CONF-951057

DEPARTMENT OF ENERGY PRETREATMENT OF HIGH-LEVEL AND LOW-LEVEL WASTES

C. Phil McGinnis and Rodney D. Hunt
Chemical Technology Division
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37831-6273

To be presented at the
Ninth Symposium on Separation Science and Technology
for Energy Applications
Gatlinburg, Tennessee
October 22-26, 1995

RECEIVED
FEB 05 1996
OSTI

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

---

*Managed by Lockheed Martin Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Dle

DEPARTMENT OF ENERGY PRETREATMENT OF HIGH-LEVEL AND LOW-LEVEL WASTES

C. Phil McGinnis and Rodney D. Hunt*
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6273

ABSTRACT

The remediation of the 1×10^8 gal of highly radioactive waste in the underground storage tanks (USTs) at five U.S. Department of Energy (DOE) sites is one of DOE's greatest challenges. Therefore, the DOE Office of Environmental Management has created the Tank Focus Area (TFA) to manage an integrated technology development program that results in the safe and efficient remediation of UST waste. The TFA has divided its efforts into five areas, which are safety, characterization, retrieval/closure, pretreatment, and immobilization. All DOE pretreatment activities are integrated by the Pretreatment Technical Integration Manager of the TFA. For FY 1996, the 14 pretreatment tasks are divided into 3 systems: supernate separations, sludge treatment, and solid/liquid separation. The plans and recent results of these TFA tasks, which include two 25,000-gal demonstrations and two former TFA tasks on Cs removal, are presented. The pretreatement goals are to minimize the volume of high–level waste and the radioactivity in low-level waste.

*Corresponding Author

INTRODUCTION

The U.S. Department of Energy (DOE) has identified its five highest–priority remediation problems, which include the remediation of the 1×10^8 gal of high-level and low-level radioactive waste in over 300 underground storage tanks (USTs) at its Hanford, Savannah River, Oak Ridge, Idaho, and West Valley sites. With the exceptions of West Valley and Idaho, the waste was generated primarily from plutonium production processes such as PUREX, REDOX, and bismuth phosphate separations. The waste in a typical UST is partitioned into three aqueous phases: saltcake, supernate, and sludge. The radioactivity of the waste averages 1×10^{11} Bq/L, or 3 Ci/L, and is primarily due to ^{137}Cs and ^{90}Sr. Major inorganic species result from $Al(NO_3)_3$ and concentrated HNO_3 that were used for metallic dissolution and from ferrocyanide that was used for Cs removal. Prior to storage at Hanford, Savannah River, Oak Ridge, and West Valley, the pH of the waste was adjusted to 10–14 with the addition of NaOH. The largest single constituent is $NaNO_3$.

The DOE's Office of Environmental Management (EM) is responsible for the remediation, waste minimization, and environmental compliance activities at all DOE sites. EM has determined that cleanup costs for the USTs would be prohibitive using the current baseline technologies. Therefore, EM has established an extensive technology development program, the main objectives of which are to reduce cost, minimize risk, and accelerate schedule. Currently, site-specific technology development projects are funded by the local Waste Management organizations at the UST sites, while the EM Office of Science and Technology (OST) utilizes the entire DOE complex to develop and demonstrate new UST remediation technologies. The OST research and development activities on waste processing are conducted by the Efficient Separations and Processing (ESP) Cross Cutting Program, while demonstrations, tests, and evaluations (DT&E) are performed by the Tank Focus Area (TFA). In addition, the TFA is responsible for the technical integration of all tank waste remediation projects of local Waste Management organizations, OST programs such as the ESP program, and other focus areas such as the Mixed Waste Focus Area.

The TFA has developed a multiyear program plan (1) and established six goals to measure the success of this new approach:

- Develop technology to meet waste tank needs across the DOE complex and apply all successfully demonstrated technologies.
- Provide an environment for cost-effective technology.
- Have an efficient management system for tank technology development.
- Clarify regulatory requirements that impact and drive technology development.
- Increase commercialization of tank technologies.
- Improve stakeholder satisfaction.

The management of TFA has divided the technology development efforts into five areas: safety, characterization, retrieval/closure, pretreatment, and immobilization. The pretreatment is a key component since the amount of waste to be immobilized and the efficiency of the selected pretreatment processes will directly impact the overall remediation costs of the USTs. During FY 1995, the TFA had eight separation tasks, which were described previously in a management plan (2). During FY 1996, the TFA has 14 pretreatment tasks. Two separation tasks, which were transferred from the TFA to the ESP, continue to directly support the TFA Cesium Removal Demonstration. The pretreatment tasks have two primary objectives:

- Demonstrate the removal of radionuclides and chemical toxicity from low-level waste (LLW).
- Demonstrate the removal of the constituents contributing to excess volume of high-level waste (HLW) from sludges and acidic wastes.

The TFA pretreatment tasks for FY 1996 are divided into three systems: supernate separation, sludge treatment, and solid/liquid separation. While the supernate system, which is shown in Fig.1, is primarily focused on Cs removal, technologies to remove other radionuclides such as Tc, Sr, and transuranics (TRUs) and processes to reduce waste volumes are also supported. Approximately half of the TFA pretreatment budget is used to support the supernate system, which is composed of the the Cesium Removal Demonstration (CRD), Cesium Qualification Studies on Hanford Waste, Technetium Qualification Studies on Hanford Waste, Acidic TRU/Sr/Tc Removal from INEL [Idaho National Engineering Laboratory] Tank Waste, and the Out-of-Tank Evaporator Demonstration. The primary goals of the supernate system are to begin a 25,000-gal Cs removal demonstration at the Melton Valley Storage Tanks (MVSTs) in Oak Ridge by the end of FY 1996, to validate technologies that could be used by the private sector to remediate the supernate at Hanford, and to process 25,000 gal of MVST supernate with a mobile, skid-mounted evaporator system. The removal of Cs from the MVST supernate is now required before any supernate can be solidified with grout. Two former TFA tasks, Comprehensive Supernate Treatment and Hot Cell Demonstration, continue to directly support the CRD through evaluation of potential Cs sorbents with batch and column tests.

