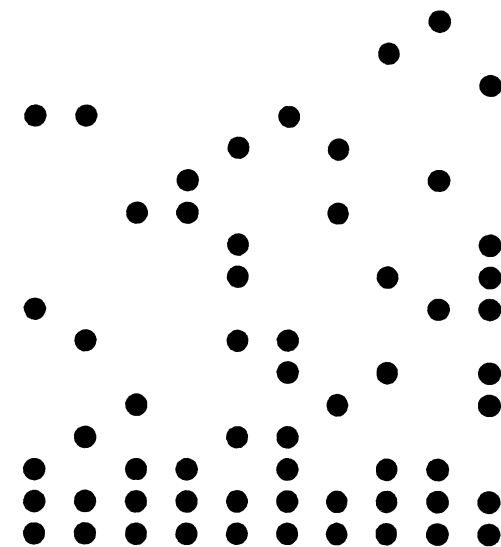


Gateway Center Water Treatment Plant, Los Angeles: Controlled Hydrogen Peroxide  
Treatment of Hydrogen Sulfide and VOC Affected Groundwater

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# CHEMICAL OXIDATION

**Technology For The Nineties**  
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## **ABSTRACT**

Groundwater affected by hydrogen sulfide and volatile organic compounds (VOCs) was removed during a temporary construction dewatering project. Treatment was required to reduce the total sulfide and VOC concentrations prior to discharge to the Los Angeles River. Hydrogen peroxide and sodium hydroxide were added to oxidize the sulfide to sulfate at pH = 9.2 in the first reaction vessel. A prototype hydrogen peroxide control system (Perox 20) was implemented to minimize the amount of hydrogen peroxide used. This was the first application of its kind in the world. The largest commercially available UV-Oxidation system was specified for organics destruction in combination with a backup carbon adsorption system for UV system maintenance, or in the event of a UV system failure. The chemical oxidation of hydrogen sulfide was successful throughout the duration (to date) of treatment plant operation. The UV-Oxidation system was successful at meeting the discharge limits at low organic loading rates, however, activated carbon was implemented at higher organic loading rates. The operation of the various components of the treatment plant with respect to the oxidation of hydrogen sulfide and dissolved VOCs (benzene) are addressed in the paper.

## **INTRODUCTION**

The Gateway Center underground parking facility will provide space for the occupants of six future office buildings and Union Station, the central hub of the Los Angeles Metropolitan Transit Authority (MTA) in downtown Los Angeles. The first stage of the development was to construct a 40+-foot deep excavation for construction of an underground parking structure in which temporary (approximately two years) dewatering was required to lower water levels approximately twenty feet over ten acres during construction. The regional groundwater in the vicinity of the site is affected by hydrogen sulfide and dissolved petroleum/chlorinated

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hydrocarbons and requires extensive treatment before the groundwater can be discharged to the Los Angeles River. The suspected source of these chemicals is a nearby former coal gasification plant which operated from the 1890s until the 1950s.

Groundwater was initially extracted from 25 extraction wells fitted with submersible electric pumps. The extracted ground water is pumped through the site piping to the treatment plant. The groundwater treatment system was designed to be capable of treating approximately 800+ gallons per minute (gpm); however, flow rates decreased once a steady state flow condition was reached and the required drawdown was obtained. There are two main aspects of the dewatering system: the groundwater extraction system and the water treatment plant. The groundwater extraction system design consisted of a pumping test and three-dimensional groundwater modeling to design the extraction system and predict its performance. The plant was designed for 1.2 MGD (~850 gpm). The design flow rates were within ten percent of the actual flows. Draw down was predicted to be three weeks, but actually occurred in approximately ten days.

In order to meet a tight construction schedule, the water treatment plant was built very quickly, two months from pre-slab to start-up. The main process consists of extensive pH adjustment and chemical addition for sulfide and VOC removal. Hydrogen peroxide and sodium hydroxide are added to oxidize the sulfide to sulfate at pH = 9.2 in the first reaction vessel. Sulfuric acid was used to lower the pH to 4.0 in the second reaction vessel. A prototype hydrogen peroxide control system (Perox 20) is in use to minimize the amount of hydrogen peroxide used, this is the first application of its kind in the world. The largest commercially available UV-Oxidation system was specified for the organics destruction and a backup carbon adsorption system is available in the event of UV-Oxidation system maintenance or a UV system failure. The pH is raised from 4.0 to 6.0 with sodium hydroxide as the final part of the treatment process. The components of the treatment plant are tied together with a Programmable Logic Control (PLC) system.

## **DESIGN CRITERIA AND DISCHARGE LIMITS**

The primary focus of the process design was the removal of VOCs and hydrogen sulfide. Discharge limits were set by a National Pollutant Discharge Elimination System (NPDES) permit from the Regional Water Quality Control Board. Although there are many VOCs in the groundwater that have discharge limits in the permit, the most significant proved to be benzene. The drinking water standard for benzene is 1.0 microgram per liter ( $\mu\text{g/L}$ ), however, the discharge limit for the project was set at 0.34  $\mu\text{g/L}$ . The design influent concentration for benzene was 35  $\mu\text{g/L}$ , based on the maximum average concentration from the groundwater monitoring network at the site. The discharge limit for total sulfides was 1 mg/L and the design concentration of total sulfides was 50 mg/L. These discharge limits are very stringent. The standard laboratory detection limits of benzene and hydrogen sulfide are 0.5  $\mu\text{g/L}$  and 1.0 mg/L, respectively. Therefore, there was effectively no margin of error in the design or operation of the plant. The pH limit was 6.0-9.0, the turbidity, 50 NTUs, and TSS, 50 mg/L.

## **FIELD TESTING AND PROCESS DESIGN**

In February 1993, field testing took place at a well in the center of the proposed excavation in the most highly affected region. This well had previously been utilized for the pumping test to quantify aquifer parameters. Approximately 60,000 gallons of groundwater had been removed from this well. On the day of the field testing, 200 gallons of water were purged from the well and batch tests at five different pH values were conducted. The purpose of these tests was to determine the optimum pH for sulfide degradation kinetics after hydrogen peroxide addition and to verify discharge limits of turbidity could be met by the addition of sulfuric acid.

Figure 1 shows the variation of first-order sulfide degradation rates as a function of pH. The initial hydrogen peroxide dose was determined by measuring the initial total sulfide concentration and adding hydrogen peroxide in excess of the stoichiometric requirement. The peroxide and total sulfide concentration were measured at regular intervals until asymptotic sulfide depletion. There was visual evidence of the production of elemental sulfur at pH = 6.5. The first-order kinetic rate of sulfide removal decreased at pH greater than 9.2 which was the result of the increase in overall flocculent formation.

