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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

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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, can be treated adequately by existing wastewater treatment facilities at Oak Ridge National Laboratory (ORNL) without producing hazardous secondary solid wastes. Previous bench-scale treatability studies indicated that ORNL treatment operations will adequately remove the contaminants although additional study was required in order to characterize the secondary waste materials produced as a result of the treatment. A 0.5-L/min pilot plant was designed and constructed to accurately simulate the treatment capabilities of ORNL full-scale (490 L/min) treatment facilities--the Process Waste Treatment Plant (PWTP) and Nonradiological Wastewater Treatment Plant (NRWTP). This new test system was able to produce secondary wastes in the quantities necessary for U.S. Environmental Protection Agency toxicity characteristic leaching procedure (TCLP) testing. The test system was operated for a 45-d test period with a minimum of problems and downtime. The pilot plant operating data verified that the WAG 6 trench waters can be treated at the PWTP and NRWTP to meet the discharge limits. The results of TCLP testing indicate that none of the secondary solid wastes 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 disposal of solid waste contaminated or potentially contaminated with radioactive and hazardous compounds. The Oak Ridge National Laboratory (ORNL) Environmental Restoration (ER) Program is examining methods for final closure of WAG 6. Plans are currently being prepared for closure of the disposal area by 1997. It is possible that the closure work will require that the waste disposal trenches be dewatered, so a method for disposing of this water is needed. Extensive characterization data are available for the trench water.[1,2] It has been proposed that these wastewaters be treated at the existing ORNL process wastewater treatment facilities.

This study was undertaken in support of the WAG 6 Record of Decision to evaluate wastewater treatment options for waste generated during the closure project. A 0.5-L/min pilot plant was designed, constructed, and operated to (1) verify the results of bench-scale tests[2] that indicated that WAG 6 trench waters could be treated to discharge limits in existing ORNL wastewater treatment systems, and (2) verify that secondary solid wastes produced at these facilities would not be considered hazardous [as defined by the Resource Conservation and Recovery Act (RCRA)] as a result of the treatment of the WAG 6 wastewater. This report describes the design of the pilot plant and the results of the treatability study.

1.1 ORNL WASTEWATER TREATMENT FACILITIES

The facilities used to remove pollutants from ORNL process wastewater include two facilities, the Process Waste Treatment Plant (PWTP) and the Nonradiological Wastewater Treatment Plant (NRWTP). The PWTP collects and treats wastewaters for removal of radioactive ^{90}Sr and ^{137}Cs. The principal contaminant, ^{90}Sr, is usually present in the wastewater at concentrations between 500 and 1000 Bq/L. Also present in the waste stream is ^{137}Cs, although the concentration is typically below regulatory concern. DOE Order 5400.5[3] limits discharges of ^{137}Cs to 111 Bq/L and discharges of ^{90}Sr to 37 Bq/L. The PWTP uses a combination of alkaline precipitation and ion exchange to remove ^{90}Sr (Fig. 1.1). 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 removed periodically from the bottom of the 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 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 ion-exchange columns downstream of the filters 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.

The PWTP effluent flows to a pumping station and is then transferred to the NRWTP. The PWTP effluent stream is received at the NRWTP nonmetals equalization tank where

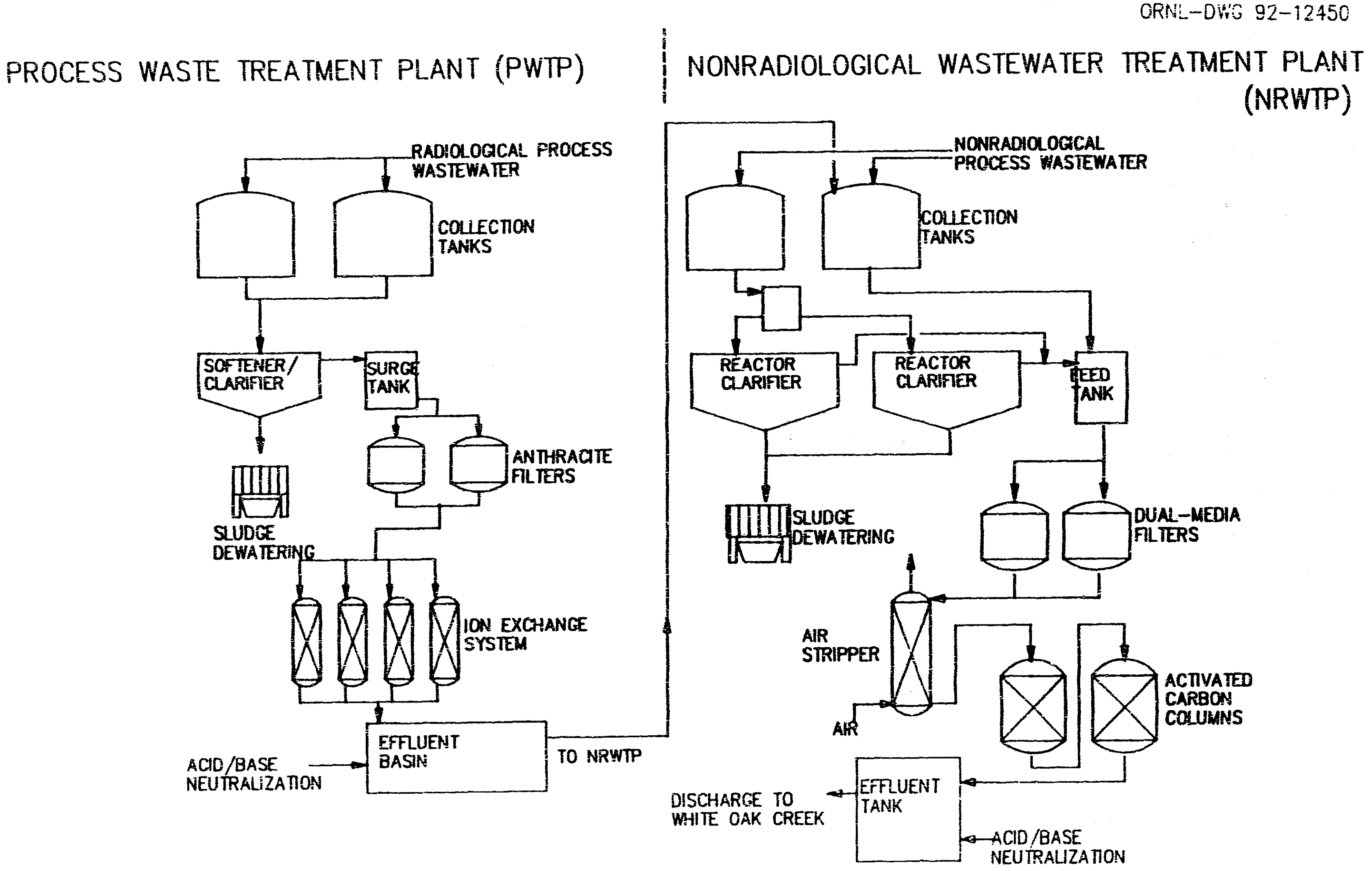

Fig. 1.1. Flow diagram of ORNL process wastewater treatment systems.

it combines with other nonradiological process wastewaters for a total average flow of 122 L/min. The wastewater is pumped through granular media filters to the air stripper. 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 the granular activated carbon (GAC) columns. The wastewater flows through two GAC columns in series and on to the effluent tank. The pH of the wastewater is adjusted as necessary in the effluent tank before final discharge to White Oak Creek. A flow diagram of the existing PWTP and NRWTP is given in Fig. 1.1.

1.2 PREVIOUS SAMPLING RESULTS

Analytical results for WAG 6 trench water are available from three previous sampling programs, including Solomon, et al. in 1986–1987,[1] B. P. Spalding in 1989 (data published in an appendix to ORNL/ER-17[2]), and Taylor in 1990.[2] Water from 23 trenches, about 5% of the total number of trenches in WAG 6, 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. Table 1.1 shows the ranges of concentrations of various contaminants for all of the trenches sampled, and Table 1.2 shows the various results for trenches T-13 and T-288, which were used to supply the water for the current treatment assessment. None of the samples showed significant concentrations of heavy metals, and only a few trenches showed significant concentrations of radionuclides, except for tritium, which was ubiquitous.

Table 1.1. Range of concentrations of radioactive contaminants in WAG 6 trench water

Contaminant	Concentration range for indicated sampling program			
	Units	1986–87[a]	1989[b]	1990[c]
^{3}H	Bq/L	310–340,000	32–11,000	180–16,000
^{90}Sr	Bq/L	0–3600	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

[a] D. K. Solomon, R. C. Haese, R. B. Dinsmore, and A. D. Kelmers, *Sampling and Analysis of SWSA 6 Trench Leachates and Groundwaters*, ORNL/TM-10813, Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 1988.