The sludge treatment system, which is displayed in Fig. 2, consists of the Enhanced Sludge Washing, Alternative Alkaline Washes of Hanford Sludges, Partitioning of Sludge Components by Caustic Leaching, Counter Current Decantation, Sludge Treatment Studies, and Caustic Recovery and Recycle. The main objectives of the sludge washing system are to determine the number of HLW glass canisters that will be needed after the enhanced sludge wash (ESW) of the Hanford HLW sludges and to provide alternatives or improvements to the ESW if too many glass canisters will be required. ESW, which consists of an inhibited water wash followed by caustic leaching, is the current pretreatment baseline for the Hanford sludges according to the Tri-Party Agreement. The 1994 and 1995 projections of the number of HLW glass canisters from Hanford after the ESW are 6800 and 7200 canisters, respectively. The 1995 projection is based on the ESW results from 15 sludge samples, which represent 23% of the Hanford sludges. The final decision on the sludge pretreatment process is scheduled to be made in March of 1998. The ESW is essentially the same processing that has been implemented at Savannah River.

The solid/liquid separation system, which is shown in Fig. 3, is composed of Solid/liquid Separation Test Equipment Development & Transfer, Solid/liquid Separation of Suspended Solids from Gunite Tanks, Crossflow Filtration Testing on Hanford Waste, and parts of the Counter Current Decantation. Solid/liquid separation is a high-priority need at each of the DOE tank sites and will be needed multiple times during the processing of the waste. Therefore, the solid/liquid separation system must address a wide variety of processing requirements, and the emphasis on and funding of this system are expected to grow in future years.

RESULTS AND DISCUSSION

Supernate Separations

Cesium Removal Demonstration by J. F. Walker of Oak Ridge National Laboratory Most of the radioactivity in the supernate and dissolved salt is due to ^{137}Cs. Therefore, Cs must be removed before millions of gallons of supernate can be immobilized and disposed as a LLW instead of a HLW. The costs to process, immobilize, and store HLW are at least an order of magnitude greater than the same costs for LLW. Clearly, Cs removal can lead to significant cost savings. This ongoing task is jointly funded by the TFA and Waste Management at Oak Ridge and will remove most of the Cs from 25,000 gal of MVST supernate. Its purpose is to provide design and operating information for implementing Cs removal treatment for underground storage tank waste using modular, mobile systems and state-of-the-art ion-exchange methods. This task will also show the relationship between bench-scale and pilot-scale performance using simulants and actual waste.

During FY 1995, the CRD selected MVST W-27 for the 25,000-gal demonstration. A 1994 analysis of the W-27 supernate has determined that the concentrations of Na, K, and Cs are 4.13, 0.29, and 0.000002 M, respectively. The ^{137}Cs level is 3.3×10^8 Bq/L, or 0.009 Ci/L, while the pH of the supernate is 7.2. Prior to CRD, the pH of MVST W-27 supernate will be raised to 12.5–13.0 with the addition of NaOH. The composition of the pH-adjusted W-27 supernate is similar to Hanford's double-shell slurry seed (DSSF) if it is diluted to 5 M Na with 2 M NaOH as expected.

In addition, the CRD completed a conceptual design study and issued an alternatives report (3). The study examined sorbents, facilities, process alternatives, and waste disposal options. Eight Cs removal technologies were identified and evaluated. The candidates included zeolites, Duolite CS-100, resorcinol-formaldehyde (RF), an engineered form of crystalline silicotitanate (CST), granular potassium cobalt hexacyanoferrate (KCCF), pillared clay, ammonium molybdophosphate (AMP), and embedded membrane technology (EMT) from 3M Corporation. The initial evaluation identified RF, CST, and KCCF as the primary candidates for the CRD based on distribution coefficient, Cs loading, estimated sorbent cost, suitability to Hanford and Savannah River, and compatibility with vitrification. However, additional information on the EMT and the results from small-column tests with actual MVST supernate are needed before the final selection of the CRD sorbent(s) can be made in early 1996. The CRD has selected the Liquid Low-Level Waste Solidification Facility as the demonstration site. This facility will not require major modifications to the building, piping, or safety documents, while the other alternatives would require major facility changes that would significantly delay the start of the CRD. Finally, the alternatives report included the following recommendations: (a) the CRD system should contain two ion-exchange columns, which should be piped to operate in parallel or in series; (b) the columns should fit into an on-site transport carrier's cavity, which is approximately 37.6 cm in diameter and 104.9 cm in height; (c) the columns should be designed to allow the sorbent to be sluiced into or out of the columns; (d) the columns should also serve as storage containers; (e) a filter should be included to remove solids from the supernate before it is processed through the sorbent; (f) provisions to remove free water from the filters and sorbent should be incorporated into the design for shipping and storage requirements; and (g) the CRD system should be skid mounted so it can be transported to a different facility.

Other recent activities included the preparation of the required documents, the design and construction of the Cold Test Loop (CTL), the completion of the specifications for the design and construction of the CRD system, and the placement of the contract to procure the system. The required documents for the CRD were identified. A safety assessment and a National Environmental Policy Act project review checklist were completed. Most of the required documentation will be completed in FY 1996. The CTL was used to examine the pressure drop, channeling, sorbent degradation, sorbent transport, rinsing, and dewatering of sorbents. The initial tests were conducted on the RF resin. Severe bleeding problems were encountered with the RF resin. Finally, a contract for the design and construction of the CRD system was placed with TTI Engineering, and the design for the system was completed and approved by October of 1995.

The CRD personnel has an aggressive FY 1996 schedule in order to meet a DOE Headquarters milestone to start processing of MVST supernate in September of 1996. The schedule includes the following: (a) finish construction of the CRD system by March of 1996 and (b) complete CRD installation and cold test by August of 1996. During FY 1997, the CRD will complete its processing campaign and send its spent sorbents to the Savannah River Site for vitrification by another TFA task, which is directed by the Immobilization Technical Integration Manager.

Comprehensive Supernate Treatment by B.Z. Egan and J. L. Collins of Oak Ridge National Laboratory This ongoing task, which has been tranferred from the TFA to the ESP, continues to perform batch tests on Cs sorbents in support of the CRD. Supernate samples from MVSTs W-25, W-27, and W-29 were retrieved and characterized. This task has also examined Sr and Tc removal technologies. Most of the batch tests were conducted on the MVST W-25 supernate (4), which is very similar to the MVST W-27 after its pH adjustment for the CRD. An analysis of the W-25 supernate has determined that the Na and K concentrations are 3.87 and 0.36 M, respectively. While the pH of the W-25 supernate is 12.6, the ^{137}Cs level is 1.2×10^9 Bq/L or 0.03 Ci/L, which represents 94% of the radioactivity. Prior to the batch tests, 1 L of MVST W-25 supernate was filtered with 0.45-micron nylon filters to remove the particulates.

