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SOUTHWEST DISTRICT
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CITRUS COUNTY DEPT. OF PUBLIC WORKS
DIVISION OF SOLID WASTE MANAGEMENT

INFORMATION PACKAGE

November 3, 1994

ZIMPRO
ENVIRONMENTAL, INC.
An Affiliate of the Black Clawson Co.
301 W. Military Road, Rothschild, WI 54474
Telephone (715) 359-7211 · FAX (715) 355-3219

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SOLID WASTE MANAGEMENT DIV

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SOLID WASTE MANAGEMENT DIV

Citrus County Dept. of Public Works
Division of Solid Waste Management
230 W. Gulf to Lake Highway
Lecanto, FL 34460-0340

Attention: Susan J. Metcalfe, P.G.

Reference: Response to Dr. Thabaraj

Dear Ms. Metcalfe:

The following discussion is in support of the recent permit modification request for the leachate treatment plant at Citrus County.

The original design for the leachate treatment plant for the Citrus County Landfill consisted of three Sequencing Batch Reactor (SBR) systems operating in parallel. Table 1 lists the design composition of the leachate. The cycle of each SBR included Fill and Aeration for control of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Even though ammonia and Total Kjeldhal Nitrogen (TKN) limits were not present on the discharge permit, it was felt that some nitrification was likely to occur, especially in the warm summer months. PACT(R) has a long-demonstrated history of nitrifying wastes that activated sludge alone could not nitrify. PACT will also nitrify at lower SRT's than activated sludge on many wastes. Since the discharge permit included a limit on nitrate, the system was equipped with submerged mixers to provide agitation during an anoxic step to remove the nitrogen. The balance of the cycle included settling, decanting to an equalization tank prior to sand filtration, wasting sludge and adding carbon to replace lost material.

In practice the system has treated the BOD to less than 5 mg/l on a consistent basis. The system also nitrified almost completely (98.5%) from an average influent ammonia nitrogen level of 100 mg/l to an effluent concentration of 1.5 mg/l. This data is given in Table 2.

Denitrification with activated sludge or with the PACT system can be readily accomplished. It is well documented that denitrification can be accomplished in waste streams that contain high levels of nitrate and COD before the "carbonaceous" removal step. Table 2 also shows influent/effluent nitrate data. This data shows that the system was not particularly successful in denitrifying.

The lack of success in denitrification is attributable to several factors. First, the PACT system is effective in organics removal which leaves virtually no assimilable organics in the treated leachate to provide a carbon source for the denitrifying bacteria. Second, mixing in each SBR tank was provided by a single 10 horsepower submerged mixer. The geometry of each tank, 12 feet wide by 48 feet long by 10.5 feet deep was not well mixed by a single device. Very good mixing was obtained at one end of the tank resulting in measurable dissolved oxygen (D.O.) during the attempted anoxic step, while at the other end of the tank, solids settled out and were not efficiently contacting the supernatant. Efficient denitrification was not taking place at the two ends of the SBR tank for these two very different reasons.

In summary, the basic problem with the existing facility is that it nitrifies very well, but denitrifies poorly due to lack of both a carbon source and adequate mixing.

The proposed alteration to the existing facility is to accomplish the nitrification in two SBR tanks operated in parallel. Denitrification is to be accomplished in the third tank which will be operated in series with the first two tanks. The missing carbon source for the denitrifying bacteria is to be provided in the form of methanol. Methanol is readily utilized by the bacteria, imposes a low BOD load to the system and is poorly adsorbed on the powdered carbon. The submerged mixers would no longer be needed in the first stage SBR tanks and would be removed. The submerged mixer in the third tank would be removed as well, but would be replaced by three top mounted low speed turbine agitators spaced evenly along the length of the tank. These mixers would provide more effective mixing without aerating the liquid as do the higher speed submerged mixers. Overall, this approach will provide a fast, effective and economical solution to the denitrification problem.

The PACT process has long been studied, tested and implemented on a variety of wastewaters. The process has consistently demonstrated resistance to toxic loads, an ability to nitrify in a single stage, and operate with stability. The following articles describe some of these studies.

Attachment A:	Includes several brochures generally describing the PACT system and our Sequencing Batch Reactor. Items of note include organics removal, especially toxic chemicals, reduction of stripping of volatile organics. A partial users list is included to indicate the numerous applications employing the PACT process.
Attachment B:	Pages 200-21 through 200-26 from our Product Manual show several tables of data where PACT is compared against the activated sludge process. PACT consistently out-performs activated sludge, especially in hard to treat wastewaters.
Attachment C:	Technical Reports 225, 077, 227 and 023 further describe the capabilities of the PACT process treating difficult wastes.
Attachment D:	Technical Reports 034, 054, 071 and Landfill Leachate Treatment Brochure discuss the application of the PACT process to landfill leachates and contaminated groundwaters.
Attachment E:	Technical Report 011 describes the use of powdered carbon in an SBR, with the basic conclusion that the carbon enhances the stability of the process.

Denitrification is well understood and explained in EPA Nitrogen Control Manual, EPA/625/R-93/010, chapters 4 and 7. The manual describes denitrification in the activated sludge process. Denitrification is also readily accomplished in the PACT process since the basic denitrification process is the same. The following information further describes research and operating experience of the PACT process on this subject.

Attachment F: Technical Report 059, brochure - "El Paso Closes the Loop" and the thesis of Jong Lee describing nitrification/denitrification in the PACT process.

El Paso has been operating as a two stage nitrification/denitrification PACT system for over ten years. It consistently meets effluent nitrate levels of less than 10 mg/l.

In summary, Zimpro has had a wide range of experience providing wastewater treatment systems that used the PACT process. We also have limited experience with providing biological denitrification systems, a process that is readily accomplished. Our experience as cited above has demonstrated the greater efficiency and cost effectiveness of the PACT process compared to other processes. Citrus County selected the PACT process for these reasons and the process has demonstrated the ability to nitrify this leachate in a single stage. The simplest and most cost effective way to provide nitrate removal at Citrus County is through biological denitrification with the proposed modification to the existing system.

Best regards,

ZIMPRO ENVIRONMENTAL, INC.

David Beula

David A. Beula
Project Manager

lg

cc Zimpro Environmental, Inc.
- J. Piccirillo
- M. R. Mayer
- K. T. Depuydt

Post Buckley Shuh & Jernigan
5300 W. Cypress St.
Suite 300
Tampa, FL 33607-1066
- Dave Weber

Table 1

	Design Composition		Discharge Permit
	Influent	Effluent	
Flow, gpd	30,000	---	---
BOD	2,000	20	20
COD	6,000	---	---
TKN	---	---	---
NH3-N	400	---	---
NO3-N	---	12	12
TSS	400	20	20
pH	6.5-8.5	---	6.5-8.5

TABLE 2

CITRUS COUNTY, FLORIDA
PACT LEACHATE TREATMENT

NITROGEN DATA

ALL VALUES MG/L

DATE SAMPLED	PACT INFLUENT AMMONIA-N	PACT INFLUENT TKN	PACT INFLUENT NITRATE-N	PACT EFFLUENT AMMONIA-N	PACT EFFLUENT TKN	PACT EFFLUENT NITRATE-N
01-06-94					1.5	100
04-14-94					2.4	240
07-06-94		85	1.1			
07-06-94	73.76	92.4				
07-07-94					1.75	69
07-13-94	66.8	110				
07-14-94					1.06	68.9
07-20-94	120	155				
07-21-94					1.8	78.4
07-27-94	125.4	170.5				
07-28-94					0.96	74.5
08-03-94	87	124.07				
08-04-94					1.96	39.44
08-10-94	55.4	88.4				
08-11-94					1.54	40.5
08-17-94	82	120				
08-18-94					1.84	113.11
08-24-94	75.5	125.5				
08-25-94					1.65	124
08-31-94	86	124.5				
09-01-94					2.11	119.77
09-08-94					0.48	154
10-05-94	239	251	0.03			
MINIMUM	55.4	85.0	0.03		0.13	39.4
MAXIMUM	239.0	251.0	1.1		2.4	240.0
MEAN	101.1	131.5	0.6		1.5	102.4

INFLUENT = UNTREATED LEACHATE
EFFLUENT = PACT SYSTEM EFFLUENT

APPENDIX A

BIG
SYSTEM
TECHNOLOGY...

Sized to Fit Small Flow Applications

New Batch-Operated PACT™ plants: Advanced wastewater treatment ideal for small flows ... and even better for your cash flow.

Now with Zimpro's new factory-built Batch PACT™ package plants, you can have the advantages of batch operation plus the *cost effectiveness* of Zimpro's patented powdered-activated carbon treatment technology. And you can get that cost-effective technology in a cost-effective size ... factory-built, ready-to-install plants ideal for small flows of industrial process discharges, contaminated groundwater, landfill leachate or surface runoff.

Batch PACT plants cut small flow wastewater treatment costs down to size.

First, and foremost, **Zimpro's new Batch PACT plants save you money because they're effective** — the PACT system handles the toughest wastewater, including organics, toxics, color and ammonia nitrogen. It uses powdered activated carbon — which has a greater adsorptive rate than granular carbon — and combines it with activated sludge. You get biological treatment and physical adsorption simultaneously.

Second, **Batch PACT plants save you money because they're a single-tank system.** The economies of the PACT system become even more significant when it's merged with the popular batch operation method of treatment. Within a treatment cycle that can be completed in less than 5 hours, wastewater is aerated, settled and decanted — all in the same tank.

The costs of separate clarification and return sludge equipment are eliminated, and you can operate the system only when you need to.

Batch PACT plants are sized for small flow operations and priced accordingly. Because Batch PACT plants are designed for small flows, you don't have to buy more treatment capacity than you actually need. And the self-contained single-unit design opens up a host of new wastewater management options.

Batch PACT plants can also save installation and start up costs. Batch PACT plants arrive on-site, ready-to-hook-up and operate. Their aboveground design reduces site preparation costs and virtually eliminates excavation and construction costs.

Technology to handle the "nastiest" wastewater.

Batch PACT plants are specifically designed for small flows of wastewater not generally amenable to straight biological treatment. Or situations where discharge requirements can't be met with biological treatment alone.

Industrial Process Waste, such as those from organic chemical, pesticide, petro-chemical, pharmaceutical and textile manufacturing. Batch PACT plants are employed for end-of-pipe treatment or for pretreatment prior to discharge to a municipal sewer. Batch PACT plants are also used to isolate and pre-treat separately problem waste streams that interfere with on-site biological treatment. Batch PACT plants have helped industries save money by eliminating expensive waste hauling or more complicated on-site biological-physical treatment systems.

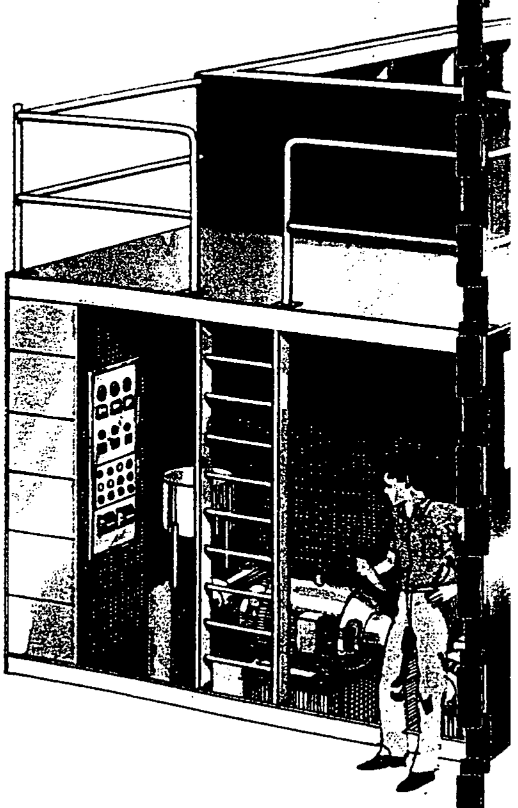
Landfill Leachates, both from Superfund sites or from municipal solid waste disposal sites. These liquids contain high levels of organics that usually resist biological treatment. Batch PACT plants are used to treat leachates on-site prior to discharge or for pre-treatment to reduce strengths and treatment tolls at a municipal wastewater plant.

Surface Runoff. As more and more groundwater protection systems are constructed, chemical terminals, refineries and other facilities are collecting surface runoff waters that contain high levels of dissolved organics. Batch PACT plants provide the means to treat runoff water and meet discharge requirements without the costs of hauling or major construction.

Contaminated Groundwater. The PACT system has an excellent record of reliability and effectiveness in removing volatile organic compounds from groundwater. Batch PACT plants are used for pretreatment or direct discharge.

Pick a unit ideal for your specific application and capacity requirements.

Batch PACT plants are prefabricated and shipped to you in five sizes designed to fit your treatment needs. The smallest unit (Model B13) measures 12′ × 10′ × 18′ and has a maximum capacity of 13,000 gallons of wastewater per day. The largest unit (Model B140) measures 12′ × 12′ × 55′ and can handle as much as 140,000 gallons per day.

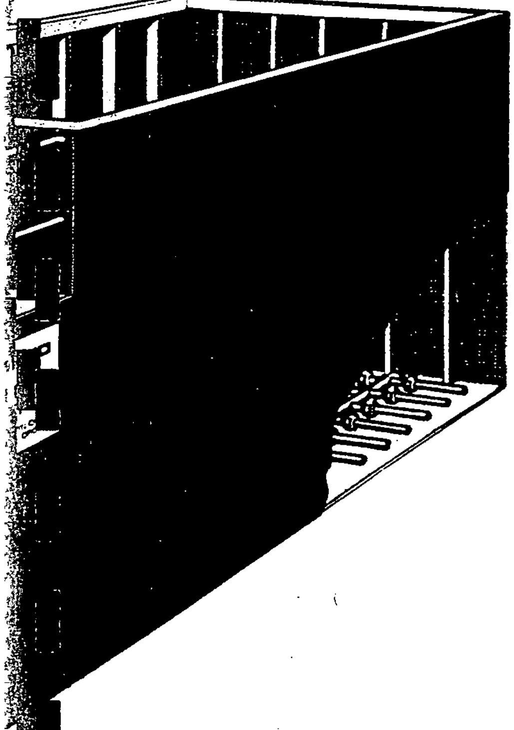


How Batch PACT Plants Work...

Step 1: Wastewater is pumped into the aeration tank where it comes in contact with a mixture of biological solids and powdered activated carbon. (An initial charge of powdered carbon and seed micro-organisms is added to the tank when a unit is operated for the first time.)

Step 2: Contents are aerated. Aeration cycle length is dependent upon the waste strength and the level of treatment desired.

During aeration, the biodegradable portion of the waste is treated biologically, while the non-biodegradable contaminants are adsorbed on the carbon particles. In short, what the "bugs" can't handle, the carbon takes care of. In addition, the combined biological and carbon treatment is synergistic; the carbon enhances biological treatment by also adsorbing biodegradables and concentrating them for efficient assimilation. At the same time, the carbon-laden mixed liquor aids the biological process further by protecting it against shock loadings.



Step 3: Aeration ceases and tank contents are allowed to settle. Solids go to the bottom of the tank while the clarified effluent is drawn off for discharge to the receiving stream, or to a sewer if the application is pretreatment. No separate clarifier is required.

The solids are retained in the tank for use with the next batch of waste, except for that portion which is periodically withdrawn for dewatering, disposal or regeneration if carbon usage warrants. Makeup powdered carbon is added directly to the tank as needed.

Minimum cycle time for the full treatment operation is 4.8 hours or 5 cycles per day.

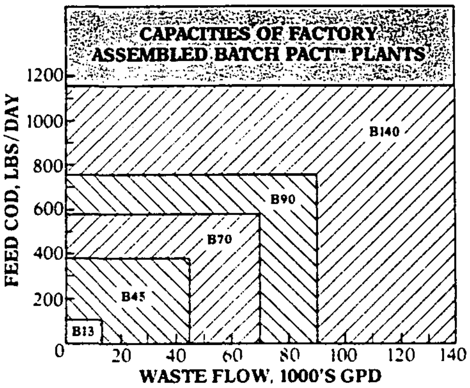
FACTORY ASSEMBLED BATCH PACT™ PLANTS	MODEL B13	MODEL B45	MODEL B70	MODEL B90	MODEL B140
Overall Plant Dimensions (Height, Width, Length - Ft)	12×10×18	12×12×21	12×12×29	12×12×38	12×12×55
Aeration Tank Dimensions (Height, Width, Length - Ft)	12×8 Dia.	12×12×16	12×12×24	12×12×32	12×12×48
Aeration Tank Volume,† Ft³	500	2,000	3,000	4,000	6,000
Maximum Design Flow,‡ GPD	13,000	45,000	70,000	90,000	140,000
Maximum COD Loading, lbs/Day	100	375	575	750	1,150
Maximum Cycles/Day‡	5	5	5	5	5
Minimum Cycle Time, Hrs	4.8	4.8	4.8	4.8	4.8

† Tank with 1'6" freeboard
‡ With feed waste at 1 g/l.

Metric Conversions:
ft × .3048 = m
lbs × .454 = kilograms
gal × .003785 = m³
ft³ × .028 = m³

*PACT™ is a trademark of Zimpro/Passavant. Purchase of a Batch PACT plant includes a paid-up license to use the PACT wastewater treatment system.

Pick a plant suited to your application.



To determine the Batch PACT plant best for your application, find the appropriate feed waste COD on the vertical axis, and the waste flow on the horizontal axis. For example, if your waste has a COD of 400 lbs./day and is generated at a rate of 60,000 gal/day, Model B70 is the right choice.

EQUIPMENT LIST† FOR FACTORY ASSEMBLED BATCH PACT™ PLANTS

Major
- Aeration Contact Tank
- Air Diffusers and Internal Air Piping
- Aeration Blower
- Polymer Storage
- Polymer Feed Pump
- Waste Sludge Pump
- Motor Control Center

Miscellaneous
- Integral Piping and Fittings
- Aeration Tank Drain
- Valves
- Instrumentation
- Decant Means

†Aeration tank and all equipment is located on one skid.

Quality, efficiency and innovation ... plus the other extras you'd expect from Zimpro.

Although Batch PACT plants are designed for easy installation and operation, Zimpro Passavant offers a wide range of waste treatment services that have made it a leading name in wastewater management.

- Zimpro's analytical laboratory and pilot plants are hallmarks of the wastewater treatment industry. They are available to clients who need to test wastewater for characteristics and treatability.
- Zimpro's operations group is prepared to assist waste generators and handlers in operating and maintaining their treatment facilities.
- Zimpro's service group is available to provide replacement parts and fast, dependable service throughout the United States and Canada.
- For flows larger than 140,000 gallons per day, Zimpro has available skid-mounted package plants or full-scale PACT systems.

Effective performance and reliability.

PERFORMANCE
BATCH PACT WASTEWATER TREATMENT PLANTS

	Organic Chemicals	Organic Chemicals	Contaminated Surface Runoff	Leachate†
Influent, mg/l				
BOD_5	187	745	94	1,530‡
COD	2,210	9,910	199	3,200‡
DOC	300	1,690	60	0
Total Toxic Organics	32.0	0	0	7.5
Effluent, mg/l‡				
BOD_5	30	16	14	31
COD	84	124	27	123
DOC	28	28	11	0
Total Toxic Organics	0.02	0	0	<0.4
Removals, %				
BOD_5	84	98	85	98
COD	96	99	86	96
DOC	91	98	82	0
Total Toxic Organics	>99.9	0	0	>95

†McShane, Sheila F., et. al., "Biophysical Treatment of Landfill Leachate Containing Organic Compounds," 41st Purdue Industrial Waste Conference, 1986.

(Organics include acetone, MEK, tetrahydrofuran, dichloroethane, methylene chloride, others)

‡Soluble Values

The PACT system has been demonstrated to deal effectively with organic chemical production waste, landfill leachates and surface runoffs. Permit-satisfying reductions are obtained, even in the face of heavy feed waste loadings.

APPLICATIONS OF BATCH PACT™ PLANTS

Industrial Pre-treatment for:
- Organic Chemicals
- Pesticides
- Pharmaceutical
- Textile/Dyes
- Others

Leachates and Contaminated Groundwater

Contaminated Surface Runoff

Whenever GAC is used or contemplated for COD ≥ 300 mg/l

The first step toward effective *and cost-effective* wastewater treatment...

If you generate or deal with small flows of industrial waste, landfill leachates, surface runoff water or contaminated groundwater, we invite you to investigate the cost saving advantages and effectiveness of Zimpro's new Batch PACT plants. For more information, contact:

Zimpro Passavant
Environmental Systems, Inc.
Military Road
Rothschild, WI (USA) 54474
Phone (715) 359-7211
Attn: PACT Product Group

ZIMPRO PASSAVANT
ENVIRONMENTAL SYSTEMS, INC.
301 W. Military Road, Rothschild, WI 54474
Telephone (715) 359-7211 · FAX (715) 355-3219

A BLACK HOLE FOR HAZARDOUS WASTEWATER

Zimpro
PACT Systems

PACT® wastewater treatment systems: The right technology at the right time.

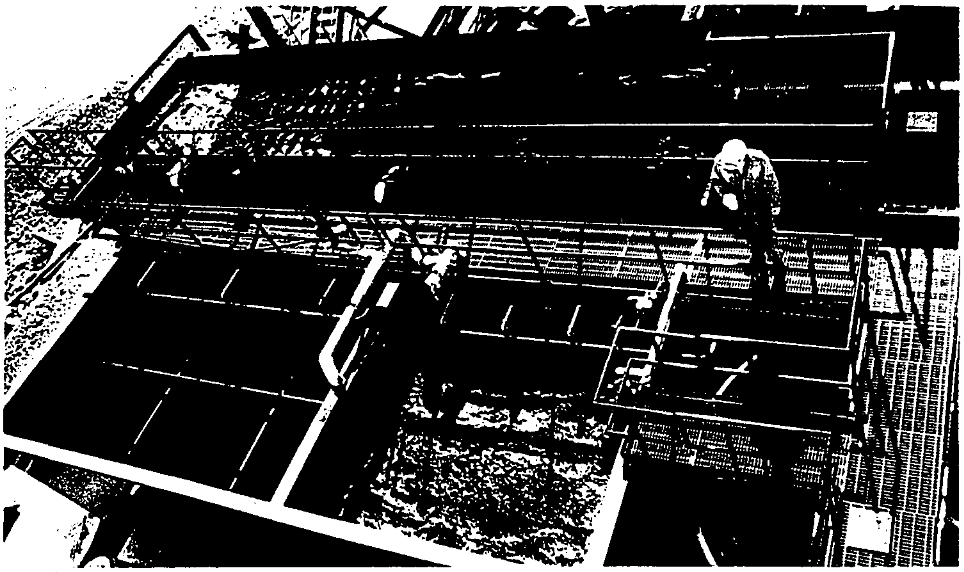
If you have to treat industrial wastewater, landfill leachate, contaminated surface water or groundwater, take a close look at the PACT® system.

