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DOE UNDERGROUND STORAGE TANK WASTE REMEDIATION CHEMICAL PROCESSING HAZARDS

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PART I: TECHNOLOGY DICTIONARY

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Acronyms

DOE	Department of Energy
HLW	high level waste
IF	Idaho Falls
LLW	low level waste
M&O	management & operations
RCRA	Resource, Conservation & Recovery Act
SAR	Safety Analysis Report
SRS	Savannah River Site
TRU	Transuranic
TWRS	Tank Waste Remediation System
UST	underground storage tank
WV	West Valley

Definitions

anion	negatively charged dissolved species
ion	charged dissolved species (positive or negative)
cation	positively charged dissolved species
supernate	liquid UST waste
salt cake	cystallized supernate
sludge	precipitated neutralized UST waste

I.0 Introduction

This document has been prepared to aid in the development of Regulating guidelines for the Privatization of Hanford underground storage tank waste remediation. The document has been prepared it two parts to facilitate their preparation. Part II is the primary focus of this effort in that it describes the technical basis for established and potential chemical processing hazards associated with Underground Storage Tank (UST) nuclear waste remediation across the DOE complex. The established hazards involve those at Sites for which Safety Analysis Reviews (SARs) have already been prepared. Potential hazards are those involving technologies currently being developed for future applications. Part I of this document outlines the scope of Part II by briefly describing the established and potential technologies. In addition to providing the scope, Part I can be used as a technical introduction and bibliography for Regulatory personnel new to the UST waste remediation, and in particular Privatization effort. Part II of this document is not intended to provide examples of a SAR Hazards Analysis, but rather provide an intelligence gathering source for Regulatory personnel who must eventually evaluate the Privatization SAR Hazards Analysis.

1.0.1 Repositories

By the late 1970s it was evident the logistics required for nuclear waste disposal in the United States necessitated federal government sponsorship. Consequently, in 1982 the United States Congress passed legislation requiring the federal government to take responsibility for providing nuclear waste repositories. It was concluded two repositories are currently required for radioactive waste disposal as outlined in Figure 1.0.1-1.

Nuclear Waste Policy Act of 1982

Congress Authorizes the Federal Government (DOE)
to Provide Nuclear Waste Repositories

Waste Isolation Pilot Plant (WIPP)

Provides for Permanent Disposal
of Transuranic Waste

Yucca Mountain

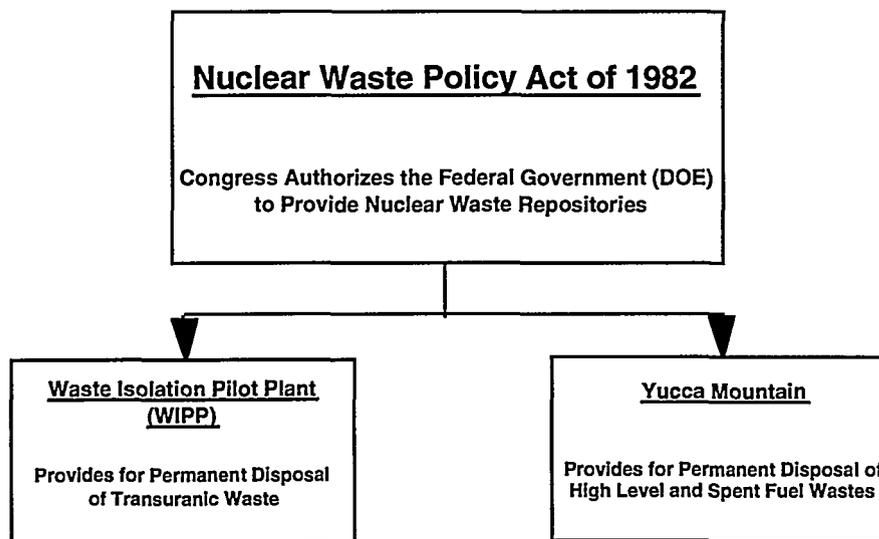Provides for Permanent Disposal of
High Level and Spent Fuel Wastes

Figure 1.0.1-1. Nuclear Waste Policy Act of 1982

The TRU waste generally consists of low-activity, long-lived radionuclides which pose a significant ingestion hazard. This waste requires very long-term deep underground disposal. The HLW generally consists of high-activity, short-lived radionuclides which pose a significant external exposure and ingestion hazard. This waste requires shorter-term deep underground disposal than TRU waste. The spent fuel consists of TRU and HLW.

The Waste Isolation Pilot Plant (WIPP) was selected as a repository for long-lived radionuclides (TRUs) excluding spent fuel, for which primary waste canister containment could not be guaranteed over the life-time of the radionuclides. Waste in this category is primarily related to weapons production. Recent plans as of 1994 were for disposal of approximately 53,000 cubic meters of waste in WIPP.[5] Some of these radionuclides have life-times well over ten-thousand years. Consequently, WIPP has been built within deep underground salt beds near Carlsbad, NM, which will serve as secondary containment.

Yucca Mountain was selected as the repository for short-lived radionuclides (HLW) and spent fuel. The spent fuel will originate primarily from commercial power plants. The HLW to be disposed of at Yucca Mountain is primarily due to spent fuel reprocessing for weapons materials and naval reactor fuel. Due to the shorter life radionuclides, the HLW disposal form (i.e. currently glass) is intended as primary containment, and the glass canister is intended as secondary containment. Yucca Mountain was originally planned for disposal of approximately 62,000 metric tons of uranium (spent fuel), and approximately 8,000 metric tons of glass (HLW), collectively not to exceed a thermal power density of 57 kW/acre.[6] More recent estimates suggest 84,000 metric tons of uranium, and approximately 60,000 metric tons of glass.[4] Depending on licensing difficulty, the final Yucca Mountain type repository may not be actually located at Yucca Mountain, Nevada. Current federal legislation limits the quantity of heavy metal in the first repository to no more than 70,000 metric tons until such time a second repository is in operation.

1.0.2 Waste

Approximately 100 million gallons (380,000 m^3) of radioactive waste is stored in underground tanks at the Hanford, Savannah River, Idaho Falls, West Valley and Oak Ridge Sites.[3] Figure I.0.2-1 shows the relative volume and radionuclide activity at these Sites. Hanford has the greatest volume of waste and Savannah River has the greatest activity. Generally speaking, this waste can not be disposed of as LLW in it's existing form. Furthermore, the volume (or mass) is much too large and consequently costly to be directly disposed of as HLW in the proposed underground repository.[4] To solve this problem, it is necessary to separate the UST waste into a small volume of HLW with most of the radionuclides, and a large volume of LLW with few radionuclides. Figure I.0.2-2 shows the variation in UST waste types across the DOE complex.
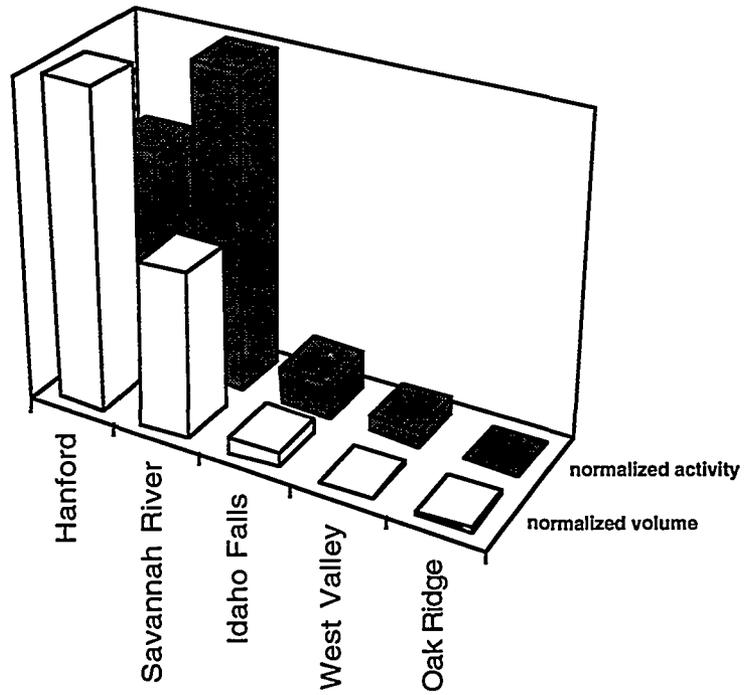
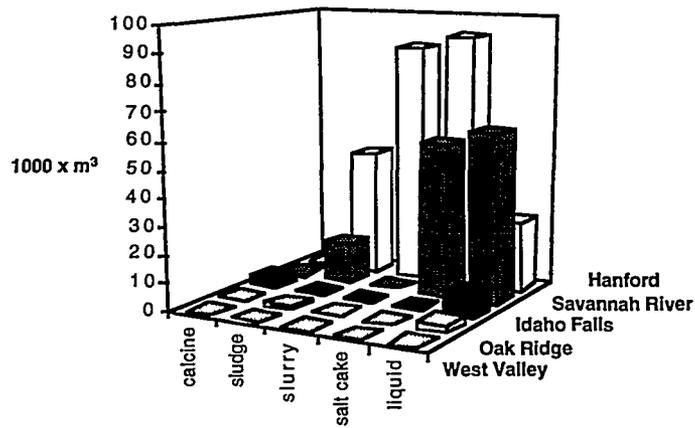Figure I.0.2-1 UST waste volume and activity at each Site

