

Improved Process Used to Treat Aqueous Mixed Waste Results in Cost Savings and Improved Worker Safety

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ABSTRACT

This paper describes an improved process implemented at Argonne National Laboratory (ANL) to treat aqueous mixed waste. This waste is comprised of radioactively-contaminated corrosive liquids with heavy metals. The Aqueous Mixed Waste Treatment System (AMWTS) system components include a reaction tank and a post-treatment holding tank with ancillary piping and pumps; and a control panel with pumping/mixing controls; tank level, temperature and pH/Oxidation Reduction Potential (ORP) indicators. The process includes a neutralization step to remove the corrosive characteristic, a chromium reduction step to reduce hexavalent chromium to trivalent chromium, and a precipitation step to convert the toxic metals into an insoluble form. Once the toxic metals have precipitated, the resultant sludge is amenable to stabilization and can be reclassified as a low-level waste if the quantity of leachable toxic metals, as determined by the TCLP, is below Universal Treatment Standards (UTS). To date, six batches in eight have passed the UTS.

The AMWTS is RCRA permitted and allows for the compliant treatment of mixed waste prior to final disposal at a Department of Energy (DOE) or commercial radioactive waste disposal facility. Mixed wastes eligible for treatment include corrosive liquids (pH <2 or >12.5) containing EPA-regulated toxic metals (As, Ba, Pb, Cd, Cr, Ag, Se, Hg) at concentrations greater than the RCRA Toxicity Characteristic Leaching Procedure (TCLP) limit. The system has also been used to treat corrosive wastes with small quantities of fissionable materials.

The AMWTS is a significant engineered solution with many improvements over the more labor intensive on-site treatment method being performed within a ventilation hood used previously. The previously used treatment system allowed for batch sizes of only 15-20 gallons whereas the new AMWTS allows for the treatment of batches up to 75 gallons; thereby reducing batch labor and supply costs by 40-60% and reducing analytical testing costs by 50-75%. Reduced treatment time also reduces worker radiation exposure to As Low As Reasonably Achievable (ALARA) levels.

Additionally, the treatment system components used previously were adapted to be used with the new AMWTS. This allowed for less dependence on personnel protective equipment (PPE) than the prior system by separating the waste handling/bulking steps of the process from the treatment steps. The AMWTS also improved worker safety by incorporating more automated engineering controls such as system logic controls; personnel safety and equipment protection interlocks, off-normal condition indicators/alarms, and system emergency stop controls.

In a time of ever-decreasing budgets, it makes sense to rethink the use of existing treatment systems. Utilizing, and possibly retooling, equipment and infrastructure may allow for reduced treatment costs and increase worker safety.

INTRODUCTION

Argonne National Laboratory Description

Argonne National Laboratory's (ANL) mission is to serve Department of Energy (DOE) and national security by advancing the frontiers of knowledge, by creating and operating forefront scientific user facilities, and by providing innovative and effective approaches and solutions to energy, environmental, and security challenges to national and global well-being, in the near and long term, as a contributing member of the DOE laboratory system.

ANL contributes significantly to DOE's mission in science, energy resources, environmental stewardship, and national security, with lead roles in the areas of science, operation of scientific facilities, and energy. In accomplishing our mission, we partner with DOE, other federal laboratories and agencies, the academic community, and the private sector. ANL's work was supported by U. S. Department of Energy, Office of Science, under contract W-31-109-Eng-38.

ANL is one of 23 Department of Energy's national laboratories and technology centers. ANL is located on 1,508 acres in DuPage County, IL, 25 miles southwest of downtown Chicago. ANL's campus includes some 105 buildings and 109 other structures.

Background / Original Design

The Aqueous Mixed Waste Treatment System (AMWTS) was originally designed and built in 1995 for operation by ANL's Waste Management Operations (WMO) organization. The system process includes a neutralization step to remove the corrosive characteristic, a chromium reduction step to reduce hexavalent chromium to trivalent chromium, and a precipitation step to convert the toxic metals into an insoluble form. Once the toxic metals are precipitated, the resultant sludge is amenable to stabilization and can be reclassified as a low-level waste if the quantity of leachable toxic metals in the stabilized sludge, as determined by the Toxicity Characteristic Leaching Procedure (TCLP), is below Universal Treatment Standards (UTS).