The distribution coefficients and percentage removal of Cs from MVST W-25 supernate using several ion-exchange materials were measured. The ion exchangers were tested RF resin from Boulder Scientific, CST from Sandia National Laboratories and UOP, Duolite CS-100 from Rohm and Haas, granular and powdered KCCF from Oak Ridge National Laboratory and Eichrom Industries, and composite microspheres containing sodium and potassium cobalt hexacyanoferrates in hydrous titanium oxide and phosphate. In a typical experiment, 10 mL of supernate was mixed with 50 mg of sorbent for periods ranging from 15 min to 144 hrs. The distribution coefficients ranged from 34 to 44 mL/g for CS-100, from 138 to 764 mL/g for the RF resin, from 451 to 958 mL/g for the powdered CST, and from 26,000 to 46,000 mL/g for the granular KCCF. In loading tests, the Cs sorption by the different exchangers was about 8 g/kg for the RF resin, 15 g/kg for the powdered CST, and 18 g/kg for the granular KCCF. These results are used by the Hot Cell Demonstration and the CRD.

This task also examined the effects of varying the Cs and K concentrations in the supernate on the sorption of Cs by the RF resin, the powdered CST, and the KCCF. An increase in the total Cs concentration from 0.2 to 180 mg/L had no effect on the distribution coefficients for the powdered CST and the granular KCCF. However, the distribution coefficient for the RF resin was reduced by 87% as its Cs capacity was exceeded.. The K concentration had little effect on the Cs sorption by the CST powder and granular KCCF, while increased K concentrations caused major decreases in Cs sorption by the RF resin.

In FY 1996, this task will complete batch tests on radionuclide removal technologies as they become available. Since the early studies have focused on the sorption of radionuclides, the emphasis will be shifted toward elution, stripping, and other ways to concentrate the recovered radionuclides on sorbents if possible. The storage or disposition of loaded sorbents that cannot be eluted will also be evaluated.

Hot Cell Demonstration by D. D. Lee of Oak Ridge National Laboratory This task, which has been transferred from the TFA to the ESP, performs small, continuous column tests with pH-adjusted MVST supernate. These results will be used by the CRD to determine the design parameters for the demonstration. The rate of removal, sorbent required, and regeneration requirements are important design parameters, and the loading capacity of each sorbent will help to determine the size of the column required and help define the final volume of solid waste to be disposed of.

This task has designed and built a small-column system, which was placed in a hot cell at Oak Ridge National Laboratory. Capabilities of this system include the ability to operate remotely, on-line monitoring of the column effluent to detect Cs breakthroughs from the material in the column, and the ability to treat ion-exchange material in the column with any desired eluent or wash solution and monitor the effluent for removal of Cs from the column. In addition, this task obtained approximately 56 L of the MVST W-27 supernate. Prior to the column tests, the pH of the supernate is increased to 12.5–12.8 using solid NaOH pellets to keep dilution to a minimum. Once the pH-adjusted supernate is transferred to the hot cell, it is allowed to settle for 3 days to allow the Ca and Mg compounds to precipitate and settle to the bottom before the solution is pumped to the column feed tank through the 0.45-

micron filter. Finally, the task has obtained the RF resin, CS-100, SuperLig 644 (IBC), SuperLig 644 with EMT from 3M, granular KCCF (Eichrom Industries), and IONSIV IE-911, which is an engineered form of CST by UOP.

For the column tests, 5–50 mL of sorbents is placed in a column, and the pH-adjusted supernate is passed continuously through the sorbent bed until the 50% breakthrough has occurred. Most of the initial experiments have used the RF resin. Single-loading tests with the RF resin were conducted at a feed rate of 2.8 and 7 column volumes (CV)/h, and based on the preliminary analysis, the 50% breakthroughs occurred at 42–43 CV and 35–40 CV, respectively. The results for these two RF experiments follow almost the same breakthrough curve. The RF resin was loaded and eluted with 0.5 M HNO_3 acid for a total of five times; the loading curves for each cycle were very comparable. In addition, CS-100 was evaluated at a feed rate of 2.9 CV/h, and 50% breakthrough occurred at 12.5 CV. Therefore, the 50% breakthrough of the RF resin was three times higher than the CS-100 50% breakthrough. An earlier Pacific Northwest Laboratory (PNL) study (5) with a neutralized current acidic waste simulant found that the 50% breakthroughs with the RF resin and CS-100 occurred at 139 CV and 22.5 CV, respectively. SuperLig 644C and IONSIV IE-911 were also tested during FY 1995. The flow rate for the initial experiment with SuperLig 644C was 2.5 CV/h, and the run was terminated before 50% breakthrough because its performance was considerable better than anticipated. The analytical results from the CST test, which was performed at 3 CV/h, are not yet available.

During FY 1996, this task will perform the initial column tests on the pH-adjusted MVST supernate with granular KCCF and SuperLig 644 with EMT from 3M. IONSIV IE-911 and SuperLig 644C will be evaluated at higher flow rates. Additional engineering tests will be performed after the sorbent selection for the CRD. After the completion of the tests for the CRD, the task will modify the MVST supernate through the addition of chemicals such as NaOH so the composition of the MVST supernate is more comparable to the supernates at Hanford. The task will evaluate new Cs, Sr, and Tc removal technologies as directed by the ESP and recommended by the TFA.

Cesium Qualification Studies on Hanford Waste—to be determined This new TFA task at Hanford and the Hot Cell Demonstration at Oak Ridge will conduct similar experiments. This duplication of tasks is necessary since insufficient quantities of supernate for column tests can be transported off-site due to Department of Transportation regulations. The column system at Oak Ridge will serve as the model for the Hanford system. This Hanford task will test the best sorbent from the Oak Ridge column tests with actual Hanford supernate in order to provide processing information for the new privatization initiative at Hanford. As part of the new privatization approach to remediate the UST wastes, DOE requires over 99% of the Cs to be removed from the Hanford supernate based on the ^{137}Cs and ^{134}Cs concentrations in the final waste form. This task will demonstrate which technologies can meet this requirement and their capacities. Thus far, the only column tests with actual Hanford supernates were performed on CS-100, the baseline Cs removal technology at Hanford. Prior to the column tests, the supernates from Hanford tanks 101-SY and 103-SY were diluted with 2 M NaOH until the Na concentrations were 5 M. Preliminary PNL results indicate that the 50% breakthroughs occurred between 30 and 40 CV (6).

