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TANK FOCUS AREA PRETREATMENT ACTIVITIES

C. P. McGinnis and T. D. Welch
Oak Ridge National Laboratory,*
and
K. L. Manke,
Pacific Northwest National Laboratory.**

with contributions from the Tank Focus Area Pretreatment Team

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If the tank wastes were contained in a manner that would preclude its escape into the environment for hundreds of years, there would no reason to disturb it. However, a number of the tanks are approaching the end of their design life. At the Hanford Site alone, at least 67 of these underground tanks have leaked or are assumed to have leaked about 1 million gallons of radioactive waste to the surrounding soil. At the Oak Ridge National Laboratory (ORNL) and SRS, approximately 30 more tanks have had structural problems (for example, cracks, leaks to the secondary containment, or infiltration of water from the environment). This situation poses a potential threat to the environment and people. As time progresses, more of these tanks are predicted to leak additional radionuclides into the environment. Because of the cumulative risk to the environment and humans, the waste must be characterized, removed, pretreated, and immobilized.

THE TANK FOCUS AREA

In January 1994, DOE's Office of Environmental Management introduced a new integrated approach for addressing environmental issues caused by waste products. This new approach centered on focus areas, or areas specifically dedicated to a specific problem, including radioactive waste tanks. The TFA was created to deliver technology to safely and cost effectively remediate the waste tanks at four DOE sites with Pacific Northwest National Laboratory (PNNL) providing the technical leadership. The TFA team partners with Laboratory staff, other national laboratories, universities, DOE, M&O contractors, industry, stakeholders, and other government agencies to focus and integrate the nation's best expertise to solve DOE's waste tank problems.

This team approach has helped fundamentally change the way DOE develops technology. The TFA team's vision and leadership transformed the process, making it more efficient and accountable, involving the user (other DOE sites and the associated contractors) in the development of the technical program. The TFA formed interactive, cooperative teams with organizations that will use, produce, and develop the technology and helped bring the national laboratory system together as a resource for problem solving bringing a systems approach to the technology development process. In particular, the team's goals are to move technology development from a site-specific effort to one with a national focus, where resources are more fully leveraged and applied as technology solutions and develop, create, and deploy technologies that will safely and effectively solve tank waste issues. A significant portion of this effort involves waste pretreatment.

PRETREATMENT

Plans call for the high-level wastes to be retrieved from the tanks and immobilized in a stable waste form suitable for long-term isolation. Chemistry and chemical engineering operations are required to retrieve the wastes, to condition the wastes for subsequent steps, and to reduce the costs of the waste management enterprise. Pretreatment includes those processes between retrieval and immobilization, and includes preparation of suitable feed material for immobilization and separations to partition the waste into streams that yield lower life-cycle costs (see Fig. 1).

