PRETREATMENT TECHNOLOGY DEVELOPMENT

Presented to:

Nuclear Waste Technical Review Board

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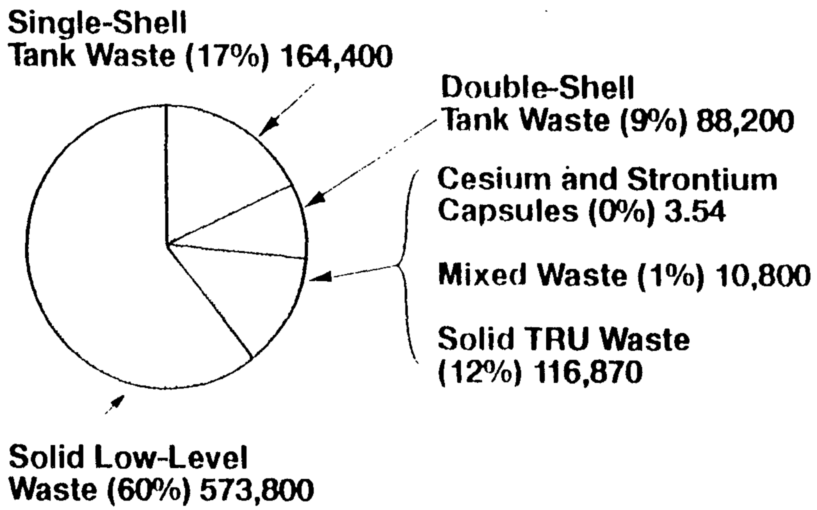
Pretreatment Technology Development

OVERVIEW

- Pretreatment to separate high- and low-level fractions of tank wastes presents some of the greatest technological challenges in the cleanup of Hanford
- Ability to separate radioactive constituents and destroy selected hazardous materials will have greatest single impact to total cost of tank waste disposal
- Recent program decisions have significant changed the focus and approach to pretreatment

Hanford Site Waste

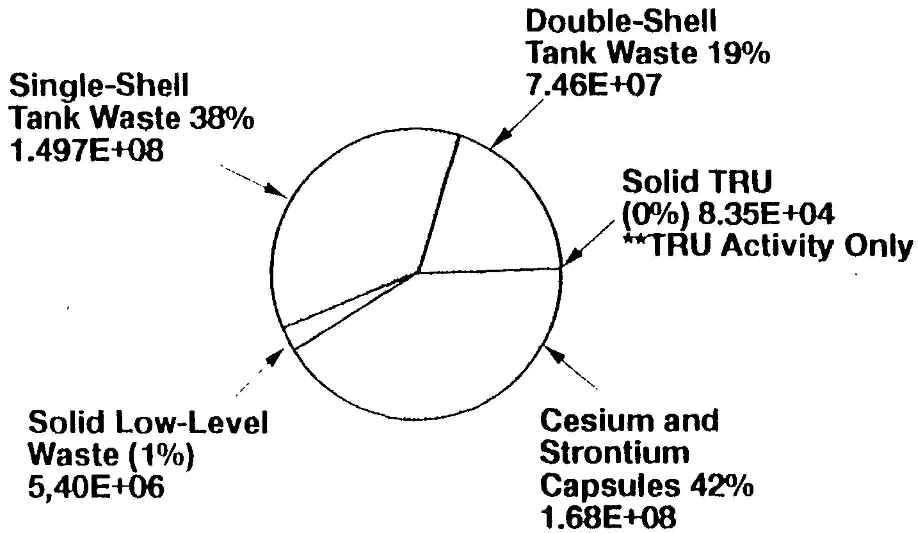
Volume



Total Volume: *954,073 m³

*Does not include past practice units and surplus facilities
Information per 1991 Integrated Data Base submittal

Radioactivity



Total Radioactivity: *3.98E+08 Ci

Key Hazardous Materials

- Nitrates
- Nitrites
- Chromium
- Cobalt
- Heavy Metals
- Cyanide
- Carbon Tetrachloride
- Selenium
- Trichlorethylene

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DST AND SST HIGH-LEVEL WASTE

