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ENVIRONMENTAL RESTORATION PROGRAM

Characterization of Secondary Solid Wastes in Trench Water in Waste Area Grouping 6 at Oak Ridge National Laboratory, Oak Ridge, Tennessee

P. A. Taylor
T. E. Kent

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Energy Systems Environmental Restoration Program
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Author Affiliations

P. A. Taylor and T. E. Kent are members of the Chemical Technology Division, part of Oak Ridge National Laboratory, Martin Marietta Energy Systems, Inc.

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ABBREVIATIONS

DCG	Derived Concentration Guidelines
DOE	U.S. Department of Energy
GAC	granular activated carbon
HEPA	high-efficiency particulate arrester
NPDES	National Pollutant Discharge Elimination System
NRWTP	Nonradiological Wastewater Treatment Plant
ORNL	Oak Ridge National Laboratory
PVC	polyvinyl chloride
PWTP	Process Waste Treatment Plant
RCRA	Resource Conservation and Recovery Act
SVO	semivolatile organics
SWSA	solid waste storage area
TCLP	Toxicity Characteristics Leaching Procedure
TH	total hardness
TOC	total organic carbon
WAG	waste area grouping
WTTF	Wastewater Treatment Facility

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EXECUTIVE SUMMARY

This project was undertaken to demonstrate that new liquid waste streams, generated as a consequence of closure activities at Waste Area Grouping (WAG) 6 and other sites, can be treated at the existing wastewater treatment facilities at Oak Ridge National Laboratory (ORNL) to meet discharge requirements without producing hazardous secondary solid wastes. Previous bench and pilot-scale treatability studies have shown that ORNL treatment operations will adequately remove the contaminants and that the secondary solid wastes produced were not hazardous when treating water from two trenches in WAG 6. This study used WAG 6 trench water spiked with the maximum concentration of Toxicity Characteristics Leaching Procedure (TCLP) constituents (chemicals that can make a waste hazardous) found in any groundwater samples at ORNL. The Wastewater Treatment Test Facility (WTTF), a 0.5 L/min pilot plant that simulates the treatment capabilities of the Process Waste Treatment Plant (PWTP) and Nonradiological Wastewater Treatment Plant (NRWTP), was used for this test. This test system, which is able to produce secondary wastes in the quantities necessary for TCLP testing, was operated for a 59-d test period with a minimum of problems and downtime. The pilot plant operating data verified that WAG 6 trench waters, spiked with the maximum concentration of TCLP contaminants measured to date, can be treated at the PWTP and NRWTP to meet current discharge limits. The results of the TCLP analysis indicated that none of the secondary solid wastes produced during the treatment of these wastewaters will be considered hazardous as defined by the Resource Conservation and Recovery Act.

1. INTRODUCTION AND BACKGROUND

Solid Waste Storage Area (SWSA) 6, which is included in Waste Area Grouping (WAG) 6, has been used since 1969 for the disposal of solid waste contaminated or potentially contaminated with radioactive and hazardous compounds. The Oak Ridge National Laboratory (ORNL) Environmental Restoration Program is examining methods for final closure of WAG 6. Because it is possible that the closure work will require that the waste disposal trenches be dewatered, a method for disposing of this water is needed. Extensive characterization data are available for the trench water (Solomon et al. 1988; Taylor 1991). It has been proposed that these wastewaters be treated at the existing ORNL process wastewater treatment facilities.

This study was undertaken to evaluate wastewater treatment options for wastewater that may be generated during closure of WAG 6. A 0.5-L/min pilot plant was used to (1) verify that WAG 6 trench water spiked with the maximum expected concentrations of Toxicity Characteristics Leaching Procedures (TCLP) contaminants could be treated to discharge limits in the existing ORNL wastewater treatment facilities and (2) verify that secondary solid wastes produced at these facilities would not become Resource Conservation and Recovery Act (RCRA) hazardous as a result of treating the WAG 6 wastewater. This report describes the design and operation of the pilot plant and the results of the treatability study.

1.1 EXISTING ORNL WASTEWATER TREATMENT CAPABILITIES

The facilities used to remove pollutants from ORNL process wastewater are the Process Waste Treatment Plant (PWTP) and the Nonradiological Wastewater Treatment Plant (NRWTP). The PWTP collects and treats wastewaters at an average flow rate of 490 L/min for removal of radioactive ^{90}Sr and ^{137}Cs. The principal contaminant is ^{90}Sr and is usually present in the wastewater at concentrations between 500 and 1000 Bq/L. Also present is in the waste stream is ^{137}Cs although the concentration is typically below regulatory concern. U.S. Department of Energy (DOE) Order 5400.5 limits wastewater discharges of ^{137}Cs to 111 Bq/L and ^{90}Sr to 37 Bq/L. The PWTP uses a combination of alkaline precipitation and ion-exchange to remove ^{90}Sr (see Fig. 1). The wastewater entering the plant is pH adjusted to 11.5 with sodium hydroxide before it enters the softener/clarifier where water hardness compounds such as calcium carbonate and magnesium hydroxide precipitate. Coagulants are added to the wastewater to increase the settling rate of the precipitated solids. The solids are periodically removed from the bottom of softener/clarifier and transferred to a sludge holding tank. The sludges are dewatered using a recessed-plate filter press. The filter cake is typically about 75% water and 25% solids. The softening process also removes about 80% of the incoming ^{90}Sr and 20% of the incoming ^{137}Cs. As a result, the sludge filter cake must be handled and stored as a low-level radioactive waste. The effluent wastewater from the clarifier flows to a surge tank where pumps are used to transfer the wastewater through granular media filters and then through ion-exchange columns where the remaining ^{90}Sr is removed. The effluent from the ion-exchange columns flows to a concrete basin where the pH is adjusted to between 7 and 8.

