

PRETREATMENT OF HANFORD PUREX PLANT FIRST-CYCLE WASTE

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ABSTRACT

A process has been developed to pretreat neutralized, first-cycle high-level waste from the fuels reprocessing facility (PUREX Plant) at the Hanford Site. The process separates solids from the supernate liquid, which contains soluble salts. The solids, including most of the fission products and transuranic elements, may then be vitrified for disposal, while the low-level supernate stream may be processed into a less expensive grout waste form. The process also includes ion exchange treatment of the separated supernate stream to remove radiocesium. A flow sheet based on these operations was completed to support a planned demonstration of the process in the Hanford Site B Plant canyon facility.

INTRODUCTION

Process technology development efforts are underway at the U.S. Department of Energy Hanford Site to minimize the amount of high-level waste that may require disposal in a borosilicate glass form. A solid/liquid separations process has been proposed to pretreat first solvent extraction cycle waste from the PUREX Plant to reduce the amount of waste components that require vitrification.

The PUREX Plant processes irradiated fuel elements to recover plutonium, uranium, and neptunium. After removal of the zircaloy cladding, the fuel elements are dissolved in nitric acid; plutonium, uranium, and neptunium are subsequently recovered in a solvent extraction process. The first solvent extraction cycle aqueous waste stream contains essentially all the fission products present in the fuel elements. This stream is denitrated and then neutralized (made alkaline) to generate neutralized current acid waste (NCAW), which is stored in underground double-wall tanks.

The NCAW is a slurry of solids, mostly iron-based compounds, containing most of the fission products and a supernate liquid with a high pH (pH 14). The NCAW slurry also contains various transuranic (TRU) elements in the solids fraction, as well as soluble salts in the supernate. A typical NCAW composition is shown in Table I.

Separation of the supernate liquid from the solids in the NCAW slurry could allow disposal of the supernate liquid (after ¹³⁷Cs removal) as a low-level waste stream in grout vaults, while the TRU-bearing solids would be disposed of in a borosilicate glass form (Fig. 1) in a geologic repository (1). This avoids vitrification of the soluble aluminum and sodium, which would contribute to much larger volumes of borosilicate glass than a waste stream containing only the solids. Disposal actions will not be implemented until a Record of Decision is reached for the Hanford Defense Waste-Environmental Impact Statement.

The estimated cost of disposal of NCAW without separating the soluble salts is approximately seven-fold higher than the cost for disposal after

