

# DOUBLE-SHELL TANK WASTE PRETREATMENT

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## ABSTRACT

Double-shell tanks contain most of the transuranic/high-level chemical processing waste generated at the Hanford Site in recent years. A small mass fraction of this waste is responsible for its characterization as transuranic/high-level waste. Pretreatment will partition the waste into a small fraction containing most of the transuranic/high-level components and a large fraction that is a low-level waste. The operations for achieving this objective include dissolution of water-soluble salts, dissolution of precipitated metal oxides in acid, clarification of the resulting dissolver liquors, transuranium element removal by solvent extraction and cesium removal by ion exchange. The primary benefit of pretreatment is a reduction in the overall cost of waste disposal.

## BACKGROUND

Most of the radioactive chemical processing waste generated at the Hanford Site over the last 45 years is still in storage either in the form of alkaline slurries or as highly concentrated, encapsulated isotopic ( $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) sources. The recent Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) between the Washington State Department of Ecology, the U.S. Environmental Protection Agency, and the U.S. Department of Energy established a schedule for the retrieval, processing, and disposal of a portion of this waste(1). As operations contractor for the Hanford Site, Westinghouse Hanford Company is taking the necessary actions to fulfill the terms of the agreement.

## INTRODUCTION

Some Hanford Site terminology used in this paper must first be defined.

**Double-shell tank** refers to the 3,785 m<sup>3</sup> (1,000,000-gallon) underground storage tanks that contain most of the chemical processing waste generated at the Hanford Site in the recent years. There are 28 double-shell tanks, 10 of which contain transuranic (TRU)/high-level waste. The bulk of the tank waste at the Hanford Site is still contained in 149 old-style single-shell tanks.

**Treatment** refers to the production of a disposable waste form. The preferred treatment for TRU/high-level waste is conversion to borosilicate glass at the Hanford Waste Vitrification Plant (HWVP). Low-level waste is treated at the Grout Treatment Facility (GTF)(2).

**Pretreatment** refers to the chemical processing that converts double-shell tank waste into treatment feed streams. Pretreatment produces a TRU/high-level waste fraction (HWVP feed) and a low-level waste fraction (GTF feed).

The GTF is currently operational. Pretreatment facilities are expected to be operational in fiscal year (FY) 1995. Construction of the HWVP is scheduled to begin in FY 1991 with startup in FY 1999.

The "critical components" mentioned throughout this paper are a group of chemical species including chromium, fluoride, noble metals, phosphorous, sulfur, and total organic carbon (TOC). The HWVP melter operations and borosilicate glass performance can be adversely effected by too much of a critical component in the glass plant feed. Pretreatment of four types of double-shell tank waste will be discussed: Neutralized Current Acid Waste (NCAW), Neutralized Cladding Removal Waste (NCRW), Plutonium Finishing Plant Waste (PFPW), and Complexant Concentrate Waste (CCW).

The presence of a small fraction by mass of radioactive species is responsible for the classification of the above waste types as TRU/high-level waste. Wholesale treatment of the double-shell tank waste at the HWVP with subsequent disposal at a geological repository would be exorbitantly expensive and unnecessary. Pretreatment technology is being developed to partition tank waste into a relatively small TRU/high-level fraction and a low-level fraction containing a high percentage of the prevalent non-radioactive metallic components (Na, Al, Fe, and Zr). Pretreatment will utilize a series of separations processes that range from mundane operations like water washing to recently developed solvent extraction technology. The effect of these operations is to reduce the volume of glass that will result from a given volume of raw waste.

Glass volume reduction is brought about by the following activities:

1. Dissolving soluble salts in water (NCAW only) or dissolving a high percentage of the precipitated metal oxides in acid
2. Clarifying the resulting solutions to remove entrained radioactive solids
3. Decontaminating the clarified solutions to low-level waste with solvent extraction and ion exchange.

The undissolved solid residues combined with the concentrated radioactive streams from solvent extraction and ion exchange make up a small TRU/high-level waste fraction relative to the initial mass of the raw waste.

## PROPOSED PRETREATMENT PROCESSES

### Pretreatment of Neutralized Current Acid Waste

The NCAW is the first-cycle raffinate from nuclear reactor fuel reprocessing. The NCAW consists of a precipitated TRU/high-level sludge that contains most of the radioactive species that are insoluble in alkaline solutions and a high-level supernate that contains most of the radioactive cesium and other soluble species. The sludges have a high concentration of aluminum and iron.