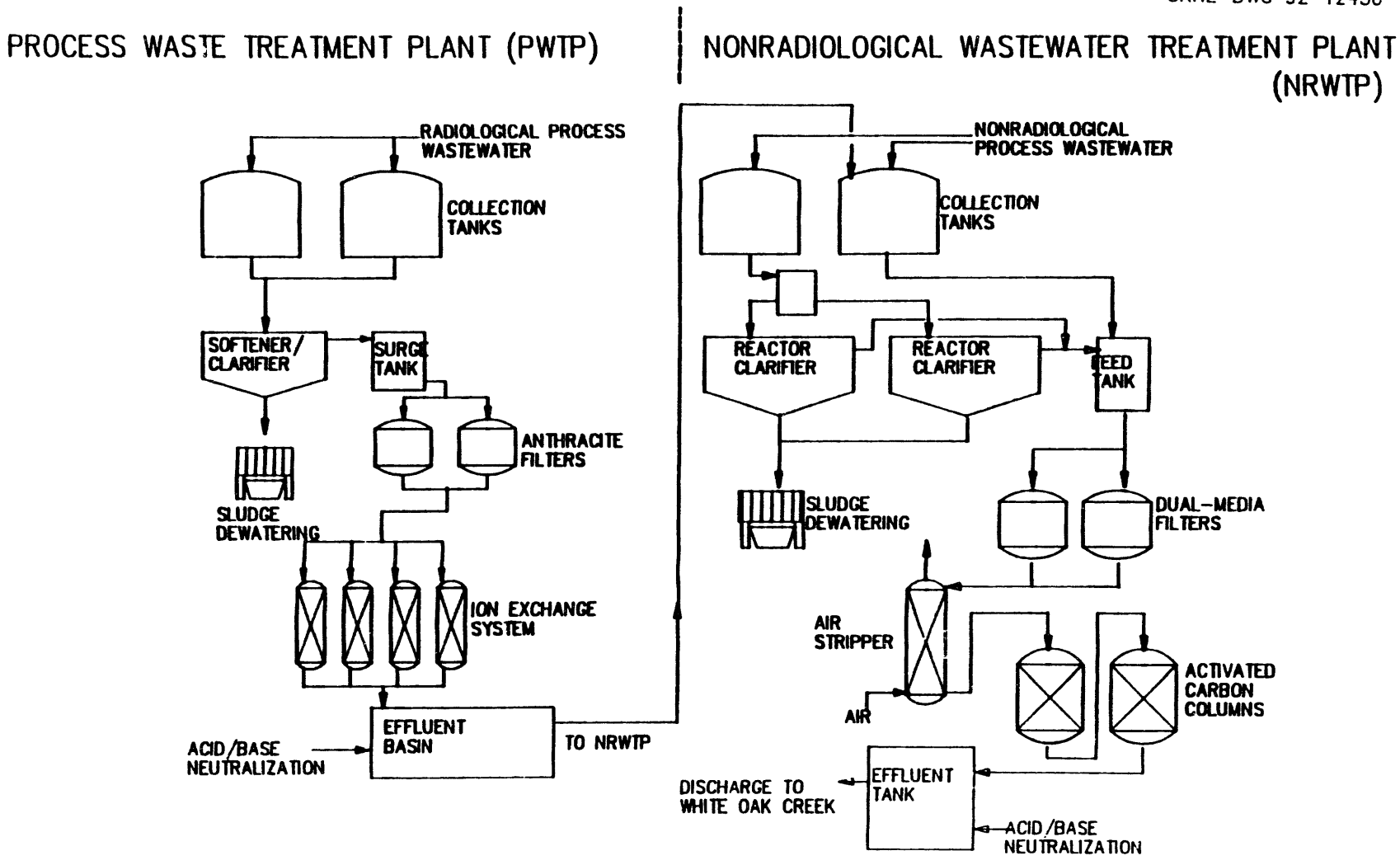

Fig. 1. Flow diagram of PWPT and NRWTP.

The PWTP effluent is transferred to the NRWTP where it combines with other nonradiological process wastewaters for a total average flow of 1200 L/min. The wastewater is pumped through granular media filters and then to an air stripper for removal of volatile organics. Just upstream from the air stripper, the wastewater passes through a pH adjustment station where the pH is adjusted to about 7.5. The air stripper has about nine net transfer units at normal operating conditions. The wastewater passes through the air stripper to a pump station for transfer through two granular activated carbon (GAC) columns in series, for removal of nonvolatile organics, and on to the effluent tank. The pH of the wastewater is adjusted as necessary in the effluent tank before discharge to White Oak Creek via a National Pollutant Discharge Elimination System (NPDES) discharge point. A flow diagram of the existing PWTP and NRWTP is given in Fig. 1.

1.2 PREVIOUS SAMPLING RESULTS

Analytical results for WAG 6 trench water are available from a previous sampling program by Soloman et al. (1988) and data supplied by B. P. Spalding and published in Taylor (1991). Water from 23 trenches in WAG 6 (about 5% of the total number of trenches) has been analyzed. The trenches for the first two sampling programs were selected independently, but those selected for the 1990 sampling program were the seven trenches with the highest levels of radionuclides or organics from the previous sampling programs (Taylor 1991). Table 1 shows the ranges of concentrations of various contaminants for all of the trenches sampled. None of the samples showed significant concentrations of heavy metals, and only a few trenches showed significant concentrations of radionuclides, except for tritium that was ubiquitous. Table 2 shows the maximum concentrations of TCLP constituents that have been measured in ORNL groundwater samples.

1.3 PREVIOUS PILOT-SCALE TREATABILITY TEST RESULTS

The Wastewater Treatment Test Facility (WTTF) was designed and constructed in 1992 to simulate the unit operations of the ORNL PWTP and NRWTP. Water from two trenches in WAG 6 was processed through the WTTF to verify that the full-scale facilities could adequately treat WAG 6 water and that treatment of these wastes would not cause the secondary solid wastes to become RCRA hazardous. About 500 L of WAG 6 wastewater was processed through the WTTF during a 45-d test program. The test system adequately simulated the ORNL process waste system and showed that WAG 6 wastewater could be treated in existing treatment facilities and continue to meet the existing NPDES discharge limits. Results of the TCLP tests showed that the treatment of WAG 6 trench waters will not significantly increase the level of RCRA contaminants in the secondary solid wastes of the system and therefore will not change the regulatory status of these wastes (Kent and Taylor 1992).

Table 1. Range of concentrations of contaminants in water from 23 WAG 6 trenches

Contaminant	Concentration range for indicated sampling program			
	Units	1986–87	1989	1990
^{3}H	Bq/L	310–340,000	32–11,000	180–16,000
^{90}Sr	Bq/L	0–3,600	0–660	0–661
^{137}Cs	Bq/L	0–130	0–36	0–100
Acetone	mg/L	0	0–8.3	0.18–0.44
Ethylbenzene	mg/L	0–0.72	0–7.8	0–3.2
Toluene	mg/L	0–1.9	0–5.0	0.2–76
Xylene	mg/L	0–3.7	0–51	0.4–26
Naphthalene	mg/L	0–1.7	0–3.6	0.02–5.1
4-Methylphenol	mg/L	0–0.09	0–1.4	0–3.8

Sources: Solomon, D. K., R. C. Haese, T. V. Dinsmofre, and A. D. Kelmers, *Sampling and Analysis of SWSA 6 Trench Leachates and Groundwater*, ORNL/TM-10813, Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 1988. Taylor, P. A. *Treatability Study for WAG 6 (SWSA 6) Trench Water*, ORNL/ER-17, Oak Ridge National Laboratory, Oak Ridge, Tennessee, August 1991.

Table 2. Maximum concentration of TCLP constituents found in ORNL groundwater samples

Contaminant	Concentration (mg/L)	Sample location
Arsenic	0.3	WAG 2
Barium	27.1	WAG 6
Chromium	1.0	WAG 2
Lead	1.2	WAG 1
Methyl ethyl ketone	0.5	WAG 6
Selenium	0.4	WAG 1
Tetrachloroethylene	6.8	WAG 6
Trichloroethylene	12.6	WAG 17
Vinyl Chloride	6.4	WAG 5

2. TEST SYSTEM DESCRIPTION

The pilot-scale test system was designed to simulate the PWTP and NRWTP systems such that the unit operations and the secondary waste solids produced will closely resemble those of the full-scale treatment plants. A wastewater flow rate of 0.5 L/min was chosen so that the required amounts of secondary solid wastes for TCLP tests could be produced in a reasonable period of time and so that the system vessels and equipment would be "off-the-shelf" and easy to procure. The materials used to construct the system are stainless steel for transfer lines and most of the process vessels. Stainless steel was chosen for corrosion resistance and for availability. The columns used for filtration, ion-exchange, air stripping, and activated carbon were constructed using clear polyvinyl chloride (PVC) with flanged heads of normal gray PVC. The clear PVC allows visual observation of the materials in the columns. Accumulation of solids on filtering surfaces, expanded height of the materials during backwashing and the extent of algae accumulation can all be observed. PVC is also corrosion resistant for the water solutions used in this application. The transfer pumps are the peristaltic type that are positive-displacement, self-priming, easy to calibrate, and deliver a relatively smooth flow of fluid. The system was equipped with several automatic control systems for wastewater flow, level control, and pH. The system was also equipped for automatic shut-down should wastewater leaks or vessel overflows occur for any reason. The test system was housed in a 48-ft long by 8-ft wide trailer located adjacent to the PWTP. The trailer was equipped with a high-efficiency particulate arrester (HEPA) filtered ventilation system and all other necessary safety and fire protection systems.