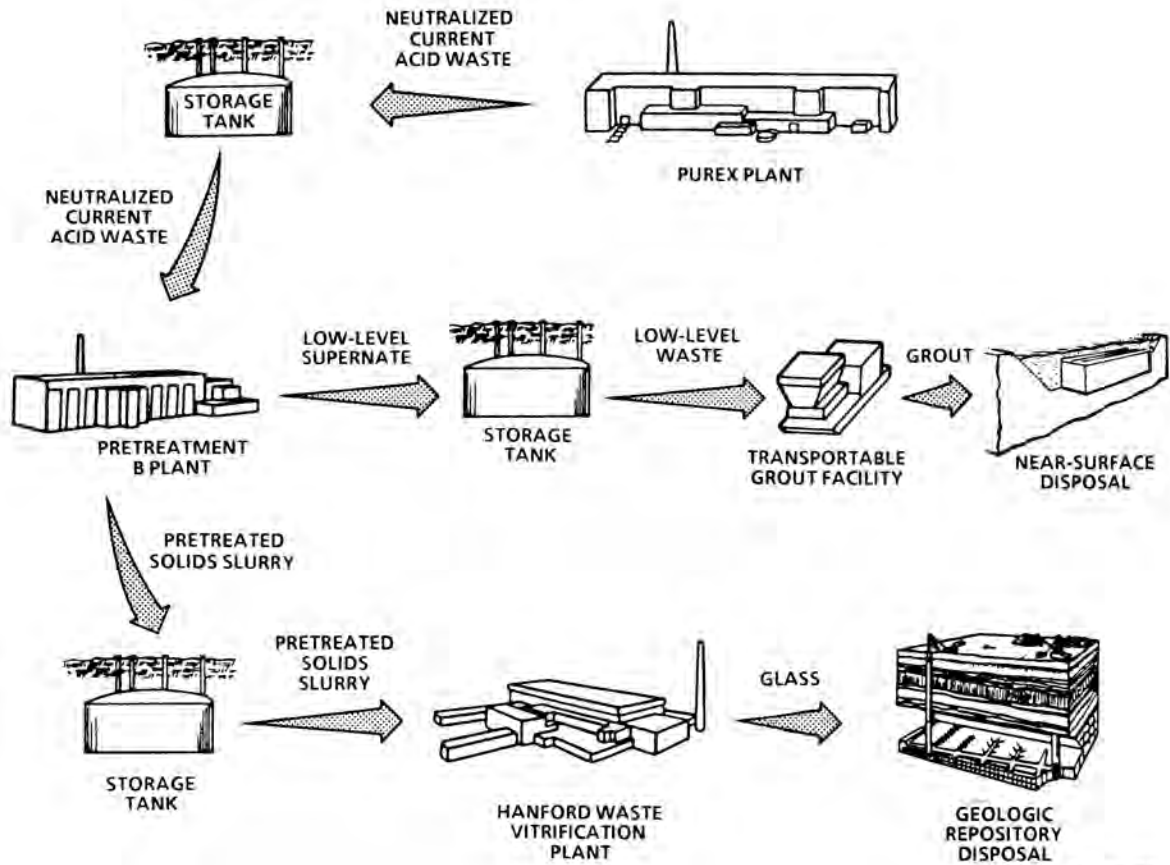
TABLE I
Typical NCAW Composition

Constituent	Concentration supernate	Concentration total slurry
Free OH ⁻	1.1M	1.0M
SO ₄ ²⁻	0.15M	0.15M
NO ₃ ⁻	1.8M	1.7M
NO ₂ ⁻	0.44M	0.43M
CO ₃ ²⁻	0.21M	0.23M
Total organic carbon	0.05 g/L	0.1 g/L
Na	4.9M	5.0M
Al	0.48M	0.50M
Fe		0.067M
²³⁹ Pu		2.6 E-03 g/L
²⁴¹ Am		2.6 E-03 g/L
Total β	1.1 E+11 Bq/mL	7.4 E+11 Bq/mL
Solids concentration		2.5-3.5 wt%
Supernate density		1.18 g/mL
Solids density		1.3 g/mL
Median particle size		1-2 μm

pretreatment, \$1.5 billion, based on the processing of 2.0 x 10⁷ L of NCAW. The economic incentive for pretreatment is, therefore, very large.

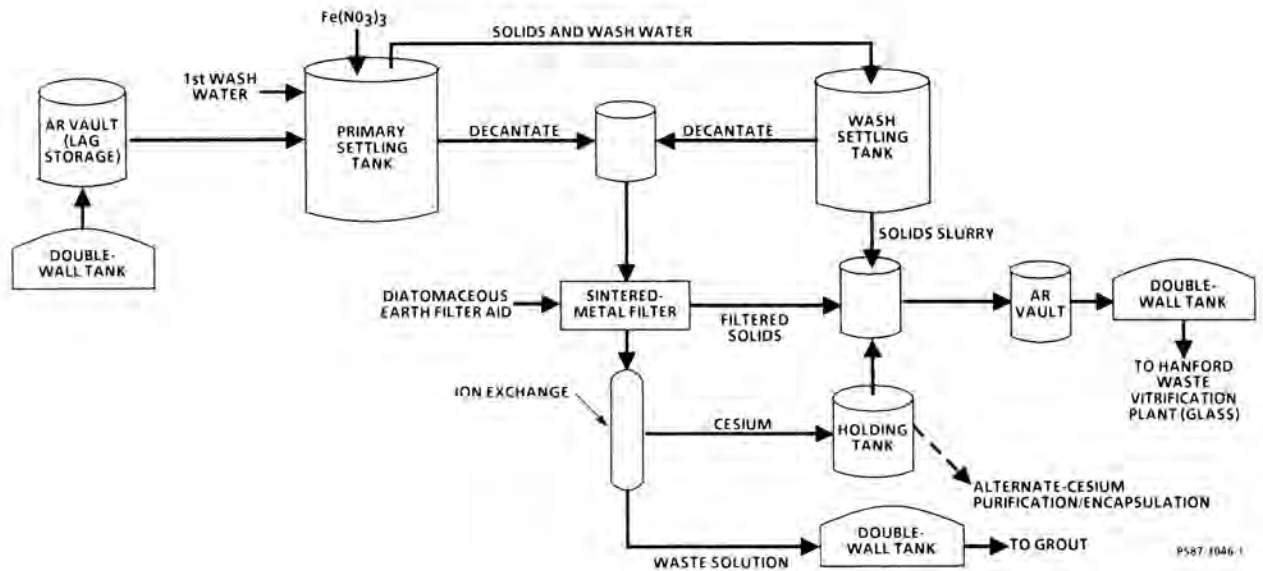
A process has been developed to separate the TRU-bearing solids and soluble cesium in NCAW from the supernate liquid (Fig. 2). Demonstration of this process is planned in the B Plant canyon facility at the Hanford Site beginning in October 1988. The process includes primary solid/liquid separation by settle/decant operations and washing of the settled solids to reduce the concentration of soluble salts remaining in the interstitial liquid. A secondary polishing filtration step using a sintered-metal filter will be performed to ensure adequate solids removal from the supernate to meet criteria for the TRU element content of low-level waste.