The AMWTS is Resource Conservation and Recovery Act (RCRA) permitted and allows for the compliant treatment of mixed waste prior to final disposal at a DOE or commercial radioactive waste disposal facility. Mixed wastes eligible for treatment include corrosive liquids (pH <2 or >12.5) containing EPA-regulated toxic metals (As, Ba, Pb, Cd, Cr, Ag, Se, Hg) at concentrations greater than the RCRA TCLP limits.

The system was designed and built as a means to accomplish ANL Site Treatment Plan Milestones for targeted waste streams and to increase automation and treatment throughput over the existing small batch system. The original design goals of the AMWTS were to develop a system to semi-automate the treatment of aqueous mixed waste corrosive with heavy metals and to replace the treatment process previously performed manually in the adjacent exhaust hood. The treatment process in the AMWTS is chemically the same process as that used in the exhaust hood system, but the batches sizes are much larger and the mixed waste and reagent chemical handling is more automated and contained (waste/chemicals were transferred by hand using the small-scale system). The system was built primarily offsite and, as such, skid-mounted on a stainless steel frame and include two tanks for chemical reaction/separation and sampling. In addition to both tanks, the system included pumps, piping and valves to allow the transfer and processing of the waste. A local control panel has all the necessary instrumentation, controls, alarms, and interlocks to operate the system.

The original system was never brought online because of incomplete system and qualification documentation, logic control problems, and design flaws. The system sat unused until late 2001 when the AMWTS project was reinitiated in an effort to reduce treatment costs for this expensive mixed waste stream.

System Component Description

The original system was comprised of the following components:

1. Waste Treatment Reaction Tank (Reaction Tank)
2. Sample Effluent Tank (Sample Tank) with effluent discharge to the building evaporator system
3. Filter Skid components that would allow for the removal of heavy metal/radioactive constituents after precipitation treatment
4. Automatic metering pumps for chemical reagent addition
5. Decant Dip Tube for effluent/sludge phase separation
6. Ancillary piping, pumps and valves
7. Control Panel and System Interlocks (pH, Temperature, Oxidation Reduction Potential [ORP])

GOALS

The original project goals were modified and the following were identified as new goals for the system:

- 1) Improve safety for workers during waste handling/transferring operations,
- 2) Increase cost effectiveness,
- 3) Remove unnecessary or improperly selected system components,
- 4) Rely less on automatic controls,
- 5) Maximize the use of existing spare parts and facilities,
- 6) Improve user interface (waste transfer components, control panel layout and system labeling)
- 7) Improve system documentation (system design description, system as-built drawings, etc.),
- 8) Document start-up testing and calibration,
- 9) Create operating procedures, and
- 10) Implement use of the system and document treatment effectiveness.

To accomplish these goals a team was assembled consisting of 1) a project manager/waste specialist, 2) a process engineer, 3) an electrical/controls engineer, 4) a nuclear facilities engineer, and 5) waste technicians. A project schedule and cost estimate was developed by the project manager with input from the project team.

PHYSICAL MODIFICATIONS

The initial evaluation consisted of determining the accuracy of the existing “as-built” drawings. Upon review, discrepancies were identified in the piping, wiring, valves, and system component labeling. Therefore, the drawings were modified and re-checked to ensure that the as-built drawings depicted actual equipment conditions. Once the drawings were accurate, the system components were labeled appropriately and the system was evaluated for improvements and modifications. This evaluation revealed areas for improvement, including equipment that was no longer needed based on the revised system goals.

The waste byproducts of treating waste in the Metal Precipitation/Filtration Unit include both an effluent liquid phase and a precipitate sludge phase. In the original system design, the effluent phase would be decanted off of the sludge and pumped through the filter skid and released to the concentrator system. It was determined that the treatment goals could be met without the filtration step since the radioactive content of the by-product sludge met the disposal site Waste Acceptance Criteria without filtration. Also, since this waste stream is small and the associated cost of disposing of nonhazardous low-level

radioactive waste is relatively inexpensive, it was determined that all treatment residuals, both the effluent and the precipitate, would be further treated in the Building 306 Mixed Waste Immobilization Unit. Since the filter skid was no longer needed, it was dismantled and disposed of.

