, solid, or gas phases, based on information on the properties of each compound of interest. An important consideration of this activity involved evaluating the degradation mechanisms for the major chemicals that produced byproducts with distinctly different properties, and assessing the effect of these new properties on the subsequent partitioning to adjacent phases. The in-depth review of the concentration mechanisms revealed a complex combination of competing effects of key parameters on the various mechanisms: high pH and high ionic strength of the aqueous phase; and a complex mixture of organic compounds with different physical and chemical properties. The evaluation of these mechanisms is organized in this report according to the principal phase involving the concentration of organics.

The organic compounds identified in the evaluation fall into several classes: hydrocarbons, ethers, alcohols, aldehydes, carboxylates, esters, amines, and sulfonates. Most of these compounds are considered to be soluble or at least sparingly soluble in water. However, the insoluble hydrocarbons could form a separate phase on top of the aqueous phase if a sufficient quantity had been added to an individual tank. This layer could extract a portion of the other organics from the aqueous phase.

Most of the hydrocarbons added to the tanks were solvents used in several operations at the Hanford Site, e.g., PUREX, REDOX, Uranium Recovery, and Waste Fractionation/Encapsulation. These solvents invariably contained substantial quantities of phosphate ester extractants, such as TBP, DBP, and D2EHPA, and would be found together in a separate organic phase. The probability of the formation of a separate phase is enhanced by the salting out effect of highly ionic aqueous solutions on organics, which can reduce the solubility of organics by at least 1 order of magnitude.

Extensive chemical and radiolytic degradation has certainly occurred in the USTs. One of the results of this degradation is the fragmentation of the organics into smaller molecules. These smaller molecules ultimately convert to more stable carboxylic acids through a number of intermediate compounds consisting of alcohols, aldehydes, and ketones. These compounds will have a lower fuel value, with respect to their carbon content, than the parent compounds, and in turn will diminish the

effect of concentration on the energetics of combustion. In a separate organic phase this trend is also observed, but another trend is the conversion of a portion of the organics to higher molecular weight molecules.

Of the concentration mechanisms evaluated in the study, five stood out in particular:

1. Concentration mechanisms involving volatilization or solubilization of the smaller and/or more polar products of degradation. These mechanisms will both deplete the organic phase and enrich it in high molecular weight compounds.
2. Precipitation of sodium oxalate. Sodium oxalate is a likely final product of degradation for many of the organics added to the tanks and was itself added in quantity to the tanks. This precipitate would reside with the other solids in the tanks.
3. Adsorption of organics onto the surfaces of the solids. Many of the organics in the tank are polar compounds and thus capable of adsorbing onto the solids surfaces of the sludge and salt cake. Among these compounds are surfactants that were used during plant decontamination operations and (C_8 or more) carboxylic acids that are products of solvent degradation and are known to have surfactant behavior. Under optimum conditions these compounds can concentrate as high as $7.5(10)^{-2}$ mol/m² of surface. This in turn can produce carbon concentrations on the solids as high as several percent if the solids have high surface areas. However, several parameters (pH, ionic strength of solution, organic compounds adsorbing, and organic compound inventory) affect the adsorption mechanism and can result in much lower concentrations at nonoptimum conditions.
4. Absorption of the organics into the interstitial spaces of the solids if a tank containing a separate organic phase were drained of free liquids. Previous experience with soils contaminated by spills of pure organic liquids has shown that the uppermost solids could achieve organic concentrations on the order of several percent.
5. Formation of foam on the surface of the tank liquids. Some of the tanks are known to generate gases, and the presence of organics with surfactant properties makes formation of a foam possible. Research on the flammability of mists suggests that propagation of a flame in a foam is possible due to the generation of a flammable organic mist as the bubbles burst.

The results of this evaluation suggest that these concentration mechanisms be considered as part of the characterization strategies for watchlist tanks. Strategies on characterization should include analysis of the overhead gas space for the presence of solvents and extractants at concentrations consistent with a separate organic phase. Samples of solids not covered by a free liquid layer should be taken near the surfaces to detect local high concentrations caused by adsorption of bulk organic liquid. Characterization of tank solids should also evaluate mineral composition and physical properties such as surface area, particle diameter, and porosity for both aqueous and organic liquids. Analyses of liquids and solids need to be capable of identifying both low and high molecular weight organic acid salts, such as sodium oxalate; salts of C_8 or greater acids; and surfactants added to the tanks. Quantitative functional group analysis and molecular weight distribution data are needed for organic constituents that cannot be separately identified.

The conclusions reached regarding the significance of the various mechanisms, however, are very subjective in nature and only provide a guide for further investigation to better quantify the significance of these concentration mechanisms and the degree of concentration to be expected from them. Research is needed on the interaction between a high ionic strength aqueous phase and a separate organic phase to better understand the behavior of surfactants, carboxylic acids, and complexants in the aqueous phase. This research should determine the solubility of the organics in both phases to better establish conditions necessary to form and maintain a separate organic phase, and for causing the precipitation of organic solids such as sodium oxalate and other carboxylic acids. The ability of surfactants and complexing agents to solubilize the inorganic ions into the organic phase and their subsequent effect on the physical chemical properties also needs to be investigated. Research involving the adsorption of organics with surfactant behavior needs to be performed to quantify the effects of pH and high ionic strength on adsorption. Because of the extremely high concentrations of electrolytes, extension of this behavior to materials not associated with surfactant activity, such as shorter chain organic acids, is also warranted. Further investigation to confirm the potential for the retention of a bulk organic phase in the solids during draining is also recommended.

Contents

Summary	iii
Abbreviations	xi
1.0 Introduction	1.1
2.0 Conclusions and Recommendations	2.1
2.1 Conclusions	2.1
2.2 Recommendations	2.4
3.0 Approach	3.1
4.0 Evaluation of Chemicals and Concentration Mechanisms	4.1
4.1 Chemicals Considered	4.1
4.1.1 Organics Added to the Tanks	4.1
4.1.2 Chemical and Radiolytic Degradation of Organic Additives	4.5
4.2 Liquid Phase Concentration Mechanisms	4.8
4.2.1 Distribution of Organics Between Aqueous and Organic Phases	4.8
4.2.2 Salting Out Organics from the Aqueous Phase	4.10
4.2.3 Volatilization	4.11
4.3 Solid Phase Concentration Mechanisms	4.11
4.3.1 Precipitation of Organics	4.12
4.3.2 Adsorption of Organics	4.14
4.3.3 Absorption of Separated Organic Phase	4.20
4.3.4 Ion-Exchange Resins	4.22
4.4 Gas Phase Concentration Mechanisms	4.24
4.4.1 Concentration of Solvents and Extractants Above a Free Organic Phase	4.25

4.4.2	Concentration Above an Aqueous Phase	4.29
4.4.3	Concentration of Organics Above an Inorganic Solid Phase	4.31
4.4.4	Concentration of Degradation Products	4.33
4.4.5	Other Concentration Mechanisms	4.33
5.0	References	5.1
	Appendix - Preliminary Assessment of Radiolytic and Chemical Degradation Products	A.1

Figures

4.1	Particle Surface Area and Carbon Concentration for Sodium Dodecylbenzene for Spherical Particles	4.17
4.2	Limits of Flammability of Hexane in Oxygen-Nitrogen Atmospheres	4.26
4.3	Effect of Diluents in Air on Flammability Limits	4.27
4.4	Vapor Pressures and Flashpoints of Selected Solvents and Extractants	4.30
4.5	Designated Regions for Vapor-phase Sorption Phenomena of Trichloroethylene as a Function of Moisture Content of Solid Surfaces	4.32

Tables

1.1	Organic Waste Tanks on Watch List	1.2
4.1	Major Chemicals Used in Hanford Site Operations	4.2
4.2	1972 Organic Waste Volumes and Projected Waste Volumes Through 1975	4.3
4.3	Tank C-103 Flammable Vapor Components	4.25

Abbreviations

BET	Multilayer adsorption model
D2EHPA	Di-(2-ethylhexyl) phosphoric acid
DBBP	Dibutyl butyl phosphonate
DBP	Dibutyl phosphate
DST	Double-shell tank
EDTA	Ethylenediaminetetraacetic acid
HEDTA	N-hydroxyethyl-ethylenediaminetriacetic acid
IDA	Iminodiacetic acid
MBP	Monobutyl phosphate
MEK	methyl ethyl ketone
MIBK	Methyl isobutyl ketone
MNBK	Methyl n-butyl ketone
NaD2EHPA	Sodium salt of D2EHPA
NPH	n-paraffin hydrocarbon
NTA	Nitrilotriacetic acid
PNL	Pacific Northwest Laboratory
PUREX	Plutonium Extraction (plant)
PZC	Point of zero charge
REDOX	Reduction-Oxidation (plant)
SST	Single-shell tank
TBP	Tributyl phosphate
TCE	Trichloroethylene
TRAC	Tracks Radioactive Components
UST	Underground storage tank
WHC	Westinghouse Hanford Company

1.0 Introduction

Between 1943 and 1987, activities at the Hanford Site generated a large quantity of high-level radioactive wastes. These wastes mainly came from plutonium production operations, as well as the production of several radioisotopes, such as cesium-137 and strontium-90, used for a variety of applications. In total, these wastes were put into 177 underground storage tanks (USTs) at the Site, 149 single-shell (SST) and 28 double-shell (DST).

Radioactive components actually constitute a very small portion of the tank waste mass (less than 0.02%), although these quantities still pose a radiation danger. Most of the tank waste is composed of nonradioactive inorganic chemicals and water. These chemicals include insoluble solids containing iron, bismuth, aluminum, silicon, chromium, zirconium, lanthanum, phosphate, carbonate, fluoride, sulfate and lesser quantities of other metals; and soluble salts, principally composed of sodium nitrate, sodium nitrite, and sodium hydroxide. The salts are found in the form of solids called salt cake and/or dissolved in aqueous liquid in the tanks.

Organic compounds constitute less than 1% of the total waste. However, the organic content of individual tanks varies widely because different processes generated the wastes in each tank. The presence of organic compounds is a concern because these compounds are reductants and can release heat and gases if oxidized. The tank wastes also contain large quantities of sodium nitrate and sodium nitrite, which are capable of oxidizing these organics under conditions of elevated temperature, above the boiling point of water following loss of tank moisture. Furthermore, because the tanks are vented to the atmosphere, oxygen in the air can diffuse into them.

Several studies have been conducted in the past to assess the potential for the organics and the nitrates and nitrites to react uncontrollably in the tanks (Beitel 1976a,b,c; Beitel 1977; Fisher 1990). These studies have generally concluded that such reactions would not take place because the tank temperatures were well below those required to initiate a reaction, and the concentrations of organics were too low to sustain a reaction. However, information released in 1989 regarding a major explosion in a radioactive waste tank in Kyshtym, U.S.S.R., in 1957 showed that the tank contained a mixture of oxidizing salts and organics (primarily sodium nitrate and sodium acetate), which were allowed to dry out and then self-heat to an explosion-initiation temperature estimated to be 380°C (Borsheim and Kirch 1991). While it was concluded that the tank conditions similar to those in the Kyshtym accident (i.e., high temperature) did not exist in any of the Hanford tanks, further review was warranted to assess the potential safety risk associated with tanks at Hanford that contained organic wastes.

A study was conducted in 1989 by Westinghouse Hanford Company (WHC) to determine an upper limit for an acceptable concentration of total organic carbon constituents in the wastes (Fisher 1990). The study recommended that an upper limit defined as "10% organic equivalent weight to sodium acetate" be used as the basis for placing tanks on a watch list. This limit corresponds to approximately 3.0% total organic carbon. A review of historical waste disposal records by Fisher (1990) and process information were used to estimate the organic content of the waste in each of the tanks. As a result, eight SSTs were identified as exceeding the limit (Table 1.1) and were placed on a watch list. The watch list may change as more information becomes available through a number of ongoing activities at Hanford, including the Organic Tank Safety Program Office established by WHC

Table 1.1. Organic Waste Tanks on Watch List

<u>Tank</u>	<u>Tank Capacity, kgal</u>	<u>Waste Volume Percent of Tank Capacity</u>	<u>Temperature, °C</u>	<u>Waste Heat Load, Btu/h</u>
241-B-103	500	20	16	< 10,000
241-C-103	500	40	55	18,000
241-S-102	750	100	43	11,900
241-SX-106	1,000	85	46	< 40,000
241-TX-105	750	85	39	20,000
241-TX-118	750	50	24	4,900
241-U-106	500	60	29	6,500
241-U-107	500	100	27	13,800

in July 1990. The activities being conducted for this program include tank sampling and further review of historical information to more accurately assess the inventory of organics in the tanks. Also, a focused program of research will be conducted to determine the behavior of real and simulated wastes containing the types and concentrations of organic chemicals potentially present in the tanks in the context of their potential for uncontrolled reactions with other waste components present.

One concern regarding the inventory of organics in the tanks is whether they could be concentrated to sufficient levels and total quantities to create a greater hazard than anticipated using average concentration values for the individual tanks. This concern will need to be coupled to the mitigating effects of aging processes that can significantly diminish the effects of concentration by reducing the fuel value of the organics in the tanks. The purpose of the study described here, which was conducted by Pacific Northwest Laboratory (PNL),^(a) was to identify and evaluate concentration mechanisms that could be occurring in the tanks and could lead to significantly elevated, localized concentrations of organics in the USTs. The results of this study will be used as a basis for further research to verify the significance of these mechanisms and to support characterization of the tank wastes to confirm whether the hypothesized local concentrations actually exist in the tanks.

This report contains the conclusions and recommendations related to the study; the approach taken; and the evaluation of liquid, solid, and gas phase mechanisms for the organic chemicals considered relevant to Hanford tank waste. The appendix provides a preliminary assessment of radiolytic and chemical degradation products.

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2.0 Conclusions and Recommendations

A number of conclusions and recommendations can be made regarding the results of this evaluation of mechanisms for concentrating organics in the tanks.

2.1 Conclusions

The organic compounds placed in the Hanford waste storage tanks fall into several classes, including: hydrocarbons, esters, alcohols, aldehydes, ethers, amines, sulfonates, and carboxylates. Most of these compounds are considered to be soluble or at least sparingly soluble in water. However, the hydrocarbon solvents are considered insoluble and could form a separate phase if a sufficient quantity had been added to a tank. Most of the hydrocarbons added to the tanks were n-paraffinic hydrocarbon solvents used in several of the major separation processes such as Plutonium Extraction (PUREX), Reduction-Oxidation (REDOX), Uranium Recovery, and Waste Fractionation/Encapsulation. These materials invariably contained substantial quantities of phosphate ester extractants, such as tributyl phosphate (TBP), dibutyl phosphate (DBP), and di-(2-ethylhexyl) phosphoric acid (D2EHPA), and would be found together in a separate organic phase. The probability of the formation of a separate phase is enhanced by the salting out effect of highly ionic aqueous solutions on organics, which can reduce the solubility of organics by at least 1 order of magnitude in the alkaline aqueous liquid within the USTs. Provided that the liquids in the tank are not undergoing significant circulation, any separate organic phase will be the uppermost liquid layer. However, it is possible with circulating liquids, due to natural circulation and/or transfer of material in or out of the tank, to produce stable emulsions of the two phases.

Extensive chemical and radiolytic degradation has certainly occurred in the USTs. One result of this degradation is the fragmentation of the organics into smaller molecules, and the fraction that does not escape will ultimately convert to more stable carboxylic acids through a number of intermediate compounds consisting of alcohols, aldehydes, and ketones. This is considered to be the dominant trend in the aqueous phase. These compounds will have a lower fuel value, with respect to their carbon content, than the parent compounds, and in turn will diminish the effect of concentration on the energetics of combustion. In a separate organic phase this trend is also observed, along with a portion of the organics converting to higher molecular weight molecules through condensation reactions and polymerization reactions. The condensation reactions involve hydrocarbon radicals produced by radiolysis; the polymerization reactions involve some intermediate products such as the aldehydes and ketones. Cleavage of larger molecules and the subsequent formation of alcohols and carboxylic acids through oxidation will tend to deplete a separate organic layer because these subsequent compounds are water soluble and more volatile. The degree of solubilization, however, will be much lower than expected because of the salting out effect of the high ionic strength solution. If a sufficient quantity exists of long chain organic acids (typically containing 8 or more carbon atoms); some surfactants used onsite; or certain organophosphate acid salts, such as dibutyl phosphate and monobutyl phosphate, there is a possibility for the formation of a separate organic phase. This second phase would also reside on top of the aqueous phase and therefore next to the hydrocarbon phase if it is also present. However, a number of other organics present in the solvent phase could solubilize these compounds and prevent formation of a third phase.

Evaporation of organics in the USTs is known to occur and will serve to deplete the inventory of organics in the tanks. This mechanism will also serve to deplete a separate organic layer. However, volatilization is also a fractionation mechanism resulting in preferential volatilization of more volatile compounds of the intermediate products of chemical and radiolytic degradation, such as alcohols, aldehydes and ketones, as well as volatile compounds added to the tank in quantity, such as acetone, methyl isobutyl ketone, and light components in the hydrocarbon solvents. A consequence of volatilization is that the remaining organics in both the aqueous and organic phases will be enriched in low-volatility materials. For a separate organic phase, this will include the high molecular weight products of chemical degradation of the solvents and extractants. In the aqueous phase, the sodium salts of the organic acids and surfactant materials will also remain because of their low volatility.

It is concluded from the evaluation of the gas phase that volatilization of the hydrocarbon solvents from a separate organic phase would provide the greatest inventory of organics in the gas phase. Using vapor-liquid equilibrium data for solvents used onsite, it appears that the concentration of these solvents will not reach their lower flammability limit for temperatures up to about 75°C. The presence of the phosphate esters, which have a much lower volatility, will raise this temperature significantly. Also, the presence of water vapor in the gas phase should raise the temperature range further by raising the lower flammability limit for the air-solvent-water vapor system. Evaporation of liquids from solids saturated with solvent would pose a similar behavior but of lesser magnitude because of the adsorption of these materials onto the solid surfaces, as well as the difficulty in replenishing organics at the top of the solids where evaporation would occur. Volatilization of organics from the aqueous phase was not considered a significant concentration mechanism. The total inventory of volatile organics dissolved in the aqueous phase would not be sufficient to fill the gas space at a significant concentration because of the salting out effect of the high ionic solutions on the solubility of organics.

The next potentially significant source of organics in the gas phase appears to be volatilization of the various volatile intermediate products of degradation of the solvent and phosphate ester extractants, such as aldehydes, alcohols, and ketones. The steady-state concentration of these compounds in the gas phase largely depends on their net generation rate due to degradation and the rate at which they can leave the tanks through the ventilation system, rather than on the temperature of the tank. The generation rate of these products is not believed to be sufficient to constitute a significant source compared with the hydrocarbon solvent, unless ventilation of a tank is obstructed. Transient conditions in the tanks from temperature excursions, atmospheric pressure changes, and turnover of tank contents could cause temporary increases in concentration of the volatile degradation compounds. However, none of these transient conditions are expected to cause significant increases.

