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TREATMENT OF COAL CONVERSION WASTEWATER WITH THE
POWDERED ACTIVATED CARBON-CONTACT STABILIZATION
ACTIVATED SLUDGE PROCESS

First Semiannual Technical Progress Report for Period August 1,
1980-January 31, 1981

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Work Performed Under Contract No. FG22-80PC30233

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U. S. DEPARTMENT OF ENERGY

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INTRODUCTION

The aqueous effluents emanating from coal conversion operations have been characterized by excessively high concentrations of phenol (200-6,600 mg/ℓ), ammonia (2,500-11,000 mg/ℓ), thiocyanate (20-1,000 mg/ℓ) and cyanide (0.1-100 mg/ℓ) (Singer et al., 1977). The simultaneous presence in coal conversion wastewaters of these four constituents renders the treatment of such wastewaters a very difficult task. Ammonia and thiocyanate have been reported to inhibit phenol biooxidation when present at concentration levels exceeding 1,700 and 250 mg/ℓ, respectively, while thiocyanate degradation was reported to be completely halted at ammonia and phenol concentrations of 1,000 and 25 mg/ℓ, respectively (Juntgen and Klein, 1977; Valiknac and Neufeld, 1978). Nitrification, on the other hand, is very sensitive to the presence of a large number of organic compounds some of which are phenol, cyanide, and thiocyanate (Juntgen and Klein, 1977; Hockenbury and Grady, 1977).

The treatment of coal conversion wastewaters has traditionally been accomplished through the use of the activated sludge process and its various modifications (Ganczarzyk and Elion, 1978; Sack and Bokey, 1978; Luthy et al., 1980). General observations made by these authors have been that phenol was degraded efficiently, however, very poor removal efficiencies of thiocyanate, cyanide, and ammonia were obtained.

The addition of powdered activated carbon (PAC) to the activated sludge process has been reported to result in a number of distinct advantages (DeWalle and Chian, 1977). Generally, however, improving the effluent water quality beyond the capabilities of conventional biological treatment and enhancing the treatability of wastewaters that inhibit or toxify biological treatment systems are the primary objectives of utilizing PAC in secondary biological treatment.

Robertaccio (1976) observed that the addition of PAC to the activated sludge process only slightly enhanced the removal of relatively nonadsorbable substrates (acetate) whereas quite significant incremental reductions in the adsorbable substrates phenol and isopropyl alcohol were obtained. Robertaccio (1976) also noted that an increase in the mixed liquor concentration of PAC resulted in an increase of the degree of enhancement in the removal of phenol in an activated sludge process. DeWalle and Chian (1977) reported an increase in the "apparent" maximum adsorptive capacity on PAC as the cell residence time of an activated sludge process was increased. They postulated that since the ratio of biomass concentration to PAC concentration increased with increasing sludge age (for a constant mixed liquor PAC concentration) a more effective regeneration of the carbon surface can occur.

The focus of the present research project is to assess the effectiveness of the powdered activated carbon-contact stabilization activated sludge process in the treatment of a coking wastewater. The purpose of the contact tank in such a process will be to provide sufficient time for the adsorbable constituents of the coking wastewater to adsorb onto the PAC. The liquor leaving the contact tank is then clarified with the concentrated underflow receiving treatment in the stabilization tank. After stabilization the sludge is returned to the contact tank. The clarifier supernatant is then nitrified in an activated sludge-type nitrification process and the nitrified effluent is subsequently denitrified in an anoxic filter.

SCOPE OF WORK

The scope of work of the present research project is to evaluate the effectiveness of the powdered activated carbon-contact stabilization activated

sludge process in the treatment of a coke oven wastewater. Nitrification and subsequent denitrification of the contact-stabilization clarifier effluent will also be evaluated. Emphasis during this research will be placed on determining the effect of sludge retention time and the PAC addition rate on the performance of the contact-stabilization process and the subsequent unit processes. Optimization of the contact and stabilization contact times will also be attempted.

EXPERIMENTAL MATERIALS AND METHODS

Experimental Apparatus

Three identical experimental apparatuses were constructed for the study, each apparatus consisting of:

- i. a contact aeration tank,
- ii. a stabilization aeration tank,
- iii. a clarifier serving the contact-stabilization aeration tanks,
- iv. a nitrification aeration tank,
- v. a nitrification clarifier,
- vi. a sump and overflow box, and
- vii. a denitrification contact column.

Aeration Tanks

The contact, stabilization and nitrification aeration tanks were constructed using 0.25" thick Plexiglas plate. Each aeration tank was fabricated as a rectangular parallelepiped having a 12" per side square base and a height of 23" (see Figure 1). Two 0.25" thick Plexiglas plates were placed in the parallelepiped in order to form an aeration volume having the form of an inverted triangular prism. The reason behind the use of this form of an aeration tank is to facilitate the maintenance of a reasonable depth of water