Developed by Zimpro Environmental, Inc., and the DuPont Co., the PACT® system combines biological treatment and carbon adsorption into a single step. That gives PACT® systems cost and performance advantages over multi-stage systems such as activated sludge and granular carbon.

There are many other benefits. PACT systems use powdered activated carbon which improves the performance of aerobic or anaerobic biological systems by stabilizing them against upsets and shock loadings. PACT systems control color and odor, and can reduce your costs for disposing of wastewater treatment residuals.

With a PACT system, you will use far less carbon than with a granular system to achieve the same or better treatment. And, because powdered carbon is used in slurry form, you won't have the problems of pre-filtration or column plugging. Further, powdered carbon costs less than granular carbon.

PACT® systems are capable of producing effluent clean enough for reuse or to meet bio-assay standards.

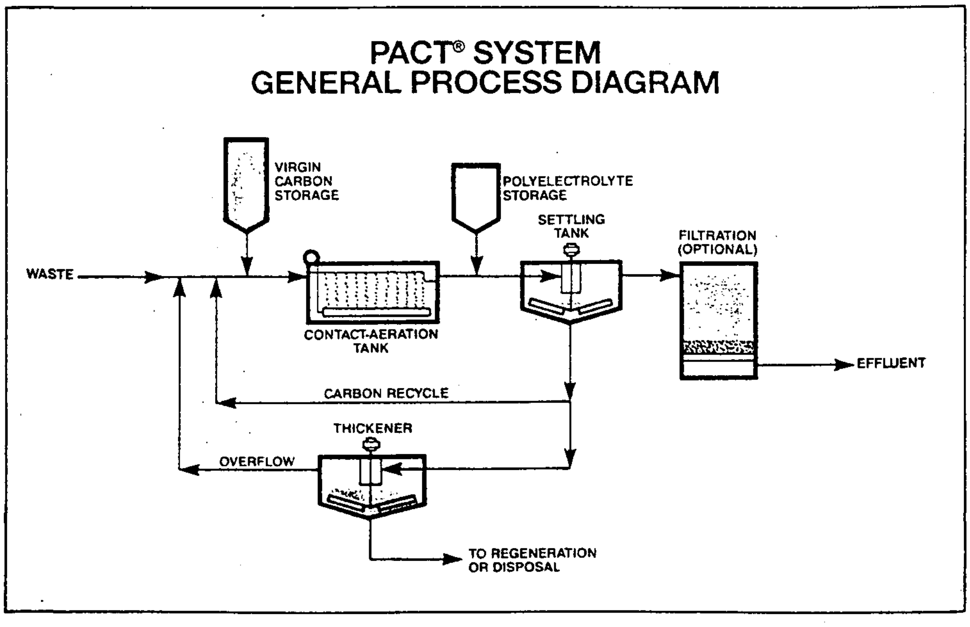


Two-stage aerobic PACT® systems, like this one at a chemical terminal, offer high levels of treatment and reduced carbon usage.

PACT systems are at work at more than 50 installations today, helping users comply with:

- New regulations for organic chemicals, plastics and synthetic fiber (OCPSF) manufacturing discharges.
- The RCRA "land ban" regulations, which forbid land disposal of wastewater, and require treatment of landfill leachates and contaminated groundwater.
- Stringent bio-assay standards for effluent discharges.
- Pre-treatment regulations controlling industrial discharges to POTWs.

These PACT systems include retrofits as well as new construction. They range from factory-built units treating 2,000 to 70,000 gallons a day, to custom-designed systems handling as much as 50 million gallons a day. Both single-stage and two-stage PACT systems are available, depending on treatment requirements.



ADVANTAGES OF AEROBIC PACT® SYSTEMS OVER ACTIVATED SLUDGE, GAC COLUMNS:

Versus activated sludge, PACT systems ...

- Remove priority pollutants, non-biodegradables.
- Maintain treatment stability in the face of complex, variable wastewaters.
- Can produce effluent that meets bio-assay standards.
- Minimize VOC stripping into the air.
- Remove color.
- Control odors.
- Increase operational flexibility of the treatment system.
- Produce less wet solids for disposal.

Versus granular carbon, PACT systems ...

- Use less carbon.
- Use less expensive carbon.
- Do not require pre-filtration for suspended solids removal.
- Offer increased operational flexibility.

Other advantages ...

- PACT systems can be aerobic, anaerobic, or anoxic.
- Single- or two-stage PACT systems are available depending on waste strength and effluent requirements.
- PACT systems cost less to build, operate, and control than multi-stage systems.
- Factory-built units are available for small flows.
- Mobile units are available for site cleanup.
- Wet air oxidation can regenerate carbon and destroy sludge.

PACT® system customers benefit from the process knowledge and pilot plant testing capabilities of Zimpro in the design of treatment projects. Zimpro has worked with the technology for more than 20 years.

GIVE YOUR BUGS A BREAK

In the PACT® system, powdered activated carbon is added to an aerobic or anaerobic biological treatment process. Physical adsorption and biological assimilation occur simultaneously. The carbon "buffers" the biological system against the effect of toxic organics in the wastewater.

In aerobic PACT® systems, influent flows to an aeration tank. Powdered carbon is added, making up a portion of the mixed liquor suspended solids. Following aeration, treated wastewater and the carbon-biomass slurry enter a clarifier where the spent carbon and biological sludge settle.

In anaerobic PACT® systems, powdered carbon is added to wastewater before the anaerobic reactor. Again, the carbon and bio-system work together to achieve a high degree of treatment. As in conventional anaerobic systems, methane gas can be recovered and used for fuel to make an energy-efficient system.

Following treatment, a portion of the recycled carbon and biomass slurry is wasted to solids handling. The choice of solids handling method will depend upon the amount of solids to be disposed of, disposal costs, and carbon use. Waste solids can be dewatered to a compact, stable cake. or can be pumped as slurry to a wet air oxidation unit where the carbon is regenerated and biological solids are destroyed. "Wet air" regeneration units can operate autothermally, recover carbon, and all but eliminate secondary sludge disposal.

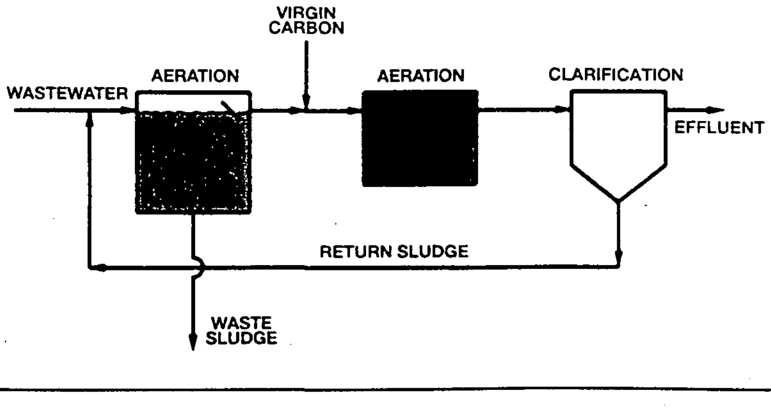
APPLES AND ORANGES

While PACT® systems are often compared to biological processes and granular carbon adsorption, there are major operational and performance differences. In aerobic PACT® systems, for example, organics are adsorbed on the carbon surfaces and are exposed to biological treatment for a longer solids residence time than in activated sludge systems (see comparison of design variables).

Versus granular carbon systems, PACT® systems are more cost effective because powdered carbon costs less than granular carbon, and you need less carbon to achieve comparable treatment. Also, you can easily change the carbon dose rate, using only what is required to achieve desired treatment results.

SI UNIT CONVERSIONS
gal/d (.003785) = m³/d
million gal/d (.04383) = m³/s
gal/min (5.4510) = m³/d
psig (.006895) = MPa

TWO-STAGE AEROBIC PACT® SYSTEM

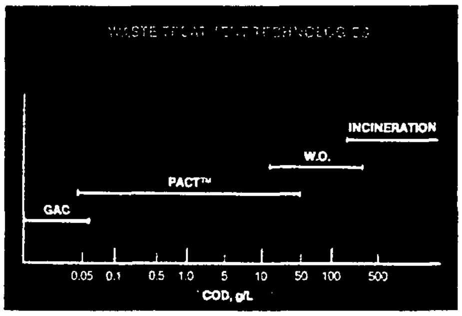


Applications and performances: a sparkling record.

PACT™ systems have been applied to a variety of wastewaters:

- Municipal.
- Joint municipal-industrial.
- Industrial.
- Hazardous.
- Leachates from landfills.
- Contaminated groundwater.
- Contaminated surface runoff.

The process is especially suited to liquids that are too toxic to be successfully treated by biological means alone, yet too dilute to be incinerated economically (see chart).



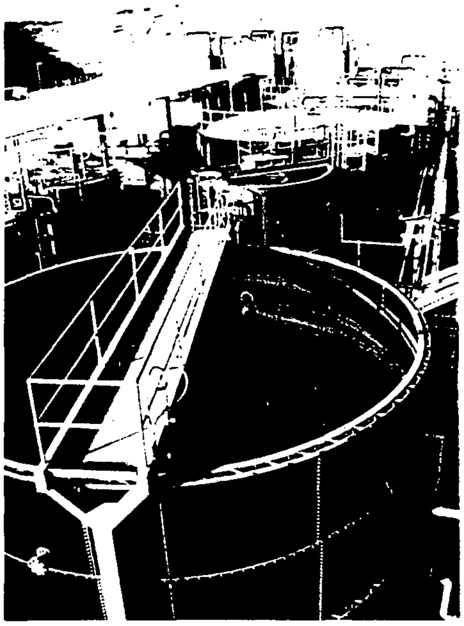
Here is a representative sampling of typical applications and performance of the PACT system:

Organic chemicals wastewaters ... PACT systems are in use at many organic chemicals, plastics, synthetic fibers, solvents, dye and pesticide manufacturing sites, both for pretreatment and direct discharge.

One of the largest industrial applications of the PACT system is at the massive Chambers Works plant of the DuPont Co. at Deepwater, New Jersey. The process treats wastewater from organic chemicals production at the site, and also a variety of wastewaters shipped in and treated on a contract basis. The flow rate through the system exceeds 35 million gallons a day.

At the Chambers Works plant, PACT systems have consistently proven to be more effective and economical in comparisons with conventional activated sludge, and activated sludge plus granular carbon columns. In a recent study concerning expanding and upgrading the Chambers Works treatment plant, the PACT system exhibited better toxicity reduction and priority pollutant removal than granular carbon. The PACT system exhibited greater flexibility in the face of changing waste streams. The performance of granular carbon was unpredictable because of desorption of organics from the columns.*

An economic analysis indicated an upgrade of the PACT system would cost less than adding granular carbon columns.



A field-erected PACT™ system for leachate treatment at a hazardous waste landfill.

COMPARISON OF DESIGN VARIABLES WHICH CONTROL TREATMENT SYSTEM PERFORMANCE:

	AEROBIC PACT SYSTEMS	ACTIVATED SLUDGE	GAC
Aeration detention time	Yes	Yes	No
Solids residence time	Yes	Yes	No
Mixed liquor content	Yes	No	No
Carbon dose	Yes	No	Yes
Carbon type	Yes	No	Yes
Carbon application point	Yes	No	No

Pesticide wastewaters ... A wastewater containing 19 pesticides in concentrations of more than 3,400 parts per million was treated with the PACT system. Major constituents were organo chlorine, organo phosphorus, carbamate, and phenolic pesticides. The PACT system achieved COD reductions of better than 99 percent, and total pesticide reduction was 99.8 percent.

Contaminated groundwater ... PACT systems have effectively treated contaminated groundwater. At a Michigan manufacturing site, a 1.5 million gallon per day PACT system has been treating groundwater contaminated by an abandoned landfill site since the mid-1980s. Two of the target contaminants are orthochloroaniline and

---

* G.J. O'Brien, Purdue Industrial Waste Conference, May, 1989.

dicholorbenzidene. The PACT system has removed these and other organic compounds consistently.

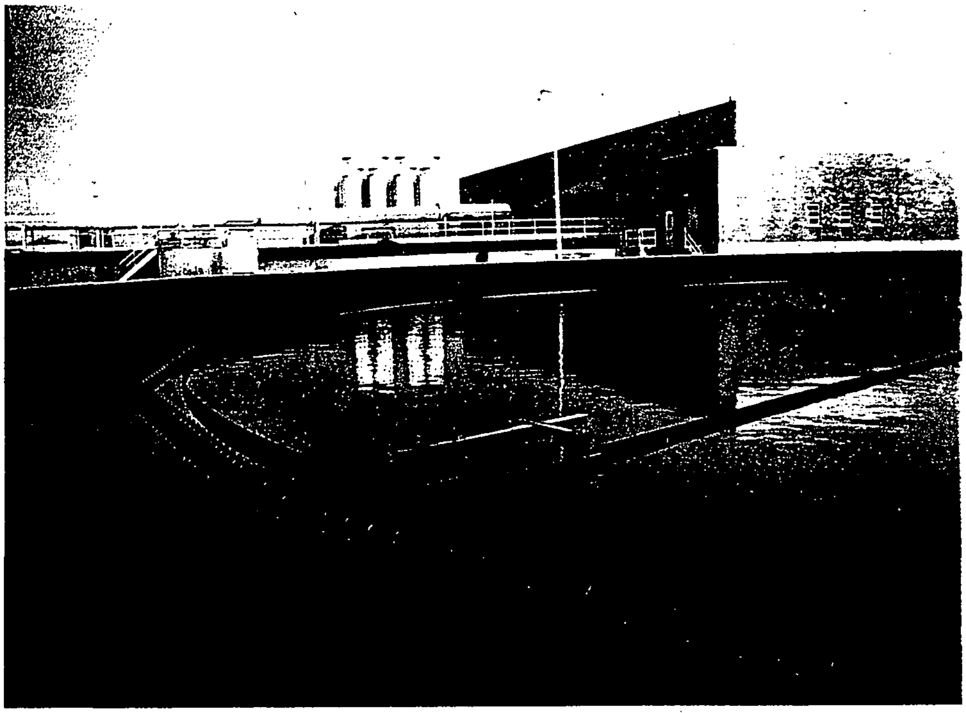
Landfill leachates ... With landfill regulations tightening, PACT systems are being applied to leachates from both municipal solid waste and hazardous waste landfills.

At a landfill site near Los Angeles, California, prior treatment methods of air-stripping and solidification were considered expensive, inadequate, and too land-intensive to meet new leachate treatment requirements. A PACT system was installed after it was evaluated lowest in cost and land usage and superior in treatment stability when compared with other systems. Since startup, the PACT system has achieved outstanding removal rates:

- COD 95-plus percent.
- BOD_5 99-plus percent.
- Volatile organic acids 99-plus percent.
- Oil and grease 93-plus percent.
- Volative organic compounds 99-plus percent.
- Pesticides 100 percent.

Anaerobic PACT systems have also proven very effective on landfill leachates. Compared with conventional anaerobic filter reactors, anaerobic PACT systems achieve higher pollutant reductions, while maintaining stable performance despite changing leachate characteristics.

Petroleum refinery and terminal wastewaters ... The PACT system is being used to treat wastewaters from petroleum refining, and contaminated surface waters at refineries and terminals.



Zimpro provided world's largest PACT™ system and carbon regeneration facility for joint municipal-industrial wastewater treatment at Kalamazoo, MI.

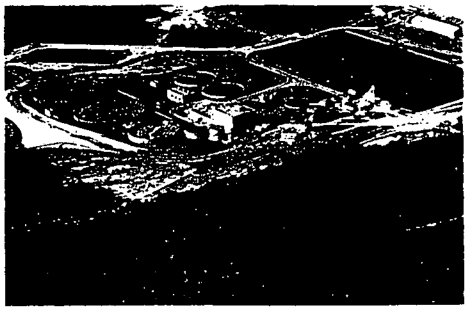
At one refinery, these results have been achieved:

PACT SYSTEM RESULTS mg/L

	Inf.	Eff.	% Rem.
COD	573	82	85.7
BOD_5	238	<6	>97.5
Sus. Solids	44	12	72.7
Oil & grease	10.1	<1.3	>87.1
Cyanide	1.29	0.04	96.9
Bio-assay (96 hr rainbow trout) 100%			

At the Powell Duffryn Terminal in Bayonne, New Jersey, a factory-built PACT unit cleans up contaminated surface runoff, and meets a stringent NPDES permit. Results have been consistent and excellent:

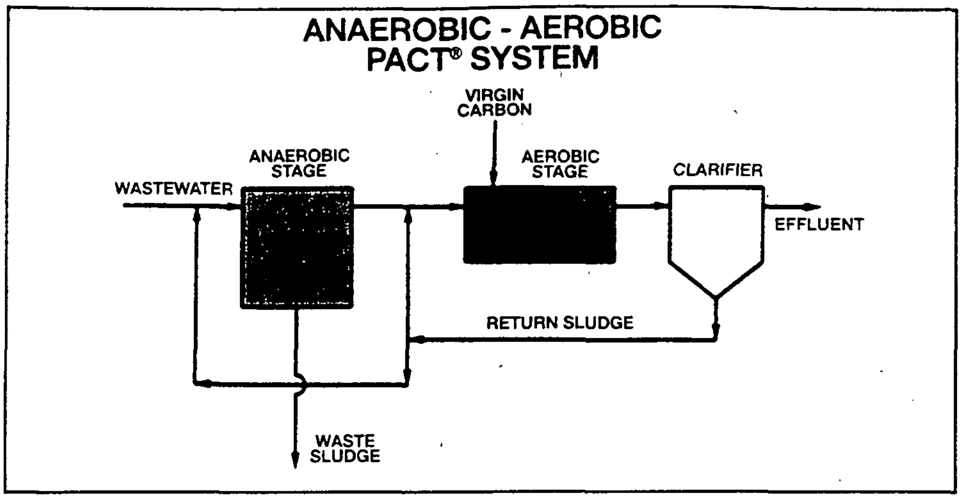
	NPDES Permit	Typical PACT Results
Oil & grease	15 mg/L	2.7 mg/L
COD	150 mg/L	44.1 mg/L
BOD	50 mg/L	18.6 mg/L
TSS	50 mg/L	17.6 mg/L
Priority pollutants	Monitor	< 0.005 mg/1
Toxicity (96 hr LC_{50})	>50% eff concent.	100% eff. concent.



Ciba-Geigy manufacturing complex uses PACT™ system to meet increased discharge requirements.

COMPARISON OF TREATMENT BY ANAEROBIC SYSTEMS WITH DIFFERENT MEDIA

PERFORMANCE	ROCK	SADDLES	PACT
COD			
Effluent g/L	5.1	3.8	2.4
% Removal	52	63	76
BOD			
Effluent mg/L	1,100	510	200
% Removal	74	89	95



NO SIZE TOO BIG OR SMALL

Zimpro supplies aerobic and anaerobic PACT® systems as continuous flow or batch operated units.

For continuous flows, Zimpro provides factory-built units for volumes from a few hundred gallons per day up to 70,000 gal/d. For higher flows, *multiple factory-built or field-erected* units, or a combination of the two can be provided.

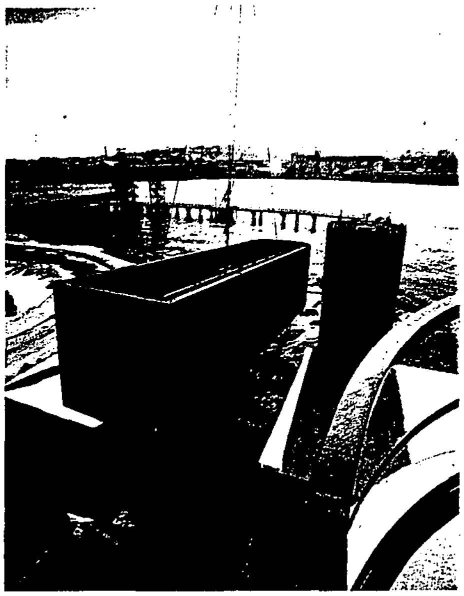
The batch PACT units are provided as prefabricated plants, with factory-built capacities up to 140,000 gal/d. Field-erected batch plants treat larger flows.

Two-stage PACT systems may be used to treat highly-concentrated wastewaters or to meet stringent discharge requirements.

PACT systems are also available as trailer-mounted units for lease or purchase.

THIS IS A TEST

In order to take full advantage of the flexibility of the PACT® system, Zimpro offers complete pilot testing and treatability studies. A testing program can be designed to suit your wastewater treatment needs.

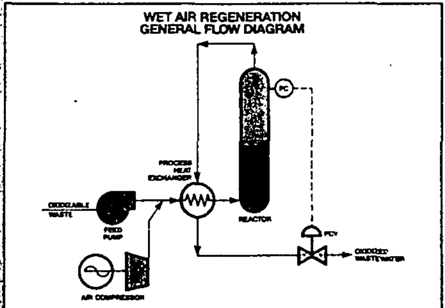


Tanks for a batch-operated PACT system are factory-built and delivered to the site by Zimpro.

Treatability testing equipment includes bench scale and frame-mounted pilot units which can be operated at our test facilities in Wisconsin or at your site. In addition, portable PACT system pilot plants are available, with or without carbon regeneration. Testing can be done in all modes: aerobic, anaerobic, single-stage or two-stage.

The pilot equipment is supported by Zimpro's analytical laboratory –

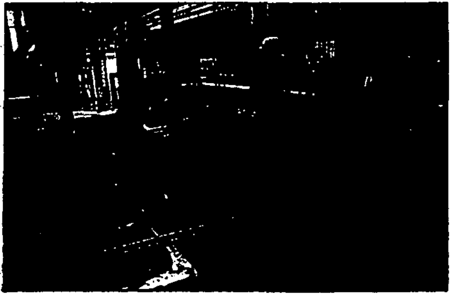
REGENERATING SPENT CARBON



Zimpro's wet air oxidation process successfully regenerates spent carbon from the PACT® systems, and simultaneously oxidizes biological sludge associated with the carbon. You can recover the carbon and use it again, and simultaneously reduce biological sludge to a small amount of ash for disposal.

In the process, the spent carbon sludge from the PACT system is gravity thickened and pumped into the regeneration unit heat exchangers at approximately 800 psig.

Compressed air is added to the slurry, and the air-slurry mixture passes into the regeneration reactor. Here an exothermic reaction takes place, raising temperatures. Organics are oxidized, with a minimum loss of carbon. The wet air oxidation process can be autothermal, requiring no auxiliary fuel after startup.



Interior view of a 10 gallon per minute wet air carbon regeneration unit serving a specialty chemical manufacturer.

Ash formed in oxidation can be separated from the carbon, removed and disposed of.