[b] B. P. Spalding (data published in an appendix to P. A. Taylor, *Treatability Study for WAG 6 (SWSA 6) Trench Water*, ORNL/ER-17, Oak Ridge, Tennessee, August 1991).

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

Table 1.2. Organic contaminants in trenches T-13 and T-288

Contaminant	Contaminant concentration (mg/L)				
	Trench T-13[a]		Trench T-288		
	1989	1990	1986–87	1989	1990
Acetone	0.14	0.18	<0.01	<0.01	0.2
Ethylbenzene	7.8	3.3	0.72	<0.01	<0.01
Toluene	4.3	6.7	1.9	0.18	0.18
Xylene	51.0	26.0	<0.01	0.50	0.42
Naphthalene	<0.01	1.4	1.7	0.06	0.02
4-Methylphenol	1.4	1.4	<0.01	0.02	<0.01

[a] Trench T-13 was not sampled in 1986-87.

1.3 PREVIOUS BENCH-SCALE TREATABILITY TEST RESULTS

Water from four trenches in WAG 6 was used for the bench-scale treatability tests. The trench water was treated full strength rather than diluted with process water as it would be at the full-scale treatment facilities.

The water-softening process used at the PWTP was performed in batch mode using a 2-L glass beaker. A small ion-exchange column (1.6 cm ID by 20 cm high) filled to a height of 6.5 cm with 13 mL of HCR-S resin was used to model the ion-exchange columns at the PWTP.

A bench-scale air stripper (8 cm ID by 60 cm high) filled to a height of 35 cm with ceramic saddles (0.6 cm) was constructed. A distributor screen and a packing support were fabricated from stainless steel screen. This air stripper provided a capacity equal to about 75% of a single net transfer unit at the NRWTP (the air stripper at the NRWTP has nine net transfer units). A water flow rate of 0.5 L/min and an air flow rate of 20 L/min were used for the air stripper. Data on the design and performance of this air stripper were later used in designing the larger-scale test system air stripper with nine net transfer units.

A 9.5-cm-ID column filled to a height of 28 cm with 2 L of GAC (Cecarbon GAC-30, Atochem, Inc.) was used to model the carbon columns in the NRWTP. All of the columns used in the treatability tests had the same aspect ratio (height to diameter ratio) as the corresponding columns in the full-scale treatment plants, and the flow rates for the laboratory units were chosen so that the contact time between the water and the treatment media (ion-exchange resin or activated carbon) was the same as for the full-scale units.

The precipitation and ion exchange tests reduced the ^{90}Sr concentration in T-41 trench water from 260 Bq/L to 0.2 Bq/L, indicating that the trench water did not contain any chelating agents that would interfere with ^{90}Sr treatment.

The laboratory-scale air stripper removed an average of 50% of the volatile organics (mostly toluene and xylene) from three different trench waters, compared with 68% from pure water. These tests showed that something in the trench water interfered slightly with air stripping. The activated carbon column removed all of the remaining organics from the trench water.

The discharge limits for process wastewater are established in the existing National Pollutant Discharge Elimination System (NPDES) permit and are based on the best available technology for the metal finishing industries. The levels of heavy metal contaminants in the WAG 6 trench water were much lower than allowable discharge limits based on the total toxic organic (TTO) limit of 2.13 mg/L given in the permit. After air stripping and activated carbon treatment, however, the organic contaminants were reduced to levels well below the TTO limit. A new permit is currently being negotiated and will likely be based on Tennessee water quality criteria, which are far more restrictive than the existing permit. Ethyl benzene and toluene are specifically limited by the water quality criteria at levels of 3.28 mg/L and 424 mg/L respectively for recreational water usage. Based on the test results, these limits could easily be met.

Bench-scale treatability testing[2] indicated that the ORNL treatment facilities could remove adequately the radioactive and organic contaminants from WAG 6 wastewaters. However, the bench testing could not produce enough secondary solid wastes to determine if the wastes would be hazardous by RCRA definition. A larger scale test system was built and operated to produce the amount of secondary solid waste required for the TCLP analysis used to determine whether these solids would be hazardous by RCRA definition.

2. TEST SYSTEM DESCRIPTION

The pilot-scale test system was designed to simulate the PWTP and NRWTP operations so that 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 could be produced in a reasonable time and so that the system vessels and equipment would be "off-the-shelf" and easy to procure. Stainless steel was chosen for use in construction of the transfer lines and most of the process vessels because of its corrosion resistance and availability. The columns used for filtration, ion-exchange, air stripping, and activated carbon were constructed of clear polyvinyl chloride (PVC) with flanged heads of gray PVC. The clear PVC allows visual observation of the materials in the columns. The accumulation of solids on filtering surfaces, the expanded height of the materials during backwashing, and the extent of algae accumulation can all be observed. PVC is also corrosion resistant for this application. The transfer pumps are the peristaltic type, which are positive displacement, self-priming, and easy to calibrate, and they 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 shutdown 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 adjacent to the PWTP. The trailer was equipped with a high-efficiency particulate air filtered ventilation system and with all other necessary safety and fire protection systems.

A flow diagram of the test system is shown in Fig. 2.1. 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 wastewater and WAG 6 wastewater. Wastewater 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 waste 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 removed periodically 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 mixed 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, which is routed to the PWTP sump for recycling to the PWTP feed tanks. Further detailed design information for the test system is available in ORNL/ER-136.[4]

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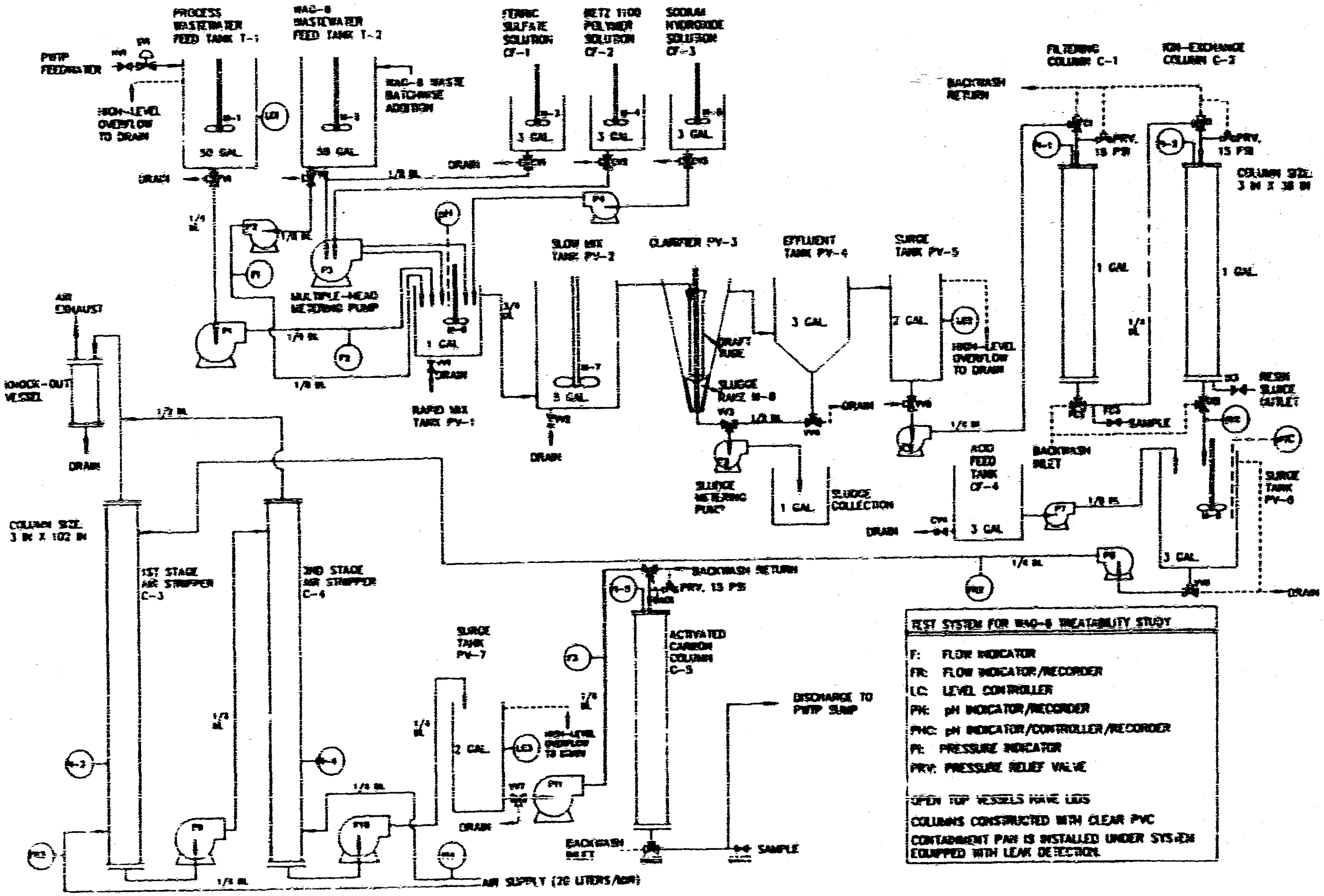

Fig. 2.1. Flow diagram of WAG 6 treatability assessment flow system.

