

# KANSAS CITY PLANT ULTRAVIOLET/OZONE/HYDROGEN PEROXIDE GROUNDWATER TREATMENT SYSTEM OVERVIEW

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## ABSTRACT

The Kansas City Plant (KCP) has committed to the utilization of a groundwater treatment system, for removal of volatile organic compounds (VOCs), that discharges a minimal amount of pollutants to the environment. An advanced oxidation process (AOP) system utilizing ozone, ultraviolet radiation, and hydrogen peroxide serves in this capacity. Packed tower aeration and activated carbon filtration are listed as best available technologies (BATs) by the Environmental Protection Agency (EPA) for the removal of VOCs in water. The disadvantage to these BATs is that they transfer the VOCs from the water medium to the air or carbon media respectively.

Operation of the system began in May 1988 at a flow rate of 22.7 liters per minute (lpm) (6 gallons per minute (gpm)). An additional 102.2 lpm (27 gpm) of flow were added in October 1990. Various efforts to optimize and track the treatment unit's efficiency have been carried out. A maximum influent reading of 26,590 parts per billion (ppb) of total VOCs has been recorded. Following the addition of flows, removal efficiency has averaged approximately 95%. Both air and water effluents are factored into this calculation.

## INTRODUCTION

### Historical

Constructed in 1942 as an aircraft engine manufacturing plant, the Kansas City Plant (KCP) is part of the United States Department of Energy's (DOE) Albuquerque Field Office. The Atomic Energy Commission (AEC), predecessor to the DOE, began production of components for nuclear weapons at the KCP in 1949. Subsequent defense related research and manufacturing operations have resulted in the release of contaminants to the environment.

### GROUNDWATER UNDER TREATMENT

Three plumes of groundwater contaminated by VOCs are being remediated by a pump and treat system at the KCP. Groundwater contamination resulted from the operation of a solvent recovery still in the Trichloroethene Still Area (TCESA) and from leaking underground storage tanks, which contained solvents and petroleum products in the Underground Tank Farm Area (UTFA). Groundwater contamination in the Northeast Area (NEA) is thought to have occurred from using several small disposal ponds for liquid wastes. The principal contaminants are TCE and its degradation products, 1,2-dichloroethene and vinyl chloride (chloroethene).

The three plumes are shown on Fig. 1 along with approximate plume boundaries and extraction well locations. Previous hydrogeologic site characterizations of the KCP identified

these areas and assisted in determining extraction well locations.

Storage tanks at the UTFA and associated contaminated soil down to the groundwater table at 4.57 meters (15 feet) have been removed. The TCESA and NEA are currently being investigated under the KCP's Resource Conservation and Recovery Act (RCRA) 3008 (h) Administrative Order on Consent and are in the RCRA Facility Investigation (RFI) phase. The groundwater treatment system is operated under an interim measures plan, as required by the consent order.

## TREATMENT UNIT

### Decision To Use An Advanced Oxidation Process (AOP)

Packed tower aeration and activated carbon filtration are listed as best available technologies (BATs) by the EPA for the removal of VOCs in water. The disadvantage of these BATs is the transfer of VOCs from the water medium to air or carbon media respectively. In the interest of waste minimization, the KCP chose to pursue the use of an AOP groundwater treatment system for the removal of VOCs.

AOPs include ozone (O<sub>3</sub>) at high pH values, O<sub>3</sub> with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), O<sub>3</sub> with ultraviolet (UV) radiation, UV with H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. (1) The KCP realized, however, that risk was involved with the utilization of a relatively new technology. Highly developed operation and maintenance costs were unavailable, and long term system reliability was unknown. In 1986, manufacturers and vendors