Advantages of wet air regeneration include:

- No sludge dewatering prior to regeneration.
- The process can operate autothermally.
- Carbon recovery is efficient – in the range of 90 percent.
- Wet air regeneration emits no oxides of nitrogen or sulfur and no particulates.
- No secondary sludge disposal is required.
- Separated ash is stable, non-leaching.

Some 20 PACT systems are coupled with wet air regeneration units.

one of the best-equipped facilities in the United States for analysis of industrial, municipal, and hazardous wastewaters, waters, and sludges. Also, for handling and storage of waste samples, Zimpro operates a fully RCRA-permitted Part B TSD facility.

Zimpro has years of experience conducting treatability studies of the PACT® system on a complete range of wastewaters. Zimpro can work with you on conceptual designs, screening your wastewater, and designing a cost-effective system to bring your operation into compliance with environmental regulations. The company's experience assures reliable scaleup from laboratory and pilot plant data to sound working designs.

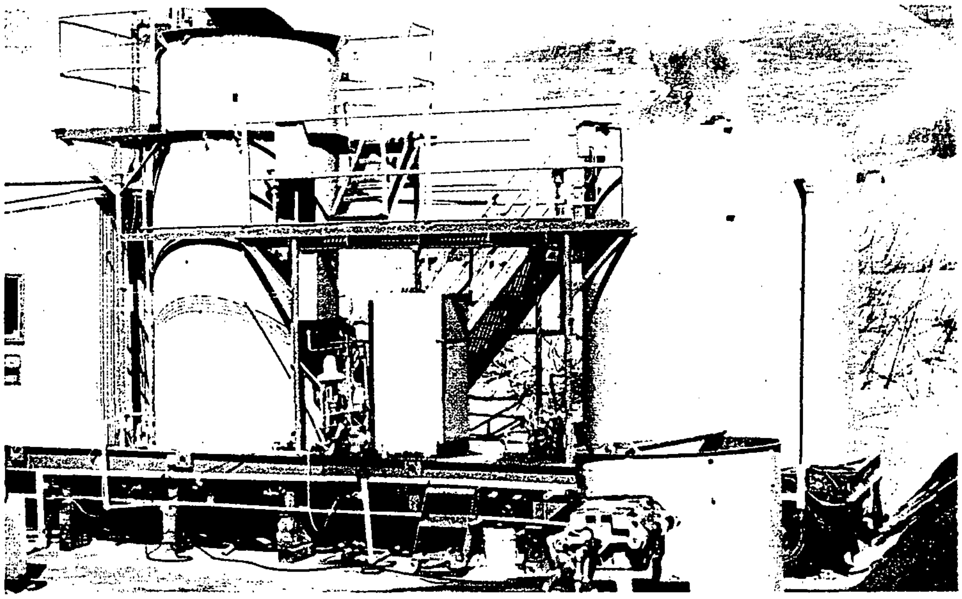
Following system design, Zimpro has full construction management capability, and can provide you with startup, training, operations, and maintenance services after mechanical completion of the project.

COST EFFECTIVENESS

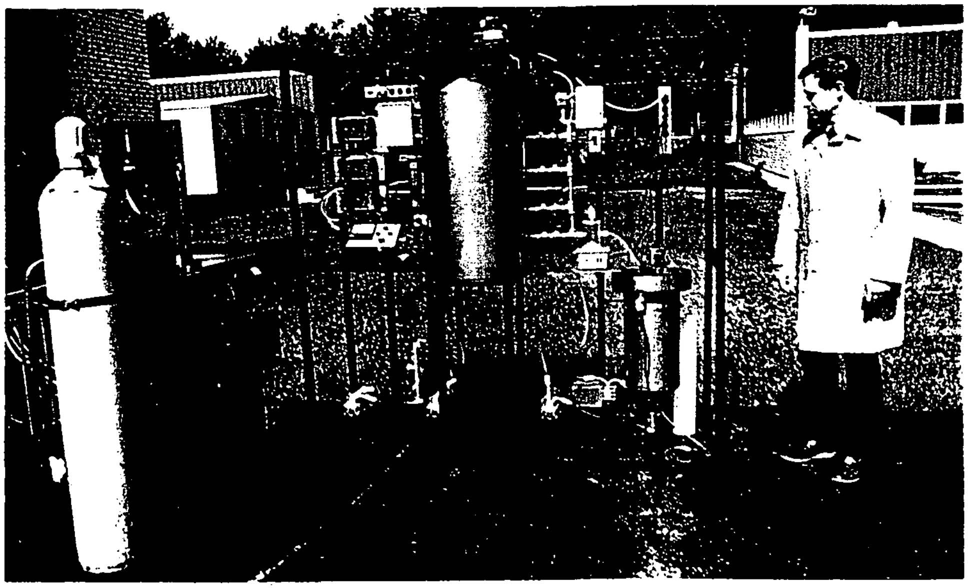
When compared with other technologies capable of achieving the same or similar effluent quality, PACT® systems win the cost effectiveness evaluation. The lower operating costs of the PACT system versus granular activated carbon are born out in this comparison at a hazardous waste landfill, based on flows of 60 gallons per minute, and 1984 dollars:

	PACT	GAC
Capital cost	$1,700,000	$1,200,000
Operating costs per year		
Chemicals	80,000	75,000
Carbon*	70,000	1,800,000
Power	65,000	30,000
O/M	220,000	150,000
TOTAL	$435,000	$2,055,000
Annual Costs (2 yrs., 10%)		
Amortized capital	980,000	691,000
O/M	435,000	2,055,000
TOTAL	$1,415,000	$2,746,000

* Powdered carbon @ $.40/pound, granular carbon @ $.95/pound.



Zimpro offers mobile PACT® units which are capable of treating contaminated waters at landfills, industries, or Superfund sites.



Zimpro has extensive knowledge and facilities for testing the PACT® system on a variety of wastes. This frame-mounted pilot system can be used for on-site testing.

PACT® SYSTEM USERS (PARTIAL LIST, 1990):

DuPont Co.
General Electric
Lomac Chemical*
Exxon
Burlington, NC (East plant)*
Upjohn
Alcoa
Crompton & Knowles
Ciba-Geigy
Powell Duffryn Terminals
ICI United States
Koppers
Rollins Environmental Services
Kalamazoo, MI*
BKK Landfill
Tosco
Mt. Holly, NJ*
Unocal*
Burlington County Landfill, NJ
Bethlehem Steel
Nalco Chemical
Domtar Papers
Safety-Kleen
El Paso, TX*
Aldrich Chemicals
Waste Management of North America
Vernon, CT*
Tenneco
US EPA Site program*
BPCL Refinery, India*
Medina County, OH*
Citrus County (FL) Landfill
Elixir Industries
Resource Conservation Corp.
Phillips 66
Charlotte County (FL) Landfill
Bostik, Inc.
Reilly Industries

* Carbon regenerated by wet air oxidation.

MORE INFORMATION

If you would like more information about the PACT® system, contact the PACT® system applications group at Zimpro, 301 W. Military Rd., Rothschild, WI (USA) 54474. Use our toll-free phone line: 1/800-826-1476, or FAX: 1/715-355-3219. Or, talk with your local Zimpro sales representative.

Bulletin #P-100 (S & A 5,000)

ZIMPRO
ENVIRONMENTAL, INC.
An Affiliate of the Black Clawson Co.

APPENDIX B

210.4 PACT™ Treatment Performance

The synergistic treatment effect of powdered carbon when maintained at high concentrations in an aeration tank of an activated sludge system is real and was originally felt to be solely related to the capability of the carbon to concentrate organics and oxygen. Microbiologists now feel the synergistic treatment effect to also be catalytic - specifically alleocatalytic. The sorptive effect of carbon inhibits the dilution of a microorganism's secreted enzymes thus enabling the organism to be more efficient in assimilation of soluble organics. Slow-to-degrade soluble compounds are unlikely to pass through a PACT™ system since they will be retained by the carbon for the operating solids residence time of the system. Thus, if compounds are slow to degrade, they will likely pass to regeneration (if used) and be destroyed. By contrast, in an activated sludge process, difficult to biologically treat organics will appear in the final effluent since they are only in contact with biological solids for the hydraulic residence time.

210.41 Treatment Performance

Performance of the PACT™ system treating a wide variety of wastewaters is shown in Table 210.4-I. Though not a complete list, this information is provided to illustrate general performance levels.

TABLE 210.4-I

PACT Treatment System Performance

	Domestic Wastewater(a) (Nitrification)			Domestic Wastewater(b) (Nitrification)
Operating Conditions	PACT*	PACT*	Activated Sludge	Full Scale PACT*
Aeration Time, hrs.	3.2-4.5	4.6	4.2/6.2	
SRT, days	13	16	16	~7
Temperature, °C	20	10	20	20
Performance Results				
Influent, mg/l				(Raw)
BOD_5	134	72	128	142
COD	364	263	320	—
TKN	39.4	28.3	32.0	—
NH_3-N	19.5	16.4	19.8	15.2
Total N	40.4	31.2	34.5	—
Effluent, mg/l		(Clarifier Effluent)		(Filter Effluent)
BOD_5	1.2	0.4	24	6
COD	50	30	63	—
TKN	3.7	2.8	6.4	3.6
NH_3-N	0.2	0.1	3.6	1.6
Total N	20.2	8.8	22.2	—
Removals, %				
BOD_5	>99	>99	81	96
COD	89	88	80	—
TKN	91	90	80	—
NH_3-N	>99	>99	82	89
Total N	50	72	36	—

*Includes Wet Air Regeneration.

(continued)

Table 210.4-I continued

	Domestic Wastewater (Nitrogen Removal)	Domestic Wastewater(c) (Nitrogen Removal)				
Operating Conditions	PACT*	PACT	PACT	PACT	Activated Sludge	Activated Sludge
Aeration Time, hrs.	4.5	3.9	6.1	7.2	22.1	17.0
SRT, days	10	13	19	38	25	36
Denitrification Time, hrs.	2.5	1.4	2.2	3.0	8.0	6.2
SRT, days	6	26	26	65	21	30
Temperature, °C	18	10	8	5	10	10
Performance Results						
Influent, mg/l						
BOD_5	152	198	198	198	198	198
COD	364	291	291	291	291	291
TKN	33.1	27	27	27	27	27
NH_3-N	20.7	12	12	12	12	12
Total N	34.3	27	27	27	27	27
Nitrification Stage Effluent, mg/l						
BOD_5		10	7	3	—	—
COD		67	36	27	—	92
TKN		—	—	—	—	—
NH_3-N		0.5	0.1	1.1	1.9	7.7
NO_3-N		16.8	12.9	7.5	10.5	5.3
Total N		—	—	—	—	—
Effluent, mg/l	(Filter Effluent)				(Filtered)	
BOD_5	10**	6	10	—	—	21
COD	36**	32	33	12	—	157
TKN	0.70	—	—	—	—	—
NH_3-N	0.41	0.3	0	0.9	2.6	8.3
NO_3-N	—	0.3	0.4	0.3	0.2	0.1
Total N	1.76	—	—	—	—	—
Removals, %						
BOD_5	93	96	95	—	—	89
COD	90	89	88	96	—	46
TKN	98	—	—	—	—	—
NH_3-N	98	97	100	92	78	31
Total N	95	—	—	—	—	—

*Includes Wet Air Regeneration.
**Pilot plant did not include aerobic polishing step following denitrification.

	Domestic/Pharmaceutical Wastewater(d)(e) (Nitrification)		Domestic/Organic Chemicals Waste(f) (Organic Removal)		Domestic/Textile Wastewater(g) (Organic Removal)
Operating Conditions	PACT*	Oxygen A.S.	PACT*	Activated Sludge	Full Scale PACT*
Aeration Time, hrs	6.5	4.5	2.5	9	5
SRT, days	16	16	—	9	5-10
Temperature, °C	14-25	—	22	22	10-20

(continued)

Table 210.4-I continued

Performance Results	PACT*	Oxygen A.S.	PACT*	Activated Sludge	Full Scale PACT*
Influent, mg/l					(Raw)
BOD_5	268	92	114**	102**	275
COD	680	249	323	263	900
TKN	32.0	19.9	—	—	—
NH_3-N	17.9	17.0	—	—	—
Total N	33.6	—	—	—	—
P	7.6	—	—	—	—
SS	—	—	37	86	440
Effluent, mg/l	(Filter Effluent)		(Clarifier Effluent)		
BOD_5	0.2	15	3	>25	4
COD	76	92	63	116	65
TKN	5.5	18.6	—	—	—
NH_3-N	2.0	19.3	—	—	—
Total N	15.6	—	—	—	—
P	2.2	—	—	—	—
SS	—	—	24	56	10
Removals, %					
BOD_5	>99	85	97	75	97
COD	89	63	80	56	93
TKN	83	7	—	—	—
NH_3-N	89	—	—	—	—
Total N	53	—	—	—	—
P	71	—	—	—	—
SS	—	—	35	35	97

*Includes Wet Air Regeneration.
**Soluble BOD_5.

	Night Soil(h)		Night Soil(h)	Organic Chemicals(i)
Operating Conditions	PACT*	Activated Sludge	Full Scale PACT*	Full Scale PACT***
Aeration Time, hrs.	12	18	18	8
SRT, days	3.3	11	5.5	45
Temperature, °C	—	—	—	—
Performance Results				
Influent, mg/l				
BOD_5	836	715	666	182
COD	1455	1350	1146	—
P	—	—	11.9	—
Color, APHA	—	—	—	1450
Effluent, mg/l				
BOD_5	2	26	8	12
COD	73	412	59	—
P	—	—	7.1	—
Color, APHA	—	—	—	476
Removals, %				
BOD_5	>99	96	98	93
COD	95	69	95	—
Color	—	—	—	67

*Includes Wet Air Regeneration.
***Includes multiple hearth carbon regeneration.

(continued)

Table 210.4-I continued

	Organic Chemicals(j) (Organic Removal)		Synthetic Fuels(k) (Lurgi)	Synthetic (l) (H-Coal)
Operating Conditions	PACT*	Activated Sludge	PACT*	PACT*
Aeration Time, days	6	6	1.0	1.0
SRT, days	25	>45	36	25
Temperature, °C	25	25	20	20
Performance Results				
Influent, mg/l				
BOD_5	4,035	4,035	1350	700
COD	10,230	10,230	2270	1780
TKN	120	120	99	186
NH_3-N	76	76	70	149
Phenol	8.1	8.1	2.6	227
Cyanide	—		7.5	1.1
Chlorinated Hydrocarbons	5-67	5	—	—
Effluent, mg/l	(Filtered)		(Filter Effluent)	(Filter Effluent)
BOD_5	11	17	<6	<7
COD	102	296	45	300
TKN	4	—	5.5	9.8
NH_3-N	0.8	—	<1	<2.4
Phenol	0.01	0.22	<0.1	0.9
Cyanide	—	—	0.08	0.39
Color	9.4	820	—	—
Chlorinated Hydrocarbons	0.1	0.9	—	—
Removals, %				
BOD_5	>99	>99	>99	99
COD	99	97	98	83
TKN	96	—	94	94
NH_3-N	98	—	98	98
Phenol	>99	97	96	>99
Cyanide	—	—	98	65
Color	—	—	—	—
Chlorinated Hydrocarbons	>98	82	—	—

*Includes Wet Air Regeneration.

(continued)

Table 210.4-I continued

	Coke Oven Gas Liquors		Toxic Waste	Refinery Waste$_{(m)}$	
Operating Conditions	PACT*	Activated Sludge	PACT*	PACT	Activated Sludge
Aeration Time, hrs.	17	—	144	15	15
SRT, days	7	—	—	60	60
Temperature, °C	25	—	25	14	14
Performance Results					
Influent, mg/l					
BOD$_5$	1050	650	9,000	—	—
TOC	—	—	—	74	74
COD	2359	1329	19,200	295	295
NH_3-N	13	600	—	19.3	19.3
Phenol	468	150	—	4.0	4.0
SCN	279	130	—	—	—
Cyanide	7	—	—	—	—
EOCL**	NA	NA	8-150	—	—
Effluent, mg/l	(Filtered Effluent)		(Filtered Effluent)		
BOD$_5$	4	10	10	—	—
TOC	—	—	—	12	25
COD	289	436	630	28	66
NH_3-N	<1	731	—	0.1	5.1
Phenol	<1	<1	—	0.002	0.019
SCN	<2	3.5	—	—	—
Cyanide	1.2	—	—	—	—
EOCL	—	—	<0.05	—	—
Removals, %					
BOD$_5$	>99	98	>99	—	—
TOC	—	—	—	84	66
COD	88	67	96	91	78
NH_3-N	—	—	—	99	74
Phenol	>99	>99	—	>99	>99
SCN	99	97	—	—	—
Cyanide	83	—	—	—	—
EOCL	—	—	>99	—	—

*Includes Wet Air Regeneration.
**Extractable organic chlorine.

References:

[a] Berndt, C. L. and Polkowski, L. B., "A Pilot Test of Nitrification with Powdered Activated Carbon." Presented at the 50th Annual Meeting of the Central States Water Pollution Control Association, Milwaukee, Wisconsin, May 18-20, 1977.

[b] Ohio EPA NPDES Discharge Monitoring Reports for Medina County, Ohio. (June-August, 1983).

[c] Lee, J. S. and Johnson, W. K., "Carbon Slurry Activated Sludge for Nitrification Denitrification." Journal Water Pollution Control Federation, Volume 51, No. 1, 1979.

[d] Sampayo, F. and Swets, D., "Powdered Carbon Treatment at Kalamazoo, Michigan." Presented at the Wastewater Equipment Manufacturers Association Pollution Conference, St. Louis, Missouri, April, 1978.

e) Sampayo, F. F. and Hollopeter, D. C., "The Influence of Industrial Waste on Nitrification." Proceedings of the 33rd Industrial Waste conference, Purdue Univeristy, May, 1978.

f) Foresman, M. R. and Sago, W. L., "Case History Joint Municipal/Industrial Wastewater Treatment for Metro East Saint Louis, Illinois." Presented at the 53rd annual Water Pollution Control Federation Conference, Las Vegas, NV, 1980.

g) Pitkat, C. and Berndt, C., "Wastewater Treatment with Powdered Activated Carbon; The PACT™ Process and Wet Air Regeneration at Vernon, CT." Public Works, October, 1981.

h) Meidl, J.A., Berndt, C.L., and Nomoto, K., "Experience with Full Scale Wet Oxidation of Spent Carbon From The PACT™ Process." Presented at the 51st Annual Water Pollution Control Federation Conference, Anaheim, CA, October, 1978.

i) Dunn, G.F., "PACT™—An Improvement in Wastewater Treatment." Presented at the 54th Annual Water Pollution Control Federation Conference, Detroit, MI, October, 1981.

j) Rollins, R.M., Ellis, C.E., and Berndt, C.L., "PACT™/ Wet Air Regeneration Treatment of an Organic Chemicals Wastes." Proceedings of the 37th Industrial Waste Conference, Purdue University, May, 1982.

k) Berndt, C.L., Rollins, R.M., Soukup, C.L., Canney, P.J., "Synfuels Waste Treatment by the PACT™ Process." Presented at the 55th Annual Water Pollution Control Federation Conference, St. Louis, MO, October, 1982.

l) Churton, B.M., Skrylov, V., "Studies to Treat Process Wastewater from a Coal Liquefaction Plant." Presented at the Summer National Meeting of the American Institute of Chemical Engineers, Cleveland, OH, 1982.

m) Grieves, C.G., Stenstrom, M.K., Walk, J.D.; and Grutsch, J.F.; "Effluent Quality Improvement by Powdered Activated Carbon in Refinery Activated Sludge Processes." Presented at the API Refining Department 42nd Midyear Meeting, May, 1977.

210.42 Cost and Energy Effectiveness

Though the PACT™ system is an advanced wastewater treatment system, its cost compares very favorably with conventional treatment systems that cannot produce effluent treated to the same level. Studies by others have shown that anytime carbon adsorption is considered in a treatment facility, powdered activated carbon should be applied to the aerator.*

Also, anytime secondary sludge incineration is considered in municipal wastewater treatment, the PACT™ system should prove to be cost effective. Documented cost comparisons indicating such are presented in the following paragraphs.

210.421 EPA Cost Evaluation

The cost effectiveness of powdered carbon treatment of municipal wastewater has been reviewed in detail by Culp and Shuckrow in 1977.** Primary objectives of the EPA sponsored study were to review the state-of-the-art of these technologies and compare the costs of the various processes.

Several wastewater treatment processes were selected for evaluation, including the PACT™ wastewater treatment system, and cost examined at plant design capacities of 1, 5, 10, 25 and 50 mgd. The wastewater characteristics and design parameters are shown in Tables 210.4-II and 210.4-III.

The results of their study (updated to 4th Quarter 1983 dollars) are shown graphically in Figure 210.4-A. The results indicate that the PACT™ system is cost effective compared to conventional activated sludge and single stage activated sludge nitrification. Significant cost savings were shown for use of the PACT™ system in lieu of two stage activated sludge for nitrification or granular carbon adsorption. In comparison with activated sludge, PACT™ systems are cost effective in the 3 and 4 mgd range, depending on the sludge handling systems included. The recent selection of a PACT™ system to upgrade treatment at Bedford Heights, OH, USA (3.0 mgd design flow), confirms these results.

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*Culp, G.L. and Shuckrow, A.J.; "What Lies Ahead for PAC?" Water and Wastes Engineering, February, 1977.

**Culp, G.L. and Shuckrow, A.J.; "Appraisal of Powdered Activated Carbon Processes for Municipal Wastewater Treatment," EPA-600/2-77-156, September, 1977.

Table 210.4-II

Wastewater Characteristics
EPA Cost Effectiveness Study

Parameter	Raw	Primary Effluent
BOD_5, mg/l	200	140
COD, mg/l	500	
TKN, mg/l	40	32
NH_3-N, mg/l	25	
P, mg/l	10	
SS, mg/l	200	70

APPENDIX C

TECHNICAL REPORT NO. 225

BIOPHYSICAL AND WET AIR OXIDATION TREATMENT OF TOXIC EFFLUENTS

By:

Dr. J. C. Mishra and K. Ravindranath; Larsen & Toubro Limited,
Bombay, India

Presented At:

Envirotech '91 International Conference;
Symposium on: "Pollution Abatement - Equipment, Monitoring and Control Systems", October 31, 1991.

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ENVIROTECH '91 INTERNATIONAL CONFERENCE

SYMPOSIUM ON : " POLLUTION ABATEMENT — EQUIPMENT, MONITORING AND CONTROL SYSTEMS "

DATE : **THURSDAY, OCTOBER 31, 1991**

TITLE OF THE PAPER :

BIOPHYSICAL AND WET AIR OXIDATION TREATMENT OF TOXIC EFFLUENTS

TO BE PRESENTED BY **DR. J. C. MISHRA & K. RAVINDRANATH**
Larsen & Toubro Limited
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The Synopsis

Liquid toxic wastes which are to dilute for economical incineration and too toxic for conventional biological treatment can be treated effectively by two State - of - the Art technologies - Biophysical process or Powdered Activated Carbon Treatment (PACT) and Wet Air Oxidation (WAO).