3. TEST SYSTEM OPERATION

3.1 GENERAL PERFORMANCE

The test system began operation on May 4, 1992, and continued through June 18, 1992, without significant downtime. Only minor problems that typically resulted in less than 1 h of downtime were encountered. During the first 5 d of operation, the system was monitored by laboratory technicians for 24 h/d; then the monitoring was reduced to 16 h/d, 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. Process wastewater from the PWTP feed pipeline was routed to drum T-2. A solenoid valve connected to a float-type level switch was used to maintain a volume of about 40 gal in the drum. Through the use of a peristaltic pump, a 500 mL/min flow of process wastewater was fed from T-2 to the rapid-mix vessel, PV-1. Wastewater from the SWSA trenches was collected in 20- to 25-gal quantities in a 30-gal stainless steel drum, transported by pickup truck to the trailer site, and transferred to T-1. From T-1, the trench water was metered at a rate of 8 mL/min to the rapid-mix vessel, PV-1, to simulate the overall average addition of 3000 gal/d expected in full-scale operations. The two wastewaters combined in vessel PV-1, where dilute NaOH, ferric sulfate, and flocculating agent were also added in the first step of the wastewater softening operation. Some difficulty was encountered during the first several days with the variable area flow meters for the two wastewater feeds. Suspended solids in both wastes tended to accumulate and plug the flow meters. The rotometers were cleaned; however, they continued to plug after short run times. It was decided to bypass the rotometers and depend on a downstream magnetic flow meter and periodic volumetric flow checks to ensure continuous and accurate flows. Fig. 3.1 shows the feed wastewater flow rate vs time for the test. The average process wastewater flow during the test was 504 mL/min. The smaller diameter trench water feed line also became plugged, and a periodic 1.5-gal batch addition of the trench water directly to the process wastewater drum T-2 was initiated on May 9. The batch addition adequately simulated the full-scale addition of 3000- to 4000-gal batches of trench water to the process waste feed tanks, which typically maintain an operating level of 100,000 gal. This procedure was used for the remaining 45 d of the test. A total of 31,950 L of process wastewater and 503 L of trench water was treated during the test program.

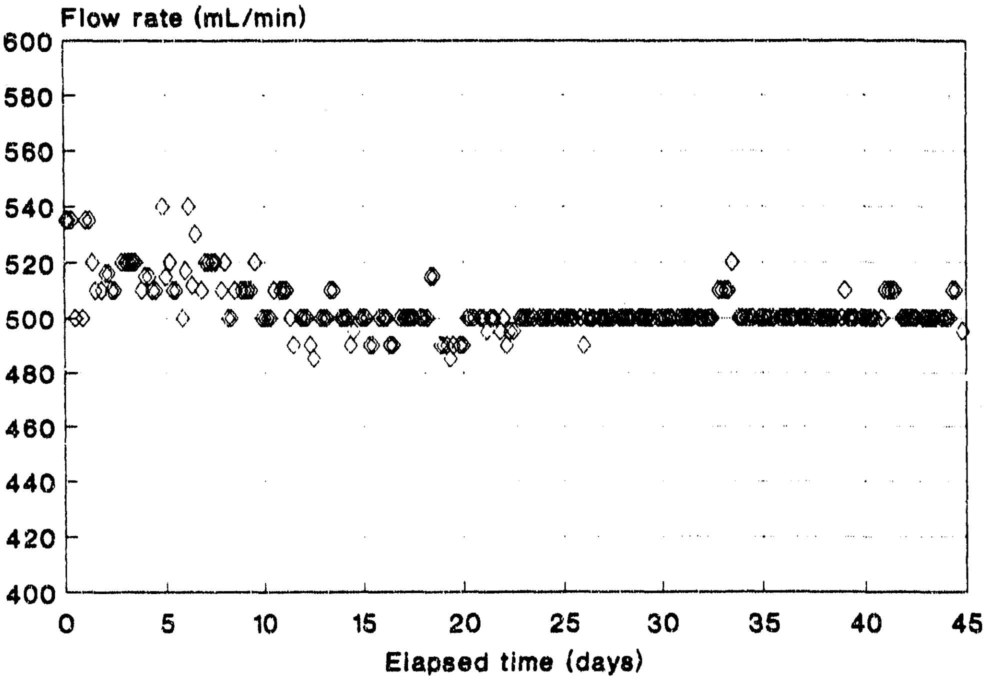

Fig. 3.1. Process wastewater feed flow rate.

SWSA 6 trench water and the combined trench water/process wastewater mixture were sampled during the test program and analyzed for organics, metals, and radionuclides. Samples from each batch of trench water and periodic samples of the combined wastewater feed were taken and submitted to the ORNL Analytical Chemistry Division for analysis. Table 3.1 is a list of the volatile and semivolatile organic compounds analyzed for. Only those that were detected are given in the compiled sample results. As shown in Tables 3.2-3.4, the trench water contaminants detected in the highest concentrations include naphthalene, toluene, xylene, 4-methylphenol, 2,4-dimethylphenol, ethylbenzene, and unknown phenol derivatives; heavy metals and radionuclides were not detected in significant quantities. In the combined wastewater samples, small quantities of xylene, naphthalene, toluene, lead, and mercury were detected. Though the contaminants were low in concentration or undetected, they could potentially concentrate in secondary solid wastes, resulting in wastes characterized as hazardous by RCRA. Analyses for radioactive contaminants indicated very low concentrations in the trench waters and typical gross beta and ^{137}Cs levels contributed by the process wastewater in the combined wastewater feed samples.

Table 3.1. 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
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
		Anthracene	10
		Di-*n*-butylphthalate	10
Semivolatile Organics		Fluoranthene	10
		Pyrene	10
1,2,4-Trichlorobenzene	10	Butylbenzylphthalate	10
Naphthalene	10	3,3'-Dichlorobenzidine	20
4-Chloroaniline	10	Benzo[a]anthracene	10
Hexachlorobutadiene	10	Chrysene	10
4-Chloro-3-methylphenol	10	Bis(2-ethylhexyl)phthalate	10
2-Methylnaphthalene	10	Di-n-octylphthalate	10
Hexachlorocyclopentadiene	10	Benzo[b]fluoranthene	10
2,4,6-Trichlorophenol	10	Benzo[k]fluoranthene	10
2,4,5-Trichlorophenol	50	Benzo[a]pyrene	10
2-Chloronaphthalene	10	Indeno(1,2,3-cd)pyrene	10
2-Nitroaniline	50	Dibenzo[a,h]anthracene	10
Dimethyphthalate	10	Benzo[g,h,i]perylene	10
Acenaphthylene	10		
2,6-Dinitrotoluene	10		
3-Nitroaniline	50		

Table 3.2. Wastewater feed characterization data: semivolatile and volatile organics

Compound	T-13 trench water 5/4/92	T-288 trench water 5/19/92	T-13 trench water, 6/2/92	T-13 trench water, 6/16/92	Combined wastewater feed 5/5/92	Combined wastewater feed 5/19/92
Semivolatile organic analysis results, µg/L						
2,4-Dimethylphenol	120	7	17	40	[a]	
2-Methylphenol		2^J				
4-Methylphenol	130		2^J			
Naphthalene	560				13	
2-Methylnaphthalene	3^J					
Butylbenzylphthalate		1^J			2^J	2^J
Bis(2-	23	6^J	2^J	12		
ethylhexyl)phthalate	2^J					
Di-*n*-octylphthalate			8^J			
Ethanol derivatives	536^J		6^J		13^J	
Benzene derivatives	471^J	435^J	145^J	13^J		5^J
Phenol derivatives	863^J	412^J	166^J	465^J		
Unknowns						
Volatile organic analysis results, µg/L						
Acetone	13^B		40^J			
Toluene	560^Y	73	13^J		6	
Xylene	7300^Y	53	575		69	
Chloroform					5^J	
Benzene	18					
Tetrachloroethene	2^J					
Carbon disulfide	5^J					
Ethylbenzene	110					
Naphthalene			900^J		43^J	
Unknowns		62^J	162^J		22^J	
Total organic carbon, mg/L	78.0	30.0	NA[b]	52.5	4.7	2.0

[a] Where a result is not entered, the compound was not detected.

[b] NA: not analyzed

Key to qualifiers:

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

"B" indicates that the compound was detected in both the sample and the associated blank.

"Y" indicates that the concentration of the compound initially exceeded the calibration range of the instrument, but was diluted and reanalyzed to quantify the reported result.