Figure I.0.2-2 UST waste type at each Site

I.1. Generic Flowsheet

The UST waste can be divided into two categories with regard to chemical processing. These categories are liquid-based processing and solids-based processing. Essentially, all waste other than sludge will undergo liquid-based processing, if processed at all. For instance, if it is decided direct vitrification of calcine at Idaho Falls produces too much HLW, it will be dissolved in acid prior to radionuclide separation. Salt cake will be essentially dissolved in the liquid added to retrieve the waste from tanks, has similar chemistry as supernate, and consequently will be processed for radionuclide separation with liquid-based processing. Figure I.1-1 shows the division of UST waste as that requiring liquid-based or solids-based processing.
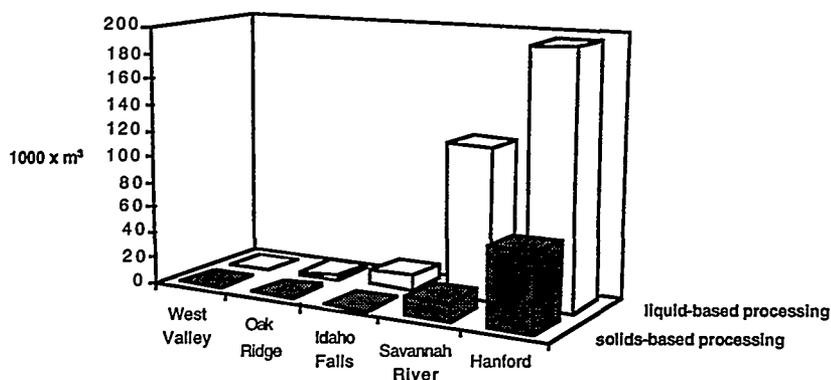
Figure I.1-1 UST waste requiring liquid-based or solids-based processing[3]

A generic flowsheet representing remediation of UST waste at all DOE Sites, in addition to the proposed responsibilities for Privatization activities at Hanford, is shown in Figure I.1-2. The solids (primarily sludge) are precipitates of the neutralization process used to prevent acidic corrosion of carbon steel USTs. This was accomplished by adding a sodium-based caustic to the original acid-based waste resulting from nuclear fuel reprocessing. Since the sludge is difficult to handle, it is intended to limit processing to a caustic wash which partially removes chemical species such as sodium, aluminum, phosphorus and/or chromium from the radionuclides. The liquids (including dissolved salt cake and possibly calcine) are processed such that most of their material can be disposed of as LLW. This generally involves separating the cesium, and/or strontium, and/or technetium, and/or TRUs from the nonradionuclides.
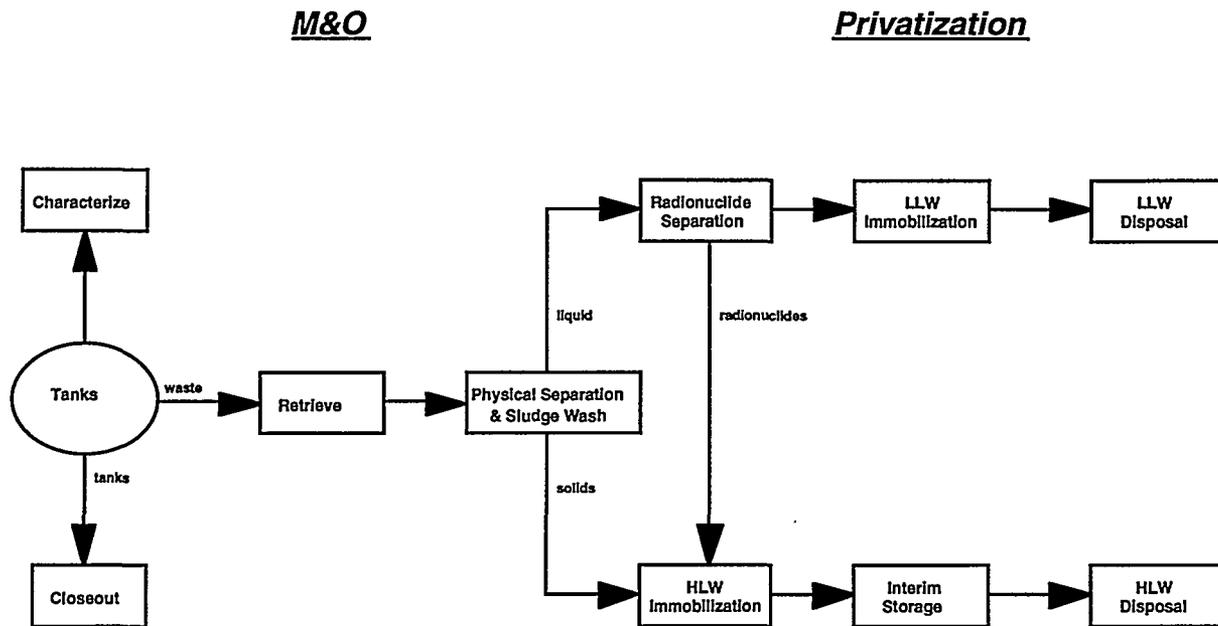
M&O   **Privatization**

Figure I.1-2 UST waste remediation process model as related to Hanford Privatization

The TWRS Process Flowsheet[7] was developed by Westinghouse Hanford Company as the Tri-Party Agreement[10] baseline for Hanford UST waste remediation, and can be used as an example for all DOE Sites to demonstrate which UST waste types (from Figure I-0.2-2) contribute most to the final HLW form prepared for the repository. Based upon the TWRS flowsheet, after liquid-based processing the UST supernate and salt cake generate approximately 12% of the final HLW form, and after solids-based processing the UST sludge generates the remaining 88%.[8] Even with the liquid-based and solids-based processing, the nonradionuclides dictate the final HLW form volume. If processing were performed to the degree of maximum radionuclide loading in the final HLW form, such that the nonradionuclides do not dictate the final HLW form volume, approximately a ten-fold volume reduction in the final HLW form could be realized.[9] Section I.3.7.2 of this document discusses the final HLW glass form in greater detail.

I.2. DOE Site Flowsheets

I.2.1 Savannah River

Approximately 35-million gallons (130,000 m³) of radioactive UST waste currently exists at the Savannah River Site (SRS).[3] This is a concentrated sodium/nitrate-based alkaline waste similar to that at Hanford, and is stored in 51 underground tanks all which have some type of secondary containment, but do not necessarily meet full RCRA requirements. The contents of these tanks consists of sludge, salt cake, and supernate. SRS waste differs from Hanford by it's age and chemical diversity. Hanford waste is older than SRS waste; and consequently, it's sludge may be more difficult to retrieve. Additionally, since Hanford was in operation before SRS, a greater variety of reprocessing methods were used as new technologies were developed. Therefore, the Hanford UST waste chemistry has greater variety and consequently requires greater characterization.
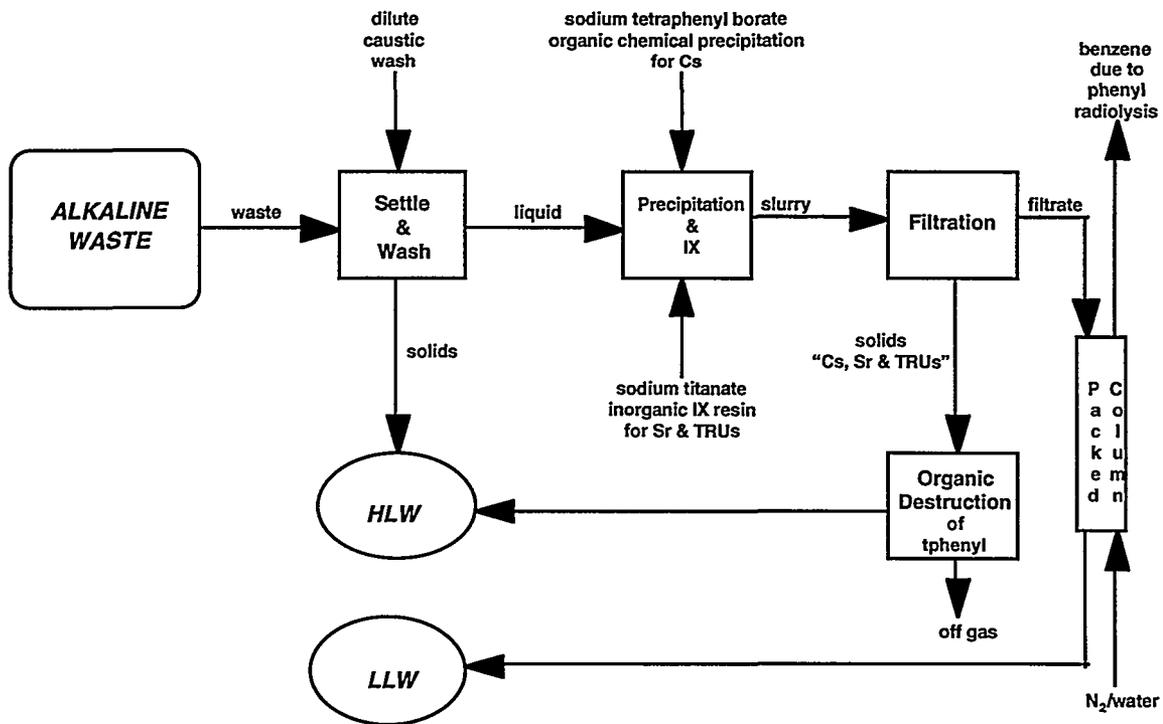
Figure I.2-1 Savannah River[11]