One concentration mechanism of the gas phase involved the formation of mists and sprays. Mists are formed from the condensation of vapor in the gas space. Sprays, on the other hand, are generated by atomization of a liquid in the gas phase. It appears to be possible to lower the flammability limit of an organic vapor constituent if it consists of small droplets on the order of 10 μm . However, information on this mechanism did not involve conditions similar to those in the tank, the most important being the likely simultaneous formation of water droplets in the same space which should tend to offset the effect. Another potentially more significant mechanism for forming mists occurs upon the collapse of an organic foam on a liquid surface. As foam bubbles burst, aerosols are formed from the rupturing skin of the bubble. Apparently, this phenomenon can result in the

propagation of a flame through an organic foam generated from air bubbles (Zabetakis 1965). It would seem likely that this phenomenon would be aggravated further if the bubbles were formed from hydrogen gas.

Evaluation of concentration mechanisms in the solid phase identified several that could be important, because individually or together they could increase the localized concentration of organics well above that dissolved in the interstitial liquids of the solids, and would persist in the salt cake and/or sludge at these concentrations even if the (drainable) aqueous liquids are drained from the tank. Subsequent drying of these solids and heating to high temperatures could cause the nitrate solids and organics to ignite. The explosion potential of such a mixture would depend on several factors including the fuel value of the organics and the concentration of inert solids. First, it was concluded that sodium oxalate either added to a tank or formed as a relatively stable product of chemical degradation could achieve sufficient quantities to cause precipitation from the aqueous phase to form a solid. This precipitate would form anywhere in the tank solids. This mechanism would increase the concentration of organics in the salt cake and sludge above that attributed to organics dissolved in the interstitial liquids.

Adsorption onto the tank solids of organic acids and other surfactants added to the tanks may be a significant concentration mechanism. Apparently, once these materials adsorb onto the surfaces they also concentrate other organics near the surface by forming admicelles that solubilize these other organics. The maximum quantity of organic carbon that could be concentrated in the solids by this mechanism was found to approach levels on the order of several percent by weight. However, the actual quantity of materials that deposit on the solids could be much lower and thus insignificant depending on a number of important parameters, including the quantity, mineralogy, and surface area of the solids; pH and ionic strength of the aqueous phase; and the type of organic acid or surfactant involved and its concentration in the solution. There is not enough information regarding this mechanism under conditions in the tank to make a realistic estimate of the actual amount of concentration that would likely occur.

Absorption of organics from a separate organic layer and into the solids during dewatering of a tank was also found to be a mechanism of potential importance. This mechanism is known to occur in unsaturated soils from petroleum spills and has produced residual levels of organics on the order of several percent by volume in the soils. This mechanism is analogous to retention of water in the pores of solids after water is drained from water-saturated soil. The only difference is that the liquid is an organic that displaces free water as it passes through the solids. This particular mechanism will occur in the uppermost solids in the tank that the organic layer passes through during draining of a tank. The depth of penetration depends on the porosity of the soil, the hydrocarbon involved, and the depth of the separate organic phase before draining. It is estimated that a depth of 30 to 60 cm would result from a 2.5-cm layer of free organic.

Displacement of water-saturated solids with an organic liquid, as the water is drained, will not necessarily follow the scenario described for unsaturated soils but could result in the displacement of the free water. This mechanism could also result in a significant quantity of organic in the solids just above the level of water-saturated solids. The rate of displacement of organic liquid into the solids by either mechanism depends on the properties of the solids and liquids, as they relate to their hydraulic conductivity in the solids, and the forces acting on the liquids. In solids consisting of micron-size particles this rate could be very slow and may be insignificant.

The conclusions reached regarding the significance of the various mechanisms are very subjective in nature and only provide a guide as to those needing further investigation. The number of unknown parameters regarding the composition and physical properties of the tanks, as well as an absence of experimental data encompassing the anticipated conditions in the tank, preclude a quantitative evaluation of the consequences of the various mechanisms except in a few cases. In these cases, worst-case or order-of-magnitude estimates can be made.

The simultaneous conditions of high pH, high ionic strength aqueous solutions, and a complex mixture of organic polar and nonpolar compounds, including those with surfactant properties, is unusual. Consequently, there is very little information on the behavior of the organics under these conditions. However, these parameters have a dramatic effect on the behavior of both the solids and the aqueous phases that affect potentially important concentrating mechanisms such as salting out of organics and adsorption of organics onto the tank solids.

The presence of potentially significant quantities of a mixture of organics with surfactant properties introduces the potential for very complex behavior for all of the mechanisms involved. Surfactant materials are known to have widely ranging behavior for different systems because of variations in the mineral solids, electrolytes present, and pH. Furthermore, even simple mixtures involving surfactants, water, and immiscible organics can cause a number of different behaviors: solubilization of immiscible organic in the water; solubilization of the water in the immiscible organic, solubilization of the surfactant into either phase; formation of an emulsion; and formation of a second organic phase. What actually occurs can vary simply by changing the relative quantities of the three components. The introduction of electrolytes and complexing agents, or more complex mixtures of organics, further complicates prediction of the behavior of the surfactants, one of which is the concentration of inorganic anions and cations into the immiscible organic phase. This could be very important because it could change the reaction chemistry of the organic phase.

2.2 Recommendations

The results of this evaluation suggest that these concentration mechanisms be considered as part of the characterization strategies for watchlist tanks. Strategies on characterization should include analysis of the overhead gas space for the presence of solvents and extractants at concentrations consistent with a separate organic phase. Samples of solids not covered by a free liquid layer should be taken near the surfaces to detect local high concentrations caused by adsorption of bulk organic liquid. Characterization of tank solids should also evaluate mineral composition and physical properties such as surface area, particle diameter, and porosity for both aqueous and organic liquids. Analyses of liquids and solids need to be capable of identifying both low and high molecular weight organic acid salts, such as sodium oxalate; salts of C_8 or greater acids; and surfactants added to the tanks. Quantitative functional group analysis and molecular weight distribution data are needed for organic constituents that cannot be separately identified. The results of this study also suggest a need for additional experimental data to better quantify the degree of concentration from these mechanisms that can be expected under actual tank conditions.

The interaction between the aqueous phase and a separate organic phase needs to be investigated in the context of the behavior of surfactants, complexants, and the inorganic ions in the aqueous phase. Solubility of the organics in both phases, in the presence and absence of organics with

surfactant properties, needs to be better understood to establish conditions necessary to form and maintain a separate organic phase, and to cause the precipitation of organic acids. The ability of surfactants and complexing agents to solubilize the inorganic ions into the organic phase and their subsequent effect on the physical and chemical properties also need to be investigated. Research involving the adsorption of organics with surfactant behavior needs to be performed to quantify the effects of pH and salting out on adsorption. Because of the extremely high concentrations of electrolytes, extension of this behavior to materials not normally associated with surfactant activity, such as shorter chain organic acids, is also warranted. Further investigation to confirm the potential for the retention of a bulk organic phase in the solids during draining is also recommended.

3.0 Approach

The overall goal of this study was to provide an initial evaluation of the processes that could lead to significant localized concentrations of organics within the tanks. The scope of the study was limited to a review of relevant literature in conjunction with scientific judgment. The literature served as a basis for documenting the organic chemicals of interest and their properties, as well as documenting concentration mechanisms for selected constituents. Scientific judgment served as a basis for making assumptions regarding tank chemistry and chemical properties in lieu of actual data, as well as assessing the significance of the various concentration mechanisms. Information gaps requiring experimental research were identified in the study but not investigated.

Four areas of investigation were identified:

- the major chemicals of interest in the tank wastes
- the types of concentrating mechanisms possible
- the distinct phases (gas, liquid, and solid) produced by these concentration processes and assignment of their location with respect to one another
- the probability of significant concentration of the assigned organic chemicals to each phase.

The study was conducted in two parts. The first part consisted of a scoping activity, including a preliminary review of each of the four elements and screening of concentration mechanisms for an in-depth review, the second part. The preliminary review involved a general survey of available information on potentially significant sources of organics, including those added to the tank waste in large quantities, and their major chemical and radiolytic degradation products. The preliminary review also scoped the literature for evidence of concentration mechanisms that were either known or suspected to occur in the tanks. Concentration mechanisms were screened for in-depth review.

The in-depth review was a detailed study of each concentration mechanism identified in the first review. This in-depth review focused on each major phase (gas, liquid, and solid) known or suspected to exist in the tank. Probable organic constituents were assigned to each phase based on information regarding the properties of each compound of interest. An important consideration of this activity involved evaluating the degradation mechanisms for the major chemicals that produced byproducts with distinctly different properties, and assessing the effect of these new properties on the subsequent partitioning to adjacent phases. An example would be degradation of a nonvolatile, water-insoluble organic chemical into fragments that are either volatile or water soluble. During the in-depth review, new concentration mechanisms or chemicals of interest were added to the study as they were identified.

Section 4.0 details the results of the PNL evaluation, which produced a wide range of technical information on the complex and variable interactions occurring within the tanks. The appendix gives an overview of expected degradation products, although degradation is also discussed in Section 4.0.

4.0 Evaluation of Chemicals and Concentration Mechanisms

This section combines the results of the overall evaluation. An overview of the chemicals and chemical classes is given here, along with concentration mechanisms for the liquid, solid, and gas phases separately. For each phase, the chemicals of particular interest and the concentration mechanisms that add or, in some cases, remove significant quantities of organics are discussed. When possible, an assessment is made of the importance of each concentration mechanism for the phase.

4.1 Chemicals Considered

The organic chemicals screened for consideration in the study included those that were used in significant quantities and either known or suspected to have been added to the USTs. Also considered are the degradation products of these chemicals. In many instances chemicals fall under both categories. Each source of chemicals is discussed below.

4.1.1 Organics Added to the Tanks

The inventory of chemicals added to the USTs has come from a number of different operations conducted over the years. Klem (1990) prepared a list of 229 chemical compounds and 68 chemical products that were used at Hanford production plants and support operations and that are known or suspected to have been disposed in the USTs. Sixty-three of the chemicals compounds were organic and 23 of the chemical products contained organic compounds, including four that were organic resins.

In an earlier report, Allen (1976) estimated chemicals added to underground tanks resulting from each major activity and attempted an estimate of tank sludge compositions. Anderson (1990) compiled a comprehensive history of the tank farms, noting the dates and descriptions of material additions and transfers to individual tanks. The TRAC program (Jungfleisch 1984) used a computer code to predict existing tank compositions. As a result of these and other evaluations, a fair picture of the organic materials added to various tanks emerges. Table 4.1 lists those chemicals that were used in significant quantities on the Site and that either are known or believed to have been added in significant quantities to the USTs.

By far the largest source of organics in the tanks is the solvent extraction processes that were used to recover uranium and plutonium from spent reactor fuel. These processes include Uranium Recovery (tributyl phosphate), REDOX, and PUREX. Documented tank inventory of solvents and extractants in 1972, as well as projected tank inventory (through 1975) from the ongoing PUREX, Waste Fractionation/Encapsulation (B-Plant), and Plutonium Finishing Plant (Z Plant) operations, is shown in Table 4.2 (Hall 1972). These large volumes confirm the significance of solvents and extractants as a major source of organics in the USTs. However, some of the inventory has since been retrieved, treated, and disposed.

Table 4.1. Major Chemicals Used in Hanford Site Operations

Solvents

- Hydrocarbon (kerosene, Soltrol, n-paraffin)
- Carbon tetrachloride
- Tetrachloroethane

Extractants

- Tributyl phosphate (TBP)
- Dibutyl butyl phosphonate (DBBP)
- Di-(2-ethylhexyl) phosphoric acid (D2EH₂PA)
- Methyl isobutyl ketone (MIBK)

Complexing Agents/Organic Acids

- Ethylenediaminetetraacetic acid (EDTA)
- N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA)
- Nitritotriacetic acid (NTA)
- Glycolic acid
- Citric acid
- Tartaric acid
- Oxalic acid
- Acetic acid

Miscellaneous Process Chemicals

- Sugar
- Sodium gluconate
- Sodium acetate
- Ion-exchange resins
- Formic acid
- Formaldehyde

Miscellaneous Organic Components of Cleaning Agents

- Diethylene glycol monobutyl ether
- Monohydroxyethyltrihydroxypropylethylenediamine
- Triethanolamine
- Dichloromethane
- Toluene
- Butyl benzyl phthalate
- Isopropanol
- Acetone
- Octylphenoxypoly(ethyleneoxy) ethanol

The organic solvent used in the greatest amount was probably the hydrocarbon diluent used with TBP and D2EHPA. For the most part this was n-paraffin hydrocarbon (NPH), a product produced largely from petroleum stock by molecular sieve separation to remove aromatic hydrocarbon impurities. It was the solvent used in latter operation of PUREX Plant (as the diluent for TBP), and the Waste Fractionation/Encapsulation Plant, as the diluent for D2EHPA. Kerosene solvents, such as Shell E-2342 and Shell Spray Base, were used as the diluent for TBP in the Uranium Recovery process and in the early PUREX process (before the mid-1960s). These products, which were produced by petroleum fractionation, consist of a very complex mixture of hydrocarbons with a boiling range of about 190°C to 260°C (Burger 1955), and an aromatic content of less than 1%. Soltrol-170, another synthetic solvent produced by polymerization, was also used in significant quantities onsite.

Undiluted methyl isobutyl ketone (MIBK) was used as both extractant and solvent in the REDOX process. This extractant was sold under the trade name Hexone.

Table 4.2. 1972 Organic Waste Volumes and Projected Waste Volumes Through 1975 (Hall 1972)

<u>Source</u>	<u>Rate of Generation, gal/yr</u>	<u>Inventory at Shutdown, gal</u>	<u>Composition</u>	<u>Total Through FY 1975, gal</u>
PUREX	6000	30,000	TBP-NPH	48,000
B Plant	--	10,000	TBP-NPH-D2EHPA	10,000
Z Plant	1700	400	TBP-DBBP Bottoms	<u>3,700</u>
				61,710

<u>Storage</u>	<u>Present Inventory (1972), gal</u>	<u>Composition</u>	<u>Total Volume, gal</u>
241-C-102	36,000	TBP-NPH	36,000
241-C-104	8,000	TBP-NPH	8,000
276-S-141	18,300	MIBK (Hexone)	18,300 ^(a)
276-S-142	12,720	MIBK-TBP-NPH-D2EHPA	12,720
234-S	2,000	Lard Oil-TBP	<u>2,000</u>
			77,020

(a) Retrieved, treated, and disposed in 1990-1991.

Carbon tetrachloride, the only halogenated material used as a process solvent onsite, was used in the Reflux Solvent Extraction (Recuplex) process used to produce purified plutonium metal in the Plutonium Finishing Plant and later in the Plutonium Reclamation Facility. This process used 15% TBP diluted in carbon tetrachloride to extract the plutonium (Cleveland 1967) from solution, followed by extraction of americium using 30% DBBP in carbon tetrachloride (Kingsley 1965).

In addition to the solvents and extractants used onsite, several organic chelating agents were used in large quantities in the Waste Fractionation/Encapsulation process. In this process, several organic chelating agents (EDTA, citric acid, HEDTA, and glycolic acid) were added to the waste to complex iron, aluminum, and other inert metals to prevent their co-extraction along with the strontium. Allen (1976) estimated the amounts of some of the major complexants that have been added to the waste:

Glycolic acid - 9.0×10^6 moles	(684,000 kg)
Citric Acid - 3.3×10^6 moles	(633,000 kg)
HEDTA - 2.7×10^6 moles	(745,000 kg)
EDTA - 0.57×10^6 moles.	(166,000 kg)

In addition to the above solvent extraction systems, a number of other organic chemicals were added in these processes. Some examples are oxalic acid, which was used to precipitate plutonium (Bismuth Phosphate, Plutonium Finishing Plant); and sugar and formaldehyde, which were added in the PUREX process to denitrate a portion of the nitric acid. These chemicals were largely consumed in the process. Other organic chemicals used in quantity in the PUREX process were sodium gluconate and sodium acetate.

Ion-exchange resins were employed in many processes onsite. Some disposal was by burial, but some may have entered the waste tanks. A separate discussion of ion-exchange resins is provided in Section 4.3.4.

Large quantities of organic compounds were also added to the tanks from plant decontamination operations. These operations used large quantities of cleaning agents. Some of these consisted of organic surfactants, solvents, and chelating agents. For example, one N-Reactor decontamination campaign in FY 1983 used 20,000 gal of Turco 4512-14A containing over 10 wt% organics, according to J. S. Schofield and R. E. Smith, Rockwell International. Table 4.1 lists miscellaneous organic components found in concentrations of 5 wt% or greater in the various detergents used in decontamination operations. In addition, several of the detergents used significant quantities of citric, oxalic, and acetic acids. Other organics of unknown concentration or of concentrations less than 5% include tartaric acid, sodium xylene sulfonate, sodium dodecylbenzene, aliphatic petroleum solvent, tetrahydroxy ethylenediamine, 2-butoxyethanol, dioctyl phthalate, morpholine, mineral oil, sodium gluconate, n-butanol, polyester resin, polyvinyl acetate, and nonylphenoxypoly(ethyleneoxy)ethanol.

Organic chemical waste was also generated by the various analytical and research laboratories and pilot plant activities conducted throughout the Site. These chemicals, which constitute the majority of the different organics identified by Klem (1990), were used in much smaller quantities (about 1000 times less) than those used in the major processes.

4.1.2 Chemical and Radiolytic Degradation of Organic Additives

The organic chemicals that were used in quantity onsite and disposed in the USTs were subject to chemical and radiolytic degradation during processing and/or after addition to the tank. Consequently, the tank wastes contain intermediate and final products of degradation that could have distinctly different properties from the parent chemicals.

Two conditions dominate the storage tanks, a high pH, roughly 10 to 12, and a high radiation field. These conditions are very significant. The high pH prevents nitration reactions that would otherwise occur, as sodium nitrate is a major component (Martin 1985). The high radiation field provides the energy necessary to break chemical bonds that otherwise would be unaffected at ambient conditions. It also provides a source of hydroxyl and other radicals that can slowly oxidize organic compounds.

The radiation dose for the waste tanks can roughly be estimated from the Cs-137 content. One curie of Cs is equivalent to $4.86 (10)^{-3}$ J/s. For the eight tanks mentioned in Table 1.1, the curie content ranges from about $4(10)^4$ to $8(10)^5$. For a tank of $2(10)^6$ L, the upper range would produce a dose of about 500 rad per hour. Since Cs-137 has a half life of 30 years, 10^8 rad is about the average dose received from Cs-137 in these tanks over a 30-year period. From another point of view, the $8(10)^5$ Ci is equivalent to $9.1(10)^{12}$ eV/L-g or $2.9(10)^{20}$ eV/g per year. Thus in 30 years, assuming a "G" value^(a) of 1.0, about $9(10)^{19}$ molecules per g would have decomposed, destroying perhaps 0.3% of the bonds. This is an order of magnitude estimate and is probably low. First it neglects secondary and chain reactions that may be appreciable in the two-phase system. This includes gamma activation followed by nitrite oxidation. Second, it neglects other activities that can double the dose received. Third, the G values for organic decomposition are greater than 1, in the range 2 to 6 for many processes. Thus, several percent decomposition would not be surprising. It must also be noted that some wastes, e.g., later PUREX waste, at the time of tank filling were much more radioactive than the reference value used above.

Considering the organic phase, radiation produces dehydrogenation and cleavage that result in smaller molecules and, depending on concentration, dimerization and polymerization of fragments to larger molecules. As is well known, molecular hydrogen is also a major product. Dehydrogenation can produce unsaturated groups, which provide routes to cleavage or, depending on structure, dimer- and polymerization. Further chemical reaction of unsaturated fragments is possible although not as significant in the high pH solution as in acid media. A discussion of chemical degradation of the components in a separate organic phase is provided in the appendix.