Separation of the soluble fission product ¹³⁷Cs from the supernate by ion exchange is also planned. Since the ion exchange resin previously used at B Plant for cesium removal is no longer manufactured, a replacement resin was identified and



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Fig. 1. Disposal Alternatives for Neutralized Current Acid Waste.



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Fig. 2. Schematic of Neutralized Current Acid Waste Pretreatment Process.

process parameters developed to allow separation of ^{137}Cs . Removal of ^{137}Cs from the supernate liquid is required to meet thermal and radiation criteria for a grout waste form. Storage of the separated ^{137}Cs in a concentrated form at B Plant will provide a future option of either combining the ^{137}Cs with the NCAW solids for vitrification or purifying the ^{137}Cs for encapsulation as a commercial radiation source.

A key element in the pretreatment of NCAW slurry was the requirement to determine TRU element levels in the feed and product streams. High-activity fission products interfered with standard alpha energy analysis (AEA) techniques. Ion exchange and liquid/liquid extraction methods were developed to separate the TRU elements from the high-activity fission products, which allows the use of AEA techniques to determine TRU element levels in the feed and product streams.

SOLID/LIQUID SEPARATION TECHNOLOGY

CENTRIFUGATION AND CROSS-FLOW FILTRATION TECHNIQUES

During the early planning for NCAW pretreatment, a conceptual flow sheet was developed based upon the use of centrifugation for primary solids removal. To ensure that TRU and radioisotope removal requirements were met, the supernatant liquids from the centrifuges would be passed through a cross-flow filtration (also known as inertial filtration) system to remove the last traces of solids material. After filtration, the low-level supernatant would be processed through a cation ion exchange system to remove soluble ^{137}Cs . The resulting product would then be suitable for near-surface disposal. Solids from both the centrifuges and the inertial filter would be washed to dilute soluble salts in the interstitial supernatant liquid, and then stored as feed for vitrification prior to final disposal.

Laboratory and pilot scale studies were initiated in 1985 to demonstrate the feasibility of the conceptual NCAW pretreatment process. Verification studies for solids separation by both the centrifuge and inertial filtration steps were performed using a nonradioactive simulated waste; the composition and pertinent physical properties of this simulated waste are provided in Table II. Use of a nonradioactive substitute for the NCAW allowed hands-on pilot plant and laboratory work to be performed at lower costs and with more extensive tests than radioactive simulants would have allowed.