I.2.2 West Valley

Approximately 300-thousand gallons (1200 m³) of liquid HLW existed at West Valley.[3] This was predominantly high-sodium alkaline waste stored in one underground carbon steel tank. Of the 300-thousand gallons, most of the supernate (95% of original waste) has currently been processed for cesium removal via zeolite ion exchange. The liquid was concentrated following cesium removal to form 10,393 drums (at 71 gal/drum or 270 L/drum) of LLW grout.[12] The remaining sludge (5% original waste) had not yet been processed at the beginning of FY-1996.
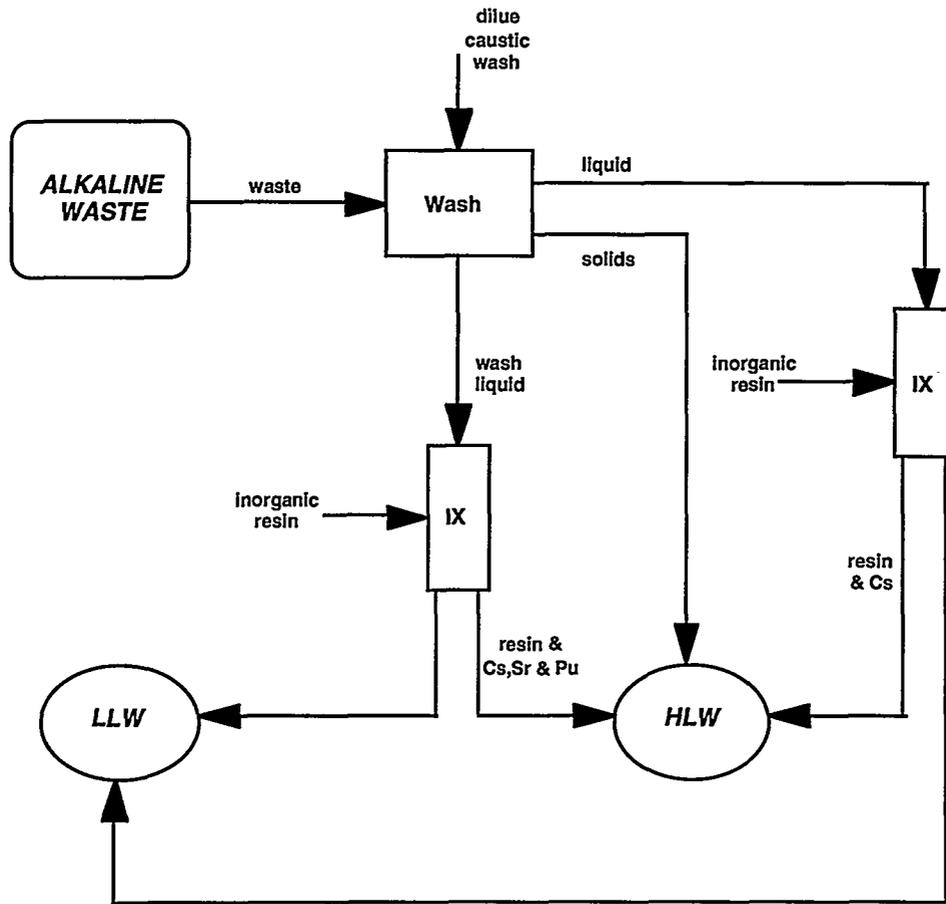
Figure I.2-2 West Valley[12]

I.2.3 Idaho Falls

The waste at Idaho Falls consists of 2.2-million gallons (10,000 m^3) of acidic liquid HLW and 3800 m^3 of calcine.[3] The liquid waste is stored in 11 underground steel tanks (resistant to acid corrosion) with concrete vault secondary containment. These tanks do not all meet full RCRA requirements. The calcine is stored in six Calcine Solids Storage Facilities, a seventh is empty. The calcine facilities have been designed for a 500-year lifetime; however, not all meet most recent seismic requirements. The composition of the liquid and calcine waste is highly variable and is essentially either aluminum, zirconium, fluorine or sodium based.
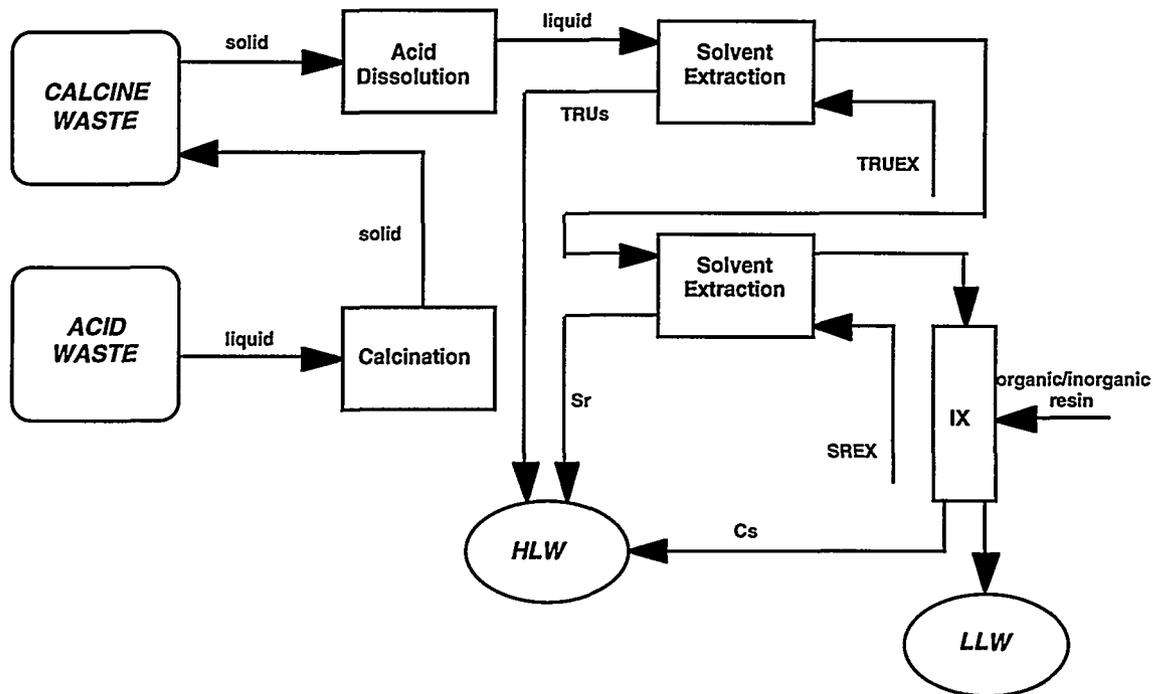

Figure I.2-3 Idaho Falls[13]

I.2.4 Hanford TWRS

Approximately 67-million gallons (250,000 m^3) of radioactive waste is currently stored in 149 single-shell and 28 double-shell underground tanks at Hanford.[3] This waste is predominantly a concentrated sodium/nitrate-based alkaline mixture. It has been determined that many of the single-shell tanks have or are leaking. The contents of the single-shell tanks consists of sludge (i.e. settled solids), salt cake (i.e. crystallized supernate), and supernate (i.e. liquid). To minimize leaking, an effort is underway and nearly complete to transfer the supernate from single-shell tanks to the double-shell tanks. The contents of the double-shell tanks consists of a slurry essentially composed of unsettled solids and supernate. In addition to the UST HLW, 1345 cesium capsules and 597 strontium capsules also exist at Hanford from prior processing of the salt cake, and may require repository disposal as well. The cesium and strontium have been immobilized as salts in the capsules.
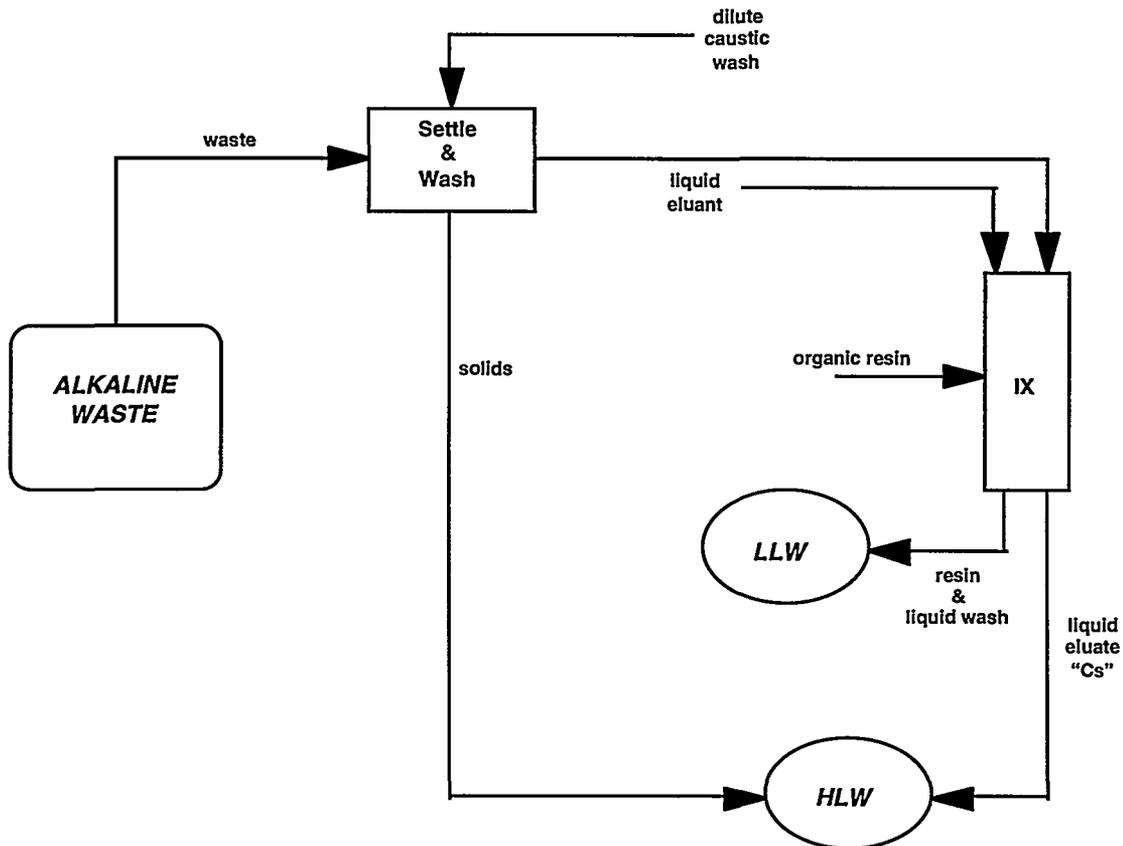
Figure I.2-4 Hanford TWRS[7]

