

APPENDIX D

Example Treatability Test Procedures

INTRODUCTION

The following test procedures have been excerpted from Section 4.0 of the report *Pilot-Scale Tests of the Universal Treatment System for the Pesticides Formulating, Packaging, and Repackaging Industry*, September 1996 (DCN F7938). The report details the results of a series of pilot-scale treatability tests conducted by the U.S. Environmental Protection Agency during development of the Pesticide Formulating, Packaging, and Repackaging effluent limitations guidelines and standards. These tests evaluated the effectiveness of a flexible treatment train that was referred to as the Universal Treatment System (UTS).

The UTS is simply a term used to describe a simple, flexible system that consists of standard wastewater treatment equipment: tanks, pumps, piping, and activated carbon columns that can be purchased individually off-the-shelf from vendors. This equipment can be used to conduct the following physical/chemical treatment steps: emulsion breaking, hydrolysis, activated carbon adsorption, chemical oxidation, and precipitation.

4.0 TEST PROCEDURES

This section provides a discussion of the equipment, procedures, and operating parameters used to perform the three pilot-scale UTS treatability tests. Each pilot-scale test consisted of a bench-scale emulsion-breaking pretest, emulsion breaking (where it was determined via bench-scale pretesting that emulsion breaking would be effective) or settling, hydrolysis, and activated carbon adsorption.

To characterize the performance of each UTS treatment step, samples were collected before and after each step to gather data on the overall effectiveness of the UTS in treating PFPR wastewater. Each of these samples was analyzed for pesticide active ingredients (PAIs), volatile organics, semivolatile organics, and classical wet chemistry parameters. The influent to and effluent from the UTS system were also analyzed for metals.

Samples were also collected throughout hydrolysis treatment; these samples were analyzed for PAIs and classical wet chemistry parameters. The PAI analytical results were used to prepare hydrolysis half-life curves, which are presented in Section 6.0. Samples were collected throughout activated carbon treatment and analyzed for PAIs. The analytical results were used to prepare carbon breakthrough curves for each of the PAIs, which are also presented in Section 6.0.

Section 4.1 provides a discussion of the test equipment used in all three UTS treatability tests. Because each type of wastewater treated in the pilot-scale UTS differed in composition and treatability, the UTS procedures were modified slightly for each test to achieve adequate treatment. Sections 4.2 through 4.4 describe the procedures and design and operating parameters for each UTS test.

4.1 Test Equipment

The pilot-scale UTS treatability tests were conducted at Radian Corporation's Milwaukee, Wisconsin laboratory facilities. The following subsections describe the equipment used to perform the pilot-scale tests, as well as the emulsion-breaking pretest.

4.1.1 Emulsion-Breaking Pretest

The bench-scale emulsion breaking pretest was conducted in glass beakers. Hot plates were used to heat the aliquots. Magnetic stirrers with Teflon®-coated stirring bars mixed the aliquots.

4.1.2 Tanks

The pilot-scale emulsion-breaking tests and hydrolysis tests were conducted in two 190-liter stainless steel tanks with open tops. These tanks were heated using electric band heaters wrapped around the tanks. Aluminum foil was used to cover the tops of the tanks during portions of the tests to reduce evaporative losses. Several plastic tanks and a 40-liter graduated plastic tank were used to hold and measure the volume of the wastewater. Plastic tanks were used to hold the supernatant from the emulsion-breaking step while the sludge layers were measured and washed out of the stainless steel tanks. The graduated plastic tank was used to measure the volume of wastewater added to the plastic activated carbon feed tank.

4.1.3 Mixers

The wastewater tanks used for the pilot-scale emulsion breaking step were mixed using milk-jug hand mixers, an electrically powered paddle mixer, or an electrically powered Lightning® mixer. Each milk-jug mixer consisted of a long stainless steel rod attached to the center of a stainless steel disc with holes punched in it. Mixing was conducted by submerging the disc in the liquid and moving it up and down. The paddle mixer consisted of an electric motor that rotated a stainless steel paddle. The motor was clamped to a board placed across the opening of a tank. The paddle remained submerged in the liquid in the tank. The Lightning® mixer consisted of an electric motor that rotated a stainless steel rod with a small, warped stainless steel disc at its tip. The Lightning® mixer was clamped to the side of a tank so that the rod and the disc remained submerged in the liquid in the tank.

4.1.4 Pumps

Wastewater was transferred into and out of the various tanks and the activated carbon column either by pouring it or by pumping it through one of three pumps: a sump pump (submersible pump), a centrifugal pump, and a

peristaltic pump. The sump pump consisted of a motor located in a plastic housing with an open bottom. The motor was attached to a rope and was lowered into the liquid to be pumped until the open bottom of the housing was submerged in the liquid. The liquid was pumped through a tube at the top of the motor housing. The sump pump had the highest flow rate but its speed was not adjustable, and it tended to cause settled solids to resuspend during pumping.

The centrifugal pump was used by attaching tubes to the pump inlets and outlets. The open end of the tube attached to the inlet was submerged in the liquid to be pumped, and the open end of the tube attached to the outlet was placed in the empty container. The centrifugal pump had a variable speed motor, which could be adjusted to minimize the resuspension of settled solids.

The peristaltic pump was used to pump the wastewater from the activated carbon feed tank through a length of flexible tubing and into the carbon column. This pump was operated by wrapping a piece of flexible tubing around a gear. As the gear rotated, the tubing was compressed, which caused the liquid to flow through the tubing.

4.1.5 Activated Carbon Column

The activated carbon column consisted of a clear glass tube seven feet high and one inch in diameter. The ends of the column were capped with plastic plugs that had openings for stainless steel fittings. These fittings were used to attach flexible tubing to the column inlet and outlet. For each UTS test, the column was packed with 680 grams of granular activated carbon that had been washed and deaerated. The carbon used in each of the three tests was pulverized Filtrasorb 300, manufactured by Calgon Corporation. The carbon had a mesh size of 300 to 400.