Due to the hardness of the groundwater, scale formed as a result of the increase in pH. The removal of this scale became a critical design issue. In order to evaluate both the nature of the scale/flocs and the degree to which they could be dissolved, laser particle counting was implemented from the batch tests and duplicate samples were acidified with sulfuric acid to dissolve the particles. Figure 2 shows variation in concentration of particles as a function of average particle diameter for the acidified and non-acidified samples. The concentration was estimated from the number of particles within selected particle ranges, assuming the particles were spheres and had a specific gravity of 1.4. The results of these calculations compared very well to independent measurements of total suspended solids (TSS). The turbidity and suspended solids concentration of the acidified samples were well within the discharge limits. The removal of the particles was also necessary to ensure the proper operation of downstream processes.

## **PROCESS DESCRIPTION**

The treatment process is generally divided into three steps that can be identified as (1) the sulfide oxidation phase, (2) the VOC treatment phase, and (3) the discharge phase. In the sulfide oxidation phase, sulfide in the groundwater is oxidized to sulfate by the addition of hydrogen peroxide at pH=9.2. The pH is then lowered to prepare for the VOC treatment phase. In the VOC treatment phase, VOCs are either destroyed in an ultraviolet oxidation (UV/Ox) system or removed by carbon adsorption. In the discharge phase, the pH is raised so that the treated water is suitable for discharge. Figure 3 shows the process flow diagram of the treatment plant. Figure 4 is the layout of the equipment on the pad which clearly indicates the effect of

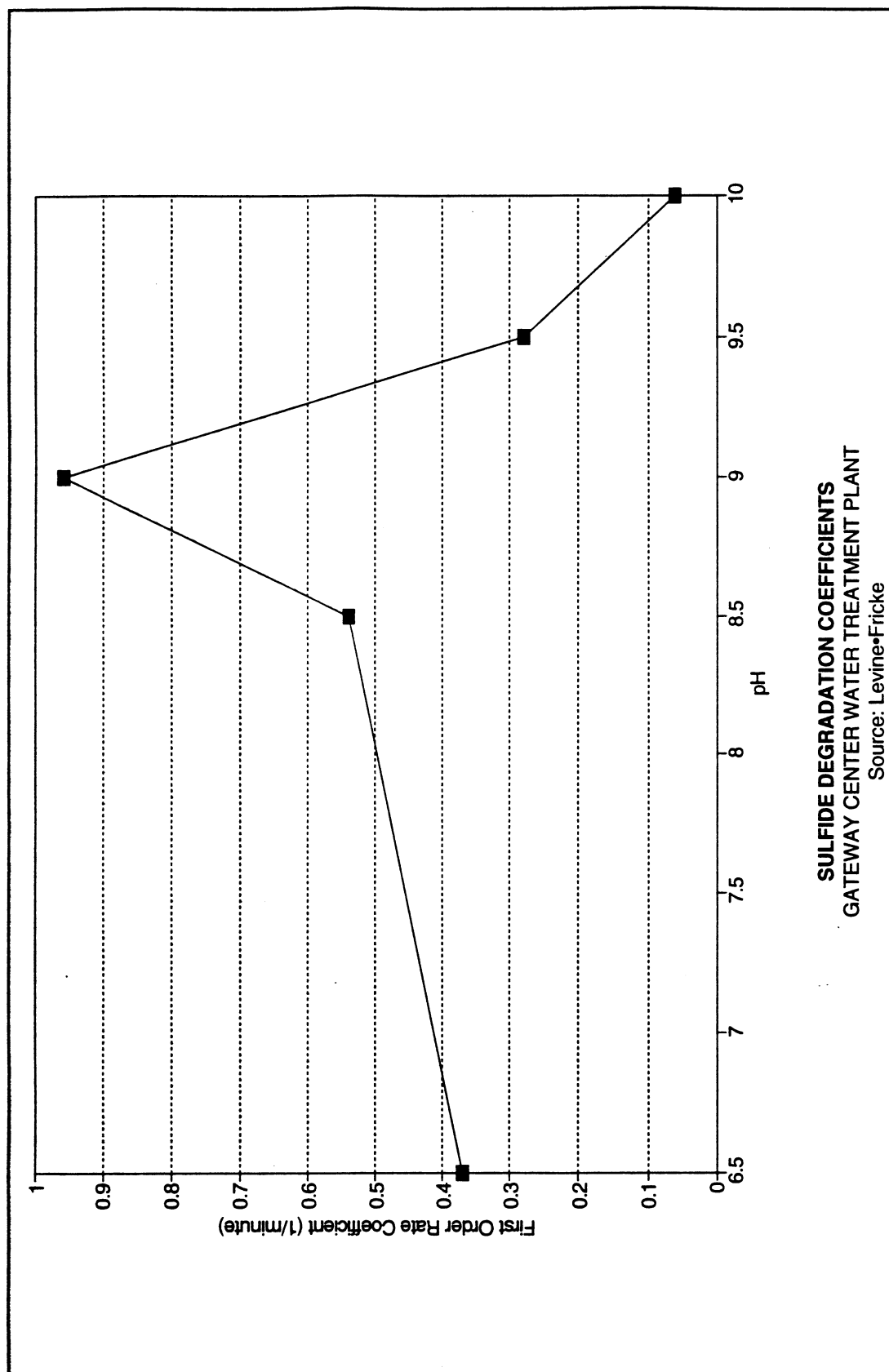
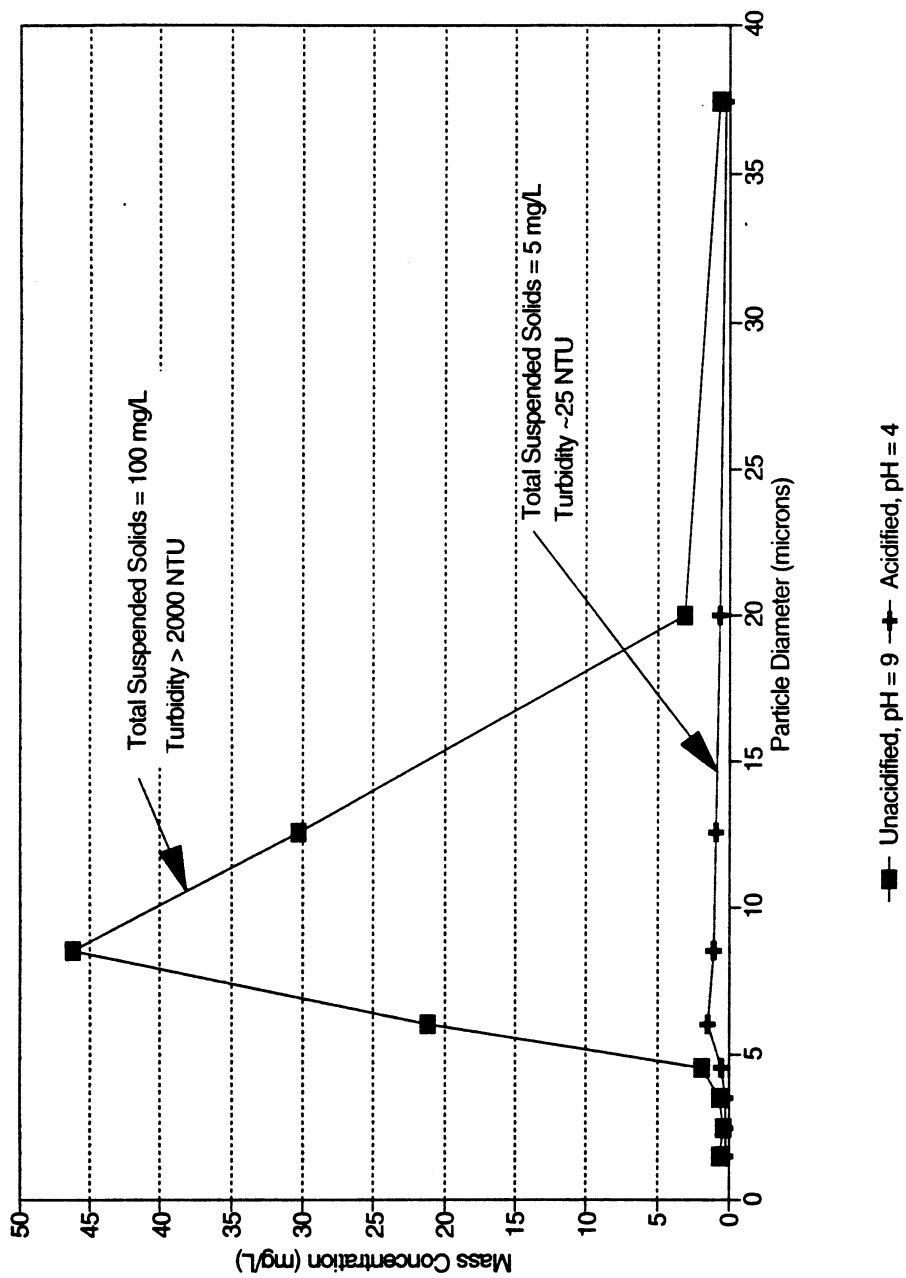