TABLE II
Composition and Physical Properties
of Synthetic NCAW

Component	Concentration
Free OH^-	1.0M
SO_4^{2-}	0.17M
NO_3^-	1.0-2.0M
Na	5.0M
Al	0.88M
Fe	0.11M
Solids concentration	~3.5 wt%
Density: slurry	1.12 g/mL
supernate	1.17 g/mL
solids	1.3 g/mL
Median particle size	1.5 μm

Pilot-scale test results using centrifugation and inertial filtration were not encouraging. An overall solids-liquid separation efficiency of greater than 99.4% would be required to ensure a low-level waste stream. The best overall separation efficiency achieved by the two operations in series was 90% to 95%; at projected plant operating conditions dictated by required process throughput rates, 50% to 60% separation efficiency would be expected. Based upon these results, the original conceptual flow sheet would not be acceptable.

Many of the problems encountered in centrifuging NCAW solids appeared to be caused by the small discrete particle size of such solids and by the small difference in density between the solids and the mother liquid. The synthetic NCAW solids exhibit a high tendency to agglomerate to form larger effective particle sizes in low-shear environments; high-shear forces produced in a centrifuge tend to overcome the weak interparticle attractive forces and break down the agglomerates. Inertial filtration difficulties were thought to center on the highly compressible nature of the solids and the actual inertial filtration process itself.

SETTLING AND CAKE FILTRATION TECHNIQUES

Settling and cake filtration processes were identified as potential alternative methods to provide the required separation efficiency of NCAW solids from solution. A series of bench-scale settling tests were performed using various solids concentrations and a number of polyelectrolyte flocculating agents. Several useful observations were made during these experiments. Samples of both the initial slurry and the supernate liquid during settling exhibited identical discrete particle size distributions. Polyelectrolyte flocculating agents had little effect on separation efficiency or settling time for solids. Solutions of synthetic NCAW solids in demineralized water, representing the solids-washing steps of the process, settled faster than solutions of solids in mother liquid. Addition of polyelectrolyte flocculating agents improved settling rates slightly. The settling behavior of the synthetic NCAW slurries was consistent with hindered settling models used for high-solids slurries in other applications (2,3). Most important, supernatant solutions contained only about 200 ppm solids after settling, corresponding to a solids separation efficiency of >99%.

Additional experiments with synthetic waste using various ratios of solution height to vessel diameter yielded hindered settling rates of 0.10 to 3.0 cm/h. These data are in agreement with the range of rates observed at the Savannah River Plant for underground storage tank settling processes for first-cycle high-level waste treatment (4). The effects of various inorganic flocculating agents on settling rates were also investigated. Treatment of the waste with 200 ppm $\text{Fe}(\text{NO}_3)_3$ increased hindered settling rates from 1.8 cm/h to between 2.5 to 5.1 cm/h. These rates are consistent with those needed to meet required plant throughputs. Solids separation efficiencies of >99% were achieved in these pilot-scale tests.

Pilot-plant scale cake-type filtration tests of a pneumatic hydropulse filter (Mott Metallurgical Corp.) were also conducted. In the pneumatic hydropulse filter, solids are passed through a sintered-

metal element in perpendicular flow. Solids trapped by the filter are removed by periodic backflushing, by forcing small amounts of the filtrate back through the filter element with 0.69 MPa air. To aid in filtration, diatomaceous earth is used to precoat the filter element with a porous solids cake. Diatomaceous earth is also added to the NCAW feed in small amounts to aid in the formation of a stable, more porous filter cake. The pneumatic hydropulse filter differs from the inertial filter because most of the solids separation occurs through the depth of the filter cake, and not on the surface of the element. Depth filtration is expected to overcome the problems encountered in inertial filtration.

The filter used in the pilot-scale tests contained a sintered-metal cartridge with a 0.15 m² filtration area and a 0.5- μ m nominal rating. Scoping studies with this filter showed that it was capable of filtering synthetic NCAW feeds containing 50 to 2,000 ppm solids at flux rates of 0.035 to 0.18 L/min-m². At all feed solids concentrations evaluated, the filtrate contained <10 ppm solids.