In NCAW, virtually all of the TRU components are contained in the precipitated solids. Most of these solids will settle into a sludge layer given sufficient time, but some of the solids remain suspended. The first step in the pretreatment of retrieved NCAW is achieved by simply allowing the bulk of the solids to settle out, followed by decanting of the supernate. The settled solids are then washed with three volumes of water, settled, and decanted. The water washing operation dilutes the concentration of dissolved solids in the interstitial liquid of the sludge and removes critical components. The washing is done twice because two stages of washing generate less than half as much wash volume as an equivalent single stage of washing. Settling rates have been measured in cold pilot studies and partially confirmed in a hot plant test. The settling rates in the diluted solutions are considerably higher than in the raw waste.

The decanted solutions contain greater than 300 ppm TRU solids but must contain less than 50 ppm solids to be acceptable for grouting. The suspended solids are very fine and tend to foul most filter media very quickly. After testing a number of different approaches to clarification, a Pneumatic Hydropulse Filter was selected. A diatomaceous earth precoat and body feed will be used with this 0.5-m sintered metal filter to extend the filtration cycle and prevent fouling. As the name implies, a pneumatic pulse is used to periodically discharge the precoat and filter cake. Performance testing has shown that the filter is better than required, producing filtrate with less than 10 ppm solids. The precoat and body feed add only 0.16 wt% to the residual solids.

The alkaline filtrates are high-level waste because of the presence of soluble radioactive cesium. About 94% of the cesium is recovered by ion exchange with a cation resin and eluted with dilute nitric acid (HNO<sub>3</sub>). The eluted cesium is passed through a second cycle of ion exchange to reduce the sodium content of the final eluate. The cesium stream is combined with washed NCAW solids and comprises the feed to the HWVP.

The NCAW pretreatment process is summarized in Fig. 1. The process results in an eight fold reduction in the amount of glass.

### Pretreatment of Neutralized Cladding Removal Waste, Plutonium Finishing Plant Waste, and Complex Concentrate Waste

The NCRW and PFPW, though chemically dissimilar, have TRU sludge layers with relatively low levels of radioactive fission product contamination. Much of the supernate volume has been decanted and processed as low-level waste, leaving behind mostly sludge. The NCRW is a high-zirconium waste derived from the chemical decladding of nuclear fuel. The PFPW comes from solvent extraction and other plutonium processing operations and contains high aluminum and iron concentrations.

Much of the TRU/high-level tank waste generated before 1984 was processed to remove a large fraction of the cesium and strontium. The resulting depleted waste streams, containing organic complexants from strontium recovery, were concentrated and are now called CCW. Over the years, tank space requirements led to the mixing of some CCW with other waste types so that CCW can be chemically dissimilar from one tank to another. The CCW is typically high in both organic complexants and TRU content.

The NCRW, PFPW and CCW are going to be processed somewhat differently from NCAW. Pretreatment involves acidifying the alkaline waste to dissolve waste sludges and create acidic, TRU solutions. Many of the waste components that are not soluble in a water wash are soluble in acid. Therefore, sludge volumereducations are very high compared to water washing. The acidic solutions are then clarified and partially decontaminated by a new solvent extraction process developed by scientists at Argonne National Laboratory (ANL), the transuranic extraction (TRUEX) process(3). The TRUEX process is capable of removing most of the TRU contamination from the acidic solutions. The TRUEX process raffinate is suitable for grouting with one exception. The raffinate from CCW processing will have to be processed to remove cesium and possibly organic carbon. Technology for the destruction of organics is being developed but will not be discussed in this paper. Extracted actinides and the solids from clarification are combined as feed to HWVP. The pretreatment process for NCRW, PFPW, and CCW is depicted in Fig. 2.

Laboratory studies with actual waste have determined the tentative conditions for sludge dissolution. Because of the high fluoride content of the waste, NCRW dissolves in 2 hours at room temperature at a relatively moderate HNO<sub>3</sub> concentration, about 1M. No settle-decant is planned for NCRW because the waste is so soluble and settling would add unnecessary processing time. The PFPW sludge will probably be processed by settling and decanting so the settled sludge can be exposed to a stronger acid, 6M HNO<sub>3</sub> and 0.1M hydrofluoric acid (HF). Dissolution time is about 6 hours. The decanted alkaline solution will