TYPE	INVENTORY AND SOURCE	CHARACTERISTICS
Single-Shell Tanks		
• Saltcake and Sludge	164,000 m^3 (37 million gal) Fuel processing	The saltcake is almost entirely $NaNO_3$, $NaNO_2$, Na_3PO_4, $NaAlO_2$, and NaOH. The Sludge consists of metal oxides and hydroxides precipitated during neutralization.
Double-Shell Tanks		
• Neutralized Current Acid Waste (NCAW)	5,300 m^3 (1.4 million gal) PUREX, 1st Cycle Extraction	High heat. Sludge is principally iron hydroxide (20 vol%) contaminated with ^{90}Sr and actinides. The alkaline supernate contains Na and Al salts, and is contaminated with ^{137}Cs.
• Neutralized Cladding Removal Waste (NCRW)	3,400 m^3 (0.9 million gal) PUREX, fuel cladding dissolution	Low heat. The sludge contains Zr contaminated with TRU. The alkaline supernate is LLW.
• Plutonium Finishing Plant (PFP)	400 m^3 (100,000 gal) Plutonium Finishing Plant	Low heat. Sludge is principally metallic compounds contaminated with insoluble TRU compounds. The alkaline supernate is LLW.
• Complexant Concentrate (CC)	16,300 m^3 (4.3 million gal) Prior Sr and Cs Recovery Operations	The sludge contains metal compounds, degraded complexants and precipitated TRU elements. The alkaline supernate contains ^{137}Cs and TRU solubilized with complexants.

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HANFORD DOUBLE-SHELL TANK WASTE COMPOSITIONS

Chemical Components (M)	NCAW Slurry	NCRW Sludge	PFP Sludge	CC Sludge	CC Supernate
A1	0.50	0.20	0.85	2.50	0.40
Cr[b]	0.012	0.016-04	0.40	.001-15	.004-008
Fe	0.07	0.02	0.20	0.04	0.04
K	0.12	0.35	0.08	0.10	0.05
Na	5.00	6.50	2.20	15.00	10.00
PO	0.025	NA	0.3	.06-12	.02-05
Zr	0.04	1.04	NA	0.001	0.001
OH	1.00	0.80	1.00	2.00	0.10
TOC	0.14	0.50	NA	3.30	3.30
Radioactive Components (uCi/L)					
Cs-137	2E6	7E4	1E5	6E5	4E5
Sr-90	2E6	NA	1E4	1E5	1E5
Pu-239	160	700	1E6	100	100
Am-241	8900	300	3E6	800	800
Volume[a] (10^6 Gal)	1.4	0.8	0.25	0.6	4.1

(a) No Future PUREX or PFP operations assumed.
(b) Shaded areas identify chemical components which limit waste loading in glass.

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ESTIMATED TOTAL SINGLE-SHELL TANK WASTE CONTENTS DISTRIBUTION

Compound or Nuclide	Total Weight Mg	wt% of Total Waste	wt% of Total Waste (water free basis)
Non-Radioactive			
$NaNo_3$	132,500	58.3	72.6
Na_3PO_4	14,800	6.6	8.1
$NaNO_2$	7,200	3.1	3.9
NaOH	6,940	3.0	3.8
$NaAlO_2$	4,350	1.9	2.4
Na_2CO_3	2,400	1.1	1.4
Na_2SO_4	2,440	1.1	1.3
Other Solids	10,390	4.6	5.7
Water	44,800	19.7	---
Total Non-Radioactive	226,000	99.4	99.2

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ESTIMATED TOTAL SINGLE-SHELL TANK WASTE CONTENTS DISTRIBUTION (CONT)

Compound or Nuclide	Total Weight Mg	wt% of Total Waste	wt% of Total Waste (water free basis)
Radioactive			
Radionuclides			
^{238}U	1,400.	0.6	0.8
^{235}U	9.40	--	--
^{93}Zr	1.60	--	--
^{99}Tc	0.93	--	--
^{239}PU	0.36	--	--
^{90}Sr	0.33	--	--
^{135}Cs and ^{137}Cs	0.22	--	--
Other TRU	0.06	--	--
Other Radionuclides	0.20	--	--
Total Radionuclides	1,413.	0.6	0.8
Total Compounds and Nuclides	227,413.	100.0	100.0

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BACKGROUND

- Degree of pretreatment dramatically impacts quantity of glass canisters produced
  - >200,000 canisters with no separations
  - >40,000 canisters with removal of soluble salts only
  - 10,000-15,000 canisters with selected radionuclide separation
- Current estimate of canister disposal costs (approximately $350K/canister) indicates need for aggressive pretreatment strategy