The carbon was weighed and washed by measuring a small amount of carbon into a glass flask. Distilled water was added to the flask and swirled to cause the carbon fines to be suspended, which generated a black water above the granular carbon. The water was decanted from the carbon. These steps were repeated until the swirling no longer suspended many fines and the water remained relatively clear after swirling. The carbon was then deaerated by placing the flask under a vacuum of about seven inches of mercury using a vacuum pump. The flask was swirled to help release air bubbles from the carbon. The vacuum and swirling were continued until the water above the carbon became relatively free of air bubbles. The carbon was then scooped from the flask or washed from the flask using distilled water, and loaded into the carbon column.

4.1.6 Measurements

Measurements of pH were performed using an electronic pH meter, which was calibrated daily, or using disposable pH strips. Temperature measurements were conducted using a portable electric thermocouple or a mercury-filled glass thermometer. Prior to use, all equipment was washed using water, detergent solution, scrubbers, and scouring pads, as needed, and was triple-rinsed with distilled water.

4.2 Facility A Treatability Test

Facility A is a toll formulator that formulates and packages home insecticides, insect repellents, and pet-care products such as flea and tick shampoos. Wastewater collected from Facility A for treatability testing included formulation vessel interior rinsates from the formulation of four separate products (referred to in this report as Rinsates 1, 2, 3, and 4) and floor wash water from a mechanical floor scrubbing machine used to clean floors in the facility's product formulation areas. The wastewater was collected between March 27 and March 29, 1995 and placed for transport in one of seven plastic carboys. Table 4-1 provides a summary of the wastewater collection at Facility A.

Table 4-1
Summary of Wastewater Collection for UTS Treatability Testing at Facility A

Carboy Number	Carboy Contents (Pesticide Active Ingredients)	Carboy Volume (Liters)	Wastewater Appearance
Carboy #1	Rinsate 1 (permethrin, methoprene)	60	Milky-white, opaque
Carboy #2	Rinsate 2 (linalool)	60	Light green, translucent
Carboy #3	Rinsate 2 (linalool)	50	Light green, translucent
Carboy #4	Rinsate 3 (pyrethrins, piperonyl butoxide)	60	Light green, translucent, foamy
Carboy #5	Rinsate 3 (pyrethrins, piperonyl butoxide)	60	Light green, translucent, foamy
Carboy #6	Rinsate 4 (permethrin, methoprene)	35	Milky-white, opaque, foamy
Carboy #7	Floor Wash Water (permethrin, methoprene, linalool, limonene, pyrethrins, piperonyl butoxide)	20	Black, opaque

Rinsate 1 was generated from the interior cleaning of a tank used to formulate an insecticide spray that contains the PAIs permethrin and methoprene. The operator used about 95 liters of hot water in 10 minutes to clean the tank. Sixty liters of the wastewater were collected into Carboy #1 from a valve connected to the bottom of the tank. The wastewater had an opaque, milky-white appearance.

Rinsate 2 was generated from the interior cleaning of a tank used to formulate an insecticidal pet shampoo that contains the PAI linalool. The operator used about 230 liters of hot water in 20 minutes to clean the tank. Using a hose connected to a valve at the bottom of the tank, wastewater collection personnel put 60 liters of the wastewater into Carboy #2 and 50 liters of the wastewater into Carboy #3. The wastewater had a translucent, slightly green hue and contained surfactants from the raw materials used to formulate the product.

Rinsate 3 was generated from the interior cleaning of a tank used to formulate another insecticidal pet shampoo that contains the PAIs pyrethrin and piperonyl butoxide. The operator used about 150 liters of hot water in 10 minutes to clean the tank. Sixty liters of the wastewater were collected into Carboy #4 and 60 liters were collected into Carboy #5 using a hose connected

to a valve at the bottom of the tank. The wastewater was foamy and had a translucent, slightly green hue, and contained surfactants from the raw materials used to formulate the product.

Rinsate 4 was generated from the interior cleaning of a tank used to formulate an insecticide spray that contains the PAIs permethrin and methoprene. The operator used about 35 liters of hot water to clean the tank. Wastewater collection personnel placed all 35 liters of the wastewater into Carboy #6 using a valve connected to the bottom of the tank. The wastewater was foamy and had an opaque, milky-white appearance.

Floor wash water was collected from a mechanical floor scrubber that is used to clean the floors in the Facility A pesticide products packaging area. The floor in the formulation area is rarely washed; however, the rest of the facility, including the floors surrounding the packaging lines, is cleaned periodically. While personnel were on site to collect wastewater, the floors in the packaging area were cleaned using a mechanical floor scrubber. Wastewater collection personnel collected 20 liters of wash water into Carboy #7 from the water reservoir in the floor scrubber. This water was generated over two floor washings, with approximately 10 liters generated per washing. The wash water had the potential to contain all of the PAIs used in the products packaged at the facility, including the PAIs in Rinsates 1 through 4, and the PAI limonene, which is contained in another product that is packaged at the facility. In addition, the wash water contained detergents used in the floor scrubber to help clean floors, as well as surfactants from products that may have leaked or spilled during packaging. The wastewater had an opaque, black appearance.

The wastewater was shipped via air cargo to Radian's Milwaukee, Wisconsin laboratory facilities and was immediately placed in cold storage (approximately 4°C). The UTS treatability testing of Facility A wastewater began on March 30, 1995 and was completed by April 9, 1995. Table 4-2 lists the sample point description, Sample Control Center (SCC) sample number, date and time of sample collection, pH, and temperature and collection methods for the samples collected during the Facility A treatability test.

4.2.1 Emulsion-Breaking Pretest

Table 4-3 lists the composition of each aliquot for the emulsion breaking pretest, including the initial pH and appearance, the volume of acid or base added, the resulting pH, and the observations of the effects of the emulsion-breaking pretest.