I.3. Waste Processing Technologies

I.3.1 Solid/Liquid Separations

I.3.1.1 Settling/decant

The settling time of UST waste following a sludge wash is dependent on the solid particle diameter and liquid waste density. The most simple approach to estimating this time is to assume spherical solid particles which obey Stoke's law. Stoke's law requires the Reynold's number to be less than 0.3, which is not unreasonable for very small solid waste particles with densities similar to the surrounding liquid. The terminal velocity based on Stoke's law (Equation I.3.1.1a) is reached when the drag force between the particle and liquid is equal to the gravitational force on the particle.

(I.3.1.1a) $$V_t = g d_p^2 (\rho_p - \rho_l)/(18\mu)$$

where V_t = terminal velocity
d_p = particle diameter
ρ_p = particle density
ρ_l = liquid density
g = gravitational force
μ = liquid viscosity

The particle diameter is best defined by a probability distribution as shown by Figure I.3.1.1-1, where P is the probability of occurrence.
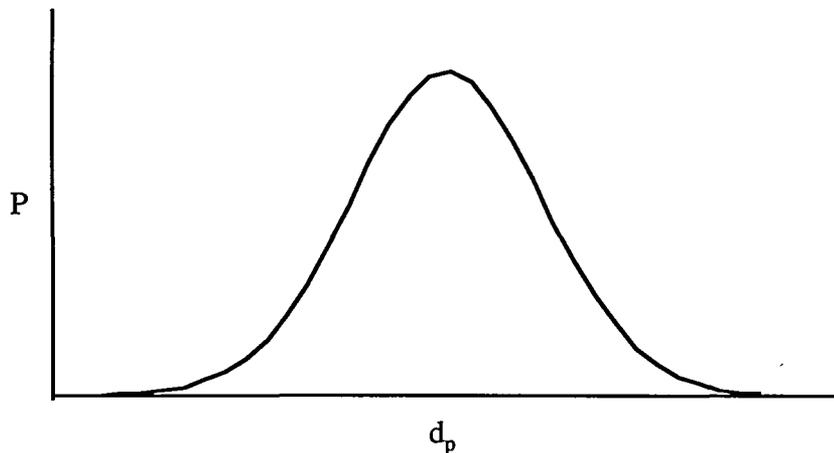

Figure I.3.1.1-1 Distribution of particle size

The settling time can be simply defined by the relationship:

$$V = \Delta l / \Delta t$$

where upon rearranging,

$$t_s = h_t / V_s$$

where h_t is the height which the particle settles from and V_s is the average velocity during settling. These can be approximated as follows:

$$h \sim \text{tank height}$$
$$V_s \sim V_t$$

since (1) the tank height is many orders of magnitude greater than the particle density and (2) the particle and liquid densities are similar. Consequently, the settling time can be represented by Equation I.3.1.1b as a first approximation. Equation I.3.1.1b is shown qualitatively by Figure I.3.1.1-2.

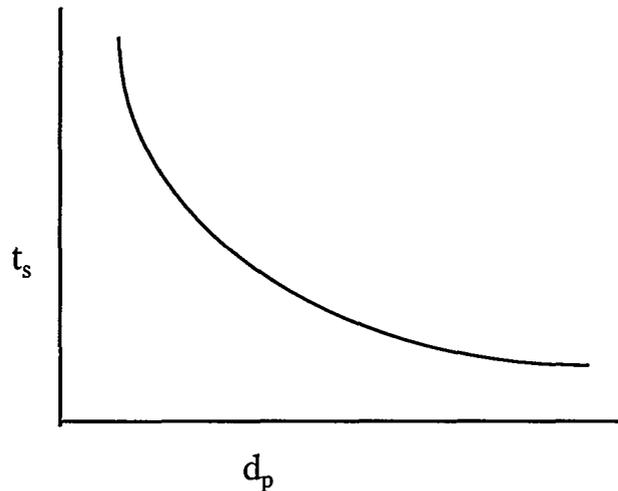$$(\text{I.3.1.1b}) \qquad t_s = 18\mu h / [g d_p^2 (\rho_p - \rho_l)]$$

Figure I.3.1.1-2 Settling time versus particle size

Figure I.3.1.1-1 and Equation I.3.1.1b can then be used to estimate the settling time required for any given fraction of total solids suspended.

I.3.1.2 Filtration

Cross-flow filtration as shown in Figure I.3.1.2-1 is a continuous process whereby the liquid portion of a slurry is passed through a semi permeable barrier. The passage of liquid through the barrier can be achieved by maintaining a lower downstream pressure in the waste liquid versus the waste solids. After an extended period of operation some cleaning of the barrier may be required. This can be accomplished by simple washing of the surface, or backflow through the barrier.
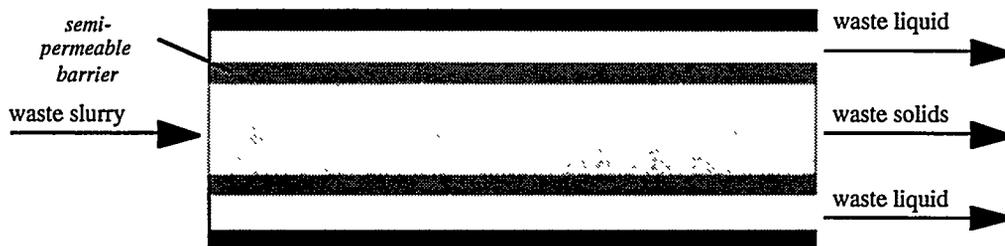
Figure I.3.1.2-1 Cross-flow filtration

Cross-flow filtration is planned for the separation of, cesium tetraphenyl borate precipitate and sodium titanate ion-exchange resin, from the processed liquid-based waste at SRS.[15]

I.3.2 Radionuclide Separations

Figure I.3.2-1 displays the planned and potential liquid-based radionuclide separation processes for the DOE Sites. The z-axis represents in-tank and out-of-tank processing, which is driven primarily by the UST integrity. In-tank processing requires less capital cost; however, it also requires a high degree of tank integrity. The x-axis represents the type of chemical processing which must be conducted batch-wise with in-tank processing, or can be conducted column-wise with out-of-tank processing. The column-wise processing. Solvent extraction has been suggested for IF since their waste is acid-based making it amenable to classical nuclear-fuel reprocessing techniques. Ion-exchange has been suggested for much of the alkaline waste across the DOE complex due to it's equipment and operational simplicity. Chemical precipitation has been selected at SRS due to it's potential simplicity based on in-tank processing and potential for minimizing the final volume of HLW by organic destruction. The y-axis represents the use of organic or inorganic chemicals for the separations. The inorganics are generally more stable than organics, but tend to contribute more to the final volume of HLW; whereas, the organics can often be destroyed and disposed of as other than HLW.
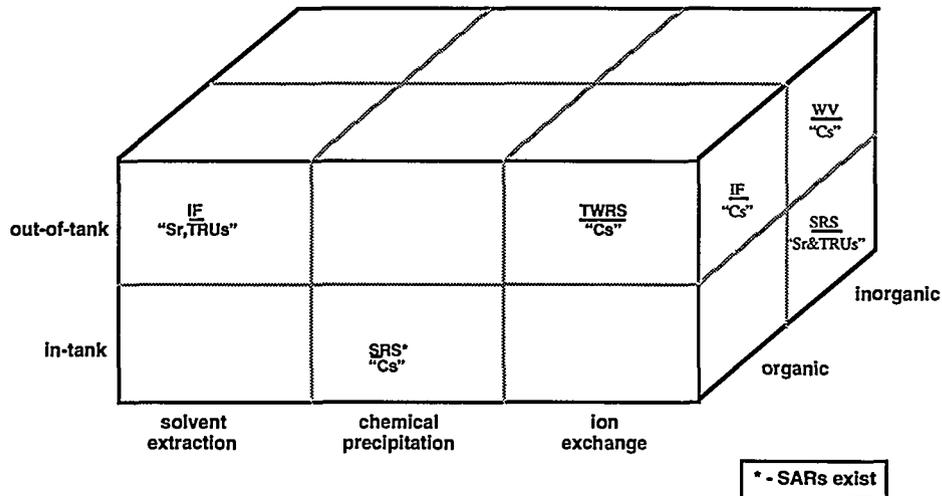