Studies were also performed to optimize filtration parameters, especially precoat and bodyfeed usage. The NCAW solids/diatomaceous earth ratios can significantly impact the final cost of waste disposal. Use of diatomaceous earth at the optimal concentration increased by a factor of 10³, the total amount of NCAW solids that could be loaded onto the filter. Careful control of filter flowrates and differential pressures, particularly at the start of filtration, also yielded a significant increase in the amount of simulated NCAW solids that could be loaded onto the filter. Filtration runs of up to 8 h between backpulses with an average filtrate clarity of <10 ppm were achieved for feeds containing 1,000 ppm solids. Feeds containing 7,500 ppm solids, simulating potential process upsets, were also successfully filtered.

To verify pilot-plant-scale results obtained with the simulated NCAW material, plant-scale tests with actual NCAW were initiated in May 1986. To simulate the projected plant process, 19,000-L vessels at B Plant were filled with NCAW slurry containing ~3 to 4 vol% settled solids. These solutions were allowed to settle for periods of 24, 48, and 72 h, at which time the supernatant liquid was decanted to an adjacent tank.

In the plant-scale tests, effective settling rates of >5 cm/h were achieved without the use of flocculating agents. Solids separation efficiencies of up to 90% were also demonstrated. In all cases, about 90% of the TRU elements were removed. A 0.04-m² filtration area pneumatic hydropulse filter installed at the Waste Encapsulation and Storage Facility is currently being tested with the actual NCAW feed. Preliminary results confirm the high solids separation and long filtration times seen during pilot-plant-scale tests with simulated NCAW waste. These results indicate a low-level waste supernate can be produced.

CESIUM ION EXCHANGE

Cation exchange resin technology has long been used at the Hanford Site for removal of ¹³⁷Cs from various alkaline waste streams (5). Typically, an (NH₄)₂CO₃ solution is used to elute sorbed ¹³⁷Cs. As a result of subsequent Cs₂CO₃ product concentration, evolved NH₃ and ¹³⁷Cs are present in the process condensate effluent stream. The presence of NH₃ in the process condensate complicates its treat-

ment and disposal. To overcome the difficulties encountered with (NH₄)₂CO₃ elution, a HNO₃ elution process is proposed for use in removing ¹³⁷Cs from the cation exchange resin used to sorb ¹³⁷Cs from the NCAW supernate liquid.

Initial laboratory tests involved identification of ion exchange materials that exhibited favorable ¹³⁷Cs adsorption characteristics in this waste matrix. Seven materials were tested by batch contacts (Table III). Duolite CS 100^m resin (Rhom and Haas Co.) was selected for further flow sheet development tests.

Radiation doses up to 10⁶ Gy had no effect on the cesium sorption capacity of the Duolite CS 100 resin. Preliminary tests also show that contact with 1M HNO₃ at 25 °C does not degrade the Duolite CS 100, but significant degradation occurs when the resin is contacted with 6M HNO₃. The proposed process uses 0.5M HNO₃ to elute the ¹³⁷Cs.

TABLE III
Cesium Sorption Capacities.

Resin	Cesium sorption (g-Cs/g-resin)
Zeolon 900 ^m *	0.0055
Duolite ARC 9359 ^m *	0.0035
Duolite CS100 ^m	0.0025
Durasil 10 ^m	0.0009
Durasil 210 ^m	0.0009
Vitrokele 55 ^m	<0.0009
Duolite ES286 ^m	<0.0009

*No longer manufactured.

Development tests of both the HNO₃ and (NH₄)₂CO₃ elution processes included variations of flowrate, concentration of cesium eluent, and the volumes of feed, sodium scrub, and cesium eluent solutions passed through the column. Initial results of the HNO₃ elution process show that a second ion exchange cycle is necessary to achieve the desired final sodium-to-cesium ratio. A second ion exchange cycle involves concentration of the first-cycle cesium eluent to minimize storage volume and adjustment of the acidic eluent to pH 10 before being returned to the ion exchange column. Table IV lists results obtained with both the HNO₃ and (NH₄)₂CO₃ elution schemes. Both elution schemes give similar cesium recovery. The (NH₄)₂CO₃ eluent, however, yields a lower, more desirable Na/Cs product ratio.