The emulsion-breaking pretest was initially conducted on six 1-liter aliquots, with five aliquots of the individual wastewater and one aliquot of commingled wastewater from all carboys. The five aliquots of individual wastewater and the commingled aliquot were lowered to a pH of approximately 2 and raised to a temperature of 60°C for 1 hour as they were mixed; the aliquots were then allowed to cool and settle overnight. Observations indicated that emulsion breaking was not effective on the interior equipment rinsates or on the commingled wastewater. However, emulsion breaking did appear to be effective on the aliquot that consisted only of floor wash water; a distinct sludge phase settled out following heat and acidification.

Table 4-2
Summary of Wastewater Sampling for UTS Treatability Testing of Facility A Wastewater

Sample	SCC Number	Sample Date	Sample Time	pH	Temp. (°C)	Collection Method
Commingled Influent to Hydrolysis	27767	04/04/95	10:15	6.10	12.5	Scooped from tank using glass measuring cup
Commingled Influent to Hydrolysis (duplicate)	27768	04/04/95	10:15	6.10	12.5	Scooped from tank using glass measuring cup
Hydrolysis (first batch, 6-hour)	27770	04/05/95	19:15	NA	60.7	Scooped from tank using glass measuring cup
Hydrolysis (first batch, 12-hour)	27771	04/06/95	1:15	NA	55.1	Scooped from tank using glass measuring cup
Hydrolysis (first batch, 24-hour)	27772	04/06/95	13:13	NA	57.9	Scooped from tank using glass measuring cup
Hydrolysis (second batch, 24-hour)	27769	04/07/95	19:45	7.46	21	Scooped from tank using glass measuring cup
Activated Carbon (60-liter)	27773	04/07/95	21:30	NA	NA	Collected in 4-L glass jar from carbon column effluent tubing
Activated Carbon (120-liter)	27774	04/08/95	8:15-10:00	NA	NA	Collected in 9.6-L glass jar from carbon column effluent tubing
Activated Carbon (180-liter)	27775	04/08/95	19:30-21:15	NA	NA	Collected in 4-L glass jar from carbon column effluent tubing
Activated Carbon (240-liter)	27776	04/09/95	8:38-1:30	NA	NA	Collected in stainless steel tank from carbon column effluent tubing

NA - Information not available.
 SCC - Sample Control Center.

To determine whether alkaline conditions increased the effectiveness of emulsion breaking for the commingled wastewater, a second commingled aliquot was prepared from the post-emulsion breaking aliquots of the five individual wastewaters. The pH of this second commingled aliquot was raised to approximately 12 and heated to a temperature of 60°C for 1 hour as it was mixed. This aliquot was then allowed to cool and settle overnight. The emulsion-breaking pretest results indicated that emulsion-breaking using alkaline conditions was not effective on the second commingled aliquot. Therefore, pilot-scale emulsion breaking was performed only on the floor wash water (Carboy #1).

Table 4-3
Emulsion-Breaking Pretest Data for UTS Treatability Testing of Site A Wastewater

Aliquot Number	Rinsate	Sample Composition	Initial Appearance	Initial pH	Material Added To Adjust pH	pH	Observations
1	Interior Rinse #1	1,000 ml Carboy #1	Milky-white, opaque	8.17	0.4 ml H ₂ SO ₄ (50% w/w)	1.98	No separation
2	Interior Rinse #2	500 ml Carboy #2 500 ml Carboy #3	Light green, translucent	6.65	0.4 ml H ₂ SO ₄ (50% w/w)	1.95	No separation
3	Interior Rinse #3	500 ml Carboy #4 500 ml Carboy #5	Light green, translucent	8.19	0.2 ml H ₂ SO ₄ (50% w/w)	1.98	No separation
4	Interior Rinse #4	1,000 ml Carboy #6	Milky-white, opaque	7.11	0.3 ml H ₂ SO ₄ (50% w/w)	1.98	No separation
5	Floor Wash	1,000 ml Carboy #7	Black, opaque	7.26	0.5 ml H ₂ SO ₄ (50% w/w)	1.99	Settling of black sludge
6	First Commingled Aliquot	177 ml Carboy #1 165 ml Carboy #2 165 ml Carboy #3 170 ml Carboy #4 170 ml Carboy #5 100 ml Carboy #6 55 ml Carboy #7	Milky-white, opaque	7.19	1.9 ml H ₂ SO ₄ (50% w/w)	1.98	Minor settling of black material; may just be solids from floor sweepings
7	Second Commingled Aliquot	177 ml Beaker #1 330 ml Beaker #2 340 ml Beaker #3 100 ml Beaker #4 55 ml Beaker #5	Milky-white, opaque	1.99	3.1 ml NaOH (10 N)	12.03	Slight separation, small amount of thick, viscous sludge at bottom

4.2.2 Emulsion Breaking

Based on the results of the emulsion-breaking pretest, the pilot-scale emulsion breaking step was conducted only on the floor wash water. The 16 liters of floor wash water remaining after the emulsion-breaking pretest were poured into a 19-liter stainless steel bucket, the pH was adjusted to 2 using 70 ml of 50% weight of acid per weight of water (w/w) sulfuric acid, and the bucket was heated to 60°C as it was stirred with a magnetic stirring bar. The bucket was maintained at 60°C for one hour as the stirring continued. The stirring was then stopped, and the wastewater was allowed to cool and settle overnight. After one hour of cooling, a noticeable settling began to occur. After 24 hours, the supernatant was pumped into a plastic tank using the peristaltic pump. The supernatant became progressively darker as the upper layers were pumped into the plastic tank. However, a distinct sludge layer had settled to the bottom of the bucket, and this layer began to resuspend as the superna-

tant was pumped out of the tank and the pump approached the level of the sludge. The volume of the sludge and the supernatant that could not be pumped out without resuspending the sludge was about 3 liters.