Figure I.3.2-1 Preferred technologies for chemical separation of radionuclides

I.3.2.1 Ion Exchange (IX)

Ion exchange (IX) is typically used for extracting species at low concentrations. The classical IX process is a chemical reaction where one ion in a liquid is exchanged for another in a solid. These exchanges follow classical chemical thermodynamic rules, which are used to establish the concentration relationship between the extracting species in the liquid and that in the solid. The solid material (or resin) can exist in a granulated powder-form for batch-wise contacting, or the granulated powder can be compacted to form larger shapes which can then be packed in a column. When batch-wise contacting is used the IX resin loading can not exceed the equilibrium concentration related to the waste following the extraction. If multiple columns are used in series, the IX resin loading can reach the equilibrium concentration related the original waste composition. Consequently, column-wise IX can achieve greater resin loading than batch-wise IX.

It is often possible to reverse the chemical reaction following resin loading. This permits separate disposal of the radionuclides as HLW and the resin as LLW, plus multiple use of the resin itself. The process of reversing the reaction and removing the extractants is referred to as elution. Following elution, the resin must be prepared for reuse. This process is referred to as regeneration. The three primary process steps for a reusable resin are then (1) loading, (2) elution, and (3) regeneration. Generally speaking, organic resins are more easily reused than inorganic resins.

With the exception of technetium, the primary radionuclides present in UST waste exist as cations. Technetium exists as an anion due to the complexes it forms in basic solutions. IX resins have been developed to exchange cations or anions.

I.3.2.1.1 *Zeolite IX Resin*

Zeolites are a well defined class of naturally occurring alumino-silicate minerals. Zeolite molecular frameworks are generally very open with channels and cavities containing water and cations. This allows for the ion exchange behavior. Many naturally occurring zeolites can be produced synthetically, and some zeolites with no known natural counterpart have been made synthetically. Materials with zeolite behavior, but not composed of alumino-silicate are refereed to as zeotypes. Figure I.3.2.1-1 displays the typical structure for a zeolite. The West Valley Site has used a zeolite IX resin[19] with column-based processing to separate cesium from it's liquid-based UST waste.[14] Generally speaking, the zeolites are not easily elutable such that the bulk of their mass is disposed of as HLW with the radionuclides. This is the case at West Valley where the processed IX resin has been stored with the sludge in a UST awaiting HLW vitrification.

[SiO_4]^{4-} and [AiO_4]^{5-} Form Basic Tetrahedra Building Block of all Zeolites

[Si]^{4+} and [Al]^{3+} are located at the center of the tetrahedra

Other cations (non Si and Al) and water molecules are sited (trapped upon formation) within the cavities and channels formed by the combining of tetrahedra. Below is an example of such a cavity or channel.

The number of cations present within a zeolite structure is determined by the number of [AlO_4]^{5-} or [SiO_4]^{4-} tetrahedra included in the framework.
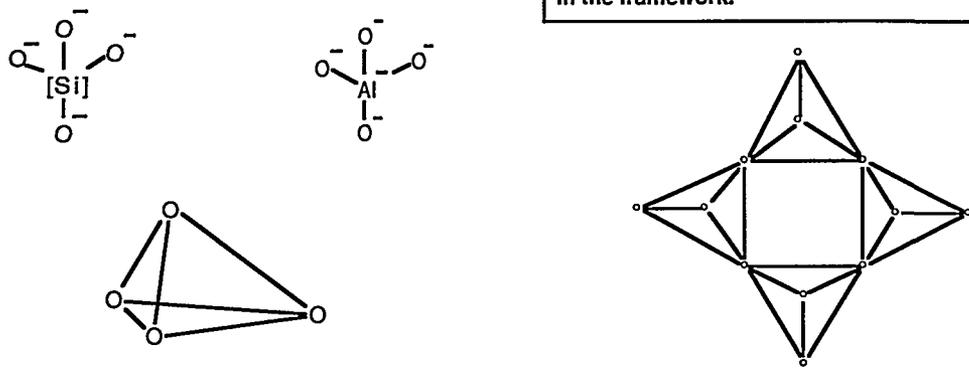
Figure I.3.2.1-1 Inorganic zeolite based resin

I.3.2.1.2 *inorganic IX resin*

A non zeolite inorganic IX resin differs from a zeolite (also inorganic) IX resin by exchanging ions which are part of the base resin molecule, rather than ions trapped within channels and cavities of the base resin molecule. As shown by Figure I.3.2.1-2 titanate is the base molecule for the sodium-titanate resin which is used at the Savannah River Site for strontium and TRU separation.[15] In this particular case, two sodium ions are exchanged for one strontium ion and/or a similar exchange of sodium ions occurs for the TRUs. Since the separations at SRS are conducted in-tank, no attempt is made to reuse the cesium loaded titanate resin.

Another non zeolite inorganic IX resin, which has been proposed for column-based IX at Hanford, is crystalline silico-titanate (CST).[16]

$$Na^+(Ti_2HO_5)^- + Sr^{2+} \longrightarrow Sr^{2+}(Ti_2HO_5)_2 + 2Na^+$$

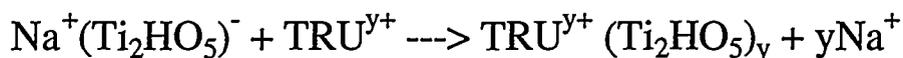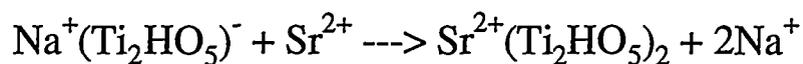$$Na^+(Ti_2HO_5)^- + TRU^{y+} \longrightarrow TRU^{y+}(Ti_2HO_5)_y + yNa^+$$

Figure I.3.2.1-2 Inorganic nonzeolite sodium-titanate resin

I.3.2.1.3 Organic IX Resin

Many types of organic IX resin exist today for cation and anion exchange. A classical form of cation exchange resin is based on the phenol-formaldehyde polymer shown in Figure I.3.2.1-3. This is also the resin-base proposed for separation of cesium from liquid-based UST waste at Hanford by the TWRS Flowsheet.[7] The specific resin recommended is CS100 manufactured by Rohm & Haas. Resorcinol differs from phenol by an additional OH-group on the carbon ring.[17] Resorcinol-formaldehyde based resins have also been proposed for separating cesium from UST liquid-based waste.[18] Generally speaking, the organic resins are easily elutable such that the bulk of their mass can be disposed of as LLW.

Hydrogen atoms can be replaced by cations.
For instance:
• Na⁺ from NaOH willreplace H⁺ (regeneration)
• Cs⁺ from CsNO₃ (waste) will replace Na⁺ (loading)
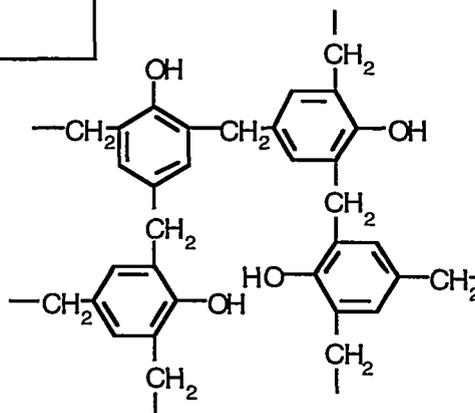• H⁺ from HNO³ will replace the Cs⁺ (elution)

Figure I.3.2.1-3 Organic phenol-formaldehyde based resin

Phenol-formaldehyde and resorcinol-formaldehyde are eamples of organic IX resin for processing of cations in alkaline liquids. An example of an organic IX resin for processing of cations in acidic liquids is ammonium molybdophosphate (AMP). This resin has been proposed for cesium separation of the acid-based waste at Idaho Falls,[13] as shown by Figure I.3.2.1-4. Polyacrylonitrile has been proposed as an engineered support for the AMP.

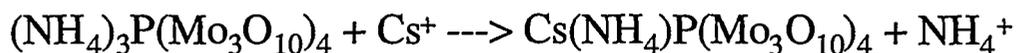$$(NH_4)_3P(Mo_3O_{10})_4 + Cs^+ \longrightarrow Cs(NH_4)P(Mo_3O_{10})_4 + NH_4^+$$

Figure I.3.2.1-4 Organic ammonium molybdophosphate resin

I.3.2.2 Solvent Extraction

Generally speaking, the principles behind solvent extraction require the formation of (1) first a neutral aqueous complex and (2) second a neutral aqueous plus organic complex. This aqueous/organic complex is then soluble in the organic phase. For the case of the Purex process, the metal cation to be extracted (such as uranium) is first complexed with nitrate anions, and then the metal-nitrate complex is further complexed with tributyl phosphate (TBP) from the organic phase. This can occur within the aqueous phase (due to the small but significant TBP solubility in the aqueous phase), or at the aqueous/organic interface. Solvent extraction (SX) has the advantage over IX of greater loading per mass of extractant or resin, since much of the IX resin particle is inaccessible. However, SX processing equipment is generally more complex and consequently more expensive to fabricate and operate than IX equipment.