Radiolysis in aqueous systems is exceedingly complicated. In concentrated solutions and at high doses the situation is still worse. Thus, dozens of papers have dealt with the nitrate reactions. Daniels (1968) was one of the first to attempt the analysis of this system. Radiation will convert nitrate to nitrite with an equilibrium position being somewhere around 30% to 40% NO_2^- . The product is O_2 . Radiolysis tends to produce an oxidative environment in these systems since the OH radical ($\text{O}^\cdot$ at high pH) produced from water is very reactive. A discussion of the hydroxide radical and its conjugate base O^- is presented in the appendix. The product of the hydroxide radical, hydrogen peroxide, is also more reactive than the reducing component, H_2 , which can more easily escape.

(a) Number of molecules produced per 100 electron volts absorbed.

Because of the high pH, hydrolysis is an important reaction for degrading many of the parent chemicals in the aqueous phase. For example, phosphate esters are converted to phosphates and alcohols. As noted above, radiolysis of nitrate produces an oxidizing environment in the aqueous phase, leading to chemical oxidation of both parent and intermediate organic (including ketones, aldehydes, and alcohols) compounds with carboxylic acids being the reasonably stable end of the chain of events. However, some alcohols, such as n-butanol, are quite stable in saturated sodium nitrate solution. Thus, it is not surprising that radiolysis of compounds such as carbohydrates gives high yields of organic acids as the extensive studies of Phillips have shown (e.g., Phillips and Moody 1959).

If any generalization can be induced from the above, it must be that there may be a degradation of high-fuel-value organics, with considerable loss due to formation of light fragments, oxidation of some fraction to CO_2 , an increase of lower-fuel-value carboxylates (especially oxalates), some polymer formation, and a general increase in the aromatic fraction of the remaining organic constituents. In addition small, possibly steady-state, quantities of alcohols, ketones, and aldehydes will be maintained as intermediate products of degradation. The degradation should produce a trend towards increased solubility in the aqueous phase. However, it must be noted that there is a very great decrease in aqueous solubility due to the very high ionic strength, as discussed earlier.

Specific comments on the behavior of the organic compounds added to the tanks are given in the following sections according to compound class.

4.1.2.1 Hydrocarbons

The G value ranges from as high as 5 for paraffin hydrocarbons to as low as 0.1 for molecules having a large aromatic content (Boldt and Carroll 1963). Polymer formation is surprisingly efficient with G values ranging from about 1 to 8. Even though polymer formation is appreciable, loss of lighter molecules cannot be prevented. For n-hexane, for example, G values are H_2 , 5; CH_4 , 0.13; C_2H_2 , 0.15; C_2H_4 , 0.63; C_2H_6 , 0.63; and C_3H_8 , 0.67.

Oxidation of radiolysis fragments produces alcohols, aldehydes, and ultimately carboxylic acids and CO_2 . For many compounds, radiolysis in the initial stages produces similar materials as does hydrolysis.

The chemical reactions of the parent hydrocarbons in the high pH aqueous environment should be very small. Secondary reactions in the two-phase system produce alcohols, aldehydes, and carboxylates. The intermediates, e.g., alcohols and ketones, could be quite reactive.

4.1.2.2 Ketones, Aldehydes, Alcohols, and Ethers

The largest contribution in this class is probably from Hexone (MIBK). It is quite volatile, b.p. 115.9°C , and also forms a water azeotrope containing 75.6% Hexone and boiling at 89.9°C . However, it can form isovaleric acid, isobutyric acid, acetic acid, and CO_2 . Thus, some degradation products may be present. Other ethers, ketones, alcohols, etc., will react somewhat differently but produce similar products.

For radiolysis the most labile bond in esters is the carbon alkoxy bond, in ketones the C-carbonyl bond, in ethers the C-O bond, and in alcohols the C-O bond (Boldt and Carroll 1963). The

C-H bond is a close second in many of the compounds, giving rise to H_2 . High yields of hydrocarbons corresponding to the alkyl group present is characteristic of ethers, ketones, and esters. Continued degradation will lead to additional carboxylic acids.

4.1.2.3 Phosphorus-containing Solvents

Hydrolysis of the phosphate esters in an alkaline medium tends to stop after the first alkyl group is removed (Burger 1955). Thus, the DBP anion may be a stable species except for radiolytic decomposition. Decomposition products of both TBP and DBBP are nearly the same. For TBP the initial and major products from radiolysis are the same as for hydrolysis; they include butyl alcohol and dibutyl phosphate (Burger and McClanahan 1958; Wagner et al. 1959). Subsequent decomposition gave yields for the acids: DBP, 2.52; monobutyl phosphoric acid (MBP), 0.30, and H_3PO_4 , 0.07. As for other materials that contain alkyl groups, radiolysis of TBP also produces hydrogen, methane, and other light hydrocarbons including alkenes. Also identified are polymeric materials (Kinderman and Samuel 1963). Polymer formation from radiolysis of TBP is appreciable, and Wagner et al. (1959) found G values of 0.91 for material having a molecular weight of 840.

For DBBP the first, and more stable, product would be butyl butylphosphonate, leaving the P-C bond intact. For radiolysis, Kinderman and Samuel (1963) observed the following yields (G values) from pure DBBP: H_2 , 1.42; $n-C_4H_{10}$, 0.12; C_3H_8 , 0.05; CH_4 , 0.04; butanol, 0.27; butenes, 0.04; and a total of 1.40 for the acids. Radiolysis will also produce the other products described above for TBP.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) was used in fission product recovery. A major decomposition product is the mono(2-ethylhexyl)phosphoric acid ester (Schulz 1971). Schulz ascribes the decrease in extraction ability to polymer formation, although the polymer content was not measured. Presumably, ethylhexyl alcohol is also formed.

4.1.2.4 Amines and Ammonia Derivatives

Amines should exist as the free bases. Decomposition products include, besides the usual fragments, alcohols and acids based on the alkyl groups. The C-N bond seems to be especially vulnerable to attack.

4.1.2.5 Organic Acids and Their Salts

The organic acid salts are reasonably stable but in time will degrade to smaller entities. Oxalic and formic acid are two of the more stable products.

4.1.2.6 Ion-Exchange Resins

Organic ion-exchange resins are organic polymers, and their behavior under radiolysis demonstrates all the expected phenomena: gas evolution, cleavage, scission of the exchange functional groups, production of new exchange groups such as -OH and -COOH, crosslinkage, and higher polymer formation. Gangwer, Goldstein, and Pillay (1977) have summarized reported results on radiolysis of ion-exchange materials. Degradation is extensive at doses of greater than $(10)^8$ rad. Organic molecules containing an aromatic ring are far more stable towards radiation than other

organics. It is notable that most of the organic ion-exchange resins contain divinylbenzene, polystyrene, or other aromatic groups. Thus, the aromatic materials may leave organic residues after other alkyl materials have disappeared as water and CO₂.

4.2 Liquid Phase Concentration Mechanisms

The liquid phase(s) added to the USTs over the years constitutes the major organics now in the tanks. Many of the organics were added as trace quantities dissolved or entrained in the aqueous phase. Others were added as a separate phase. Depending on the quantity added to a specific tank, it is possible to form a separate organic phase in the tank. Degradation of the parent organic compounds, and/or the addition of different classes of organics to the same tank, and evaporation of water from the tanks can result in concentration processes involving redistribution of organics between aqueous and separate organic phases. Other processes such as evaporation, precipitation, and adsorption can deplete the inventory of organics in the liquid phase, leading to a redistribution to the solid and gas phases. This section describes those mechanisms that lead to concentration of organics in aqueous and separate organic phases and depletion of the total inventory of organics in the liquid phase. Further concentration involving the gas and solid phases is discussed separately in Sections 4.3 and 4.4.

4.2.1 Distribution of Organics Between Aqueous and Organic Phases

Many of the major organic compounds that were added to the tanks are quite insoluble in water. These compounds include the hydrocarbons, the ion-exchange resins, the halogenated solvents, and the higher alkyl amines. Of these compounds the hydrocarbon solvents are the most likely to have been added to the tanks in sufficient volume to create a separate organic layer, as evidenced by the apparent presence of a separate organic layer in Tank C-103 that appears to be predominantly NPH and TBP.

Slightly water-soluble compounds, less than 1 g/L, include the phosphorus-containing solvents, most of the chlorinated compounds, and most alkyl amines. The higher alcohols and ethers, e.g., dibutyl carbitol, are borderline, the latter having a solubility in water of 2.7 g/L. A general rule for the polyether-diols is that if only one hydroxy hydrogen is replaced by an R group, the substance is water soluble. If both are replaced by C₂ or larger alkyl groups, then it is insoluble in water and miscible with organics. Hexone (MIBK) is more soluble, 17 g/L in water at 25°C. The sparingly water-soluble organics, by the very nature of their hydrophobic character, will also distribute to the organic phase if it is present.

The acids, including the carboxylic amine derivatives such as NTA, are soluble in water and slightly to moderately soluble as the sodium salt in the resultant liquid. As the aqueous phase disappears, some may form as a solid sodium salt. These salts are generally not highly crystalline compounds, and the sodium salts of the larger organic acids are essentially soaps. These are generally soluble in water, exhibiting micelle formation, with the solubility increasing rapidly as the temperature is raised. Sodium decanoate has a solubility of 2.1 wt% at 24°C, 42 wt% at 50°C, and 66 wt% at 60°C (Stephen and Stephen 1963). These compounds are considered relatively insoluble in nonpolar solvents. However, the presence of alcohols or other very polar compounds greatly increases the solubility in the organic phase.

Surfactants present, in addition to these sodium salts, include the various detergents that were used as decontaminating agents. These are predominantly aqueous soluble, although some will be dissolved in the organic phase, especially if the organic has a large proportion of polar compounds. The nonionic surfactants are largely based on polyether structures and are aqueous soluble but, again, will partition to the organic phase.

At low concentrations, all surfactants will concentrate at interfaces and could interfere with phase separation, especially if there is any liquid circulation in the tanks. At higher concentrations, surfactants in the aqueous phase will form micelles that can solubilize hydrophobic organic into the aqueous phase. Alternatively, however, they can lead to the formation of water-in-oil microemulsions as are found during enhanced oil recovery operations. In an organic phase, the solubilization mechanism proceeds through inverted (or reversed) micelles and is capable of solubilizing water and water-soluble components in an organic phase. Reverse micelles of nonionic surfactants, such as nonylphenoxypoly(ethyleneoxy) ethanol and octylphenoxypoly(ethyleneoxy) ethanol, are even capable of solubilizing salts in an organic phase with no water present (Boutonnet et al. 1982).

The presence of surfactants in organic/water systems also allows the possibility of enhanced reaction rates among components in the two phases. Accelerated reaction rates for hydrolysis, substitution, and decarboxylation reactions have all been reported (Bunton, Mhala, and Moffatt 1986). Of particular interest are the reports of accelerated substitution reactions involving such species as the azide ion (Bunton, Moffatt, and Rodenas 1982) or halide species (Br or Cl) (Al-Lohedan, Bunton, and Moffatt 1983). Accelerated rates for anionic species in micellar media appear to occur for micelles formed from cationic surfactants, while anionic surfactants (sodium dodecylbenzene sulfonate) inhibit such reactions (Bunton and Huang 1972). The effect of micelles formed from nonionic surfactants on reaction rates is not clear, although the potential for increased reaction rates (such as among organic species and either nitrates or nitrites) exists.

There is little reason to expect more than one liquid organic phase. The possible exception might result from a large amount of metal salts of long-chain carboxylic acids or organophosphorus acids, which can form a separate organic phase under some conditions. Solvent extraction systems containing D2EHPA, for example, can form a separate phase slightly more dense than the hydrocarbon layer if a sufficient "modifier," such as a polar organic, is not present to increase its solubility in the hydrocarbon phase (Richardson and Schulz 1967). It is not likely to occur here, since TBP is expected to be present wherever D2EHPA is present and will modify its solubility. Alcohols, esters, and ethers are also excellent solubilizing agents.

The degradation of the various parent chemicals in the USTs will also affect the distribution of organics between the aqueous phase and the organic phase. In general, the intermediate products such as the aldehydes, ketones, and alcohols, and the final organic acid products are more hydrophilic than the parent chemicals because they are smaller molecules and contain functional groups that are polar in nature. Furthermore, acids formed from fragments of the alkane solvent will have surfactant properties if they are sufficiently large (generally 8 carbon atoms or greater), and they may solubilize a portion of the hydrophobic organic components by forming admicelles in the aqueous phase. On the other hand, polymeric compounds formed in the organic phase will be even more hydrophobic and will tend to remain in the organic phase. Taken together, the net effect of the formation of these products is to gradually deplete the inventory of the organic phase material while enriching it in higher molecular weight material.

The density is important because not only does it determine the location of the organic phase, perhaps as a layer if enough is present, but along with viscosity and interfacial tension, it determines the ease and degree of phase separation. Except for the halogenated solvents and the sodium salts, the density of the compounds discussed and expected to be present in significant quantity falls in the range 0.8 to 1.1. As noted, halogenated compounds should be negligible. The sodium compounds may vary from 2.27 (sodium oxalate) and 1.53 (sodium acetate) to about 1.2 for the higher organic salts. However, sodium oxalate is insoluble in the organic phase, and sodium acetate has a low solubility (unknown). It is reasonable to expect then that a liquid organic phase would have a density of about 1.0 or, at a maximum, less than that of the aqueous phase. As a minimum the latter would be about 1.4 or the density of 40% NaOH. Actual data for Tank 103-SY show a density of 1.54 (Bryan et al. 1992). Thus, we expect a liquid organic layer to be at the upper surface of a waste tank unless it is mechanically trapped by solids.

4.2.2 Salting Out Organics from the Aqueous Phase

The solubilities of organics are greatly diminished by the addition of electrolytes to an aqueous phase, which can cause the organics to form into a separate phase. This separation is referred to as salting out. This trend has been shown for various ethers, carbitols, ketones, and aromatics (Marcus and Kertes 1969; Dack 1975). The decrease in solubility normally follows the Setchenov rule:

$$\ln S/S_0 = -kC$$

where S is the solubility in a salt solution of concentration C compared with that in pure water, S_0 . The value of the constant k varies with the compound in question but is much more dependent on the particular salt in solution. An approximate value will lead to a factor of 2 reduction in solubility for an ionic strength of about 3 (Harned and Owen 1943). The sodium salt of D2EHPA (NaD2EHPA) presents an extreme illustration of the Setchenov relation. The salt is soluble in water, but only to the extent of 325 mg/L in a 0.38 M Na^+ solution and only 7 mg/L in a 2.8 M solution (Richardson and Schulz 1967). A part of this decrease is due to the common ion effect. The solubility of TBP has been examined by many workers and was reviewed by Burger (1984). Higgins et al. (1959) measured Setchenov constants for a variety of electrolyte solutions. Unfortunately, only NaOH in their list is applicable to the present case. Their value of 0.65 ($\log_{10}$ basis, 1.5 $\ln$ basis) would predict a solubility decrease by a factor of 400 for a 1 M solution and greater than $(10)^5$ for 8 M . Alcock and coworkers (1955) measured the solubility in sodium nitrate solutions. They obtained a value for k for the $\ln S/S$ equation of 0.81, for concentrations up to 5 M . Although an extrapolation to 10 or 15 M is uncertain, reductions in solubility of TBP and many other organic compounds of $(10)^4$ to $(10)^5$ are predicted. Unfortunately, k values for most compounds are not available.

Sodium DBP is a similar compound to NaD2EHPA and along with the MBP salt may be present in appreciable amounts in tanks that received large amounts of TBP. Very large amounts may result in a solid organic phase.

It is interesting to note the reported soluble organic content for the Hanford tanks. This is of the order of a few tenths to a few molar in soluble organic carbon according to M. J. Klem of WHC. As an example, 2 M C would be 1 M acetate or 0.25 M DBP. This would most surely precipitate if the solution were concentrated, e.g., reduced in volume by evaporation by a factor of 10.

4.2.3 Volatilization

Mechanisms that will have led to volatilization include: deliberate evaporation or distillation of the wastes before or after they were placed in tanks; and radiolytic and hydrolytic decomposition leading to smaller, more volatile organic molecules that subsequently evaporate in the tanks.

The first mechanism would be the most effective because of the higher temperature, i.e., the boiling point, and the benefit of steam distillation. Steam distillation permits distillation of a two-phase mixture when the sum of their vapor pressures is P_{atm} ; i.e.,

$$P_{atm} = P_{Water}^0 + P_{Organic}^0$$

from which the weight ratio distilling is

$$W_{Org}/W_{Water} = 18fP_{Water}^0/M_{Org}X_{Org}P_{Org}^0$$

Here f is the activity coefficient of the water in the aqueous phase, X is the mol fraction of the organic of vapor pressure P_{Org}^0 in a nonvolatile organic phase, and M_{Org} its molecular weight. Thus, 10 mol% decane in contact with pure water at about 95°C would produce a distillate that is about 58 wt% decane, even though the partial pressure of decane from the organic solution is less than 2% of that of pure water. TBP under similar conditions would produce a distillate that is about 0.2% TBP.

It is predicted that volatilization processes will have accommodated the depletion of light organic fractions in the organic phase. The range of vapor pressures of the various organic compounds entering the tanks is great. As an example, at 80°C the vapor pressure of decane is 25 torr and of tetradecane about 1.2 torr. Both are constituents of the NPH diluent used with TBP. To further raise the higher molecular weight fraction there is some polymer formation as a result of radiolysis. Thus, although there is a constant formation of hydrogen and light hydrocarbon fragments, there may be a trend with time towards higher molecular weight organic material.

If we consider the case where the aqueous phase gradually disappears by evaporation, nonvolatile organic compounds dissolved in the aqueous phase will eventually either partition to the organic phase or form a new phase, either solid or liquid, due to additional salting out as previously described.

4.3 Solid Phase Concentration Mechanisms

Concentration mechanisms involving the solid phase are important because individually or together they could increase the localized concentration of organics well above that dissolved in the interstitial liquids of the solids, and would persist in the salt cake and/or sludge at these concentrations even if the (drainable) aqueous liquids are drained from the tank. Subsequent drying of these solids and heating to high temperatures could cause the nitrate solids and organics to ignite. The explosion potential of such a mixture would depend on several factors, including the fuel value of the organics and the concentration of inert solids.

A major portion of the total inventory of chemicals in the USTs are solids that either were added to or generated within the tanks over the years, and thus vary in composition among the different tanks. At the present time, the inventory of salt cake and/or sludge in individual SSTs and DSTs ranges from 0% to 100%. The term "salt cake" is used to describe the solids that are considered to be soluble in water. Major constituents of salt cake are sodium nitrate and sodium nitrite. "Sludge" describes the solids considered to be insoluble in water. These solids contain iron, bismuth, aluminum, silicon, chromium, zirconium, lanthanum, phosphorous, inorganic carbon, fluorine, sulfate, and lesser quantities of other metals. A large portion of these solids is in the form of hydroxides, with lesser amounts of carbonates, phosphates, zirconates, fluorides, and sulfates. Both salt cake and sludge contain substantial quantities of water that fills the pores.