4.2.3 Hydrolysis

Following the emulsion breaking of the floor wash water, the contents of Carboys #1 through #6 were poured into a plastic tank with the floor wash supernatant, and the tank was mixed with the milk-jug mixers. Influent and influent duplicate samples were collected from the commingled wastewater in the plastic tank by scooping the water from the tank using a glass measuring cup and pouring it into the appropriate sample bottles. Approximately 293 liters of commingled wastewater remained in the tank following sample collection, and was hydrolyzed in two treatment batches.

Batch 1—A volume of 171 liters of the well-mixed commingled influent was pumped into a stainless steel tank using the sump pump. Electric band heaters were used to heat the tank, and 175 ml of 10 N sodium hydroxide were added to the tank to raise the pH of the wastewater to 12. Aluminum foil was used to insulate the tank and reduce evaporation during the heating, and the paddle mixer was used to keep the wastewater mixed throughout the hydrolysis testing. After about three hours of heating, the tank achieved a temperature of 60°C. The temperature of the tank varied between 51°C and 82°C over the next 24 hours. The variation in temperature was due to a malfunctioning automatic temperature controller. The temperature had to be checked periodically using an electronic thermocouple or a glass thermometer. The control knobs on the band heaters were adjusted manually based on these temperature readings, with the goal of maintaining the temperature at 60°C.

Samples of the hydrolysis wastewater were collected at 6, 12, and 24 hours after the tank initially reached 60°C. Samples were collected by scooping water from the tank into a glass measuring cup, and then pouring it into the appropriate sample bottles. Approximately 26 liters of wastewater were collected for the three sample volumes, an additional 12 liters were lost due to evaporation and about 133 liters of wastewater remained in the tank.

After the 24-hour hydrolysis sample was collected, the tank was cooled by submerging a length of stainless steel tubing in the wastewater; noncontact cooling water was circulated through the tubing while the tank contents were stirred with the paddle mixer. Cooling the tank from 56°C, its temperature at the time of collection of the 24-hour sample, to 27°C required about 1.5 hours, at which point the stainless steel cooling coil was removed from the tank and cleaned for reuse. The pH of the wastewater was adjusted from 11.4 to 7.3 using 62 ml of 50% (w/w) sulfuric acid. The wastewater, which was originally milky white, turned turbid yellow during pH adjustment. The wastewater was then pumped from the hydrolysis tank through a 10-mm filter to the plastic activated carbon feed tank using the submersible sump pump. The 10- μ m filter was used to remove filterable solids that could cause plugging problems in the carbon column. The stainless steel tank, paddle mixer, and sump pump were cleaned for reuse. Table A-1 in Appendix A¹ lists the operating data for the first hydrolysis treatment batch.

¹ This is referring to Appendix A of *Pilot-Scale Tests of the Universal Treatment System for the Pesticides Formulating, Packaging, and Repackaging Industry*, September 1996 (DCN F7938).

Batch 2—The remaining wastewater (about 122 liters) that had not been treated with the first batch was transferred to the cleaned stainless steel tank for hydrolysis treatment. Electric band heaters were used to heat the tank, and 160 ml of 10 N sodium hydroxide were added to the tank to raise the pH of the wastewater to 12. Aluminum foil was used to insulate the tank and to reduce evaporation during the heating, and the paddle mixer was used to keep the wastewater mixed throughout the hydrolysis testing. After about 2.5 hours of heating, the tank achieved a temperature of 60°C. The temperature of the tank varied between 39°C and 73°C over the next 24 hours.

A final sample of the hydrolysis wastewater was collected about 24 hours after the tank initially reached 60°C by scooping water from the tank into a glass measuring cup and then pouring it into the appropriate sample bottles. No interim samples were collected at 6- and 12-hour intervals as was done for the first batch. Approximately 4 liters of wastewater were collected for the sample and an additional 8 liters were lost due to evaporation; about 110 liters of wastewater remained in the tank upon completion of the treatment step.

Unlike the first hydrolysis batch, the tank was cooled, and the pH of the wastewater was adjusted to a neutral level prior to collection of the 24-hour sample. The tank was cooled by submerging a length of stainless steel tubing in the wastewater; non-contact cooling water was circulated through the tubing while the tank contents were stirred with the paddle mixer. The cooling of the tank from 62°C to 22°C required about 1.5 hours. The pH of the wastewater was then adjusted from 11.8 to 7.5 using 50% (w/w) sulfuric acid. The wastewater turned from milky white to a turbid yellow during the pH adjustment. The 24-hour sample was then collected, and the wastewater was pumped from the hydrolysis tank through a 10-mm filter to the plastic activated carbon feed tank using the sump pump. The stainless steel tank, paddle mixer, and sump pump were cleaned for reuse. Table A-2 of Appendix A¹ lists the operating data for the second hydrolysis treatment batch.

4.2.4 Activated Carbon Adsorption

Treatment of the wastewater from the first hydrolysis batch through activated carbon adsorption was initiated during the hydrolysis treatment of the second batch of wastewater. The wastewater from the activated carbon feed tank was pumped by the peristaltic pump through flexible tubing into the top of the column. The wastewater passed down through the column, out the bottom of the column, and into another length of flexible tubing from which samples were taken. The wastewater flow rate through the column was maintained at a rate of 82 to 88 milliliters per minute throughout the test. Samples were collected after 60, 120, 180, and 240 liters of wastewater had passed through the column by collecting the column effluent into glass jars and pouring the treated effluent from the glass jars into the appropriate sample bottles.

The wastewater from the second hydrolysis batch was pumped into the activated carbon feed tank after about 56 liters of water from the first batch had passed through the column and about 76 liters of wastewater from the first batch remained in the feed tank. About 100 liters of wastewater from the

¹ This is referring to Appendix A of *Pilot-Scale Tests of the Universal Treatment System for the Pesticides Formulating, Packaging, and Repackaging Industry*, September 1996 (DCN F7938).

second hydrolysis batch were added to the feed tank. The first activated carbon wastewater sample (i.e., the 60-liter sample) was collected immediately after the wastewater from the second hydrolysis batch was added to the activated carbon feed tank. The activated carbon effluent did not have the turbid, yellow color of the influent, but it did have a milky-white color. In addition, some white deposits were observed on top of the packed carbon and in the pore spaces between the carbon granules.