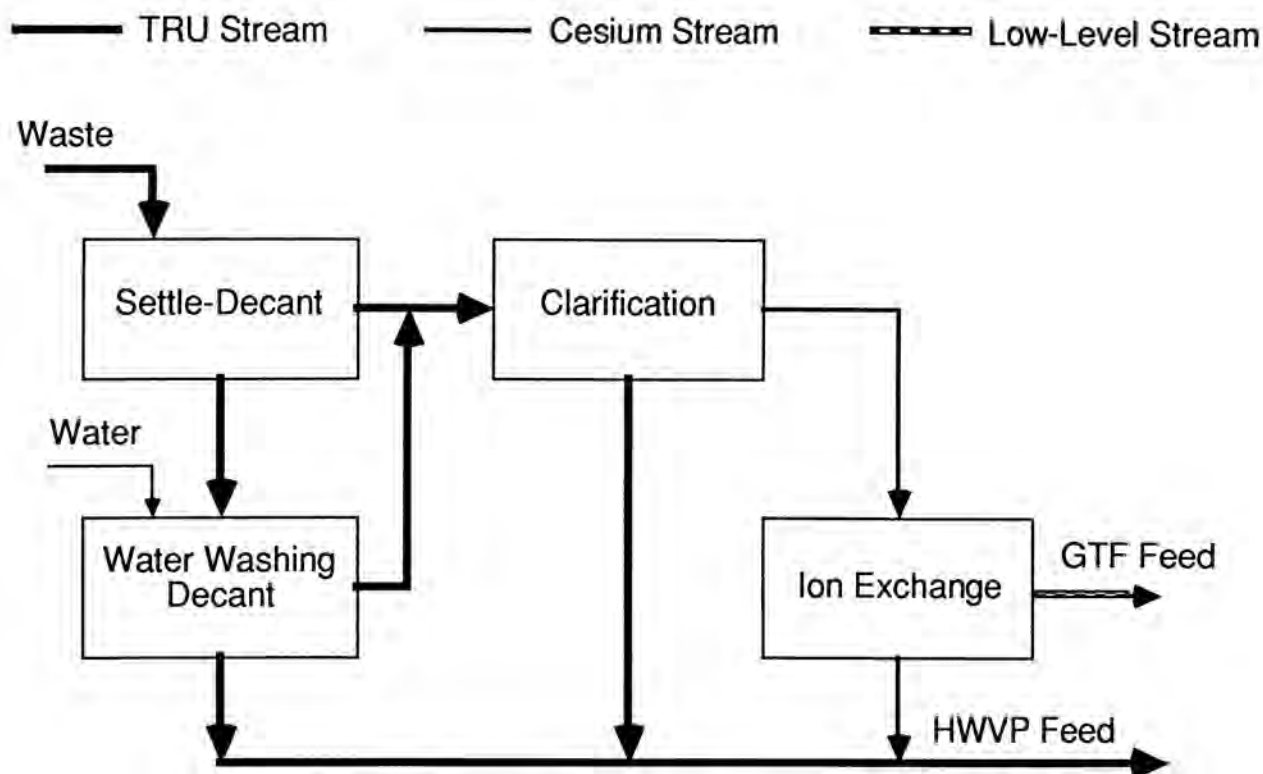


Fig. 1. NCAW Pretreatment.

either be discarded or used to adjust the acid concentration of the TRU EX feed to about  $1\text{M HNO}_3$ . For the time being, plans are to settle and decant CCW before acidification. The CCW solids dissolve very well in concentrated  $\text{HNO}_3$ . The decanted solution from CCW, highly buffered with carboxylic anions and carbonate, are used to adjust the acid concentration. Some of the CCW may dissolve quite readily in low-concentration acid, in which case no settling and decanting would be necessary.

The conditions for dissolution are summarized below:

NCRW $1\text{M HNO}_3$	No settle-decant
PFPW $6\text{M HNO}_3$ and $0.1\text{M HF}$	Settle-decant
CCW $12\text{M HNO}_3$	Settle-decant
or	
$1\text{M HNO}_3$	No settle-decant.

Laboratory work to date has established that greater than 90% of the NCRW sludge can be dissolved. Typical dissolution efficiencies for the major components in NCRW are shown in Table I. Virtually complete dissolution of aluminum and chromium were achieved at  $100^\circ\text{C}$ , but large fractions of zirconium and uranium precipitated.

TABLE I  
Primary Dissolution of NCRW  
(Room Temperature,  $\sim 0.5\text{M Acid}$ )

Element	Dissolution (%)
Zr	93-98
U	98-99
Al	72-76
Cr	71-96
Fe	85-95

Plutonium Finishing Plant Waste and CCW dissolution is still being evaluated in the laboratory. Quantitative results were not available as of this writing, but the percentage of dissolution appears to be high.