The two processes either individually or in combination cover treatment of a broad and specific range of COD where no other technology or system is effective.

This paper describes process, advantages and applications of Biophysical & Wet air oxidation process, and also deals with PACT and WAO systems highlighting the characterization of toxic waste, process design concepts, operating plant data, the efficiency of treatment and the special features. The effective combination of the two processes to achieve the treated effleunt pollutant limits as per Minimum National Standards (MINAS) for a refinery in Bombay is presented as a case study.

About the Author

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BIOPHYSICAL AND WET AIR OXIDATION TREATMENT OF TOXIC EFFLUENTS

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ABSTRACT :

Liquid toxic wastes which are too dilute for economical incineration and too toxic for conventional biological treatment can be treated effectively by two State-of-the-Art technologies - Bio-physical process or Powdered Activated Carbon Treatment (PACT) and Wet Air Oxidation (WAO).

PACT process provides a synergistic effect of biological oxidation and physical adsorption applicable to difficult-to-treat wastes having variable concentration and composition of inhibitory materials potentially toxic to biological growth encountered in refinery, petrochemical, synthetic fuels, pharmaceuticals, dyes, organic chemical industry etc.

Wet air oxidation is the liquid phase oxidation of organics and oxidizable inorganic compounds at elevated temperature and pressure. This process is applicable for spent caustic liquors, cyanides, Sulphides, phenolic and acrylonitrile wastes, spent solvent waste, coke oven waste liquor, pesticide/herbicide wastes and other hazardous and priority pollutants.

This paper covers PACT and WAO processes highlighting characterization of toxic waste, special features, process design aspects, performance/operating plant data and the efficiency of treatment. The effectiveness combination of the two processes to achieve treated effluent pollutant limits as per Minimum National Standards (MINAS) for a refinery is presented as a case study.

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... treat... process ... t technologies such as activated ... ent and ... biotowers, granular activated ... OD seg... incineration have limitations in ... COD of ... viz. 1000 to 50,000 mg/lit. ... ration o... a waste too dilute for economical ... ent. Tw... o toxic for conventional biological process ... State-of-the-Art technologies ... (PACT) a... Powdered Activated Carbon ... specifically ... Wet Air Oxidation (WAO) ... for ma... the above range of COD of the toxic wastes. PACT process can treat COD in the range of 50 mg/lit to 50,000 mg/lit and WAO can treat 20,000 mg/lit to 400,000 mg/lit. The principle of wet air oxidation is extended further to regenerate the carbon spent in the PACT process and this process is termed as Wet Air Regeneration (WAR). WAR in conjunction with PACT has the ability to handle extremely toxic and concentrated waste streams.

WASTE WATER CHARACTERIZATION-TOXIC EFFECTS

Various parameters of waste water that can be considered to have toxic effects on the biota of receiving streams are organic content expressed in terms of chemical oxygen demand and total organic carbon; sulphides; phenols; NH_3-N; TKN; and certain specific constituents termed as priority pollutants such as chlorinated hydrocarbons like trichloroethylene, dichlorobenzene, dichlorophenol, nitrophenol, Methylchloride, Orthochloroaniline, dichlorobenzidine and aromatics like benzene, toluene etc. The toxicity can also be assessed from the values of BOD_5 and COD. Very low ratios of BODS to COD (less than 0.4) indicates that the waste is of toxic nature. Values of COD, TOC and concentrations of specific known pollutants can be used to decide on the toxic nature of the waste.

POWDERED ACTIVATED CARBON TREATMENT (PACT)

Essentially PACT process involves addition of powdered activated carbon to the aeration basin of the activated sludge process. This process, developed by DuPont and Zimpro, takes advantage of the synergistic effect of adsorption capability of fine activated carbon and biological oxidation of toxics simultaneously. The benefits of both the treatment methods can be combined in the removal of highly biodegradable, non-adsorbable compounds as well as highly adsorbable but poorly biodegradable compounds.

System Description

General process diagram is similar to that of an activated sludge flow scheme. Additional input to the system is only powdered activated carbon to the aerator. Mixed liquor carbon levels are maintained in the range of 3000 mg/lit to 10,000 mg/lit depending on the waste characteristics. After effecting good contact between carbon, biomass and the waste in presence of diffused air, the solids are separated in a clarifier. The overflow goes to discharge and the underflow clarifier solids are pumped in concentrations ranging from 2 to 4% solids back to the aeration tank. Wasting of excess solids out of the PACT process is accomplished from the recycle stream. Waste solids consist of a mixture of spent carbon, biomass, adsorbed organic material and inert matter and are directed to solid processing system which could be simple dewatering using centrifuge or filter press or regeneration by wet oxidation (WAR). The regenerated carbon is sent back to the aeration tank. To avoid build up of inert material (ash) in the system, a part of the solids are removed in the regeneration step.

Advantages/Special Features.

Some of the major concerns while selecting a treatment system are minimum COD levels that can be achieved, effect of discharge concentrations on the biota of receiving streams, controlling the levels of priority pollutants, sludge generation/handling and volatiles emission. PACT system offers advantages over other system in all these areas:

- Powdered carbon facilitates the adsorption of toxic and inhibitory substances which enhances the bio-oxidation potential.
- Adsorbed organics are retained in the system for the period of time equivalent to solids residence time (SRT) rather than hydraulic detention time as would occur in conventional biological processes.
- Availiability of large quantity of carbon adsorbent provides stability against shock and variable pollutent loadings.
- Specific toxics such as chlorinated aromatic hydrocarbons and other priority pollutants can be removed to very low levels.
- PACT process can effectively reduce the toxicity with higher Lc_{50} value of discharge effluent concentration to biota of receiving streams.
- Performance can be improved simply by adjusting the carbon dosage.
- Volatiles stripped from waste water while aerating are effectively adsorbed on the suspended carbon, thereby controlling organic emissions.
- Improved oxygen transfer due to strong affinity of carbon towards the gaseous oxygen.
- Activated carbon provides favourable environment for nitrification in a single stage.
- Excess biosludge is converted to carbon dioxide and water in the process of regenerating spent carbon from PACT process by oxidation in WAR unit, compared to the residual sludge carrying concentrated toxic requiring to be incinerated in conventional system.

Process Design Aspects

The key process parameters used in the design of PACT system are :

(i) Mixed liquor suspended solids - volatile carbon, biomass and suspended ash (MLSS)

(ii) Solids residence time (SRT)

(iii) Hydraulic detention time (HDT)

(iv) Powdered carbon dose rate

(v) Biomass growth rate or net yield of volatile solids

(vi) Dissolved oxygen concentration based on oxygen transfer rate.

The above critical parameters are waste specific and are derived based on biokinetic study in the laboratory. Though broad guidelines are evolved for typical industrial wastes, laboratory tests would help in optimising the set of parameters. For example, biomass growth rate depends on various constituents of waste and is derived from laboratory experiments and correlation of biokinetic coefficients such as yield coefficient, decay coefficient and Monod constant.

Apart from the type of waste, two ither issues controlling the design are carbon characteristics and microbiology.

Powdered Activated Carbon

PAC serves as a sorbent for toxic and inhibitory substances, provides surface for concentration of oxygen, adsorbed organics, microorganisms and microbial enzymes and forms the nuclei for the biofloc. The important characteristics of carbon are the base material used, particle size distribution, bulk density, ash content and adsorptive capacity in terms of surface area and pore size distribution, and regenerability in terms of loss during oxidation and enhancement in adsorptivity and withstanding repeated regenerations. The surface area and pore size distributions are also correlated from various adsorbate numbers such as Iodine no., Methylene blue no. and Molasses no. In addition, experiments on specific carbons are carried out to check the amount of pollutant that can be adsorbed (physical adsorption isotherm) and the residual amounts that can be achieved in presence of carbon and biomass (biophysical isotherm). Typical adsorption isotherm for refinery waste water is shown in **Fig.1.**

Microbiology

An optimum microbial environment is required to enhance removal of biodegradables. Biological degradation is more predominant in PACT due to longer time periods available for adsorbed, but slowly biodegradable organics. High efficiency toxic removal system are found to have a diverse mixture of versatile bacteria. Predominantly the microbial environment is made up of protozoans including flagellates and both free swimming and stalked ciliates. These are indicator microorganisms as they can thrive only in non-toxic, aerobic and low BOD_5 environments. They also ingest free bacterial cells thus improving effluent clarity. Rotifers are generally not present, but filamentous species are present in very low levels.

Relative predominance of the indicator microorganisms is given in **Fig.2.**

Pact Performance

The objective of PACT process is mainly to attain low levels of COD, TOC and organic priority pollutants in the discharge streams and to control stripping of organic compounds. The superiority of treatment achieved by PACT vis-a-vis conventional activated sludge process for some typical industrial wastes is presented in **Table 1.**

From the table, it can be seen that activated sludge process treatment is effective only in removing BOD while PACT is very effective in treating COD, TOC, specific organic pollutant removal and colour apart from improved removal of BOD.

LC_{50} values, (i.e. effluent pollutant concentrations as a percent which produces death or immobilization of 50% of test species) for PACT are far better than for conventional activated sludge.

High treatment that can be achieved in PACT in removing priority pollutants compared to activated sludge is shown in **Table 2.** Most of the toxic organics are removed to 99% and above levels in PACT process.

PACT performance for selected industrial wastes is shown in **Table 3** along with the process conditions maintained. The low levels achieved for toxic, high COD containing wastes demonstrate the superiority of the technology. Volatile organics removal in activated sludge process are deceptively indicated as low values in treated effluent, whereas they are actually stripped out of the aeration basin as shown in **Table 4.** If the amount stripped is taken into account, percent treatment is very low. In PACT process volatiles are effectively handled by the powdered carbon due to the adsorption phenomena.

The effluent levels can further be lowered by adjusting the carbon dose levels to PACT system. This can be demonstrated by **Fig. 3.** For toxic organic waste the correlation between higher mixed liquor volatile corbon levels and lower effluent COD and TOC concentrations are seen in this figure.

Thus it can be seen from the sample systems presented in this section that the advantages mentioned above can be fulfilled for most of the industrial wastes.

Wet Air Oxidation (WAO)

Wet air oxidation is the process of aqueous phase oxidation of dissolved and suspended organic and inorganic substances at elevated temperature and pressure. The temperature controls the oxidation reaction and the high pressure (20-200atm) maintains water in the liquid state which makes the oxidation occur at relatively lower temperatures of 175-325 degC. In this process, developed by Zimmermann, numerous hazardous and toxic compounds are readily destroyed by a series of oxidation and hydrolysis reactions. Water, apart from being the main force by removing excess heat by evaporation and providing an excellent heat transfer medium making the process to be thermally self-sustaining even with relatively low organic feed concentrations. Also the enhanced solubility of oxygen in aqueous solution at elevated pressure provides a strong driving force for oxidation. This process when used for regeneration of spent carbon and destruction of associated biological matter, is called wet air regeneration. However, the principle involved in both WAO and WAR is the same.

System Description

The stream containing oxidizable material or spent carbon with associated biomass is pumped using a high pressure pump and mixed with air from a compressor. The feed stream is preheated in a heat exchanger by the hot oxidized effluent from the reactor, and enters the vertical bubble column type of reactor which provides the desired residence time for the oxidation reaction. The reaction time and temperature of oxidation very depending on the type of the waste water and the treatment objectives. The heat of oxidation raises the reactor temperature to the desired operating level. Hot oxidized effluent from reactor is cooled in the preheat exchanger and depressurised through a pressure control valve assembly. Liquid and non-condensable gases are disengaged in an atmospheric separator and discharged separately.

Energy Efficiency

The distinct feature of wet air oxidation process is energy conservation. The only comparable alternative to this technology is thermal oxidation such as incineration with associated air pollution control equipment. However, wet oxidation consumes far less fuel than incineration where not only the sensible heat and heat of vaporization of the liquid need to be supplied, but also heat the water vapour, combustion products and excess air to combustion temperatures in the range of 800-1100 degC. In the wet air oxidation process, the wastes used are unconventional for normal burning because of their high water content and low fuel value. A convenient measure of the fuel value of an aqueous dispersion of organic matter is its chemical oxygen demand (COD). The energy requirements (Deficit or Surplus) as function of COD value are given in **Fig. 4** for both wet oxidation and thermal oxidation processes. It can be seen that a feed COD of 15,000mg/lit is sufficient for wet oxidation to proceed autogenously (self sustaining, with no auxiliary fuel) whereas a COD of 300,000-400,000 mg/lit is required for autogenous incineration.

Other benefits

The wet air oxidation process is adaptable to variations in feed characteristics and can process practically any oxidizable matter. Apart from energy efficient processing of dilute waste streams, WAO process offers many advantages.

- WAO process covers the range of waste waters which are too toxic to microorganism or too dilute for economical incineration.
- This process is readily applied to a wide variety of difficult-to-treat toxic and hazardous industrial waste waters such as those from the manufacture of herbicides, pesticides, organic chemicals, petrochemicals and coke oven plants.
- The oxidation products are innocuous and the gas discharged consists mainly of spent air and carbon dioxide and is essentially free of any air polluting constituents.
- Organic nitrogen is converted primarily to NH_3.
- The organic compounds remaining after wet oxidation are comprised of low molecular weight oxygenated compounds, predominantly carboxylic acids.
- Because of aqueous phase oxidation, no oxides of nitrogen or sulphur exit in the off gases as in incineration.
- Metals are generally converted to their highest oxidation state and remain in the aqueous phase as dissolved or suspended solids.
- Halogens also stay in the aqueous phase.
- Wet oxidation reduces the toxicity 15-4060 fold.
- The effluent from the wet air oxidation process is generally readily treatable by biological methods.

Process Parameters

The key process parameters used in the design of wet air oxidation/regeneration are :

(i) Oxidation temperature.

(ii) Reactor pressure.

(iii) Residence time

(iv) Residual oxygen concentration.

In case of wet air regeneration, additional parameters to be considered are :

(i) Percent volatile solids in the feed.

(ii) Regeneration efficiency of carbon.

(iii) Recovery efficiency of carbon.

All the critical parameters are waste specific and are derived based on laboratory autoclave studies and optimization of time - temperature combination.

WAO Performance

The objective of wet air oxidation process is to

mplete destruction of toxic com-
down COD to significantly low
e waste water amenable to bio-
e cases direct discharge to receiv-
effectiveness of wet air oxidation
o wide range of toxic and hazar-
ented as the performance of WAO
ndustrial wastes in **Table 5**. The
s in terms of temperature, pres-
me and the corresponding reduc-
specific toxic pollutants amply
perior treatment offered by wet

REFINERY WASTE WATER
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PACT/WAO outlined have been
tment of waste water originating
plant using the PACT/WAR tech-
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e. The waste water comprise of
The concentrated waste water
our condensates from the catalytic
and Fluidized catalytic cracking
ent caustic from the Kero-Merox
ream consists of process waste
de distillation unit (CDU), Bitumi-
(BBU) and Aromatics plant. The
of the combined waste water is
he principal pollutants are BOD_5,
in the form of oil, sulphides and

sists of equalisation and subse-
the combined equalized waste
of a free oil and emulsified oil
followed by an aeration basin
ation system for PACT. The aera-
d by a clarifier and guard pond
discharge. Wasting of spent
a thickener and after storing in
nt to the WAR unit comprising of
heat exchangers, reactor, pres-
atmospheric separator and scrub-
all amount of sludge generated is
ntrifuge and trucked off. Process
T/WAR plant is given in **Fig. 5**.

Performance

The design and operating parameters for the PACT/WAR system are given in **Table 6**. The performance of the plant achieved after stabilization isgiven in **Table 7**. From the table, it can be seen that all the MINAS parameters are met in the treated effluent. Additionally an effluent COD of 78 mg/lit was achieved with an influent COD of 1494 mg/lit. COD level is the treated effluent is much below the value specified by ISI, thus demonstrating the effectiveness of PACT system in removing COD and specific pollutants like phenol and sulphide.

Operational Flexibility

Various benefits obtained in the plant apart from achieving stringent treatment objectives and the response of the plant to the wide variations in the influent characteristics are as under :

- The sludge generated in the plant is almost negligible and the only sludge is sterile ash from the reactor blowdown.
- War unit operation is thermally self sustaining at solids concentration of 7% which includes about 3.5% of biomass indicating the energy efficiency of the system.
- When carbon levels from the aeration basin dropped down due to continuous wasting but without regeneration for short duration, it was noticed that the biomass became inactive affecting the treatment. When carbon is brought back to aeration tank after regeneration, quick revival of performance was seen, thus demonstrating the importance of the combined effect of carbon and biomass for certain toxic waste waters.
- The plant was able to withstand shock loads as well as spikes in some pollutant levels very effectively. For example COD upto 4000 mg/lit (longer period), sulphide upto 300-500 mg/lit (short duration) and phenol upto 900 mg/lit (short duration) posed no problem in achieving required treated effluent quality.
- Very high influent sulphide levels resulted in sulphur reducing bacteria converting the same to sulphur and storing in the cells. Subsequent reduction in influent Sulphide levels have made biomass oxidise the stored sulphur to sulphate causing reduction in pH. This has shown the importance of controlling sulphide levels within the specified limits at all times.

CONCLUSION

The treatment of toxic organics and hazardous industrial waste by two advanced technologies viz. PACT and WAO/WAR has been shown to be an effective means of controlling liquid, solid and gaseselected industries of both the processes are presented in the article.

The high performance levels that can be achieved by PACT in conjunction with WAR and the operational flexibility are presented in the case study of refinery waste water treatment.

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Table 1 : Comparison of Treatment Performance Pact vs. Activated Sludge

Sl. No.	Tyts of waste water	Influent characteristics (mg/lit)		Effluent characteristics (mg/lit)	
				Activated sludge	PACT
1.	Organic chemical industry	BOD$_5$	4035	17	11
		COD	10230	296	102
		TOC	2965	65	0.10
		R-Cl	5.08	0.91	0.01
		Phenol	8.1	0.22	94 APHA
		Color	-	820 APHA units	
2.	Chemicals manufacturing industry	BOD$_5$	320	3	2
		TOC	245	81	17
		Colour	5365	3830	125
		LC$_{50}$	-	11	>87
3.	Pharmaceutical & Fine Organic chemicals	BOD$_5$	7470	55	11
		COD	11840	540	280
		TKN	690	595	31
4.	Synthetic fuels production	BOD$_5$	6220	650	27
		COD	23700	8430	2510
		DOC	4950	2990	840
		Phenols	71.4	2.88	0.2
		Cyanide	60.1	39.3	0.65
		Thiocyanate	191.7	>190	16.2

Table 2: Priority Pollutant Removal - Performance Comparison

Pollutant	Feed ppb	Percent removal	
		Activated sludge	PACT System
1,2 - dichlorobenzene	18	90.6	>99
2.4 - Dinitrotoluene	1000	31.0	90
2,6 - dinitrotoluene	1100	14.0	95
Nitrobenzene	330	95.5	>99.9
1,2,4 - trichlorobenzene	210	>99.9	>99.9
1,4 - dichlorophenol	19	0	93
2,4 - dinotrophenol	140	39.0	>99
4 - nitropenol	1100	25	97
Methylchloride	1770	-	100
Chlorobenzene	1720	-	98
Toluene	519	-	99
Benzene	105	-	99.2
Orthochloroaniline	6500ug/1	-	99.8
Dichlorobenzidene	400ug/1	-	99.5

Table 3 : PACT Performance For selected Industrial Waste Water

Type of waste	1 Concentrated toxic waste	2 Contaminated ground water	3 Organic Chemicals	4 Chemicals	5 Refinery	6 Synthetic fuels
Operating conditions						
Solids residence time, days						
Hydraulic detention time, days,						
Mixed liq. volatile carbon, mg/1						
Mixedf liq. volatile biomass, mg/1						
Performance						
COD, mg/1						
Feed	18,800	1788	11,840	5520	616	2341
Effluent	563	467	284	66	129	62
% removal	97	74	97.6	98.8	79.1	97.4
BOD$_5$ mg/1						
Feed	9880	55	7470	569	149	1391
Effluent	11	5	7.5	<6	<6	5
% removal	>99	91	99.9	98.9	>96	99.6
Others:	Eod	DOC	TKN	DOC	Cyanide	TKN
Feed	75	550	690	879	4.78	103
Effluent	<0.05	154	31	30	0.554	3.6
% removal	>99	72	95.5	96.6	96.8	96.5

Table 4: Off-Gas Quality - Control of Toxic Organic Emission By PACT

(% of influent)

Compound	Activated sludge			Pact (@100mg/1 carbon dose)		
	Effluent	Off-gas	(% Treatment)	Effluent	Off-gas	(% Treatment)
Benzene	<1	16	83	<1	14	85
Toluence	<1	17	82	<1	0	99
O-xylene	<1	25	74	<1	0	99
1,2 - dichlorobenzene	6	59	35	<1	6	94
1,2,4 - Trichlorobenzene	10	90	0	<1	6	94

Table 5 : WAO Performance For Selected Industrial Waste Waters

Type of waste water	Operating conditions			Performance data			
				Concentration, mg/lit			
	Temp. (degC)	Pressure (kg/cm2)	Reaction time(min)	Assay	Feed	Effluent	%Destruction
Spent caustic from Ethylene plant	315	130	50	COD	2400	800	96.7
				Sulphide	9000	<0.1	99.9
Acrylonitrile waste water	250	70	90	COD	37000	15000	65
				Cyanide	400-900	<0.1	99.9
Coke oven waste liquor	270	75	60	Thiocyanate	33000	1000	97
Metal plating waste water	280	140	60	COD	97000	5300	94.5
				Cyanide	33000	2.4	99.99
Herbicide waste water	280	140	60-90	COD			
				Dipropyl-formamide	600-1200	2.2	99.8
Pesticide waste	270	133	90	COD	40514	1020	97.5
Phenolic waste from plastics plant	270	150	60	COD	60870	1552	97.5
				Phenol	16850	195	98.84
Sulphide waste from pharmaceutical ind.	200	82	60	COD	6977	176	97.5
Spent caustic from refinery	230	100	60	COD	39827	4090	98.7
				Sulphide	14208	12.5	99.9
Organic Chemical industry	314	135	128	COD	77500	9400	87.9
				DCB	2213	29	98.7
				PCE	4000	0.9	99.9
				MEK	6000	1.0	99.9

Table 6 : PACT/WAR for Refinery Waste :