4.3 Facility B Treatability Test

Facility B formulates and packages pesticide products primarily for use in the agricultural market. The wastewater collected from Facility B for treatability testing consisted of an interior cleaning rinsate from the washing of formulating and packaging equipment dedicated to a product that contains the PAI tetrachlorvinphos. The product also contained molasses, and the rinsate was expected to have high BOD₅ and TOC levels. The operator cleaned the interior of the formulation vessel using a hot, high-pressure washer and about 430 liters of water over a 50-minute timeframe. The wastewater was allowed to drain by gravity from the formulation vessel through the packaging equipment, and it was collected from a hose connected to a manifold at the bottom of the formulation equipment and from nozzles on the packaging equipment. Wastewater collection personnel placed about 350 liters of the wastewater into 5-gallon carboys. The wastewater had an opaque, brown appearance.

The wastewater was collected on June 27, 1995, and was transported to Radian's Milwaukee, Wisconsin laboratory facilities via Federal Express, where it was placed in cold storage (approximately 4°C). The UTS treatability testing of Facility B wastewater began on June 29, 1995 and was completed by July 11, 1995. Table 4-4 lists the sample point description, SCC number, date and time of sample collection, pH, temperature, and collection method for the samples collected during the Facility B treatability test.

4.3.1 Emulsion-Breaking Pretest

Upon receipt in Milwaukee, the wastewater was poured from the carboys into two stainless steel tanks, Tank 1 and Tank 2. The wastewater was dark brown, and clumps of solids had settled to the bottoms of the carboys. After the wastewater was poured into the stainless steel tanks, the tanks were vigorously mixed using the milk-jug mixers to resuspend the solids, and two 1-liter aliquots were collected for the emulsion-breaking pretest. The tanks were then placed in a walk-in refrigerator at 4°C to prevent biological growth from occurring. Emulsion breaking at pH 2 and 60°C was performed on one of the aliquots, and the second aliquot was used as a control sample.

The first aliquot of wastewater was lowered to a pH of 1.98 by adding 15.8 ml of 36 N sulfuric acid to the wastewater and was raised to a temperature of 60°C for one hour as it was mixed; the aliquot was then allowed to cool and settle overnight. The aliquot turned a slightly lighter shade of brown as the pH was adjusted downward. The second aliquot was simply allowed to settle overnight with no heating, mixing, or pH adjustment. The emulsion-breaking pretest results indicated that emulsion breaking by adding acid and heat did not significantly improve the settling of the solids or the clarity of the supernatant over the control sample. However, solids did settle out of both

Table 4-4
Summary of Wastewater Sampling for UTS Treatability Testing of Facility B Wastewater

Sample	SCC No.	Sample Date	Sample Time	pH	Temp. (°C)	Collection Method
UTS Influent	28918	06/30/95	11:30	NA	NA	Half of sample volume measured from each tank using glass measuring cup
UTS Influent (duplicate)	28919	06/30/95	11:30	NA	NA	Half of sample volume measured from each tank using glass measuring cup
Settling Supernatant	28920	07/04/95	11:20	5.85	NA	Half of sample volume measured from each tank using glass measuring cup
Hydrolysis (6-hour)	28921	07/05/95	20:00	NA	57 ^a	Half of sample volume measured from each tank using glass measuring cup
Hydrolysis (12-hour)	28922	07/06/95	2:14	NA	64.5 ^a	Half of sample volume measured from each tank using glass measuring cup
Hydrolysis (24-hour)	28923	07/06/95	14:00	10.6 ^a	63 ^a	Half of sample volume measured from each tank using glass measuring cup
Activated Carbon (60-liter)	28924	07/10/95	8:20-8:45	7.04	NA	Collected in 4-L glass jar from carbon column effluent tubing
Activated Carbon (120-liter)	28925	07/10/95	19:08-20:30	7.02	NA	Collected in 9.6-L glass jar from carbon column effluent tubing
Activated Carbon (180-liter)	28926	07/11/95	7:22-9:47	7.00	NA	Collected in 4-L glass jar from carbon column effluent tubing
Activated Carbon (240-liter)	28927	07/11/95	14:55-19:15	7.05	NA	Collected in stainless steel tank from carbon column effluent tubing

^aAverage of both tanks.

NA - Information not available.

SCC - Sample Control Center.

the emulsion-breaking aliquot and the control aliquot; therefore, a settling step was used instead of an emulsion-breaking step for the pilot-scale UTS treatment test.

4.3.2 Settling

After the emulsion-breaking pretest, the stainless steel tanks were removed from the refrigerator and their contents were remixed. Tank 1, which contained 156 liters of wastewater, was mixed using the paddle mixer, and Tank 2, which contained 163 liters of wastewater, was mixed using the Lightning®

mixer. Both mixers effectively mixed the contents of the tanks, so the difference in mixer types should not have affected the test results. After mixing, the influent and influent duplicate samples were collected by scooping the well-mixed wastewater into a glass measuring cup and pouring it into the appropriate sample bottles. For each sample bottle, a volume of wastewater equal to half of its capacity was collected from one tank, and the remainder of the volume was collected from the other tank.

The wastewater was allowed to settle overnight. After settling, the supernatant from Tank 1 was pumped into a plastic tank using the submersible sump pump. The supernatant volume was about 92% of the original Tank 1 volume. The supernatant from Tank 2 was pumped into a separate plastic tank. The supernatant volume was about 91% of the original Tank 2 volume. The stainless steel tanks, sump pump, and Lightning® and paddle mixers were cleaned for future use.

A sample of the supernatant was collected by scooping water from the plastic tanks into a glass measuring cup and pouring the wastewater into the appropriate sample bottles. For each sample bottle, a volume of wastewater equal to half of its capacity was collected from one tank, and the remainder of the volume was collected from the other tank. The wastewater was then pumped back into the stainless steel tanks and placed in the walk-in refrigerator.