A flow diagram of the test system is shown in Fig. 2. The system consists of a series of process vessels designed to simulate the unit operations of the ORNL PWTP and NRWTP. Two 55-gal drums were used to separately collect ORNL process water and WAG 6 wastewater. Water from the feed drums was metered to a 1-gal rapid mix vessel where the wastewaters combine with the treatment chemicals used for the softening process. From the rapid mix vessel, the water flows to a larger 5-gal slow mix vessel where residence time is provided for the softening reaction and flocculation of precipitated solids. The effluent from the slow mix vessel flows to the clarifier where further softening occurs as a result of upflow contact with the sludge blanket and where separation of the sludge and wastewater is accomplished. Sludge that accumulates in the clarifier is periodically removed from the bottom of the vessel and transferred to a holding container. The clarifier effluent flows to an effluent tank that is provided for settling of any solid particles that may carry over from the clarifier. The effluent tank flows to a surge vessel that provides flooded suction for a metering pump that transfers the wastewater through the granular media filter and ion-exchange column. The effluent from the ion-exchange column flows to a stirred vessel used for pH adjustment of the wastewater before transfer to the air stripper. The air stripper is composed of two packed columns in series. Metering pumps are provided to transfer wastewater from the first stage to the second stage air stripper and on to a surge vessel. This vessel provides flooded suction for the pump that transfers the wastewater to the GAC column. The GAC column effluent stream flows to the test system drain that is routed to the PWTP sump for recycle to the PWTP feed tanks. Further detailed design information for the test system is available in a previous report (Kent and Taylor 1992).

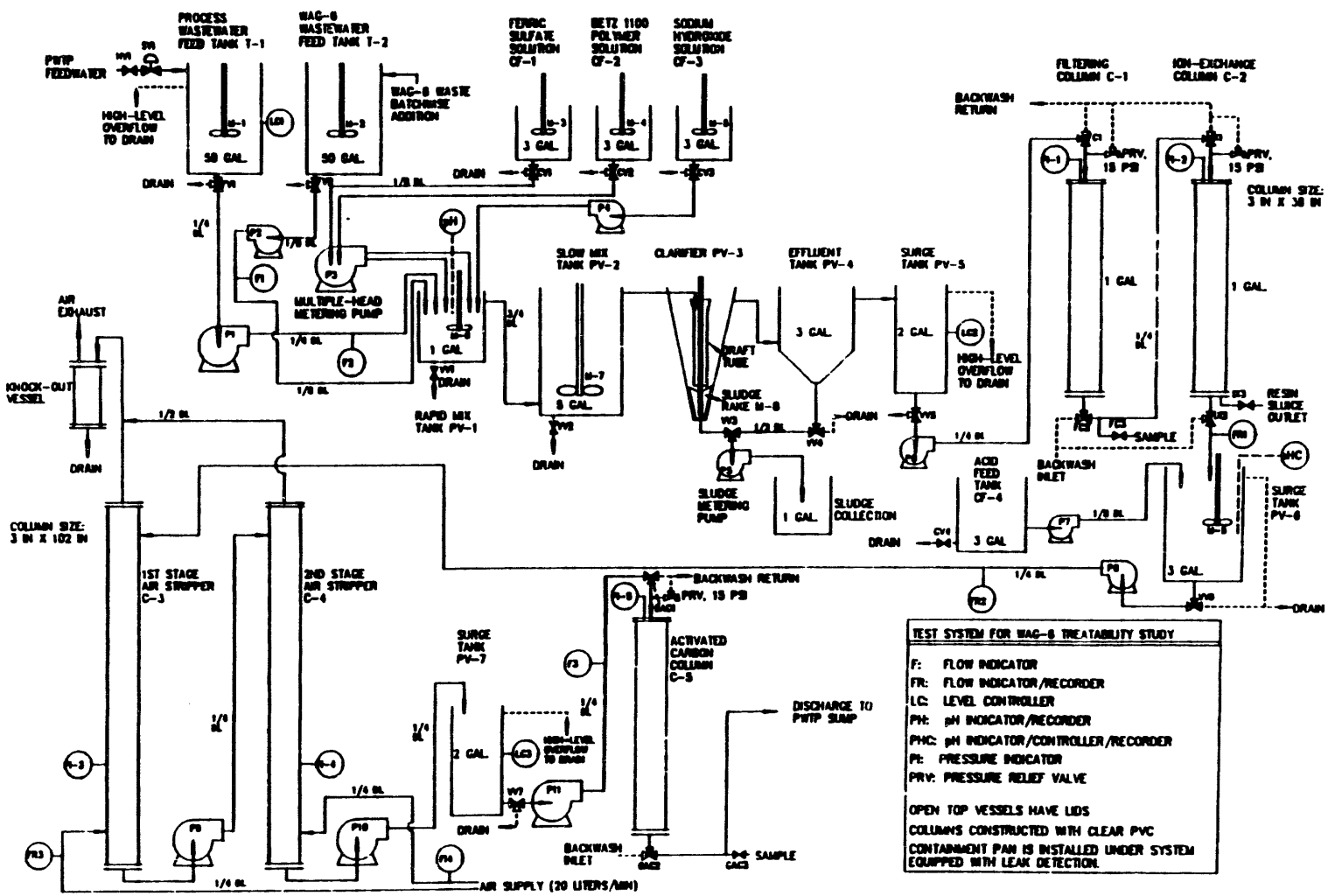

Fig. 3. Flow diagram of WAG 6 treatability assessment flow system.

3. TEST SYSTEM OPERATION

3.1 GENERAL PERFORMANCE

The test system began operation on April 26, 1993, and continued until June 24, 1993, without significant downtime. Only minor problems were encountered that typically resulted in less than 1 h of downtime. The system was monitored by laboratory technicians for two 8-h shifts per day with 4 h of unattended operation between each shift. Technicians monitored and logged test data, performed wet titrations, adjusted equipment settings, calibrated instruments, and performed preventative maintenance and repairs as necessary. A sampling and monitoring program was carried out to evaluate the operation of the system and to verify adequacy of PWTP and NRWTP simulation. No emergency shutdowns or unusual occurrences were encountered during the test. Secondary solid wastes were collected during and after the test program to submit for TCLP analysis.

3.2 WASTEWATER FEED SYSTEM

The wastewater feed system consists of two 55-gal stainless steel drums equipped for level control, mixing, and metering of wastewater. For this test, process water was fed directly from a supply line through a needle valve to the rapid mix tank at a rate of 0.5 L/min, so the T-1 drum was not used. Water from trench T-13 in WAG 6 was collected in a 30-gal stainless steel drum, transported by pickup truck to the trailer site, and transferred to tank T-2 about once a week. Spike solutions were added to each batch of WAG 6 trench water to supply the concentrations of TCLP constituents listed in Table 2, except for the vinyl chloride that was not available. The trench water was pumped from T-2 at a rate of 10 mL/min to the rapid mix vessel (PV-1) to simulate the overall average addition of 3000 gal/d of WAG 6 wastewater to the process wastewater system, which is the maximum expected in full-scale operations. The two wastewaters combined in vessel PV-1 where dilute NaOH, ferric sulfate, and flocculating agent (Betz 1100 polymer) were added in the first step of the wastewater softening operation. Fig. 3 shows the wastewater flow rates for the test. The average flow rates during the test were 508.3 mL/min of process water and 10.0 mL/min of WAG 6 water. A total of 42,500 L of process water and 850 L of trench water were treated during the test program.