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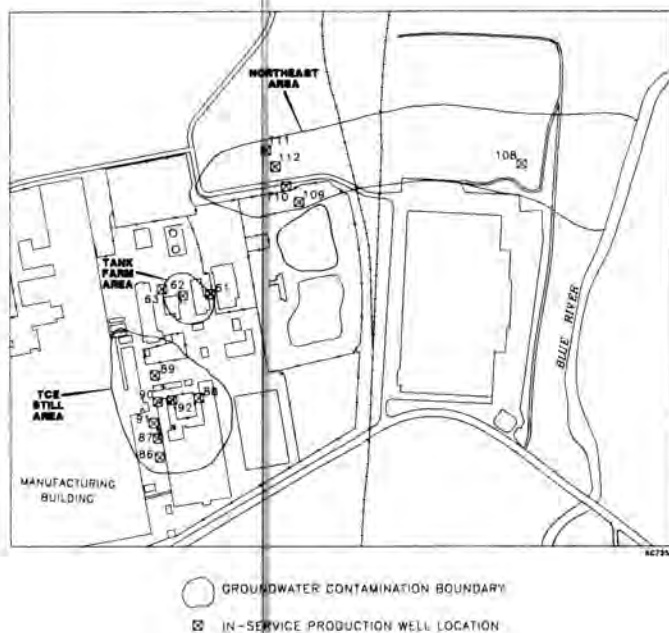


Fig. 1. Extraction well locations.

in the groundwater treatment field were given KCP specifications for a groundwater treatment system.

#### Description Of Unit

A UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> unit, rated at 94.63 lpm (25 gpm), is operated by the KCP for treatment of groundwater. This unit is composed of:

- an ozone generator, rated at 9.53 kilograms (21 pounds) per day of ozone at two percent by weight,
- a hydrogen peroxide feed unit rated at 2.84 liters per hour (0.75 gallons per hour),
- 72 low-pressure mercury vapor lamps, rated at 65 watts each, and
- a stainless steel reaction chamber with a volume of 2.9 m<sup>3</sup> (90 ft<sup>3</sup> or 725 gal) partitioned into six stages by baffles.

Costs of a bench-scale study, pilot plant study, and construction of the treatment plant, including the building used to house the treatment unit, were approximately \$304,000.

Each stage contains an ozone sparger and 12 UV lamps. Hydrogen peroxide is metered into the groundwater through an in-line mixer immediately before the groundwater enters the reaction chamber. A simplified schematic of the unit is shown in Fig 2. Various components were later added to the system and are described under "Actions Taken."

Groundwater flows in series through the reactor stages, entering stage 1 and exiting stage 6. A serpentine pattern is produced which provides the longest flow path through the reactor. This flow produces the greatest contact time between contaminants and the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, yielding a higher contaminant destruction percentage.

A headspace at the top of the reaction chamber vents residual ozone to an ozone destroyer where the offgas is treated and exhausted to the atmosphere. Effluent water from the treatment system is discharged under a pretreatment permit to the city of Kansas City, Missouri, sanitary sewer. The maximum discharge limit of 0.16 mg/l of total organic halogen (TOX) is of most concern when treating VOCs.

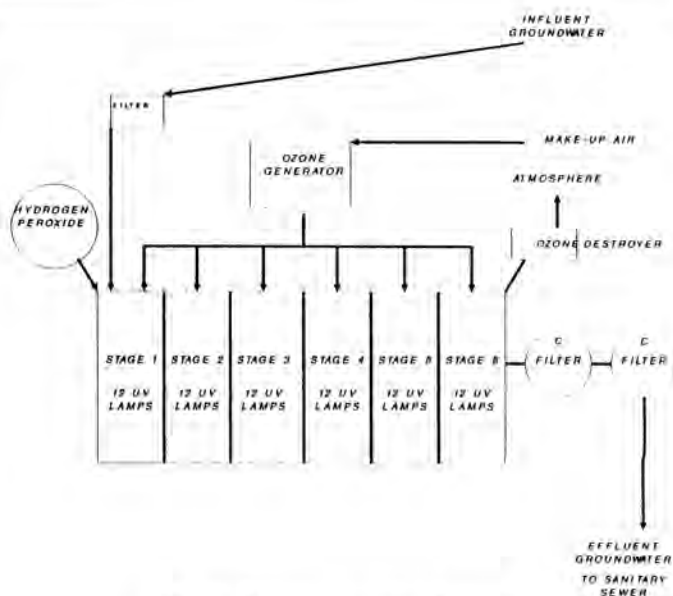


Fig. 2. Treatment unit schematic.