4.3.3 Hydrolysis

A volume of 146 liters of wastewater was contained in each stainless steel tank at the start of the hydrolysis testing. Electric band heaters were used to heat the tanks, and 5.3 liters of 40% sodium hydroxide (w/w) were added to the Tank 1 to raise its pH from 5.81 to 12.02. The pH of Tank 2 was raised from 5.78 to 12.04 through the addition of 4.9 L of 40% sodium hydroxide (w/w). Aluminum foil was used to insulate the tanks and to reduce evaporation during the heating. The Lightning® mixer (Tank 1) and the paddle mixer (Tank 2) were used to mix the wastewater throughout the hydrolysis test. After about five hours of heating, the tanks achieved the target temperature of 60°C. The temperatures of the tanks varied between 52°C and 74°C over the next 24 hours. Table A-3 of Appendix A lists the operating data for the hydrolysis test.

Samples of the hydrolysis wastewater were collected at 6, 12, and 24 hours after the tanks initially reached 60°C by scooping the well-mixed wastewater into a glass measuring cup and pouring it into the appropriate sample bottles. For each sample bottle, a volume of wastewater equal to half of its capacity was collected from one tank, and the remainder of the volume was collected from the other tank. Approximately 20 liters of wastewater were collected for the samples from each tank; about 135 liters of wastewater remained in each tank following completion of hydrolysis. The volume of wastewater lost due to evaporation during the hydrolysis step was negligible.

After the 24-hour hydrolysis sample was collected, the pH of Tank 1 was reduced from 10.6 to 6.4 using 1.22 L of 36 N sulfuric acid, and the pH of Tank 2 was adjusted from 10.8 to 7.2 using 1.22 L of 36 N sulfuric acid. The wastewater was pumped from each of the hydrolysis tanks through a 10-mm

filter into separate plastic tanks using the sump pump. The filter became clogged several times with solids from the wastewater and was replaced twice during the pumping of each tank. The wastewater was pumped from the plastic tanks back into the stainless steel tanks, and was then placed in the walk-in-refrigerator to prevent biological growth. The plastic tanks, paddle mixer, and sump pump were cleaned for reuse.

4.3.4 Activated Carbon Adsorption

The wastewater was removed from the walk-in refrigerator and approximately 38 liters were pumped from each tank into the plastic activated carbon feed tank. The stainless steel tanks were then returned to the walk-in refrigerator to prevent biological growth. The wastewater from the activated carbon feed tank was pumped using the peristaltic pump through flexible tubing into the top of the column. The wastewater passed down through the column, out the bottom of the column, and into another length of flexible tubing from which samples were taken. The wastewater flow rate through the column was maintained at a rate of 85 to 98 milliliters per minute throughout the test. Samples were collected after 60, 120, and 180 liters of wastewater had passed through the column. The column effluent was collected into glass jars and poured from the glass jars into the appropriate sample bottles. A final sample was collected after 240 liters of wastewater had passed through the column. Throughout the test, the activated carbon effluent had the same brownish color as the influent.

Additional wastewater from the stainless steel tanks was pumped into the activated carbon feed tank after the first 60 liters had been treated and about 12 liters of wastewater remained in the feed tank. Approximately 38 liters of wastewater were pumped from each tank into the plastic activated carbon feed tank. The stainless steel tanks were then returned to the walk-in refrigerator to prevent biological growth. About 27 liters remained in the activated carbon feed tank following collection of the 120-liter sample. Another 38 liters of wastewater were pumped from each stainless steel tank into the plastic activated carbon feed tank. The stainless steel tanks were then returned to the walk-in refrigerator to prevent biological growth. About 17 liters of wastewater remained in the feed tank following collection of the 180-liter sample, and the remaining wastewater in the stainless steel tanks was pumped into the plastic activated carbon feed tank. About 22 liters were pumped from Tank 1, and about 34 liters were pumped from Tank 2.

4.4 Facility C Treatability Test

Facility C formulates and packages fertilizer and herbicide products, and toll formulates products for other companies. The products formulated in the dry formulations area contain the PAIs ametryn, atrazine, cyanazine, ethalfluralin, metolachlor, and pendimethalin. For four to five weeks prior to sample collection, Facility C accumulated interior cleaning water from the washing of formulating and packaging equipment for dry products and wash water from floor washings in the dry formulation area. This wastewater was stored on site in a 20,000-gallon stainless steel tank and based on the odor and scum content, this wastewater supported biological growth. During wastewater collection, the wastewater was allowed to drain by gravity from the storage

Table 4-5
Summary of Wastewater Sampling for UTS Treatability Testing of Facility C Wastewater

Sample	SCC No.	Sample Date	Sample Time	pH	Temp. (°C)	Collection Method
UTS Influent	29769	07/28/95	10:30	7	13	Half of sample volume measured from each tank using glass measuring cup
UTS Influent (duplicate)	29770	07/28/95	10:30	7	13	Half of sample volume measured from each tank using glass measuring cup
Emulsion-Breaking Supernatant	29771	07/30/95	9:30	2.09	33	Half of sample volume measured from each tank using glass measuring cup
Hydrolysis (6-hour)	29772	07/31/95	20:15	12	NA	Half of sample volume measured from each tank using glass measuring cup
Hydrolysis (12-hour)	29773	08/01/95	2:30	NA	NA	Half of sample volume measured from each tank using glass measuring cup
Hydrolysis (24-hour)	29774	08/01/95	2:00	12	59	Half of sample volume measured from each tank using glass measuring cup
Activated Carbon (60-liter)	29775	08/02/95	7:50-8:40	7	21	Collected in 4-L glass jar from carbon column effluent tubing
Activated Carbon (120-liter)	29776	08/02/95	22:15-23:00	7	18	Collected in 9.6-L glass jar from carbon column effluent tubing
Activated Carbon (200-liter)	29778	08/03/95	9:00-14:30	7.9	NA	Collected in stainless steel tank from carbon column effluent tubing

NA - Information not available.
 SCC - Sample Control Center.

tank through a hose connected to a valve at the bottom of the tank into fourteen 30-liter carboys. Approximately 420 liters of wastewater were collected. The wastewater had an opaque, gray appearance and a strong odor.