In general, very little organic solids were added to the tank. The only large quantity that would have been added is ion-exchange resins. Precipitated salts of certain organic acids, such as sodium oxalate, may have been added if they were in sufficient concentration and were neutralized prior to disposal in the tanks. Small quantities of other organic solids were added to the tanks, but are not believed to be significant.

Even though the solids in the tanks are almost all inorganic compounds it is very possible for organics in the tank to concentrate in this phase over time through precipitation, adsorption, or absorption. These mechanisms are described in this section. The chemical degradation of organic resins in the tank is also discussed; these resins constitute a potentially important organic solid added to the tanks.

4.3.1 Precipitation of Organics

Precipitation of organic compounds as solids from concentrated wastes containing crystalline NaNO_3 and/or NaNO_2 is a mechanism by which solid organic-oxidant mixtures could be produced with organic-to-oxidant ratios significantly different from the waste tank average ratios. Precipitated organics could form mixtures with NaNO_3 - NaNO_2 either by crystallization of NaNO_3 - NaNO_2 simultaneously with precipitation of the organics or by drainage of the bulk aqueous phase followed by evaporation of NaNO_3 - NaNO_2 -containing interstitial liquid in the already precipitated organics.

The chemicals of interest in the USTs are those polar, water-soluble compounds that can form metal salts. A large number of organic compounds normally thought of as water soluble have entered the waste tanks. These compounds include sucrose for denitration and a large number of organic acids or their sodium salts used for complexation and pH control. These acids include oxalic, glycolic, citric, tartaric, gluconic, EDTA, HEDTA, and others, many of which were added in large quantity in such operations as B-Plant fission product recovery. In addition to these acids, smaller quantities of numerous other water-soluble organics were added as components of commercial cleaning and related agents. Klem (1990) lists about 40 tradename materials used in the 221-T Plant decontamination facility. Some contain at least several, and perhaps more, organic compounds in varying quantity. The water-insoluble compounds are present largely for degreasing (chlorinated organics) or for dissolution of organic films, cruds, or varnishes (toluene), whereas the water-soluble compounds are present largely as metal complexing agents (oxalate, citrate, tartrate, etc.); weak acids (acetic acid); surfactants for both cleaning action and for keeping immiscible solvents and corrosion inhibitors dispersed in the cleaning agent itself (sodium xylene sulfonate, nonylphenoxypolyethoxy ethanol); and corrosion inhibitors (2-mercaptobenzothiazole, etc.).

In addition to the large number of organic compounds added to the wastes in widely varying amounts, these compounds have no doubt degraded to produce an even greater variety of compounds through both radiolytic and chemical attack. Numerous organic compounds have been identified in Hanford waste tanks (Toste et al. 1988; Hendrickson 1990; Lokken et al. 1986), and many are reasonable degradation products of the major organics added to the wastes. A very prominent degradation product is oxalic acid. Indeed, it was the most abundant organic compound identified in Tank AN-103 constituting (by weight) about half of the approximately 40 organic compounds identified (Hendrickson 1990). Oxalic acid is produced by nitrate oxidation of sugar and is a likely product of degradation (radiolytic and chemical) of tartrate, citrate, glycolate, and perhaps of amino-polyacetate chelating agents, and was also added directly in some cases. Other degradation products include fragments of chelating agents such as EDTA (Lokken et al. 1986; Toste et al. 1988; Hendrickson 1990). These fragments are often themselves chelating agents. Other degradation products include various carboxylic and dicarboxylic acids. Degradation of nonpolar solvents and extractants will also produce organic acids that will form sodium salts in the aqueous phase. These include carboxylic acids from alkane solvent oxidation and oxidation of alcohols from organo-phosphoric acid salts such as those of DBP and MBP.

Although sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) is considered a soluble compound, its solubility is only 37 g/L in water at 20°C. Its solubility is even lower in aqueous solutions containing excess Na^+ concentration. The solubility given by Seidell (1953) in essentially saturated NaNO_3 solution is 0.051 g/100 g solution, at 15°C with 45.86 g NaNO_3 /100 g solution. At 50°C, the solubility is 0.047 g/100 g solution and 53.66 g NaNO_3 /100 g solution. Using density data from Hodgman (1947) yields a solubility value of 0.0052 M $\text{Na}_2\text{C}_2\text{O}_4$ at 7.43 M NaNO_3 at 15°C and a value of 0.0051 M $\text{Na}_2\text{C}_2\text{O}_4$ at 9.05 M NaNO_3 at 50°C. Many of the waste tanks are saturated with NaNO_3 and NaNO_2 and because many have significant amounts of the very soluble NaOH as well as NaAlO_2 , it can be expected that the Na^+ concentration is higher than those shown above. Thus, for Tank SY-103, the reported concentration of Na^+ in the interstitial liquid is 11.3 M (Bryan et al. 1992). Under these conditions, the solubility of $\text{Na}_2\text{C}_2\text{O}_4$ can be expected to be significantly less than the values from Seidell shown above.

It should be noted that other cations (such as Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , lanthanides, and others) form even less-soluble oxalates. These metals are, however, present in much smaller quantities than Na^+ is and they form other even less-soluble compounds with some or all of certain other anions which may be present in widely varying amounts. These anions include phosphate, carbonate, and hydroxide. These metals, then, can be expected to precipitate oxalate only if their concentrations exceed the concentrations of inorganic anions with which they form even less-soluble salts. These metals will also not precipitate oxalate if they are complexed by adequate amounts of chelating agents (including certain degradation products of the original chelating agents). Based on what is known of tank compositions (pH, phosphate concentration, etc.) it seems that other metals such as alkaline earths and actinides will probably have little effect in controlling oxalate solubility.

An overall oxalate concentration of 2.6 mg/g waste has been reported for Tank AN-103 or about 0.045 M (Hendrickson 1990). This is at least 10 times the expected solubility based on the discussion above. However, the reported 36 mg/g of aluminum in this waste may account for the high oxalate concentration, because it is known to form oxalato-hydroxo compounds.

The solubilities of salts of other organic acids derived from complexing agents, buffering agents, and diluents are less easy to predict. Not only are the solubilities of the sodium salts of many of

these acidic materials high, but many are also present in considerably smaller amounts than is oxalate. The solubilities of the sodium salts of chelating agents such as EDTA and HEDTA are high, both being purchased as 40% solutions (Buckingham 1967). Sodium citrate, tartrate, glycolate, butyrate, and salts of longer chain mono- and dicarboxylic acids are generally quite soluble. Data are limited or nonexistent for other organic compounds which have been identified in the waste, particularly for very high salt concentration. One example of the effect of high Na^+ concentration is the solubility of sodium butyrate, which decreases from 207 g/kg solution at 169 g Na_2O /kg solution to 7.7 g/kg solution at 406.2 g Na_2O /kg solution (Seidell 1953). This lowest solubility is still greater than the probable abundance of butyrate in the waste. The solubility of alkaline earth, uranyl, and other polyvalent cation salts of long chain carboxylate acids (soaps) is quite low, but again it is questionable whether they would form because these metals may be preferentially tied up with phosphate, carbonate, chelating agents, etc.

The longer chain acids and surfactants will also have the potential to salt out of solution in highly ionic solutions encountered in the tanks, but they will exhibit soap characteristics and will not form a precipitate as discussed in Section 4.2.1. Similarly, the sodium salts of D2EHPA and the degradation products of TBP (DBP and MBP) will also tend to salt out of the aqueous solution and possibly form a separate organic phase as previously discussed.

In summary, precipitation of sodium oxalate in waste tanks containing more than a few thousandths molar total average oxalate concentration is expected in the absence of aluminum. Precipitation of other salts of organic acids cannot be as clearly predicted, although it cannot be clearly ruled out either. Co-crystallization of salts or related organic compounds might occur in which the sum of the concentrations of isomorphous compounds exceeds the overall solubility product.

4.3.2 Adsorption of Organics

Adsorption of organics onto the tank solids is a probable concentration mechanism, because the surfaces of solids are known to adsorb a number of organic compounds from aqueous solutions. Cleaning with soaps and detergents; flocculation; ore flotation; and water purification using adsorbents such as activated carbon are all based on this mechanism. This is because most inorganic solids carry a surface charge, and polar organics with an opposite charge will be strongly attracted to the surface and will likely be adsorbed. The adsorption mainly occurs due to strong electrostatic attractions between the charged surface and polar molecules in solution. Nonpolar organics such as the alkanes are also attracted to the polar solid surfaces by weaker forces such as Van der Waals forces, but they normally will not preferentially adsorb in water because they do not compete effectively with water or electrolytes in solution.

Hanford wastes contain significant amounts of organic compounds with polar groups that might be expected to adsorb on inorganic surfaces. These compounds include in particular, but are not necessarily limited to, many of the chelating agents and their degradation products, carboxylic and dicarboxylic acids from oxidation of NPH or other sources, detergents and surfactants from decontaminating agents, and corrosion inhibitors also from decontaminating agents Toste et al. 1988; Lokken et al. 1986; Hendrickson 1990). These materials can be expected to be adsorbed through

their polar ends to inorganic solids in the USTs. In fact, molecules like dicarboxylic acids and possibly some of the chelating agents or fragments might actually attach to two solid particles and act as flocculants.

Evidence of this mechanism is suggested by recent research using simulated Hanford waste designed to simulate the waste in double-shelled Tank SY-101 (Bryan et al. 1992). This research was conducted to determine the influence of the chelating agents EDTA, HEDTA, and citric acid on the gas generation and "slurry growth" in Tank SY-101. Comparison was made of simulated wastes containing EDTA and HEDTA; simulated solutions containing only the inorganic constituents; and simulated solutions containing the inorganic constituents and HEDTA, EDTA, and citric acid separately. Floating, nonrigid "crusts" due to gas bubble attachment were formed in the solutions containing either EDTA or HEDTA but not in the other two solutions when the solutions were sparged with fine N₂ bubbles and allowed to stand for 30 min. In addition, a much larger fraction of the solids remained in suspension in the solutions containing EDTA or HEDTA than in the control or in the citrate solution. There was evidence (NO_x evolution) that citrate had decomposed. This gas bubble attachment is attributed to the adsorption of these two organic compounds onto the inorganic surfaces through their polar (carboxylate groups). The floating crusts observed in this research also illustrate the potential for surfactants to cause tank solids to float to the surface of the aqueous phase.

The concentration of organics caused by adsorption on solids in the salt cake and sludge depends on a number of factors that can affect the amount of adsorption and resulting concentration by several orders of magnitude. Physical properties of the solids including porosity and the surface-to-volume ratio have a direct impact on the concentration mechanism. The discussion of these properties in Section 4.3.2.1 suggests that the concentration could vary by 2 or more orders of magnitude, depending on the surface-to-volume ratio alone. Sections 4.3.2.2 and 4.3.2.3 discuss the concentration mechanisms involving adsorption and the maximum possible concentration of organics in the sludge and salt cake that could occur due to these mechanisms. Calculations of maximum concentrations caused by these mechanisms suggest that total organic carbon concentrations could be 100 g/L or greater for solids with specific surface areas of 100 m²/g. There are, however, a number of competing physical/chemical effects that can reduce the degree of adsorption by several orders of magnitude: the type and molecular weight of the organics present; the pH of the aqueous phase; and the concentration of electrolytes in the aqueous phase. Each of these effects is discussed in Section 4.3.2.4. Furthermore, it must be emphasized that an insufficient inventory of adsorbable organics relative to the inventory of solids can place a more restrictive upper limit on the achievable concentration. This factor alone could override all other considerations for this mechanism where the organic-to-solids ratio is very low.

The likelihood of achieving the high concentrations possible is probably not great, given competing interactions described. However, the fact that adsorption does occur in relatively simple simulated waste (Bryan et al. 1992) and the magnitude of this estimated value indicates that, without further data, adsorption of organics on solids must be assumed to be capable of significant concentration of organics in the waste tanks. Only with further experimental work and analytical work on tank sludges can the actual degree of concentration of organics by this mechanism be determined.

4.3.2.1 Effect of Surface Area on the Concentration of Organics

Adsorption is a surface phenomenon. Therefore, the degree of concentration of surfactants caused by adsorption on the tank solids depends on the available surface-to-volume ratio. Assuming a simple case of spherical particles not containing pores, and assuming that the solids content of the salt cake and sludge is 60% by volume with the balance being supernate, the unit surface area (cm^2/cm^3) can be calculated as a function of particle diameter. Figure 4.1 shows the inverse relationship between the particle size and the unit surface area of the sludge solids. The corresponding relationship between organic carbon concentration and the particle diameter is also illustrated in the figure for the maximum adsorption of dodecylbenzene sulfonate, which is further discussed in Section 4.3.2.2.

Solids in the USTs consist of two classes of materials, strongly ionic nitrate and nitrite salts and weakly ionic insoluble salts, such as the phosphates, carbonates, and hydroxides. The insoluble solids in the sludge are generally believed to be composed of very small particles. Some particle size distribution data have been obtained for sludge solids in Tanks 101-SY, U-110, and B-110 (Herting et al. 1992; Jones et al. 1990; and Westinghouse Hanford Company 1990). The data for B-110 showed a mean particle diameter of $0.91\ \mu\text{m}$, on a number basis, with 56% of the measured particles less than $1\ \mu\text{m}$ in diameter and over 80% less than $2\ \mu\text{m}$ in diameter. On a volume density basis, however, the mean diameter was $15.2\ \mu\text{m}$ with 50% of the total volume less than $14\ \mu\text{m}$, and over 80% less than about $23\ \mu\text{m}$. The mean diameter, on a number basis, ranged from 0.91 to $1.89\ \mu\text{m}$ for data from the analysis of five core sample segments from U-110. The average mean diameter for the five samples on a volume basis ranged from 8.48 to $12.64\ \mu\text{m}$. Data from Tank 101-SY appeared to show similar trends with over 50% of the particles having a diameter of $1\ \mu\text{m}$ or less and over 80% having a diameter of $4\ \mu\text{m}$ or less.

The above data, while limited, suggest that the particle diameters in the range of 1 to $20\ \mu\text{m}$ could be characteristic of the sludge and possibly the salt cake in some cases. Using Figure 4.1 for this range of particle diameters, the surface-to-volume ratio would be on the order of about 1800 to $36,000\ \text{cm}^2/\text{cm}^3$ (180 to $3600\ \text{m}^2/\text{L}$). This range of surface-to-volume ratios represents a lower limit for the solids in the tank in this particle diameter range.

The insoluble solids consist of a number of minerals, including hydroxides, silicates, carbonates, and phosphates. Particles made from these materials will have surface areas larger than predicted by measuring their apparent diameter, because particles are not spherical and may possess internal pores, providing additional surface area. This may be particularly true for the very insoluble hydrous oxides of metals such as Al, Fe, Zr, Cr, Ni, and various fission products. As examples of the surface areas that might be expected, gelatinous alumina (boehmite) may have surface areas in the range 400 to $600\ \text{m}^2/\text{g}$ after drying at 120°C and from 250 to $400\ \text{m}^2/\text{g}$ after drying even at 500°C (Lippens 1970). Other types of activated alumina possess surface areas on the order of 200 to $300\ \text{m}^2/\text{g}$ (Perry and Chilton 1973). Zirconia formed by precipitation of zirconyl chloride solution by base followed by boiling with base and drying at 120°C produces materials with a surface area of about $370\ \text{m}^2/\text{g}$ (Rijnten 1970). Other very insoluble hydrous oxides present in the waste tanks may be expected to have similar surface areas. Various silicas are available with surface areas of 200 to $600\ \text{m}^2/\text{g}$ even after heating to temperatures as high as 500°C (Okkerse 1970). It is assumed that silica gels could only form in the lower pH tanks. The common minerals, kaolinite and montmorillonite, have surface areas on the order of 11 and $97\ \text{m}^2/\text{g}$ (Ong and Lion 1991).

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Figure 4.1. Particle Surface Area and Carbon Concentration for Sodium Dodecylbenzene for Spherical Particles

It should be noted that the surface areas of the oxides such as alumina and zirconia quoted above are measured by the BET methods (N_2 adsorption). Some of the surface area measured by this method may not always be available for adsorption of larger organic molecules because of steric effects in crevices and pores. For this reason, only an upper limit estimate for amount of adsorption can be made here based on the assumption of complete covering of the surface with a monolayer of organic molecules.

The nitrate salts in the salt cake are generally believed to consist of large particles and would not provide a significant surface area for adsorption. Typically, if $NaNO_3$ were crystallized from water, essentially smooth surface crystals of 1 mm or more on a side and a corresponding surface area of the order of $0.01 \text{ m}^2/\text{g}$ or less might be expected. It should be noted, however, that analyses of the particles measured in the U-110 and B-110 tanks suggest that a portion of the solid particles may be nitrates. The possibility of smaller diameters for nitrates in these solids could be explained by the fact that the insoluble solids present a very large surface area for nitrate crystals to grow on, thus limiting their growth. Alternatively, it is known that adsorption of trace levels of various materials on growing crystals can very markedly alter the morphology of the crystals produced, if organics in the waste tanks were present at the time of crystallization of these salts. Preferential adsorption on certain crystal planes can very markedly alter the shape and size of the crystals produced. Therefore, it is far from certain that the surface area of solid salts such as $NaNO_3$ and $NaNO_2$ formed in the complex mixtures present in the waste tanks might not have larger surface areas than expected from crystallization from water solutions.

It can be seen from the analysis that a specific surface area on the order of $100 \text{ m}^2/\text{g}$ or greater could be plausible for the tank solids. Assuming that the tank sludge contains 60% solids, by volume, and that those solids have a specific gravity of 3.0, then a specific surface of $100 \text{ m}^2/\text{g}$ would correspond to a surface-to-volume ratio of total of $1.8(10)^6 \text{ cm}^2/\text{cm}^3$ ($180,000 \text{ m}^2/\text{L}$) of sludge. This value is 36 to 670 times larger than the ratio that can be attributed to the diameter of the particles.

4.3.2.2 Maximum Concentration Due to Surfactant Adsorption

An approximate maximum loading of surfactants on the surface of solids can be made by assuming a $50\text{\AA}^2$ surface area occupied by a surfactant molecule at saturation conditions. This value is typical of alkyl sulfate and sulfonate surfactants. Using sodium dodecylbenzene sulfonate as an example of a surfactant added to the tank wastes, the surface loading on the solids would be $3.3(10)^{-10} \text{ moles}/\text{cm}^2$. This corresponds to a loading of about $1.1(10)^{-7} \text{ g}/\text{cm}^2$ of surfactant or about $7.1(10)^{-8} \text{ g}/\text{cm}^2$ of organic carbon. Assuming a $180,000 \text{ m}^2/\text{L}$ surface area as discussed in Section 4 3.2.1 a surfactant concentration of $0.4 \text{ mol}/\text{L}$ can be achieved for dodecylbenzene sulfonate. This corresponds to a total organic carbon value of $129 \text{ g}/\text{L}$.

Carboxylic acids, which are also believed to be present in the tanks as degradation products, also have some surface activity. Generally, linear carboxylic acids need to contain 8 or more carbon atoms in order to display surfactant character (Schwartz and Perry 1949). The cross-sectional area for an aliphatic chain is about 0.22 nm^2 as determined by the behavior of molecules such as stearic, palmitic, and cerotic acids and cetylalcohol at an interface (Daniels 1948). Using this value, it can be calculated that if the surface is completely covered by a monolayer there will be about $7.5 \times 10^{-10} \text{ mole of organic}/\text{cm}^2$ of surface. Again assuming a $180,000 \text{ m}^2/\text{L}$ surface area, a surfactant concentration of $1.4 \text{ mol}/\text{L}$ can be achieved for a linear chain carboxylic acid. This

corresponds to a total organic carbon value of 162 g/L for a C_{10} carboxylic acid. It should be noted, however, that branched chain organics will occupy more space per molecule. In fact tristearin, $[(C_{18}H_{35}O_2)_3C_3H_5]$, a three-chain molecule, occupies 0.66 nm^2 when adsorbed (Daniels 1948).