Each batch of spiked WAG 6 trench water was sampled and analyzed for organics and metals by the Analytical Chemistry Division. Samples of the combined trench water/process water were analyzed periodically for organics and metals. Table 3 gives a list of the volatile and semivolatile organic compounds analyzed. Only those that were detected are listed in the compiled sample results. As shown in Tables 4 and 5, the spiked trench water contaminants detected in the highest concentrations include naphthalene, toluene, and xylene, plus the contaminants added in the spike solutions. In the combined trench/process feed samples (shown in Tables 6 and 7), small quantities of barium, chromium, naphthalene, toluene, xylene, and zinc were detected. Although the TCLP contaminants were low in concentration or undetected, they could potentially concentrate in secondary solid wastes resulting in RCRA characteristically hazardous wastes.

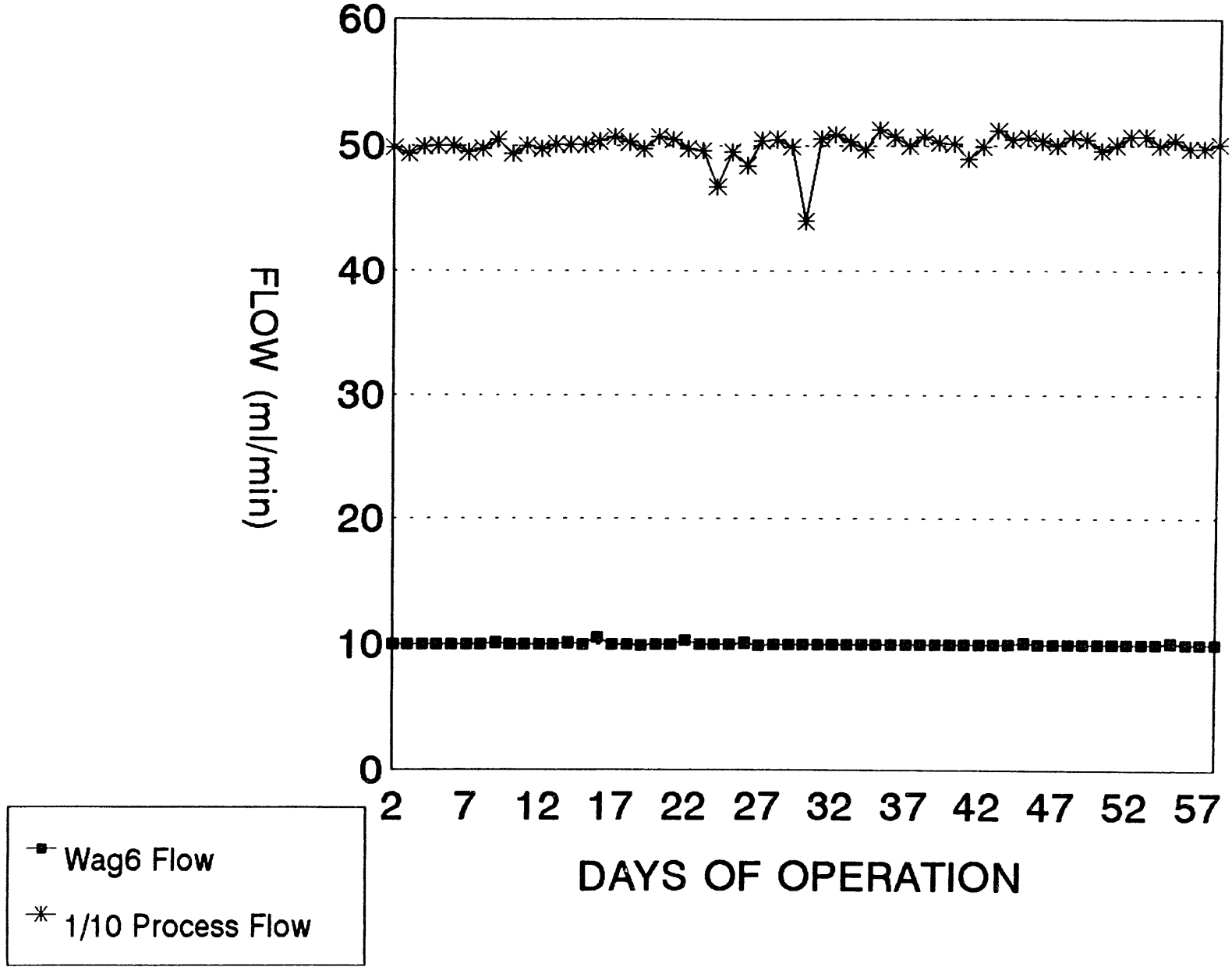

Fig. 2. Test system flow diagram.

Table 3. List of volatile and semivolatile organics analyzed for wastewater characterization and evaluation of test system performance

Compound	Detection limit (μg/L)	Compound	Detection limit (μg/L)
Volatile organics		Semivolatile organics	
Chloromethane	10	Acenaphthene	10
Bromomethane	10	2,4-Dinitrophenol	50
Vinyl chloride	10	4-Nitrophenol	50
Chloroethane	10	Dibenzofuran	10
Methylene chloride	5	2,4-Dinitrotoluene	10
Acetone	10	Diethylphthalate	10
Carbon disulfide	5	4-Chlorophenyl-phenylether	10
1,1-Dichloroethene	5	Fluorene	10
1,1-Dichloroethane	5	Phenol	10
1,2-Dichloroethene (total)	5	Bis(2-chloroethyl)ether	10
Chloroform	5	2-Chlorophenol	10
1,2-Dichloroethane	5	1,3-Dichlorobenzene	10
2-Butanone	10	1,4-Dichlorobenzene	10
1,1,1-Trichloroethane	5	Benzyl alcohol	10
Carbon tetrachloride	5	1,2-Dichlorobenzene	10
Vinyl acetate	10	2-Methylphenol	10
Bromodichloromethane	5	Bis(2-chloroisopropyl)ether	10
1,2-Dichloropropane	5	4-Methylphenol	10
cis-1,3-Dichloropropene	5	n-Nitroso-di-n-propylamine	10
Trichloroethene	5	Hexachloroethane	10
Dibromochloromethane	5	Nitrobenzene	10
1,1,2-Trichloroethane	5	Isophorone	10
Benzene	5	2-Nitrophenol	10
trans-1,3-Dichloropropene	5	2,4-Dimethylphenol	10
Bromoform	5	Benzoic acid	50

Table 3 (continued)