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PURPOSE / OBJECTIVE

- Resolve tank safety issues by destroying organics and ferrocyanides

- Minimize glass volume and disposal costs through efficient separation of radionuclides and inert material

- Provide feed for vitrification and grout within allowable feed specifications

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PROCESS FUNCTIONS

- Soluble Salts Removal
- Soluble Fission Product Removal
- Insoluble Fission Product Removal
- Actinide Separations
- Organic/Ferrocyanide Destruction
- Nitrate/Nitrite Destruction (TBD)

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PROCESS OPTIONS

- Soluble Salt Removal
  - Liquid/solids separation
  - In-tank sludge washing

- Soluble Fission Product Removal
  - Ion exchange
  - Solvent extraction
  - Precipitation

- Insoluble Fission Product Removal
  - Sr extraction
  - Precipitation

- Actinide Separations
  - TRUEX
  - Solvent extraction other than TRUEX
  - Selective leaching
  - Ion exchange/solid sorbants
  - Precipitation
  - Salt splitting

PROCESS OPTIONS (CONT)

- Organic/Ferrocyanide Destruction
  - Thermal oxidation
  - Chemical oxidation
- Nitrate/Nitrite Destruction
  - Thermal oxidation

THREE PHASED APPROACH FOR PRETREATMENT

- Near Term Processes -- generally proven technologies implemented mostly in-tank (or "modules")
  - Organic/ferrocyanide destruction
  - Sludge wash
  - Ion exchange/cesium removal

- Intermediate Term Processes -- more complex, evolving technologies implemented in-tank (or "modules")
  - Chrome leaching
  - Aluminum leaching
  - Transuranic leaching

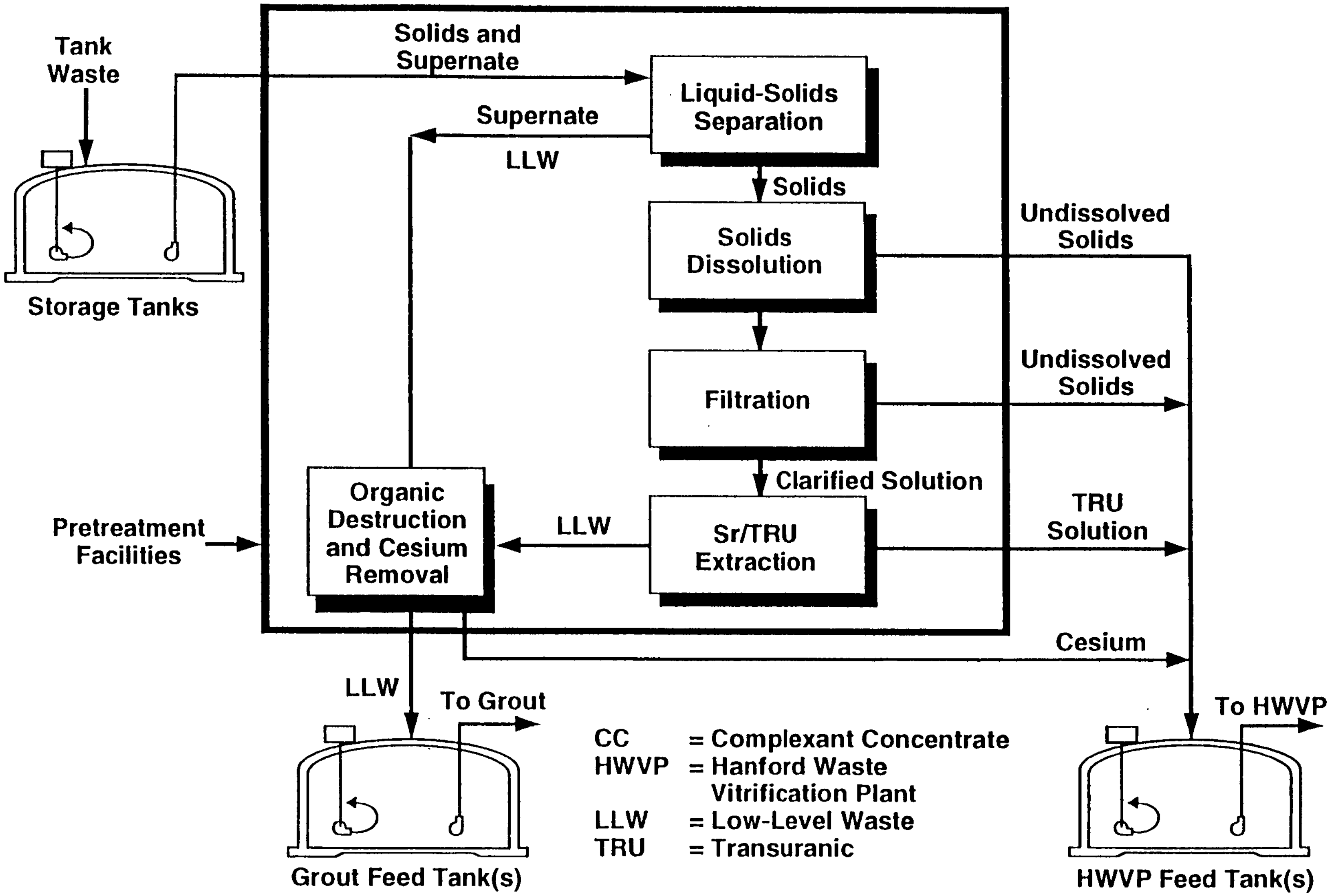
THREE PHASED APPROACH FOR PRETREATMENT (CONT)