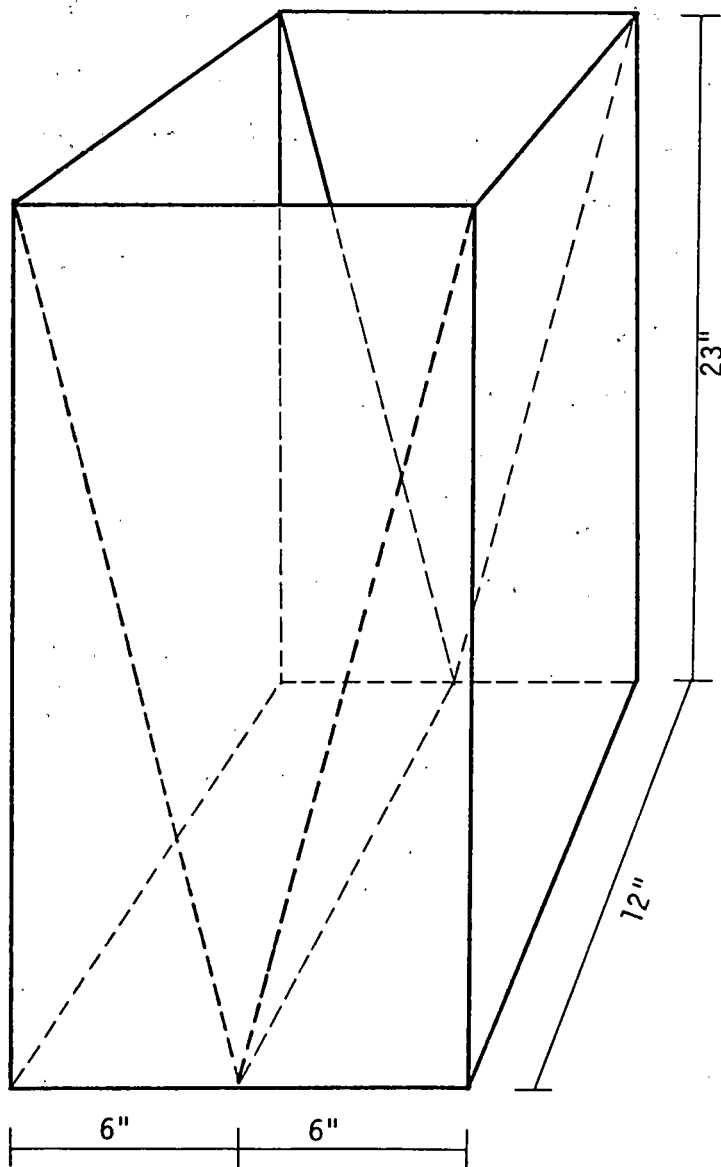


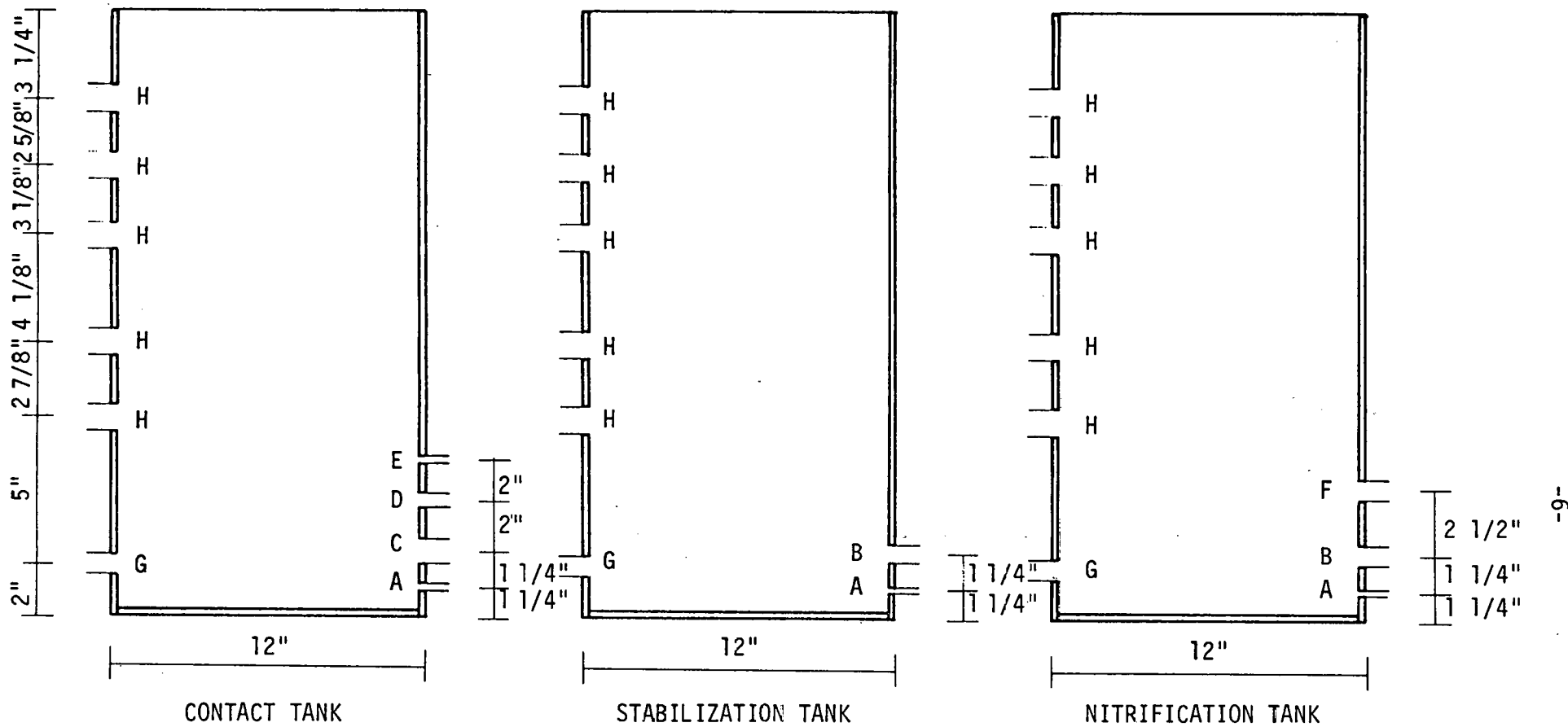
Figure 1. SCHEMATIC OF AERATION TANK

within the tank when lower contact volumes are desired. To allow for the attainment of different water depths in the aeration tanks, each tank was provided with five 1" NPT Swagelok Tube Fittings (Crawford Fitting Company, Solon, OH) at levels of 7, 9 7/8, 14, 17 1/8, and 19 3/4 inches from the bottom of the aeration tank (see Figure 2). Each tank was also provided with a 3/4" NPT Swagelok Tube Fitting (Crawford Fitting Company, Solon, OH) drain port situated 2" from the bottom of the tank and a 1/4" NPT Swagelok Tube Fitting situated 1 1/4" from the bottom and serving as an inlet port for a 5/16" OD plastic tube diffuser.

The contact aeration tanks were also provided with a 1/2" NPT Swagelok Tube Fitting for the raw wastewater influent line, a 1/4" NPT Swagelok Tube Fitting for the powdered activated carbon feed line and a 1" NPT Swagelok Tube Fitting for the stabilized sludge return line. These three fittings were situated 4 1/2, 6 1/2, and 2 1/2 inches from the bottom, respectively. The stabilization and nitrification aeration tanks, on the other hand, were provided with 3/4" NPT Swagelok Tube Fittings situated 2 1/2" from the bottom and serving as sludge feed ports. The nitrification aeration tanks had an additional 3/4" NPT supernat tank.

Clarifiers

Two clarifiers were constructed for use in each of the three experimental apparatuses; one serving the contact stabilization process while the other serving the nitrification phase of the units. The main body of each clarifier was constructed of a 40" long, 8" OD 1/4" wall Plexiglas tube (see Figure 3). Mixed liquor was introduced into each clarifier through an 18" long 2 1/4" OD



- A - 1/4 NPT Air Line Fitting
- B - Sludge Inlet From Clarifier Underflow
- C - Stabilized Sludge Return
- D - Wastewater Feed Line
- E - Powdered Activated Carbon Feed Line
- F - Influent To Nitrification Tank
- G - Drain Line
- H - Effluent Line