4.3.2.3 Effect of Admicelle Formation on Concentration

In addition to the loading of the solid surfaces with surfactant it is possible for the surfactant to further concentrate by forming admicelles by the attraction of the nonpolar end of the adsorbed surfactant to the nonpolar end of a surfactant in solution. As a result of this attraction, a second layer of surfactant can be adsorbed to the first layer, effectively doubling the concentration of organic carbon on the solid surfaces. This additional layer of adsorption occurs when the aqueous solution is saturated with surfactant. This condition is considered possible in the USTs because carboxylic acids and other surfactants containing 10 or more carbon atoms are relatively insoluble in water. For example, sodium dodecyl benzene sulfonate achieves saturation at about 10^{-3} M (its critical micelle concentration) in water and would be even lower in the presence of electrolytes.

The formation of admicelles also makes it possible to further increase the concentration of organics at the solid surfaces by extracting hydrophobic organics such as the longer carbon chain alkanes from the aqueous phase and into the admicelles. Data obtained by Dr. R. L. Zollars, Washington State University, when examining the solubilization of monomers, as well as data reported by Smith et al. (1989), indicate that for materials of very low water solubility, approximately two molecules of sodium dodecyl sulfate are required to solubilize one organic molecule. The number of surfactant molecules necessary to solubilize a molecule of an organic decreases as the normal solubility of the organic increases.

Complexing agents like EDTA will also partition into organic phases such as the admicellized alkane. The exact amount of complexants that will dissolve into the admicellized alkanes is unknown. Gu, Wasan, and Li (1988) observed this behavior in experiments with emulsion membranes to extract EDTA from an aqueous phase into an emulsified organic phase admicellized by a surfactant membrane. In these experiments, about five times as much complexant as surfactant by weight was used. However, the system investigated did not fully represent admicelle conditions expected at a solid surface. Thus, the 5-to-1 ratio is speculative, but provides a gross indication of the potential for the surfactant to concentrate complexing agents near the solid surface.

The effect of this extraction phenomenon on organic carbon concentration depends in part on both the size of the organic molecule adsorbed and the number of molecules adsorbed per molecule of surfactant. If it is assumed that one molecule of organic, containing the same number of carbon atoms as the surfactant molecule, is extracted for every two (C_{10}) surfactant molecules, then this mechanism will increase the organic carbon concentration at the surface by 50% over that attributed to the double layer of surfactant alone.

4.3.2.4 Other Parameters Affecting Adsorption of Organics

The adsorption of surfactants onto the solid surfaces involves competition among the surfactant, other polar molecules, and electrolytes in solution for adsorption sites on the solid surface. Usually, in order for a surfactant to be strongly adsorbed to a solid surface, the surface charge is opposite to that of the surfactant. The net surface charge on a solid occurs due to the net charge of the lattice ions at its surface. The net surface charge may be positive or negative depending on the

concentration of the corresponding counter ions in solution that are in equilibrium with the surface. At the point of zero charge (PZC), the concentration of these ions is such that the surface possesses no net charge. In the case of the hydroxide-based solids as are found in the tanks, the pH of the solution (and thus the hydroxide ion concentration) is compared with the pH at the PZC in order to determine the surface charge. For many hydroxide minerals in water, the PZC ranges from about 4.5 to 9.5 (Somasundaran and Ananthapadmanabhan 1987). The PZC of other minerals, such as calcium carbonate and silicates, is also influenced by pH. The pH at the PZC for silicates ranges from 2.7 to 7.9. For calcium carbonate the pH at the PZC ranges from 8 to 10.8.

The influence of surface charge on the amount of surfactant adsorbed can be significant. Somasundaran and Ananthapadmanabhan (1987) presented data that indicate a decrease in adsorption density of over 3 orders of magnitude for alumina as the PZC is approached due to pH changes.

Other factors besides electrostatic attraction can influence the adsorption behavior of surfactants. Iwasaki, Cooke, and Choi (1960) noted that increasing the number of carbon atoms in the surfactant can translate the ability of a surfactant to adsorb to higher pH values. They observed that while the flotation of goethite ($\text{FeO} \cdot \text{OH}$) with dodecyl sulfate or sulfonate would occur up to a pH of 6.7 as would be expected by its PZC, flotation with a surfactant possessing 18 carbon atoms would occur up to a pH of 10. Some other interactions that can affect adsorption include lateral associative interactions between adsorbed species at high concentrations, covalent bonding between the surfactant and the mineral lattice, and hydrogen bonding.

Another potentially significant consideration in evaluating surfactant adsorption is the effect of electrolyte concentration on the behavior of the surfactant. As previously discussed in Section 4.2.2, increasing the ion strength of an aqueous solution causes organics to salt out of solution. This is known to apply to the surfactant-type organics as well. As a consequence, the surfactant will be driven out of the aqueous phase and into a separate organic phase or to either the gas-liquid interface or the gas-solid interface. In the latter case the surfactant will concentrate on the solids by adsorption. As often happens in mineral processing, the most stable alignment will be with the hydrophilic end attached to the surface and the hydrophobic end forming admicelles as previously described.

4.3.3 Absorption of Separate Organic Phase

Another potential mechanism involves the interaction between a separate organic phase and the solids. Many of the SSTs have been drained of free liquids by pumping them from the bottom of the tank. A separate organic layer, floating on the surface of the free liquids in the tank, would eventually come into contact with the tank solids if the free liquid were to be drained. A potential consequence of this scenario would be the concentration of organics in the interstitial spaces between the solids.

The interaction between bulk hydrocarbon phases and solids has been a subject of considerable interest in the transport of hydrocarbons in soils. In oil spills on soil, the bulk hydrocarbon phase will infiltrate unsaturated soil, filling up a portion of the pore space by displacing air and free (drainable) water. If organic compounds have adsorbed onto the solid surfaces, as discussed in the previous section, then interstitial (nondrainable) water may also be displaced by a floating organic layer as a tank is drained. If the layer encounters the capillary fringe of the water table, the weight of the

organic phase will collapse a portion of the capillary zone and depress the water table. The net effect is that as the hydrocarbon infiltrates the soil, a portion of it is retained by the soil at a residual saturation level. It is interesting to note that when bulk hydrocarbons constitute the solvent in soils and clays, the hydraulic conductivity tends to increase, making infiltration more easily achieved (Dragun 1988). This behavior is attributed to the effect of the bulk hydrocarbon on the interparticle spacing. Among those hydrocarbons demonstrating this behavior are kerosene, motor oil, naphtha, and paraffin oil.

The residual saturation level for a hydrocarbon is defined as the maximum fraction of the soil pore volume that is occupied by the immobilized hydrocarbon in the soil (Palmer and Johnson 1989). This value ranges from about 0.1 for gasoline to 0.15 and 0.2 for diesel fuel and heavy fuel oil, respectively (Dragun 1988). For comparison, the residual saturation level of water is about 0.33. Soil porosity ranges from about 20% to 60% of the bulk soil volume but generally averages about 40%. Assuming a similar porosity for the tank solids, and a specific gravity of 1.0 for the hydrocarbon mixture in the organic phase, this would translate into a concentration ranging from 40 g/L to 80 g/L in the solids over the zone where the organics were deposited in the solids

If the absorption takes place uniformly in the solids, this concentration would occur at the uppermost portion of the solids that the organic passes through, extending downward to the point where the total inventory of the hydrocarbon layer has been retained at the residual saturation level. For an initial thickness of the separate organic phase of 2.5 cm, this depth would be about 30 to 60 cm. In fact, the solids surface will contain fissures and macropores leading to preferential paths for draining the organics, and localized concentrations will penetrate to greater depths. It has also been noted that if the organic saturated zone is again flooded with water, only a portion of the organic will be displaced because it will remain at the residual saturation level (Palmer and Johnson 1989). It is this phenomenon that has made remediation of soils and groundwater containing nonaqueous phases so difficult. The water will resolubilize a portion of the organic, however.

If the organic is allowed to penetrate to the point where free organic phase contacts a strata containing free water that was not drained from the tank, then it will float on the surface of the capillary fringe of this strata and migrate laterally. If there are localized seams or pockets of coarser-grained solids, just below the capillary fringe above the water level, they may trap free product. This behavior was observed in thin sand seams interbedded in fine-grained silty clay sediments at two different sites by Krueger and Portman (1991). In the context of the tanks, this particular phenomenon would only be applicable where there was sufficient organics relative to the quantity of solids to make it possible for the organics to reach the bottom of the tank as a free phase and either encounter a layer of undrained water or subsequently encounter a refilling of the tank with water.

Displacement of water-saturated solids with an organic liquid, as the water is drained, will not necessarily follow the scenario described for unsaturated soils. However, a second possible consequence could be the displacement of the free water. In this case, the organic would not necessarily be retained at a residual concentration and would reside just above the level of water-saturated solids. Assuming that the residual water is 33% of the pore volume in this zone then approximately 67% of the soil pore volume will consist of free water that could be displaced by the organic liquid. In fact the porosity could change due to changes in the interparticle spacing. By the same logic as described for the unsaturated soil, the concentration of organic could be as high as 270 g/L in the bed of solids and would penetrate to nominal depth corresponding to about 3.7 times the original thickness of the organic layer.

In both mechanisms, the rate of penetration depends on the properties of the solid and liquid phases and the forces acting on the fluids. If the hydraulic conductivity of the solids for the organic liquid and/or water is very low, then the rate of displacement will be correspondingly slow. For example, a hydraulic conductivity of 10^{-7} cm/s is typical of water in clays composed of micron-size particles, and the draining rate of water because of gravity would be only about 3 cm/yr (HMCRI 1987).

4.3.4 Ion-Exchange Resins

Ion-exchange resins constitute a potentially significant source of organic solids that were added to the USTs. It would appear that as much as 5,000 to 10,000 gal (20,000 to 40,000 L) of resin were added to Hanford waste tanks; most was Duolite ARC-359. All the organic ion-exchange resins that are believed to have been used onsite in significant quantities can be expected to have actual particle densities of about 1.1 g/mL to about 1.3 g/mL, with the densities varying somewhat with the resin and with the ionic strength of the solution it is contacting. Since typical high salt wastes have densities of about 1.4 to 1.6 g/mL, all of these resins remaining as solids can be expected to be in a layer floating on top of the aqueous phase. Draining the tank liquid could then be expected to leave a layer of ion-exchange resin on top of any sludge layer present.

The main mechanism affecting the concentration of ion-exchange resins is radiolytic and chemical degradation into water-soluble polyelectrolytes. The degree of degradation depends both on the type of resin and the radiolytic and chemical environment. Ion-exchange resins were used in the PUREX, REDOX, B-, and Z- (Plutonium Plutonium and Waste Treatment) Plants and in the tank farms evaporation so idification project. Consequently, each encountered different tank environments and will have undergone different degrees of degradation.

Permutit SK and its chemically identical successor, Ionac A-580 anion-exchange resin, are polyvinyl pyridine resins with methyl groups attached to some of the nitrogen rings. They were used in both PUREX and REDOX for final plutonium processing through part of the life of each plant. Permutit SK or Ionac A-580 was used in rather small quantities in PUREX and REDOX in Higgins-type semi-continuous contactors. The inventory per contactor was probably less than 100 L and the spent resin was discharged no more frequently than about every 2 months, amounting to probably less than 600 L/yr discard at each of the two plants. Both Dowex 21K and Amberlite XE-270 are polystyrenedivinyl benzene anion-exchange resins with trimethylammonium groups attached that were used in PUREX for final Np purification. The Dowex 21K and Ambertite XE-270 resins were used in static columns, and the annual discard levels should have been less than for the Pu processing resins because of the lower alpha radiation damage produced by Np than Pu and because the mass of Np processed was much less than the mass of Pu processed.

It appears that all of the anion-exchange resins used in PUREX and REDOX were discarded to the high-level waste tanks along with the waste being produced at the time. It is expected that this resin (which was only used for a portion of PUREX or REDOX Plant operating life) would have been dissolved by radiolytic and chemical attack well before the present. At 1-year cooling, typical irradiated Hanford reactor fuel produced about 380 Watts/ton U (Van Tuyl 1967) and about 500 L of neutralized waste were produced per ton U (PUREX Manual 1955). This 0.76 W/L corresponds to about 2×10^9 rad/yr, which is probably about twice the radiation dose expected to be required to completely dissolve the more radiation-resistant of these resins (Permutit SK or Ionac A-580), since it

is known that these resins are extensively decrosslinked at $< 5 \times 10^8$ rad (Ryan and Wheelwright 1959). It should also be noted that these anion-exchange resins are particularly susceptible to chemical degradation by hydroxide solutions, especially at elevated temperature, and it is recommended by the manufacturers that they not be used above about 50°C to 60°C in the hydroxide form or in hydroxide solutions. The tanks containing fresh PUREX or REDOX waste were at or near boiling and were very alkaline. Based on both radiolytic and chemical attack, it is expected that the anion-exchange resins have been dissolved to produce very soluble polyelectrolytes. Whether these polyelectrolytes have been completely depolymerized by now is less certain, but the existence of much smaller organic molecules derived from these resins is probable.

Duolite ARC-359, a sulfonated phenolic cation-exchange resin, was used for Cs removal both in B-Plant and in the tank farm evaporation-solidification process. In the former case Cs was removed from the alkaline high-level waste, and in the latter it was removed from condensate produced by waste evaporation-crystallization. Duolite ARC-359 cation resin was used in B-Plant in an approximately 6500 to 8500 L column for removal of Cs from alkaline high-level waste. This resin was changed out about every 2 to 3 years and at least part of it ended up in a high-level waste tank containing wastes already treated for Cs and Sr removal. (A March 1, 1979, internal Rockwell letter written by J. S. Buckingham states that this resin went to tank BX-101 having a radioactive heat production rate of 0.02 W/L.) It is also the recollection of others associated with B-Plant that during a significant part of B-Plant operation resin was dewatered and buried.

Duolite ARC-359, a sulfonated phenol-aldehyde condensation polymer, is considered to be quite radiation resistant, showing only slight capacity losses at 5×10^8 rad (Kalkwarf 1977). It can then be expected that radiolysis alone at a level of 0.02 W/L would not have destroyed or dissolved this resin. These resins are only moderately stable to alkali and dissolved oxygen though (Helfferic 1962), and it is not certain that they will have survived chemical attack. Chemical breakdown of the resin should solubilize any remaining organic material since sodium salts will be formed with both the sulfonate and phenol groups at high pH. These groups would have to be removed without forming carboxylate groups in their place in order to form insoluble organic compounds from resin fragments.

Quite small amounts of Dowex 50 were used for Am-241 recovery in the Plutonium Reclamation Facility in Z-Plant. In addition, at an earlier time, a larger (presumably annular) column of Dowex 50 was used in Z-Plant to remove trace levels of Pu (and Am) from a large volume, low acidity, low ionic strength waste referred to as "sump water." Also at one time, Permutit SK was used to recover Pu from oxalate supernate in Z-Plant. It seems almost certain that all of these resins in contact-operated alpha facilities were disposed of as solid transuranic waste and were never introduced to the high-level waste tanks.

In addition to these routes of introduction of resin into the high-level waste tanks, a small amount came from Pm-147, Sr-90, and Pu-238 recovery operations in the 325 A Building hot cells in 300 Area. E. J. Wheelwright, who was closely associated with this operation, estimates a total of less than 100 gal (380 L) of resin went to tanks by this route, of which ~20% (76L) was Dowex 1, X-3 or Dowex 1, X-4 anion exchanger, and the remainder was Dowex 50. It is not known which tanks this material was routed to.

4.4 Gas Phase Concentration Mechanisms

The overhead space in the passively ventilated USTs could allow volatile organic compounds to preferentially concentrate to flammable levels. Because the ventilation system is open to the atmosphere, air enters the tanks and provides a source of oxygen for combustion. On the other hand, the ventilation system provides a path for organics in the overhead space to leave the tank, thereby reducing the amount of volatile organics.

The primary organics concentrating in the gas space are expected to be from the free surface liquid phases or the solid phase if the free liquids have been drained. The major depletion mechanism is due to convective or diffusive transport of gases to the outside air, through ventilation ducts. Another consideration affecting concentration mechanisms in the overhead space is the potential condensation of vapors in the gas space and onto surfaces enclosing the overhead space. However, the inventory of condensate that has not returned to the surface of the free liquids should be relatively small and should behave in a manner similar to that in the free liquid phase.

The main safety issue, in evaluating concentration mechanisms for organics in the vapor space, is whether a combustible mixture will result. In order to conduct a complete evaluation of this condition other inorganic fuels such as hydrogen and ammonia should be considered, as well as the concentration of oxidants in the overhead gas. Borsheim and Kirch (1991) conducted an assessment of organic solvent flammability that considered the interactions of a mixture of organics using gas phase data obtained for Tank C-103, which is known to contain a significant inventory of TBP and NPH. Table 4.3 taken from their report illustrates contributions of key organic and inorganic flammable vapor components to the vapor mixture. It can be seen that ammonia and hydrogen could make up over 97% of the flammable mixture. The calculated lower flammability limit of the mixture is 11.8% using Le Châtelier's rule, which also shows the influence of these components on the lower flammability limit of the mixture. It should be noted that this value may not be truly representative of the actual flammability limit for Tank C-103 because the values for the organic constituents were obtained using an unproven sampling method that was not validated and is now believed to have produced suspect data.

The concentration of oxidants in the vapor space is also a major consideration in assessing the flammability of vapors in the vapor space. Like the fuels there are limits to the amount of oxidant that must be present in a mixture in order to sustain combustion. Upper and lower flammability limits cited in the literature assume a fuel-air mixture. However, if the oxygen concentration of the mixture is lower due to the presence of nonflammable components other than those in the air, then the two limits converge until a point is reached, as shown for hexane in Figure 4.2 (Fawcett and Wood 1982), where no combustion will occur regardless of the concentration of the fuel components. Carbon dioxide and water vapor are examples of diluents that could dilute the oxygen concentration in the vapor space in the tanks. Burger (1956) showed the effect of these diluents on the flammability of kerosene, hexane, and propane (Figure 4.3). Differences in the limits for the two diluents is attributed to differences in their molar heat capacities.

A rigorous evaluation of the concentration of organics in the vapor space requires vapor-liquid equilibrium data for anticipated mixtures of organics either as a separate phase or dissolved in an aqueous phase containing specific concentrations of dissolved inorganic salts. These data are

Table 4.3. Tank C-103 Flammable Vapor Components (Borsheim and Kirch 1991)

<u>Constituent</u>	<u>Flash-point, °C</u>	<u>Lower Limit of Flammability^(a)</u>	<u>Volume Percent</u>	<u>Percent of Combustibles^(c)</u>	<u>C/L^(d)</u>
Acetone	9.4	2.6	1.34 E-04 ^(b)	0.518	0.199
Ammonia		15.5	2.39 E-02	92.333	5.957
MEK	-4.4	2.0	3.91 E-04 ^(b)	1.511	0.756
MNBK	35	1.2	5.17 E-05 ^(b)	0.200	0.167
MIBK	17	1.4	7.75 E-06 ^(b)	0.030	0.021
Hydrogen		4.0	<u>1.4 E-03</u>	<u>5.409</u>	<u>1.352</u>
			0.02588	100.0	8.452

(a) Percent-by-volume.