- Long Term Processes -- aggressive new technologies to minimize disposal costs, likely implemented in new facilities
  - Sludge dissolution
  - Transuranic extraction
  - Strontium extraction
  - Technetium removal - ion exchange
  - Organic destruction

ALTERNATIVE PROCESSES

- Innovative technologies being pursued which have performance and/or cost incentives; e.g.:
  - HLW/LLW splitting by salt crystallization
  - Solid sorbants
  - Nitrate destruction
  - Leaching/dissolution
  - Calcination/leaching

Typical Pretreatment Flow Diagram



CC = Complexant Concentrate
HWVP = Hanford Waste Vitrification Plant
LLW = Low-Level Waste
TRU = Transuranic

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PRETREATMENT FOR TANK SAFETY ISSUES

Problem

- Hydrogen, ferrocyanide, and organic salts tanks are all on the safety watch list due to the combination of a fuel (hydrogen, ferrocyanide, or organic salts) and an oxidizer (nitrate) in the tanks

Solution

- If remediation is required after mitigation is complete, all three categories would be treated by some form of oxidation process

POTENTIAL OXIDATION PROCESSES

- Ozonization
- High temperature/high pressure wet oxidation
- Electrochemical oxidation
- Calcination
- Other

SLUDGE WASHING

- Simple process
  - Gravity settling of solids
  - Water washing

- Not a new concept

- Similar to processing at Savannah River, West Valley, and previous Hanford HLW

- In-tank washing planned for NCAW

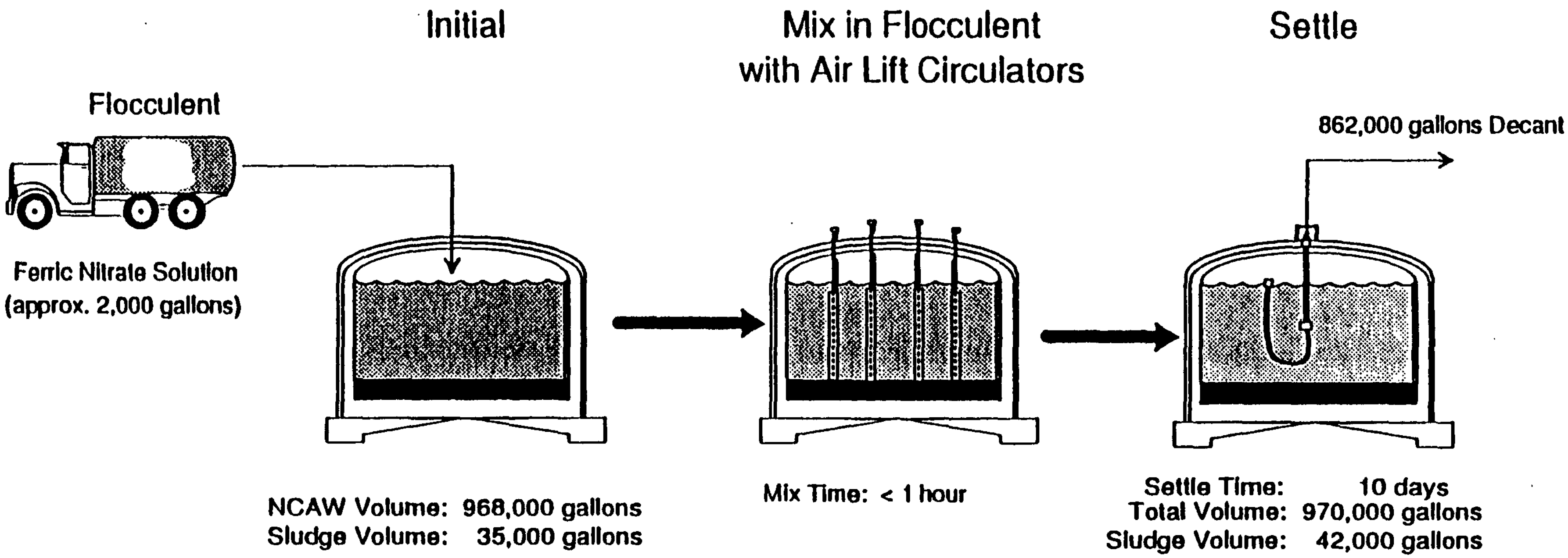
- Other candidates include 101-AY, 106-C, and 105-C
  - Additional candidates under consideration