Table 3.3. Wastewater feed characterization data: metals

Compound		T-13 trench water, 5/4/92	T-288 trench water, 5/19/92	T-13 trench water, 6/16/92	Combined wastewater feed, 5/5/92	Combined wastewater feed, 5/19/92
Metal	**DL**[a]	**Total metals, mg/L**				
Ag	0.005	*b*				
Al	0.05	0.16	0.23	0.3	1.6	0.074
As	0.05					
B	0.08					
Ba	0.001	0.26		0.41	0.065	0.032
Be	0.001					
Ca	0.01	100	97	97	55	46
Cd	0.005			0.0054		
Co	0.004	0.012				
Cr	0.004			0.011	0.019	
Cu	0.005	0.13	0.051	0.07	0.27	0.018
Fe	0.01	60	23	47	2.5	0.94
Hg	5E-05	0.00017		0.00002	0.0037	
Li	15					
Mg	0.03	22	18	24	34	9.7
Mn	0.001	8.3	6.5	4.4	0.29	0.098
Mo	0.04					
Na	0.03	5.2			38	15
Ni	0.004	0.0069		0.0098	0.71	0.0063
P	0.1	1.6		0.31	5.0	0.34
Pb	0.03				0.069	
Sb	0.05					
Se	0.04			0.098		
Si	0.05	9.6	4.4	10	13	2.7
Sn	0.05			0.071		
Sr	0.005	0.17	0.13	0.21	0.13	0.11
Ti	0.02					
V	0.002	0.0063	0.0026			
Zn	0.005	0.59	0.14	4.6	1.0	0.098
Zr	0.02					

[a] DL: detection limit, mg/L

[b] Where a result is not entered, the compound was not detected.

Table 3.4. Wastewater feed characterization data: radionuclides

Compound	T-13 trench water, 5/4/92	T-288 trench water, 5/19/92	T-13 trench water, 6/2/92	T-13 trench water, 6/16/92	Combined wastewater feed, 5/5/92	Combined wastewater feed, 5/19/92
	Radionuclides, Bq/L					
Gross alpha	0.09 ±0.34	0.058 ±0.07	Not analyzed	-0.42 ±0.46	6.3 ±2.4	4.8 ±0.5
Gross beta	0.5 ±1.5	2.7 ±0.3	1.4 ±1.3	4.2 ±2.8	680 ±20	660 ±10
Co-60	-0.5 ±2.7	-0.4 ±1.3	0.31 ±0.15	0.4 ±1.3	4.2 ±1.0	2.5 ±1.0
Cs-137	0.2 ±2.3	1.5 ±0.8	0.45 ±0.13	5.0 ±1.2	140 ±10	280 ±10
Eu-152	*a*				14 ±5	11 ±5
Eu-154					8.8 ±4.7	
Eu-155					3.7 ±2.2	

[a] Where a result is not entered, the compound was not detected.

3.3 SOFTENING AND CLARIFICATION OPERATIONS

The softening and clarification operation of the system 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. The purpose of this operation was to remove cations that would otherwise interfere with the ion-exchange removal of radioactive ^{90}Sr. 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 continuously, using an in-line pH electrode and recorder. Every 4 h, the pH was verified by sampling and checking with a bench-top pH meter. The rapid-mix tank flowed by gravity to the slow-mix tank, PV-2, which provided time for the softening reaction and for flocculation of precipitates. PV-2 flowed by gravity to the clarifier, where separation of the flocculated precipitates was accomplished. The wastewater and suspended precipitates entered the draft tube of the clarifier, which directed the flow to the bottom of the conical 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 carryover 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 Building 3541 for dewatering by vacuum filtration. The dewatered sludge sample was then submitted for TCLP analysis.

The softening and clarification systems performed well and adequately simulated the PWTP full-scale operations; pH control for the softening reaction compared well with that experienced at the PWTP during the same time period. Figure 3.2 shows pH profiles for both the test system and the PWTP during the 45-d run. The pH averages about 11.6, with a standard deviation of 0.08 for both the PWTP and test system operation. The feed flow rates of ferric sulfate and polymer solutions were adequate for the treatment and varied between 3.5 and 4.0 mL/min throughout the test program. 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 carryover to PV-4 rarely occurred. The vacuum filtration operation worked well in producing a dewatered sludge "cake" with a solids content comparable 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 to determine the amount of calcium carbonate and other hardness compounds that precipitate during the treatment were performed periodically by test system operators. As shown in Fig. 3.3, the feed wastewater TH

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[*] Trademark of Betz Laboratories, Inc.

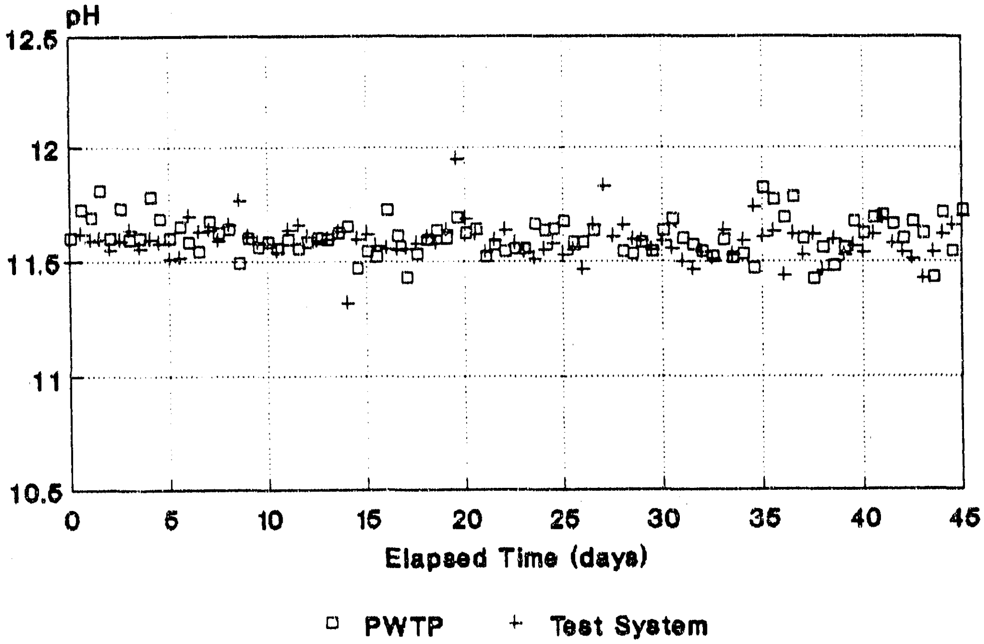

Fig. 3.2. The pH of wastewater during softening.

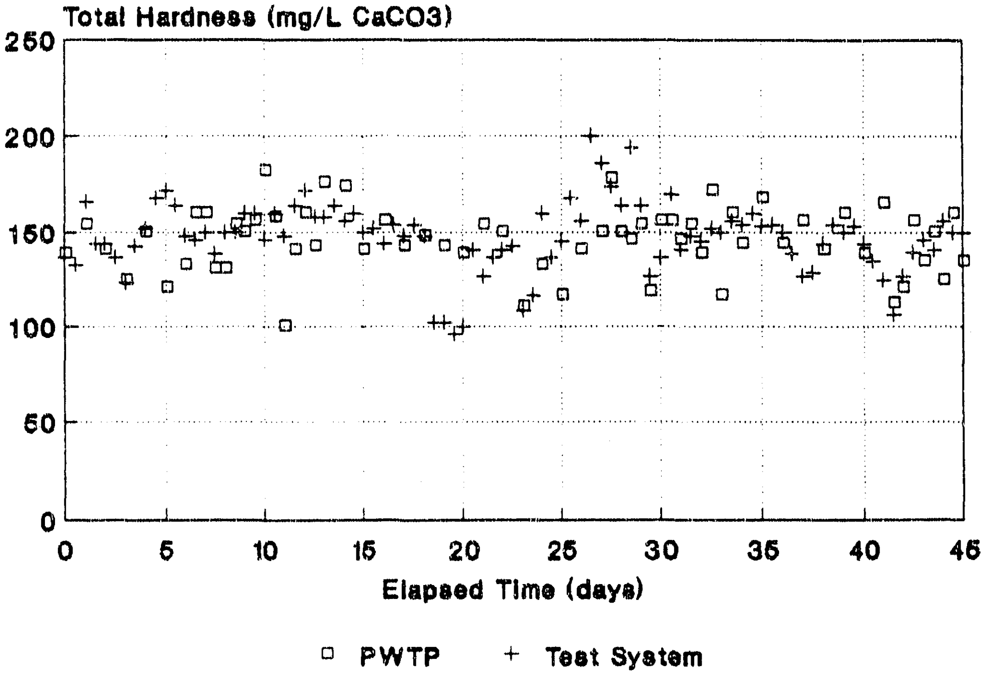

Fig. 3.3. Wastewater feed total hardness concentration.

levels were comparable, with mean concentrations of 145 mg/L for the PWTP and 147 mg/L for the test system. Overall, the TH levels in the test system clarifier effluent were moderately higher than those in the PWTP clarifier effluent because of the slightly longer reaction time and deeper sludge blanket available in the full-scale system (Fig. 3.4). PWTP clarifier effluent TH averaged 26 mg/L, and the test system clarifier effluent averaged 44 mg/L. This factor, however, impacts only the rate of sludge generation and not the resultant sludge composition. Two samples of the clarifier effluent were taken and analyzed for dissolved metals. Table 3.5 compares the dissolved metals in the combined wastewater feed and in the clarifier effluent. As expected, the levels of calcium, magnesium, iron, and other heavy metals were lower in the effluent stream, indicating precipitation of the metal carbonates and hydroxide compounds. 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 of the wastewater continue to precipitate onto the filter media after clarification. PWTP and test system filter effluents averaged 13.3 and 17.2 mg/L respectively. As shown in Fig. 3.5, the TH vs time trends are similar for both PWTP and test system filter effluents, particularly near the end of the test program. Accumulation of calcium carbonate onto the granular anthracite was clearly visible in the test system filter column. A total of three samples of sludge from the test system softening operation were collected, dewatered, and submitted for TCLP analysis. For comparison purposes, two additional samples of dewatered sludge were collected from the PWTP and submitted for TCLP analysis.