The system was further simplified by replacing the existing chemical reagent metering pumps, that were automatically actuated using system logic controls (e.g., low pH would result in metered alkaline chemical addition), with peristaltic pumps that would be manually operated as warranted using the treatment batch instructions in conjunction with the pH, ORP and temperature indicators. Since appropriately-sized peristaltic pump tubing was utilized in other operations, these pumps were selected to simplify overall operations and still meet design requirements.

Another design improvement involved the waste transfer components and piping. Where appropriate, quick connect fittings were added to flexible hoses. A water supply spigot was installed to aid in the dilution of reagent chemicals and as a suction line flush water source. A drum suction wand was designed and fabricated that would be reusable, upon decontamination. The new AMWTS was connected to the existing small-scale batch system housed in the adjacent fume hood via piping. This connection allows for bulking smaller quantity containers in the “bulking tub” and then transferring the waste to the Reaction Tank using the tank pump and newly installed piping. This effectively limits loose contamination and contact handling of waste liquids to the area in and around the fume hood. A simplified flow diagram of the system is included as Figure 1.

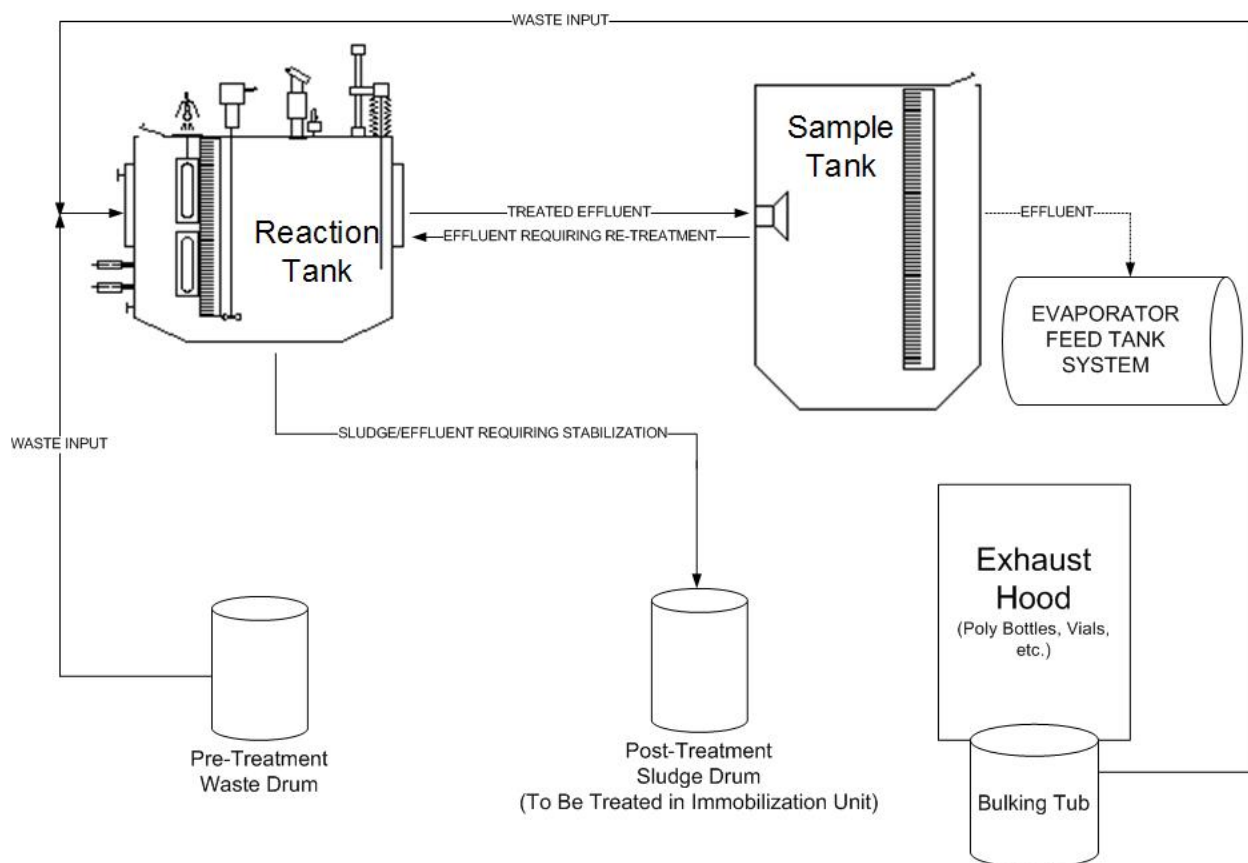


Fig. 1. AMWTS Simplified Waste Flow Diagram

SYSTEM QUALIFICATION AND PROCEDURALIZATION

The system was qualified for use by systematically testing each of the system components including:

- Pumps and motors
- Pressure relief valve
- Mixers
- Piping, joints, and elbows
- Valves
- Controls, interlocks and alarms
- pH and ORP probes and indicators/controllers
- Thermocouples
- Level transducers

The AMWTS was designed for flexibility in treating aqueous corrosive waste; therefore, multiple operating procedures were created as follows:

1. AQUEOUS MIXED WASTE TREATMENT SYSTEM - CORROSIVES WITH METALS (NO DECANT)
2. AQUEOUS MIXED WASTE TREATMENT SYSTEM - CORROSIVES WITH METALS (WITH DECANT)
3. AQUEOUS MIXED WASTE TREATMENT SYSTEM – ACIDS ONLY

Additionally, a procedure was created for the routine maintenance and calibration of the system entitled, “AQUEOUS MIXED WASTE TREATMENT SYSTEM - ANNUAL MAINTENANCE AND INSTRUMENT OPERATION VERIFICATION”

The procedures were systematically written and valve line-ups were checked at the desktop and tested by performing dry runs of the procedures to ensure procedure accuracy. The procedures were written to include logical break points between the waste loading, treatment and offloading steps to allow for different personal protective equipment (PPE) requirements and possible downgrade of PPE if conditions warranted. Also, since fissionable materials were going to be introduced into the system, special consideration was given to procedurally flushing the system to prevent holdup of material.

Final Upgraded Design Description

All modifications were completed in March 2004 and the final upgraded AMWTS was put into service in September 2004 (see Fig. 2).