(b) Data were obtained using an unproven sampling technique that was not validated and is now considered suspect.

(c) Volume percent of flammable constituent (i/sum of volume percent of all flammable constituents).

(d) C/L - Percent of combustibles/lower limit of flammability.

necessary to account for nonideal effects introduced by multicomponent mixtures. However, this information is not available for the USTs, and simplifying assumptions must be made to estimate the significance of vapor phase concentration. In addition, the kinetics of evaporation at the liquid surfaces, the kinetics of generation of volatile organic products of chemical and radiolytic degradation, and the rate of depletion in the overhead space caused by diffusion and convection of vapors from the tank are also not known and would need to be determined to accurately predict steady-state values.

The chemicals considered in the evaluation conducted for this report were the solvents, extractants, and degradation products that were expected to be volatile or semivolatile in the tank. Ionic or complexed organic species in highly alkaline supernate (carboxylic acid and the various complexants) were not considered because they exhibit very low vapor pressure and are considered to be nonvolatile. The principal degradation products are the ketone, aldehyde, and alcohol intermediates produced during the degradation of TBP and NPH. Using data from the vapor space in Tank C-103 as a guide (Ulbricht 1989), acetone and 2-butanone are representative ketones; butanal is a representative aldehyde; and butanol is a representative alcohol.

4.4.1 Concentration of Solvents and Extractants Above a Free Organic Phase

It was assumed that a separate organic layer could be produced by one of the solvents, as is the case with Tank C-103. It was also assumed that the solvent would contain one or more of the principal extractants and small quantities of the organics produced from degradation with varying degrees

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Figure 4.2. Limits of Flammability of Hexane in Oxygen-Nitrogen Atmospheres (Fawcett and Wood 1982)

of concentration. Solvents and extractants of interest are: NPH, TBP, DBBP and MBIK. D2EHPA was not of interest because it is expected to form a sodium salt in the highly alkaline supernate and would have a flashpoint much higher than its acid form, 196°C. Properties for DBBP were not found during this study, precluding a quantitative evaluation of its behavior in liquid-vapor equilibrium. However, in a review of the properties of various esters of the acids of phosphorus, Burger (1957) noted that the phosphates, phosphonates, and phosphinates with the same number of carbon atoms had about the same boiling point. Using this observation as a basis, it is assumed that TBP and DBBP would have approximately the same liquid-vapor equilibrium behavior and flashpoint. Carbon tetrachloride was also not considered because it is not flammable in air over the range of temperatures of interest. Furthermore, carbon tetrachloride behaves as a diluent in the same manner as water and carbon dioxide, so its presence in the vapor space will be to increase the lower flammability limit of the mixture.

The approach taken in evaluating the overhead space was to examine the system under simplifying assumptions, recognizing that deviations from these assumptions will have an effect on the degree of concentration predicted. The assumptions are as follows:

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Figure 4.3. Effect of Diluents in Air on Flammability Limits (Burger 1956)

- The gas phase is in equilibrium with the liquid phase.
- The total pressure of the vapor space is 1 atm, with air making up the balance of the gas phase at equilibrium.
- The temperature in the overhead space is uniform and the same value as the liquid surface. The temperature range of concern is from 20°C to 100°C.
- Individual components in the organic mixtures behave ideally.

The assumption of equilibrium implies that the transfer of organics between the liquid and vapor phase is so rapid that equilibrium is achieved. However, if ventilation of gas to or from the tank is sufficiently rapid then it is possible that the gas phase concentrations of organics could be much lower than that predicted by equilibrium. In those tanks with passive ventilation this represents a reasonably accurate assumption. The assumption of equilibrium is considered to be conservative because it would represent the highest concentration of organic present.

One atmosphere of total vapor is assumed to represent the average conditions in the tank. The composition assumption that the balance of gases is air ignores the presence of other diluents such as water vapor and carbon dioxide in the overhead space and inorganic fuel gases such as ammonia and hydrogen. This assumption is not expected to significantly affect the analysis in terms of concentration mechanisms, but would likely affect the safety consequences of vapor concentration.

The assumption of uniform temperature in the vapor space is a simplifying assumption for purposes of analysis. In an actual tank, temperature gradients would be likely to occur due to temperature differences along the vapor space dome surfaces, and infiltration of ambient air. The range of temperature being considered in the report is based on the tank temperatures reported in a tank farm surveillance report for October 1991 (Hanlon 1992), which listed temperatures for tanks on various categories of watch lists. These temperatures ranged from 20°C in Tank B-103 to 93.9°C in Tank SX-108, which is a high-heat tank.

The assumption regarding ideal behavior of the organics is made to allow an approximation of the expected concentrations for each organic of concern in the overhead space. This assumption may not be entirely conservative but is considered sufficient for describing the concentration mechanisms.

With these simplifying assumptions, the vapor phase concentration of the pure volatile organic compounds can be approximated by using the Clapeyron Equation:

$$\ln (p/p_o) = \Delta H/RT_o - \Delta H/RT$$

where p_o and p are the vapor pressures corresponding to the temperatures T_o and T , respectively, and ΔH is the molar heat of vaporization.

Raoult's Law can be used to approximate ideal vapor-liquid equilibrium between selected binary systems such as two miscible organic liquids or an organic liquid dissolved in the aqueous phase. According to Raoult's Law:

$$P_1 = P_1^o x_1$$

where P_1^o is the pure phase vapor pressure of the component of interest, and P_1 is the vapor pressure of that component at a mole fraction x_1 in the liquid phase. Raoult's law is generally used to approximate the vapor pressure of the solvent of a binary mixture as its concentration in the liquid phase approaches 100%. However, Raoult's law generally does not accurately apply to solutes as they approach 0% concentration in the mixture, except in those rare instances where the mixture behaves ideally. Instead, Henry's law

$$P_1 = K_1 x_1$$

is used where K_1 , Henry's constant is calculated experimentally. Henry's constants can be found in the literature for organic-water mixtures, but these values are not valid for the highly nonideal, multi-component aqueous mixtures found in the tanks.

Figure 4.4 shows the vapor pressure curves for decane, dodecane, a number of NPH solvents used onsite, MIBK, and TBP, which was used in conjunction with NPH at concentrations up to 30%. Also shown are the flashpoints for these solvents and the approximate temperature at which the lower

flammability limit is reached. It can be seen from this figure that pure NPH could present a safety problem above about 58°C, depending on the exact composition. It is likely, however, that the actual temperature of concern is closer to 75°C to 85°C, as shown for N-dodecane and Soltrol-170, because over time the lighter fraction of the solvent would preferentially evaporate and leave behind a solvent with a much lower vapor pressure. Pure MIBK exceeds its flashpoint at 18°C and becomes a hazard in the vapor space. At 61°C, however, its vapor pressure exceeds its upper flammability limit and would not sustain combustion with air entering the tank from outside. From a perspective of tank safety, exceeding the upper flammability limits is not considered a desirable safe condition. Pure TBP does not achieve its flashpoint until 146°C and would not be a safety concern over the range of interest. Since it is less volatile than any of the alkane solvents, it would also reduce the vapor pressure of a mixture of alkane solvent containing TBP and in turn increase the flashpoint temperature. Furthermore, as evaporation occurs over time, the mixture of the two would become more enriched in TBP, producing an even lower vapor pressure and higher flashpoint.

A key consideration inherent in estimating an equilibrium vapor pressure for the pure vapor phase is that a sufficient inventory of the solvent is available to fill the necessary vapor space and make up losses to the atmosphere through the ventilation system without significantly lowering the liquid phase concentration. In the case of the less volatile solvents such as NPH and TBP, the loss of liquid phase inventory over time would be relatively modest and the assumption of a separate phase is reasonably probable. This is supported by analysis of Tank C-103, which appears to have a separate organic layer and accompanying vapor phase concentrations of NPH and TBP indicative of a separate layer. However, in the case of MIBK, the corresponding pure vapor phase concentration is 7 times more volatile than shell spray base and more than 25 times more volatile than dodecane. The probability of maintaining sufficient inventory of pure MIBK to create a separate phase is considered to be very low, because of its high vapor pressure, and the fact that substantial quantities of water evaporating from the tanks since plant operation using MIBK was discontinued in 1966 would have stripped the tank of a separate MIBK phase. According to Borsheim and Kirch (1991), the maximum concentration of MIBK in aqueous solution discharged from the REDOX process was 0.3 ppm. However, 18,300 gal of the undiluted spent extractant was stored separately in Tank S-141 (Hall 1972).

4.4.2 Concentration Above an Aqueous Phase

Vapor-liquid equilibrium behavior involving organics dissolved in an aqueous phase will be very similar to that described above for a separate organic phase. As solvents and extractants such as NPH and TBP approach their saturation concentrations, the corresponding vapor pressure will approach that for a pure phase organic. The main difference between the two situations is that it is not necessary to produce a separate organic phase to achieve vapor phase concentrations approaching that of a pure organic phase. Therefore, the assumption of a separate organic phase provides a worst case for concentration involving the aqueous phase.

One important consideration worth noting, however, is the aqueous phase inventory at which pure organic phase behavior is achieved. It is well established that solvents and extractants, such as dodecane, MIBK, and TBP, are not very soluble in water. In fact low solubility is a desirable

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Figure 4.4. Vapor Pressures and Flashpoints of Selected Solvents and Extractants

property in solvents and extractants for treating aqueous solutions. Solubilities of NPH and TBP in water are 5 mg/L and 390 mg/L, respectively. Hexone is more soluble with a solubility of 17 g/L. As discussed in Section 4.2.2, organics become even less soluble in highly ionic solutions as is the case with the alkaline supernate in the USTs.

Because of the low solubilities of the solvents and extractants in the aqueous phase, saturation can be achieved at concentrations on the order of 1 to 10 mg/L for TBP/NPH mixtures. At these concentrations the total inventory of either solvent in the aqueous phase would be on the order of 1 to 10 kg in a million gallons of solution and would be insufficient for achieving the lower flammability limit for all but a small space, even if all of the organic vaporized. The presence of significant complexants or surfactant-type organics in the aqueous phase could increase the inventory of hydrophilic compounds if they solubilized TBP or NPH. In the case of Hexone or degradation products such as acetone that have a relatively high solubility in water, the total inventory of the organic could be 1 or more orders of magnitude higher and be sufficient to fill the vapor space at the lower flammability limit.

4.4.3 Concentration of Organics Above an Inorganic Solid Phase

In the USTs that have had the free liquid phase removed there remains behind nondrainable liquid filling the interstitial spaces between the solids particles and within the pores of these particles. The organic constituents in the nondrainable liquids will be the same as those present in the free liquid prior to draining it, including a free organic liquid should it have been in the tank. Over time, the amount of liquid remaining in the solids may slowly diminish due to evaporation in vapor spaces within the solids. Therefore, in describing the partitioning of volatile organics between the vapor phase and the solids, three conditions must be considered: between the solids and the vapor, between the nondrainable liquids and vapor phase, and a combination of the two.

Adsorption of organics on the solids involves both physical adsorption and chemisorption. The forces attracting gas molecules to the solid surfaces are relatively weak, and the heat evolved for physical adsorption is of the same order of magnitude as the heat of condensation (Smith 1970). The effect of physical adsorption on the concentration of organics in the vapor phase is not significant. Chemisorption, on the other hand, is specific and involves forces much stronger than in physical adsorption, because of chemical interaction with the surface molecules of the solids. This behavior is very pronounced for coverage of the surface by a monolayer of competing gases, but it is rapidly diminished for each added monolayer so only physical adsorption dominates after several monolayers of coverage. Where all of the void space in the solids is occupied by liquids, the behavior of organics is essentially the same as that encountered for the free liquid phases, following either Raoult's law or Henry's law, depending on the concentration of the organics in the liquid phase. Between the two extremes there is a transition region in which only a fraction of the voids in the solids are filled with liquid and the remainder with gas. Ong and Lion (1991) conducted research on this condition for adsorption of trichloroethylene (TCE) vapor onto moist solids.

Figure 4.5 shows the general behavior of the distribution coefficient for TCE between the moist solids and the gas phase (K_d) observed by Ong and Lion for several solids as a function of the moisture content of the solids. According to their research, the water phase dominated the mechanism of adsorption of TCE from the gas to the water according to Henry's Law for moisture

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Figure 4.5. Designated Regions for Vapor-phase Sorption Phenomena of Trichloroethylene as a Function of Moisture Content of Solid Surfaces (Ong and Lion 1991). Coverage by water: Region 1 - Oven dry 0 to 1 monolayer; Region 2 - 1 to ≈ 5 monolayers; Region 3 - > 5 monolayers

concentrations corresponding to 5 monolayers or more of coverage on the solid surfaces. Thus, there is a linear dependence between the total inventory of TCE and the inventory of water in the solids. At moisture contents corresponding to less than 1 monolayer chemisorption dominated, but since water is more strongly adsorbed than TCE, the water displaces the TCE into the vapor phase. Thus, there is an inverse relationship between the inventory of TCE and that of the water in the solids.

The phenomena involving the adsorption of organics onto the solids suggest that the evaporation of organics from the solids exposed to the gas phase will be no worse than that experienced for free liquids with the same composition. Furthermore, convective mixing of the liquids within the solid bed is very limited, and diffusion is a significant mechanism for transporting organics. Thus, diffusion of the organics to the upper layer of the solids in the tank will result in potentially significant concentration gradients in the solids below this layer. Consequently, the concentrations at the top layer of the solids phase in the tank will be lower than the average value for the liquid/solids mixture and will correspondingly reduce the concentration of organics in the gas space.

4.4.4 Concentration of Degradation Products

Degradation products can also be present in either a separate organic solvent or an aqueous phase but in relatively low concentrations. A key factor affecting their concentration in either phase is that they are generated by radiolytic or chemical degradation. Thus, the total inventory of these components in the vapor phase of any tank will depend on the rate of depletion of the component via the ventilation system and the net rate of their generation according to the equation:

$$dM/dt = M_{\text{gen}} - M_{\text{out}}$$

where dM/dt is the rate of accumulation of the organic in the tank, M_{gen} is the net rate of generation of the organic from radiolytic and chemical degradation mechanisms, and M_{out} is the rate at which the organic leaves the tank through the ventilation system.

For the degradation products that are essentially nonvolatile, such as organic acid salts and polymeric materials, the rate of depletion through the ventilation will be very low and could be lower than their generation rate. Thus, their corresponding inventory (and concentration) in the tanks could be relatively high and still increasing. However, since they are nonvolatile, these components would not be expected to concentrate to a significant degree in the vapor phase. For volatile degradation products, the rate of depletion through the ventilation system will eventually reach a steady-state condition that equals the net rate of generation, and the inventory of the organic in the vapor remains constant. At steady state, the concentration of organics in the vapor directly affects the rate of depletion due to convection and diffusion through the ventilation system. The corresponding liquid phase concentrations will adjust to maintain equilibrium with the vapor phase. Under steady-state conditions those organic compounds generated at lower rates will require a lower corresponding concentration in the vapor phase in order to maintain steady state.

Because the inventory of organic components in several tanks has not been completely depleted over a time frame of many years, it is reasonable to assume that the generation rates of individual degradation products are very low, and the resulting inventory of those with a reasonably high volatility would be significantly lower than any of the solvents or complexants in the tanks. However, without a rigorous evaluation of the generation and depletion rates, it is not possible to estimate actual quantities. It is possible, however, to draw some general conclusions regarding the relationship of the vapor phase concentration of the less volatile degradation products to the inventory of the organic in the organic liquid. For example, in order for butanol to be at its lower flammability limit at 25°C it would have to approach pure phase concentrations, requiring it to approach 100% of the organic inventory. This would be very unlikely considering that a primary source of butanol is TBP, and as TBP is depleted the generation rate of butanol is similarly reduced. At 100°C, butanol would only have to account for approximately 2.2 mol% of the organic phase, and the constraint is less certain. For a high-volatility degradation product, the constraint is even less definite. For example, the organic phase concentrations corresponding to the lower flammability limit of acetone at 25°C and 100°C are 2.5 mol% and 0.04 mol%.

4.4.5 Other Concentration Mechanisms

Three other concentration mechanisms were considered in the evaluation: concentration during transient conditions; transport to other tank gas spaces; and aerosol formation. A key assumption in

the evaluation of the concentration of volatile degradation products was that steady-state conditions exist in the tank. This assumption dictates both the inventory and corresponding concentration of the volatile organic in the liquid phase. If a transient condition occurs in the tank, such as a temperature increase in the liquid phase, the evaporation rate of organics from the liquid to the gas phase will become temporarily greater than the net degradation rate, and the vapor phase concentration will temporarily increase. Eventually the vapor phase will return to concentrations very nearly that for the original temperature, and the liquid phase will achieve a lower concentration to reestablish equilibrium with the vapor phase at the higher temperature. The magnitude of the concentration excursion depends on both the magnitude and rate of change of the temperature excursion. However, in the tanks it is not expected to be a likely mechanism because of the large thermal mass in the tanks relative to heat sources.

Transient behavior can also occur through changes in the convection of gases into or out of the tanks because of atmospheric pressure. These transients are also expected to cause only minor changes. Finally, transient behavior can be caused by a sudden turnover of stagnant liquid or liquid-saturated solids in the bottom of the tanks. In a stagnant solution, where degradation products are produced, a concentration gradient is created between the bottom and the surface of the solution in order to cause diffusion of volatile components to the surface where they evaporate. During turnover, solutions with these higher concentrations will be transported by convection to the surface and result in a sudden release of volatiles to the vapor phase. The transient behavior of Tank 101-SY is an extreme case involving hydrogen generation rates in a stagnant zone of sludge, causing hydrogen to eventually exceed saturation of the solution and produce a separate gas phase trapped in the sludge. The resulting periodic turnover in the tank produces a concentration excursion of hydrogen and other gases.

Another concentration mechanism involves the interconnection of the ventilation systems of a series of tanks. In this case the concentration mechanism involves diffusion and convection of the organics from a tank with high concentrations of volatile organics and into a tank with lower concentrations of these gases. Furthermore, a portion of these gases will subsequently condense to establish equilibrium with the liquid phase in the organic-deficient tank, thus increasing its inventory above that predicted from disposal records. This concentration mechanism is not considered to be a major safety concern other than spreading the inventory of volatile organics to other tanks, because the resulting concentrations in the deficient tank would not exceed those concentrations found in the tank serving as the source of organics.