The acidic dissolver liquors must be clarified to avoid interfacial crud formation and poor phase separation in the TRU EX process. Because the TRU EX process can only extract dissolved metals, the presence of undissolved TRU solids also limits the decontamination factor. Fig. 3 shows the particle size profiles of the three waste types after acid dissolution. Clarification of acidic solutions with as much as  $1\text{M F-}$  and extremely fine particles is a challenging

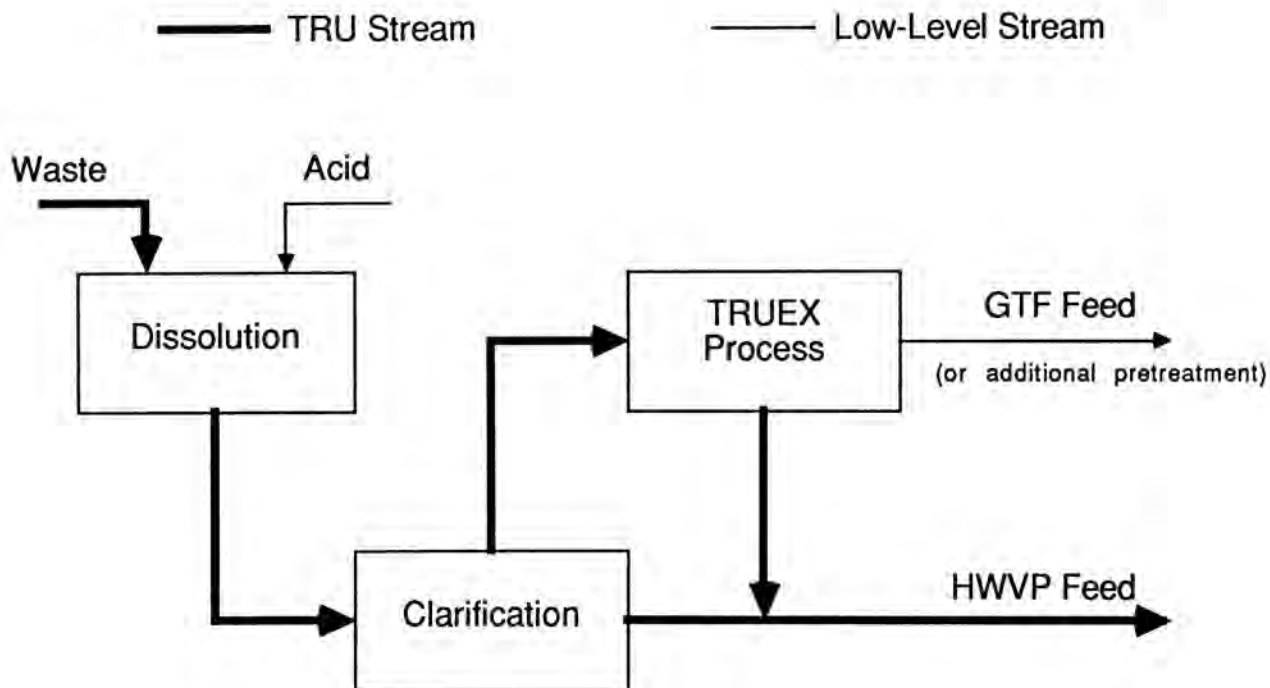


Fig. 2. NCRW, PFPW and CCW Pretreatment.

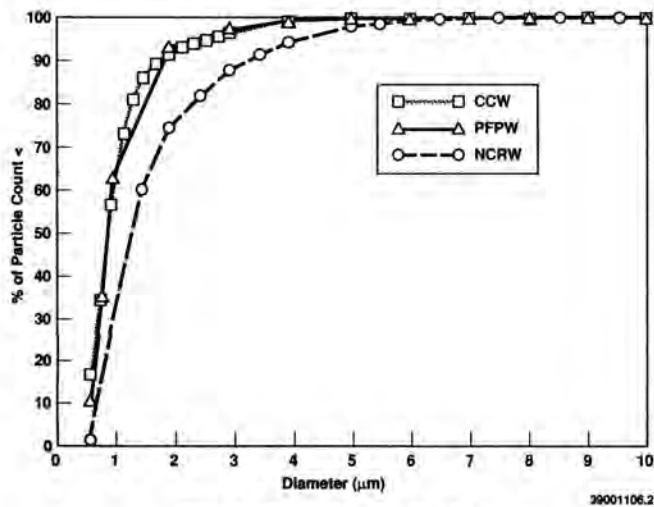


Fig. 3. Particle Size Profile.

problem that will have to be resolved. Studies are under way to identify materials that can be used for the filter medium.