During FY 1996, this task will place a full operational column system in a properly shielded facility and obtain liter quantities of DSSF supernate. Preference will be given to the tanks that are part of the privatization effort. The first small-column test, which will use 2–10 mL of sorbent, is expected to begin in spring of 1996. The treated supernate will then be provided to the Technetium Qualification Studies on Hanford Waste task.

Technetium Qualification Studies on Hanford Waste—to be determined This new TFA task is also directed at the new privatization effort to remediate Hanford UST wastes. DOE requires an average of 90% of the Tc to be removed from the Hanford supernate based on the Tc concentration limit for the final waste form. Recent results from Los Alamos National Laboratory (LANL) indicate that this level of decontamination may be difficult to achieve with technologies designed to remove the pertechnetate anion, TcO_4^-. The CS-100 treated supernates from Hanford tanks SY-101 and SY-103 were sent to Los Alamos, and batch tests were performed with the Reillex-HPQ resin and the SY-103 supernate. The first measurements of distribution coefficients indicated that 75% of Tc could not be removed.

During FY 1996, this task will use a column system for Tc studies and obtain Cs-treated Hanford supernates from the Cesium Removal Column Tests with Actual Hanford Supernates task. A minimum of two Tc removal technologies, which include Argonne National Laboratory (ANL) crown ether technology and the best commercially available resin based on earlier LANL studies, will be tested.

Acidic TRU/Sr/Tc Removal from INEL Tank Waste by T. A. Todd of Idaho National Engineering Laboratory This new task, which is jointly funded by the TFA and Waste Management at Idaho, will focus on the removal of TRUs, Sr, and Tc from Idaho Chemical Processing Plant wastes. The TRUEX and SREX processes, which were developed at ANL, are considered the baseline TRU, Sr, and Tc treatment technologies for the HLW calcine and all future acidic Na-bearing liquid waste that is produced after the year 2015. Previously, TRUEX and SREX have been tested on a very limited basis with actual waste. These solvent extraction technologies are now ready to use on actual Idaho tank waste in a continuous countercurrent extraction demonstration.

During FY 1996, this task will use a 24-stage bank of 2-cm diameter centrifugal contactors to verify the effectiveness of the TRUEX process for the removal of TRUs and Tc from acidic wastes. Actual tank waste will be used as the aqueous feed to the contactor assembly in the Remote Analytical Laboratory hot cell. The TRUEX solvent will be a mixture of 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide in 1.4 M tributylphosphate in Isopar L. The process will be operated continuously until steady-state operation is achieved, and then exit-stream samples will be taken. At the completion of the TRUEX demonstration, each stage will be sampled to determine the individual stage distribution coefficients and the concentration profiles for all 24 stages. The goal of the TRUEX process is to reduce the actinide concentration to below 10 nCi/g, which is the limit for Nuclear Regulatory Commission Class A LLW. A SREX demonstration is tentatively scheduled for FY 1997.

Out-of-Tank Evaporator Demonstration by A. C. Lucero of Oak Ridge National Laboratory This ongoing task between the TFA and Waste Management at Oak Ridge will demonstrate the feasibility of a mobile evaporator for the treatment of supernate. The Out-of-Tank Evaporator Demonstration (OTED) will process 25,000 gal of supernate from a MVST tank. Approximately 19,000 gal of concentrate will be returned the MVST, while 6000 gal of condensate will be collected and transferred to the process waste system. The OTED has chosen to evaporate the supernate from W-24 based on preliminary characterization data on the MVSTs because the nitrate concentration would remain below 5 M even after a 25% volume reduction. The current concentrations of Na, NO_3^-, K, and ^{137}Cs in MVST W-24 are 3.25 M, 3.18 M, 0.53M, and 1,100,000 Bq/mL, respectively. Personnel at ANL have performed tests with a W-24 simulant and a small bench-scale evaporator that is comparable to the OTED evaporator. The ANL results indicate the potential for a 50% volume reduction of the supernate without precipitation, and foaming and scaling are not expected to cause an operational problem. These ANL experiments identified potential problems and will be used to determine the relationship between the performance of small-scale evaporators on surrogate solutions and full-scale units on actual supernate. Finally, a skid-mounted single-stage subatmospheric evaporator unit was designed and built by Delta Thermal Inc., and it was delivered to Oak Ridge in September of 1995.

During FY 1996, the evaporator will be installed in the Liquid Low-Level Waste Solidification Facility. Temporary shielding, heating and cooling systems, and tanks for the OTED will be added as necessary to meet Oak Ridge National Laboratory safety requirements. The OTED should complete its evaporation phase by the end of 1996. The evaporator will then be decontaminated and transferred to the local Waste Management organization for additional evaporation campaigns. The OTED will determine processing capabilities such as decontamination factors, identify potential operation/maintenance problems with remotely operated evaporators, and evaluate the feasibility of decontaminating the evaporator systems for hands-on maintenance or movement to another site.

Sludge Treatment

Enhanced Sludge Washing by D. J. Temer of Los Alamos National Laboratory and G. J. Lumetta of Pacific Northwest Laboratory This new TFA task was transferred from the Tank Waste Remediation System (TWRS) and will continue to examine the effectiveness of the ESW, which consists of an inhibited H_2O wash and a hot caustic leach. The objective of the ESW is to dissolve only nonradioactive components such as Na, Al, Cr, phosphate, and sulfate from the HLW sludges. If these inert bulk constituents can be successfully removed, then the number of

HLW glass logs will be significantly reduced. Earlier results (7–9) from TWRS tasks at PNL and LANL indicated that sludge wash and enhanced sludge wash will generate 19,000 and 7200 canisters, respectively. The combined sludge leaching assumptions for single-shell tanks and double shell tanks result in overall enhanced sludge leaching efficiencies of 68, 64, 74, and 25% for Al, Cr, phosphate, and Na, respectively. This TFA task will help to verify these assumptions.