An alarm panel for the groundwater pumping wells and treatment unit was installed at the east boiler house control room, which is continually manned. If a problem develops, an alarm is sent to the east boiler house panel. The east boiler house operator then notifies appropriate personnel who investigate and correct any problems. The following conditions activate the alarm panel:

- shutdown of the ozone generator,
- high ballast temperature of the UV lamps,
- high water level in the treatment building sump,
- out-of-limits (high or low) temperature of the ozone destroyer, and
- high ozone concentration in the treatment, and building's ambient air.

#### PERFORMANCE OF TREATMENT UNIT

##### Start-up

System components were delivered and setup in February 1988. Initially, flows of 22.7 lpm (6 gpm) from the UTFA only were introduced to the system. Extraction wells and the delivery system were not in place for operation of the TCESA and NEA. Batch operations were conducted during February and March 1988 to ensure that the effluent from the treatment unit would meet the specifications of the discharge permit. Effluent from the batch operations was not discharged to the Kansas City sewer until analytical results were received ensuring the requirements of the permit were met and verifying that the treatment unit was operating successfully. At that time, it was demonstrated that the treatment unit could meet the discharge specifications and the continuous operation phase could be started.

##### Operations (FY 1988-90)

Continuous operations were initiated May 1988 and have continued to present. Operations were initially reviewed under DOE's Hazardous Waste Remedial Actions Program (HAZWRAP) and in late 1989 were grandfathered into the Technology Development (TD) program. During 1988, 1989, and 1990, the treatment unit was operated on a continuous

basis at a flow rate of 15.1 to 22.7 lpm (4 to 6 gpm), with flows from the UTFA only. The treatment unit was very effective at routinely removing VOCs to below the detection limits of 5 ug/l (Table I) as compared to the influent levels.

#### Problems Encountered

According to the manufacturer, minimal system maintenance would be required for efficient operations. A full-time operator was not available to routinely check and maintain the system until February 1990. Prior to this time an operator spent approximately one hour each day on routine maintenance and monitoring activities.

Equipment malfunctions resulting in a high percentage of downtime plagued the unit during the first two years of operation. Some of the major problems encountered were wet air feed to the ozone generator, ozone leaks, iron and manganese oxidation (yielding clogged filters and sparger tubes and coated lamp sheaths), cavitating peroxide pumps, damaged interceptor pumps in the extraction wells, freezing of lines and equipment, and iron bacteria build-up that still plagues some wells. In addition:

- frequent downtime was required to acid clean the reactor,
- the ozone generator produced at only 20% of rated capacity,
- the unit lacked sufficient instrumentation to routinely monitor and record unit operations, and
- the system did not have, for continuous operations, the necessary control mechanisms (instrumentation, valves for flow and pressure control, sample taps, alarms, and pump controls).

All of these problems contributed to the extended learning curve experienced with the unit.

#### Actions Taken

As knowledge and experience were gained, extensive modifications were made during 1989, and 1990 that helped to improve the reliability of the groundwater recovery system. These included the following major actions:

- replaced, repaired, or modified spargers,
- installed air dryer,
- overhauled ozone generator,
- completed major overhaul by manufacturer,
- modified H<sub>2</sub>O<sub>2</sub> and installed feed tank system,
- acid cleaned the reaction chamber, and
- installed indicator lights for UV lamps.

The treatment unit was down for approximately six weeks in June and July 1989 for major servicing and overhauling by the manufacturer. This was necessitated by the excessive downtime being experienced and the inability of the unit to operate at rated capacities. When the unit was brought back on-line, major problems were experienced with wet air and ozone leaks but were corrected by month end.