Design/Operating Parameters

PACT

Major design parameters		Actual operation conditions	
SRT	: 7-13 days	SRT	: days
HDT	: 18-45 days	HDT	: days
MLSS	: 10-20 g/lit	MLSS	: g/lit
D.O	: 2-4 mg/1	D.O	: 2.5 mg/1
pH	: 6.5 - 8.5	pH	: 7
		Oxygen uptake rate	: 11.2mg/lit/hr

WAR

Major design conditions		**Actual autothermal operating conditons**	
Reactor inlet temp.	: 205-220 degC	Reactor inlet temp.	: 205-210 degC
Reactor outlet temp.	: 240-247 degC	Reactor outlet temp.	: 240-243 degC
Process HX tube outlet temp.	: 230 degC	Process H.X. tube outlet temp.	: 232-235 degC
Reactor pressure	: 63-45 kg/cm²g	Reactor pressure	: 64.5 kg/cm²g
Solids conc. in slurry	: 6 - 8%	Solids conc. in slurry	: 7.6%
Residual oxygen	: 3%	Residual oxygen	: <10%

Table 7 : PACT/WAR Plant For Refinery Waste - Performance Data

Parameter	Influent		Treated Effluent			
	Design. (mg/1)	Actual (mg/1)	Design MINAS for oil refinery		Actual	
			Max. conc. (mg/1)	Max. quantum Kg/1000 T crude processed *	Concn. (mg/1)	Quantum Kg/1000 T crude processed *
BOD$_5$	808	718	15	10.5	7.0	0.756
Phenolics	257	70	1	0.7	NIL	NIL
Sulphide	120	142	0.5	0.35	NIL	NIL
Oil & grease	7535	-	10	7	2	0.216
Suspended solids	57	75	20	14	6	0.648
pH	6-10	8	6-8.5	-	6.6	
COD	1172	1494	(250 as per ISI)		78	

* Crude processing capacity = 20,000tpd

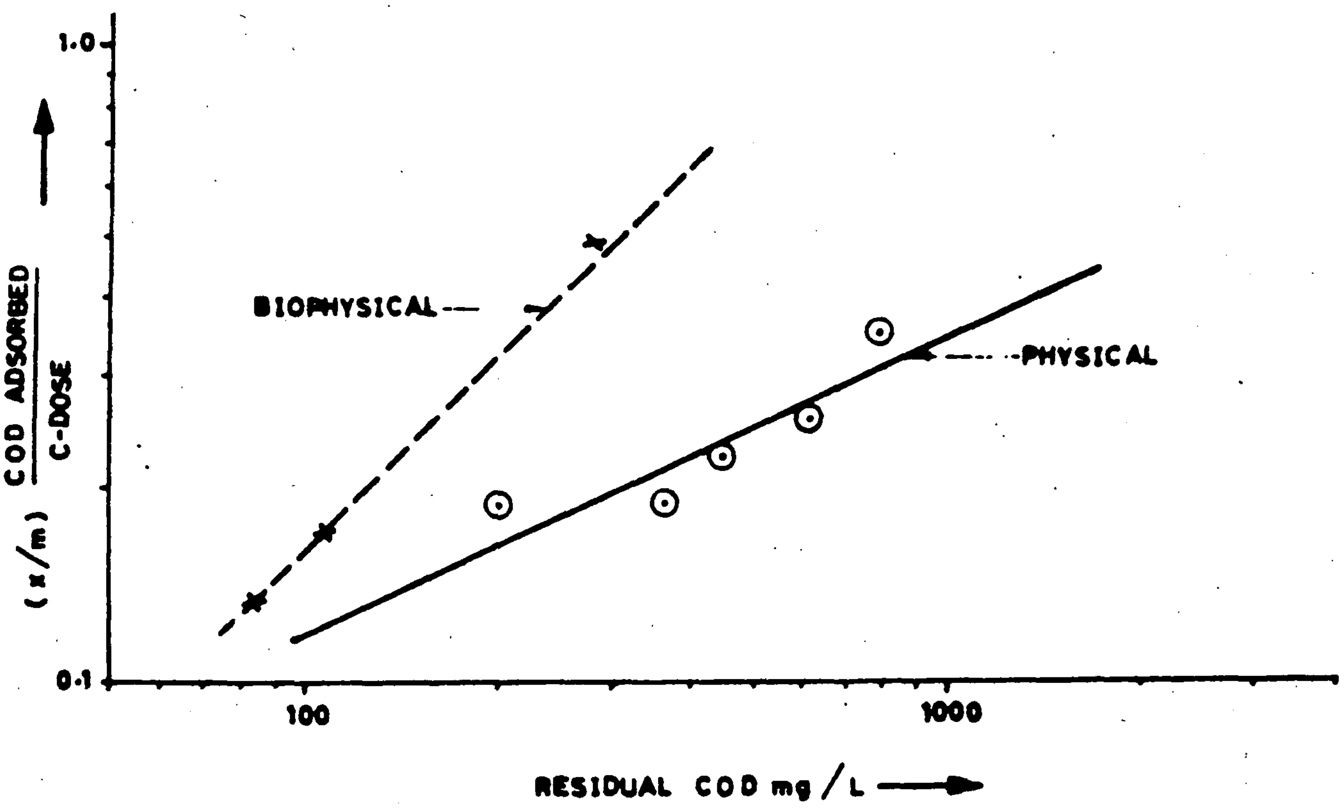

FIG. 1 PHYSICAL/BIOPHYSICAL ADSORPTION ISOTHERMS REFINERY WASTEWATER

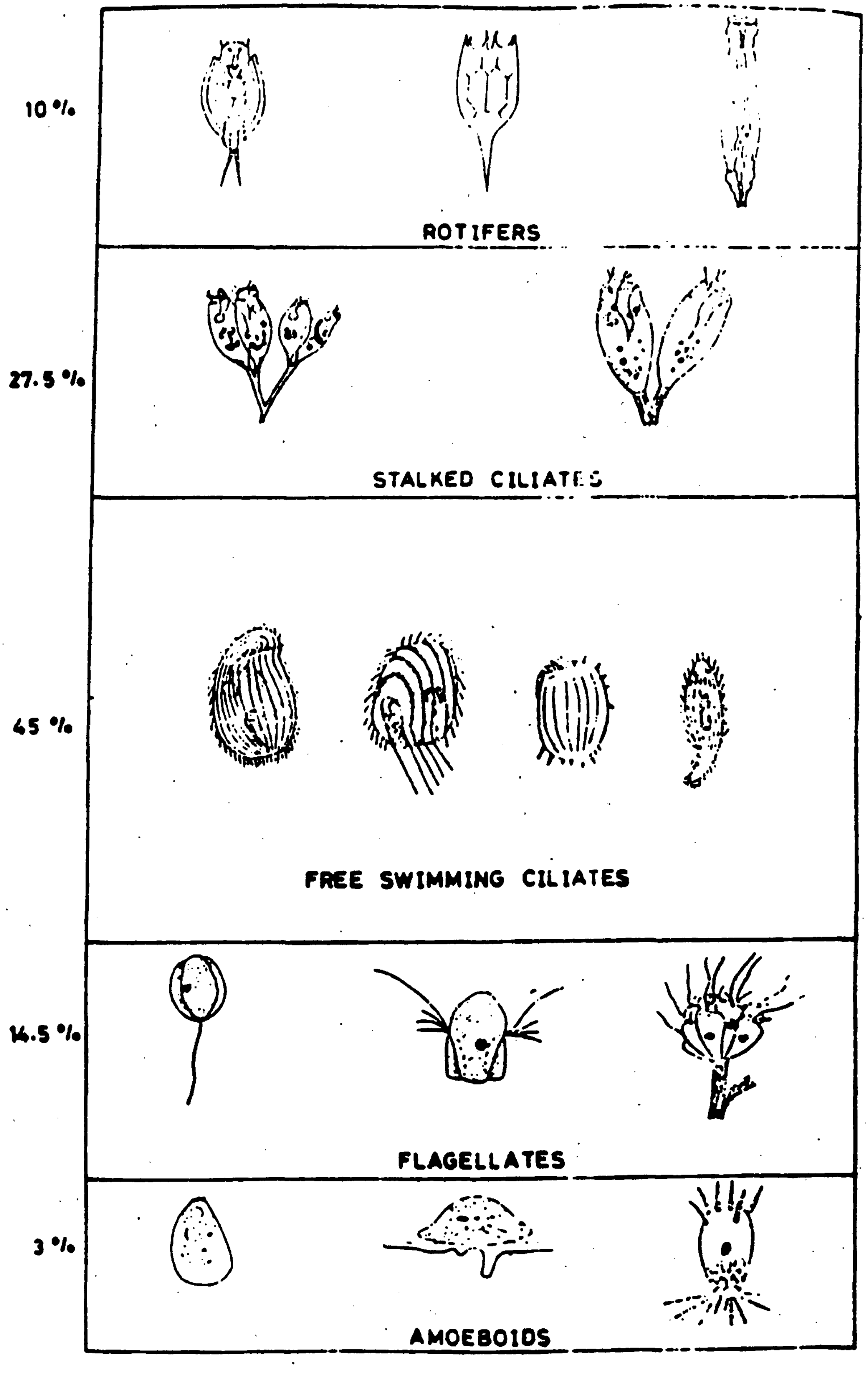

FIG. 2 PREDOMINANCE DIAGRAM OF MICROORGANISMS

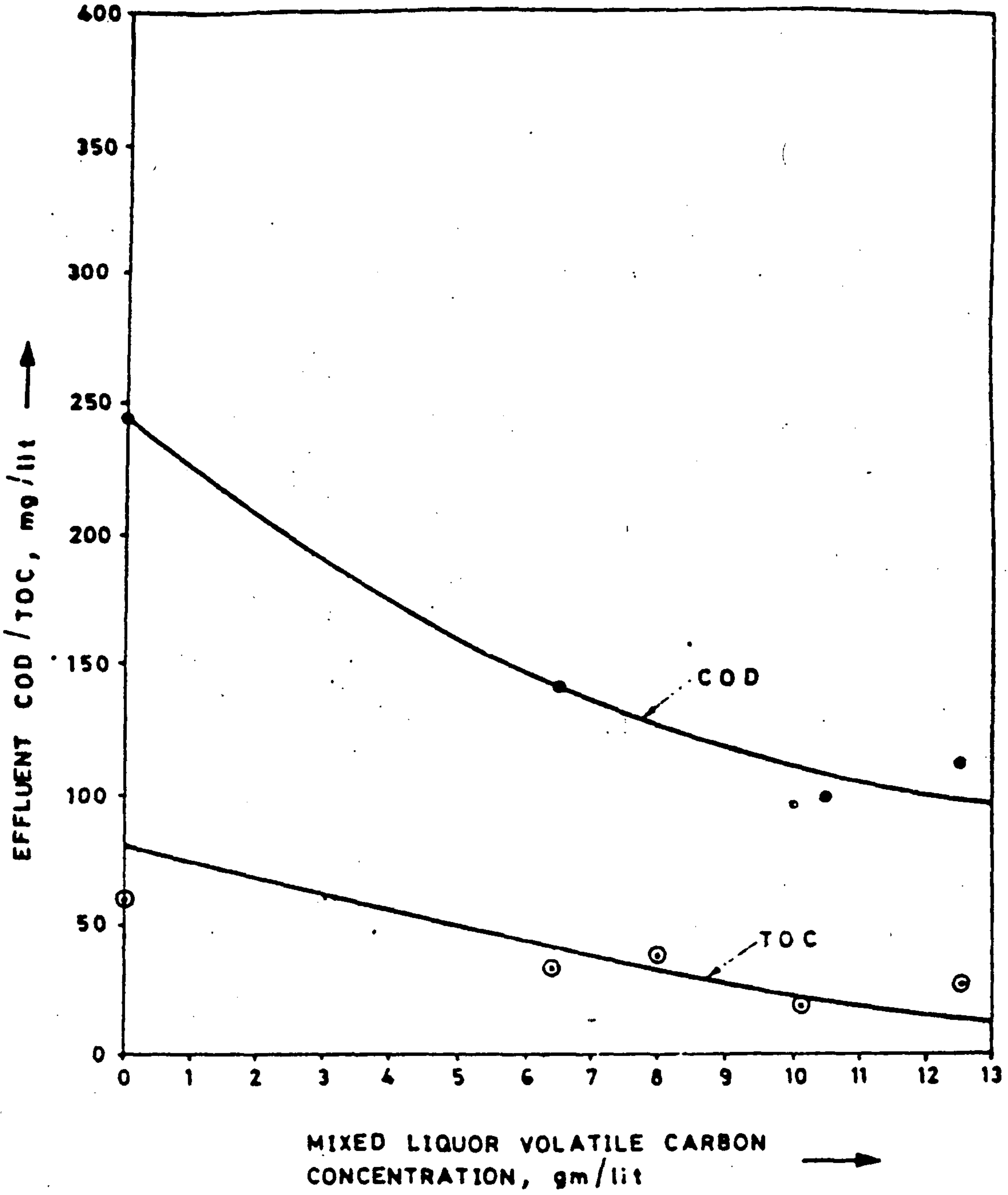

FIG. 3 CARBON LEVELS Vs EFFLUENT QUALITY FOR TOXIC ORGANIC WASTE

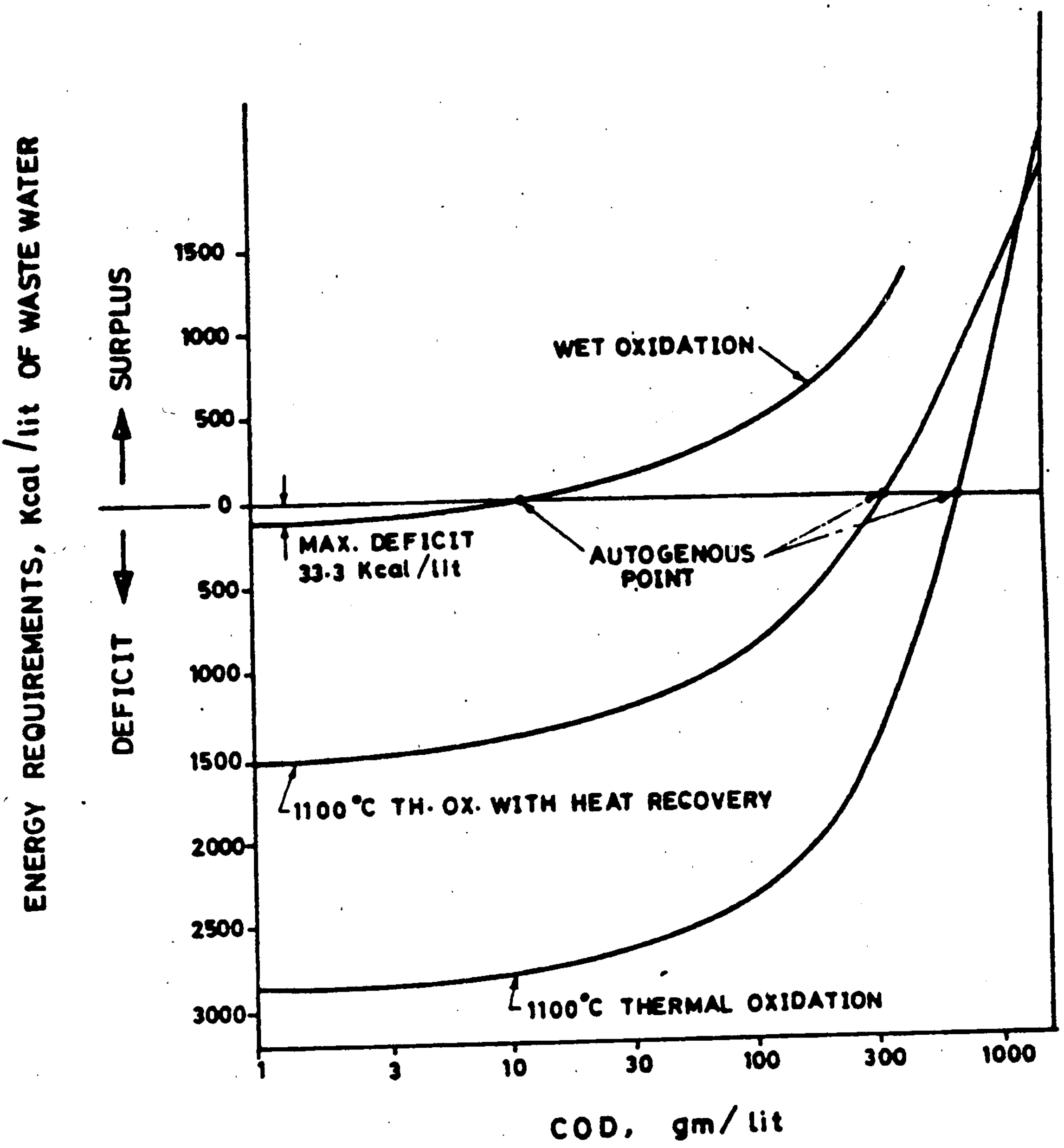

FIG. 4 ENERGY REQUIREMENTS AS FUNCTION OF COD THERMAL Vs WET OXIDATION

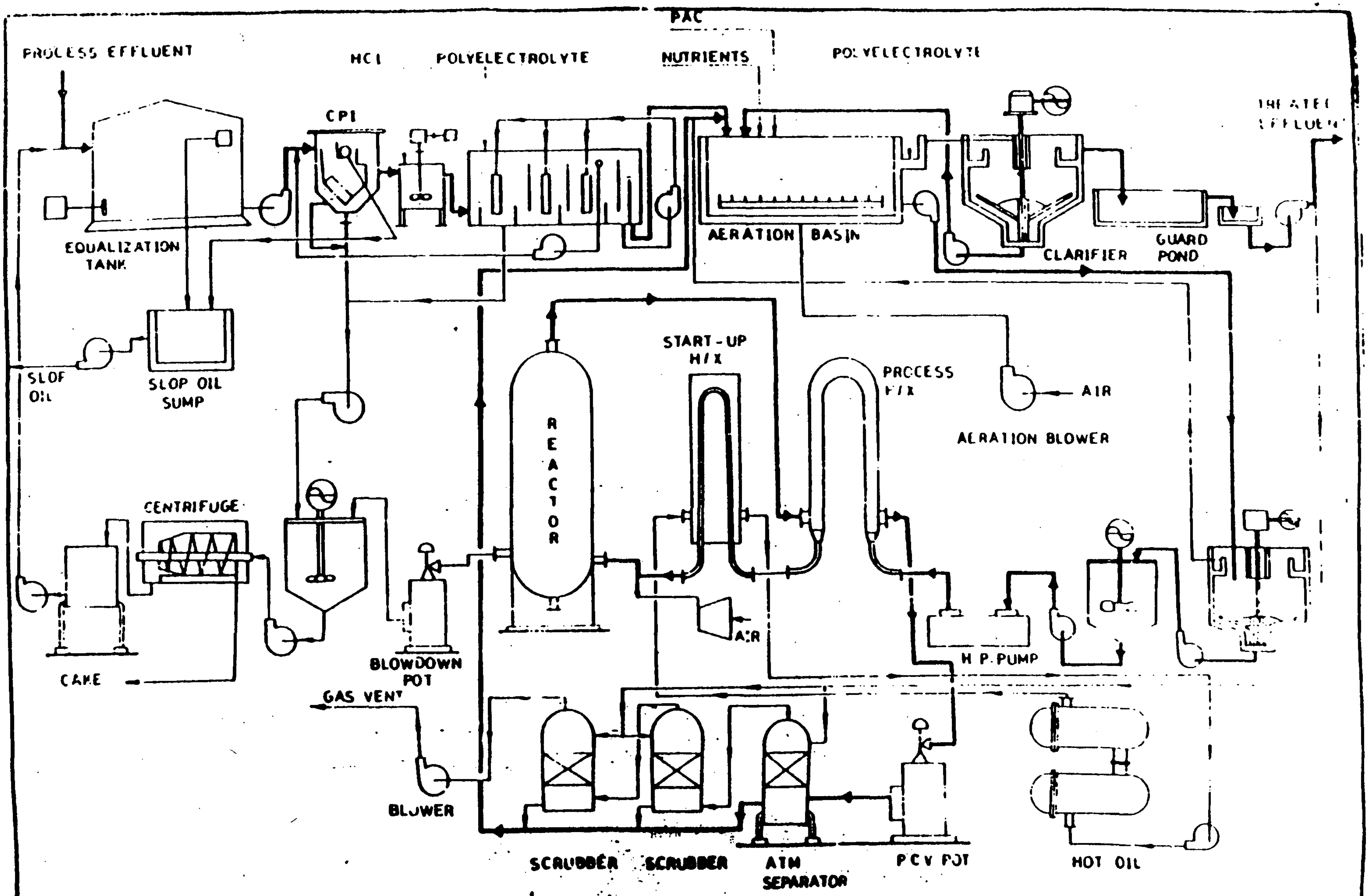

FIG.5 REFINERY WASTE WATER TREATMENT PLANT (PACT / WAR)

TECHNICAL REPORT NO. 007

BIOLOGICAL TREATMENT OF WASTEWATERS DERIVED FROM THE FUEL INDUSTRY USING THE PACT^R PROCESS

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Presented At:
1988 Symposium
Oil Waste Management Alternatives:
Minimizing, Recycling, and Treatment of Oil Wastes

Oakland Convention Center
Oakland, California

April 28-29, 1988

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ABSTRACT

In the present study, bench scale and pilot plant treatability testing of the PACT^{TM} process was demonstrated on a variety of wastewaters that are derived from the fuel industry. Treatment results from a total of six different wastewaters are discussed. The wastewaters treated were from refinery operations and various synthetic fuels processes.

The PACT process utilizes biological treatment combined with physical/chemical adsorption of pollutants on powdered activated carbon. The results from the present study indicate that the PACT process is highly effective in removing organic pollutants and toxic components from these fuel derived wastewaters.

INTRODUCTION

The treatment of wastewaters that are derived from the fuel industry (oil refineries and coal conversion) has received much attention. Since these wastewaters contain biologically toxic components, a high level of treatment is usually required to substantially reduce the toxic pollutants. Standards for treatment of these wastewaters are slowly evolving. The common elements that appear in most standards that have been developed to date consist of a combination of numerical criteria for pollutant concentrations and a biological assessment of the toxicity impact. The chemical methods for analysis of pollutants are well defined. The biological assessment usually requires acute toxicity testing on two or more test species, preferably a vertebrate and an invertebrate.

Test species for toxicity testing are usually specified by state standards which strive to use species that are resident in the specific receiving waters.

The wastewater treatment requirements to meet these standards are rather stringent. They often involve the use of a combination of biological and physical/chemical processes. One process that combines biological treatment with physical/chemical adsorption is the PACT^{TM} process. In the PACT process, powdered activated carbon is added to a

PACT^{TM} SYSTEM DESCRIPTION

The PACT wastewater treatment system involves the addition of powdered activated carbon to the aeration basin of the activated sludge process. The PACT system combines biological oxidation and assimilation with powdered carbon adsorption to provide effective treatment of wastewaters in a single process as shown in Figure 1.