During FY 1996, this task will conduct ESW experiments on small sludge samples from four different tanks that have not been previously evaluated. The distributions of key components such as sulfate, phosphate, Al, Cr, and radionuclides among the wash and leach solutions and the leached residue will be determined.

Alternative Alkaline Washes of Hanford Sludges by G. J. Lumetta of Pacific Northwest Laboratory This new TFA task will examine potential improvements to the ESW, which is perceived as easy and inexpensive to implement. However, the number of HLW glass logs from the ESW may still significantly exceed the limit for the HLW repository. This task will evaluate alternative alkaline washes that are still relatively easy to implement and can reduce the number of HLW glass logs.

During FY 1996, this task will initially focus on the dissolution of Cr by $KMnO_4$. A dilute NaOH wash is expected to remove only 30% of the Cr from sludge in Hanford tank SY-102. However, a combination of dilute NaOH leaching and KMnO4 results in the 96% removal of Cr from a SY-101 sludge sample (10). The $KMnO_4$ oxidizes the insoluble Cr(III) to the alkaline soluble Cr(IV). This method will be extended to other sludge samples that have high Cr concentrations. This Cr process will also be optimized with respect to time, temperature, and $KMnO_4$ concentration. Finally, this task will investigate the use of ultrasound to improve the performance of the ESW on real sludge samples. Ultrasound is capable of imparting high energy into a chemical system under mild temperature and pressure conditions.

Partitioning of Sludge Components by Caustic Leaching by B. Z. Egan of Oak Ridge National Laboratory This task, which was transferred from the ESP to the TFA, continues evaluate washing and caustic leaching of HLW sludges in an effort to provide improvements to the ESW at Hanford. Previously, procedures were developed for the preparation of Hanford surrogate sludges and for analysis of sludge solids and dissolution solutions. These Hanford simulants were leached under different conditions, such as temperature and NaOH concentrations. In addition, an actual sample of MVST W-25 sludge was leached with 3 M NaOH followed by 6 M NaOH at ambient temperature. The percentage of Al and Cr removed by the caustic leaching was much less from the MVST sludge than from the Hanford surrogate sludges. The caustic leaches also removed about 8% of the ^{137}Cs, 100% of the sulfate, and 0% of the phosphate. Another sample of MVST W-25 sludge was leached with 3 M NaOH for 4 h at 95°C. Analyses indicated that 11% of the Al and 100% of the Cr were removed from the solids. Approximately 15% of the Cs, 0.56% of the Co, and 0.78% of the Eu were also removed. In other tests, samples of the MVST W-25 sludge were leached with 1 M NaOH for 4.2 h at 95°C; the leaching and washing dissolved about 16% of the solids along with 12% of the Cs. A similar test with 3 M NaOH removed 17% of the solids and 15% of the Cs. When the residue from the 3 M NaOH leach was leached with 6 M NaOH, an additional 27% of the Cs was removed. In the same test, the sequential leaching of the sludge removed about 18% of the Al and 16% of the Cr. As expected, the amounts of these components that were removed increased significantly at the higher temperature, compared to a 6 M NaOH leach at room temperature. However, the Cs was still very difficult to remove from the sludge.

During FY 1996, this task will perform bench-scale tests on the solubility of combinations of specific sludge components such as calcium and aluminum hydroxides. In addition, the caustic dissolution behavior of actual sludge samples from Oak Ridge and Hanford will be examined with an emphasis on amphoteric elements. These results will be compared with the results from the other caustic sludge projects to determine if easily implemented improvements to the ESW are possible.

Counter Current Decantation by R. A. Peterson of Westinghouse Savannah River Company This new TFA task will evaluate the effectiveness of a countercurrent decantation circuit for sludge treatment at Savannah River, Hanford, and Oak Ridge. Sludges at these DOE sites will be water washed primarily to remove Na salts and then leached to remove Al, Cr, sulfate, and phosphate. Hanford and Savannah River personnel are examining the potential of in-tank clarification of the sludge treatment solutions. This process is inherently inefficient since clarification requires long time intervals. The in-tank process is also inefficient in mixing and contacting the treatment solutions with the sludge. Fortunately, countercurrent decantation (CCD), which is an industrial process, can more effectively treat the sludges and clarify liquids that are used in the washing. CCD uses a number of clarifiers to cascade wash and leach, concentrate the sludge from the final clarifier, and produce a concentrated effluent that has very low solids content. CCD can greatly reduce processing time and the volumes of spent wash water that will require subsequent treatment.

During FY 1996, this task will review existing results prior to the initiation of tests for the design of the CCD circuit. The Savannah River tests will focus on the use of tank waste samples and on the selection of a flocculent. An industrial partner will identify operating parameters for the CCD circuit. Once these parameters have been identified, a process flow sheet and a cost estimate will be prepared.

Sludge Treatment Studies by E. C. Beahm of Oak Ridge National Laboratory This task, which was transferred from the ESP to the TFA, performs a comprehensive evaluation of sludge treatment options, which include caustic leaches and acid dissolution. These results will be used in the 1998 decision on the Hanford sludge pretreatment process. During FY 1995, acid dissolution of MVST sludge revealed important aspects about sludge chemistry and treatment strategies. Gel formation in leachates was observed as early as 2 days after leaching. Studies of colloid concentrations in leachates found that few or no colloids were present during the first 2 days. However, after this latent period, colloid concentration steadily increased for approximately 10 days. At this point, the colloid concentration remained the same and enhanced gel formation occurred. Gelation in leachates is unacceptable because it could prevent mixing and pumping, retard separations, coat surfaces, and clog filters.

Caustic leaching of MVST sludge was not found to be an effective technique for Al removal. This sludge contains a relatively high concentration of Ca, which can form calcium aluminates and calcium aluminosilicates in caustic solutions and thereby restrict dissolution of aluminum oxide/hydroxide.

During FY 1996, this task will continue its tests on Hanford and Oak Ridge sludges and its modeling of sludge behavior to evaluate sludge processing. The distribution of chemical species between aqueous solutions and solids will be examined, and problems due to chemical interactions that could result in processing difficulties or safety concerns will identified and addressed.