Solvent extraction is being considered for separation of Sr and TRUs from UST waste at Idaho Falls due to their acidic waste conditions.[13] Classical SX related to the nuclear industry has been developed for acid-based solutions from fuel reprocessing. For TBP and CMPO, the aqueous based TRU cations are probably complexed with the electron-rich surface of the oxygen atom, thereby making the complex soluble in the organic phase.[20] In the case of crown ether, the strontium cation preferentially fits within the crown structure and probably complexes with the electron-rich surface of the oxygen atoms.[20]

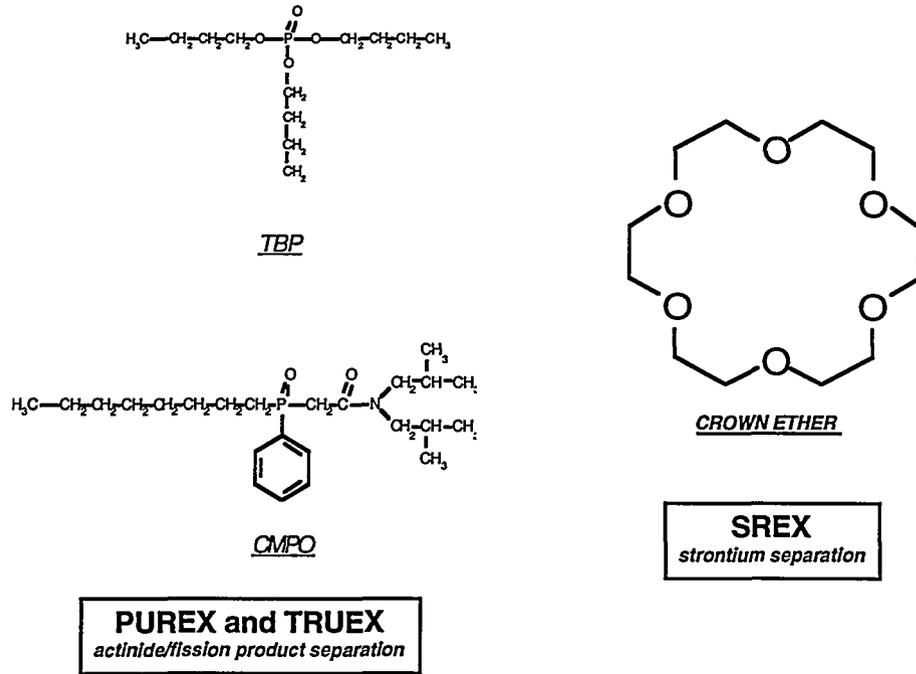Figure I.3.2.2-1 Typical solvent extractants

Acronym definition:

PUREX	plutonium and uranium extraction
TRUEX	Transuranic extraction
SREX	strontium extraction
TBP	tri-butyl phosphate
CMPO	carbamoylmethylphosphine oxide

I.3.2.3 Chemical precipitation

The chemistry of precipitation is similar to ion exchange. The precipitation process selected by SRS for cesium separation from the liquid-based waste involves the exchange of sodium in sodium tetraphenyl borate (Na-TPB) molecule with cesium in solution, shown in Figure I-3.3.3-1.[15] Whereas the Na-TPB is soluble in the waste at the concentrations utilized, the Cs-TPB is insoluble at all significant concentrations. The purpose for using the organic chemical precipitation process is to minimize HLW disposal by destruction of the organic phenol leaving only cesium and boron for final HLW disposal.
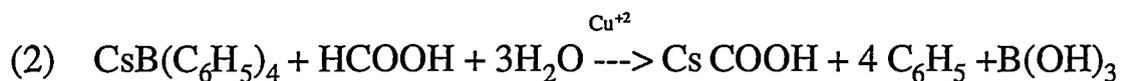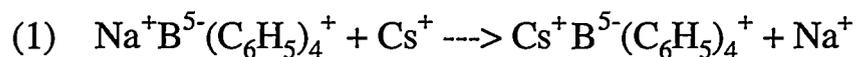
$$(1) \quad Na^+ B^{5-}(C_6H_5)_4{}^+ + Cs^+ \ ---> \ Cs^+ B^{5-}(C_6H_5)_4{}^+ + Na^+$$

$$(2) \quad CsB(C_6H_5)_4 + HCOOH + 3H_2O \ \xrightarrow{\ Cu^{+2}\ } \ Cs\ COOH + 4\ C_6H_5 + B(OH)_3$$

Figure I.3.3.3-1 Chemical precipitation

I.3.3 Nonradionuclide Separations

I.3.3.1 Sludge processing

Due to the transport difficulty associated with UST waste solids, minimum handling and consequent processing is desired. However, a simple wash and caustic leach has been proposed to reduce the amounts of selected species which can individually dictate the final volume of HLW glass. These species are primarily (1) sodium due to neutralization, (2) aluminum from fuel cladding, (3) chromium due to the glass sensitivity towards it, (4) phosphate from the Bismuth-Phosphate separation process at Hanford, and (5) sulfate at West Valley. Table I.3.3.1-1 shows the individual species HLW. These constraints are due to either (1) formability concerns during melting or (2) glass crystallization concerns during permanent disposal.

	maximum wt%[7]
Al as Al_2O_3	11.0
Cr_2O_3	0.5
Na_2O	12.5
P as PO_4	4.0
SO_4[14]	0.3

Table I.3.3.1-1 HLW glass constraints at SRS and Hanford

Generally speaking, the wash and leach are actually two different operations. The wash is used primarily to remove the interstitual liquid between the solid waste particles; whereas, the leach actually involves partial dissolution of the solid waste. Since the sludge of interest for UST waste remediation is due to alkline neutralization, the wash is generally a dilute caustic and the leach a more concentrated caustic. The leach step is not to be confused with sludge dissolution which involves nearly complete dissolution of the sludge by acid. In the case of UST waste, NaOH is the primary candidate for wash and leach; whereas, nitric acid is the primary candidate for dissolution.

I.3.3.2 Crystallization

Crystallization can be used to decrease the amount of nonradionuclide material disposed of as HLW. This can be accomplished by at least two different appoaches. These are (1) increasing the concentration of radionuclides prior to radionuclide separations such as ion exchange, or (2) removing some of the nonradionuclides following radionuclide separations. Both of these approaches involve precipitating principally some of the sodium nitrate which is at near saturated conditions prior-to and following radionuclide separations, as shown in Figure I.3.3.2-1. This is easily acomplished for UST waste since most of the metal nitrates (radionuclides and nonradionuclides) present have similar solubilities (approximately within an order of magnitude), and sodium concentrations are approximately 10^5 - 10^6 (Hanford) times greater than radionuclide concentrations. Consequently, if the near-saturated waste liquid is cooled the sodium readily precipitates before the radionuclides. Other candidates for precipitation from UST waste include as an example aluminum nitrate. If crystallization is used prior to radionuclide separation, advantages and disadvantages exist. The primary advantage is concentration of the radionuclides which permits higher loading of ion exchange resins or extractant in solvent extraction. The disadvantage is operation of the crystallizer with significant radionuclides present, requiring additional shielding and operating care.
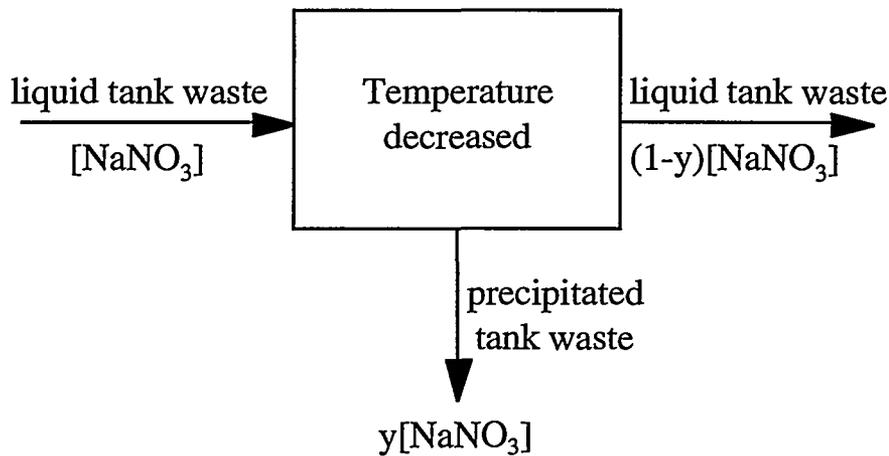

Figure I.3.3.2-1 Principal nonradionuclide separated by crystallization

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I.3.5 Recycle and Volume Reduction