Compound	Detection limit (µg/L)	Compound	Detection limit (µg/L)
Volatile organics		Semivolatile organics	
4-Methyl-2-pentanone	10	Bis(2-chloroethoxy)methane	10
2-Hexanone	10	2,4-Dichlorophenol	10
Tetrachloroethene	5	4-Nitroaniline	50
1,1,2,2-Tetrachloroethane	5	4,6-Dinitro-2-methylphenol	50
Toluene	5	n-Nitrosodiphenylamine (1)	10
Chlorobenzene	5	4-Bromophenyl-phenylether	10
Ethylbenzene	5	Hexachlorobenzene	10
Styrene	5	Pentachlorophenol	50
Xylene	5	Phenanthrene	10
Semivolatile organics		Anthracene	10
1,2,4-Trichlorobenzene	10	Di-n-butylphthalate	10
Naphthalene	10	Fluoranthene	10
4-Chloroaniline	10	Pyrene	10
Hexachlorobutadiene	10	Butylbenzylphthalate	10
4-Chloro-3-methylphenol	10	3,3'-Dichlorobenzidine	20
2-Methylnaphthalene	10	Benzo(a)anthracene	10
Hexachlorocyclopentadiene	10	Chrysene	10
2,4,6-Trichlorophenol	10	Bis(2-ethylhexyl)phthalate	10
2,4,5-Trichlorophenol	50	Di-n-octylphthalate	10
2-Chloronaphthalene	10	Benzo(b)fluoranthene	10
2-Nitroaniline	50	Benzo(k)fluoranthene	10
Dimethyphthalate	10	Benzo(a)pyrene	10
Acenaphthylene	10	Indeno(1,2,3-cd)pyrene	10
2,6-Dinitrotoluene	10	Dibenzo(a,h)anthracene	10
3-Nitroaniline	50	Benzo(g,h,i)perylene	10

Table 4. WAG 6 trench water organic characterization data

Compound	Unspiked trench water 4/26/93	Spiked trench water 4/27/93	Spiked trench water 5/4/93	Spiked trench water 5/11/93	Spiked trench water, 5/20/93	Spiked trench water 5/26/93	Spiked trench water 6/3/92
Semivolatile organic analysis results, μg/L							
2,4-Dimethylphenol	170	NA[a]	32	NA	8[J(b)]	NA	250
2-Methylphenol	10	NA	39	NA	3[J]	NA	78
4-Methylphenol	72	NA	8	NA	28	NA	42
Naphthalene	610	NA	*c*	NA	670	NA	
Benzene derivatives	1135	NA	233[J]	NA	1375[J]	NA	1237[J]
Phenol derivatives		NA		NA	114[J]	NA	95[J]
Unknowns	666	NA	564[J]	NA	540[J]	NA	587
Volatile organic analysis results, μg/L							
Tetrachloroethylene		5011	2300	3900	640	610	880
Toluene	1615	1256	670	670	510	770	810
Trichloroethylene		30260	5600	8300	3200	2000	2400
Xylene	2146	1933	3200	3400	3700	5200	6300
Total organic carbon, mg/L	38	35.2	15.1	NA	25.1	NA	9.3

[a]NA = not analyzed.

[b]"J" indicates that the quantitative value is estimated. This qualifier usually appears after a value that is below the quantification limit or after a value given for a tentatively identified compound.

[c]Where a result is not entered, the compound was not detected. Detection limits given in Table 3.

Table 5. WAG 6 trench water metals characterization data

		Unspiked trench water 4/26/93	Spiked trench water 4/27/93	Spiked trench water 5/4/93	Spiked trench water 5/11/93	Spiked trench water 5/20/93	Spiked trench water 5/26/93	Spiked trench water 6/3/93
Metal	DL[a]	Total metals concentration (mg/L)						
Al	0.05	*b*		0.18	0.33	0.32	0.15	0.074
As	0.05		0.16	0.11		0.16	0.14	
Ba	0.001	0.23	32	10	39	38	12	0.032
Ca	0.01	78	78	85	78	93	43	46
Cr	0.004	0.027	0.70	0.64	0.71	1.5	0.53	
Fe	0.01	40	33	25	40	40	22	0.94
Hg	0.00005	NA[c]	NA		NA	NA	NA	
Mg	0.03	17	17	18	17	19	8.9	9.7
Mn	0.001	6.8	6.5	7.8	6.8	7.6	3.6	0.098
Na	10							15
Ni	0.004							0.0063
Pb	0.03		0.63	0.19	0.77	1.5	0.49	
Sr	0.005	0.14	0.14	0.13	0.14	0.15	0.075	0.11
Zn	0.005	0.63	0.5	0.47	0.80	0.76	0.33	0.098

[a]DL = detection limits (in milligrams per liter).

[b]Where a result is not entered, the compound was not detected above the indicated detection limit.

[c]NA = not analyzed.

Table 6. Pilot plant feed water organic characterization data

Compound	5/4/93	5/20/93	6/3/92
Semivolatile organic analysis results, μg/L			
2,4-Dimethylphenol	*a*		
2-Methylphenol			
4-Methylphenol			
Naphthalene	25	33	53
Benzene derivatives	40[J(b)]	47[J]	93[J]
Phenol derivatives			
Unknowns	47[J]	4[J]	30[J]
Volatile organic analysis results, μg/L			
Tetrachloroethylene	61[J]	10[J]	14[J]
Toluene		13[J]	15[J]
Trichloroethylene	140[J]	55	41
Xylene	74[J]	59	102
Total organic carbon, mg/L	2.0	1.7	2.1

[a]Where a result is not entered, the compound was not detected. Detection limits given in Table 3.

[b]"J" indicates that the quantitative value is estimated. This qualifier usually appears after a value that is below the quantification limit or after a value given for a tentatively identified compound.

Table 7. Pilot plant feed water metals characterization data

		5/4/93	5/20/93	6/3/93
Metal	DL[a]	Total metals concentration (mg/L)		
Al	0.05	0.18	0.21	0.069
As	0.05	*b*		
Ba	0.001	0.60	0.67	0.51
Ca	0.01	42	40	41
Cr	0.004	0.020	0.026	0.0065
Fe	0.01	0.52	0.63	0.55
Hg	0.00005		NA[c]	NA
Mg	0.03	10	11	10
Mn	0.001	0.13	0.13	0.15
Na	5	5.3	5.6	6.1
Ni	0.004			
Pb	0.03			
Sr	0.005	0.099	0.098	0.10
Zn	0.005	0.23	0.22	0.20

[a]DL: Detection limits (are in milligrams per liter).

[b]Where a result is not entered, the compound was not detected above the indicated detection limit.

[c]NA = not analyzed.

3.3 SOFTENING AND CLARIFICATION OPERATIONS

The softening and clarification step of the process involves elevating the pH of the wastewater to 11.5 with sodium hydroxide to precipitate hardness compounds, such as calcium carbonate, magnesium hydroxide, and smaller amounts of other metal compounds. Sodium hydroxide was added to the combined wastewater in the rapid mix vessel PV-1. Also added were two other treatment chemicals, ferric sulfate and Betz 1100* polymer, which were used to coagulate and flocculate the precipitated hardness compounds. The pH of the wastewater in PV-1 was monitored and recorded at least twice each shift. The rapid mix tank gravity-flowed to the slow mix tank PV-2 that provided time for the softening reaction and for flocculation of precipitates. PV-2 gravity flowed to the clarifier where separation of the flocculated precipitates was accomplished. The wastewater and suspended precipitates entered the draft tube of the clarifier that directed the flow to the bottom of the conical shaped vessel. As the wastewater flowed upward toward the clarifier outlet, the widening cone caused a gradual decrease in the upflow velocity. The upflow velocity decreased to the point where the flocculated precipitates were no longer suspended by the wastewater and an interface or "sludge blanket" was formed. The depth of the sludge blanket increased as the precipitates accumulated in the clarifier. The function of the sludge blanket was to provide nucleation sites for further precipitation of hardness compounds and also to act as a filter for finely suspended particles. The sludge blanket level was controlled by periodic removal of sludge from the bottom outlet of the clarifier. To obtain the maximum benefits of the sludge blanket, the level was maintained as high as possible without carry-over of precipitates into the effluent tank PV-4. The sludge removed from the softener was collected in a 1-gal plastic container. When the container was full, the sludge was transferred to a larger plastic carboy for temporary storage. At selected times during the test program, a 1-gal sample of the sludge was moved to Bldg. 3541 for dewatering using vacuum filtration. The dewatered sludge sample was then submitted for TCLP analysis.