Figure 1.



**PARTICLE SIZE DISTRIBUTIONS**  
 GATEWAY CENTER WATER TREATMENT PLANT  
 Source: Levine•Fricke

Figure 2.

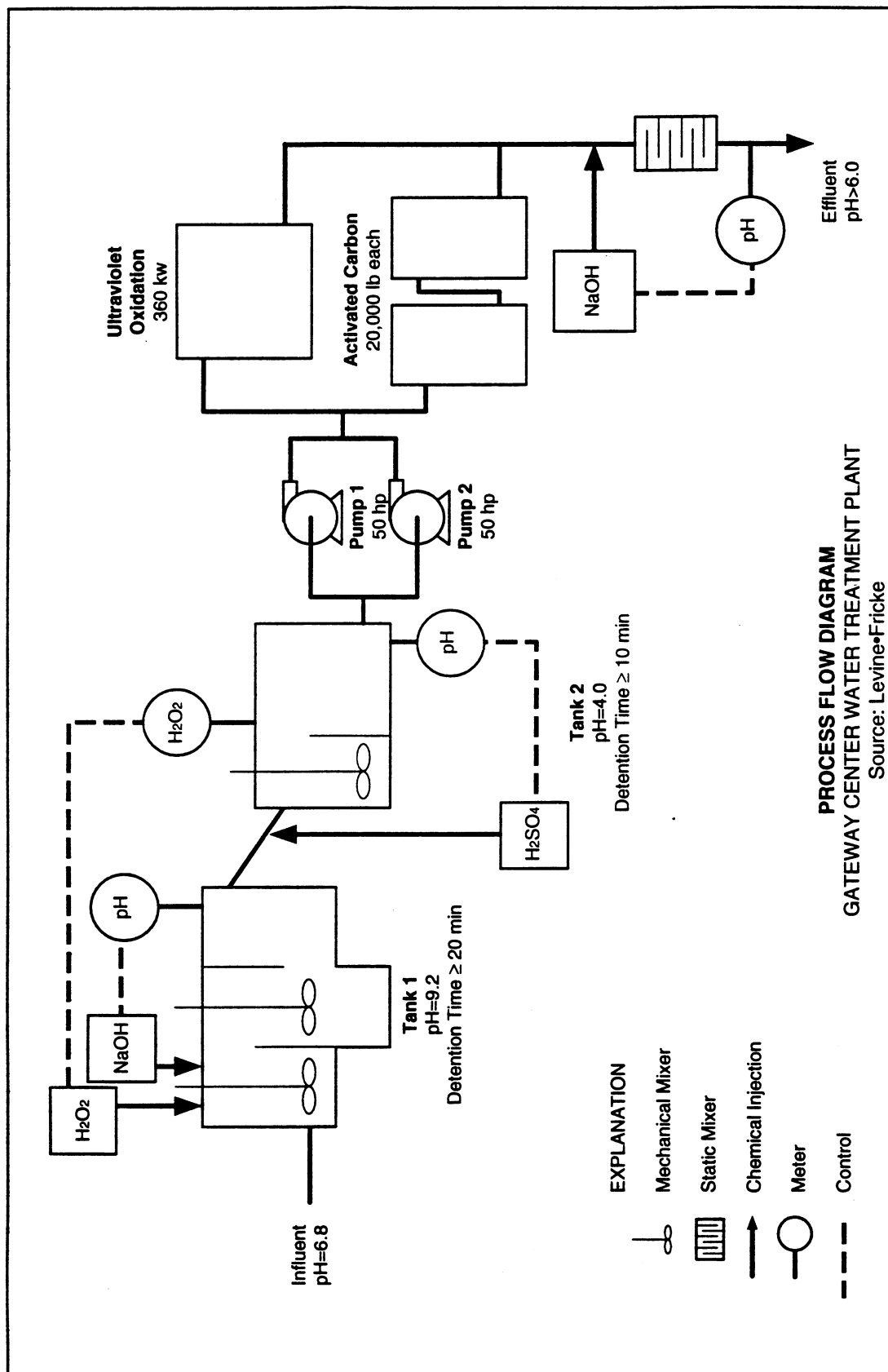


Figure 3.