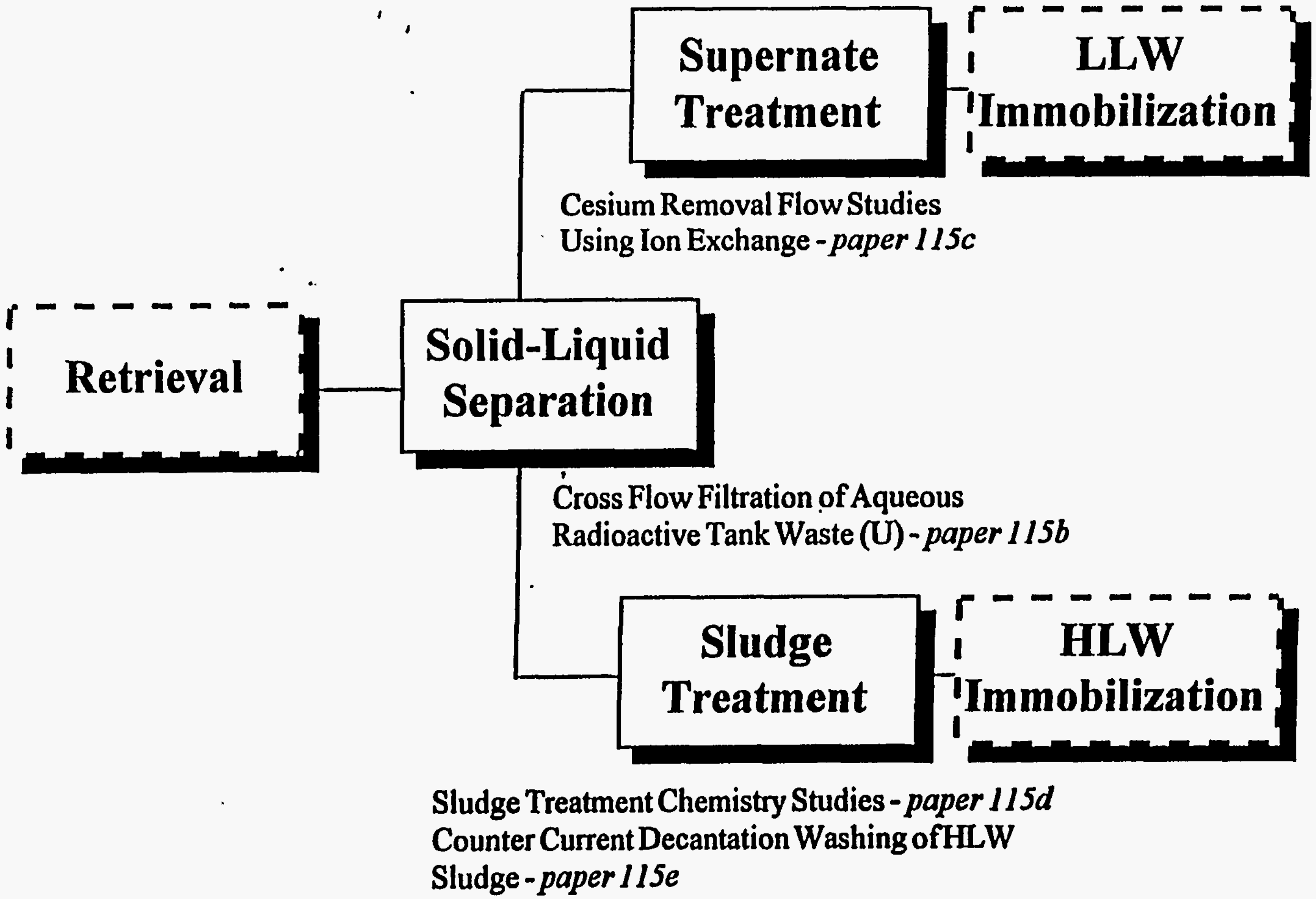

Fig. 1. Tank Focus Area Pretreatment Activities

The expanded flowsheet in Fig. 2 presents a more complete picture. Retrieved wastes consist of a solid-liquid mixture of sludge and supernate. This slurry is separated into a sludge stream and a liquid stream. The liquid stream is processed to remove cesium and other high-activity radionuclides. To reduce the volume of high-level waste, sludge is treated to remove the high-volume, nonradioactive components, such as aluminum. Another concern is that some constituents in the wastes, such as chromium, can result in undesirable glass properties if their concentration is too high.

The technologies for treating tank wastes must be developed. The TFA is developing, demonstrating, and deploying these pretreatment technologies at sites across the DOE complex. Figure 3 highlights how the program is meeting existing site needs with its portfolio of technology development, demonstration, and deployment projects.

The following sections describe some of the technologies being developed by the TFA to process these wastes. These technologies fall roughly into three areas: (1) solid/liquid separation (SLS), (2) sludge pretreatment, and (3) supernate pretreatment.