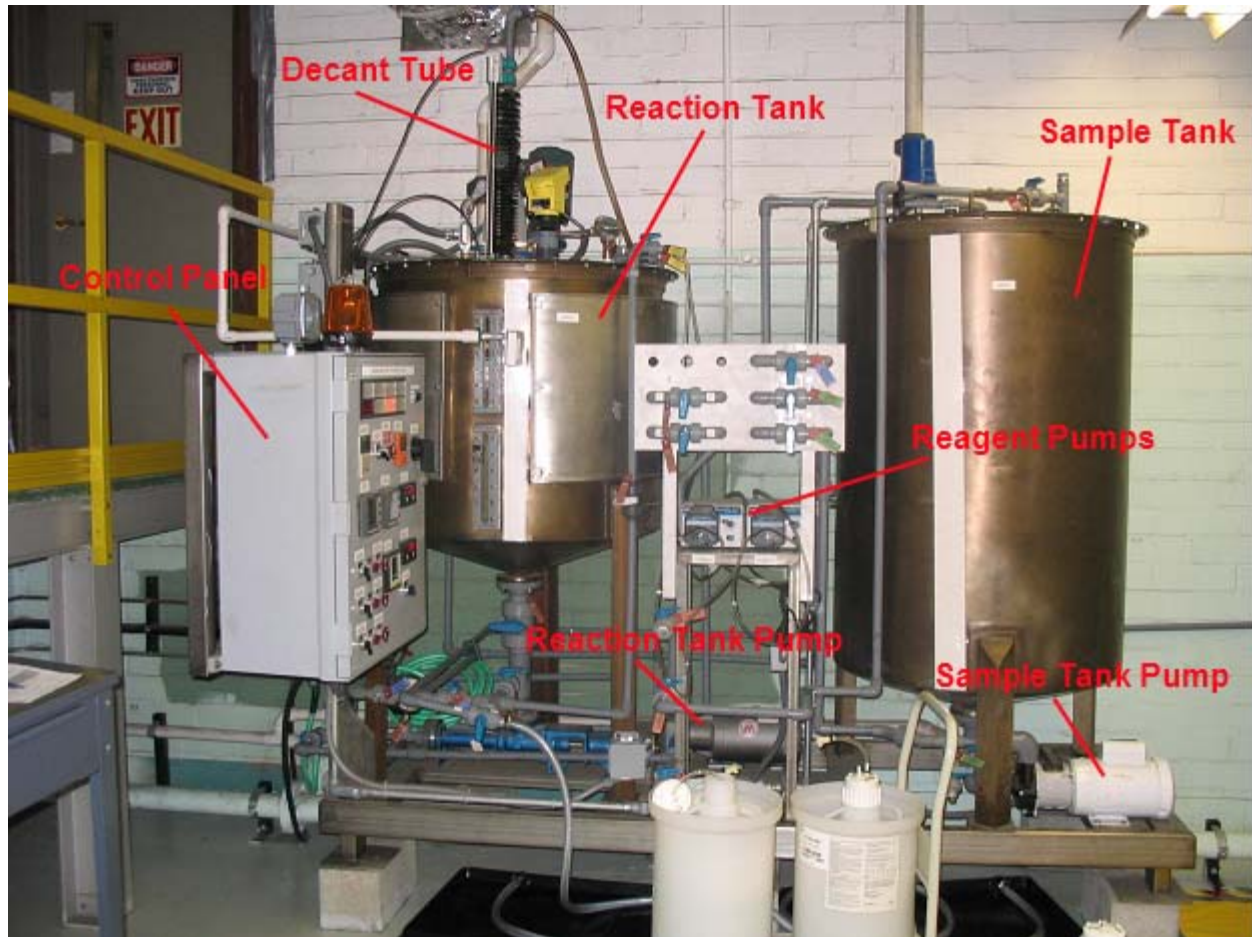


Fig. 2. Aqueous Mixed Waste Treatment System (AMWTS)

A description of the final system is as follows:

The Reaction Tank is a 148 gallon stainless steel tank with an internal Kynar® coating to protect the stainless steel against extreme corrosive conditions. The Reaction Tank is equipped with an externally mounted mixer motor, pneumatically operated decant tube, temperature sensor, pH and ORP probes and an ultrasonic level sensor. The fresh water supply line to the Reaction Tank is mounted on the top of the tank and passes through a spray nozzle inside the tank. The AMWTS Reaction Tank pump is a progressive cavity positive displacement pump with a remote operator control mounted on the electrical control enclosure. Reaction Tank pump interlocks are actuated during high and low tank levels and high temperature levels. The Reaction Tank is equipped with a Decant system that can remove the top layer of liquid from the Reaction Tank. The Decant system is a CPVC pipe that is lowered or raised via a pneumatically actuated rodless cylinder.

The Sample Tank is a 243 gallon stainless steel tank with an internal Kynar® coating to protect the stainless steel against extreme corrosive conditions. The Sample Tank is equipped with an externally mounted ultrasonic level sensor and an internally mounted mixing eductor. A magnetic drive centrifugal pump transfers waste in and out of the Sample Tank. Sample Tank is controlled a remote operator control mounted on the electrical control enclosure. Sample Tank pump interlocks are actuated during high and low tank levels and high temperature levels.

There are two chemical reagent peristaltic pumps equipped with quick connect tubing fittings. Primarily the chemical reagents used with these pumps are reagent grade Sodium Hydroxide (for pH adjustment), Ferrous Sulfate (for reduction of hexavalent chromium to trivalent chromium), and Sodium Sulfide (for precipitation of heavy metals) solutions which are pump to the Reaction Tank according to batch instructions.

All aqueous mixed waste process lines are CPVC schedule 80 socket welded except for connections at the pumps, pressure gauges, and some tank connections. The piping valves include 3-piece full port true union manual ball valves.

The AMWTS control cabinet incorporates a fiberglass enclosure with electrical power and control wiring in flexible PVC Sealtite® and/or rigid conduit. The fluid transfer control systems for the AMWTS are manually operated with some automated interlocks, as described above. Many of these interlock can be overridden with an operator holding two control buttons or switches simultaneously.

Small quantity waste (<5-gal.) bulked in the 15-gallon exhaust hood bulking tub is transferred to the Reaction Tank using the hard-piped discharge line and the Reaction Tank Pump. The suction line must be primed with water prior to use by back flowing clean water through the line into the drum expelling any air space in the suction line.

Waste contained in 5 to 15-gallon carboys is transferred into the Reaction Tank using the Reaction Tank Pump. The suction line must be primed with water prior to use by back flowing clean water through the line into the carboy expelling any air space in the suction line.