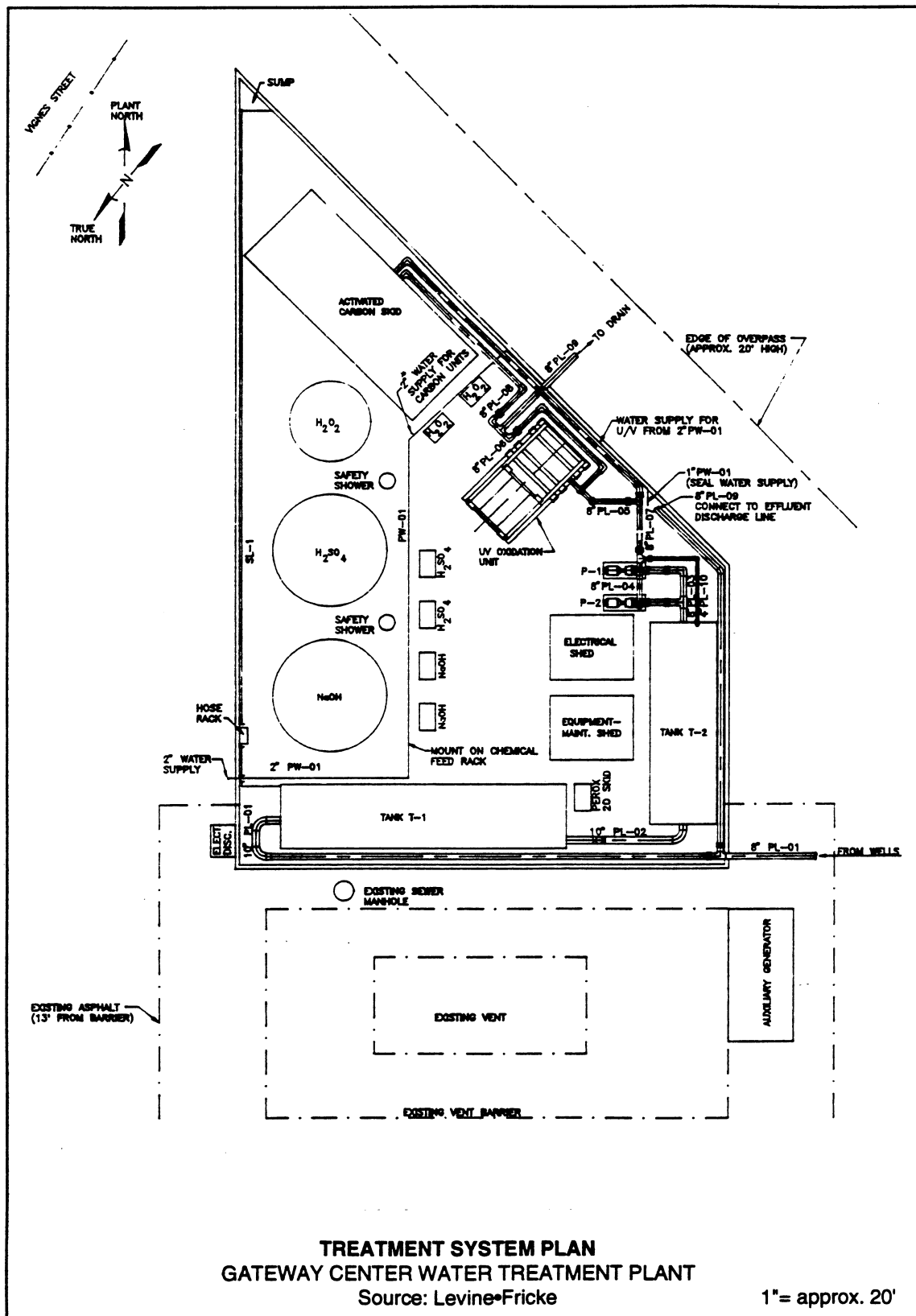


Figure 4.



space limitations. Figure 5 is the overall site layout which shows the relationship of the treatment plant with respect to the dewatering wells and the ultimate point of discharge of the treated groundwater.

## SULFIDE OXIDATION PHASE

The ground water was pumped from 25 dewatering wells through a common header to the plant. Sodium hydroxide is added and mixed to raise the pH to approximately 9.2. Hydrogen peroxide is added and mixed to act as an oxidizing agent. At pH 9.2, the hydrogen peroxide oxidizes sulfide to sulfate. This reaction occurs in Tank 1, a 500-barrel (21,000-gallon) tank which provides over 23 minutes of detention time at 800 gpm for the sulfide oxidation reaction to occur. Tank 1 has two vertical baffles and two mechanical agitators in the first two of three cells created by the baffle arrangement. The addition of hydrogen peroxide is controlled by the Perox 20.

The process water flows from Tank 1 to Tank 2 by gravity flow. Between Tank 1 and Tank 2 sulfuric acid is added to lower the pH to approximately 4.0. The pH is lowered to redissolve the solids that precipitate out of solution at pH 9.2. The sulfuric acid is mixed by a mechanical agitator in the front end of Tank 2. Tank 2 is a 320-barrel (13,440-gallon) tank with one baffle which separates the front section of the tank which contains the mixer. The sulfuric acid addition is controlled by a pH probe located at the outlet of Tank 2.

## VOC TREATMENT PHASE

Pumps 1 and 2 pump the process water from Tank 2 through either the UV/Ox system or the carbon system to the discharge point. The UV/Ox system bombards the process water with ultraviolet light in the presence of hydrogen peroxide. The ultraviolet light energizes a reaction which destroys the VOCs in the water by bombardment of them with hydroxy-radicals. A flow control valve may divert the process flow to the granular activated carbon adsorption system in which case the VOCs in the process water attach (or adsorb) onto the carbon. When the carbon is saturated with VOCs, it is removed from the vessel and replaced with clean carbon. In the event of a power failure, the VOC treatment is performed by the carbon adsorption system and a standby generator provides power to the system.