ORNL DWG 97C-105

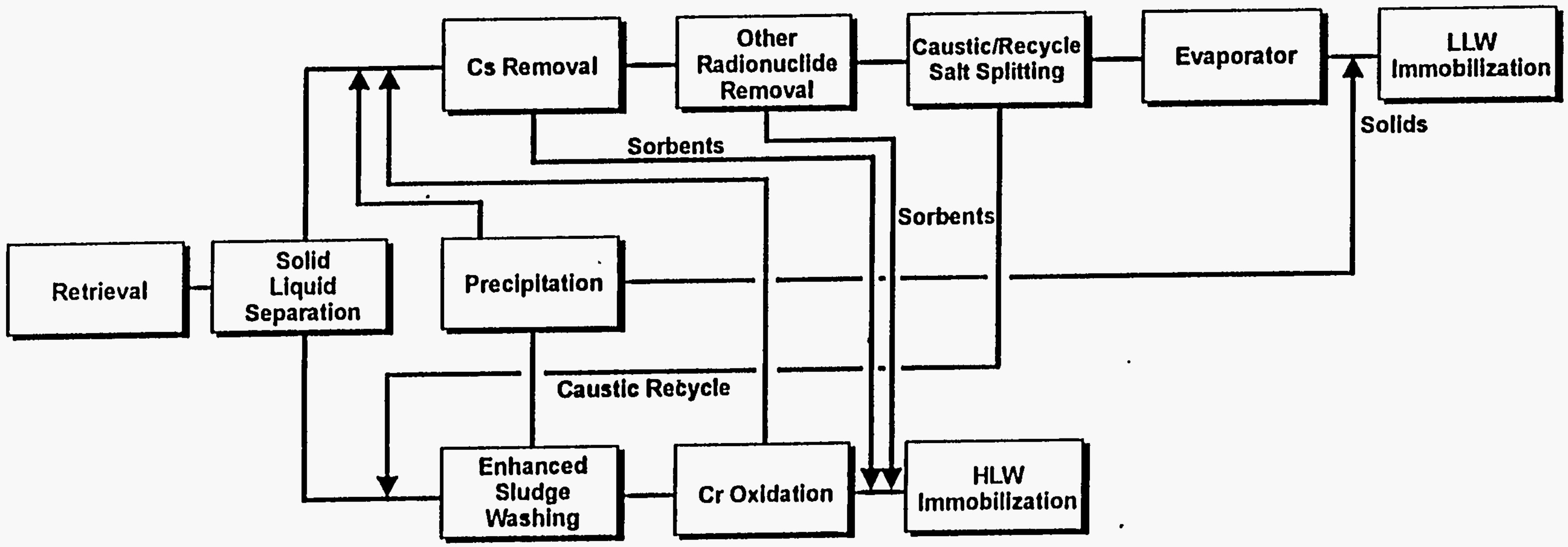

Fig. 2. Expanded pretreatment flowsheet.