Aerosol formation is also a potential concern because it can increase the inventory of inorganics in the vapor space above that predicted for the gas phase. Aerosols can be formed as mists or sprays in the tank. Mists could form as a result of condensation of vapors in the vapor space, most likely due to an increase in atmospheric pressure causing cooler outside air to enter the tanks through the vents. Studies reported by Zabetakis (1965) showed that mists consisting of very fine droplets can decrease the lower flammable limit of a combustible vapor. This conclusion was based on the observation by Burgoyne and Cohen (1954) that the droplets tend to fall towards the flame front of an upward propagating flame, producing a local concentration at the flame front corresponding to the lower flammable limit. Data presented for kerosene mists ranging up to 10 μm in diameter showed no significant decrease in the lower flammable limit. For kerosene spray droplets greater than 60 μm diameter, the lower flammability limit increased above that for the vapor. However, the spray droplet tests were conducted in the same manner as the mist tests and were more representative of an internal combustion engine. No data were reported for kerosene droplet diameters between 10 μm

and 60 μm . Experiments with tetralin mist showed a continual significant decrease in the limit for droplet diameters ranging from 10 to $>135 \mu\text{m}$, suggesting that the flammability limit could be lowered for kerosene droplets larger than 10 μm . An important consideration in evaluating these results is that tests were conducted using the flammable organic in air. In the USTs there should be a significant concentration of water vapor in the gas space that should form a mist at the same time as any organics above their saturation point in the vapor space. These droplets will also fall as a mist and would tend to dilute the concentration of both organic and oxygen near a flame.

Liquid aerosols can also be dispersed into the vapor space if the surface of the tank is agitated mechanically or pneumatically using gas bubbles. Stordeur (1982) conducted experiments to generate aerosols from TBP/NPH mixtures using a vaned disk aerosol generator. He produced aerosols with droplet diameters ranging from 314 to 664 μm . Using these results, he calculated that it was not possible to generate enough spray droplets in the vapor space to increase the concentration of the TBP/NPH mixture (both droplets and vapor) to the lower flammability limit for temperatures at least as high as 60°C, because the aerosols had such high settling rates.

Another mechanism mentioned by Zabetakis for forming mists is the collapse of foams on the surface of a flammable liquid. As gas bubbles reach the surface of a liquid, foam bubbles may form that consist of a thin skin of organic liquids, such as surfactants. As the foam bubbles burst, organic aerosols are formed from the rupturing skin of the bubble. Zabetakis reported that when ignited foam can propagate a flame. No specific information was found on the generation of foams in the USTs. Similarly, there is little information on gas bubble formation in the liquids (or slurries) in any of the tanks except 101-SY, although several tanks are known to produce significant quantities of gas. However, should significant foams be found on the liquid surface of any of the tanks, further study of the mechanism may warrant consideration.

5.0 References

- Alcock, K., S. S. Grimley, T. V. Healy, J. Kennedy, and H.A.C. McKay. 1955. "The Extraction of Nitrates by Tri-n-Butyl Phosphate (TBP)." *Trans. Faraday Soc.* 52:39.
- Allen, G. K. 1976. *Estimated Inventory of Chemical Added to Underground Waste Tanks, 1944 Through 1975*. ARH-CD-610B, Atlantic Richfield Hanford Company, Richland, Washington.
- Al-Lohedan, H., C. A. Bunton, and J. R. Moffatt. 1983. *J. Phys. Chem.* 87:332.
- Anderson, J. D. 1990. *A History of the 200 Area Tank Farms*. WHC-MR-0132, Westinghouse Hanford Company.
- Beitel, G. A. 1976a. *Chemical Stability of Salt Cake in the Presence of Organic Materials*. ARH-LD-119, Atlantic Richfield Hanford Company, Richland, Washington.
- Beitel, G. A. 1976b. *Final Report on Investigation of Stability of Organic Materials in Salt Cake*. ARH-LD-126, Atlantic Richfield Hanford Company, Richland, Washington.
- Beitel, G. A. 1976c. *Sodium Nitrate Combustion Limit Tests*. ARH-LD-123, Atlantic Richfield Hanford Company, Richland, Washington.
- Beitel, G. A. 1977. *Exothermic Potential of Sodium Nitrate Salt Cake*. ARH-LD-163, Atlantic Richfield Hanford Company, Richland, Washington.
- Boldt, R. O., and J. G. Carroll. 1963. *Radiation Effects on Organic Materials*. Academic Press, New York.
- Borsheim, G. L., and N. W. Kirch. 1991. *Summary of Single-Shell Tank Waste Stability*. WHC-EP-0347, Westinghouse Hanford Company, Richland, Washington.
- Boutonnet, M., J. Kizling, P. Stenius, and G. Maire. 1982. *Colloids Surf.* 5:209.
- Bryan, S. A., L. R. Pederson, J. L. Ryan, R. D. Scheele, and J. M. Tingey. 1992. *Slurry Growth, Gas Retention, and Flammable Gas Generation by Hanford Radioactive Waste Tanks: Synthetic Waste Studies, FY 1991*. PNL-8169, Pacific Northwest Laboratory, Richland, Washington.
- Buckingham, J. S. 1967. "Aqueous and Organic Makeup." Chapter VI in *Waste Management Technical Manual*, ed. J. S. Buckingham. ISO-100, DEL, Isochem, Inc., Richland, Washington.
- Bunton, C. A., and S. K. Huang. 1972. *J. Org. Chem.* 37:1790.
- Bunton, C. A., M. M. Mhala, and J. R. Moffatt. 1986. *Surfactants in Solution*, eds. K. Mittal and P. Botharet, Vol. 5, p. 625. Plenum Press, New York.
- Bunton, C. A., J. R. Moffatt, and E. E. Rodenas. 1982. *J. Am. Chem. Soc.* 104:2653.

- Burger, L. L. 1955. *The Chemistry of Tributyl Phosphate-A Review*. HW-40910, General Electric, Hanford Atomic Products Operation, Richland, Washington.
- Burger, L. L. 1956. *The Flammability of Vapors Above Purex Systems*. HW-40820, General Electric, Hanford Atomic Products Operation, Richland, Washington.
- Burger, L. L. 1957. *The Esters of the Acids of Phosphorous as Solvents*. HW-44888, General Electric, Hanford Atomic Products Operation, Richland, Washington.
- Burger L. L., and E. D. McClanahan. 1958. "Gamma Radiolysis: Tributyl Phosphate and Its Diluent Systems." *Ind. Eng. Chem.* 50:153.
- Burger, L. L. 1984. "Physical Properties." *The Science and Technology of Tributyl Phosphate*, eds. W. W. Schulz and J. D. Navratil. CRC Publications, Boca Raton, Florida.
- Burgoyne, J. H., and L. Cohen. 1954. "The Effect of Drop Size on Flame Propagation in Liquid Aerosols." *Proceedings of the Royal Society of London* 225:375-392.
- Cleveland, J. M. 1967. "Plutonium Recovery and Waste Disposal." In *Plutonium Handbook*, ed. O. J. Wick, Vol. II. Gordon and Breach, Science Publishers, New York.
- Dack, M.R.J. 1975. "Importance of Solvent Internal Pressure and Cohesion to Solution Phenomena." *Chemical Society Reviews* 4:211229.
- Daniels, F. 1948. *Outlines of Physical Chemistry*, pp. 547-561. John Wiley & Sons, Ltd., New York.
- Daniels, M. 1968. "Radiolysis and Photolysis of Aqueous Nitrate Systems." *Advances in Chemistry* 81:153.
- Dragun, J. 1988. *The Soil Chemistry of Hazardous Materials*. Hazardous Materials Control Research Institute, Silver Spring, Maryland.
- Fawcett, H. H., and W. S. Wood. 1982. *Safety and Accident Prevention in Chemical Operations*, 2nd ed. John Wiley & Sons, Ltd., New York.
- Fisher, F. D. 1990. *The Kyshtym Explosion and Explosion Hazards with Nitrate-Nitrite Bearing Wastes with Acetates and Other Organic Salts*. WHC-SD-CP-LB-033, Westinghouse Hanford Company, Richland, Washington.
- Gangwer, T. E., M. Goldstein, and K.K.S. Pillay. 1977. *Radiation Effects on Ion Exchange Materials*. BNL-50781, Brookhaven National Laboratory, Upton, New York.
- Gu, Z. M., D. T. Wasan, and N. N. Li. 1988. "Surfactants in Chemical/Process Engineering." *Surfactant Science Series*, Vol. 28, p. 127. Marcel Dekker, Inc., New York.

- Hall, J. C. 1972. *Engineering Study Liquid Organic Waste Collection and Disposal*. ARH-2424, Atlantic Richfield Hanford Company, Richland, Washington.
- Hanlon, B. M. 1992. *Tank Farm Surveillance and Waste Status Summary Report for October 1991*. WHC-EP-0182-43, Westinghouse Hanford Company, Richland, Washington.
- Harned, H. S., and B. B. Owen. 1943. *The Physical Chemistry of Electrolytic Solutions*. Reinhold, New York.
- Harned, H. S., and B. B. Owen. 1950. *The Physical Chemistry of Electrolytic Solutions*. Reinhold, New York.
- Hazardous Materials Control Research Institute (HMCRI). 1987. Superfund Series. *Hazardous Materials In Situ Stabilization*. Silver Spring, Maryland.
- Helfferic, F. 1962. *Ion Exchange*, p. 30. McGraw-Hill, New York.
- Hendrickson, D. 1990. *Methods and Data for Use in Determining Source Term for Grout Disposal Program*. WHC-SD-WM-TI-355, Westinghouse Hanford Company, Richland, Washington.
- Herting, D. L., D. B. Brechtold, B. A. Crawford, and T. L. Welsh. 1992. *Laboratory Characterization of Samples Taken in May 1991 from Hanford Waste Tank 241-SY-101*. WHC-SD-WM-DTR-024, Westinghouse Hanford Company, Richland, Washington.
- Higgins, C. E., W. H. Baldwin, and B. A. Soldano. 1959. "Effects of Electrolytes and Temperature on the Solubility of Tributyl Phosphate in Water." *J. Phys. Chem.* 63:113.
- Hodgman, C. D., ed. 1947. *Handbook of Chemistry and Physics*, 13th ed. Chemical Rubber Publishing Co., Cleveland, Ohio.
- Iwasaki, I., S.R.B. Cooke, and H. S. Choi. 1960. *Trans. AIME* 217:237.
- Jones, T. E., S. G. McKinley, J. M. Tingey, and T. M. Longaker. 1990. *SST Waste Characterization Project, Core 3 Data Report, Revision 1*. Pacific Northwest Laboratory, Richland, Washington.
- Jungfleisch, F. M. 1984. *Preliminary Estimation of the Waste Inventories in Hanford Tanks Through 1980*. SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington.
- Kalkwart, D. R. 1977. *Safety Evaluation of Cation Exchange Resins*. BNWL-2391, Pacific Northwest Laboratory, Richland, Washington.
- Kinderman, E. M., and A. H. Samuel. 1963. *Radiation Stability of Organic Liquids*. SRI A-101, Stanford Research Institute, Menlo Park, California.
- Kingsley, R. S. 1965. *Solvent Extraction Recovery of Americium with Dibutyl Butyl Phosphonate*. RL-SEP-518, Hanford Atomic Products Operation, Richland, Washington.

- Klem, M. J. 1990. *Inventory of Chemicals Used at Hanford Site Production Plants and Support Operations (1944-1980)*. WHC-EP-0172, Westinghouse Hanford Company, Richland, Washington.
- Krueger, J. P., and M. E. Portman. 1991. "Mechanism for Migration of Light Nonaqueous Phase Liquids Beneath the Water Table." In *HMC-Northeast '91 Conference Proceedings*. Hazardous Materials Control Research Institute, Greenbelt, Maryland.
- Lippens, B. C., and J. J. Steggerda. 1970. "Active Alumina." In *Physical and Chemical Aspects of Adsorbents and Catalysts*, ed. B. G. Linsen, pp. 171-211. Academic Press, New York.
- Lokken, R. O., R. D. Scheele, D. M. Strachan, and A. P. Toste. 1986. *Complex Concentrate Pretreatment FY 1986 Progress Report*. PNL-7687, Pacific Northwest Laboratory, Richland, Washington.
- Marcus, Y., and A. S. Kertes. 1969. *Ion Exchange and Solvent Extraction of Metal Complexes*. John Wiley & Sons, Ltd., New York.
- Martin, E. C. 1985. *Complexant Stability Investigation. Task 2-Organic Complexants*. PNL-5453, Pacific Northwest Laboratory, Richland, Washington.
- Morgan, L. J., P. Somasundaran, and S. Partyka. 1987. *Colloids Surf.* 27(1-3):15.
- Okkerse, C. 1970. "Porous Silica." In *Physical and Chemical Aspects of Adsorbents and Catalysts*, ed. B. G. Linsen, pp. 213-264. Academic Press, New York.
- Ong, S. K., and L. W. Lion. 1991. "Mechanisms for Trichloroethylene Vapor Sorption onto Soil Minerals." *J. Environ. Qual.* 20(1):180-188.
- Palmer, C. D., and R. L. Johnson. 1989. "Physical Processes Controlling the Transport of Non-Aqueous Phase Liquids in the Subsurface." Chapter 3 in *Transport and Fate of Contaminants in the Subsurface*. EPA/625/4-89/019, U.S. Environmental Protection Agency, Cincinnati.
- Perry, R. H., and C. H. Chilton. 1973. *Chemical Engineer's Handbook*. McGraw-Hill Book Company, New York.
- Phillips, G. O., and G. J. Moody. 1960. "Radiation Chemistry of Carbohydrates, Part III. The Effect of Gamma Radiation on Aqueous Solution of d-Fructose." *J. Chem Soc.* 754.
- PUREX Technical Manual. 1955. HW-31000, General Electric Company, Richland, Washington.
- Richardson, G. L., and W. W. Schulz. 1967. "Process Chemistry and Engineering." Chapter VI in *Waste Management Technical Manual*, ed. J. S. Buckingham. ISO-100DEL, Isochem, Inc., Richland, Washington.
- Rijntjen, H. Th. 1970. "Formation, Preparation and Properties of Hydrous Zirconia." In *Physical and Chemical Aspects of Adsorbents and Catalysts*, ed. B. G. Linsen, pp. 315-372. Academic Press, New York.

- Ryan, J. L., and E. J. Wheelwright. 1959. *The Recovery, Purification and Concentration of Plutonium by Anion Exchange in Nitric Acid*. HW-55893, General Electric Company, Richland, Washington.
- Schulz, W. W. 1971. *Effects of Radiolysis on the Hanford B Plant Fission Product Extractant*. ARH-SA-60, Atlantic Richfield Hanford Company, Richland, Washington.
- Schwartz, A. M., and J. W. Perry. 1949. *Surface Active Agents Their Chemistry and Technology*. Interscience Publishers, Inc., New York.
- Seidell, A. 1953. *Solubilities of Inorganic and Metal Organic Compounds*, 3rd ed., Vol. 1. D. Van Nostrand, New York.
- Smith, G. A., S. D. Christian, E. E. Tucker, and J. F. Scamehorn. 1989. *J. Colloid Interface Sci.* 130(1):254.
- Smith, J. M. 1970. *Chemical Engineering Kinetics*. McGraw-Hill Book Publishing Company, New York.
- Somasundaran, P., and K. P. Ananthapadmanabhan. 1987. "Bubble and Foam Separations-Ore Flotation." In *Handbook of Separation Process Technology*, ed. R. W. Rousseau. John Wiley & Sons, Ltd., New York.
- Stephen, H., and T. Stephen. 1963. *Solubilities of Inorganic and Organic Compounds*, Vol. 1. McMillan, New York.
- Stordeur, C. M. 1982. *Organic Aerosols in Purex Agitated Solvent Tanks*. SD-RE-TI-047, Rockwell Hanford Operations, Richland, Washington.
- Toste, A. P., T. J. Lechner-Fish, D. J. Hendren, D. J., R. D. Scheele, and W. G. Richmond. 1988. "Analysis of Organics in Highly Radioactive Nuclear Wastes." *J. Radio- anal. Nucl. Chem.* 123:149.
- Ulbricht, W. H. 1991. *Report on 241-C Tank Farm Sampling Results of 1989*. WHC-SD-WM-RPT-019, Westinghouse Hanford Company, Richland, Washington.
- Van Tuyl, H. H. 1967. "Nuclear Reactions, Transuranic Elements and Fission Products" In *Waste Management Technical Manual*, ed. J. S. Buckingham. ISO-100 DEL, Isochem, Inc., Richland, Washington.
- Wagner R. M., E. M. Kinderman, and L. H. Towle. 1959. "Radiation Stability of Organic Compounds." *Ind. Eng. Chem.* 51:45.
- Westinghouse Hanford Company. 1990. *222-S/RCRA Analytical Laboratories, Single-Shell Tank Waste Characterization, 241-U-110 Core 8 Composite*. Richland, Washington.
- Zabetakis, M. G. 1965. "Flammability Characteristics of Combustible Gases and Vapors." Bulletin 627, U.S. Bureau of Mines, Washington, D.C.

Appendix

Preliminary Assessment of Radiolytic and Chemical Degradation Products

Appendix

Preliminary Assessment of Radiolytic and Chemical Degradation Products

Evaluation of concentration mechanisms for degradation products is very constrained by the dearth of characterization data for organics in all but the following tanks: AN-107; C-102 and C-103; and AN-101, AN-103, and AW-101 (Lokken et al. 1986, Ulbricht 1991, Hendrickson 1990). Even these data are incomplete, with significant portions of the organics unaccounted for, or only tentatively identified. Furthermore, because of incomplete inventories of organics added to specific tanks, many of the identified constituents cannot be confirmed as degradation products rather than as chemicals added to the tank.

The information presented here is not intended to be a rigorous or complete examination of references of chemical and radiolytic degradation mechanisms and their resulting products. Instead it is a preliminary assessment, based on a review of chemistry literature, to provide insight into the types of chemicals to be expected, due to these mechanisms, in the absence of complete and validated characterization data. The purpose of providing this information is so that physical behavior of these organic components can be considered in the evaluation of concentration mechanisms within the waste tanks.

Because of the various waste configurations, such as crystalline salt layers, and the high pH of the systems, which the organic components encounter, it is difficult to extend assumptions very far without further experimental results. The assumed conditions of the waste tanks are high pH, high nitrate/nitrite concentrations, and an oxidizing environment.

General Chemistry of Radiolysis

A hydroxyl radical is formed within the tanks by the radiolysis of water. The hydroxyl radical is a powerful oxidant, having a standard reduction potential of 2.7 V in acidic solution and 1.8 V in neutral solution (Buxton et al. 1988). However, in strongly alkaline solution, the hydroxyl radical is rapidly converted to its conjugate base $\cdot\text{O}^-$, as shown:

The oxide radical anion reacts more slowly than the hydroxyl radical with several inorganic anions, and the rate is immeasurably slow with Br^- , CO_3^{2-} , and $\text{Fe}(\text{CN})_6^{4-}$, although these ions are all rapidly oxidized by $\cdot\text{OH}$. In its reactions with organic compounds, the hydroxyl radical behaves as an electrophile, whereas the oxygen radical anion is a nucleophile. Both forms of the radical abstract H from C-H bonds, and this can result in the formation of different products when the pH is raised to where $\cdot\text{O}^-$, rather than $\cdot\text{OH}$, is the reactant. For example, if an aromatic molecule with an aliphatic

group, such as toluene, is attacked by $\cdot\text{O}^-$ the H abstraction occurs on the methyl group. Attack by a hydroxyl radical on toluene will add a hydroxyl to the aromatic ring.