## DISCHARGE PHASE

Following the VOC treatment phase, the pH of the process water is still approximately 4.0. In the discharge phase, sodium hydroxide is added and mixed to raise the pH to greater than 6.0 as required to comply with the discharge limits. The addition of caustic soda is controlled by a pH probe located downstream of an in-line static mixer.

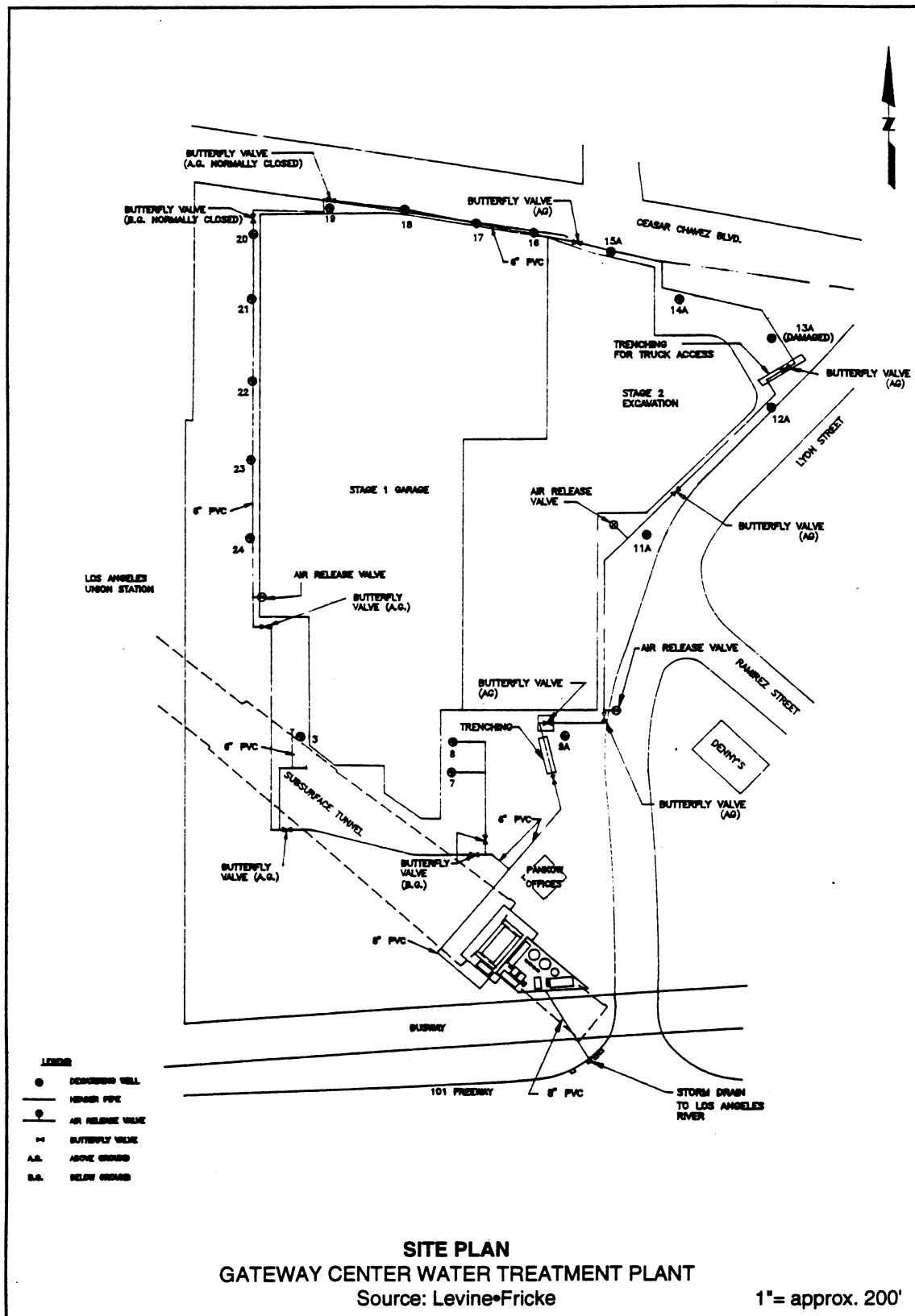


Figure 5.

## **PLANT PERFORMANCE AND CHANGES IN GROUNDWATER CHEMISTRY**

Figure 6 is a graph of the flow to the treatment plant from June 1993 through November 1994. The flow decreased from start-up until September 1993 as steady-state flow developed. The flow varied slightly until June 1994 as construction either allowed groundwater levels to rise or fall. In June 1994, the excavation was expanded and additional areas were dewatered initiating a second approach to steady-state. The maximum total sulfide concentration to enter the treatment plant was 65 mg/L, which was reduced to less than 1 mg/L during the sulfide oxidation phase.

Figure 7 illustrates the variability in influent benzene concentration and benzene loading with respect to the flow to the treatment plant. As depicted in the figure, there has been an overall steady increase in benzene loading to the treatment plant. The source of the increased benzene loading is suspected to be from off-site. The increase in benzene loading to the treatment plant exceeded the design loading to the UV system and resulted in poor performance. In order to compensate, the primary VOC treatment was switched to activated carbon in October 1993.

Figures 8A, 8B and 8C show the time varying usage rates of caustic soda, sulfuric acid and hydrogen peroxide. The overall trends in all the usage rates reflect the changes in flow.

## **SUMMARY AND CONCLUSIONS**

The Gateway Center Water Treatment Plant was designed to oxidize hydrogen sulfide and dissolved VOCs produced from groundwater dewatering. The oxidation of hydrogen sulfide with hydrogen peroxide was a success in that the full-scale system operated per design parameters determined from field testing. The implementation of a hydrogen control system combined with the results of initial kinetic testing was successful at reducing chemical and labor costs for the optimum oxidation of hydrogen sulfide. The UV-Oxidation system was successful at meeting the discharge limits at low organic loading rates, however, activated carbon was implemented at higher organic loading rates. The initial field testing for chemical kinetic parameters combined with aquifer testing and groundwater flow modeling formed the basis of treatment system design. An unanticipated increase in benzene concentrations required operation of the initial back-up system to become the primary method of VOC removal. The UV-oxidation system is used at very low flow rates, i.e. low benzene loading rates.