ORNL DWG 97C-110

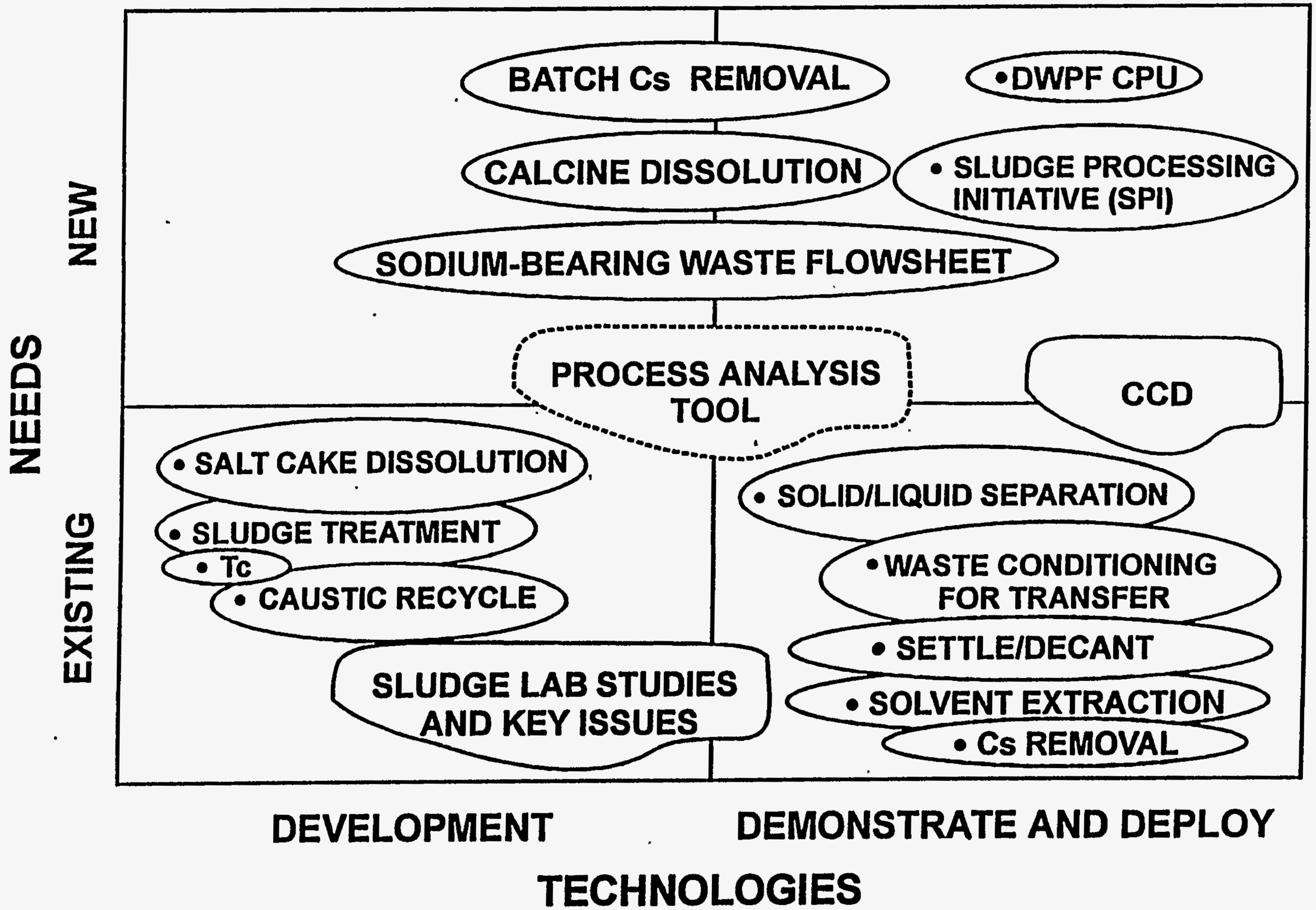

Fig. 3. The matrix of pretreatment needs and technologies.

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Oak Ridge National Laboratory,

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BACKGROUND

The legacy of the nuclear weapons production effort in the United States is being felt today and will continue to impact the nation for generations. One aspect of this legacy is the waste stored in the underground storage tanks. It is the problems posed by these tanks that the Tanks Focus Area is working to resolve. The Tanks Focus Area is working to characterize, retrieve, pretreat, and immobilize the radioactive waste stored in 273 tanks at four locations. The focus area is also working to close these tanks. These tanks are located at the Hanford Site, Richland, Washington; Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, Idaho; Oak Ridge Reservation (ORR), Oak Ridge, Tennessee; and Savannah River Site (SRS), Aiken, South Carolina. These four sites are within the U.S. Department of Energy (DOE) complex.

The 273 tanks that are the concern of the Tanks Focus Area contain approximately 100 million gallons of high- and low-level radioactive waste and mixed waste, predominantly sludge and liquid. So, how much waste is this? If you spread all of this waste across a football field, it would reach to the top of a 28-story office building.

SOLID-LIQUID SEPARATION

SLS is needed to prepare the supernate for radionuclide processing and the sludge for washing processes. This has been listed as a critical need by all of the TFA sites.

Cross-Flow Filtration (Daniel McCabe, Westinghouse Savannah River Company. SRS has a decade of experience designing, testing, and operating SLS for in-tank precipitation, sludge washing, and effluent treatment that is being transferred to the other sites to meet their needs. The work at Savannah River supports the ORNL Gunite and Associated Tanks (GAAT) demonstration and the Hanford tank waste flowsheet development. Testing of SLS techniques with radioactive waste testing are planned at both of these sites. Construction of a filter unit designed for remote radioactive service at INEEL is also part of this task. Limited testing is also being performed using simulants to evaluate the solid-liquid separation parameters for treatment processes proposed for underground storage tank wastes. Testing for Hanford Tank Waste Remediation System and ORNL GAAT waste including simulant benchmark comparison testing for radioactive wastes tested on the Cells Unit Filters (CUF) at Hanford and ORNL. This will allow performance correlations between radioactive waste and simulant.

Solid/liquid separation OR-GATT (Jim Wilson and Tim Kent, ORNL). Westinghouse Savannah River Company conducted an initial survey of SLS methods for GAAT application, performed laboratory and bench-scale testing with waste simulants, and developed the preliminary design for the SLS demonstration system in FY96. Meanwhile, ORNL performed settling and cross-flow filtration tests in a hot cell using GAAT sludge samples, prepared equipment specifications for the SLS demonstration system, and selected a vendor to develop a detailed design and fabricate the SLS demonstration system.