Waste contained in 30 and 55-gallon drums is transferred into the Reaction Tank using the Reaction Tank Pump suction line a suction wand attachment. The suction line must be primed with water prior to use by back flowing clean water through the line into the drum expelling any air space in the suction line.

Treated sludge is transferred from the Reaction Tank to a 55-gallon treated sludge drum using the Reaction Tank Pump. Treated effluent may be transferred directly from the Sample Tank to the Building 306 Evaporator Feed Tank System (EFT). This discharge line output utilizes gravity to drain the Sample Tank to the EFT.

The Control Panel includes pumping/mixing and pneumatic decant controls; tank level, temperature and pH/ORP indicators; system logic controls; personnel safety and equipment protection interlocks, off-normal condition indicators/alarms, and system emergency stop control (see Fig. 3).



Fig. 3. AMWTS Control Panel

OUTCOMES

Goals Met

All of the goals identified at the beginning of the project were met. Worker safety improved due to less contact-handling of waste liquids. Implementation of the system was more cost effective than utilizing the previous system. The system relies less on automatic waste transfer (metering pumps) and more on worker experience and procedures. The system also incorporates system logic controls. Unnecessary system components were removed (e.g., filter skid system) and existing facilities (exhaust hood bulking tub) were utilized. Also, the user interface (waste transfer components, control panel layout and system labeling) was improved over the existing system.

System design documentation was brought to an as-built condition and system qualification, and testing and calibration were conducted and documented.

The system was put into service and treatment effectiveness has been proven (see below).

Safety

Utilizing simple quick connect fittings on chemical reagent and waste transfer lines reduced exposure to chemical and radiological hazards. Also, adapting the old small-scale system reaction vessel inside of the adjacent exhaust hood as the new “bulking tub” allowed for less dependence on PPE than the prior system by separating the waste handling/bulking steps of the process from the treatment steps. The AMWTS also improved worker safety by incorporating more engineering controls such as system logic controls; personnel safety and equipment protection interlocks, off-normal condition indicators/alarms, and system emergency stop controls.

By breaking the treatment process into three steps: loading, treatment, and offloading, worker exposure time and fatigue were reduced. This reduced treatment time also reduced worker radiation exposure As Low As Reasonably Achievable (ALARA). Also, the better containment system (i.e., fully enclosed reaction vessel) reduced airborne contamination as seen in retrospective air sampling data.

Cost Savings

The prior treatment system allowed for batch sizes of only 15-20 gallons, whereas the new AMWTS allows for the treatment of batches up to 75 gallons; thereby reducing batch labor and supply costs by 40-50% and reducing analytical testing costs by 70-80%. For the first year of operation this saved ANL approximately \$56K and in subsequent treatment batches, the cost savings should be approximately \$7K per batch. Also, due to the high fissile content of the waste, a savings of approximately \$24K, per batch, over commercial treatment is also realized. A cost comparison, comparing commercial treatment, prior treatment system and the new AMWTS is included as Table I.

Table I. Corrosive Waste Treatment Comparison

Commercial Treatment	
Resource	Cost
Mechanic Effort	\$618
HP Tech Effort	\$206
Commercial Treatment	\$15,000
Fissile Surcharge	\$15,000
Drums	\$116
Total	\$30,116

Assumes 75 gallon bulking by ANL and treatment/disposal by commercial vendor.

Hood System (prior treatment system)	
Resource	Cost
Staff Effort	\$515
Mechanic Effort	\$824
HP Tech Effort	\$206
Drums	\$58
Supplies	\$150
Analytical Testing	\$1,500
Mixed Waste Debris Disposal	\$294
Total	\$3,547
3.75 Events (75 gal) Total	\$13,301

Assumes treatment of ~20 gallons (one event) X 3.75 events (75 gal) for comparison.

Table I. cont'd

AMWTS	
Resource	Cost
Staff Effort	\$618
Mechanic Effort	\$2,060
HP Tech Effort	\$515
Drums	\$232
Supplies	\$150
Analytical Testing	\$1,500
Mixed Waste Debris Disposal	\$1,176
Total	\$6,251

Assumes treatment of ~75 gallons (one event).