## **ACKNOWLEDGEMENTS**

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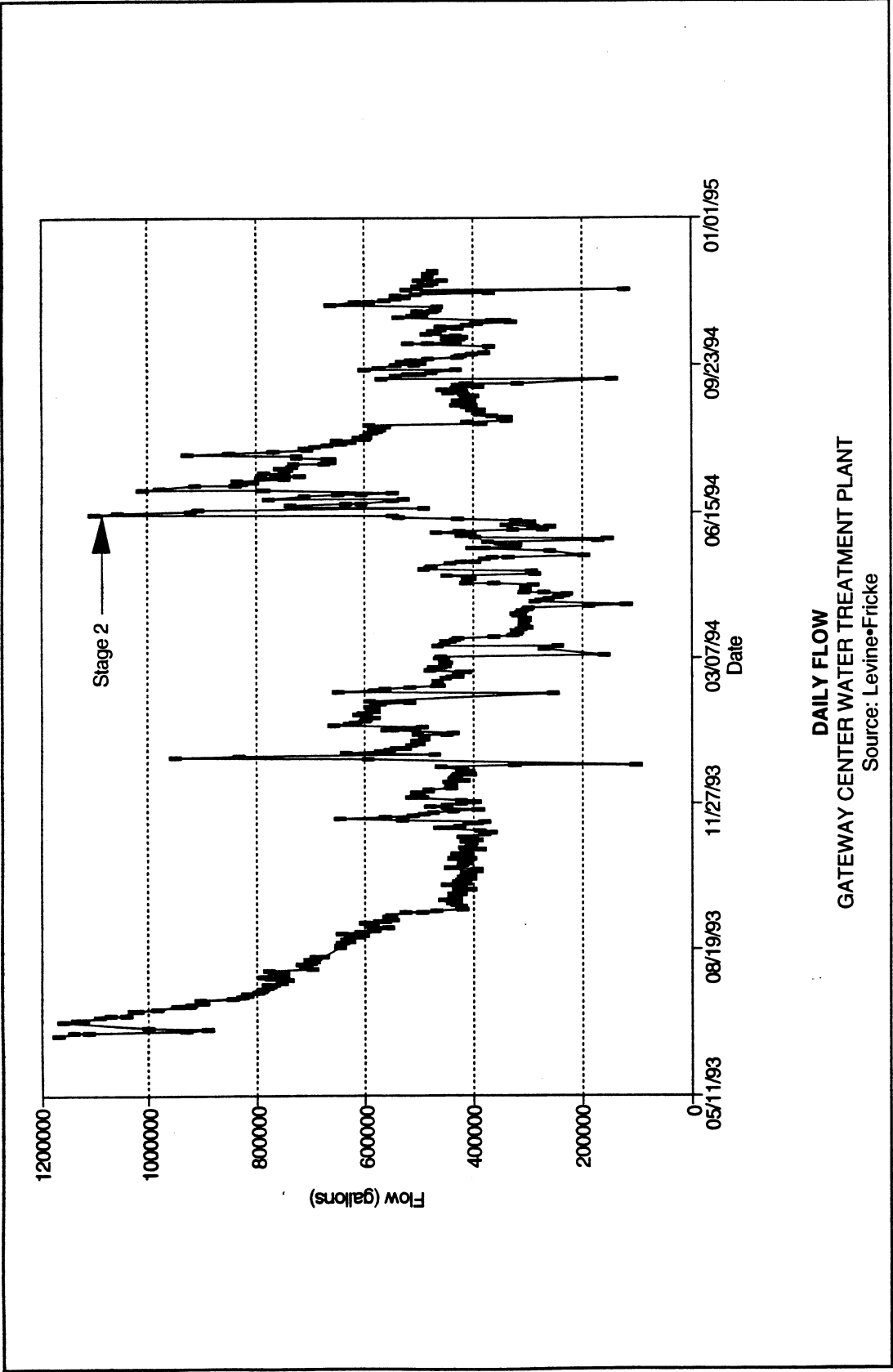


Figure 6.