SLUDGE WASHING (CONT)

- Significant development work completed
  - Pilot plant test with synthetic NCAW
  - Lab test with actual NCAW
  - Process testing with actual NCAW at B Plant

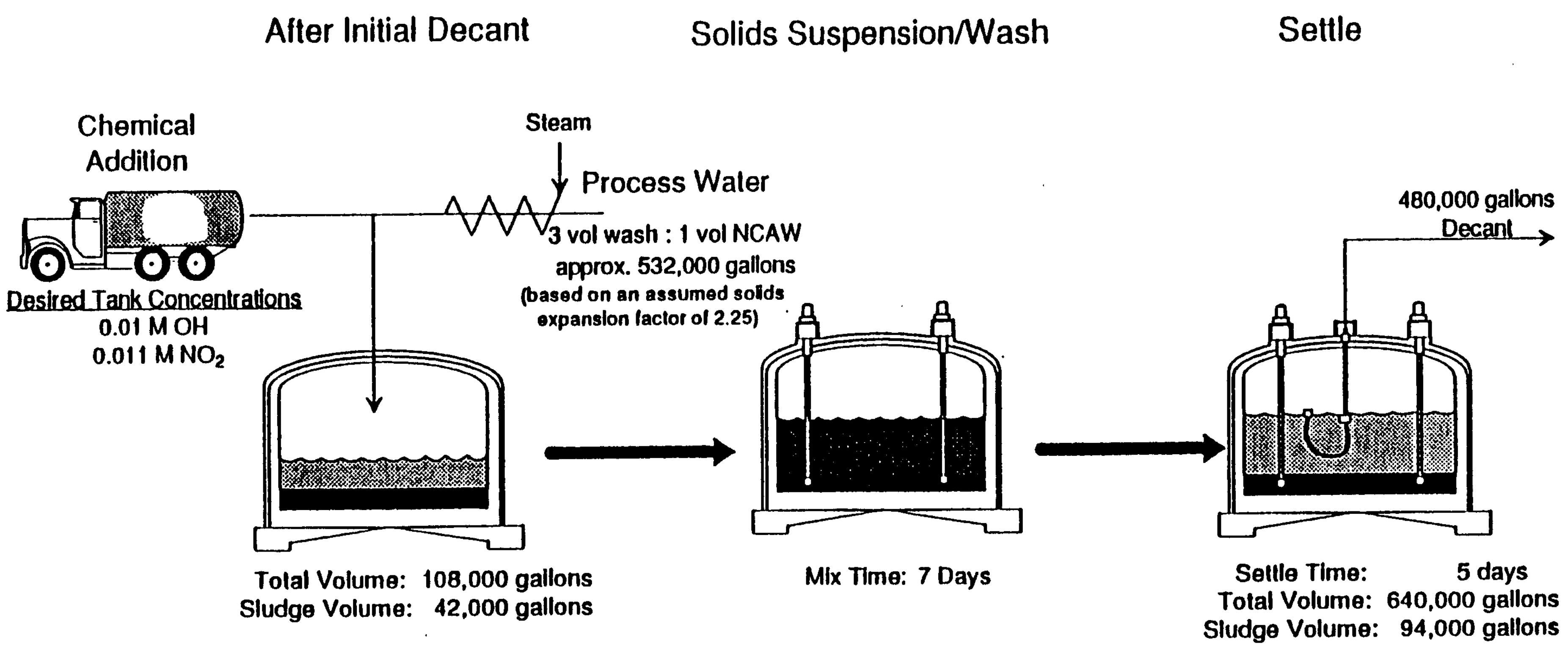
NCAW In-Tank Sludge Washing

Initial Treatment & Decant of Tank 241-AZ-101



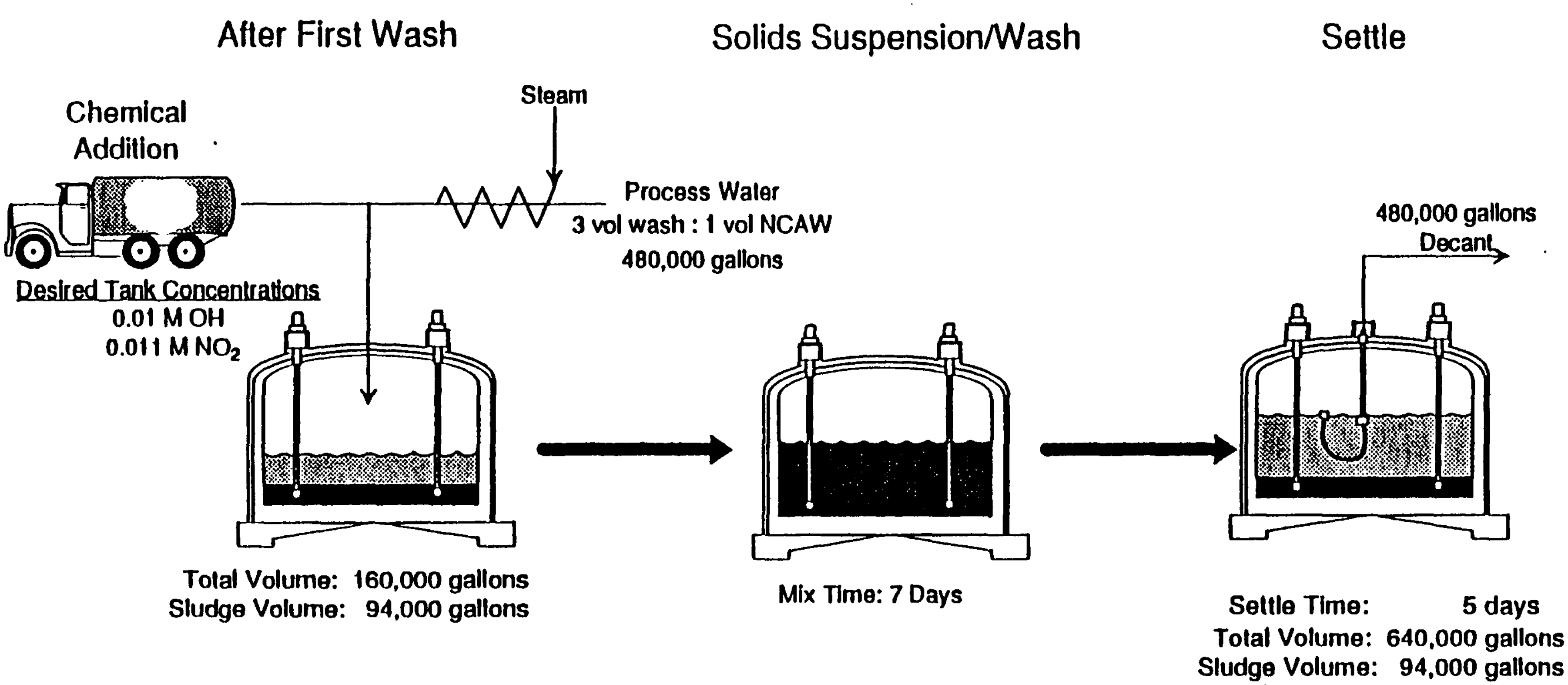