In spite of the problems, the groundwater recovery system operated more than 65% of the time each month of fiscal year (FY) 1988, except September 1988. The system was down much of September for sparger repairs and feed-gas modifications. The groundwater recovery system operated 61% of the time in FY 1989, excluding the month of January when it was down because of ozone generator problems, and the months of June and July when it was down for servicing and modification by the manufacturer. The operating time percentage increased overall throughout FY 1989; and during FY 1990, it increased to 89%. A more complete discussion and analysis of treatment unit operations, problems, maintenance, and modifications during FY 1988 and 1989 is presented in documents by ORNL. (2,3)

TABLE I

VOCs in the Groundwater Treatment Unit's Influent Water-ug/L<sup>a,b,c</sup>

VOC Constituent	Fiscal Year			
	1988 <sup>d</sup>	1989 <sup>d</sup>	1990 <sup>d</sup>	1991
1,1,1-Trichloroethane	14	18	6	<5
1,2-Dichloroethane	<5	<5	<5	<5
Vinyl chloride	15	42	>9	311
1,1-Dichloroethene (1,1-DCE)	14	12	19	<5
1,1-Dichloroethane (1,1-DCA)	19	15	13	<5
Carbon tetrachloride	<5	<5	<5	<5
1,2-Dichloroethene (1,2-DCE)	714	697	953	1753
Trichloroethene (TCE)	520	329	327	6843
Tetrachloroethene	42	32	18	138
Total VOC	1338	1155	1415	9070

<sup>a</sup> These values represent averages for grab sample analyses.

<sup>b</sup> Detection limit for vinyl chloride is 10 ug/l and 5 ug/l for all

<sup>c</sup> Only VOCs that were detected are listed.

<sup>d</sup> The influent groundwater came from the UTFA only.

### Capacity Study

When the system was originally purchased, characterizations of the TCESA and NEA contaminated groundwater plumes were not complete. As the areas of contamination were further identified, an interceptor system was designed for each area. The anticipated interceptor systems would add 12 additional extraction wells, which would introduce an additional flow of 102.2 lpm (27 gpm) for a potential total flow of 125 lpm (33 gpm). This exceeds the manufacturer's rated capacity of 94.6 lpm (25 gpm) by 30.3 lpm (8 gpm).

During FY 1989, an evaluation of the capacity of the treatment unit was commissioned with Gary Peyton, a private consultant who is a recognized authority in the AOP field. The purpose of this study was to determine the following:

- Is the existing system capable of treating the additional flow?
- Could operation of the existing unit be optimized?

During Peyton's capacity study, ozone peroxide treatment was identified as the primary treatment mechanism and it was determined that the ozone generator was not operating at full capacity. The generator was subsequently overhauled, and monitors were added to determine the ozone output of the generator and to measure ozone concentrations in the offgas (headspace gas of the reaction chamber). These two readings could then be used to determine the mass transfer efficiency of ozone during the treatment process.

Mass transfer efficiency is a measure of the unit's ability to transfer the generated ozone into solution where it is needed for the treatment of groundwater. (4) Transfer efficiency ( $e_t$ ) is calculated as follows:

$$e_t = C_{g \text{ in}} - C_{g \text{ out}} / C_{g \text{ in}} \quad (\text{Eq. 1})(4)$$

$C_{g \text{ in}}$  = concentration of ozone in feedgas to the reactor

$C_{g \text{ out}}$  = concentration of ozone in the offgas

Peyton determined that the system should be capable of treating the projected flow rates and concentrations of VOCs if the transfer efficiency were 60 to 80 percent and the ozone generator were producing the rated yield. In arriving at this conclusion, Peyton made numerous assumptions. His feasibility study (4) should be consulted for a detailed discussion regarding transfer efficiency and ozone generator output calculations.

For optimization of the treatment system, Peyton recommended several routine maintenance activities, one of which was installation of ozone monitors to measure offgas and feedgas concentrations. Another recommended maintenance activity was routine cleaning of the spargers. One indicator of the necessary frequency of this maintenance is the transfer efficiency. A reduction in transfer efficiency could indicate clogged sparger tubes due to the precipitation of iron and manganese by the oxidation process.