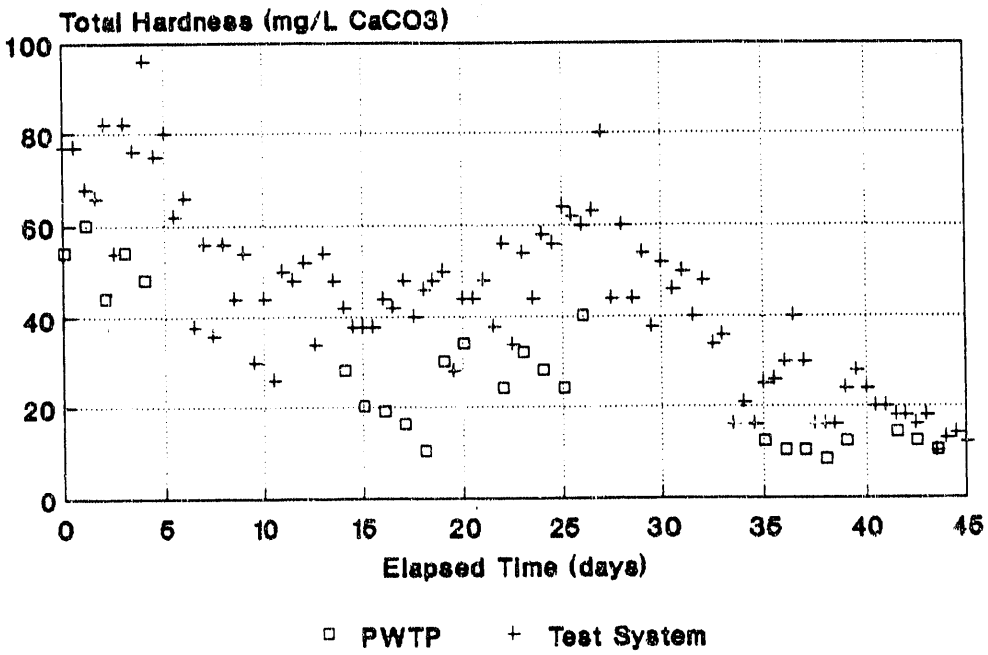

Fig. 3.4. Clarifier effluent total hardness concentration.

Table 3.5. Wastewater dissolved metals during test system softening operation

Metal	Detection limit (mg/L)	Combined wastewater feed, 5/5/92	Clarifier outlet wastewater, 5/5/92	Combined wastewater feed, 5/19/92	Clarifier outlet wastewater, 5/19/92
Ag	0.005	[a]			
Al	0.05	1.6		0.074	
As	0.05				
B	0.08				
Ba	0.001	0.065	0.012	0.032	0.009
Be	0.001				
Ca	0.01	55	31	46	14
Cd	0.005				
Co	0.004				
Cr	0.004	0.019			
Cu	0.005	0.27		0.018	
Fe	0.01	2.5	0.12	0.94	0.14
Hg	5E-05	0.0037		0.0003	0.00005
Li	15				
Mg	0.03	34	1.1	9.7	0.64
Mn	0.001	0.29	0.0029	0.098	
Mo	0.04				
Na	0.03	38	160	15	200
Ni	0.004	0.71	0.004	0.0063	
P	0.1	5.0		0.34	
Pb	0.03	0.069			
Sb	0.05				
Se	0.04				
Si	0.05	13	2.1	2.7	2.2
Sn	0.05				
Sr	0.005	0.13	0.085	0.11	0.051
Ti	0.02				
V	0.002				
Zn	0.005	1.0	0.019	0.098	
Zr	0.02				

[a] Where no result is indicated, the metal was not detected.

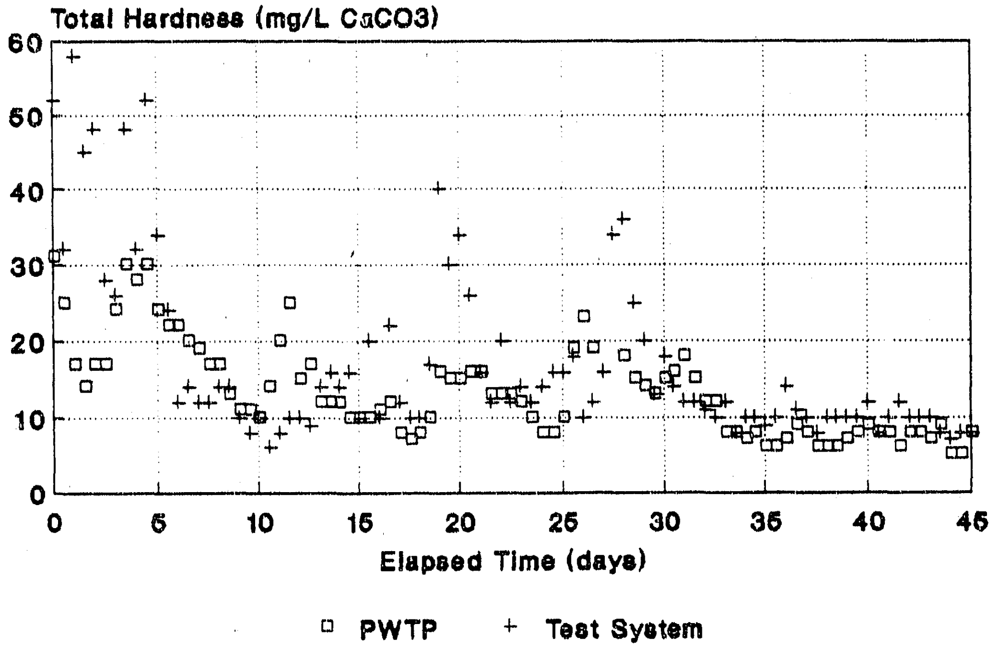

Fig. 3.5. Filter effluent total hardness concentration.

3.4 ION-EXCHANGE PROCESS

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 (DGC) given in DOE Order 5400.5.[3] To remove additional amounts of strontium, ion-exchange treatment at the PWTP uses a strong-acid cation exchange resin, Dowex HCR-S*. In the test system, this treatment is simulated by using 2.5 L of the Dowex HCR-S loaded in an 8-cm (3-in.)-diam, 91-cm (36-in.)-tall column. Prefiltering of the wastewater to remove suspended solids before ion-exchange is performed at the PWTP by using a granular anthracite pressure filter. An 8-cm (3-in.)-diam, 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 during each shift to prevent column plugging. As seen in the PWTP operation, a significant reduction in TH occurs as wastewater is passed through the filter.

The progress of ^{90}Sr loading of the ion-exchange resin closely follows that of the TH loading, thus the TH titration is used to test the column effluent and determine the extent of resin exhaustion. The TH concentration of the ion-exchange system effluent is typically at or below 0.5 mg/L in the PWTP operation. For the test system, the average TH of the

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*Trademark of the Dow Chemical Co.

ion-exchange column effluent was 2.5 mg/L (Fig. 3.6). Though this is somewhat higher than the PWTP ion-exchange effluent levels, gross breakthrough of TH and ^{90}Sr did not occur, and the slightly elevated TH caused no detrimental impacts on downstream air stripping and activated carbon system operations. As shown in Table 3.6, the ion-exchange effluent gross beta and ^{137}Cs concentrations were comparable for the test system and the PWTP ion-exchange operations except for samples taken on May 5. The removal of cesium and its associated beta activity on May 5 resulted from use of fresh ion-exchange resin, which was initially in the hydrogen form. The hydrogen exchange sites on the resin are initially displaced by sodium, the dominant cation in the wastewater. Cesium also displaces hydrogen on the resin until the resin is entirely converted to the sodium form. Cesium breakthrough occurs, as shown in other samples, after all of the hydrogen is displaced and the exchange sites occupied. Calcium, magnesium, and strontium displace the sodium and cesium on the exchange sites as the resin exhausts. The test system was designed so that the resin would exhaust in 7 to 10 d. As part of routine operation, the resin was removed and replaced with freshly regenerated resin every 7 d. To regenerate the resin, it was sluiced from the test system column and transported to a laboratory where it was contacted with 2.7 *N* nitric acid for several hours. A bed volume of freshly regenerated resin was kept on standby to minimize downtime during resin replacement. After removal of the spent resin, the column was immediately reloaded with freshly regenerated resin and the system placed back on-line.