Planned activities in FY97 originally include monitoring, designing, fabricating, and installing activities for the SLS demonstration system, obtaining the necessary regulatory approvals, preparing safety documentation and procedures, and operating the demonstration. The task is being adapted to serve evolving site user needs.

Cross Flow Filtration (Bruce Reynolds, PNNL). Isotopes such as strontium and various transuranics "follow" the fine solids and colloidal particles through to the treatment process. Thus, fine solids and colloidal particles must be separated from Hanford supernates to assure that the supernate meets the definition of low-level waste. There are limited filtration processes that can remove particulates less than one micron. Cross-flow filtration can remove particulates down to 0.2 microns.

Cross-flow filtration is being demonstrated on Hanford streams. During FY96, a CUF was acquired from SRS, run with simulants, and operated with two types of actual Hanford tank waste. In FY97, these tests are being expanded to permit testing of as many as three different types of Hanford waste to ensure cross-flow filtration can meet performance requirements on the different Hanford waste types. Also, radiocolloid and radionuclide testing of the filtrates from

FY96 cross-flow filtration of tank waste C-106 (non-leached) and cross-flow filtration on up-to-three additional Hanford tank wastes will be done.

CESIUM REMOVAL FROM SUPERNATE

Cesium Flow Studies at Hanford (Dean Kurath, PNNL). Hanford is required to treat tank supernate to remove cesium so that the resultant waste can meet waste acceptance criteria. The baseline requirement that the cesium activity in the final waste form must be less than $1 Ci/m^3$ requires decontamination factors of greater than 1000. This level of removal has not been demonstrated on Hanford supernates. This task evaluates sorbents on a range of waste types to ensure waste acceptance can be met in a flow system. In FY96, the equipment was designed, installed, tested, and used to conduct tests on a double-shell slurry feed (DSSF) tank supernate. In FY97, three additional supernates are being tested with one sorbent each. These tests will demonstrate the cesium selectivity and load capacity of crystalline silicotitanate (CST) using actual Hanford DSSF, neutralized current acid waste (NCAW) and concentrated complexant (CC) waste. This information is being compared to similar data gathered using simulants and will be used to validate the simulant data's use in the designing of a cesium removal pretreatment process.

Cesium Removal Demonstration (CsRD) (Joe Walker, ORNL). The CsRD activities continue to evaluate the ability to process radioactive waste using mobile, modular systems (compact processing units) available for deployment near the site on an "as needed" basis. Radioactive cesium, a common contaminant of DOE underground storage tank wastes, emits gamma radiation that complicates and increases the cost of handling and disposal of tank wastes. A technology is needed whereby radioactive cesium can be selectively removed and concentrated into a small-volume, stable waste form. The treated waste liquids may then undergo further treatment for disposal in a safer and less expensive manner. Operability of a full-scale treatment system for an extended duration is required before routine deployment as per agreement with the user. This type of system may find potential for use at other DOE sites such as Hanford and SRS.

Project planning and design of the CsRD demonstration were performed in FY95. In FY96, the demonstration system was fabricated, cold testing was performed with the selected ion exchanger, the demonstration system was installed, and hot operations initiated. In FY97, the system has continued to operate to remove cesium from up to 25,000 gallons of Melton Valley Storage Tank (MVST) supernate. The supernate is a 4 to 5 M sodium nitrate-based liquid contaminated with cesium and other radionuclides. Waste processing will continue; followed by system decontamination, testing to determine the feasibility of hands-on maintenance and transporting the system to an interim storage location or another DOE site.

SLUDGE PRETREATMENT

Caustic Recycle (David Hobbs, SRS). Significant quantities of sodium hydroxide (caustic) will be required to retrieve and treat high-level wastes (HLW) and leach sludges at Hanford and SRS. Addition of fresh caustic for these operations will significantly increase the quantity of waste requiring disposal. HLW solutions contain large quantities of caustic that could be used for these operations if separated from other salts present in the waste, thus reducing life-cycle costs. Moreover, the volume of low-level waste (LLW) can lead to fewer saltstone vaults at the SRS, thus reducing life cycle costs.