The softening and clarification systems performed well and adequately simulated PWTP full-scale operations. The precipitates coagulated and flocculated well and the resulting sludge blanket formed in the clarifier was well-defined and stable. The level of the sludge blanket was easy to control and carry-over to PV-4 rarely occurred. The vacuum filtration operation worked well in producing a dewatered sludge "cake" with comparable solids content to that produced in filter press operations at the PWTP. Filter cake from the PWTP filter press is typically 20 to 30 % solids as was the cake produced from the laboratory vacuum filter. Total hardness (TH) titrations were performed by test system operators on a periodic basis to determine the amount of calcium carbonate and other hardness compounds in the clarifier effluent and the filter column effluent. Table 8 shows the dissolved metals concentrations of the clarifier and filter column effluents. These samples indicate that metals will be removed to concentrations well below the existing NPDES permit limits. The test system granular anthracite filter also behaved similarly to the PWTP anthracite filters. As expected from PWTP experience, the hardness compounds in the wastewater continue to precipitate onto the filter media after clarification. As shown in Fig. 4, the clarifier effluent averaged 25.9 mg/L TH, and the filter column effluent averaged 9.1 mg/L. Accumulation of calcium carbonate onto the granular anthracite was clearly visible in the test system filter column. Two samples of sludge from the test system softening operation were collected, dewatered, and submitted for TCLP analysis.

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*Trademark of Betz Laboratories, Inc.

Table 8. Clarifier and filter effluent metals characterization data

		Clarifier effluent 5/4/93	Filter effluent 5/4/93	Clarifier effluent 5/20/93	Filter effluent 5/20/93	Clarifier effluent 6/3/93	Filter effluent 6/3/93
Metal	DL[a]	Total metals concentration (mg/L)					
Al	0.05	0.076	*b*	0.087			
As	0.05						
Ba	0.001	0.35	0.003	0.32	0.007	0.2	0.006
Ca	0.01	19	0.68	12	1.1	13	1.4
Cr	0.004	0.006		0.011	0.006		
Fe	0.01	0.34	0.12	0.66	0.12		
Hg	0.00005			NA[c]	NA	NA	NA
Mg	0.03	3.2	0.36	3.7	0.49	5.5	0.25
Mn	0.001	0.037	0.005	0.05	0.005		0.001
Na	5	220	230	300	300	270	280
Ni	0.004						
Pb	0.03						
Sr	0.005	0.058		0.046		0.05	0.005
Zn	0.005	0.064	0.021	0.078	0.008		

[a]DL: Detection limits (in milligrams per liter).

[b]Where a result is not entered, the compound was not detected above the indicated detection limit.

[c]NA = not analyzed.

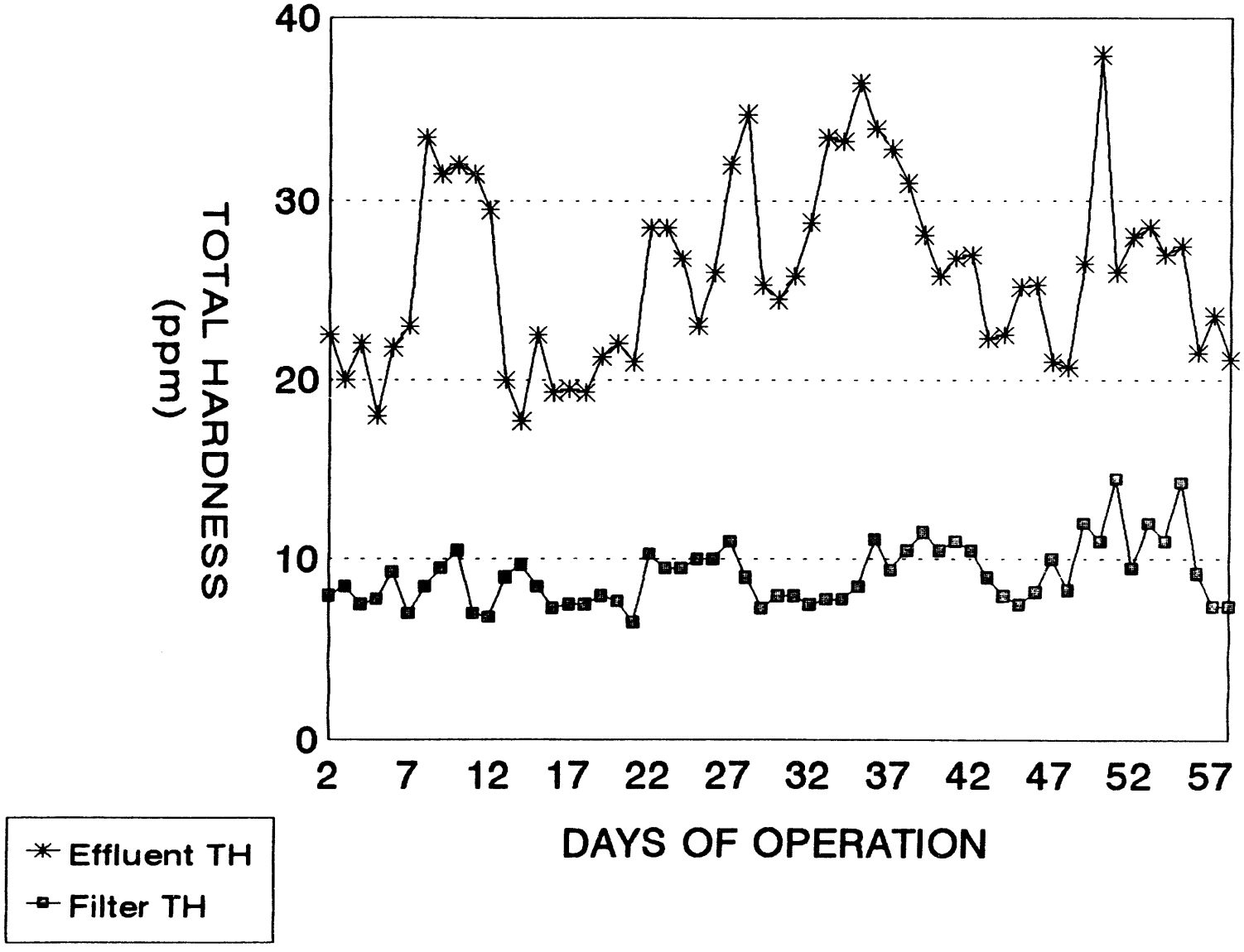

Fig. 4. Total hardness of clarifier and filter column effluents.

3.4 ION-EXCHANGE PROCESS

At the PWTP the softening process removes a large portion of the radioactive ^{90}Sr from the wastewater; however, additional treatment is necessary to meet the Derived Concentration Guidelines (DCG) given in DOE Order 5400.5. To remove additional amounts of strontium, a strong-acid cation exchange resin, Dowex HCR-S* is used. This treatment is simulated in the test system using 2.5 L of the Dowex HCR-S loaded in an 8 cm (3 in.) diameter, 91 cm (36 in.) tall column. Prefiltering of the wastewater to remove suspended solids before ion-exchange is performed at the PWTP using a granular-anthracite pressure filter. A 8 cm (3 in.) diameter, 91 cm (36 in.) tall column loaded with 2 L of granular anthracite is used as a prefilter in the test system. The prefilter and ion-exchange column were operated in series during the test. As discussed in Sect. 3.3, the performance of the prefilter closely resembled that of the PWTP prefilter during the run. The pressure drop across the filter increased with time as suspended solids and scaling of anthracite particles occurred. The filter was backwashed with process water once a day to prevent column plugging. As seen in the PWTP operation, a significant reduction in TH occurs as wastewater is passed through the filter.