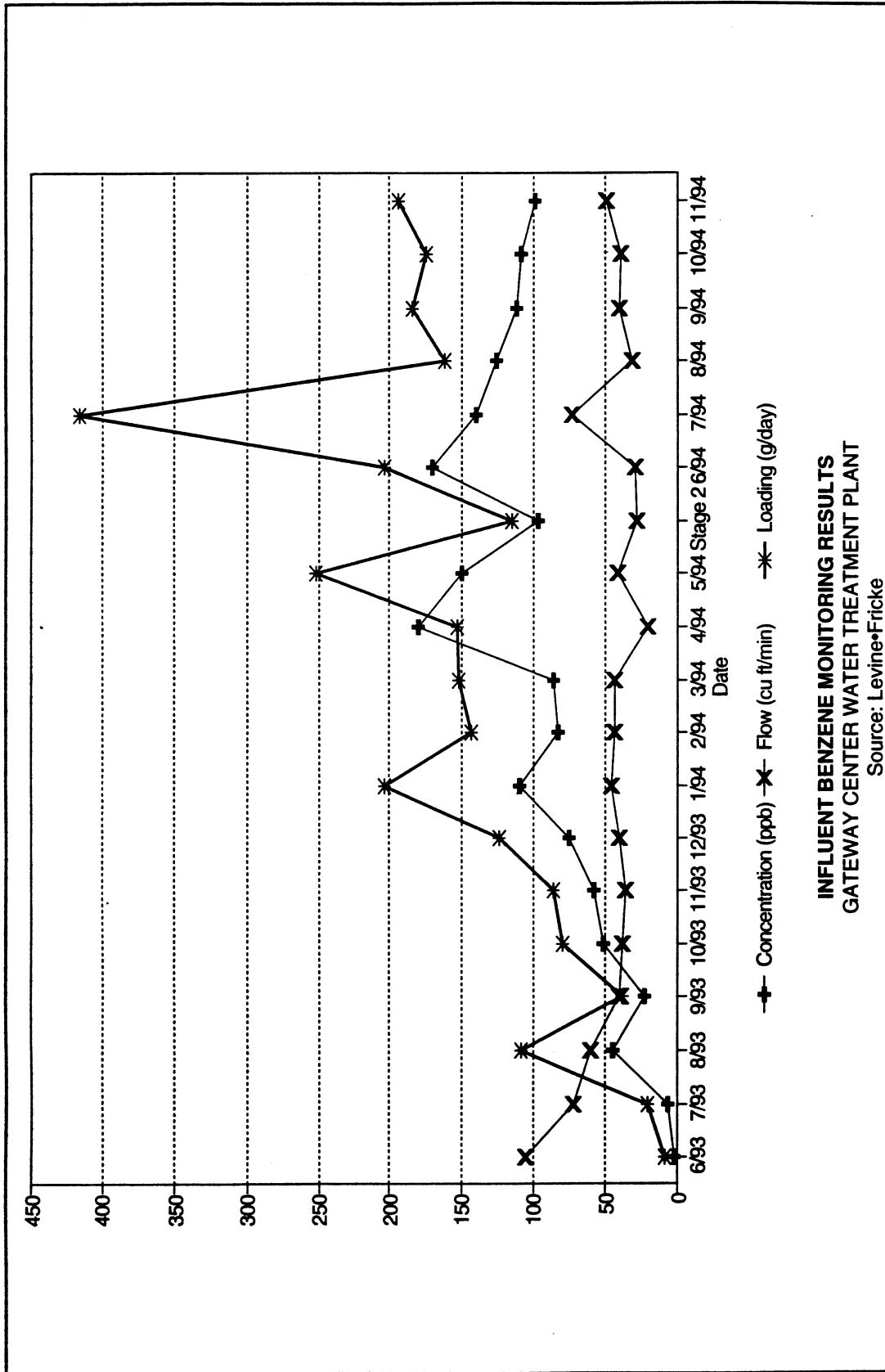


Figure 7.

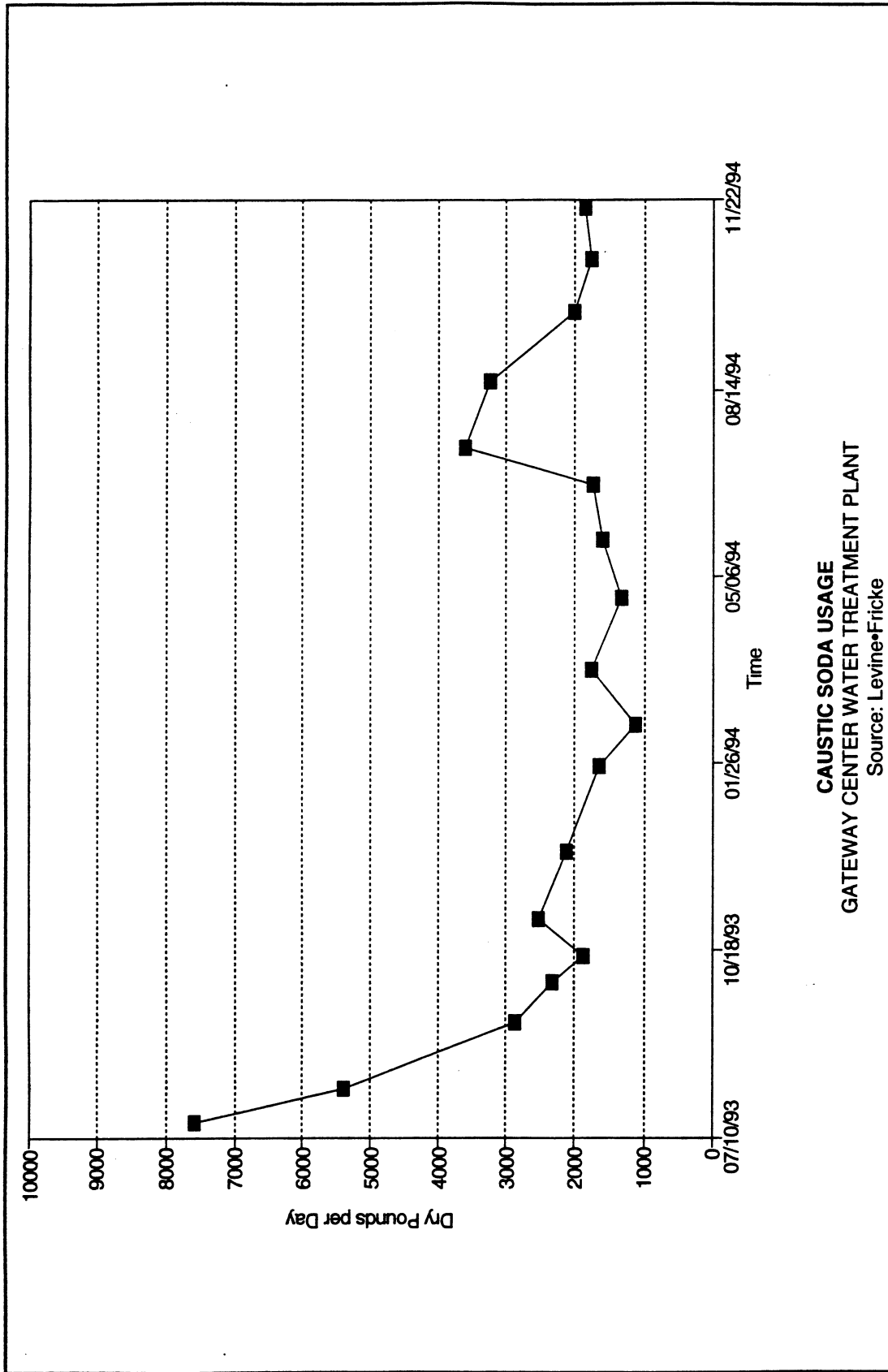
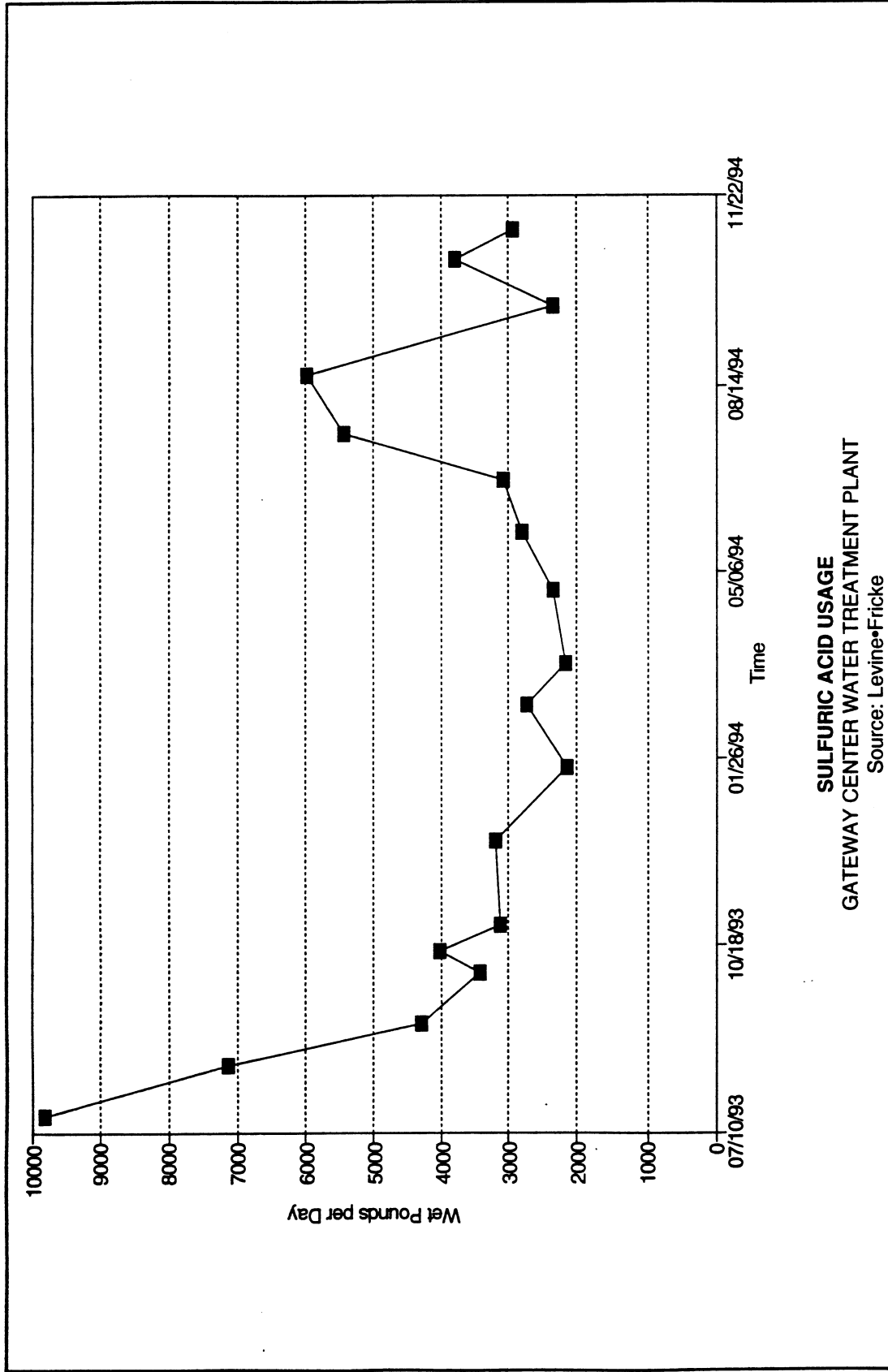