The Dowex HCR-S resin is a very stable product and may be used for several years before resin degradation begins to occur. If the resin is degraded, it is regenerated, unloaded from the column, dewatered, and disposed of as solid low-level waste. This occurs very infrequently at the PWTP, and there is currently no available data indicating RCRA characteristics of the degraded resin. Although there is no comparison data available, a sample of the test system regenerated resin was submitted for TCLP analysis to determine if any of the contaminants from the SWSA 6 trench water tend to concentrate on the resin matrix.

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 air flows upward through the column. The packing material spreads 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, by Lantec Products, Inc., Agoura Hills, California]. Correlations supplied by the packing manufacturer show that the air stripper should have about nine net transfer units at normal operating conditions. Since 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 laboratory-scale treatability tests[2] 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,

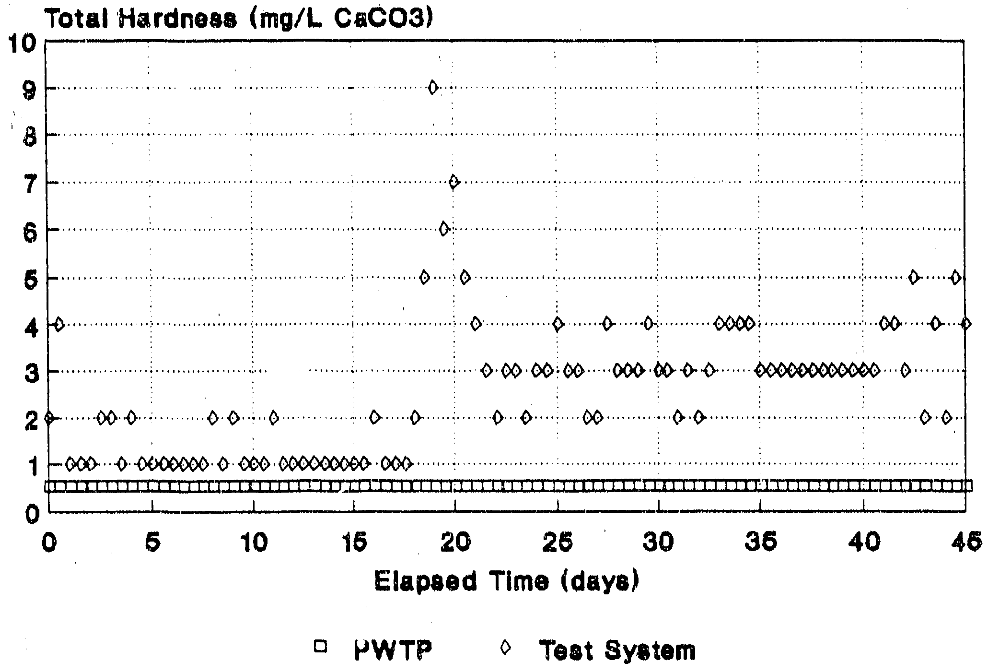

Fig. 3.6. Ion-exchange column effluent total hardness concentration.

Table 3.6. Radionuclide analysis of ion-exchange column effluent wastewater

Radio-nuclide	Ion-exchange effluent, (Bq/L)[a]							
	5/5/92		5/19/92		6/2/92		6/16/92	
	Test system	PWTP[b]	Test system	PWTP	Test system	PWTP	Test system	PWTP
Gross Beta	0.5 ±2.0	90	110 ±10	145	810 ±20	1170	390 ±10	483
^{137}Cs	0.46 ±0.15	92	200 ±10	185	890 ±10	1170	560 ±10	485
^{60}Co	0.3 ±0.13	<10	0.6 ±0.52	<10	0.69 ±0.2	<10	0.7 ±1.9	<10

[a] Since the analysis of ^{90}Sr is complex and time consuming, ion-exchange breakthrough is monitored in the PWTP operation by the total hardness titration and gross beta results. Gross beta concentrations in the above samples are due to the ^{137}Cs also detected in the gamma scan. If the gross beta concentrations are significantly higher than the ^{137}Cs, ^{90}Sr breakthrough is suspected and appropriate actions are taken.

[b] PWTP results are the average of several samples taken from two ion-exchange columns.

will provide the same organic removal as the NRWTP air stripper. The test air stripper consists of two 8-cm (3-in.)-diam columns, each 2.43 m (8 ft) in height and packed with ceramic saddles.

In the test system operation, the ion-exchange column effluent flowed to a mixed-surge vessel, PV-6, used to decrease the pH of the wastewater to a level between 7 and 8. From PV-6, the wastewater was transferred to the first stage of the air stripper. The wastewater entered the top of the first stage air stripper and onto the column packing, where it was dispersed and exposed to an upward-flowing 20-L/min air stream. The wastewater effluent from the first-stage column was transferred to the top of the second-stage column with a peristaltic pump. The effluent from the second stage 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 knockout container to remove any water droplets from the air stream. From the knockout container, the air was routed to the trailer ventilation system exhaust duct, where it was passed through a high efficiency particulate air filter before discharging to the atmosphere.

Prior to tests with actual wastewater, the air stripper was tested with clean process water and later with a sample of process water spiked with 32 mg/L of xylene. During the test with clean process water, water began to accumulate in the air stripper packing section. To eliminate this condition, the air flow into the bottom of the air stripper had to be reduced from 20 L/min to a level of 5 L/min, which reduced the gas-to-liquid ratio to 10:1. This reduced the number of transfer units and likewise the organic removal capacity of the stripper. The removal of xylene during the test using the spiked process water indicated that the stripper provided four transfer units. The reduced number of air stripper transfer units results in additional quantities of volatile organic contaminants being fed to the downstream activated-carbon operation. The additional organics removed by the activated carbon increases the likelihood that the carbon will contain RCRA hazardous constituents. After the test program, the air stripper problem was investigated and found to be caused by the packing support plate in the bottom of the air stripper. The size of the openings in the support plate were too small to allow free flow of both air and wastewater.

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 that the mixing characteristics of the vessel remain constant, with a minimum of level variation. To ensure good pH control, it was decided in the design plan to control the level by providing a simple overflow line. The flow into PV-6 was adjusted manually to a value slightly higher than the flow out of PV-6 to the air stripper, thus placing the vessel in constant overflow to the test system drain. Figure 3.7 shows the flow profile for wastewater entering the air stripper. The average wastewater flow through the air stripper was 453 mL/min. Figure 3.7 also shows a trend of steadily decreasing flow for the first 15 d of the test program. The flow profile for the air stripper feed is slightly lower than that for the wastewater feed and follows the same trend—that is, it decreases somewhat during the first 2 weeks of the test (Fig. 3.1). The decreasing trend is the result of manual adjustment error, drift in the pump speed control, and variation in flowmeter readings. Based on the average flow of wastewater feed (504 mL/min) and air stripper feed (453 mL/min), the targeted overflow rate for PV-6, about 50 mL/min, was achieved adequately. This system performed well during most of the test program, as indicated by the pH profile shown in Fig. 3.8. The

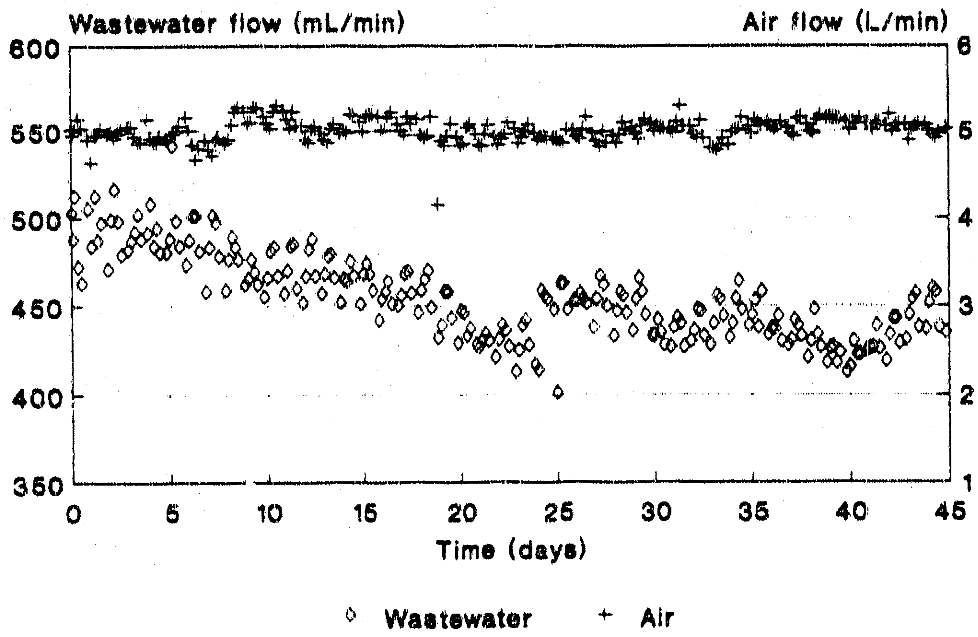

Fig. 3.7. Test system air stripper waste water and air flows.