Caustic Recovery and Recycle by D. T. Hobbs of Westinghouse Savannah River Company This new TFA task will develop a cost-effective process for the recovery and recycle of NaOH from the HLW, which contains a large amount of Na salts. This Na can be separated from other components of the HLW by electrochemical salt splitting. In this electrochemical process, Na^+ cations migrate across a cation-selective membrane into the anolyte under the influence of an applied electrical potential. Hydroxide is produced at the anode by the oxidation of water. Therefore, the anolyte product is a NaOH solution. Currently, the baseline retrieval and sludge washing processes at Savannah River and Hanford require a significant addition of fresh NaOH, which will also increase the volume of LLW. At Hanford, a trade study (11) has projected that the new NaOH for the enhanced sludge washing is expected to increase the volume of LLW by 13–16%. The trade study has determined that electrochemical salt splitting is more cost-effective than crystallization or the plasma torch.

During FY 1996, this task will conduct bench-scale tests on electrochemical salt splitting with Hanford and Savannah River simulants to demonstrate the recovery of NaOH. These tests will then be repeated with actual Savannah River and Hanford wastes. The results for these experiments will be used in an engineering study on the cost-effectiveness of the NaOH recycle technology.

Solid/liquid Separation System

Solid/liquid Separation Test Equipment Development & Transfer by D. J. McCabe at Westinghouse Savannah River Company This ongoing task conducted solid/liquid separation experiments on simulants for several Oak Ridge and Hanford waste streams. Surrogates of mobilized sludges from the Hanford tank S-103 and the Gunite tanks as well as the newly generated liquid LLW at Oak Ridge were tested.. The Experimental Lab Filter (ELF) and the Parallel Rheology Experimental Filter were used during the evaluations. Work also continued on improvements to the Cell Unit Filter (CUF), which is a small hot cell system for tests with actual wastes. Finally, this task provided a comprehensive summary document (12) of solid/liquid separation needs and potential applications useful for planning the FY 1996 work.

For FY 1996, this task will expand this support to all five tank sites. A CUF will be provided along with operational procedures to both Idaho and Hanford for tests with actual wastes. Hanford and Oak Ridge have both requested extensive testing and engineering support in preparation for demonstrations at the sites. In addition, the full-scale remediation efforts at Savannah River and West Valley are under way, and this task will address solid/liquid separation problems as they arise.

Solid/liquid Separation of Suspended Solids from Gunite Tanks by T. E. Kent at Oak Ridge National Laboratory This new TFA task will address the solid/liquid separation needs of Environmental Restoration Program during its remediation of the Gunite tanks at Oak Ridge. This remediation project is planning to use a suspension agent such as bentonite during its sludge retrieval operations so the sludge will not plug the only transfer line to Melton Valley. After the transfer has been completed, solid/liquid separation is required before the Gunite sludge solutions can be sent into the MVSTs. Because of an agreement between DOE and the state of Tennessee, solids must be sent to the old MVSTs, and only liquids can be sent to the new MVSTs.

During FY 1996, this task will evaluate a variety of filtration methods that can meet the requirements of this agreement and easily handle large volumes of suspended material. After the evaluation, the most suitable filtration technologies will be tested with simulants that are formulated with the assistance of the Environmental Restoration personnel. In later years, the most promising technology will be evaluated with actual Gunite tank waste, and a full-scale demonstration will begin as soon as retrieval activities begin.

Crossflow Filtration Testing on Hanford Waste by B. A. Reynolds of Pacific Northwest Laboratory This new TFA task will examine the solid/liquid separation requirements for sludge sluicing activities. Effective solid/liquid separation is required before the liquids can be sent to the LLW vitrification facility. The primary solid/liquid separation will be made in-tank by settling solids and decanting the liquid phase. Settling and decantation will provide a gross separation of phases; however, the liquid phase will still contain some suspended solids and require additional solids removal. This second "polishing" phase separation is expected to require a filtration technology such as crossflow filtration.

During FY 1996, this task will install a CUF unit from Savannah River into a PNL hot cell. The CUF unit will be used to determine the effectiveness of crossflow filtration to remove solids from suspended sludge. Through the use of sluicing methods 1.5 L of actual Hanford sludge from tank C-107 will be mobilized. The suspended sludge solution will then be sent to the ELF for solid/liquid separation. An examination of operational parameters such as separation efficiencies and throughput will be conducted. Various crossflow filters will be tested.

CONCLUSIONS

The greatest technical and financial challenge facing DOE is the remediation of the USTs. In an effort to reduce remediation costs, improve safety, and minimize delays, the TFA has been conducting DT&E on new waste treatment technologies. Its current pretreatment tasks focus on supernate separation, sludge treatment, and solid/liquid separation. The supernate separations system are primarily designed to support the 25,000-gal CRD and OTED at Oak Ridge and the new privatization initiative at Hanford. The objectives of the sludge treatment system are to determine the effectiveness of the ESW and to provide improvements or process alternatives to the ESW. The tasks on solid/liquid separation system is directly addressing key needs that have been identified by the tank sites. The TFA and its Pretreatment Technical Integration Manager have and will continue to impact the selection of the processes for the full-scale remediation of the HLW and LLW.

ACKNOWLEDGMENTS

The Pretreatment Technical Integration is a component of the Tank Focus Area, which is funded by DOE's Office of Science and Technology. The authors gratefully acknowledge the contributions from the principal investigators and input from the site users.