The wastewater was collected on July 27, 1995, and was transported by van from Facility C to Radian's Milwaukee, Wisconsin laboratory facilities. The wastewater arrived on July 27 and was placed in the walk-in refrigerator until treatability testing began. The UTS treatability testing of Facility C wastewater began on July 28, 1995 and was completed by August 3, 1995. Table 4-5 lists the sample point description, SCC number, date and time of sample collection, pH, temperature and collection method for the samples collected during the Facility C treatability test.

4.4.1 Emulsion-Breaking Pretest

On July 28, 1995, the wastewater in twelve of the carboys was poured into two stainless steel tanks, Tank 1 and Tank 2. The wastewater in the remaining two carboys was held in reserve. The wastewater was an opaque, gray color. After the wastewater was poured into the stainless steel tanks, the tanks were vigorously mixed using the milk-jug mixers, and the influent and influent duplicate samples were collected by scooping the well-mixed wastewater into a glass measuring cup and pouring it into the appropriate sample bottles. For each sample bottle, a volume of wastewater equal to half of its capacity was collected from one tank, and the remainder of the volume was collected from the other tank.

After the influent and influent duplicate samples were collected, three 1.5-liter aliquots were collected for the emulsion-breaking pretest. The tanks were then placed in a walk-in refrigerator at 4°C to prevent biological growth.

The pH of the first aliquot of wastewater was lowered from 7.38 to 2.01 by adding 1.1 ml of 36 N sulfuric acid. The temperature was raised to 60°C for one hour as it was mixed; the aliquot was then allowed to cool and settle overnight. Visible settling of a brown flocculent began to occur when the mixing was stopped. After settling overnight, a compact gray sludge had settled out of a translucent, yellow supernatant. The sludge occupied approximately 3% of the original aliquot volume of 1.5 liters.

The pH of the second aliquot of wastewater was raised from 7.07 to 11.74 by adding 6.1 ml of 10 N sodium hydroxide. The temperature was raised to 60°C for one hour as it was mixed; the aliquot was then allowed to cool and settle overnight. Visible settling of a brown flocculent began to occur when the mixing was stopped; however, this settling was not as dramatic as the settling that occurred in the first aliquot. After settling overnight, a gray sludge had settled out of an opaque, brown supernatant. The sludge occupied approximately 7% of the original aliquot volume of 1.5 liters, but was not as compact as the sludge in the first aliquot. The third aliquot was simply allowed to settle overnight with no heating, mixing, or pH adjustment. No visible settling occurred immediately; however, after settling overnight, about 750 ml (50% of the original volume) exhibited signs of settling. As with the second aliquot, the settling that was observed was not as complete and the sludge was not as compact as the first aliquot.

4.4.2 Emulsion Breaking

Because the pretest of the first aliquot resulted in more complete settling of the solids and a clearer supernatant, pilot-scale emulsion breaking using heat and acid was conducted on the Facility C wastewater. Each of the two stainless steel tanks of wastewater, which contained approximately 170 liters of wastewater, were removed from the walk-in refrigerator. The pH of the tanks was adjusted from 7.2 to 2.1 using 175 ml of 36 N sulfuric acid per tank. The tanks were heated from their initial temperature of 7°C using the band heaters. During the heating, Tank 1 was stirred with the paddle mixer and Tank 2 was stirred with the Lightning® mixer. After about six hours the tanks reached 60°C; the tanks were maintained at a temperature between 60°C and 70°C for one hour as the stirring was continued. A 50-ml aliquot of Tank 1 waste-

water was collected in a 50-ml glass graduated cylinder for the purpose of more accurately identifying the volume of sludge that would settle out of the wastewater. The mixers were then stopped, and the wastewater was allowed to cool and settle overnight.

A noticeable settling of a brown flocculent in a translucent yellow supernatant began to occur as soon as the mixers were stopped. After settling overnight the supernatant in Tank 1 appeared to be a translucent yellow color, while the supernatant in Tank 2 appeared to be a slightly turbid green color. The 50-ml aliquot taken from Tank 1 contained a translucent, yellow supernatant with 2 ml (or 4%) of gray sludge.

The emulsion-breaking effluent sample was collected from the tanks by scooping the supernatant into a glass measuring cup and pouring it into the appropriate sample bottles. For each sample bottle, a volume of wastewater equal to half of its capacity was collected from one tank, and the remainder of the volume was collected from the other tank.

The supernatant from Tank 1 was pumped into a plastic tank using the sump pump. However, turbulence from the sump pump caused the sludge to resuspend. The supernatant was then pumped back into Tank 1, and the emulsion-breaking process was repeated by heating the tank back to 60°C and stirring its contents with the paddle mixer. While Tank 1 was reheating, the supernatant from Tank 2 was pumped to a plastic tank using a centrifugal pump, which did not cause the supernatant to resuspend. About 8 liters (or 4.7%) of sludge remained in the tank after the supernatant was pumped from Tank 2.

Because Tank 1 was already at a pH of about 2, no pH adjustment was required prior to performing the emulsion-breaking step on Tank 1 a second time. The tank was reheated to 60°C and the temperature was maintained for one hour as the contents of the tank were mixed with the paddle mixer. The mixer was then turned off and the tank was allowed to cool and settle for about three hours. A translucent, yellow supernatant was then pumped from Tank 1, using the centrifugal pump, into a separate plastic tank, which left about 4 liters (or 2.3%) of gray sludge in Tank 1. The sludge from both Tank 1 and Tank 2 was disposed of, and the tanks, mixers, and pumps were cleaned for future use. The plastic tanks of supernatant were cooled overnight.