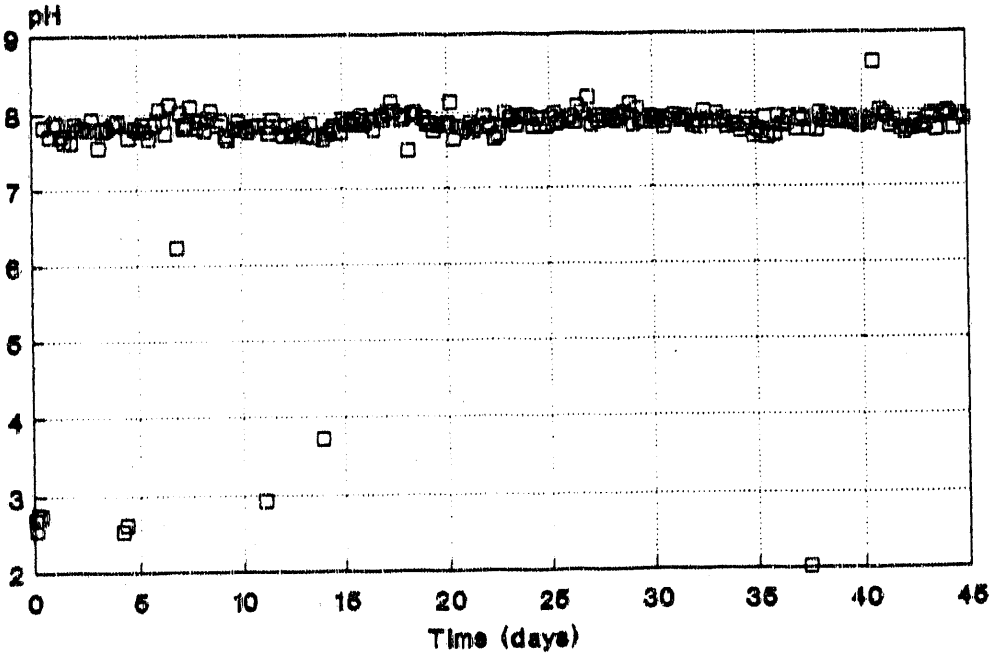

Fig. 3.8. Air stripper wastewater pH.

average pH for the test program was 7.64. There were several short-lived occasions when the pH was significantly lower than specified, however. This was caused by the replacement of spent ion-exchange resin with fresh resin supplied in the acid or H^+ form. When the resin is initially placed in service, the H^+ ions are replaced by Na^+ ions that are then displaced by divalent cations such as calcium, magnesium, and strontium. The displaced H^+ ions cause the acidic wastewater pH to prevail until the resin is converted to the Na^+ form. After the experience with the initial batch of resin, subsequent pH excursions were minimized by converting the resin to the sodium form in the laboratory before loading the regenerated resin into the column. The low pH is not expected to have had significant detrimental effects on the air stripping or activated carbon operations.

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 5 L/min. Figure 3.7 shows a profile of air flow as a function of time. The average air flow for the test program was 5.01 L/min.

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. In only two cases were any measurable levels of organics detected. The results of these two samplings are compiled in Table 3.7 and indicate that only extremely low levels of organics existed in both feed and effluent samples. The samples taken on May 5 indicate removal of xylene from 60 μg/L to the detection limit of 5μg/L and also the removal of some 19 μg/L of unknown volatiles. The samples taken on June 16 indicate only slight removal of acetone from 19 to 15 μg/L. This data is insufficient for quantitative evaluation of the air stripper performance.

Table 3.7. Organic content of air stripper inlet and outlet wastewater

	Air stripper samples, 5/5/92 (μg/L)		Air stripper samples, 6/16/92 (μg/L)	
Compound	Inlet	Outlet	Inlet	Outlet
Chloroform	5^{J}	*a*	3^{J}	
Toluene	6			
Xylene	60			
Naphthalene	9^{J}	7^{J}		
Unknowns	19^{J}			
Acetone			19	15
4-Methylphenol	1^{J}	2^{J}		
Benzene derivative	11^{J}	10^{J}		

[a] Where a result is not given, the compound was not detected.

Key to qualifier: "J" indicates that the quantitative value is estimated. This qualifier usually appears after a value which is below the quantitation limit or after a value given for a tentatively identified compound.

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 the 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 GAC system consists of a surge vessel, a metering pump, and a 15-cm (6-in.)-diam, 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 is necessary to perform the U.S. Environmental Protection Agency (EPA) TCLP test. In the case of the carbon waste from the GAC system, it will be 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 30 months, has not been replaced to date. Though the sorption capacity of activated carbon varies widely, a carbon that will remove 10% of its weight of an organic contaminant would be considered adequate for wastewater treatment. In the initial planning of the test program, it was assumed that 100 g of 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 is 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 45 d was chosen. At termination of the test, two 200-ml samples (approximately 100 g each) of activated carbon were to be removed from the top surface of the carbon bed for the TCLP testing. The GAC column carbon bed was not backwashed or otherwise disturbed during the test period.

During the test program, GAC column inlet and outlet samples were collected and analyzed for semivolatile organics (SVO) and total organic carbon (TOC). The results shown in Table 3.8 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 about 1.0 mg/L TOC during the test program. With a total throughput of 29,218 L, about 29 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 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 3.8. Organic content of GAC column inlet and outlet wastewater

Date	Organic compound	GAC column samples	
		Inlet	Outlet
5/5/92	4-Methylphenol, μg/L	2^{J}	[a]
	Naphthalene, μg/L	7^{J}	
	Benzene derivative, μg/L	10^{J}	7^{J}
	TOC, mg/L	3.2	2.2
5/19/92	TOC, mg/L	1.4	0.6
6/2/92	TOC, mg/L	2.7	1.3
6/16/92	TOC, mg/L	1.45	0.6

[a] Where a result is not given, the compound was not detected.

Key to qualifier: "J" indicates that the quantitative value is estimated. This qualifier usually appears after a value which is below the quantitation limit or after a value given for a tentatively identified compound.

4. SECONDARY WASTE TCLP RESULTS

Nine samples of secondary solid wastes were submitted for TCLP analysis during the test program. The protocol given in Method 1311 in Appendix II of 40 CFR 261.[5] Five of the samples are sludge cake samples: three from the test system and two from the PWTP. One sample each of the anthracite filter media, ion-exchange resin, and activated carbon taken from the test system were also submitted. TCLP data for the anthracite and ion-exchange resin at the PWTP were not available for comparison with pilot plant data. A sample of activated carbon taken from an NRWTP GAC column in January 1992 was submitted for TCLP metals analysis in July 1992. Total semivolatile organic and pesticide analyses (no leach performed) were performed on the sample in January within recommended sample hold times. The results of the NRWTP carbon sample were used for a qualitative comparison with the pilot plant carbon. The manner in which the samples were handled during the analyses was determined by the radiochemical nature of the material. The sludge samples, anthracite filter media, and activated carbon samples were contaminated with ^{90}Sr and ^{137}Cs and were sent to a radiochemical laboratory where special procedures and facilities are provided for handling contaminated materials. The ion-exchange resin, which was not significantly contaminated, was sent to another laboratory where it could be handled as a nonradioactive sample. The results of the analyses are given in Tables 4.1 and 4.2.

The results in Table 4.1 indicate that the concentration of RCRA contaminants in the softener sludge did not change significantly as a result of the trench water treatment. Cadmium, chromium, and silver were detected routinely in the sludge, though the concentrations were far below the RCRA limits. None of the TCLP organic contaminants were detected in the sludges. Though PWTP comparison data are not available for the ion-exchange resin and the anthracite filter media, the levels of TCLP contaminants in these two wastes were extremely low or undetectable (Table 4.2). It is unlikely, therefore, that the future addition of SWSA 6 trench water will increase the RCRA contaminants in either of these wastes to problematic levels. Cadmium and chromium were detected in both activated carbon samples. The levels of these two metals in the NRWTP carbon were significantly higher in concentration, though well below the regulatory limits. Results of many of the TCLP organic compounds for the NRWTP carbon were not available for comparison with the test system carbon analysis. Like the other samples, organic contaminants were not detected in TCLP analysis of the test system activated carbon. None of the four different secondary wastes showed significant concentrations of TCLP contaminants. Based on these results, it is very unlikely that the addition of WAG 6 trench wastewater to the ORNL process waste system will change the regulatory status of the secondary solid wastes.