### OPERATIONS (FY 1991)

During FY 1991, flows to the system were to be increased by 102.2 lpm (27 gpm), bringing the total flow to 125 lpm (33 gpm), which exceeded the manufacturer's rated capacity of 94.6 lpm (25 gpm) by 30.3 lpm (8 gpm).

### Addition of TCESA and NEA

The KCP added flows from the NEA and TCESA to the treatment system on October 1, 1990. Three start-up tests,

conducted in July and August 1990, determined that requirements of the pretreatment discharge permit were met. During test events, all effluent water was contained until laboratory analyses indicated that permit levels had been achieved. During start-up tests, the highest influent level recorded was 1807 ppb of total VOCs; the corresponding effluent VOC level was 108 ppb. Because of the system's below expectation performance, daily influent/effluent VOC samples were collected during startup. The total-organic-halogen parameter of the permit was exceeded on two occasions during October.

### Problems and Actions Taken

Flows to the system were subsequently reduced from 125 lpm (33 gpm) to 56.8 lpm (15 gpm), and efforts to add a carbon polishing step were initiated. In addition, approximately one-half of the UV lamps and six sparger tubes were replaced. Following these maintenance activities, the KCP began to add flows to the system incrementally. By February 1991, all wells had been added to the system, producing a flow of 125 lpm (33 gpm) when all wells were in operation.

Clogging of the carbon polishing filters became a problem due to naturally occurring high levels of iron and manganese precipitation following oxidation in the reactor. In-line filters (3 micron) were placed upstream of the carbon vessels to capture these precipitates. A backwashing procedure was also initiated to extend the life of the carbon filters by removing iron and manganese not captured by the in-line filters.

The influent water line contains an in-line filter (5 micron) to remove suspended particles prior to treatment. With the addition of flows from the NEA and TCESA, this filter became clogged frequently. The major cause of this problem is iron bacteria build-up at the extraction well. This is a naturally occurring phenomenon that has required frequent treatment of the extraction wells. Typically, the well's capacity to produce is not restricted; rather, the influent becomes highly loaded due to the iron bacteria build-up. Wells are now chemically treated to correct this problem. Pretreatment processes for removal of suspended solid loads have been considered.

The ozone destroyer had, until October 1990, eliminated any ozone present in the reactor offgas. However, following increase of the ozone generator's output in October 1990, due to the addition of flows, the destroyer did not effectively destroy residual ozone prior to being exhausted. Investigations indicated that the ozone destroyer might be too small to process the increased concentration of ozone being utilized. When the vendor was contacted and the situation explained, it was determined that a larger capacity destroyer would cost approximately \$40,000. To minimize this cost, the KCP designed, constructed, and installed a new, larger ozone destroyer for approximately \$2,000. The new destroyer effectively reduces exhaust gas ozone concentrations.

### Increasing Influent VOC Concentrations

Following the addition of all extraction wells to the system in February 1991, influent VOC concentrations continued to increase. Average monthly VOC concentrations increased from 6,200 ppb to 17,500 ppb from October 1990 to September 1991. Increased loading of this magnitude was not anticipated during Peyton's feasibility study. A maximum influent total VOC concentration of 26,590 ppb has been recorded.

### VOC Removal Efficiency

Beginning in November 1990, exhaust gas samples for VOCs were collected. This sampling was initiated both to verify the manufacturer's claim that the system would not air strip the VOCs under treatment and to calculate the overall VOC removal percentage. The total VOC removal efficiency percentage (% RE) is calculated in the following manner:

$$\% RE = \frac{I - (E_a + E_g)}{I} \times 100 \quad (\text{Eq. 2})$$

I = total VOC influent

E<sub>a</sub> = effluent, aqueous VOC

E<sub>g</sub> = effluent, gaseous VOC

The average removal efficiency for FY 1991 and October 1991 was 94.6%. The effluent gas contained approximately 3.7% of the total effluent VOCs and the effluent water approximately 1.7%. Removal efficiency reflects only the removal of VOCs by the UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. Carbon polishing routinely removes all detectable VOCs from the water effluent.