I.3.5.1 Evaporation

Evaporation is used to separate volatile from much less volatile components. This is in contrast to distillation which is used to separate two or more similarly volatile components from each other. An example of this process for UST waste remediation might be the separation, and consequent recovery for recycle, of water from the much less volatile sodium hydroxide used in the sludge wash. While the vapor pressure of water is 760 mm-Hg at 100 C, the vapor pressure of sodium hydroxide is less than 1 mm-Hg at 100 C. A typical evaporator is shown in Figure I.3.5.1-1, where liquid feed enters the boiling section, is forced through tubes, and then separates into a liquid and vapor phase. A portion of liquid is recycled to achieve the desired concentration for the less volatile component.
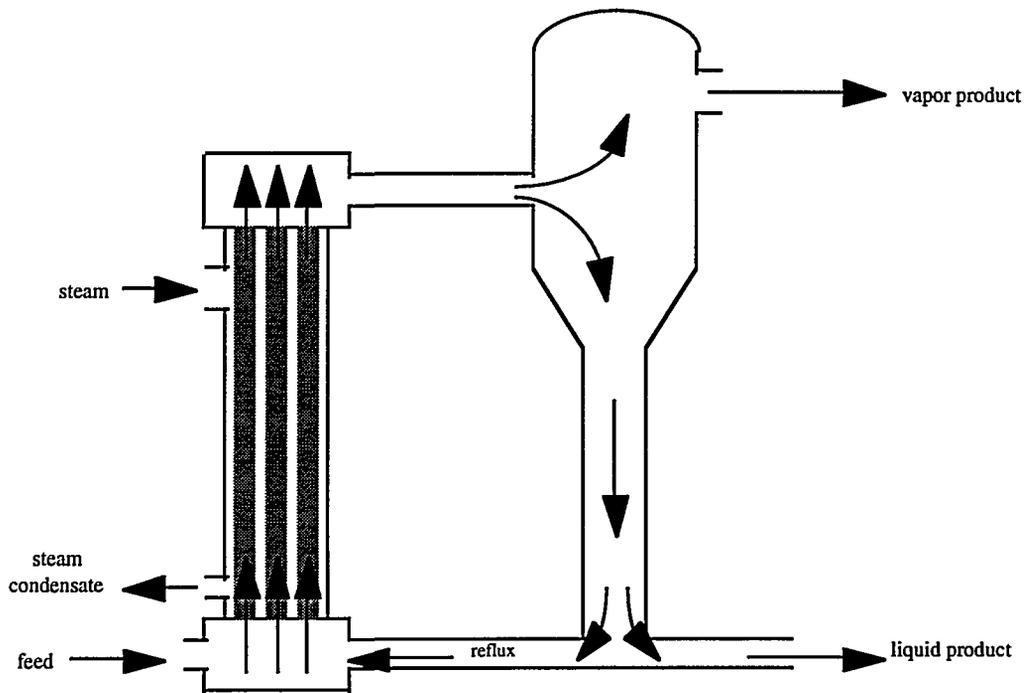
Figure I.3.5.1-1 Evaporator operation

I.3.5.2 Distillation

Distillation is used for the separation of two similarly volatile components. An example of this process for UST waste remediation might be the concentration of nitric acid used for dissolution of calcine-based wastes or the sludge of alkaline wastes. If it is decided that sludge dissolution is required to minimize the final volume of HLW, a distillation step may be required for acid recycle. Following dissolution of the sludge, radionuclides will be separated leaving a nitric acid and water based LLW. Acid concentration and recycle could be performed to minimize the final volume of LLW. While the vapor pressure of water at 100 C is 760 mm-Hg, that of nitric acid is similar at 1282 mm-Hg. As shown in Figure I.3.5.2-1, the vapors are passed upward through many perforated plates where the more volatile components are preferentially passed upward, and the less volatile component are preferentially condensed and passed downward.
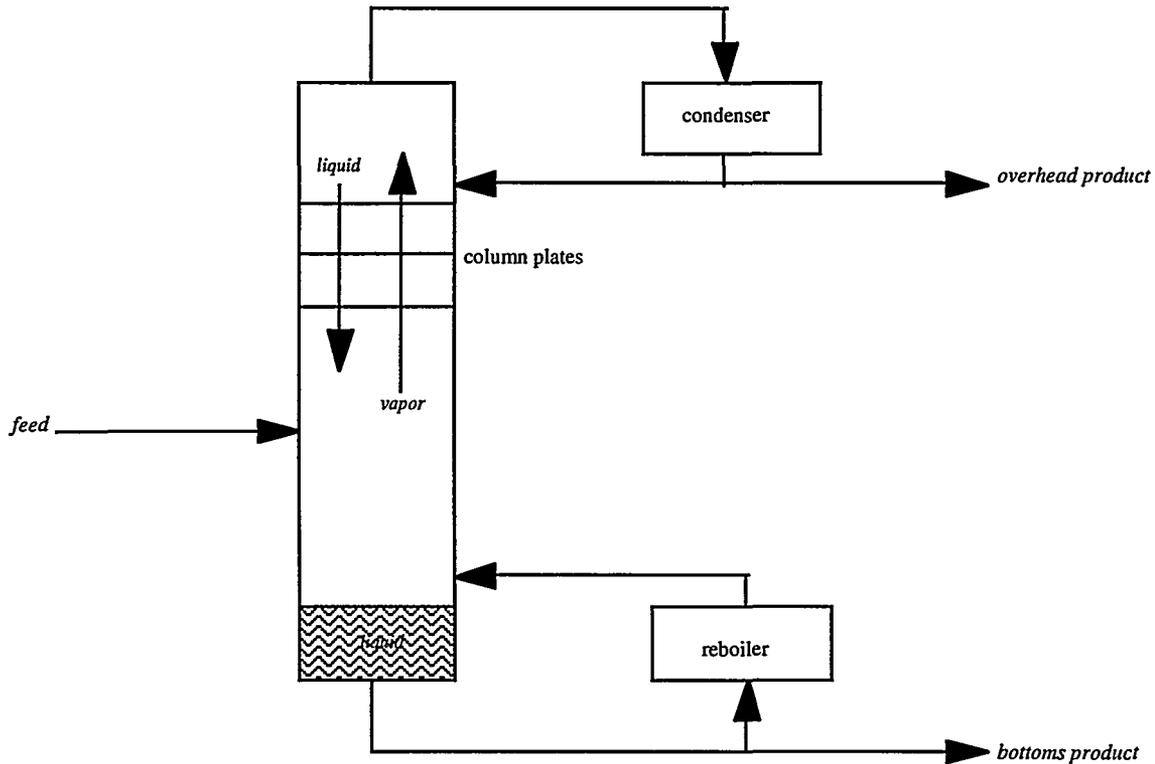
Figure I.3.5.2-1 Distillation operation

I.4 Immobilization Technologies

The classical immobilization methods for radioactive waste disposal are cementation/grout for LLW and vitrification/glass for HLW. It is essentially it's amorphous characteristic which makes glass preferred over grout for HLW immobilization. While the objective with cementation/grout is formation of stable minerals incorporating the radionuclides, these minerals are of a crystalline nature which are susceptible to leaching due to grain boundaries and typical crystalline defects such as dislocations. Glass on the other hand does not form a crystal or any ordered molecular pattern; consequently, it is much more impervious to outside influences which can cause leaching.

I.4.1 CementationGrout

Immobilization of radioactive wastes by incorporation in cement/grout has been practiced for many years. However, current day state-of-the-art technology has emphasized the focus on developing cement/grout mixtures which form stable minerals with radionuclides. The intent is to produce cement/grout with superior resistance to leaching by formation of specific crystalline types.

I.4.2 Vitrification

The three most significant technology concerns related to glass use for HLW or LLW disposal are (1) handling during formation, (2) multiphase formation and (3) divitrification with time. Handling is generally addressed by careful control of the melt viscosity. Multiphase formation is dependent on the limiting maximum concentration of any one particular waste species, and the total concentration of the cumulative waste species. And finally, divitrification (or crystallization) over time is generally due to chemical reactions which can be enhanced due to radionuclide heating and consequent increased chemical kinetics and diffusivity. Divitrification can be controlled by the glass chemistry. Generally speaking, based on the composition of UST wastes, sodium has the greatest impact on glass formation by affecting the melt viscosity, and species such as aluminum, chromium, and phosphorus have the greatest impact on additional phase formation.