Figure 2. INLET AND OUTLET DETAILS FOR AERATION TANKS

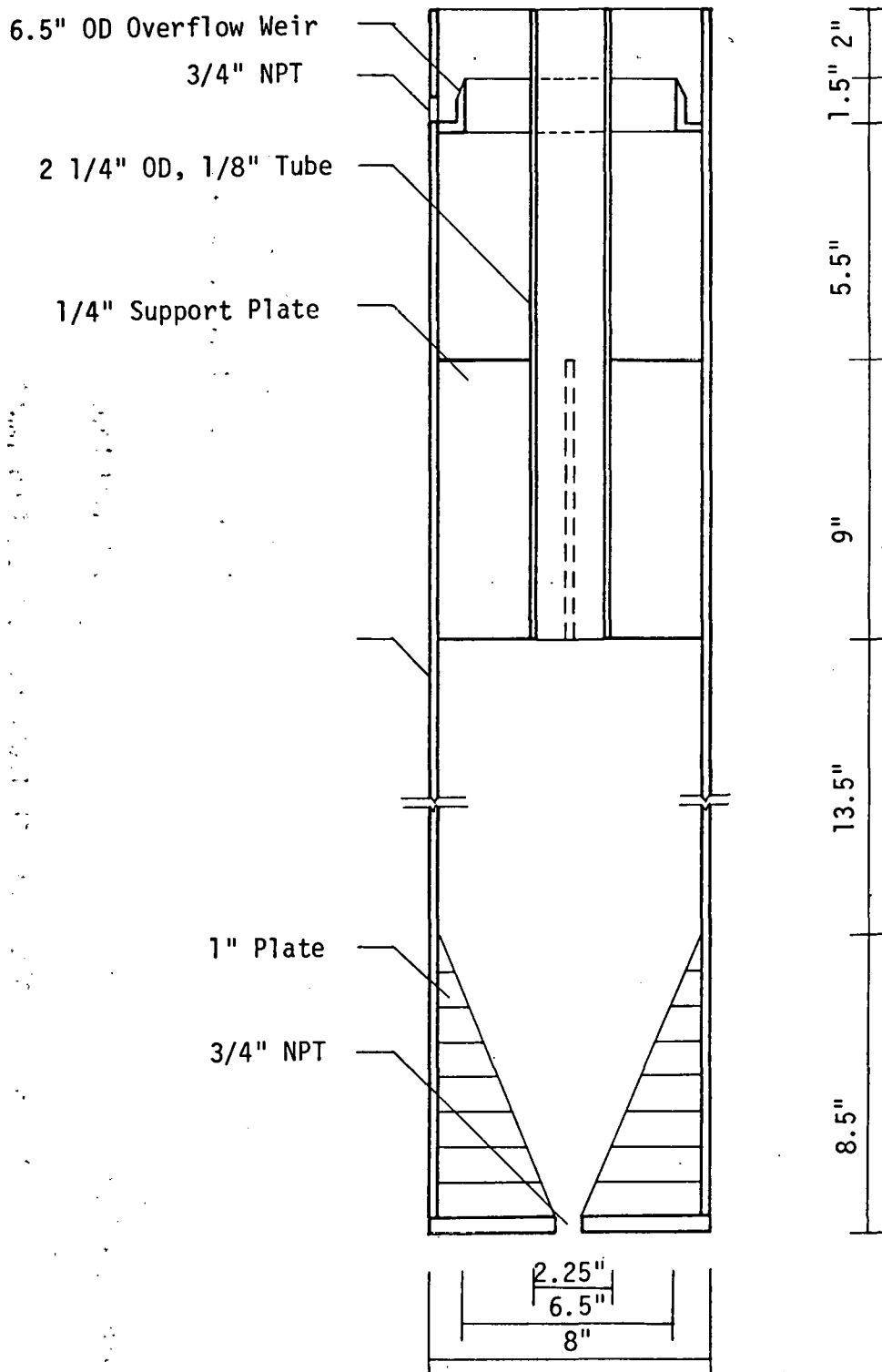


Figure 3. SCHEMATIC OF CLARIFICATION TANK

1/8" wall Plexiglas tube supported centrally within the clarifier. A funnel-shaped base constructed of eight 1" plates was placed at the base of each clarifier. The inner walls of the base funnel are sloped at 3.56:1 and are used for the collection and concentration of the biological flocs prior to recycle. The overflow weir structure was constructed of a 6 1/2" OD 1/4" wall Plexiglas tube section 1.5" in length. The top part of the weir was bevelled to provide a sharp water contact while the outer wall of the weir tube and the inner wall of the clarifier tube were joined by a 1/4" thick plate to provide an effluent collection channel. The supernatant from the clarifier was withdrawn through a 3/4" NPT opening situated flush with the effluent channel bottom while the concentrated underflow was withdrawn through another 3/4" NPT opening situated at the center of the base of the clarifier (see Figure 3).

Denitrification Feed Sumps

The effluent from every nitrification clarifier is collected in a sump with an overflow weir and the corresponding denitrification column is fed from this sump at a flow rate which is lower than the clarified effluent. The purpose of the sump is to provide a water seal between the clarifier and the denitrification column and aid in avoiding the introduction of air into the denitrification column. The sump also provided a reservoir volume of 4 l of nitrified effluent (see Figure 4).

Each sump was constructed of 1/4" Plexiglas plate. The square base of the sump was 8" on the side while the height was 12". An 8" square 1/4" thick Plexiglas plate was used to divide each sump into two compartments. One compartment served to receive the nitrified effluent and a 1/2" NPT Swagelok