### OPERATIONS (FY 1992)

In October 1991, the headspace of the stainless steel reaction chamber developed numerous pinhole leaks due to corrosion. This condition is prevalent at or just above the water line. Possible causes are under investigation and may be attributed in part or whole to:

- weak acids, formed as by-products of treatment, reacting with products of corrosion caused by the precipitation of iron, and
- residual ozone attacking the stainless steel.

These leaks have been temporarily patched, and the system has remained operational with minimal downtime. The manufacturer is working on a possible protective coating. Another remedial option is to replace the reaction chamber;

however, the cause of the problem needs to be determined and corrected to prevent its reoccurrence.

### COSTS

Operating and Maintenance (O & M) costs calculated by Oak Ridge National Laboratory (ORNL) for the system's present configuration and monitoring plan are \$15.51/3785.4 liters (1000 gallons). (5) These O & M costs were developed based upon the following considerations: (5)

- operating labor costs: wages, training, overhead, and benefits associated with labor requirements for normal operations,
- maintenance costs: labor, parts, supplies, and other resources associated with routine maintenance,
- purchased services: sampling and analytical services for performance monitoring and permit compliance,
- utilities,
- raw materials,
- administrative costs: for management oversight,
- no contingency funds utilized, and
- no depreciation or amortization costs included.

Table II, Operating and Maintenance Cost Comparison, compares costs of the KCP system to those of air stripping and carbon treatment. A detailed discussion of cost comparison and qualifications has been prepared by ORNL. (5)

### REFERENCES

1. W. H. GLAZE and JOON-WUN KANG, "Advanced Oxidation Processes for Treating Groundwater Contaminated with TCE and PCE: Laboratory Studies," *J. Am. Water Works Assoc.*, 80, pp. 57-63 (May 1988).
2. S. B. GARLAND II, "An Evaluation of the Use of a Combination of Ozone, Ultraviolet Radiation, and Hydrogen Peroxide to Remove Chlorinated Hydrocarbons from

TABLE II

Operating And Maintenance Cost Comparison

	KCP 10/90 to 4/91 <sup>a</sup>	KCP 10/90 to 4/91 <sup>b</sup>	HAZWRAP Air Stripping Modified <sup>c</sup>	HAZWRAP GAC Modified <sup>d</sup>
Flow rate-gpm	25	70	70	70
Cost Component				
Labor	\$27,958	\$27,958	\$37,100	\$37,100
Maintenance	18,100	50,680	28,100	29,700
Purchased services	45,500	45,500	78,000	78,000
Utilities	5,987	16,764	23,300	27,600
Raw materials	13,935	39,018	13,300	22,300
Administrative	6,880	6,880	-----	-----
Contingency	-----	-----	54,000	58,400
TOTAL COSTS	\$118,360	\$186,800	\$233,800	\$253,100
COSTS PER 1,000 GAL.	\$15.51	\$8.73	\$6.35	\$6.88

<sup>a</sup> For 10/90 to 4/91 using the June 1991 monitoring program and adjusted to 70 gpm.

<sup>b</sup> One year costs adjusted.

<sup>c</sup> No exhaust gas treatment charges.

<sup>d</sup> No disposal cost of spent carbon.

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3. S. B. GARLAND II, and G. R. PEYTON, "An Evaluation of the Use of an Advanced Oxidation Process to Remove Chlorinated Hydrocarbons from Groundwater at the U. S. Department of Energy Kansas City Plant, Fiscal Year 1989 Annual Report," Oak Ridge National Laboratory (October 1990).
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5. OAK RIDGE NATIONAL LABORATORY, "Department of Energy, Kansas City Plant, Ultraviolet/Ozone/Hydrogen Peroxide Groundwater Treatment System Fiscal 1991 Annual/Final Technology Development Report," (August 1991).