The classical varieties of glass melters are (1) in canister versus continuous melter and (2) induction heated -versus joule-heated. Canister forming involves melting of the waste in the final canister for disposal. A continuous melter forms the glass outside the final disposal canister. Induction-heating refers to heating from outside the melt mixture; whereas, joule-heating refers to electrical resistance heating within the melt mixture. Figure I.4.2-1 shows in very general terms a joule-heated glass melter made of either a ceramic or metallic refractory material.
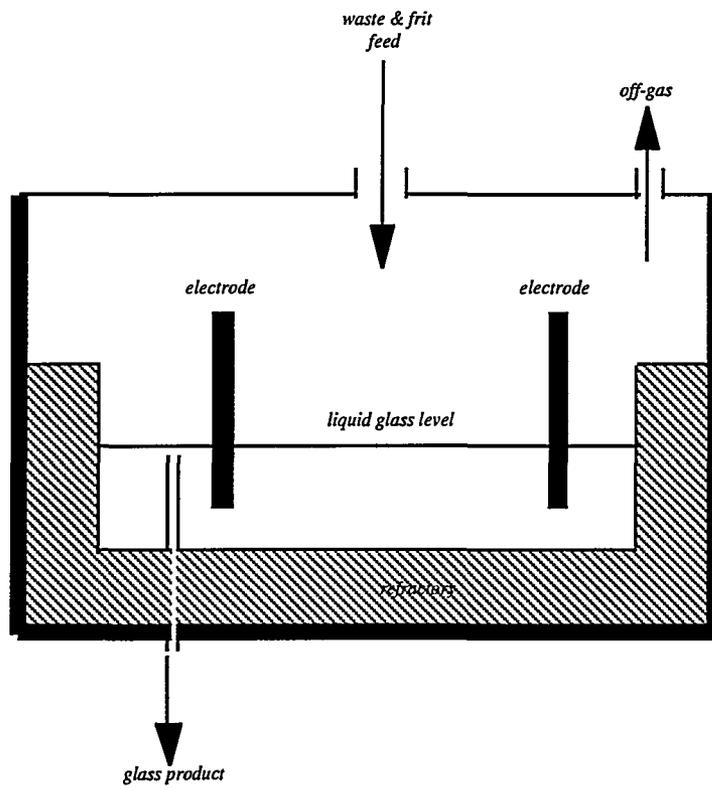
waste & frit
feed

off-gas

electrode

electrode

liquid glass level

refractory

glass product

Figure I.4.2-1 Joule heated melter

I.5 Off Gas Technologies

The primary UST waste remediation process requiring off gas treatment is vitrification. This is due to it's temperatures being higher than the other processes; and consequently, it's associated higher vapor pressures. Off gas of concern involves solid and liquid airborne aerosols, plus vapors. Particles and aerosols are generally divided into two classes (1) those larger than 3-microns diameter which are relatively easy to separate by scrubbers, demisters, cyclones or electrostatic precipitators, and (2) those smaller than 3-microns diameter which can be separated by filters. Vapors include radionuclide hazardous species such as cesium, ruthenium, technetium and mercury. The processes with which these species are removed depends on the volatile compounds they form. Absorption and adsorption are commonly used.[21]

I.5.1 Filters

In general, filters are used to remove aerosols and particles with diameters less than 3-microns. Two primary types of filters are used for aerosol and particulate removal related to UST waste remediation off gas treatment. These are (1) prefilters and (2) high efficiency particulate (HEPA) filters.[21] Prefilters ere available in three groups ranging from low to high separation efficiency. HEPA filters are used when very high separation efficiency is required. These filters are a disposable, dry-fiber medium in a rigid frame.

I.5.2 Electrostatic Precipitation

Electrostatic precipitators are used for removing particles less than 2 microns diameter from gas streams with high efficiency. The principle of operation is ionization of the gas stream with high-voltage electrodes. The charged particles are then collected at the appropriate electrode.

I.5.3 Absorption

Absorption is defined in a broad sense as dissolution of a solid particle, liquid aerosol or vapor in a liquid phase absorbent. A common absorption process is scrubbing. Figure I.5.3-1 shows a packed-column which is a common type of process equipment used for absorption, where the absorbing liquid generally flows countercurrent to the gas or vapor. Some of the UST waste remediation off-gas species which can be separated by absorption include nitric acid vapor, No_x gases, technetium vapors and mercury vapors.

A specific de-absorption application relate to UST waste remediation is the removal of benzene from liquid-based waste at Savannah River. Benzene is produced by hydrolysis and radiolysis of tetraphenyl borate used to precipitate cesium. This benzene is removed by gas stripping with humidified nitrogen in a packed-column.[22]
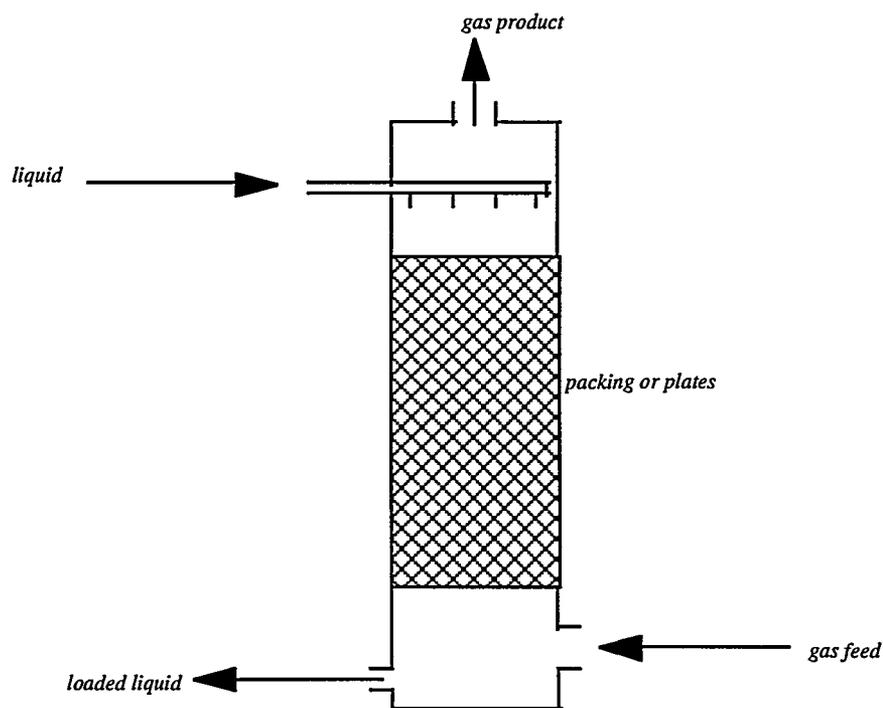
Figure I.5.3-1 Absorption by packed column

I.5.4 Adsorption

Adsorption is defined in a broad sense as a surface attachment between a liquid aerosol or vapor with a solid-phase adsorbent. A common adsorption medium is activated charcoal. Figure I.5.4-1 shows a fixed packed-bed which is a common type of process equipment used for adsorption, where the adsorbing medium can be fixed or flow countercurrent to the gas or vapor as in a fluidized bed. One of the important UST waste remediation off-gas species which can be separated by adsorption is ruthenium on a silica-gel bed.
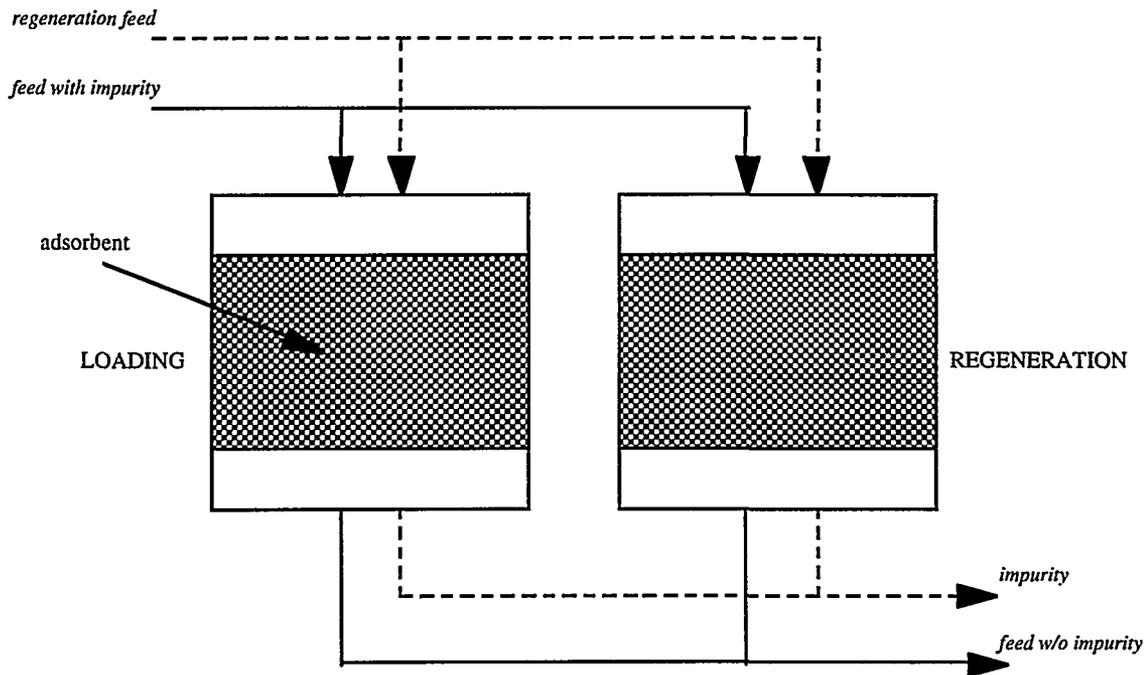
Figure I.5.4-1 Adsorption fixed packed-bed

21. Edited by T.E. Carleson, N.A. Chipman and C.M. Wai, *Separation Techniques in Nuclear Waste Management: Chapter 13 - Treatment of Off-Gases from process Operations*, CRC Press, New York, 1996.
22. T.P. Gaughan and G.A. Taylor, *Decontamination and Treatment of High Level Liquid Mixed Waste to Meet Regulatory Compliance Issues Outlined in Federal Facilities Agreements (U)*, Westinghouse Savannah River Company, WSRC-MS-93-380, 1993.*

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