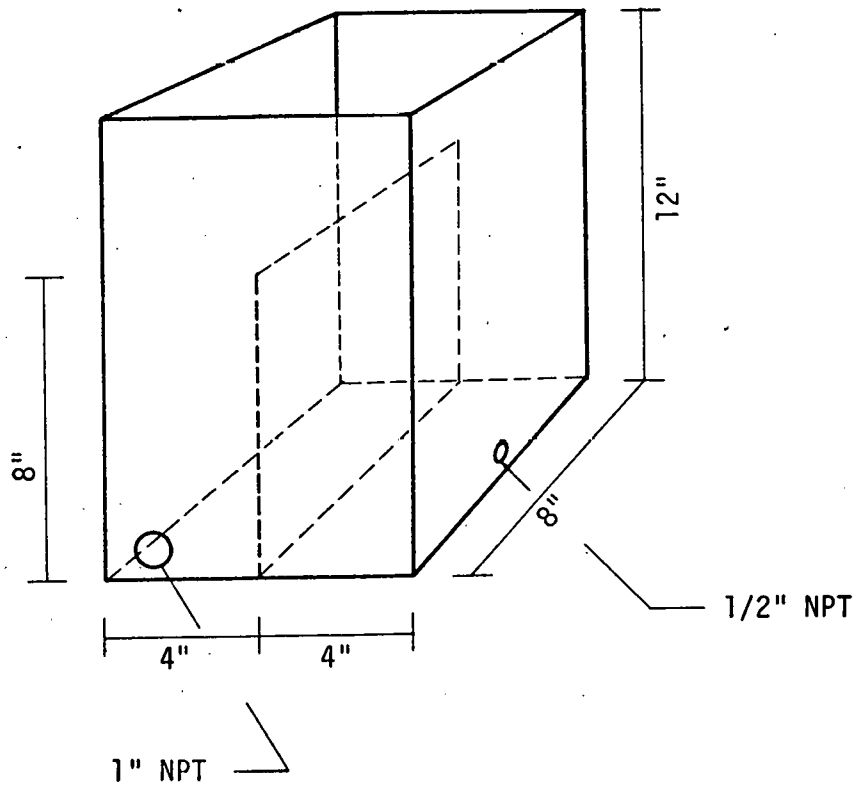


Figure 4. SCHEMATIC OF DENITRIFICATION COLUMN FEED SUMP

Tube Fitting was placed at the outer wall of this compartment to provide the feed to the denitrification column. The other compartment served to receive the excess nitrified effluent and a 1" NPT fitting was used to conduct this excess flow to the drain.

Denitrification Columns

Each denitrification filter consists of a water jacketed column. The inner tube which is 48" long was constructed using a 4 1/2" OD 1/4" wall Plexiglas tube (see Figure 5). A 1/2" thick flange, 6 1/2" in diameter was attached to each end of the tube. These two flanges serve to connect the main body of the column to the influent and effluent structures. A 45" long water jacket was constructed around the main body of the column using a 6" OD 1/4" wall Plexiglas tube. The influent header (see Figure 5) was constructed using a 6 3/8" long inner tube section. The inside of the tube was tapered to an inverted conical shape using ten pieces of 1/2" plate in order to allow for better distribution of the influent flow. A 1/2" thick flange, similar to the ones attached to the inner tube provided the means for attaching the influent header to the main column. A similar header was used for the effluent structure of the column. The influent, effluent, and gas withdrawal ports were all 1/2" NPT Swagelok Tube Fittings. The gas collection system for every column which consisted of a 6.5 l gas buret, two 4 l leveling bottles and a sampling port was used to monitor gas production and composition.