PROCESS CONTROL

A key objective for pretreatment of NCAW slurry is its separation into high- and low-level waste streams. The TRU element content of the low-level waste stream must be determined to ensure process control and to meet criteria for low-level waste disposal. Standard AEA techniques were found to be ineffective for detection of TRU elements in NCAW slurry and supernate liquid. High-activity fission products interfered with AEA detection. To resolve these difficulties, an alternate analytical method was developed that separated the fission products from the TRU elements before AEA was performed.

Plutonium-241 and ²³⁹Np can be loaded on a Biorad AG-1 x 4^m ion exchange resin, then eluted and detected by AEA. Americium-241 can then be extracted from the ion exchange effluent solution

TABLE IV
Comparison of ¹³⁷Cs Ion Exchange Processes.

First-cycle eluent	Waste streams (% of feed)		Product stream (% of feed)		Bed volumes		Column loading	Product ratio
	Cs	Na	Cs	Na	feed	¹³⁷ Cs elution	Bq ¹³⁷ Cs/g-resin (x 1.0 E-10)	Na/Cs
HNO ₃	2.6	99.0	97.4	1.0	45	8	1.92	120
(NH ₄) ₂ CO ₃	0.5	99.8	99.5	0.2	45	6	1.92	19
Second-cycle eluent								
HNO ₃	3.2	95.6	96.8	4.4	18	5	9.47	7.8
(NH ₄) ₂ CO ₃	7.0	NA	93.0	NA	10	6	35.2	1.9

using a liquid/liquid extractant, octyl (phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide [O₈D(IB)CMPO] and detected by AEA. This method has shown good reproducibility and will be the standard method for use on NCAW samples.

FLOW SHEET DEVELOPMENT

An integrated process flow sheet for pretreatment of the NCAW slurry was modeled to allow sensitivity studies and adjustment of parameters as the results of further plant process tests and demonstrations become available. The estimated compositions of the separated NCAW solids and supernate streams resulting from the pretreatment process are listed in Table V.

The reference flow sheet for pretreatment of NCAW slurry is designed to produce satisfactory feed stocks to both the Hanford Waste Vitrification Plant (HWVP) and the Transportable Grout Facility (TGF). Present criteria specify that feed to the TGF

and washed NCAW solids are expected to be well within acceptable concentrations for feeds to the HWVP.

SUMMARY

A flow sheet for pretreatment of Hanford Site NCAW has been developed, which includes settle/decant and washing operations for primary separation of the TRU-bearing solids from the supernate. A sintered-metal filter, using diatomaceous earth filter aid, is specified as a secondary filtration device to ensure that TRU levels in the separated supernate stream meet criteria for low-level waste disposal. Cesium-137 is also removed from the supernate stream by ion exchange using an organic resin, Duolite CS 100.

The requirements of the downstream facilities, which will process the streams resulting from pretreatment of the NCAW slurry to glass and grout waste forms, were considered in the technology development efforts. Other site requirements were also integrated into the flow sheet, including considerations of process rates and double-wall tank storage availability, routing between facilities, and waste retrievability. The process proposed for demonstration in B Plant will meet all known requirements.

TABLE V
Composition of Pretreated NCAW Streams.

Constituent	Pretreated NCAW solids	Pretreated supernate liquid
Free OH ⁻	3.2 E-02M	1.4M
SO ₄ ²⁻	1.1 E-02M	0.13M
NO ₃ ⁻	7.3 E-02M	1.7M
NO ₂ ⁻	9.8 E-02M	0.4M
Na	0.45M	5.0M
Al	0.11M	0.42M
Fe	0.14M	5.3 E-05M
Total organic carbon	8.7 E-02 g/L	0.1 g/L
²³⁹ Pu	2.5 E-03 g/L	2.2 E-06 g/L
²⁴¹ Am	2.4 E-03 g/L	2.0 E-06 g/L

contain <4.9 E+09 Bq ¹³⁷Cs/L and that the grout produced in the TGF contain <3.7 E+03 Bq TRU elements per gram of grout. Based on the pilot-plant tests and computer modeling, the low-level liquid stream resulting from pretreating NCAW slurry will contain about 2.2 E+09 Bq ¹³⁷Cs/L; the grout made from the low-level waste is expected to contain only about 330 Bq TRU elements per gram of grout. The amounts of sulfate and chromium in the separated

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