Treatment by the PACT system involves more than a simple combination of carbon adsorption and biological treatment. Carbon adsorption of toxic or inhibitory components provides a mechanism for removing these compounds and as a result enhances biological treatment performance. In addition, biodegradable but adsorbable organics are retained in the PACT system for a period of time approaching the solids residence time (SRT) rather than the hydraulic detention time (HDT) as in conventional biological treatment processes. The presence of a large quantity of activated carbon adsorbent in the PACT system provides stability to shock and variable organic loadings.

Other advantages associated with the PACT wastewater treatment system versus conventional activated sludge include the ability of the PACT system to achieve effective color removal, achieve consistent nitrification, improve mixed liquor solids settling characteristics and suppress stripping of volatile organics during aeration. In addition, excess

Make-up powdered activated carbon, through the addition of either virgin or wet air regenerated carbon, is required to maintain the desired PACT system aeration basin carbon concentration. The carbon addition rate is determined by treatment requirements, waste load and wastewater characteristics.

Operation of the PACT system is controlled by adjustment of specific process parameters. These parameters are:

1. Hydraulic Detention Time (HDT)
2. Solids Residence Time (SRT)
3. Mixed Liquor Carbon Concentration (MLCC)
4. Carbon Dose (CD)

In operating the PACT system, selection of initial process conditions is usually made based on knowledge of the characteristics of the waste to be treated, the desired treatment results (effluent quality), and past experience with application of the PACT system.

WET AIR REGENERATION PROCESS

Wet air regeneration is often an economical alternative for carbon recovery and biological solids disposal in larger PACT systems. The wet air regeneration process is based on the principles of wet air oxidation, which is an aqueous phase oxidation process occurring at elevated temperatures (typically 150-325°C) and pressures (typically 300-3000 psig).

Wet air regeneration of excess sludge from the PACT system destroys the excess biological solids and adsorbed organics, simultaneously reactivating the activated carbon for reuse within the PACT system. Thus, the potential costs associated with disposal of the excess biological solids and spent carbon are reduced or eliminated by wet air regeneration. Likewise, only minimal amounts of virgin powdered carbon, generally less than 10 percent of the total carbon dose, are required to maintain the desired activated carbon concentration in the aeration basin.

The wet air regeneration system shown in Figure 2 is typically used in PACT wastewater treatment systems. Excess sludge from the PACT system - a mixture of spent carbon, biological solids and suspended ash - is gravity thickened in excess of 6.0 percent suspended solids. The thickened solids are then transferred to the high pressure pump and into the wet air regeneration unit heat exchangers.

organics, e.g. acetic acid, are readily biodegradable and easily treated when returned to the PACT system aeration basin.

TEST METHODS

In this paper, application of the PACT wastewater treatment system for wastewaters derived from the fuel industry will be reviewed. The data presented were obtained from five pilot-scale treatability studies and one bench-scale treatability study performed on various refinery and synfuels wastewaters. A general description of the test equipment used for these treatability studies is included in the following sections.

Pilot System Description

The pilot-scale treatability studies were performed using frame-mounted, continuous-flow PACT pilot systems. The PACT pilot systems are fully operational wastewater treatment systems complete with aeration tank, clarifier, single media sand filter, feed, recycle and sampling pumps and all necessary auxiliary equipment. An illustration of a typical PACT system pilot unit is shown in Figure 3.

The pilot unit aeration basins are stainless steel tanks having valved effluent ports which allow for varying treatment volumes. Fine bubble air diffusion is provided by sintered stainless steel tubing located at the bottom of the aeration basin. Air is metered to the aeration basin by a

The regeneration unit is used to destroy biological solids and simultaneously regenerate the spent powdered activated carbon. This is achieved by heating a mixture of thickened mixed liquor and air to the reaction temperature, holding the mixture at elevated temperature and pressure for a designated time period, then cooling the treated mixture to ambient conditions. The recovered carbon slurry is then removed from the autoclave and returned to the PACT system aeration basin. A small amount of virgin carbon, generally less than 10 percent of the carbon dose rate, is also added to the PACT system to replace carbon lost due to sampling, oxidation, and effluent solids losses.

Bench-Scale System Description

An illustration of a typical bench-scale PACT system is shown in Figure 4. The major components of the bench-scale system include a 2.0 to 4.0 liter cylindrical aeration tank with mechanical mixer, external conical clarifier, and peristaltic feed and mixed liquor recycle pumps. Mixed liquor dissolved oxygen levels are maintained above 2.0 ppm using an air diffuser located at the bottom of the aeration tank.

Daily operation of the PACT system includes measuring feed and effluent volumes and mixed liquor pH, D.O. and oxygen uptake rates. Mixed liquor is wasted directly from the aeration basin on a daily basis in order to maintain the desired SRT. When wet air regeneration is used for carbon

PACT SYSTEM PERFORMANCE RESULTS

In the folowing sections, PACT™ system performance is discussed for six different wastewaters derived from the fuels industry. The performance results were obtained from five pilot-scale and one bench-scale treatability study performed on various petroleum refinery and synfuels wastewaters. In all cases, the wet air regeneration process was used for destruction of excess biological solids and recovery of spent activated carbon.

The treatability studies discussed in this paper were typically performed over a several month period and included two or more periods of steady state operation. The data presented in the following sections represent performance results obtained while the PACT systems were operating at steady state conditions reflecting optimum design or performance levels.

Study A: In Study A, a pilot-scale PACT™ system was used to evaluate treatment of a refinery wastewater. The refinery wastewater treated by the PACT system consisted of a mixture of a phenolic stripper system effluent and a dissolved air flotation (DAF) system effluent. Operating conditions and treatment performance obtained for the refinery wastewater are summarized in Table 1.

Operating conditions used during treatment of the refinery wastewater included an HDT of 26 hours and SRT of 10

Study B: A second refinery wastewater was treated in Study B using a pilot-scale PACT system. The influent wastewater to the PACT system consisted of all refinery wastewater streams after pretreatment for oil and grease removal. PACT system operating conditions and performance results for Study B are shown in Table 3.

Operating conditions during Study B included an 8.0 hour HDT, 11.0 day SRT and 230 mg/l carbon dose provided by wet air regeneration of spent PACT mixed liquor.

The PACT system achieved a very high effluent quality during Study B, easily meeting the refinery's NPDES discharge limits. Overall removals achieved by the PACT system included 79.1 percent for COD, >96.0 percent for BOD_5, 77.4 percent for suspended solids and >93.2 percent for NH_3-N. Other constituents easily treated by the PACT system included cyanide (96.8 percent removal), phenols (99.4 percent removal), and oil and grease (95.3 percent removal). Color removals obtained during Study B averaged 65.1 percent.

In addition to the above performance, the PACT system also demonstrated excellent toxicity reduction during Study B. For example, toxicity measurements using the Microtox^R toxicity system showed the influent refinery wastewater to have EC50 values in the range of 0.30 to 4.00 percent. PACT system effluent during Study B had EC50 values of 92 to >100 percent, indicating the PACT effluent to be virtually nontoxic to the luminescent bacteria used in the Microtox test.

Excellent treatment of the Sasol/Mobil M synfuels wastewater was accomplished during Study C by the two-stage PACT system. Removals of the organic constituents of the wastewater were very high as shown by 97.4 percent COD removal, 99.6 percent BOD_5 removal and 97.5 percent DOC removal. The PACT system also achieved nearly complete nitrification, reducing the influent NH_3-N level of 65 mg/l to only 0.7 mg/l NH_3-N in the treated effluent. Excellent treatment of specific components in the wastewater was also obtained with 98.5 percent phenols removal, 99.2 percent cyanide removal and 96.4 percent thiocyanate removal.

Study D: Wastewater generated by the H-Coal process, which converts coal to hydrocarbon liquids such as gasoline and fuel oil, was treated in Study D. The H-Coal wastewater was ammonia and hydrogen sulfide stripped and phenol extracted prior to PACT treatment. As with Study C, a two-stage PACT system with wet air regeneration was used for the treatability study.

Operating conditions and performance results obtained during treatment of the H-Coal wastewater are shown in Table 5. The two-stage PACT system was operated using a 9.2 hour first stage HDT and 21.8 hour second stage HDT. SRT's for the first and second stages were 16.7 and 40.0 days, respectively. The entire carbon dose of 400 mg/l was added to the second stage with second stage waste solids returned to the first stage system.

nitrification was not an objective during Study E, the high NH_3-N concentration of above 800 mg/l for the SGL wastewater did not interfere with treatment performance.

Volatile acids contained in the SGL wastewater were easily treated by the PACT system with total volatile acids removal averaging 96.2 percent. Removals of specific volatile acids ranged from 80.8 percent for isobutyrate to 97.2 percent for formate.

Study F: A shale oil retort wastewater derived from a pilot-scale synthetic fuels production facility was treated in Study F using a bench-scale PACT system. Included in Study F was a parallel conventional activated sludge bench-scale system operated at conditions equivalent to the PACT system. Operating conditions and treatment results achieved during Study F are shown in Table 7.

Operating conditions for both the PACT and activated sludge systems were approximately 5 days HDT and 9 days SRT. The carbon dose of 4260 mg/l used for the PACT system consisted of virgin and wet air regenerated carbon.

The shale oil retort was a very high strength wastewater having COD, BOD_5 and DOC concentrations of 23,700, 6220 and 4950 mg/l, respectively. Specific components present in the wastewater included high concentrations of phenols (71.4 mg/l), cyanide (60.1 mg/l), and thiocyanate (191.7 mg/l). The bench-scale PACT system achieved a high level of treatment of the shale oil retort wastewater with 89.4

CONCLUSIONS

The results obtained from pilot and bench-scale treatability studies have shown the PACT wastewater treatment system to be highly effective for treatment of wastwaters derived from the fuel industry. The PACT system can provide excellent treatment of conventional wastewater parameters such as COD and BOD_5, as well as specific constituents including phenols, cyanide, thiocyanate and oil and grease. The PACT system also provides exceptional performance with respect to nitrification and toxicity reduction.

Table 1

Study A: PACT^{TM} SYSTEM TREATMENT OF A REFINERY WASTEWATER

Operating Conditions:

Days of Operation	38
HDT	26 hours
SRT	10 days
Carbon Dose	140 mg/l
MLCC	1300 mg/l
ML Biomass	860 mg/l
ML Suspended Solids	2380 mg/l
F/M (COD Basis)	0.56 g/g biomass • day

Treatment Performance	PACT Influent	PACT Effluent	Percent Removal
COD, mg/l	573	82	85.7
NPOC, mg/l	160	16	90.0
BOD_5, mg/l	238	<6	>97.5
NH_3-N, mg/l	16.6	7.8	53.0
Suspended Solids, mg/l	44	12	72.7
Oil & Grease, mg/l	10.1	<1.3	>87.1
Phenols, mg/l	7.8	0.1	98.7
Cyanide, mg/l	1.29	<0.04	>96.9

Table 3

Study B: PACT^{TM} SYSTEM TREATMENT OF A REFINERY WASTEWATER

Operating Conditions:

Days of Operation	29
HDT	8.0 hours
SRT	11.0 days
Carbon Dose	230 mg/l
MLCC	7960 mg/l
ML Biomass	4190 mg/l
ML Suspended Solids	15,900 mg/l
F/M (COD Basis)	0.35 g/g biomass • day

Treatment Performance	PACT Influent	PACT Effluent	Percent Removal
COD, mg/l	616	129	79.1
BOD$_5$, mg/l	149	<6	>96.0
Suspended Solids, mg/l	31	7	77.4
NH$_3$-N, mg/l	16.1	<1.1	>93.2
Cyanide, mg/l	4.78	0.154	96.8
Phenols, mg/l	9.55	0.053	99.4
Color, APHA Units	109	38	65.1
Oil & Grease, mg/l	14.8	0.7	95.3
Toxicity			
- Microtox (EC50), %(1)	0.3-0.4	92->100	-
- Rainbow Trout (LC50 - 96 hours)	-	>100	-
- Sea Urchin (NOEC), %	-	>90	-
(LOEC), %	-	>90	-
- Water Flea (NOEC), %	-	90	-
(LOEC), %	-	>100	-

(1) Toxicity results determined using the Microtox system (Microbics Corp.)
EC50 = concentration of sample in water which causes a 50% decrease in light output by the luminescent bacteria used in the Microtox test.

(2) LC50 = concentration of sample in water which achieves 50% fish mortality in 96 hours

(3) NOEC = No Observable Effect Concentation

(4) LOEC = Lowest Observable Effect Concentration

Table 5

Study D: PACT^{TM} SYSTEM TREATMENT OF H-COAL WASTEWATER

Operating Conditions:

Days of Operation		31
HDT	1st Stage	9.2 Hours
	2nd Stage	21.8 Hours
SRT	1st Stage	16.7 Days
	2nd Stage	40.0 Days
Carbon Dose	1st Stage	0 mg/l
	2nd Stage	400 mg/l
MLCC	1st Stage	11,720 mg/l
	2nd Stage	15,310 mg/l
ML Biomass	1st Stage	3950 mg/l
	2nd Stage	2720 mg/l

Treatment Performance	PACT Influent	PACT Effluent	Percent Removal
COD, mg/l	1515	226	85.1
BOD$_5$, mg/l	581	<7	>98.8
DOC, mg/l	484	44	90.9
Phenols, mg/l	178.2	1.21	99.3
Color, APHA Units	10,550	1175	88.9
NH$_3$-N, mg/l	145.4	0.9	99.4
Cyanide, mg/l	1.4	0.2	85.7
Thiocyanate, mg/l	8.9	1.2	86.5

Table 7

STUDY F: TREATMENT OF SHALE OIL RETORT WASTEWATER BY PACT^{TM} AND ACTIVATED SLUDGE SYSTEMS

Operating Conditions:	PACT System	Activated Sludge System
HDT, days	5.0	4.9
SRT, days	9.4	9.0
Carbon Dose, mg/l	4260	-

Treatment Performance:	Influent	PACT System Effluent	Activated Slud System Efflue
COD, mg/l	23,700	2510	8430
Percent Removal	-	89.4	64.4
BOD_5, mg/l	6220	27	650
Percent Removal	-	99.6	89.5
DOC, mg/l	4950	840	2990
Percent Removal	-	83.2	39.6
Phenols, mg/l	71.4	0.20	2.88
Percent Removal	-	99.7	96.0
Cyanide, mg/l	60.1	0.65	39.3
Percent Removal	-	98.8	34.6
Thiocyanate, mg/l	191.7	16.2	229.6
Percent Removal	-	91.5	-

FIGURE 1

PACT® WASTEWATER TREATMENT SYSTEM GENERAL PROCESS DIAGRAM

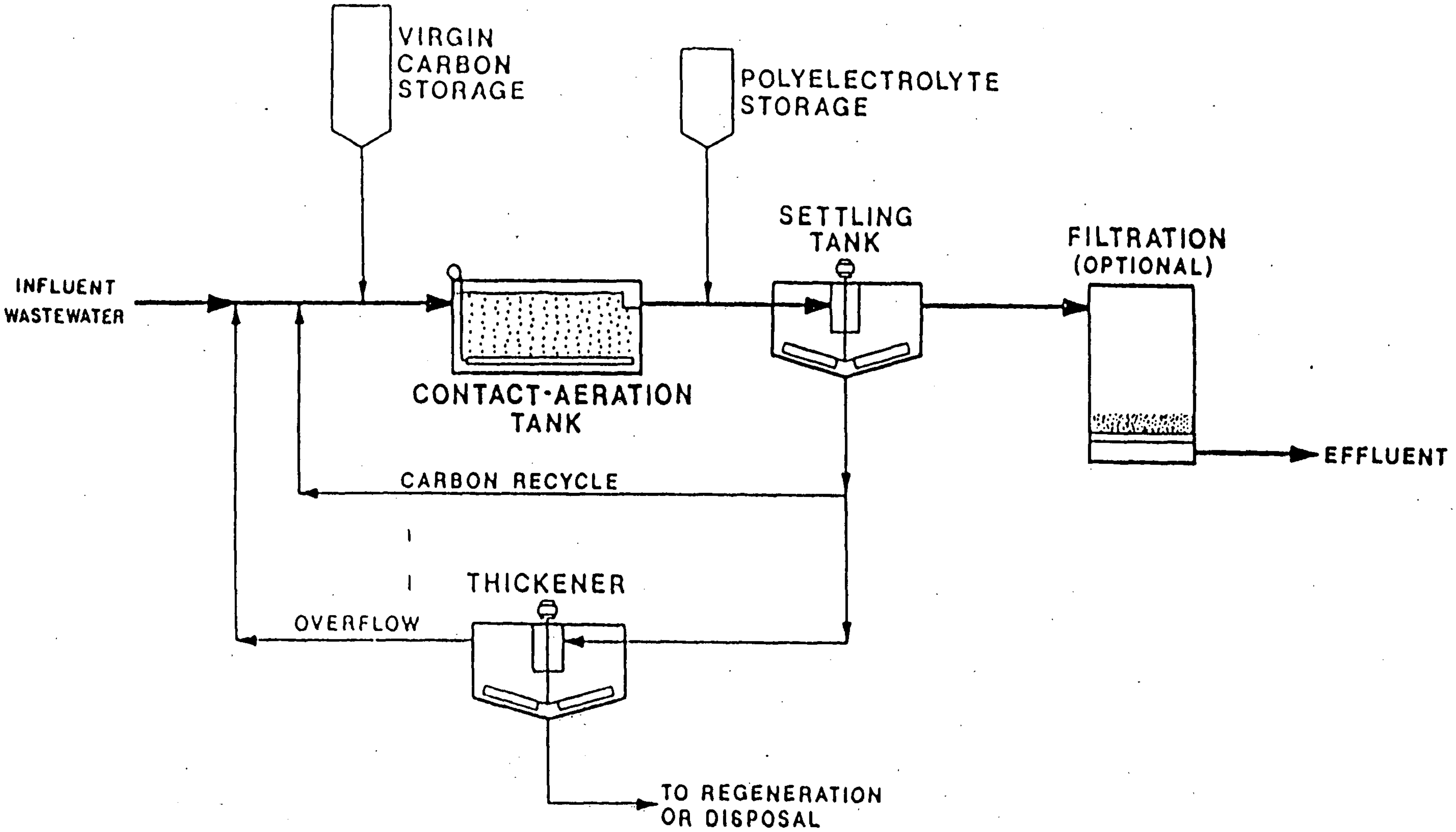


Figure 2

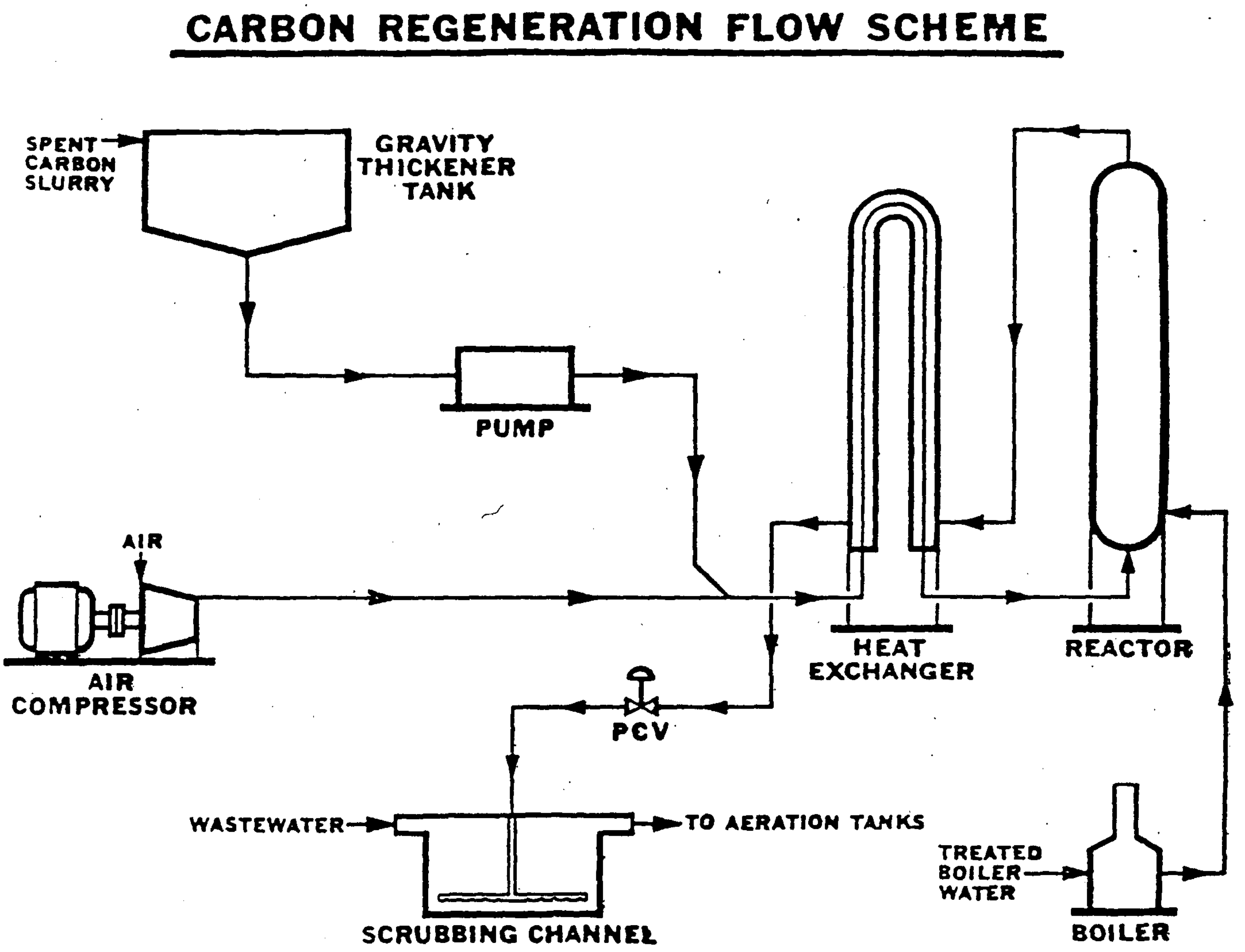

CARBON REGENERATION FLOW SCHEME
SPENT CARBON SLURRY
GRAVITY THICKENER TANK
PUMP
AIR
AIR COMPRESSOR
HEAT EXCHANGER
REACTOR
PCV
WASTEWATER
TO AERATION TANKS
SCRUBBING CHANNEL
TREATED BOILER WATER
BOILER