Operation of Experimental Apparatuses

The various unit processes of every experimental apparatus were connected as shown schematically in Figure 6. The feed wastewater was placed in a 50 l polyethylene reservoir and fed to the contact aeration tank at the feed rate

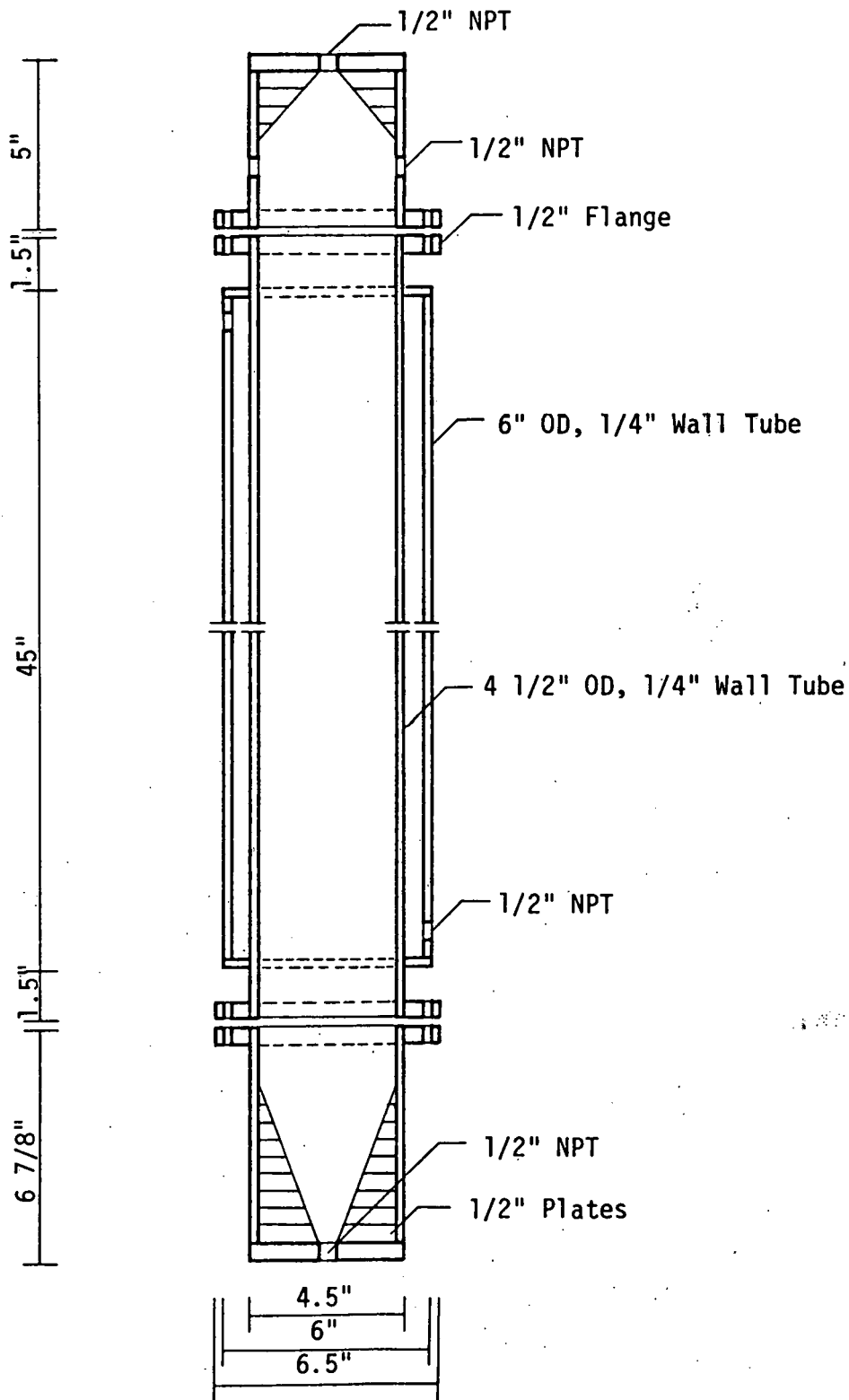


Figure 5. SCHEMATIC OF DENITRIFICATION COLUMN

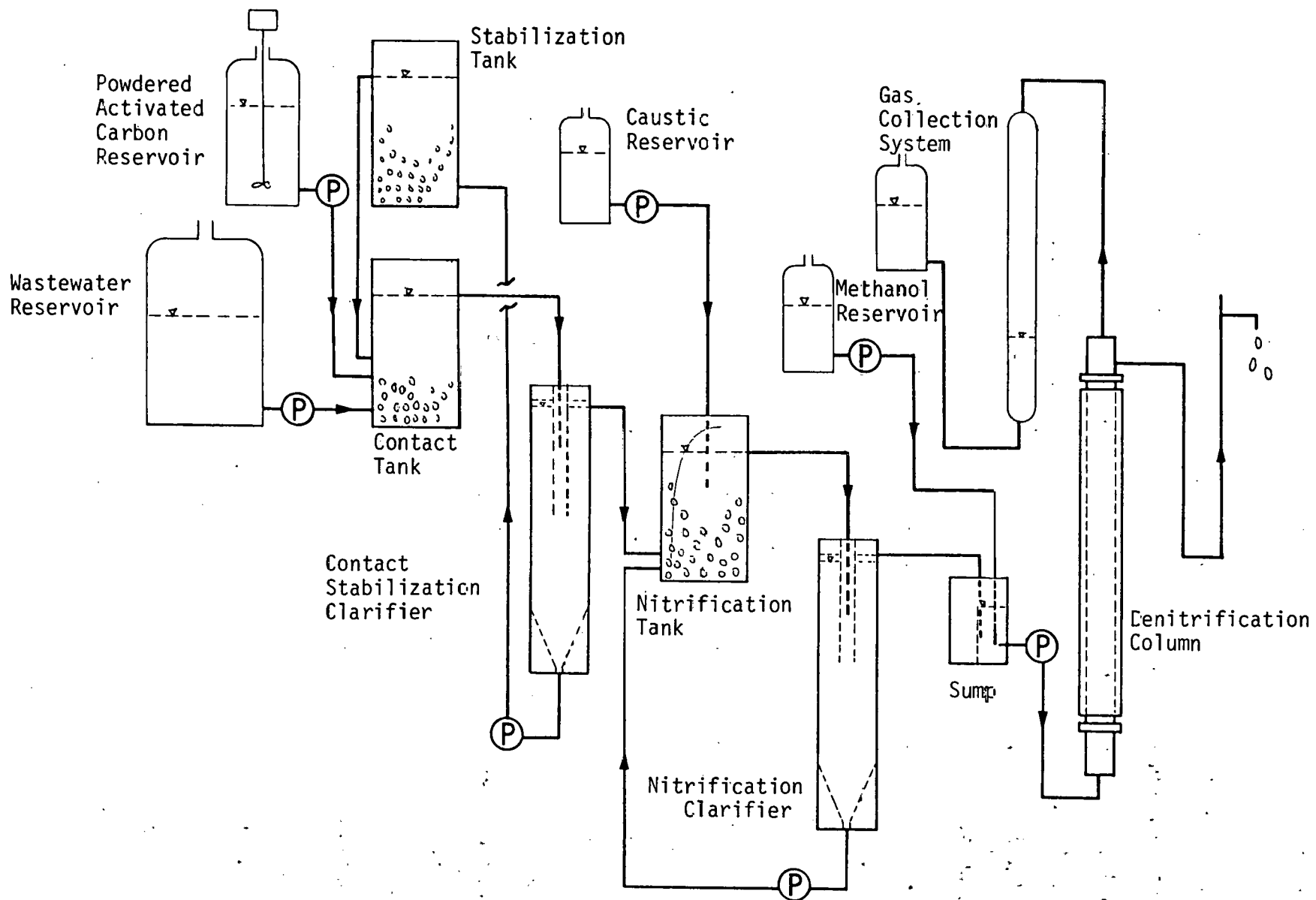


Figure 6. SCHEMATIC OF TREATMENT SYSTEM

of 13.2 ℓ /day using a model 7565-10 console Masterflex drive and a 7015-00 pump head (Cole Parmer Instrument Company, Chicago, IL). A powdered activated carbon slurry of 1,300 mg/ ℓ was prepared in a 10 ℓ glass reservoir and the suspension maintained using a Fisher Dyna-Mix Stirrer (Fisher Scientific, Chicago, IL). The powdered activated carbon slurry was pumped into the contact tank at a rate of 2.3 ℓ /day using a 7543-02 low rpm fixed speed Masterflex drive and a 7016-20 pump head (Cole Parmer Instrument Company, Chicago, IL). At the present operating conditions, the PAC addition rate to the mixed streams of wastewater and PAC slurry is maintained at 193 mg/ ℓ . The overflow from the contact aeration tank is gravity fed to the contact-stabilization clarifier through a 0.75" ID Tygon tube. The clarifier underflow is pumped to the stabilization tank using a model 7545-10 variable speed Masterflex drive and a 7018-00 pump head (Cole Parmer Instrument Company, Chicago, IL). The overflow from the stabilization aeration tank is conducted by gravity to the contact aeration tank in a 0.75" ID Tygon tube. The supernatant from the