The TRU EX process is based on the actinide extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) dissolved in tributyl phosphate and normal paraffin hydrocarbon. While many extractants are available for the removal of tetravalent and hexavalent actinides from acid solutions, CMPO is also capable of extracting trivalent <sup>241</sup>Am, a major TRU component in many TRU waste streams. The TRU EX process is capable of reducing the TRU concentration in solutions containing a wide range of HNO<sup>3</sup>, salt, and fission product concentrations.

A laboratory program began in 1989 to evaluate the applicability of the TRU EX process to the Hanford Site double-shell tank waste. The elements of a generic TRU EX flowsheet are illustrated in Fig. 4. There are several stages of extraction followed by scrub stages. A typical organic to aqueous phase ratio in extraction is 1:5. Consequently, during extraction most of the extractable TRU elements in the aqueous feed are concentrated in the organic extract and a TRU-depleted raffinate results. The extract is then scrubbed with water or dilute HNO<sup>3</sup> to reduce the acid concentration of the extract. With some waste feeds, the TRU EX

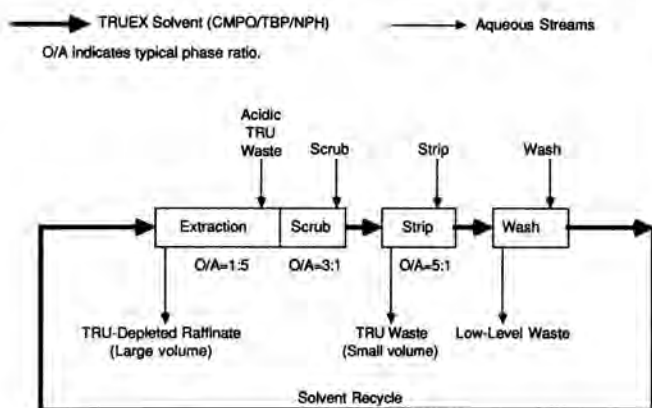


Fig. 4. TRUEX Process.

solvent may not be perfectly selective for actinides, and the scrub is also used to remove coextracted nonactinide species. A typical organic to aqueous phase ratio during scrubbing is 3:1.

Stripping, or back extraction, transfers the extracted actinides back into the aqueous phase. Americium strips easily with dilute  $\text{HNO}_3$ . Plutonium is more tightly bound and requires a dilute complexant to strip efficiently. The complexant used in most of the laboratory work 1-hydroxyethane-1,1-diphosphonic acid is effective, but other stripping agents are being tested. A number of common complexants have been used successfully. The metal oxide content of the strip stream is a small fraction of the feed to the process. The strip stream is combined with the bottoms from clarification to make up the feed to the HWVP. A typical organic to aqueous phase ratio during stripping is 5:1. Stripping can be modified to partition plutonium from the other extracted actinides.

Table II summarizes the range of extraction and stripping distribution coefficients for acidified actual waste that were measured with batch contacts during the FY 1989 laboratory program. These results were obtained using a wide range of phase ratios and acid concentrations. Although some surprising results were obtained, the laboratory work with actual waste has essentially confirmed results obtained by ANL with synthetic wastes. The distribution coefficients for extraction of americium in actual waste were much higher than those measured by ANL in synthetic waste.

The TRUEX solvent is restored to near original condition with a sodium carbonate wash. Experiments were done with CCW to determine if solvent poisoning occurs when using actual waste. Little, if any, change in solvent performance was observed after several cycles of contacting.

The next step at the Hanford Site toward full-scale TRUEX application is the development, testing, and opti-

mization of flowsheets on a pilot scale. Pilot plant design was initiated early in calendar year (CY) 1990. Laboratory optimization will continue concurrently with the pilot plant project. Pilot plant startup is expected in the FY 1993.

#### Other Pretreatment Considerations

TABLE II  
Plutonium and Americium Distribution Coefficients With Real Waste.