REFERENCES

1. Tank Focus Area (TFA), Multiyear Program Plan FY96–FY98, PNL-10650, 1995.
2. M. I. Morrison, C. P. McGinnis, W. T. Wilkenson, and R. D. Hunt, FY 1995 Program Management Plan—Pretreatment Program—Tank Focus Area, ORNL/TM-12935, 1995.
3. J. F. Walker, Jr., and E. L. Youngblood, Design Alternatives Report for the Cesium Removal Demonstration, ORNL/TM-12939, 1995.
4. J. L. Collins, B. Z. Egan, K. K. Anderson, C. W. Chase, J. E. Mrochek, J. T. Bell, and G. E. Jernigan, Evaluation of Selected Ion Exchangers for the Removal of Cesium from MVST W-25 Supernate, ORNL/TM-12938, 1995.
5. G. N. Brown, R. J. Elovich, and L. A. Bray, Evaluation and Comparison of SuperLig 644, Resorcinol-Formaldehyde and CS-100 Ion Exchange Materials for the Removal of Cesium from Simulated Alkaline Supernate, PNL-10486, 1995.
6. G. N. Brown, J. R. Bontha, C. D. Carlson, J. R. DesChane, R. J. Elovich, D. E. Kurath, P. K. Tanaka, D. W. Edmonson, D. L. Herting, and J. R. Smith, Ion Exchange Removal of Cesium from Simulated and Actual Supernate from Hanford Tanks 241-SY-101 and 241-SY-103, NL-10792, 1995.
7. G. J. Lumetta and B. M. Rapko, Washing and Alkaline Leaching of Hanford Tank Sludges: A Status Report, PNL-10078, 1994.
8. B. M. Rapko, G. J. Lumetta, and M. J. Wagner, Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1995 Studies, PNL-10712, 1995.
9. D. J. Temer and R. Villarreal, Sludge Washing and Alkaline Leaching Tests on Actual Hanford Tank Sludges: A Status Report, LAUR-95-2070, 1995.
10. G. J. Lumetta, J. L. Swanson, and S. A. Barker, Chemical Pretreatment of Nuclear Waste for Disposal, Plenum Press, New York, 1995.
11. Initial Pretreatment Trade Studies Caustic Recycle, E/B-SD-W236B-RPT-024, 1995.
12. D. J. McCabe, Evaluation and Ranking of the Tank Focus Area Solid Liquid Separation Needs, WSRC-TR-95-0337, 1995.