4.4.3 Hydrolysis

After cooling overnight, the supernatant from Tank 1 was pumped back into Tank 1, and the supernatant from Tank 2 was pumped back into Tank 2. Electric band heaters were used to heat the tanks, and 550 ml of 40% sodium hydroxide (w/w) was added to each tank to raise the pH. The pH of Tank 1 was raised from 2.05 to 11.33, and the pH of Tank 2 was raised from 2.05 to 11.43. During the hydrolysis testing, the paddle mixer was used to stir Tank 1, and the Lightning® mixer was used to stir Tank 2. After about five hours of heating, the pH reading for each tank was approximately 11; therefore, an additional 50 ml of 40% sodium hydroxide (w/w) was added to each tank to raise its pH to 12. After about five and one-half hours of heating, the tanks achieved the target temperature of 60°C. The temperatures of the tanks varied between 50°C and 70°C over the next 24 hours. The temperatures of the

tank were not recorded; therefore, no table of operating data is provided for the hydrolysis of wastewater from Facility C. About one hour after the tanks achieved their target temperature, aluminum foil was placed over the tops of the tanks to insulate the tanks and to reduce evaporation during the heating.

Samples of the hydrolysis wastewater were collected at 6, 12, and 24 hours after the tank initially reached 60°C by scooping the well-mixed wastewater into a glass measuring cup and pouring it into the appropriate sample bottles. For each sample bottle, a volume of wastewater equal to half of its capacity was collected from one tank, and the remainder of the volume was collected from the other tank. The wastewater in both tanks appeared translucent yellow throughout the hydrolysis testing. Sampling personnel noted that a small amount of brown sludge settled to the bottoms of the samples. However, this sludge became resuspended in the samples that were preserved to neutral or acidic pH, resulting in a slightly turbid brown sample.

After the 24-hour hydrolysis sample was collected, Tanks 1 and 2 were cooled by submerging a length of stainless steel tubing in the two wastewaters; noncontact cooling water was circulated through the tubing while the tank contents were stirred with the paddle mixer. Approximately 45 minutes were required to cool Tank 1 from its temperature of 59°C to 35°C; Tank 2 required about 40 minutes to lower the temperature from 55°C to 35°C.

4.4.4 Activated Carbon Adsorption

Following hydrolysis, the pH of Tank 1 was adjusted from about 12 to 7 using 100 ml of 36 N sulfuric acid. The pH of Tank 2 was also adjusted using 100 ml of 36 N sulfuric acid, which lowered its pH from about 12 to 4. An additional 60 ml of 40% sodium hydroxide (w/w) was added to Tank 2 to raise its pH to 7. The wastewater turned a slightly turbid brown color during the pH adjustment.

Using the sump pump, 30 liters of wastewater from Tank 1 were pumped through a 10-mm filter into a plastic tank with volume gradations marked on the side of the tank. The filtered water was then poured into the plastic activated carbon feed tank. This process was repeated with 30 liters of wastewater from Tank 2; however, the filter became clogged with solids from the wastewater and was replaced. An additional 30 liters of wastewater were pumped again from each tank using the same procedures, but again the filter became clogged and had to be replaced. Yellow-brown solids were caked on the filters when they were replaced. The total volume of wastewater pumped to the activated carbon feed tank was 120 liters. Tank 1 and Tank 2 were then placed in the walk-in refrigerator to prevent biological growth in the wastewater.

The wastewater from the activated carbon feed tank was pumped by the peristaltic pump through flexible tubing into the top of the column. The wastewater passed down through the column, out the bottom of the column, and into another length of flexible tubing from which samples were taken. The activated carbon effluent was initially clear, but it developed a faint yellow-green tinge after about 60 liters of wastewater had passed through the column. The wastewater flow rate through the column was maintained at a rate of 82 to 93 milliliters per minute throughout the test. A sample was

collected after 60 liters of wastewater had passed through the column by collecting the column effluent into a glass jar and pouring the treated effluent from the glass jar into the appropriate sample bottles.

About six hours after the collection of the 60-liter sample, an additional volume (35 liters) of wastewater from Tank 1 was pumped, using the submersible sump pump, through a 10-mm filter into a plastic tank with volume gradations marked on the side of the tank. The filtered water was poured into the plastic activated carbon feed tank, and the filter, which had become caked with yellow-brown solids during the pumping, was replaced. This process was repeated with 35 liters of wastewater from Tank 2 and then with the remaining 8 liters of wastewater from Tank 1 and the 22 liters from Tank 2.

About one hour after the remaining wastewater was filtered into the activated carbon feed tank, the flow rate through the carbon column decreased to about 40 milliliters per minute, and a cake of solids was visible on top of the carbon packed in the column. The wastewater in the activated carbon feed tank was then refiltered using a 5-mm filter by pumping the wastewater from the carbon feed tank through the 5-mm filter into a clean plastic tank. Yellow-brown solids accumulated on the filter during the filtration. The activated carbon column was then backwashed with about 1 liter of distilled water, which caused the caked solids at the top of the column to break apart. However, some air became entrapped in the column during the backwashing. A vacuum of about 18 centimeters of mercury was applied to the column for 15 minutes while the column was tapped with a mallet to remove the entrapped air. Some air bubbles remained in the spaces between the carbon granules following this procedure. The column was then restarted and the flow rate of wastewater from the activated carbon feed tank was adjusted to 85 milliliters per minute.

A sample was collected after a total of 120 liters of wastewater had passed through the column by collecting the column effluent into a glass jar and pouring the treated effluent from the glass jar into the appropriate sample bottles. Two additional samples of the carbon effluent were planned, one at 180 liters of effluent and one at 240 liters of effluent, but only a total of about 220 liters of wastewater was available for activated carbon treatment because wastewater was lost to evaporation during the hydrolysis and emulsion-breaking steps. Therefore, only one additional sample was taken after 200 liters of wastewater had passed through the column.