The technical feasibility of a caustic recycle process on actual waste needs to be shown and the ability to produce sodium hydroxide that meets operational specifications must be demonstrated. Electrochemical salt splitting is a possible method to recover caustic from HLW solutions. During FY95, scoping tests funded by the Efficient Separations and Processing Crosscutting Program demonstrated the feasibility of electrochemical salt splitting processes for the recovery of caustic from simulants of SRS and Hanford wastes. During FY96, additional bench-scale tests were conducted to evaluate key operating parameters on the recovery of sodium hydroxide using an organic-based ion-selective membrane. Factors investigated included current density, temperature, and the concentrations of nitrate/nitrite, hydroxide, and aluminate.

Bench-scale demonstrations of caustic recovery are being carried out at SRTC using radioactive liquid waste obtained from SRS Tank 50H, which is the feed tank for the saltstone facility. The testing includes the use of both the organic-based membrane and the ceramic membrane to better determine which system can be used in an actual waste environment.

Pilot-scale tests are also being conducted to demonstrate scale-up and address any issues concerning scale-up with respect to design activities. Process flowsheets incorporating caustic recovery are also being developed to reflect the latest available data from radioactive and pilot-scale testing.

Sludge Studies (Ed Beahm, ORNL). The purpose of this task is to determine the effect of chemistry on sludge mobilization, pretreatment, and transfer to immobilization. Efficient treatment and leaching must remove non-radioactive species that add to the volume of HLW or affect melter performance to reduce the number of logs and thus significantly reduce costs for HLW processing and disposal.

Separation techniques cannot be performed on sludge leachates if the material to be separated is not in solution or if the leachates contain gels or colloids. There are two aspects of sludge treatment and subsequent separations that should be well-delineated and predictable: (1) distribution of chemical species between aqueous solutions and solids and (2) potential chemical interactions that could result in process difficulties or safety concerns. Before any separation technology is adopted, it must be demonstrated that solutions to be treated are amenable to the process. The DOE site tank waste disposal strategy will likely include treatment of sludge with a base or an acid before further treatment. The chemical interactions both within the sludge and between the sludge and process chemicals must be better understood to plan treatment strategies such as TRUEX or vitrification.

Data on chemical interactions in caustic and acidic sludge leachates are needed to evaluate sludge processing scenarios. It is very important to assess implementation of a pretreatment process. This requires an evaluation of the overall process and not just the distribution of species between solids and liquids. The formation of solids in decanted leachates and wash solutions must be prevented. Failure to do so will result in the formation of crystalline solids and gels that are unacceptable because they will (1) prevent mixing, (2) prevent pumping, (3) retard separations, (4) coat surfaces, and (5) clog pipes, equipment, and filters. Precipitation and gelation in both caustic and acidic sludge treatment are being assessed, and viable treatment strategies are being developed.

Sludge Partitioning Chemistry (Zane Egan, ORNL). Some underground storage tanks contain high inventories of nonradioactive materials, such as aluminum, chromium, and phosphates, that can significantly increase the volume of the final HLW form for disposal. The amounts of some of the components, such as chromium and phosphate which must be limited in the HLW glass composition, can control the volume of HLW waste product from the vitrification processes. Aluminum and silicon behavior may also be related to gel formation during sludge processing. The increased solubility of some of these components under very caustic conditions could be used to partition the radioactive and nonradioactive components. DOE can reduce the costs of long-term storage and disposal of HLW in direct proportion to the amount of nonradioactive components that can be removed from the waste and hence not require immobilization and storage as HLW.

Although the amounts of sludges and their compositions vary from tank to tank, the sludges generally contain mixtures of hydrated metal oxides, hydroxides, and phosphates. Some of the amphoteric components have the potential of forming soluble chemical species under highly caustic conditions. The conditions under which hydrated metal oxides, hydroxides, and phosphates can be efficiently removed from sludge are not fully known for the range of sludge compositions within the DOE complex. Laboratory studies on actual sludge samples are needed to determine the extent of preferential solubilization, the conditions that enhance nonradioactive component removal, and the potential for volume reduction.

An objective of this task is to develop alternate process conditions for sludge partitioning on a broad range of sludge samples. The caustic dissolution behavior of various components will be determined using sludge samples from Hanford and ORNL MVST. The dissolution behavior of sludges will be determined in hot cell tests using up to 6 M sodium hydroxide solutions at temperatures of up to 95 degrees Celsius. Components of particular interest include aluminum, chromium, zinc, bismuth, cerium, strontium, zirconium, iron silver, nickel, lead, uranium, thorium, and phosphate. The work will be coordinated with related work at PNNL, Los Alamos National Laboratory (LANL), and SRS, and by possible interaction with the aluminum industry.