contact-stabilization clarifier is gravity fed to the nitrification aeration tank using a 1/2" ID Tygon tube, while the overflow from this aeration tank is fed to the nitrification clarifier in a 3/4" Tygon tube. Sludge return from the nitrification clarifier to the aeration tank is accomplished through the use of a model 7545-10 variable speed Masterflex drive and a 7015-00 pump head. Sodium carbonate is pumped from a reservoir to a nitrification aeration tank using a model 7565-10 console Masterflex drive and a 7013-00 pump head (Cole Parmer Instrument Company, Chicago, IL). The sodium carbonate is maintained at a 4 normal strength and is used to maintain the pH in the nitrification tank at around 7.5. The overflow from the nitrification clarifier is fed to the sump from which a model 7543-02 fixed speed Masterflex drive and a

7018-20 pump head (Cole Parmer Instrument Company, Chicago, IL) are used to feed the denitrification column at a rate of 10.9 ℓ /day. Methanol is introduced into the column feed using a model 7543-02 fixed speed Masterflex drive and a 7013-20 pump head (Cole Parmer Instrument Company, Chicago, IL).

The oxygen supply for all the aeration tanks is obtained from a central air compressor. Prior to introduction to the tanks, the air is humidified by bubbling through pressurized tanks containing water. The reason for prehumidification is to minimize water losses in the aeration tanks.

The unit processes, pumps, and reservoirs for every treatment apparatus are mounted on a unistrut structure in order to allow for level adjustment and gravity flow to occur.