Fig 3

PACT™ SYSTEM PILOT UNIT FLOW DIAGRAM

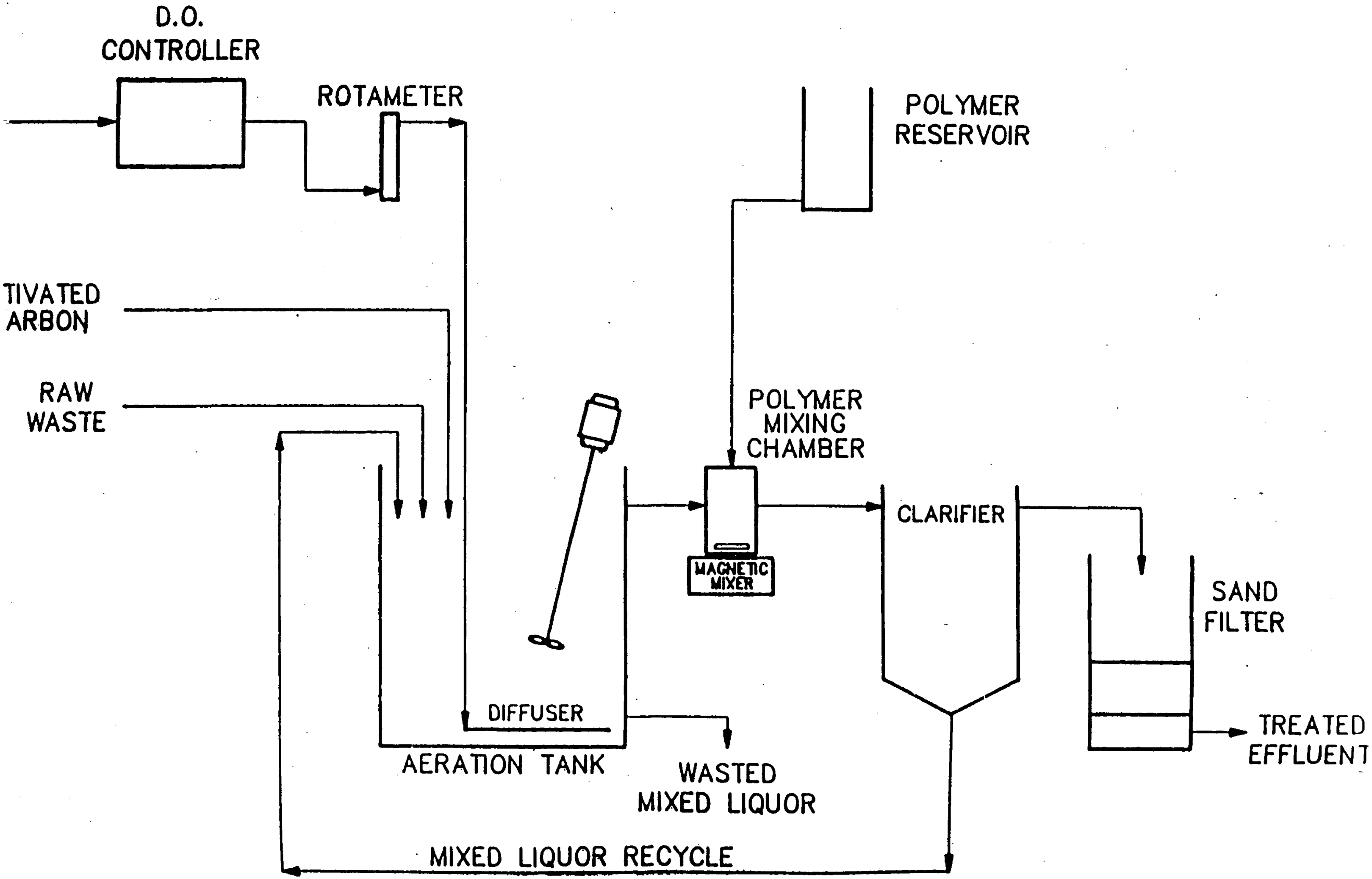
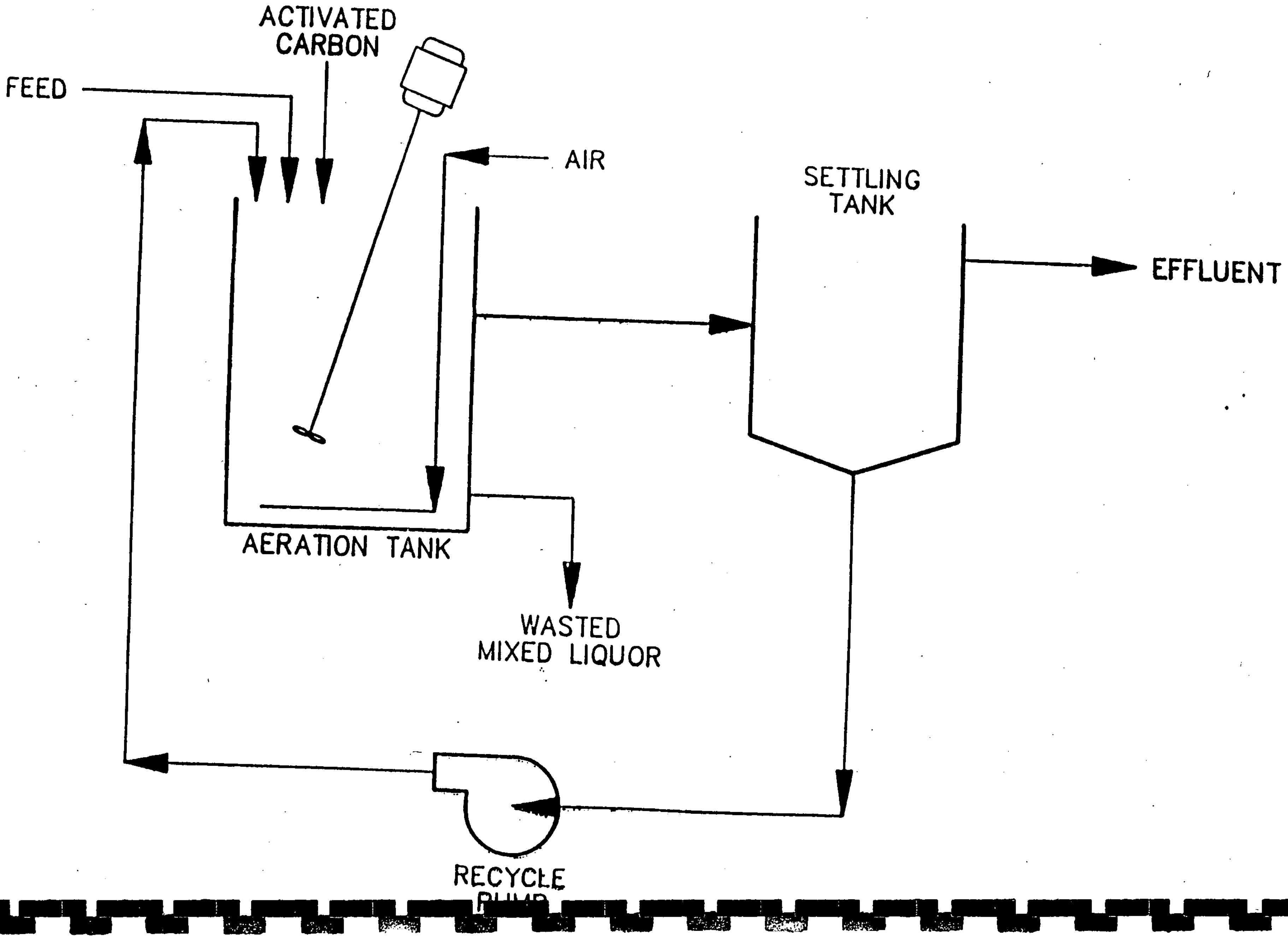


Figure 4

LABORATORY SCALE PACT SYSTEM



TECHNICAL REPORT NO. 227

NITRIFICATION IN POWDERED-ACTIVATED CARBON-ACTIVATED SLUDGE PROCESS

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Published:

Published in the *Journal of Environmental Engineering*, Vol. 113, No. 6, December, 1987.

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NITRIFICATION IN POWDERED-ACTIVATED CARBON-ACTIVATED SLUDGE PROCESS

By Adam S. Ng[1] and Michael K. Stenstrom,[2] Member, ASCE

ABSTRACT: Powdered activated carbon (PAC) has been added to activated sludge processes over the past 10 years to improve process performance in a variety of ways, including ammonia removal. Improved ammonia removal is a surprising benefit of PAC since it is not adsorbed. Investigators have speculated that PAC adsorbs inhibitory compounds or provides a media for nitrifier growth. To ascertain the mechanism of nitrification enhancement, a series of experiments were performed with adsorbable (aniline, phenol) and nonadsorbable (ethanol) inhibitors. Experimental results show that adsorption of nitrification inhibitors can dramatically improve nitrification rates in unacclimated activated sludge cultures.

INTRODUCTION

Previous investigators (2,13,15,23,30) have provided evidence that the addition of powdered-activated carbon (PAC) to nitrifying activated sludge (AS) can improve nitrification rates. Plausible, but unsubstantiated, mechanisms that have been proposed to explain PAC-enhanced nitrification include adsorption of compounds toxic to nitrifiers (13,15,23), enhanced nitrifier growth on the carbon's surface (2,30), and bioregeneration. This research was conducted to substantiate mechanisms of PAC enhancement, and experiments were conducted to evaluate adsorption, attached growth and acclimation mechanisms.

Bioregeneration

Bioregeneration is a term used to describe the synergism which is often observed in powdered-activated carbon-activated sludge (PAC-AS) processes. Various researchers (4–6,11) have noted that in specific cases, PAC-AS processes can remove an organic compound more efficiently than would be expected from either biodegradation or adsorption alone. Proposed theories of bioregeneration require that a compound be adsorbed onto the carbon's surface where microorganisms reside, and that adsorption results in higher substrate concentrations than would be expected in the bulk solution. This increase in concentration stimulates biological growth and replenishes the carbon surface for further adsorption. Once adsorbed, these compounds are in contact with the biomass for a length of time equal to the system's cell retention time. This mechanism's applicability to nitrification is questionable, since adsorption of ammonia at the pH and concentrations found in wastewater is negligible; however, bioregeneration may be important in the acclimation of heterotrophic organisms to certain slowly biodegradable inhibitors of nitrification. Adsorption of

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Note. Discussion open until May 1, 1988. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on September 15, 1986. This paper is part of the *Journal of Environmental Engineering*, Vol. 113, No. 6, December, 1987. ©ASCE, ISSN 0733-9372/87/0006-1285/$01.00. Paper No. 22030.

the inhibitor would increase the time available for heterotrophic acclimation and, ultimately, for the removal of nitrifier inhibition.

Enhanced Nitrifier Surface Growth

Up until 1955, it was generally considered that particulate materials such as calcium carbonate, which was used as a buffer in early culture experiments, were necessary for nitrifier growth. It was postulated that the solid surface in the growth media provided obligate surface sites to which nitrifying organisms adsorbed and multiplied. Although this "obligate surface" theory was later disproved by workers who successfully grew Nitrobacter (12) and Nitrosomonas (9) in clear media, the role of suspended solids in nitrification remains unclear. A stimulatory effect of suspended particles on nitrification rates has been reported by a number of investigators in studies with surface waters and soils. These investigators maintain that the enhancement mechanism involves either the particle's ability to provide a physical support medium for growth of nitrifiers (19,29) or substrate (ammonium ion) concentration at the surface of the particles (22). Conflicting evidence has been reported in which no detectable effects on nitrification rates due to suspended particles were observed (1). Other investigators (12,19) assert that while suspended solids were not essential for nitrifier growth, attachment to particles and enhancement occurred if the solids were present.

As a part of this experimental investigation, a reactor was operated using bentonite clay as a site for nitrifier attachment. Bentonite clay was added to an activated sludge reactor, identical to the reactors used in this study, to match the external surface area provided by the carbon in PAC reactors. Experiments were performed for several compounds, both adsorable and nonadsorbable over a two-year period, testing both acute and chronic inhibition. The results are reported in detail by Ng, et al. (24) and show that adding bentonite clay was not beneficial to nitrification.

Adsorption of Compounds Toxic to Nitrifiers

Many organic compounds are known to inhibit nitrification in pure (31,35,37) and activated sludge cultures (30,34,36). Some of these compounds are biologically resistant to degradation while others are resistant and highly adsorbable by activated carbon. Therefore, it is likely that the presence of activated carbon can protect nitrifiers from adsorbable, inhibitory compounds.

In summary, various mechanisms can be suggested to explain the role of adsorption in PAC-enhanced nitrification. The major purpose of this study is to further define the role of adsorption in PAC-enhanced nitrification, and to access these effects independently of biological acclimation. Emphasis is placed on the adsorption of toxics mechanisms because recent work in one laboratory (24) suggest that this is a dominant mechanism in PAC-enhanced nitrification.

EXPERIMENTAL METHODS

A series of batch assay experiments using variable activated carbon doses was performed to study PAC-AS nitrification enhancement in the presence of known nitrification inhibitors with different adsorptive characteristics. Selection of inhibitors for experimentation was based upon an

TABLE 1. Adsorption and Nitrification Inhibitory Characteristics of Compounds Tested in Carbon Dose Experiments

Compound (1)	Freundlich Parameters (2)	Langmuir Parameters (3)	Concentration Required for 75% Inhibition (4)
Aniline	K = 12.2 mg/g n^{-1} = 0.52	Q = 0.065 b = 0.324	7.7 mg/L
Phenol	K = 21.0 mg/g n^{-1} = 0.54	Q = 0.158 b = 0.176	5.6 mg/L
Cyanide	data unavailable	maximum adsorption = 2.0 mg/g at C_o = 20.0 mg/L	0.65 mg/L
Ethyl Alcohol	K = 0 mg/g	maximum adsorption = 20 mg/g at C_o = 1,000 mg/L	2,500 mg/L

[a] Freundlich adsorption data for phenol and ethyl alcohol from Dobbs and Cohen (7).
Other adsorption data for ethyl alcohol from Perrich (27).
Cyanide adsorption data from Hoffman (15).
Other inhibition data from Tomlinson, Boon, and Trotman (35).

intensive survey of all known nitrification-inhibiting compounds and their carbon adsorption properties. Potential compounds were characterized either as adsorbable-inhibitory (AI) or nonadsorbable inhibitory (NAI). Other considerations for compound selection included industrial significance and solubility. Table 1 shows the compounds selected for experimentation. Included are the compound's nitrification inhibition and adsorptive characteristics. With the exception of the adsorption parameters for aniline, which were experimentally determined, data from Table 1 were extracted from the literature and hence are subject to interpretation due to differing sets of conditions under which the values were obtained. Nonetheless, the data do provide an indication of the relative adsorptive and inhibitory properties of the compounds chosen for evaluation. For AI compounds, concentrations were selected to produce significantly more than 75% inhibition. For NAI compounds, inhibitory concentrations tested were chosen to yield approximately 75% inhibition in control assays without PAC addition. This was to ensure that nitrification would continue in any given assay and that any benefit, due to PAC addition, would be detected.

Source of Nitrifying Activated Sludge

Nitrifying mixed liquor for experimentation was drawn from a continuous flow bench scale activated sludge plant fed a synthetic substrate and operating at a mean cell retention time of nine days and a hydraulic retention time of eight hours. The reactor was constructed of 1.25 cm (0.5 in.) plexiglass, with a working volume of 12.2 L in the aeration section and 1.5 L in the solid-liquid separator. Several holes were provided in the lid of the reactor: larger holes for a pH probe and access for maintenance and smaller holes for influent, base addition, and air lines. A port hole on the side of the aeration section was used to withdraw mixed liquor for experimentation and for control of cell retention time. Air, which was added through diffuser stones located near the bottom of the mixed liquor aeration section, provided oxygen for microbial growth as well as turbulence for mixing. Airflow rates, which ranged from 0.14 to 0.28 m^3/hr., were monitored by rotameters. Reactor pH was maintained, using a saturated solution of sodium bicarbonate, at a range of 7–7.2 by means of a pH control meter (Horizons, Inc., Model 5997-20).

Synthetic Feed Composition

Due to the large quantity of substrate required, a dilution system was used whereby concentrated feed was automatically diluted before being pumped into the reactor. The liquid level in the mixing reservoir was electronically sensed by two float switches which controlled both the concentrate feed pumps to the reservoir and an external solenoid valve for the flow of dilution tap water. The diluted substrate was pumped directly from the mixing reservoir, contained in a refrigerator at 4 °C, into the reactor using a separate pump system. The feed was composed of glucose, ammonia, and other nutrients required to support the growth of heterotrophs and nitrifiers. The $CaCl_2$-$MgCl_2$ solution was separately pumped into the mixing reservoir to prevent the formation of calcium phosphate precipitates. The concentrate was diluted approximately 250 times during each cycle. The total steady state influent ammonia-N concentration was calculated and measured to be 50 mg/L. Additional details describing the reactor, substrate dilution system, and synthetic feed are available elsewhere (24,25).

EXPERIMENTAL PROCEDURE

Batch Inhibition Experiments

The general procedure for all experiments consisted of the following steps:

1. PAC (Westvaco Nuchar SA-15) was dried at 150°C for a minimum of three hours and stored in a dessicator until use.
2. Appropriate amounts of PAC were analytically weighed and placed dry into designated empty 500 ml Erylenmeyer flasks.
3. Reactor effluent ammonia-N and nitrate-N concentrations were measured.
4. A measured volume of mixed liquor was withdrawn from the reactor and divided equally into the flasks, resulting in activated carbon dosages of 500, 1,000, 2,000, and 4,000 mg PAC/L of mixed liquor added. For NAI compounds evaluated, only PAC concentrations bracketing the highest (4,000 mg/L) and lowest (500 mg/L) concentrations were tested. In all experiments, a minimum of two flasks were retained as controls and did not receive any PAC.
5. An exogenous source of ammonia-N in the form of a solution of ammonium chloride was pipetted into each flask to bring the NH_4^+-N concentration from less than <0.1 to 40–50 mg-N/L.
6. 1.0 ml of the test compound from a concentrated stock solution was pipetted into the test flasks to give the desired calculated concentration. It

should be noted that the changes in volumes brought about by the additions of PAC, ammonia-N, and the inhibitory compound were incorporated into the calculation of the final concentrations used.

7. All flasks were placed under a manifold and aerated throughout the experiment. Air was supplied through disposable, plastic aquarium diffuser stones at a flowrate of 0.1 m^3/hr.

8 One or two minutes after the start of aeration (designated as time = 0 hours), two separate 5–10-ml portions of the mixed liquor were withdrawn from each flask using volumetric pipettes and then added into a 100-ml volumetric flask, half filled with distilled water preserved. The flasks were then diluted to volume, capped, shaken, and stored for the analysis of ammonia and nitrate at the end of the experiment.

9. Step 8 was repeated for time = 2, 4, 6, and 8 hours.

10. Every hour throughout the aeration period, the pH was checked and manually adjusted, if necessary, to the range of 7.2–7.4 using 0.1 N NaOH.

In the final experiment (with 10 mg/L aniline), nitrite-N, and liquid phase inhibitor concentration were determined at various times during the aeration period.

Aniline Adsorption Isotherm

An aniline adsorption isotherm was conducted, because aniline was considered to be an "ideal" inhibitor to study PAC-enhanced nitrification. The effects of aniline on activated sludge nitrification are well documented (18,34), and it is known to be both adsorbable and biodegradable, although the extent of its adsorptive properties have not been well established. Aniline at 100 mg/L was contacted with PAC over a concentration range of 0.1–20 g/L. Sample bottles were agitated for nine hours at room temperature (27–29°C). Samples were analyzed by gas liquid chromatography following centrifugation.

ANALYTICAL METHODS

Inorganic Nitrogen

Specific ion electrodes for ammonia (Orion Model 95-10) and nitrate (Orion Model 93-07) in conjunction with an Orion Ionanalyzer (Model 407A) were used to directly measure ammonia-N and nitrate-N concentrations in influent, mixed liquor, effluent, and assay samples. The probes were calibrated at least once, using laboratory prepared standards, prior to and during each analytical run. If necessary, ammonia and nitrate samples were preserved with 1M HCl (0.1 ml/0.1 L sample) or 1M boric acid (0.1 ml/0.1 L), respectively. Sample volume analyzed was 100 ml or aliquots diluted to 100 ml. Nitrite-N was determined by a wet chemical technique described in Standard Methods (1975). All nitrite samples were preserved with 4 mg $HgCl_2$/0.1 L sample, filtered (0.45 micron), and diluted with distilled water to cover the applicable range of the method (0.01–1.0 mg nitrite-N/L). Photometric determinations were accomplished using a Bausch and Lomb Spectronic 20 (1 cm light path) at 543 nm. Standard curves were obtained for each analytical run using serially diluted nitrite standards ($NaNO_2$).

Determination of Aniline

Liquid phase aniline concentrations for the adsorption isotherm and a single batch experiment were measured by direct aqueous injection using a Varian 6000 gas chromatograph and a Hewlett Packard 3300 integrator. The capillary column used was SP 2100 (Supelco, Inc.) operated isothermally at 110°C. Optimal operational conditions for the analysis were found to be as follows: Injector temperature = 200°C; Detector (FID) temperature = 300°C; Carrier gas = Helium at 2.0 ml/min; Detector make-up gas = 30 ml/min; Air and Hydrogen at 300 and 30 ml/min, respectively; Spitless injection at 1.0 microliter sample size with purge vent opened after 0.9 min. at 100 ml helium/min. Reproducibility for a given injection was found to be within 5% for peak area response and 7% for peak height response. All determinations were based on peak area response.

A preliminary test was conducted to determine whether aniline could be recovered from the liquid phase of mixed liquor and accurately analyzed for by gas chromatography. The nature of the substrates used for reactor feed suggested that there would be little interference in the analysis of aniline by direct aqueous injection. The procedure used for the test was as follows:

1. 1.35 L of mixed liquor (MLSS = 1250 mg/L) was withdrawn from the reactor and divided equally into three stirred flasks.
2. An appropriate amount of an aniline stock solution was quantitatively added into each flask producing calculated aniline concentrations of 1.0, 5.0, and 10.0 mg/L.
3. After mixing the contents of each flask for two minutes, 10 ml of mixed liquor was withdrawn from each flask and centrifuged for three minutes or until a clear supernatant was visible. The resulting supernatant was then pipetted into 7.7 ml glass vials with Teflon lined caps and stored at 4°C until analysis. These steps were necessary to preserve the stability of aniline and were satisfactory for subsequent analysis by gas chromatography (28).