The nitrate radical, $\cdot\text{NO}_3$, can readily be formed by pulse radiolysis of both 6M HNO_3 and 5M NaNO_3 solutions (Neta and Huie 1986). It is evident that it can also be formed under source radiolysis. It should be noted that the yield of the nitrate radical is about four times higher during the pulse radiolysis of nitric acid than sodium nitrate solution. The nitrate radical abstracts hydrogen from alkanes such as isobutane to form nitric acid and the alkane radical (Neta and Huie 1986), as shown:

In general, the nitrate radical is a weaker one-electron oxidant than the hydroxyl radical. The rate constants are about 100 times less for the nitrate radical, compared with the hydroxyl radical, for hydrogen abstraction from alkanes. No information has been reported concerning the reactivity of nitrate radical in highly basic solutions.

Alkanes

Normal paraffinic hydrocarbons, such as n-dodecane, should be able to undergo radiolytic cleavage with time in the waste tanks, because this has been shown to occur with a number of related saturated organic compounds. Rate constants for the hydrogen abstraction from various saturated organic compounds, including the salts of hexanoic, malonic, succinic, adipic, and citric acids, have been reported (Neta and Schuler 1975).

The attack of the hydrogen abstracting radicals ($\cdot\text{O}^-$ or $\cdot\text{NO}_3$) should be random over the length of a compound such as dodecane; and a statistical mixture of organic radicals should be formed. Once the hydrogen radical is abstracted from an alkane, either by an oxide radical ion or a nitrate radical, a radical remains on one of the carbons of the hydrocarbon. Hydroxy radical can react with the alkane radical to form an alcohol. This reaction can occur anytime hydrogen abstraction occurs. In the presence of oxygen, the alkane radical can react with oxygen (a biradical itself) to form a peroxy radical:

Alkane peroxy radicals are not stable in acid or base. Alkyl hydroperoxides, for instance, are more acidic than alcohols and form salts with aqueous solutions of strong alkalies. A proposed mechanism for the oxidation of alkanes is presented below:

It is anticipated that the most likely product of the oxidation would be a ketone; however, the oxidative procedure probably will not stop at that step. Those ketones that are subject to enolization,

by possessing an α -hydrogen, can be degraded by oxidants in a manner similar to that of olefin cleavage (Stewart 1967). Enol anions of ketones, formed in base, readily undergo oxidation with molecular oxygen to carboxylic acids (Doering and Haines 1954). This mechanism involves an aldehyde intermediate and produces 2 moles of the carboxylic acid. This reaction is somewhat similar to the Baeyer-Villiger oxidation, which uses peracids, and converts aromatic ketones to esters (carboxylates in base).

Under conditions of high alkalinity in the presence of oxygen, it is also possible that a number of other organic oxidations can readily be achieved. For instance, several acidic-metal processes (manganese oxide, chromic acid, or ruthenium tetroxide) are available to convert alcohols to either aldehydes (from a primary alcohol) or ketones (from a secondary alcohol). These alcohol oxidations can be initiated by strong one-electron oxidants or two-electron oxidants. The alcohol functional group is not rapidly attacked by oxygen or peroxides, but it can be reacted with ozone. However, with oxygen in aqueous alkaline solutions it was shown that copper phenanthroline complexes catalyze the oxidation of primary alcohols to carboxylic acids (Tretyakov et al. 1982). This procedure probably involves singlet molecular oxygen (Foote 1968).

Primary alcohols can also be oxidized to aldehydes and carboxylates in alkaline solution by using hexacyanoferrate(III) with sodium ruthenate as a catalyst (Pandey et al. 1982). The Oppenauer oxidation (Djerassi 1951) of an alcohol involves the use of an aluminum alkoxide in the presence of a carbonyl compound, such as a quinone, which acts as a strong hydrogen acceptor. At a temperature of 300°C to 350°C, alcohols can be readily oxidized in sodium nitrate-sodium hydroxide melts to carboxylates (Shykuji, Yamano, and Eguchi 1983). It was assumed that the mechanism involved formation of a hydroperoxy anion.

If it is assumed that the concentration of alkanes in the waste tanks is not high, then the potential for recombination of the alkyl radicals or the formation of dimers, trimers, and oligomers is reduced. However, when undiluted paraffins are exposed to radiation, such dimerization to oligomerization is observed (Seguchi et al. 1991). In fact, under these conditions, the cross-linking mechanism is the preferred route.

Recent research indicated that alkane radicals either react by disproportionation or combination (de Doncker and Tilquin 1991). Dilute oxygen-free hexane solutions (in water) gave hydrogen gas, hexene, and dodecane isomers as the products. Thus, olefins have been observed in radiolysis reactions.

It should also be noted that the Kolbe oxidation of carboxylates, generally an electrolytic process, allows for the loss of carbon dioxide and the combination of two radical fragments (Stewart, Henry, and Temple 1969) as shown:

In concentrated sodium hydroxide solutions, aldehydes with two α -hydrogens are converted to high molecular weight polymers (Noller 1958). It is assumed that this process requires an aldol addition, followed by α - β dehydration and polymerization. Ketones are not affected by concentrated caustic in this manner. It should be noted that the standard aldol addition (or condensation) in base requires an aldehyde with one α -hydrogen to give the self-addition reaction that forms the dimer. This reaction does not yield polymeric since the condensation between more than two molecules is prevented by formation of a sesquiacetal between the third aldehyde and the aldol. However, it is interesting that Brite (1954) observed polymer formation with butyraldehyde and provided quite reasonable analytical support for such a product. Aldehydes without any α -hydrogens can undergo an intermolecular oxidation and reduction in strong alkali. This reaction, the Cannizzaro, allows one aldehyde molecule to act as a reducing agent and be oxidized to a carboxylate while the other acts as an oxidizing agent and is reduced to an alcohol. It should be noted that polymeric condensations can occur between mixed aldehydes and ketones in a manner similar to the condensation of formaldehyde and acetone. Under basic conditions, formaldehyde can polymerize to paraformaldehyde, a linear, yet thermally unstable material above 200°C. The fate of formaldehyde depends upon many conditions. However, two routes of formaldehyde loss include oxidation and polymerization. Formaldehyde can be oxidized to formic acid which will immediately convert to sodium formate. This molecule can then decompose to CO_2 and water.

Organic Complexants/Chelators

Organic complexants and chelating agents are known to undergo radiolytic and chemical degradation in the tank wastes at Hanford. High concentrations of citric acid, ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), methane tricarboxylic acid, and nitriloacetic acid (NTA) have been identified in various waste storage tanks, especially AN-107 (Lokken et al. 1986). A number of chelate fragments, such as ethylenediaminetriacetic acid and iminodiacetic acid (IDA), were also identified.

The radiolysis of EDTA-type chelators has been examined for a number of specific complexes. For instance, nickel(II) aminopolycarboxylates undergo hydrogen abstraction with the hydroxyl radical (Mandel et al. 1991). When Ni(II)EDTA is reacted with either $\text{OH}\cdot$ or $\text{CO}_3\cdot$ the products are glyoxylic acid (OHCCOOH) and formaldehyde (Mandel et al. 1991). For the formation of

formaldehyde, the mechanism apparently involves sequential decarboxylation of the respective four acetic acid groups of the EDTA. The remaining methylol groups can be cleaved as formaldehyde.

Glyoxylic acid is formed from the same acetic acid groups by a hydroxyl substitution on the alpha-carbon. This secondary hydroxyacetic acid can rapidly decompose to glyoxylic acid. Glyoxylic acid, under oxidative conditions, probably converts to oxalic acid. Obviously, the chelated metal ion may have substantial direction on the route of decomposition of the organic chelator.

Hydroxyl radical induced decarboxylation has also been observed with numerous dipeptides (Bobrowski et al. 1991). The peptide (coupled amino acids) structure is quite similar to that of the aminopolycarboxylates. The simplest aminopolycarboxylic acid is IDA which can serve as a model for many of the EDTA-related compounds. Cobalt-60 gamma ray exposure of IDA leads to glycine, the smallest amino acid, as well as glycolic acid, formaldehyde, and hydrogen peroxide in the presence of air (Bhattacharyya and Saha 1976). The initial step of the radiolysis is hydrogen abstraction from one of the alpha-carbons of IDA, a mechanism noted for amino acid radiolysis. In the presence of oxygen, the IDA radical forms a peroxy-compound which degrades to the carbonyl product (glyoxylic acid). The aldehyde that is formed should oxidatively form oxalic acid with time. Alkylamines can be decomposed to various fragments and ammonia. However, the amines can react with aldehydes to form imines (Schiff bases) or they can be oxidized to nitrosoamines in the presence of nitrite ion. Preliminary results by J. A. Campbell, K. H. Pool, and P. K. Melethil of PNL (1992) indicate that the nitrosoamine route is quite available for amine removal (Schiff bases).

The radiolysis of water forms both hydrogen and hydroxide radicals under acidic and neutral conditions (Bhattacharyya and Saha 1976). In aerated solution, hydrogen radical is expected to react with oxygen rather than disappearing through reactions with IDA or other products. This mechanism is assumed to proceed as:

In alkaline solutions (pH 13) the level of hydrogen peroxide will be greatly reduced since the hydrogen radical reacts readily with the hydroxide ion to form a hydrated electron. However, the same radiolysis products of IDA are noted in basic and acidic solutions. In the absence of air, the radiolysis mechanism is directed only to glyoxalic acid, through glycine.

The radiolysis of NTA has been studied with NTA as a metal complex with cobalt (Bhattacharyya and Srisankar 1977). The molecular framework of the complex provides two centers for reaction, the metal ion and the organic ligand. Thus, the reaction of Co(III)NTA with the hydroxide radical can lead to either oxidation or reduction of the metal ion in the complex, depending on whether the initial attack is centered on the metal ion or hydrogen abstraction of the ligand. The products of radiolysis are IDA. The degradation of the ligand (NTA) has been presented as the possible oxidation of Co(III) to Co(IV) by the hydroxide radical followed by oxidation of the ligand. The mechanism in the presence of oxygen involves formation of a peroxy-intermediate followed by

the carbonyl product (glyoxalic acid). Interestingly, the yields of IDA and glyoxalic acid were the same in aerated solutions and deaerated solutions.

Surfactants

Minimal information is available concerning the radiolysis of specific surface active agents (surfactants). However, due to their relation to both alkanes and chelating agents, a number of inferences can be made. The major division of surfactants is anionic, cationic, and nonionic. Anionic refers to the salt form of the major ionic group within this group of surfactants, such as carboxylate or sulfonate; an example is sodium dodecylbenzene sulfonate. Cationic surfactants are usually nitriles or amines with long-chain alkyl groups; an example is dodecylpyridinium chloride. Nonionic surfactants generally include polyethylene oxides or glycols with an attached alkylated phenol, such as the decyl(ethyleneglycol) ether of dodecylphenol.

Anionic Surfactants

Radiolysis of aliphatic carboxylic acids, one type of anionic surfactant, can involve hydrogen abstraction, usually alpha to the carboxyl group (Campbell et al. 1989). However, radiolysis of small carboxylic acids, such as butyric acid, indicates that decarboxylation is the primary reaction. It should be noted that both carbon dioxide and carbon monoxide are observed as products of decarboxylation. The major hydrocarbon product is the parent alkane, propane in this case, following the loss of the carboxyl group. These alkanes can undergo hydrogen abstraction and provide alkenes. In the presence of air (oxygen), the peroxy radical is formed which directly decomposes to the corresponding carbonyl compound. Either a ketone or aldehyde is formed depending on the position of hydrogen abstraction.

Similar mechanisms can be expected for alkylsulfonates; however, the degradation products may include sulfur trioxide, which would be detected as sulfate. The aromatic rings in the surfactants should not initially be attacked unless the energy of the system is intensive. Aromatic groups, in general, are considered quite stable to ionizing radiation, but they do not provide this stability to large alkyl groups attached to the aryl-rings.

Alkylbenzene sulfonate surfactants have been examined in the presence of gamma radiation (Makarachkina et al. 1976). The alkyl chain of the surfactant was found to be oxidized, but the products were not specified. Similar results were noted with sodium decylsulfate (Sawai et al. 1978). Sulfate ion has been identified as a final radiolysis product of sodium toluene sulfonate (Veseloyskaya 1976).

Cationic Surfactants

The radiolysis of alkylamines, especially ethylamine, propylamine, and ethylenediamine, were examined with both pulse and gamma radiolytic techniques (Delaire and Bazouin 1979). Evidence for hydrogen abstraction from the amine group was noted; i.e., RNH radicals were observed. Hydrogen was the main gas emitted during radiolysis of these amines. The radiolysis of triethanolamine in aqueous acid or base produced acetaldehyde and diethanolamine (Schwarz 1982). This type of rearrangement has been also observed with ethylene glycol (Pikaev and Kartasheva 1975). Thus,

tertiary amines, a standard group in cationic surfactants, should provide aldehydes as each alkyl group is radiolytically removed from the amine. Under oxidative conditions, these aldehydes should convert to the corresponding carboxylic acid.

As noted previously with anionic surfactants, long-chain alkyl groups will be subjected to hydrogen abstraction.

Nonionic Surfactants

Decomposition of polyethylene glycols and alkylphenyl ethers have been observed under radiolysis conditions (Spasov and Balushev 1983). The radiolysis was catalyzed by the presence of di- and trivalent ions. Polyethylene glycols may decompose to a series of aldehydes as noted previously in the case of ethylene glycol (Spasov and Balushev 1983). This may be a stepwise process or may present a random mixture of ether fragments which rearrange further to acetaldehyde.

Summary

Alkanes undergo hydrogen abstraction in strong caustic/nitrate solutions by the oxide radical anion and nitrate radical. This reaction ultimately provides smaller fragments, which form carboxylates. Alcohols, aldehydes, and ketones can also undergo oxidation to carboxylates under these severe conditions. If the alkanes are highly concentrated, radiolysis may provide for oligomerization and larger molecules. Thus, the size of the products is very dependent on alkane concentration. In general, the products tend to be carboxylates.

The organic complexants and chelating agents will tend to degrade to fragments of the parent compound by removal of one or more of the carboxylic acid groups as formaldehyde and glyoxylic acid. The formaldehyde will further react in a manner similar to those aldehydes derived from alkane degradation. The glyoxylic acid probably converts to oxalic acid.

The various classes of surfactants will generally follow chemistry similar to the alkanes and the complexing agents. The long chain alkane group that serves as the hydrophobic end of the surfactant will be split from the hydrophilic functional group (carboxylic acid, amine) and further degrade as do the alkanes. The fragment containing the hydrophilic end of the surfactant will also further degrade depending on the type of functional group. Decarboxylation of the carboxyl group in anionic surfactants will produce carbon dioxide and carbon monoxide. Nonionic surfactants containing polyethylene glycols and alkylphenyl ethers will degrade to form aldehydes. The benzene ring, however, will not further degrade.

References

- Bhattacharyya, S. N., and N. C. Saha. 1976. *Radiation Res.* 68:234.
- Bhattacharyya, S. N., and E. V. Srisankar. 1977. *Radiation Res.* 71:325.

Bobrowski, K., C. Schoneich, J. Holcman, and K.-D. Asmus. 1991. *J. Chem. Soc., Perkin Trans.* 975.

Brite, D. W. 1954. "Identification of Impurities in Process THP Solutions." HW-31630, Quarterly Progress Report, Chemistry Unit, Jan-March, General Electric Atomic Products Operations, pp. 63-64.

Buxton, G. V., C. L. Greenstock, W. P. Helman, and A. B. Ross. 1988. *J. Phys. Chem. Ref. Data* 17:513.

Campbell, K. T., D.J.T. Hill, J. H. O'Donnell, P. J. Pomery, and C. L. Winzor. 1989. "Radiolysis of Polycarboxylic Acids and Model Compounds." *In The Effects of Radiation on High-Technology Polymers*, eds. E. Reichmanis and J.H. O'Donnell, pp. 80-94. ACS Symposium Series 381, American Chemical Society, Washington, D.C.

de Doncker, J., and B. Tilquin. 1991. *Bull. Soc. Chim. Belg.* 100:107.

Delaire, J. A., and J. R. Bazouin. 1979. *Can. J. Chem.*, 57:2013.

Djerassi, C. 1951. *Organic Reactions* 6:207.

Doering, W. V., and R. M. Haines. 1954. *J. Amer. Chem. Soc.* 76:482.

Foote, C. S. 1968. *Accounts Chem. Res.* 1:104.

Hendrickson, D. W. 1990. *Methods and Data for Use in Determining Source Terms for the Grout Disposal Program*. WHC-SD-WM-TI-355, Westinghouse Hanford Company, Richland Washington.

Lokken, R. O., R. D. Scheele, D. M. Strachan, and A. P. Toste. 1986. *Complex Concentrate Pretreatment FY 1986 Progress Report*. PNL-7687, Pacific Northwest Laboratory, Richland, Washington.

Makarochkina, L. M., L. B. Upadyshev, L. V. Putrya, Y. A. Panin, M. T. Filippov, S. P. Buslaeva, I. Z. Reznichenko, and R. V. Dzhagatspaenyan. 1976. *Khim. Prom-st. (Moscow)*:589.

Mandel, P. C., D. K. Bardhan, S. Sarkar, and S. N. Bhattacharyya. 1991. *J. Chem. Soc., Dalton Trans.* 1457.

Neta, P., and R. H. Schuler. 1975. *J. Phys. Chem.* 79:1.

Neta, P., and R. E. Huie. 1986. *J. Phys. Chem.* 90:4644.

Noller, C. R. 1958. *Chemistry of Organic Compounds*, p. 207. W. B. Saunders, Philadelphia, Pennsylvania.

Pandey, N. N., H. Narayan, R. S. Shukla, and K. Behari. 1982. *Z. Phys. Chem. (Leipzig)* 263:1055.

- Pikaev, A. K., and L. I. Kartasheva. 1975. *Int. J. Radiat. Phys. Chem.* 7:395.
- Sawai, T., T. Shimokawa, Y. Miki, K. Oseka, and T. Sawai. 1978. *Radioisotopes.* 27:20.
- Schwarz, H. A. 1982. *J. Phys. Chem.* 86:3431.
- Seguchi, T., Y. Katsumara, N. Hayashi, N. Hayakawa, N. Tamura, and Y. Tabata. 1991. *Radiat. Phys. Chem.* 37:29.
- Shukuji, A., S. Yamano, and A. Eguchi. 1983. *Proc. Int. Symp. Molten Salt Chem. Technol.*, pp. 99-103.
- Spasov, S., and B. Balushev. 1983. *God. Vissh. Inst. Arkhit. Stroit.-Sofiya.* 30:153; *Chem. Abstr.* 101:10190p.
- Stewart, R. 1967. *Mechanisms: Applications to Organic Chemistry*, p. 31. American Chemical Society, Washington, D.C.
- Tretyakov, V. P., G. P. Zimtseva, E. S. Rudakov, and A. V. Bogdanov. 1982. *React. Kinet. Catal. Lett.* 19:263.
- Stewart, R., P. M. Henry, and R. D. Temple. 1969. *Organic Reactions in Organic Chemistry*, p. 3. American Chemical Society, Washington, D.C.
- Ulbricht, W. H. 1991. *Report on 241-C Tank Farm Sampling Results of 1989.* WHC-SD-WM-RPT-019, Westinghouse Hanford Company, Richland, Washington.
- Veseloyskaya, N. V., V. M. Berenfel'd, E. V. Chumaevskii, and R. V. Dzhagatpaenyan. 1976. *Tr.-Mezhdunar. Kongr. Poverkhn.-Akt. Veshchestvam*, 7th ed. pp. 332-344 (pub. 1978); *Chem. Abstr.* 91:22818d.

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