Analytical Procedures

The performance of the treatment systems in purifying the wastewater is characterized using a number of measurements. Samples collected from the feed reservoir, contact-stabilization clarifier supernatant, nitrification clarifier supernatant and the denitrification column effluent are filtered using a 0.45 μm Gelman Metrice1 membrane filters (Ann Arbor, MI) and stored at 2°C prior to analysis. Analysis on these samples and the appropriate procedures include:

- i. Chemical Oxygen Demand (COD) (Ref. 6 and 11);
- ii. Total Organic Carbon (TOC) (Ref. 11);
- iii. Total Inorganic Carbon (TIC) (Ref. 11);
- iv. Ammonia Nitrogen (Ref. 5, 6, and 11);
- v. Nitrate Nitrogen Colorometric (Ref. 11);
- vi. Nitrate Nitrogen Colorometric (Ref. 11);
- vii. Gas composition using Fisher 25V gas partitioner calibrated with certified standards;

viii. Cyanide by distillation followed by specific ion electrode
(Ref. 5 and 11);

ix. Thiocyanate colorometric after precipitation and extraction with
chloroform (Ref. 5);

x. Phenols - phenol, o, m, and p-cresols. Acid fraction extraction
followed by gas chromatography separation using an 8' long 2 mm ID
column packed with 10% SP 1200 on 80/100 Supelcoport;

xi. Total and dissolved sulfide (Ref. 5 and 11);

xii. Alkalinity (Ref. 6 and 11); and

xiii. pH.

Total and volatile suspended solids measurements are also made on the
mixed liquor in the contact, stabilization, and nitrification aeration tanks
(Ref. 11).

An estimate of the concentration of viable biological solids will be
obtained from nitrogen and organic carbon analyses on the suspended solids.

PROGRESS TO DATE

Coking Wastewater

The coking wastewater employed in this study was obtained from a steel
mill in twelve 55-gallon drums. At the present rate of consumption, it is
anticipated that a fresh batch of wastewater would be needed every three
months. Analyses on this wastewater revealed that the cyanide and thiocyanate
content of the wastewater is on the higher range of what has been reported in
the literature while the phenols were of much lower levels. The data presented
in Table I represent a chemical characterization of the full-strength wastewater.

Table I

Characteristics of the Full-Strength Coking Wastewater

<u>Parameter</u>	<u>Concentration Range</u>
pH	9.3
Alkalinity, mg/l as CaCO ₃	5,000-5,333
COD, mg/l	5,500-5,835
TOC, mg/l	1,700-1,800
TIC, mg/l	210-270
Ammonia, mg/l as N	3,720-3,850
Nitrate, mg/l as N	<2
Nitrite, mg/l as N	<2
Cyanide, mg/l	800-1,000
Thiocyanate, mg/l	800-1,000
Phenol and Cresols, mg/l	250-350
Total Sulfide, mg/l	190
Dissolved Sulfide, mg/l	42
COD to Phosphorus added	100:2

Preliminary attempts to determine the phenolic constituents of the wastewater were conducted using gas chromatographic mass spectroscopic analyses. The phenol constituents of the wastewater were extracted with methylene chloride under acidic conditions. To avoid the problem of tailing caused by the interaction of the phenolic hydroxyl group with the active sites in the column and to obtain separation not possible with the free phenols, a mixture of hexamethyldisilazane/trimethylchlorosilane/pyridine was used as a derivatizing agent. The organic extract was analyzed using a 5830 Hewlett Packard gas chromatograph interfaced with a 5985A Hewlett Packard mass spectrometer using the electron impact positive ion mode. The gas chromatograph was equipped

with a 30 m long fused silica capillary column coated with SP-2100. The resulting chromatogram is shown in Figure 7 and it serves to illustrate the preliminary GC/MS spectrum of the derivatized acid extract of the wastewater. Further analyses on using a packed column yielded the concentration of the phenols reported in Table I.

System Operation

After construction, the three experimental apparatuses were assembled, connected, and the pumps placed in line and calibrated. All the feed reservoirs were also calibrated in order to provide another control over the solution feed rates. The nine aeration tanks are seeded with mixed liquor obtained from the Champaign Sewage Treatment Plant on the 19th of October, 1980. Powdered activated carbon was added to the contact and stabilization tanks to result in initial mixed liquor PAC concentrations of 2000, 4000, and 6000 mg/l in the first, second, and third treatment systems, respectively. This level of PAC was computed to simulate the steady-state PAC concentrations that are anticipated when the three systems are operated at sludge ages of 10, 20, and 30 days, respectively. On the 20th of October, 1980, the three systems were fed the coking wastewater at a strength of only 10%. Dilution of the wastewater, which was accomplished using deionized water, was used in order to minimize the shock effects on the microbial population. This waste strength was maintained at a uniform mode until the first of November when the concentration in the feed was raised to 20%. The data in Table II represent the feed strengths of the wastewater and the duration of each such strength.