Waste Type	Extraction		Stripping	
	Pu	Am	Pu	Am
NCRW	6-400	20-200	0.03	0.04
PFPW	5-8	10-14	NA	NA
CCW	4-10	5-100	0.04	0.09

The composition of the pretreated TRU/high-level fraction as well as its mass are important factors in determining how much glass is actually generated. Under some circumstances, pretreatment may increase the concentration of certain critical components in the TRU/high-level fraction. If HWVP feed specifications are exceeded, component-specific pretreatment or an adjustment to the reference waste loading (currently 25 wt% waste oxides in glass) would be required. If the waste loading in glass changes, then a high percentage reduction in the mass of the TRU/high-level fraction does not necessarily result in the same percentage reduction in glass volume.

#### SUMMARY

The objectives of pretreatment are summarized in Fig. 5. The cost of vitrifying the entire mass of TRU/high-level double-shell tank waste is exorbitantly high. Through pretreatment, the waste will be segregated into a TRU/high-level fraction and a low-level fraction. The combined cost of pretreatment, treatment (conversion to glass and grout) of the resulting waste fractions, and disposal is significantly less than wholesale vitrification of waste.

The pretreatment operations discussed in this paper include water washing and dissolution of waste sludges, clarification of the resulting solutions, removal of soluble TRUs by solvent extraction (the TRUEX process), and cesium removal by ion exchange.

#### REFERENCES

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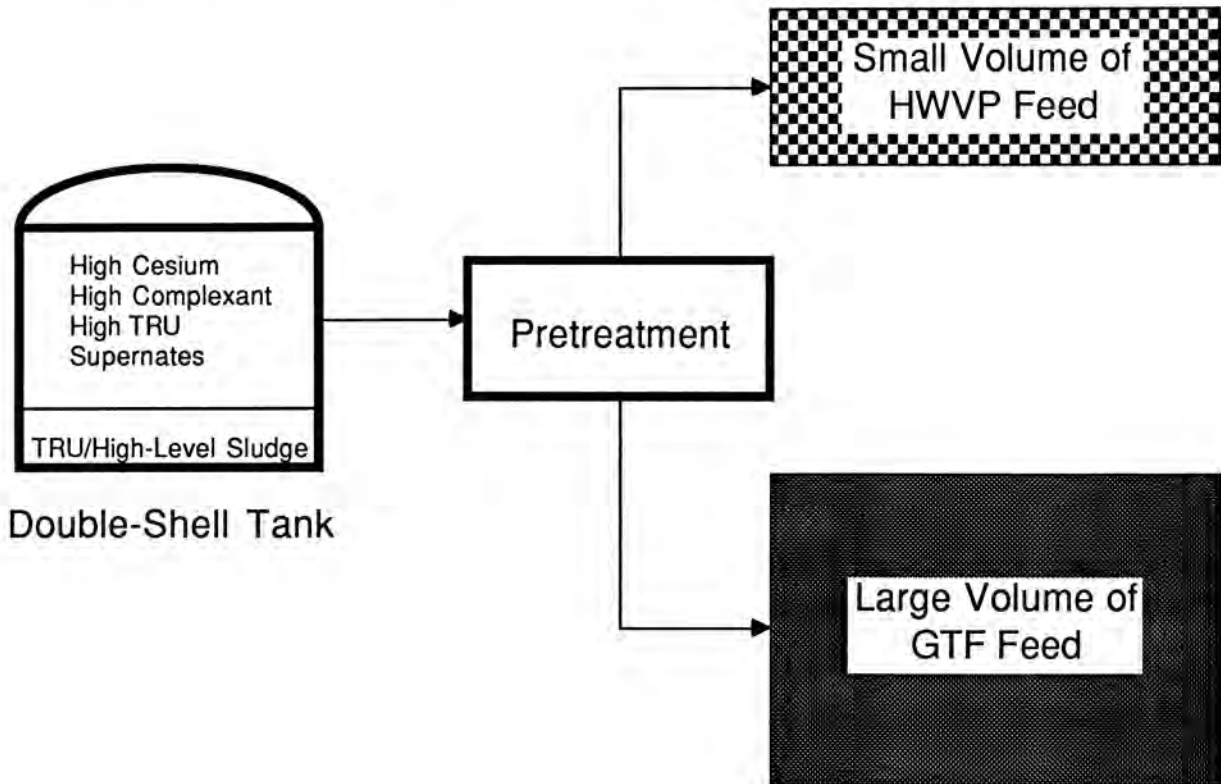


Fig. 5. Pretreatment Objectives.

2. DOE, "Final Environmental Impact Statement: Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes," DOE/EIS-0113F, U.S. Department of Energy, Washington, D.C. (1987).
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