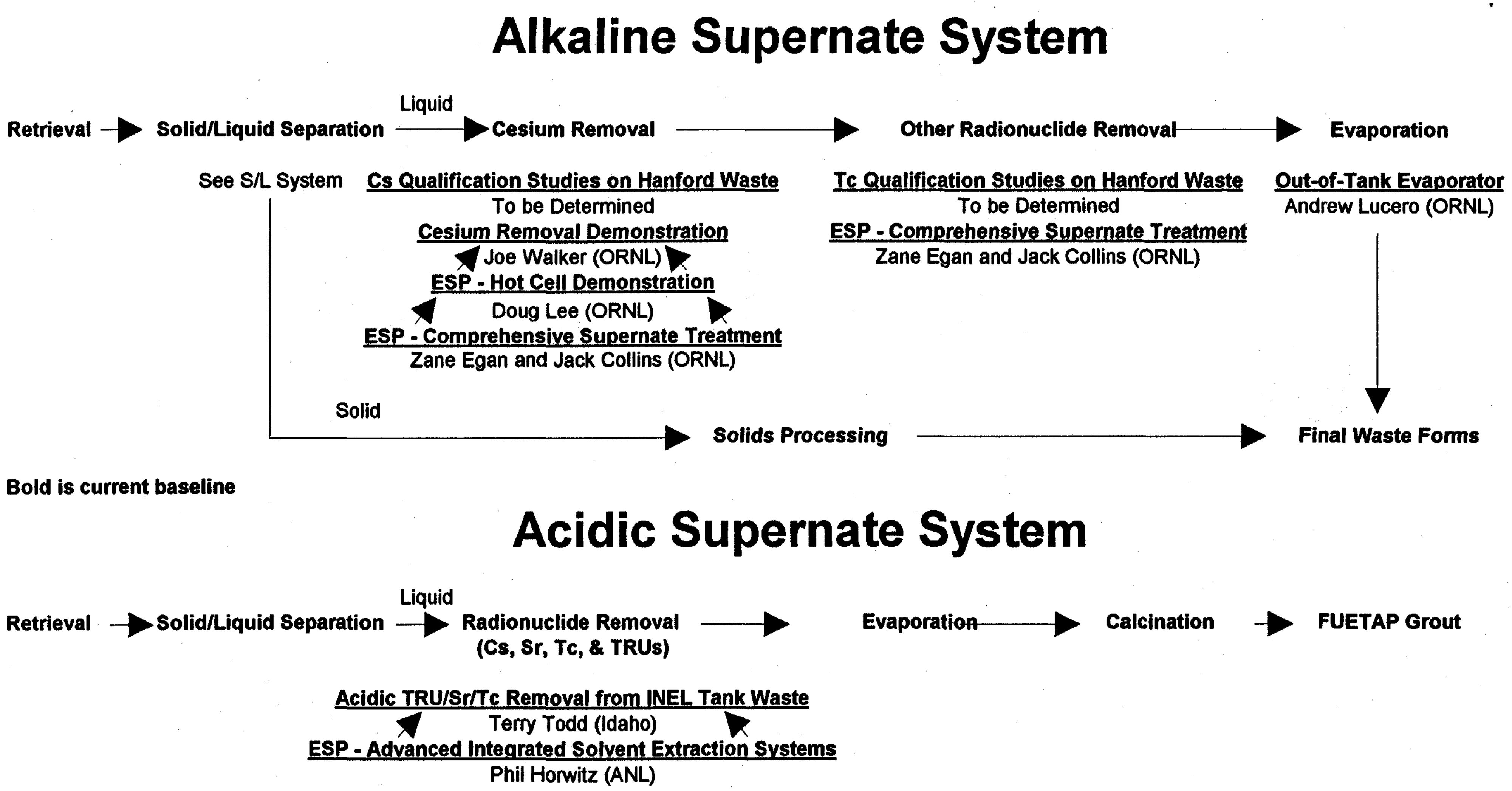


Fig. 1 System integration and process flowsheet for supernate treatment

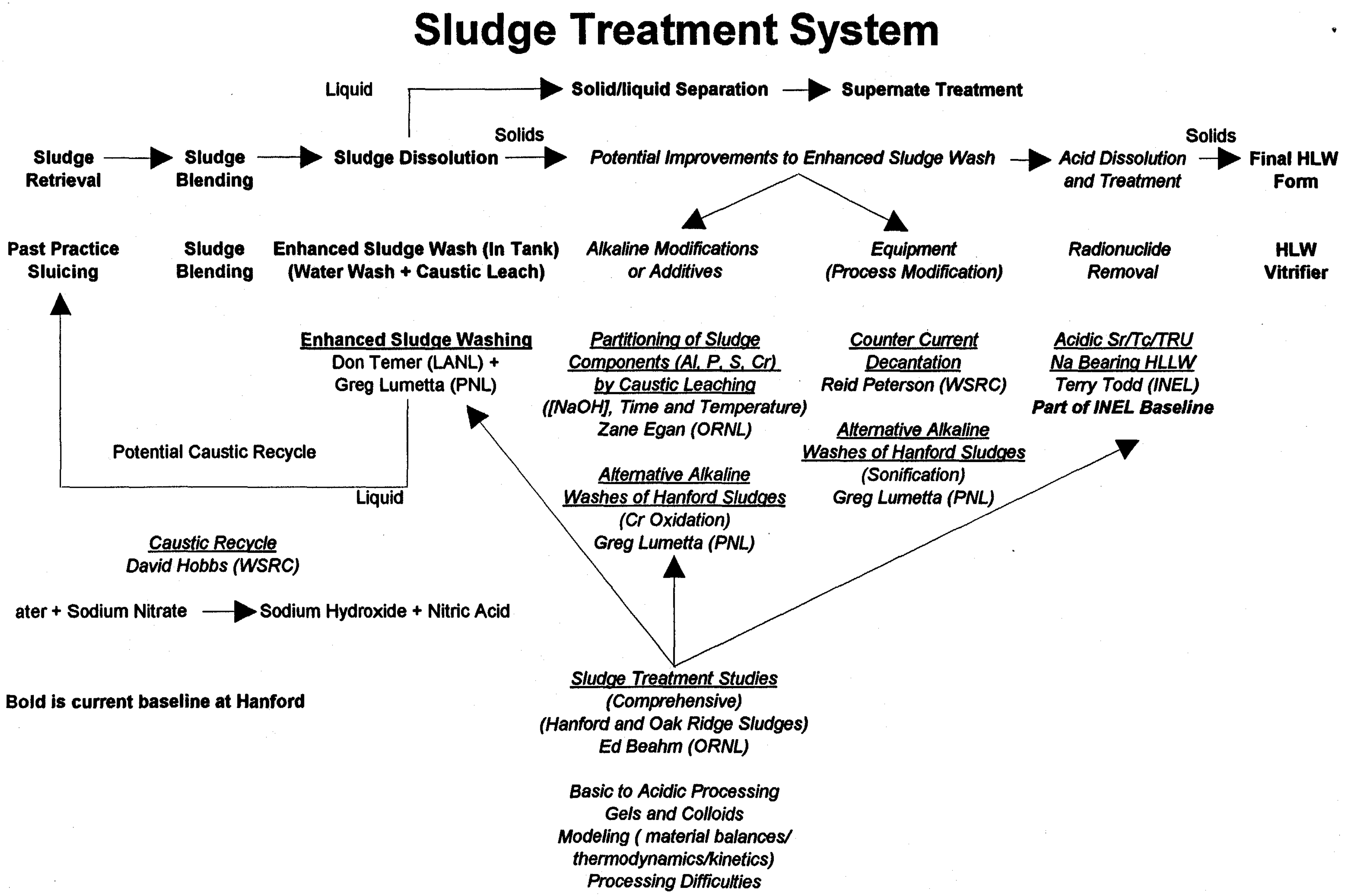
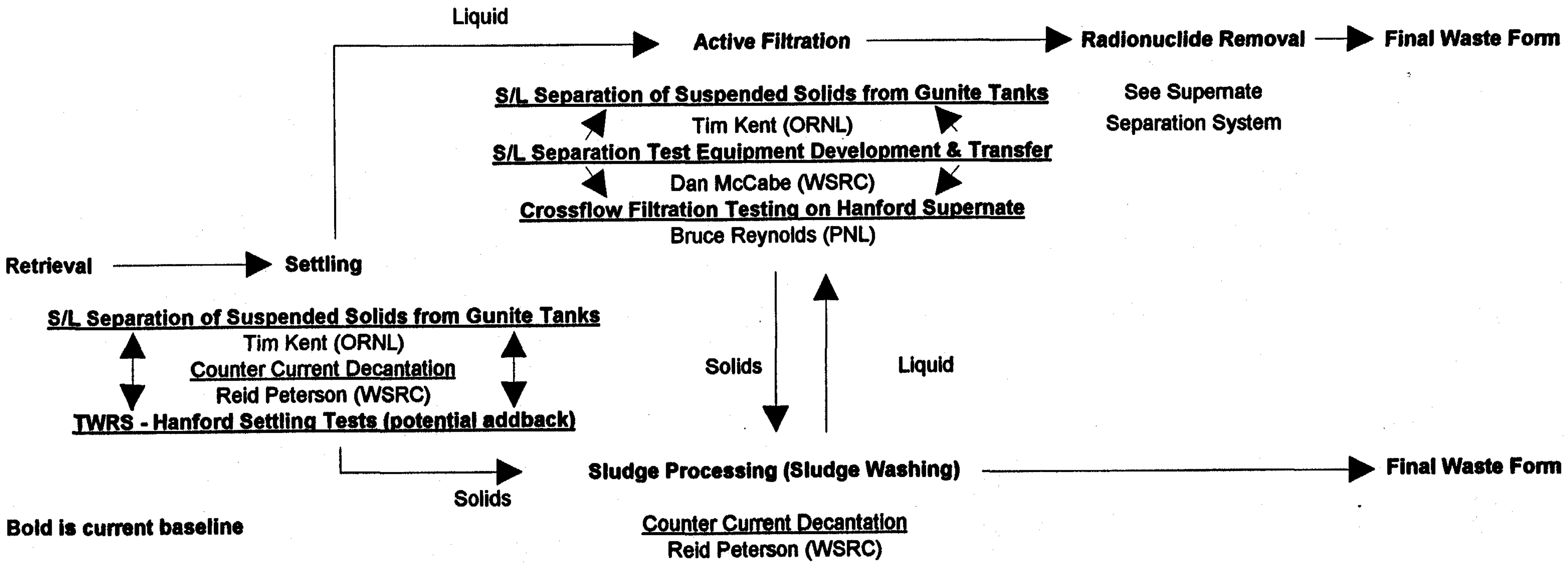


Fig. 2 System integration and process flow sheet for sludge treatment

Solid/liquid (S/L) Separation System



Bold is current baseline

Fig. 3 System integration and process flow sheet for solid/liquid separation