NCAW In-Tank Sludge Washing

First Wash Cycle



NCAW In-Tank Sludge Washing

Second Wash Cycle



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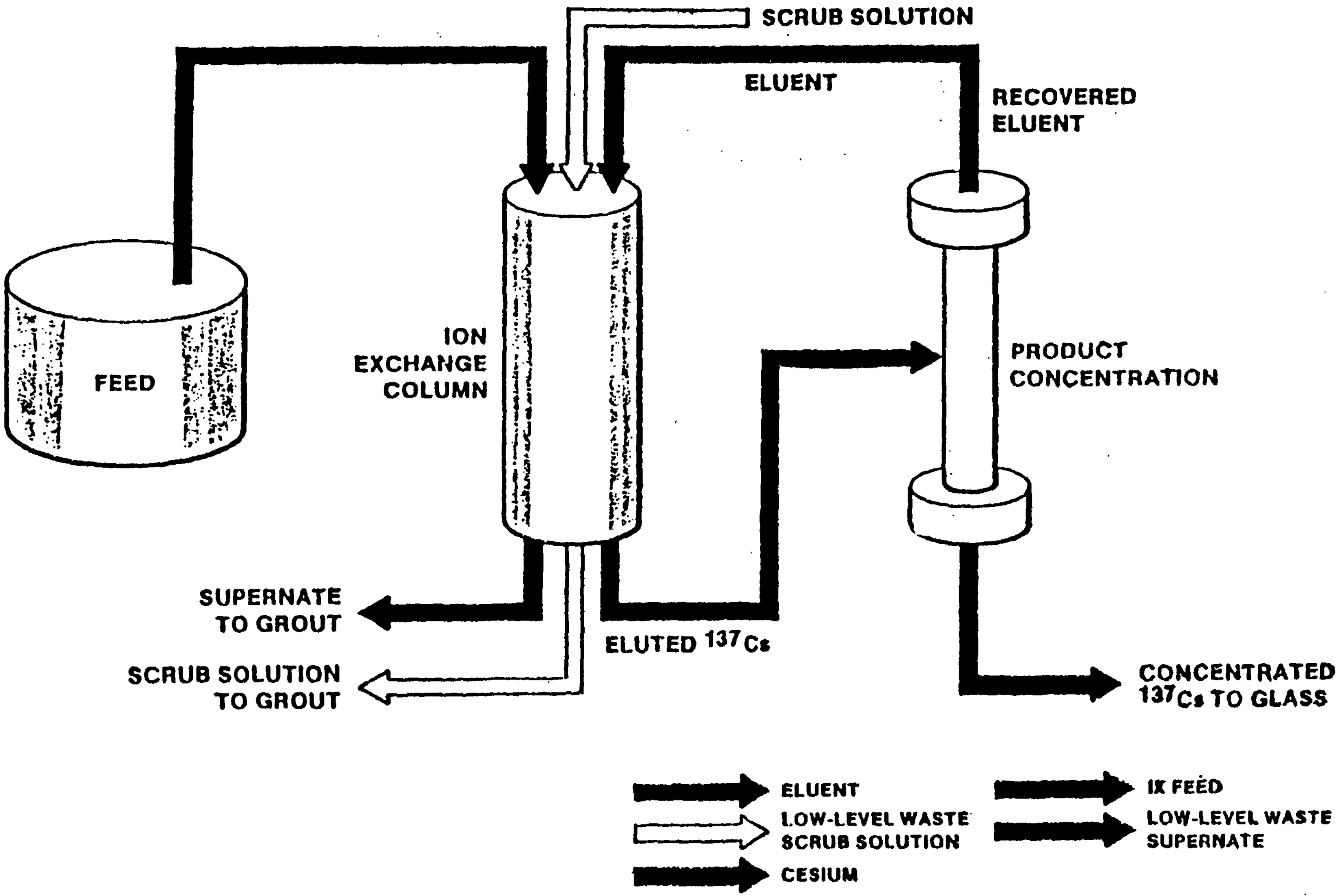
ION EXCHANGE

- Batch screening tests of eight organic and inorganic ion exchange media
  - Resorcinol/formaldehyde resin (SRL-DJ) has highest Cs capacity
  - "Duolite CS-100"™ is next best
- Radiation effect
  - Hanford data shows CS-100 resists capacity degradation better than resorcinol/formaldehyde resin
  - Recent SRL data shows resorcinol/formaldehyde resists degradation better than CS-100
  - Jury is still out on radiation stability

"Duolite CS-100 is a trademark of Rohm and Haas Company."