** SPECTRUM DISPLAY/EDIT **
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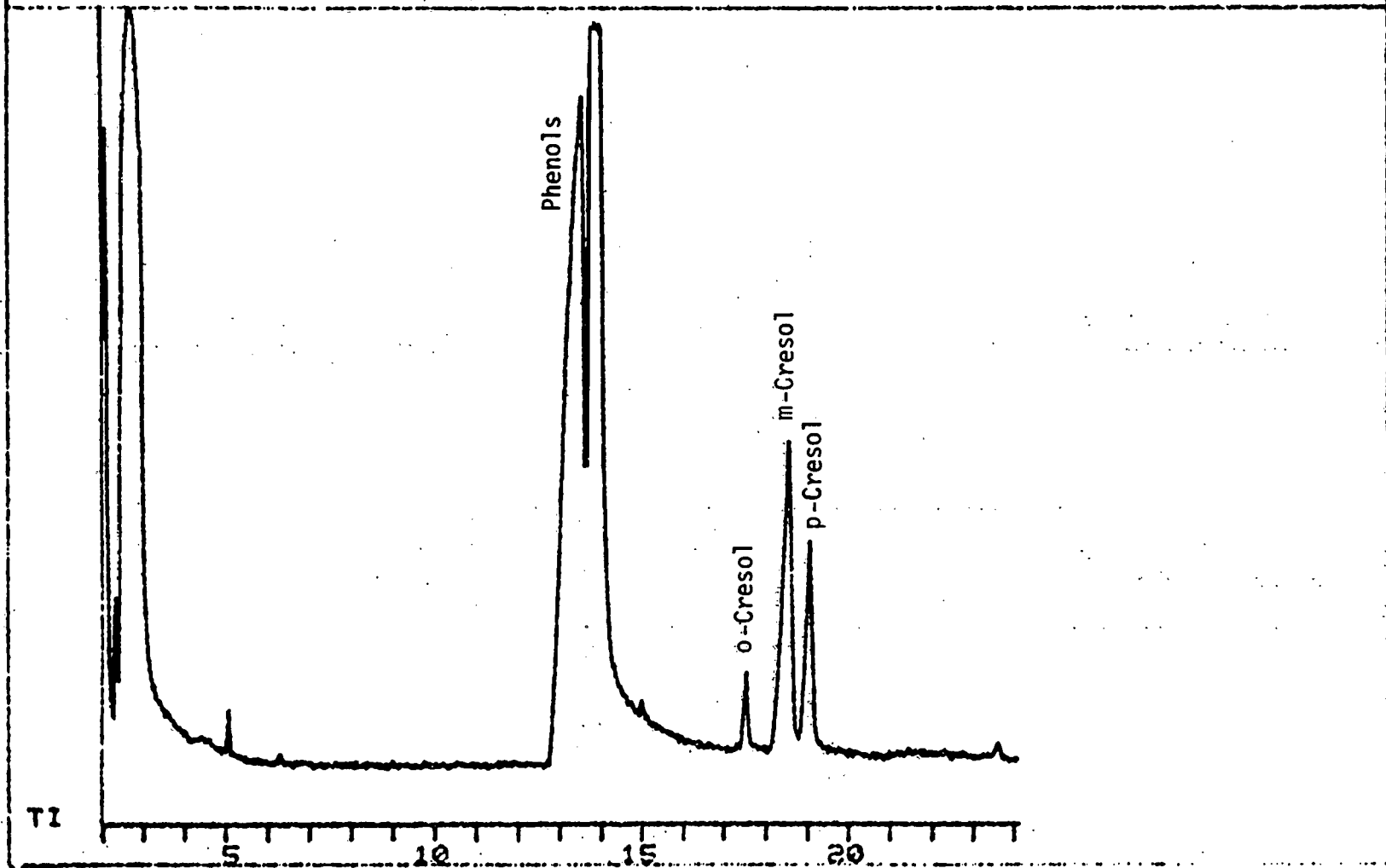


Figure 7. GC/MS SCAN OF 45% STRENGTH WASTEWATER

Table II
Percent Strength of Feed Wastewater

<u>Feed Strength (Percent)</u>	<u>Duration (Days)</u>
10	12
20	27
23	3
26	4
29	8
32	9
35	7
38	7
40	4
45	Jan. 9, 1981 - Present

The contact-stabilization portions of the three treatment apparatuses were operated with no sludge wastage during the period extending between the initiation of the experiments until January 18, at which time wastage was commenced at a rate that will result in a sludge age of 30 days. Once stable operating conditions are attained, different sludge ages will be evaluated in every apparatus.

The three contact-stabilization systems exhibited a decrease in COD and TOC removal efficiencies in response to increases in waste strength. During the period where the waste composition was held at 20% strength, the COD removal efficiency in the three contact tanks averaged 85% while the average TOC removal efficiency averaged 91%. A moderate but uniform decrease in COD and TOC removal efficiencies was observed in response to the increases in feed composition and at present COD removal from the three units is averaging

74% while the average TOC removal is 79%. COD and TOC removals were observed on the nitrification aeration tanks effluents. Ammonia removal efficiencies, on the other hand, have exhibited uniformly increasing trends and at present the three treatment systems are responsible for average ammonia removals of 76%. The contact-stabilization portions of the three systems account for only 31% of the ammonia removal and it is suspected that the majority of the ammonia removed in these tanks is due to air stripping because of the elevated pH levels in these tanks. This is confirmed by the low levels of nitrite and nitrate present in the effluents. The pH levels in the nitrification tanks, on the other hand, are much lower and are presently controlled at around 7.5 through the addition of Na_2CO_3 . Measurements for the various nitrogen species in the nitrification tank effluents revealed that most of the oxidized ammonia was in the form of nitrite nitrogen and not nitrate as would have been expected. Literature research revealed that the predominance of nitrite is indicative of stressed systems. Further chemical analyses have revealed that the thiocyanate levels in the effluents from the contact and nitrification tanks have been steadily increasing and these increased levels of thiocyanate may account for the retardation in the formation of nitrate nitrogen.

The research plan at present is to maintain the feed strength at 45% and stabilize the operation of the three systems.

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