Because the process water used in this test did not contain any ^{90}Sr, the ion exchange resin in the WTTF did not provide any treatment of the wastewater; however, the resin was left in the system to determine if it would adsorb any TCLP constituents. At the end of the test, the resin was analyzed by the TCLP procedure to determine if it had become RCRA hazardous.

3.5 AIR STRIPPER OPERATION

Air stripping is used at the NRWTP for removal of trace amounts of volatile organic contaminants from the wastewater. The treatment involves cascading wastewater downward over a tall column of packing material while flowing air upward through the column. The packing material serves to spread the wastewater over a large surface area for better contact with the air. Under these conditions, the volatile organic contaminants are desorbed from the wastewater into the air stream and are discharged to the atmosphere.

The NRWTP air stripper is filled to a height of 7.9 m (26 ft) with a high-efficiency packing [8.9 cm (3.5 in.) Lanpac, Lantec Products, Inc., Agoura Hills, Calif.]. Correlations supplied by the packing manufacturer show that the air stripper should have about nine transfer units at normal operating conditions. Because the packing used in the NRWTP air stripper is not available in small sizes, the operating conditions of the NRWTP air stripper cannot simply be duplicated in the test system. The goal is to have the same concentration of organics exiting the test air stripper as would be present in the effluent from the NRWTP air stripper treating the same wastewater. This can be accomplished by designing and operating the test air stripper to provide nine transfer units, as is the case at the NRWTP. The experimental data from the earlier bench-scale treatability tests (Taylor 1991) show that 4.6 m (15 ft) of 0.64 cm (0.25 in.) ceramic saddles, with a gas-to-liquid volume ratio of 40:1 will provide the same organic removal as the NRWTP air stripper. The test air stripper consists of two 8 cm (3 in.) diameter columns each 2.43 m (8 ft) in height and packed with ceramic saddles.

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*Trademark of the Dow Chemical Co.

Prior to entering the air stripper, the wastewater passed through pH adjustment vessel PV-6 where a solution of sulfuric acid was added to reduce the pH to a level between 7 and 8. An in-line pH electrode connected to a pH controller was used to automatically adjust pH. For pH control, it was important that the pH electrode be immersed in the wastewater at all times and also important that the mixing characteristics of the vessel remained constant with a minimum of level variation. To ensure good pH control, it was decided in the design planning to control level by providing a simple overflow line. The flow to the air stripper was manually adjusted to a value slightly lower than the flow into PV-6, thus placing the vessel in constant overflow to the test system drain.

From PV-6, the wastewater was transferred to the first column of the air stripper. The wastewater entered the top of the air stripper column and onto the packing where it was dispersed and contacted with an upward flowing 20 L/min air stream. Air flow through the air stripper was monitored and recorded continuously with a mass flow meter, while the test system operator manually adjusted air flow to maintain 20 L/min. The wastewater effluent from the first column was then transferred to the top of the second column using a peristaltic pump. The effluent from the second column was pumped to a surge vessel for transfer to the test system GAC column. The exhaust air stream from the stripper was discharged through a knock-out container to remove any water droplets from the air stream. From the knock-out container, the air was routed to the trailer ventilation system exhaust duct where it was passed through a HEPA filter before discharging to the atmosphere.

At four different time periods during the test program, samples of air stripper feed and effluent wastewater were taken and analyzed for volatile and semivolatile organic compounds. The results of these analyses are compiled in Table 9 and indicate that only extremely low levels of organics existed in both feed and effluent samples. No volatile organics were detected in the air stripper effluent.

3.6 ACTIVATED CARBON COLUMN OPERATION

Contact of the wastewater with activated carbon is provided to remove semivolatile organic contaminants. Activated carbon is a carbon-based material that is treated by oxidation to produce a highly porous material. In wastewater treatment, a wide variety of organic compounds are amenable to adsorption by activated carbon. The extent of contaminant removal by activated carbon is dependent on the particular organic compound, the type of activated carbon, the wastewater conditions, and the treatment system operating conditions.

The test system GAC system consists of a surge vessel, metering pump, and a 15 cm (6 in.) diameter, 91 cm (36 in.) tall column, filled with 10 L of Cecarbon GAC 30 activated carbon (same as that used in the NRWTP). The test system GAC column has the same aspect ratio (height to diameter ratio) and provides the same wastewater residence time as the NRWTP GAC system.

At least 100 g of solid waste are necessary to perform the U.S. Environmental Protection Agency TCLP test. In the case of the carbon waste from the WTTF GAC system, it is necessary that the carbon be at or near exhaustion to simulate that produced in the NRWTP full-scale system. The GAC at the NRWTP will be removed and discarded as a solid waste when the organics break through the column. However, the NRWTP carbon, which has been in service for 40 months, has not been replaced to date. As such, the loading capacity of the

pilot plant GAC had to be estimated. Though the sorption capacity of activated carbon varies widely, a carbon that will remove 10% of its weight of an organic contaminant is considered typical for wastewater treatment. In the initial planning of the test program, it was assumed that 100 g GAC will remove 10 g of organic carbon and that the wastewater would contain 1 mg/L of adsorbable organic carbon. The equivalent volume of wastewater necessary to provide 10 g of adsorbable carbon is 10,000 L. At a treatment flow rate of 0.5 L/min, 14 d are required to treat 10,000 L of the WAG 6/process wastewater mixture. To allow for lower concentrations of adsorbable organics, a test duration of 59 d was chosen. At termination of the test, two 200 mL samples (approximately 100 g each) of activated carbon were removed from the top surface of the carbon bed, where organic loading should be the highest, for the TCLP testing. The GAC column carbon bed was not backwashed or otherwise disturbed during the test period.

Table 9. Organic content of air stripper inlet and outlet wastewater

Compound	Air stripper samples 5/4/93 (µg/L)		Air stripper samples 5/20/93 (µg/L)		Air stripper samples 6/3/93 (µg/L)	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Tetrachlorethylene	*a*				11	
Toluene					12	
Trichloroethylene	70[J(b)]		44		30	
Xylene			11[J]		86	
Naphthalene	23	2[J]	23	2[J]	52	
Benzene derivatives	141[J]	120[J]	29[J]		102[J]	9[J]
Unknowns	38[J]	50[J]			75[J]	35[J]

[a]Where a result is not given, the compound was not detected. Detection limits are given in Table 3.

[b]"J" indicates that the quantitative value is estimated. This qualifier usually appears after a value that is below the quantification limit or after a value given for a tentatively identified compound.

During the pilot plant operation, GAC column inlet and outlet samples were collected and analyzed for semivolatile organics (SVO) and total organic carbon (TOC). The results shown in Table 10 indicate that SVO compounds in most cases were below detection limits in both inlet and outlet samples. TOC results, however, indicated an average reduction of at least 0.5 mg/L TOC during the test program. With a total throughput of 42,500 L, at least 21 g of adsorbable carbon was collected based on TOC results. Though SVO compounds were not detected, other nonspecific adsorbable compounds (including SVO compounds at concentrations below detection limits) were being removed and it is likely that the GAC at the top surface of the bed reached a significant degree of exhaustion. The analytical results of GAC column effluent samples also indicate that organic contaminant concentrations will not exceed or even approach the concentrations given in the existing NPDES permit.