ION EXCHANGE SCHEMATIC



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ION EXCHANGE (CONT)

- Column loading and elution tests with CS-100
  - As high as 45 column volumes before significant breakthrough
  - Cs recovery efficiency of the total cycle was 95%
- Aging/cycling tests with CS-100
  - After 55 elution/regeneration cycles, CS-100 had 60% of initial Cs capacity as determined by a batch contact
  - Particle attrition was apparent
- Current column loading tests with CS-100
  - NCAW supernates and wash waters

STATUS OF ION EXCHANGE PROGRAM

- Column loading experiments are in process
- Cs removal alternatives study completed
- Some engineering studies have commenced
- Parametric batch equilibrium studies have commenced

OBJECTIVES OF INTERMEDIATE-TERM WASTE PRETREATMENT PROCESSES

- Pretreat wastes to reduce canister production compared to sludge-wash only
  - Facility requirements similar to sludge-washing/ion exchange processing
- Provide suitable feeds to HWVP until long-term pretreatment approaches (sludge dissolution - Actinide separation) are available
  - Ensure cost effective, viable Tank Waste Disposal Program

INTERMEDIATE TERM PROCESS DEVELOPMENT

- Review waste characterization data to identify potential candidate tanks for intermediate processing
  - Look for high fission product/TRU tanks that would produce relatively low volumes of glass if selected components such as chrome or aluminum were removed from waste
  - Look for low fission product, high TRU wastes that would benefit from leaching TRU from waste
- Continue lab testing on actual PFP waste to remove chrome from waste
- Initiate lab tests on potential candidate wastes for those tanks that have been sampled

LONG-TERM PROCESS DEVELOPMENT

- Focus of program had been on solvent extraction (TRUEX) process for double-shell tank wastes
- Systems engineering study for disposal of single-shell tank (SST) wastes identified solvent extraction as a prime candidate for SST wastes
- Recent reviews have raised technical concerns with TRUEX process and lack of fallback options
- Program was revised to investigate other alternatives prior to selecting long-term processes
  - Three phased strategy provides the needed time to perform these investigations
- Alternatives will be evaluated by Pretreatment Technology Working Group and processes selected for investigation will be documented in Pretreatment Technology Plan

SOLVENT EXTRACTION PROCESS STATUS

- PNL and ANL have done extensive batch contacts on a variety of synthetic wastes including the following Hanford specific wastes:
  - NCAW
  - PFP Acid Waste
  - CC Waste
- ANL has done some continuous tests on synthetic waste including the PFP acid waste
- ANL has done significant work on the effect of radiation on the stability of CMPO; no significant degradation found

REMAINING SOLVENT EXTRACTION DEVELOPMENT

- Material of Construction
  - A corrosion program has been initiated
- Effect of feed composition variations to dissolution and solvent extraction processes
  - A lab program is planned which includes investigating feed variations
- Waste minimization
  - A denitrification process to reduce nitrate levels in waste is being pursued
- Confirmation of a continuous process with actual waste
  - Continuous lab tests are planned to support confirmation
  - A pilot plant is proposed to confirm the process

CURRENT ACTIVITIES IN ALTERNATE TECHNOLOGIES

- Leaching/dissolution of SST sludges
  - Strong caustic for aluminum removal
  - Carbonate leaching for TRU reduction
  - Nitric acid leaching and dissolution
- HLW/LLW splitting by salt crystallization
- Solid sorbant for actinide separation
- Salt splitting/recycle with bipolar electrodyatic membrane (LLNL)
- Destruction of organics by steam reforming (SANDIA)
- Nitrate destruction in aqueous solutions (ORNL)
- TRUEX model development (ANL)

ADDITIONAL ALTERNATE PROCESSES BEING CONSIDERED

- In-tank dissolution and precipitation
- Solid/solid separations
- Calcination/leaching
- In-tank processing
- Electro-chemical separations

ADDITIONAL ALTERNATE PROCESSES BEING CONSIDERED (CONT)

- Magnetic separations
- Nitrate destruction/conversion
- Solvent extraction alternatives
  - Initiate batch tests of DST waste using French diamide solvent
- Other
  - Initiate foreign technology exchange
  - Complete alternatives study to examine other processes

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SUMMARY

- Near-term pretreatment processes are mature and will provide several years of feed to HWVP

- Substantial development is required to implement cost-effective long-term processes which will minimize total costs of Hanford Tank Waste Disposal Program

- Three-phased approach to pretreatment provides time to complete this development