The results from this task are needed to support the March 1998 milestone at Hanford on enhanced sludge washing, to design countercurrent decantation equipment, and to plan demonstrations of continuous countercurrent technology demonstrations. This task is also to provide information on alternate process conditions and their effects on the baseline sludge process parameters in support of privatization at Hanford to reduce life-cycle costs.

Enhanced Sludge Washing (Gregg Lumetta, PNNL) and Enhanced sludge Washing Analysis (Don Temer, LANL). The baseline option for pretreating Hanford tank sludges is caustic leaching followed by washing with dilute sodium hydroxide. This process is often referred to as "enhanced sludge washing." Testing of the baseline pretreatment process with actual tank sludges is required to conform (or amend) the assumptions made in developing the process flowsheet. Collection of these data is essential to reducing the technical risks associated with the baseline tank waste disposal flowsheet and in fulfilling the Hanford Federal Facility Agreement and Consent Order target milestone M-50-03. These date are needed for phase 2 privatization at Hanford.

A series of assumptions has been made regarding the behavior of various sludge components, namely, the baseline caustic leaching process. Initially, these assumptions were based upon very limited experimental data. The assumptions are amended annually, based on the results of testing with actual tank waste (i.e., the results of this task). However, the sludge contained in the 23 single-shell tanks investigated by the end of FY 96 represents only 33% of the sludge inventory in the single-shell tanks. Furthermore, there are several classes of wastes that have not yet been tested. Collection of additional data on actual tank wastes will enhance the reliability of the planning assumptions.

The objective of this task is to develop performance data for different sludge types. This activity consists of conducting small-scale laboratory tests (5 to 20 grams) on actual sludge waste from Hanford tanks to determine the effectiveness of enhanced sludge washing for separating the key, glass-limiting components of the tank sludges from the bulk of the radionuclides. Hanford selected phase 2 sludge types will be targeted, although final sludge sample availability is determined by user schedule on core samples. The reported results from these experiments will then be used by Hanford to update the HLW glass volume projection.

Counter Current Decanting (Reid Peterson, SRS). Sludges at SRS, Hanford, and ORNL will be washed to remove salts before immobilization. The HLW sludge must be washed to remove soluble salt as a pretreatment to vitrification. Washing is done presently by a batch process with "limited" to "no reuse" of the wash water. Thus, large quantities of water are generated as waste by the washing operation. To date, most work has focused on in-tank washing of sludge solids which is inherently inefficient and slow. A more efficient technology is needed to wash solids and clarify liquids used in washing. For example, a continuous counter-current washing operation would decrease dramatically the amount of wash water required.

Technology to remove the desired components, such as aluminum and selected radionuclides from the sludge; to produce a more concentrated lower volume wash water; and to produce a more consistent treated sludge feed for vitrification are all desired. The production of a more consistent sludge feed results from the controllability and adjustments that can be affected in the process. Counter-current decantation (CCD) promises these benefits, but the technology must be demonstrated. Equipment designed and fabricated based on the latest test data and demonstration of the separation and washing capability of the countercurrent decanting circuit are needed. Demonstration of countercurrent decantation is required to support a hot deployment decision and scale-up from bench-scale to full-scale. Remote operability, reliability, and performance must be also demonstrated.

This task involves designing, fabricating, and operating full-scale, a single-stage CCD system. The task also conducts supporting laboratory tests using simulants. Supporting laboratory hot tests are being conducted to confirm data applicability from simulants. The scope of work for FY97 involves producing a full-scale, single-stage demonstration of the CCD concept. The locked-cycle test procedure will be used to simulate the single-stage circuit.

OTHER TECHNOLOGIES

We have highlighted many of the activities in TFA pretreatment. A number of other activities are ongoing including work on solvent extraction (Terry Todd, INEEL), alternative alkaline processing (Gregg Lumetta, PNNL), technetium removal flow studies (Dean Kurath, PNNL).

CONCLUSION

The TFA is addressing DOE site needs by developing and deploying pretreatment technologies. Several technologies, such as cesium removal by exchange, has progressed from research to implementation. Development and demonstration of other technologies, such as sludge pretreatment, presents a challenge we are now addressing.