Figure 8A.



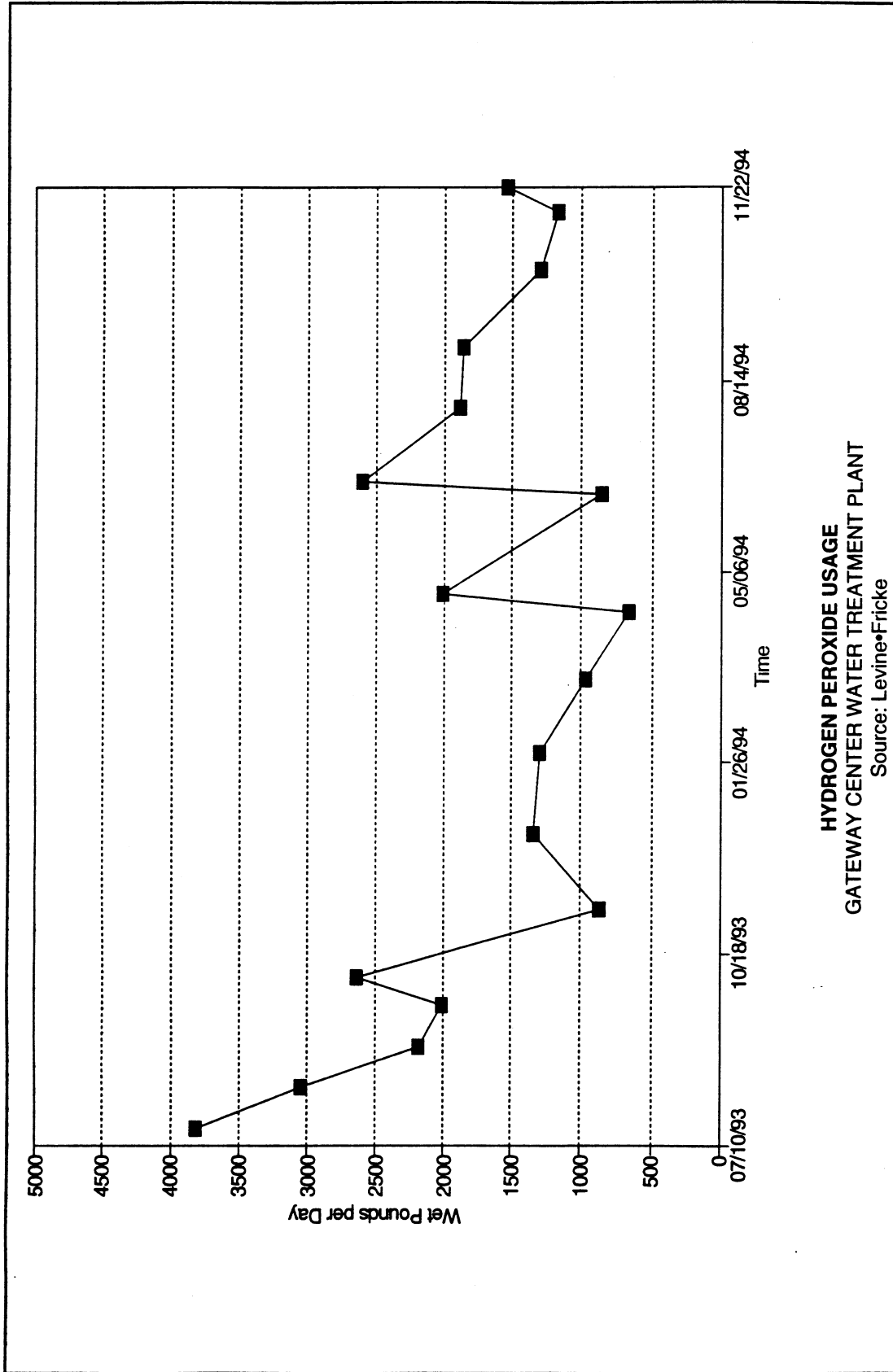


Figure 8C.



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