Table 4.1. Results of TCLP analysis of sludges from softening operation

TCLP compound	RCRA limit	Test system sludge, 5/6/92	Test system sludge, 5/19/92	Test system sludge, 6/18/92	PWTP sludge, 5/19/92	PWTP sludge, 6/18/92
Metals analysis, mg/kg						
Arsenic	5.0	0.005	<0.002	<0.002	<0.002	<0.002
Barium	100	<100	<100	<100	<100	<100
Cadmium	1.0	0.072	0.045	0.054	0.048	0.052
Chromium	5.0	0.033	0.0073	0.032	0.015	0.033
Lead	5.0	<0.094	<0.09	<0.094	<0.094	<0.094
Mercury	0.2	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Selenium	1.0	<0.002	<0.002	<0.002	<0.002	<0.002
Silver	5.0	0.021	0.015	0.01	0.012	0.0098
Organics analysis, μg/kg						
Benzene	500	<25	<25	<25	<25	<25
Carbon tetrachloride	500	<25	<25	<25	<25	<25
Chlordane	30	<30	<30	<30	<30	<30
Chlorobenzene	100,000	<25	<25	<25	<25	<25
Chloroform	6,000	<25	<25	<25	<25	<25
o-Cresol	200,000	<1,250	<1,250	<1,250	<1,250	<1,250
m-Cresol	200,000	<1,250	<1,250	<1,250	<1,250	<1,250
p-Cresol	200,000	<1,250	<1,250	<1,250	<1,250	<1,250
Cresol	200,000	<1,250	<1,250	<1,250	<1,250	<1,250
2,4-Dichlorophenoxy acetic acid[a]	10,000	NA[b]	NA	NA	NA	NA
1,4-Dichlorobenzene	7,500	<25	<25	<25	<25	<25
1,2-Dichloroethane	500	<25	<25	<25	<25	<25
1,1-Dichloroethylene	700	<25	<25	<25	<25	<25
2,4-Dinitrotoluene	130	<130	<130	<130	<130	<130
Endrin	20	<20	<20	<20	<20	<20
Heptachlor	8	<8	<8	<8	<8	<8
Hexachlorobenzene	130	<130	<130	<130	<130	<130
Hexachlorobutadiene	500	<50	<50	<50	<50	<50
Hexachloroethane	3,000	<50	<50	<50	<50	<50
Lindane	400	<400	<400	<400	<400	<400
Methoxychlor	10,000	<10,000	<10,000	<10,000	<10,000	<10,000
Methyl ethyl ketone	200,000	<100	<100	<100	<100	<100
Nitrobenzene	2,000	<100	<100	<100	<100	<100
Pentachlorophenol	100,000	<1,250	<1,250	<1,250	<1,250	<1,250
Pyridine	5,000	<1000	<1000	<1000	<1000	<1000
Tetrachloroethylene	700	<25	<25	<25	<25	<25
Toxaphene	500	<500	<500	<500	<500	<500
Trichloroethylene	500	<25	<25	<25	<25	<25
2,4,5-Trichlorophenol	400,000	<1,250	<1,250	<1,250	<1,250	<1,250
2,4,6-Trichlorophenol	2,000	<1,250	<1,250	<1,250	<1,250	<1,250
2,4,5-Trichlorophenoxy-propionic acid (Silvex)[a]	1,000	NA	NA	NA	NA	NA
Vinyl chloride	200	<50	<50	<50	<50	<50

[a] These two herbicides were not analyzed due to limitations in analytical capability. Herbicides in general have historically not been detected in SWSA-6 trench water samples, though no data are available for these two compounds. Detection of these compounds in secondary wastes was considered to be extremely unlikely.

[b] NA = not analyzed

Table 4.2. Results of TCLP analysis of filter media, ion-exchange resin, and activated carbon

TCLP compound	RCRA limit	Ion-exchange resin, 5/8/92	Anthracite filter media, 6/18/92	Granular activated carbon, 6/18/92	NRWTP granular activated carbon, 1/10/92
		Metals analysis, mg/kg			
Arsenic	5.0	<0.002	0.003	<0.002	0.005
Barium	100	<100	<100	<100	<100
Cadmium	1.0	<0.004	0.048	0.0055	0.018
Chromium	5.0	<0.005	0.031	0.0056	0.02
Lead	5.0	<0.094	<0.094	<0.094	<0.094
Mercury	0.2	<0.0002	<0.0002	<0.0002	<0.0004
Selenium	1.0	<0.005	0.0029	<0.002	<0.002
Silver	5.0	0.008	0.016	<0.002	0.019
		Organics analysis, μg/kg			
Benzene	500	<25	<25	<25	NA[a]
Carbon tetrachloride	500	<25	<25	<25	NA
Chlordane	30	<30	<30	<30	5.7^{J}
Chlorobenzene	100,000	<25	<25	<25	NA
Chloroform	6,000	<25	<25	<25	NA
o-Cresol	200,000	<1,250	<1,250	<1,250	<2900
m-Cresol	200,000	<1,250	<1,250	<1,250	<590
p-Cresol	200,000	<1,250	<1,250	<1,250	NA
Cresol	200,000	<1,250	<1,250	<1,250	NA
2,4-Dichlorophenoxy acetic acid[b]	10,000	NA	NA	NA	NA
1,4-Dichlorobenzene	7,500	<25	<25	<25	<590
1,2-Dichloroethane	500	<25	<25	<25	NA
1,1-Dichloroethylene	700	<25	<25	<25	NA
2,4-Dinitrotoluene	130	<130	<130	<130	<590
Endrin	20	<20	<20	<20	0.53^{J}
Heptachlor	8	<8	<8	<8	2.67^{J}
Hexachlorobenzene	130	<130	<130	<130	<590
Hexachlorobutadiene	500	<50	<50	<50	<590
Hexachloroethane	3,000	<50	<50	<50	<590
Lindane	400	<400	<400	<400	8.79^{J}
Methoxychlor	10,000	<10,000	<10,000	<10,000	<141
Methyl ethyl ketone	200,000	<100	<100	<100	NA
Nitrobenzene	2,000	<100	<100	<100	<590
Pentachlorophenol	100,000	<1,250	<1,250	<1,250	<2900
Pyridine	5,000	<1000	<1000	<1000	NA
Tetrachloroethylene	700	<25	<25	<25	NA
Toxaphene	500	<500	<500	<500	<282
Trichloroethylene	500	<25	<25	<25	NA
2,4,5-Trichlorophenol	400,000	<1,250	<1,250	<1,250	<2900
2,4,6-trichlorophenol	2,000	<1,250	<1,250	<1,250	<590
2,4,5-Trichlorophenoxy-propionic acid (Silvex)[b]	1,000	NA	NA	NA	NA
Vinyl chloride	200	<50	<50	<50	NA

[a] NA = not analyzed

[b] These two herbicides were not analyzed due to limitations in analytical capability. Herbicides in general have historically not been detected in SWSA-6 trench water samples, though there is no data available for these two compounds. Detection of these compounds in secondary wastes was considered to be extremely unlikely.

[c] Key to qualifier: "J" indicates that the quantitative value is estimated. This qualifier usually appears after a value which is below the quantitation limit or after a value given for a tentatively identified compound.

5. SUMMARY AND CONCLUSIONS

The ORNL ER Program is currently planning closure activities to be conducted in the WAG 6 area, which includes SWSA 6. Closure activities will generate wastewaters that will require treatment before discharge to the environment. It has been proposed that these wastewaters be collected, transported, and discharged to the ORNL process waste treatment systems for removal of contaminants before discharge to White Oak Creek. Previous bench-scale testing showed that the ORNL treatment systems could successfully treat the wastewater, though the impacts on secondary waste composition could not be determined in the small-scale tests. A larger-scale test system was designed and constructed to simulate the unit operations of the ORNL process waste system and to generate secondary solid wastes in amounts necessary for EPA TCLP testing. A 45-d test program was successfully conducted with the new test system, which adequately simulated the ORNL process waste system, and the required amounts of secondary solid wastes were generated for TCLP testing. Results of the TCLP tests indicate 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.

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7. REFERENCES

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

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

3. *Radiation Protection of the Public and the Environment*, U.S. Department of Energy, Order 5400.5, February 8, 1990.

4. T. E. Kent and P. A. Taylor, *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, September 1992.

5. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3d ed., U.S. EPA Office of Solid Waste and Emergency Response, Washington, D.C., November 1986.

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