Table 10. Organic content of carbon column inlet and outlet wastewater

Compound	Carbon column samples 5/4/93 (μg/L)		Carbon column samples 5/20/93 (μg/L)		Carbon column samples 6/3/93 (μg/L)	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Naphthalene	2[J(a)]	*b*	2[J]			
Benzene derivatives	120[J]	100[J]			9[J]	
Unknowns	50[J]	32[J]			35[J]	
TOC	1200	<500	1200	<500	1200	<500

[a]"J" indicates that the quantitative value is estimated. This qualifier usually appears after a value that is below the quantification limit or after a value given for a tentatively identified compound.

[b]Where a result is not given, the compound was not detected. Detection limits are given in Table 3.

4. SECONDARY WASTE TCLP RESULTS

Five samples of secondary solid wastes were submitted for TCLP analysis during the test program. The protocol given in Method 1311, publication SW-846 (EPA 1986) of Appendix II in 40 CFR 261 was used for the analysis. Two samples of filtered sludge cake and one sample each of the anthracite filter media, ion-exchange resin, and activated carbon were submitted to ORNL Analytical Chemistry. Duplicate samples of all but the first sludge cake sample were also sent to an off-site laboratory (CompuChem Labs, Inc., Research Triangle Park, North Carolina). The sludge sample taken on May 21, 1993, contained 24 wt% dry solids and that taken on June 24, 1993, contained 27 wt% dry solids. The ion exchange, filter media and carbon samples were drained but not dried before submitting.

For the samples sent to CompuChem Labs, all of the TCLP constituents in each of the samples was below the reporting limit, which is one half of the RCRA regulatory limit. The results from ORNL Analytical Chemistry that have been received to date are shown in Tables 11 and 12. All of these samples were significantly below the RCRA regulatory limit for TCLP constituents, so they are not hazardous wastes.

Table 11. Results of TCLP analysis of sludge samples

TCLP constituent	RCRA limit	5/21/93 sample	6/24/93 sample
Metals analysis	Concentration (mg/L)		
Arsenic	5	<0.55	0.12
Barium	100	19	17
Cadmium	1	<0.055	<0.005
Chromium	5	<0.044	0.15
Lead	5	<0.55	0.079
Mercury	0.2	0.000084	0.000055
Selenium	1	<0.55	0.20
Silver	5	<0.055	0.015
Organics analysis	Concentration (μg/L)		
Benzene	500	<25	<25
Carbon tetrachloride	500	<25	<25
Chlordane	30	<0.6	<0.6
Chlorobenzene	100,000	<25	<25
Chloroform	6,000	<25	<25

Table 11 (continued)

TCLP constituent	RCRA limit	5/21/93 sample	6/24/93 sample
Cresol	200,000	<1,250	<1,250
2,4-Dichlorophenoxy acetic acid (2,4-D)[a]	10,000	NA[b]	NA
1,4-Dichlorobenzene	7,500	<25	<25
1,2-Dichloroethane	500	<25	<25
1,1-Dichloroethylene	700	<25	<25
2,4-Dinitrotoluene	130	<0.3	<0.3
Endrin[a]	20	NA	NA
Heptachlor[a]	8	NA	NA
Organics analysis	Concentration (µg/L)		
Hexachlorobenzene	130	<0.3	<0.3
Hexachlorobutadiene	500	<50	<50
Hexachloroethane	3,000	<50	<50
Lindane[a]	400	NA	NA
Methoxychlor[a]	10,000	NA	NA
Methyl ethyl ketone	200,000	<100	<100
Nitrobenzene	2,000	<100	<100
Pentachlorophenol	100,000	<1,250	<1,250
Pyridine	5,000	<1,000	<1,000
Tetrachloroethylene	700	<25	<25
Toxaphene[a]	500	NA	NA
Trichloroethylene	500	<25	<25
2,4,5-Trichlorophenol	400,000	<1,250	<1,250
2,4,6-Trichlorophenol	2,000	<1,250	<1,250
2,4,5-Trichlorophenoxy-propionic acid (Silvex)[a]	1,000	NA	NA
Vinyl chloride	200	<50	<50

[a]These pesticides were not analyzed at ORNL due to limitations in analytical capability. They were analyzed by CompuChem Lab and were below the reporting limit.
[b]NA = not analyzed.

Table 12. Results of TCLP analysis of filter media, ion-exchange resin, and activated carbon

TCLP constituent	RCRA limit	Ion-exchange resin 6/24/93	Filter media 6/24/93	Activated carbon 6/24/93
Metals analysis	Concentration (mg/L)			
Arsenic	5.0	<0.05	0.089	<0.05
Barium	100	14	25	0.53
Cadmium	1.0	<0.005	<0.005	0.0087
Chromium	5.0	0.024	0.020	0.014
Lead	5.0	<0.05	0.052	<0.050
Mercury	0.2	0.000051	0.00024	0.000056
Selenium	1.0	0.11	0.13	<0.05
Silver	5.0	<0.005	0.014	<0.005
Organics analysis[a]				

[a]The organic analysis results have not yet been received from ORNL, but CompuChem Lab found that all organic and pesticide results for these samples were below the reporting limit.

5. SUMMARY AND CONCLUSIONS

The ORNL Environmental Restoration Program is currently planning closure activities for WAG 6, which includes SWSA 6. Closure activities may generate wastewaters that will require treatment before discharge to the environment. It has been proposed that these wastewaters be collected, transported, and treated at the ORNL process wastewater treatment facilities for removal of contaminants before discharge to White Oak Creek. A pilot plant was designed and constructed to simulate the unit operations of the ORNL PWTP and NRWTP. WAG 6 wastewater, spiked with the maximum concentrations of TCLP contaminants detected in any ORNL groundwater samples, was processed through this pilot plant to verify that the full-scale facilities could adequately treat these wastes without causing the secondary solid wastes to become RCRA hazardous. A total of 850 L of spiked WAG 6 wastewater was processed through the pilot plant during a 59-d test program. The test system adequately simulated the ORNL treatment facilities and demonstrated that WAG 6 wastewater, and other ORNL groundwaters, could be treated at these facilities to meet the existing NPDES discharge limits. Results of the TCLP analysis indicate that the treatment of WAG 6 trench waters will not change the regulatory status of the secondary solid wastes produced by the PWTP and NRWTP.

REFERENCES

EPA (U.S. Environmental Protection Agency). 1986. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, Third Edition, U.S. EPA Office of Solid Waste and Emergency Response, Washington, D.C.

Kent, T. E., and P. A. Taylor. 1992. *Characterization of Secondary Solid Waste Anticipated from the Treatment of Trench Water from Waste Area Grouping 6 at Oak Ridge National Laboratory, Oak Ridge, Tennessee*, ORNL/ER-122, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kent, T. E., and P. A. Taylor. 1992. *Design Report on the Test System Used to Assess Treatment of Trench Water from WAG 6 at Oak Ridge National Laboratory, Oak Ridge, Tennessee*, ORNL/ER-136, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Solomon, D. K., R. C. Haese, T. V. Dinsmore, and A. D. Kelmers. 1988. *Sampling and Analysis of SWSA 6 Trench Leachates and Groundwater*, ORNL/TM-10813, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Taylor, P. A. 1991. *Treatability Study for WAG 6 (SWSA 6) Trench Water*, ORNL/ER-17, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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