Performance

The first batch of waste was treated in the AMWTS on September 29, 2004 (see Fig. 4) with seven subsequent batches treated thereafter. Table II summarizes the analytical results for these first eight batches treated in the AMWTS. Six of the eight treatment batches were treated successfully. The two that were unsuccessful (AMWTS-003/004 and AMWTS-009) failed the UTS for leachable mercury (0.027 and 0.035 mg/L, respectively). These results were only slightly higher than the UTS of 0.025 mg/L. These mercury concentrations were attributed to high mercury loading in one container in each of the batches. This mercury content is considered an anomaly and is not expected in future treatment batches since this waste stream source is no longer present at ANL. These treated waste containers will be shipped to Envirocare of Utah for further stabilization treatment.



Fig. 4. Workers Bulking Less Than 5-Gallon Containers in Exhaust Hood Bulking Tub

Table II. Aqueous Mixed Waste Treatment System Analytical Results Summary

Batch #	EPA Codes Applied (Pre-Treat)	Post-Treat pH (Liquid)	Post-Treat TCLP Results (Solid) (mg/L)							
			As	Ba	Cd	Cr	Pb	Hg	Se	Ag
AMWTS-001	D002, D004, D006, D007, D008, D009, D011	8.23	<0.50	0.30	<0.05	0.24	<0.10	0.000122	<0.20	<0.08
AMWTS-002	D002, D004, D005, D006, D007, D008, D009, D010, D011	6.6	<0.50	0.16	<0.05	0.27	<0.10	0.000114	<0.20	<0.08
AMWTS-003/004	D002, D004, D005, D006, D007, D008, D009, D010, D011	7.11	<0.50	0.15	<0.05	0.42	<0.10	0.027	<0.20	<0.08
AMWTS-005	D002, D006, D007, D008, D009, D011	6.74	<0.50	0.16	<0.05	0.27	<0.10	0.000142	<0.20	<0.08
AMWTS-006	D002, D004, D005, D006, D007, D008, D009, D010, D011	6.68	<0.50	0.70	<0.05	0.50	<0.10	0.000001	0.22	<0.08
AMWTS-007	D002, D004, D005, D006, D007, D008, D009, D010, D011	8.26	<0.50	0.59	<0.05	0.51	<0.10	<0.000001	<0.20	<0.08
AMWTS-008	D002, D004, D005, D006, D007, D008, D009, D010, D011	6.7	<0.50	0.32	<0.05	0.1	<0.10	0.00011	<0.20	<0.08
AMWTS-009	D002, D004, D005, D006, D007, D008, D009, D010, D011	6.96	<0.50	0.11	<0.05	0.13	<0.10	0.035	<0.20	<0.08

Indicates failed Universal Treatment Standard

For future mercury-containing waste streams, as applicable, additional bench testing will be conducted prior to AMWTS treatment to ensure proper batch instructions and treatment success.

The improvements over the original, manual small-scale system and the modifications made from the original AMWTS have been realized. Worker feedback indicated that the system was easy to use, less labor intensive and “cleaner” than the original system.

CONCLUSION

The tank based chemical treatment system was designed and built as a means to accomplish ANL Site Treatment Plan Milestones for associated waste streams and to increase automation and treatment throughput over existing small batch system.

Even though the original design and fabrication of the system experienced problems, the system was still viable and the technology was sound. Once the system and qualification documentation were brought up to date, and the logic control problems and design flaws were corrected, the system was utilized to accomplish the original goals. Simple and relatively inexpensive modifications made to the system resulted in significant improvements over the prior, more labor intensive on-site treatment method that was being done within a ventilation hood.

Reinitiating the AMWTS project reduced treatment costs for this expensive mixed waste stream. Reduced treatment time and utilizing an enclosed reaction vessel reduced worker exposure to radiation, thereby positively impacting ALARA goals.

The previously used treatment system components were adapted to be used with the AMWTS. This innovation allowed for less dependence on PPE than the prior system by separating the waste handling/bulking steps of the process from the treatment steps. The AMWTS also improved worker safety by incorporating more engineering controls such as system logic controls; personnel safety and equipment protection interlocks, off-normal condition indicators/alarms, and system emergency stop controls.

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In a time of ever decreasing budgets, it makes sense to rethink the use of existing treatment systems. Utilizing, and possibly retooling, equipment and infrastructure may allow for reduced treatment costs and increase worker safety.