Recovery of aniline from controls averaged 89.8% of theoretical recovery. Recovery ranged from a low of 86% at 1.0 mg/L to 96.4% at 10 mg/L. It is likely that the difference between calculated and measured values were due to either inherent experimental error and/or adsorption of aniline onto the biomass. The latter explanation is reasonable, since all measured values were less than the corresponding calculated values. The largest difference (14%) noted was substantially less than the reported 75% recovery of aniline from wastewaters using the same column and a methylene chloride extraction step (28).

RESULTS AND ANALYSIS

Aniline Adsorption Isotherm

The equilibrium data for the adsorption of aniline on PAC fitted both the Freundlich (r^2 = 0.98) and the Langmuir (r^2 = 0.97) adsorption model reasonably well. Results show that approximately 12.2 mg aniline/g PAC will be adsorbed at an equilibrium aniline concentration of 1.0 mg/L. Calculated adsorption parameters from the experimental data are shown in Table 1.

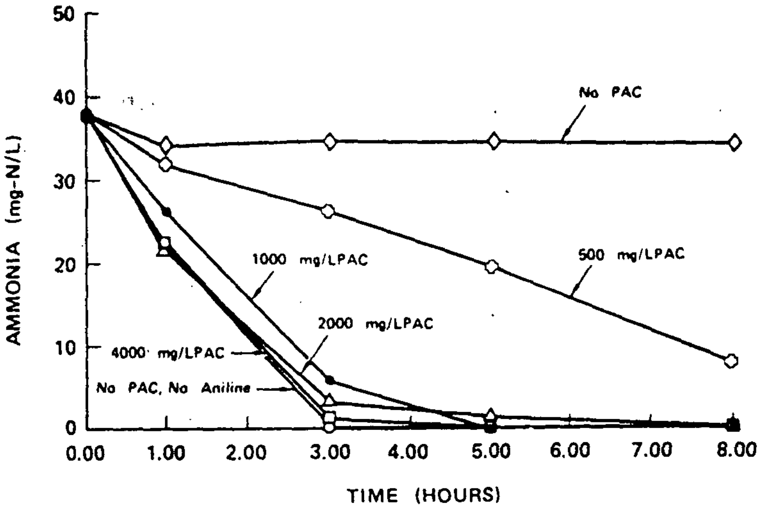

FIG. 1. NH_4^+-N versus Time for Variable Carbon Dose (10 mg/L Aniline 1-85)

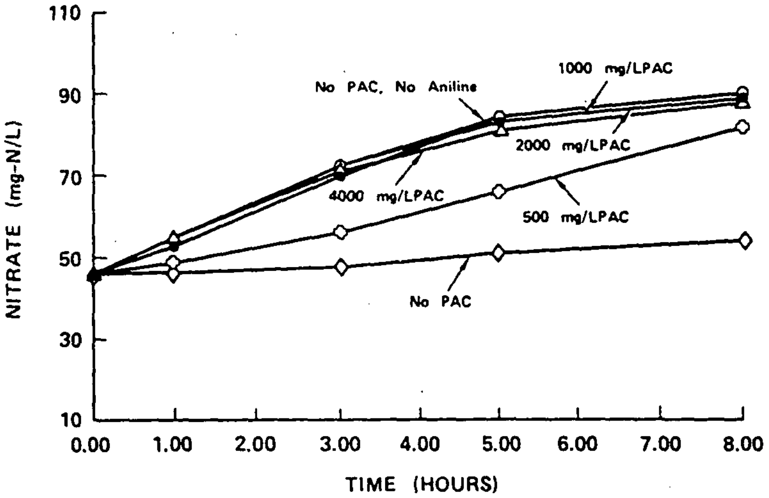

FIG. 2. NO_3^--N versus Time for Variable Carbon Dose (10 mg/L Aniline)

Batch Inhibition Experiments

Ammonia oxidation and nitrate production data generated from three separate experimental runs using 10 mg/L aniline (Figs. 1–2), 0.7 mg/L cyanide (Figs. 3–4) , and 2500 mg/L ethanol (Figs. 5–6) as inhibitors show the effect of PAC concentration on nitrification rates. Data presented in these figures are representative of the nature of data generated from other experimental runs, which are not shown here.

In order to interpret and quantify observed nitrification rates for all experiments, zero-order kinetics were used to estimate nitrification rate constants. Zero-order nitrification kinetics have been observed and used to describe nitrification under various conditions (10,17,20,25,34,36). Reported K_s values for ammonia oxidation in activated sludge typically range from 0.5–2.0 mg-N/L (3,8,32); therefore, for ammonia concentrations used in this study the kinetic expression for ammonia oxidation in a batch assay can be expressed as:

$$\frac{d\ \mathrm{NH}_4^+ - \mathrm{N}}{dt} = -K \quad \text{.........} \quad (1)$$

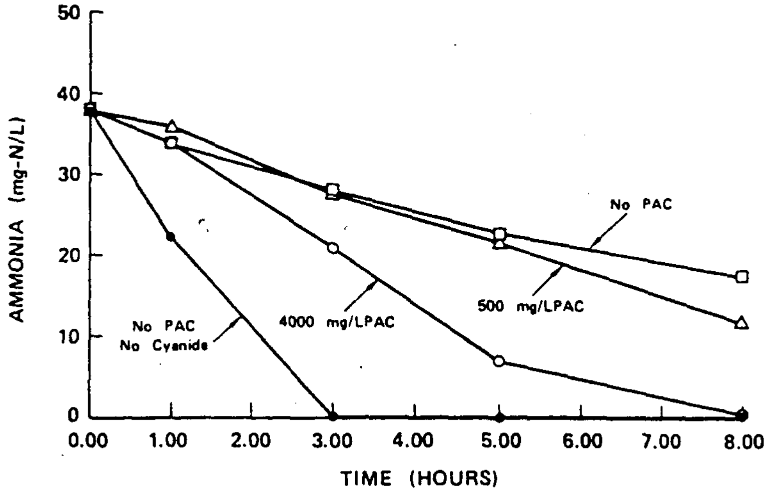

FIG. 3. NH_4^+-*N* versus Time for Variable Carbon Dose (0.7 mg/L Cyanide)

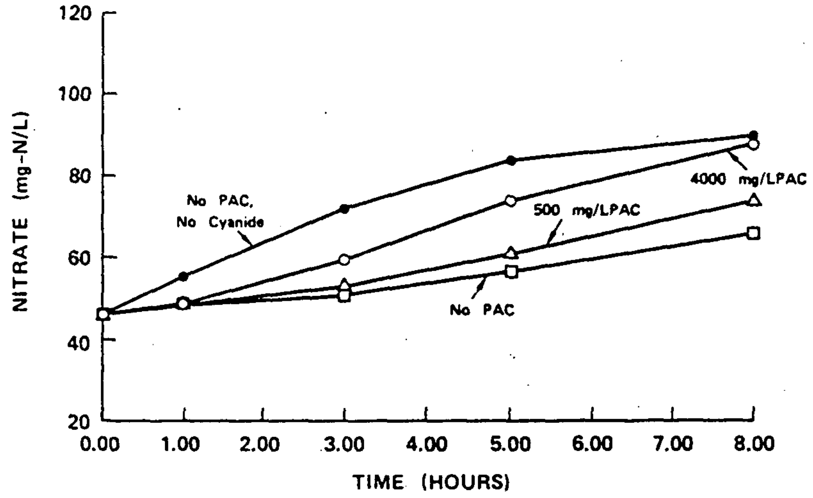

FIG. 4. NO_3^--*N* versus Time for Variable Carbon Dose (0.7 mg/L Cyanide)

Assuming that ammonia oxidation is rate limiting, the nitrate productio rate can be similarly expressed:

$$\frac{d\,\mathrm{NO}_3^- - \mathrm{N}}{dt} = K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2$$

The observed zero-order ammonia oxidation and associated nitrate production rate constants *K* were calculated under nonlimiting substrat conditions by simple linear regression and are presented for all experimental runs in Table 2. Also included in Table 2 are coefficients o determination r^2 which indicates the accuracy of fit between the data an the linear regression equation. The term zero-order here applies to reaction rate with respect to ammonia. The reaction constant *K* is dependent upo nitrifier biomass concentration. In our early deliberations about experimental design, we considered ways of estimating nitrifier biomass concentration. None of the available methods were sufficiently precise an inexpensive to be useful to us. Therefore we devised an inhibitor constan (24), which is the ratio of reaction rates obtained in experiments to the reaction constant obtained in controls, without inhibitor, but at the sam

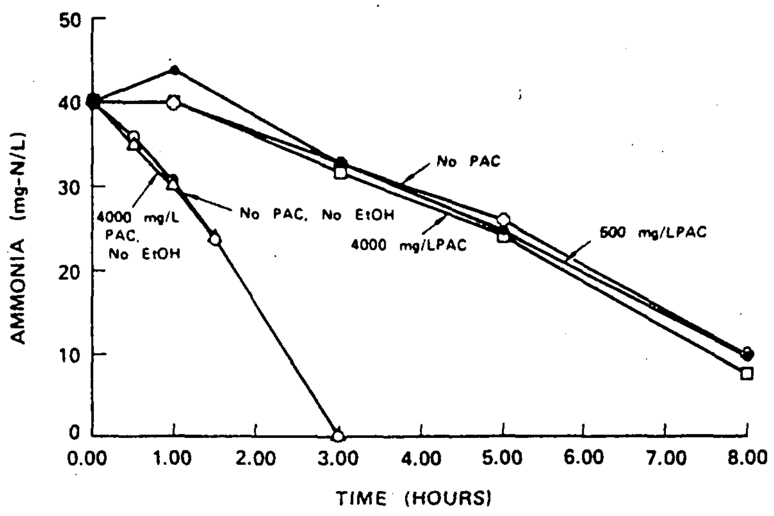

FIG. 5. NH_4^+-*N* versus Time for Variable Carbon Dose (2500 mg/L Ethanol)

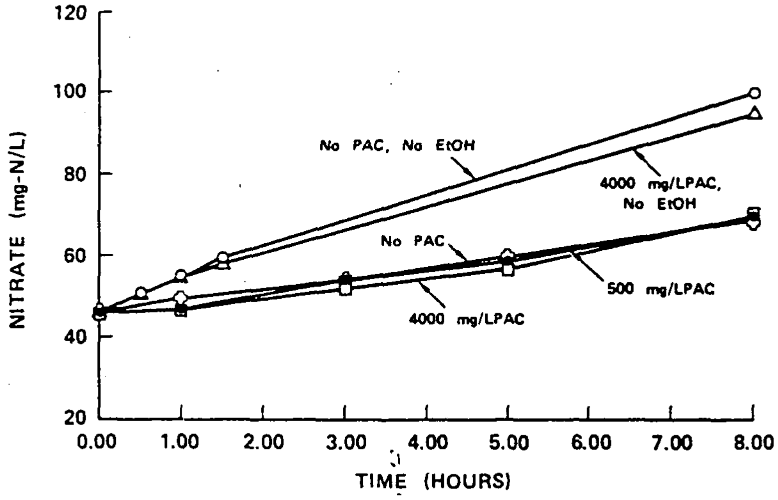

FIG. 6. NO_3^--*N* versus Time for Variable Carbon Dose (2500 mg/L Ethanol)

biomass concentration. The inhibition constants are independent of biomass concentration.

In general, nitrate production rate constants were observed to range from 60–100% of the corresponding ammonia oxidation rate constants. The discrepancy in rate constants was most evident if ammonia was oxidized relatively rapidly. This suggested an initial lag period for nitrite oxidation since measured nitrate concentrations were all within 14% of expected values (based on reaction stoichiometry and excluding heterotrophic ammonia uptake and endogenous decay) at the end of each experiment. If it had been possible to use continuous experiments, one would expect more agreement between ammonia oxidation and nitrate production rates.

Table 2 shows that for experiments performed using adsorbable inhibitors (i.e., phenol and aniline), PAC addition resulted in enhanced nitrification rates. For nonadsorbable inhibitors (i.e., ethanol and cyanide), little or no significant nitrification enhancement was observed. The results of the experiment with ethanol are in dramatic contrast to experiments using adsorbable inhibitors, where the degree of nitrification enhancement is related to PAC dosage.

TABLE 2. NH_3-*N* and NO_3-*N* Reaction Constants and r^2 for Carbon Dose Experiments

Spiked Compound (1)	Type (2)	(3)	control NA[c] (4)	control A[d] (5)	4,000 A[e] (6)	2,000 A[f] (7)	1,000 A[g] (8)	500 A[h] (9)
Aniline	AI[a]	r^2	0.99	0.99	0.97	0.99	0.99	0.99
10 mg/L		$-K(NH_3)$	12.1	0.25	12.0	11.3	10.7	3.6
(1-85)		r^2	0.99	0.99	0.99	0.99	0.99	0.99
		$K(NO_3)$	8.6	0.6	8.3	8.7	8.0	3.4
Phenol	AI	r^2	0.96	0.23	0.96	0.99	0.87	0.2
20 mg/L		$-K(NH_3)$	11.7	0.65	11.75	11.73	4.35	0.78
(1-85)		r^2	0.99	0.7	0.99	0.99	0.95	0.74
		$K(NO_3)$	8.0	0.54	7.2	7.8	3.5	0.79
Cyanide	NAI	r^2	0.99	0.99	0.99	—[i]	—	0.97
0.7 mg/L		$-K(NH_3)$	12.1	2.6	6.3	—	—	4.5
(1-85)		r^2	0.99	0.98	0.99	—	—	0.98
		$K(NO_3)$	8.6	2.44	5.5	—	—	3.5
Cyanide	NAI	r^2	0.99	0.65	0.69	—	—	0.4
1.4 mg/L		$-K(NH_3)$	10.7	−0.67	1.69	—	—	0.7
(2-85)		r^2	0.99	0.74	0.86	—	—	0.6
		$K(NO_3)$	8.84	0.59	2.2	—	—	0.43
Ethanol	NAI	r^2	0.99	0.96	0.97	—	—	0.95
2500 mg/L		$-K(NH_3)$	10.7	3.82	4.14	—	—	4.12
(2-85)		r^2	0.99	0.99	0.96	—	—	0.99
		$K(NO^3)$	8.8	2.82	3.0	—	—	2.98
Aniline	AI	r^2	0.98	0.97	0.97	0.96	0.99	0.97
10 mg/L		$-K(NH_3)$	15.9	3.16	15.0	14.4	14.1	6.1
(2-85)		r^2	0.99	0.98	0.99	0.99	0.97	0.99
		$K(NO_3)$	11.8	2.07	11.3	11.3	11.0	6.1

[a] AI = Adsorbable inhibitor.
[b] NAI = Nonadsorbable inhibitor.
[c] Control NA = Control with no activated carbon or inhibitor added.
[d] Control A = Control with inhibitor added but no activated carbon.
[e] 4,000 A = Inhibitor and 4,000 mg/L carbon added.
[f] 2,000 A = Inhibitor and 2,000 mg/L carbon added.
[g] 1,000 A = Inhibitor and 1,000 mg/L carbon added.
[h] 500 A = Inhibitor and 500 mg/L carbon added.
[i] Carbon doses not evaluated in these experimental runs.

In using ethanol, the least adsorbable inhibitor of all compounds evaluated, there was no significant difference among nitrification rates in all test assays. Dissolved oxygen concentration was measured during and after the ethanol experiment. This was done to insure that oxygen limiting conditions were not created through increased heterotrophic ethanol oxidation. All DO levels were measured to be greater than 5 mg/L.

Data (see Table 2) from the experiments involving cyanide showed enhancement due to PAC addition. The degree of enhancement was significantly less than those observed for adsorbable compounds, and suggests that the degree of nitrification enhancement is related to adsorptivity of the inhibitor.

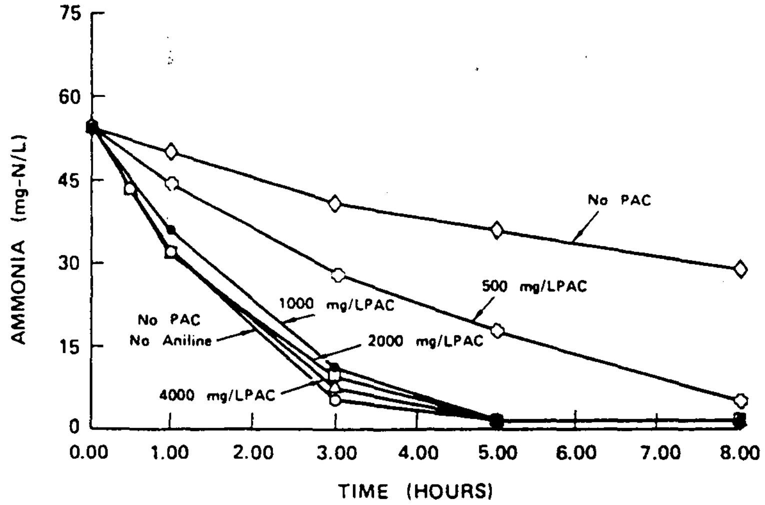

FIG. 7. NH_4^+-*N* **versus Time for Variable Carbon Dose (10 mg/L Aniline 2-85)**

In the final batch experiment with 10 mg/L aniline (Figs. 7–10), liquid phase aniline concentrations were measured by gas liquid chromatography at specific sampling periods throughout the experiment. Results show that nitrification inhibition is inversely related to PAC concentration. Since the amount of aniline adsorbed is directly related to PAC concentration, it can be shown that nitrification inhibition is directly related to liquid phase aniline concentration. It appears that for assays with no PAC addition, approximately 2 mg/L of aniline was either metabolized and/or adsorbed onto the biological mass. Figure 10 also indicates that near equilibrium conditions were rapidly established, with 80%–95% of the total adsorption occurring within 30 min.

Using the previously determined adsorption isotherm parameters for aniline, the expected liquid phase aniline concentration at each PAC dosage can be determined and compared to the corresponding measured concentration. The following equation, derived from the Freundlich adsorption model, was used to calculate expected liquid phase aniline concentrations:

$K_f G$ .... (3)

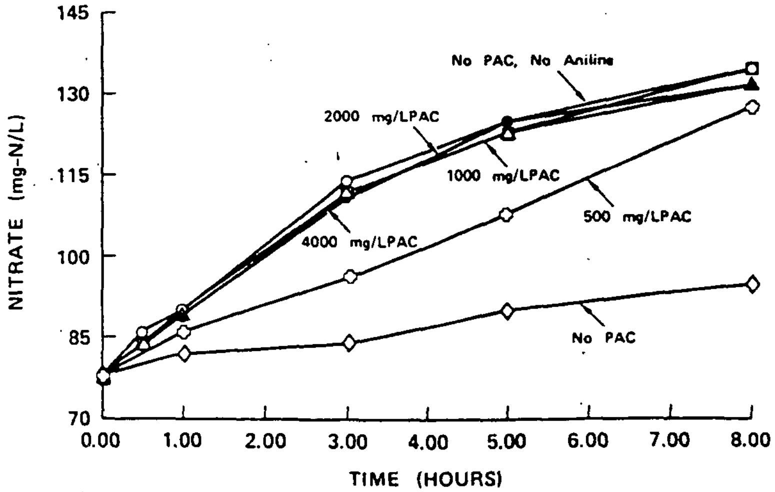

FIG. 8. NO_3^--*N* **versus Time for Variable Carbon Dose (10 mg/L Aniline 2-85)**

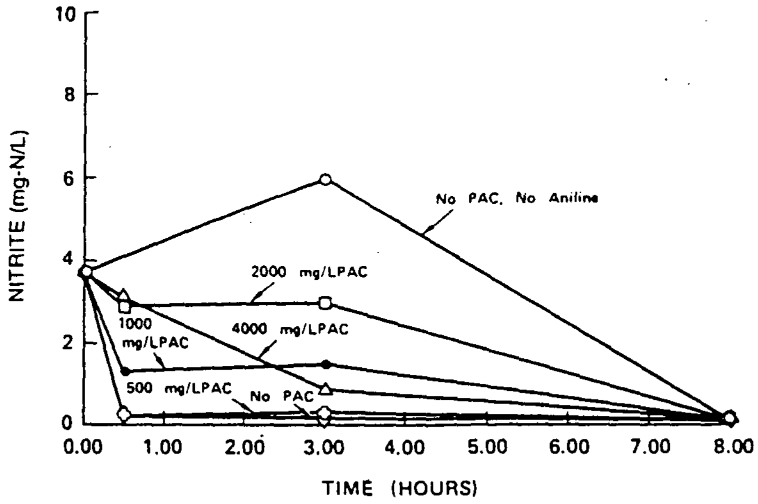

FIG. 9. NO_2^--*N* versus Time for Variable Carbon Dose (10 mg/L Aniline 2-85)

in which C_i = initial aniline concentration, 10 mg/L; C_f = final equilibrium liquid phase aniline concentration, mg/L; $1/n$ = experimentally determined Freundlich parameter (0.52); K_f = 12.2 mg/g; and G = PAC dose, g/L. The equation is implicit, requiring trial and error to determine the expected liquid phase aniline concentrations. Results are shown in Table 3 for an initial aniline concentration of 10 mg/L.

The detection limit for the gas chromatography method was 0.3 mg aniline/L. The reasons for the difference between expected and measured values are speculative. Different mixing conditions exist between activated sludge cultures and isotherm experiments. Equilibrium conditions may not have been obtained in the 30 minute period used for this experiment. Also there may have been competition for carbon sites. Martin and Iwugo (37) reported that suspended solids, particularly biological solids, could interfere with the adsorption process, both in terms of capacity and rate. They found that organic suspended solids at 500 mg/L or higher concentrations interfered with the adsorption process for single solutes and that adsorption was significantly reduced.

By interpolation of Fig. 10 (to be discussed) for the final aniline experiment on 2-85, it can be estimated that the PAC concentration at

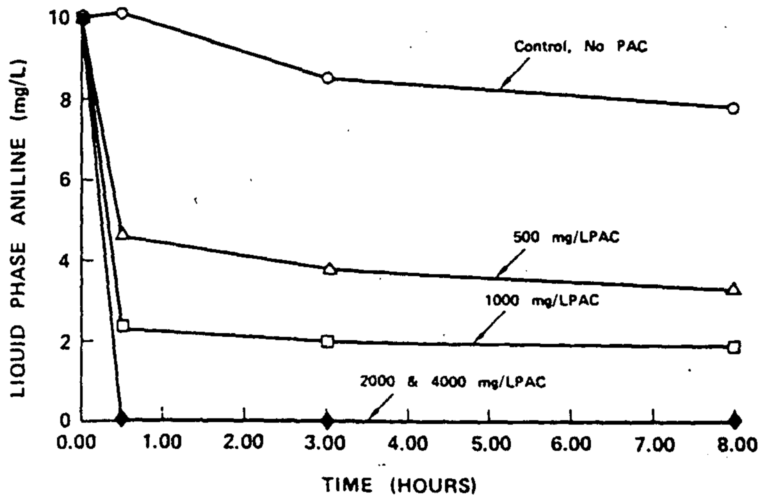

FIG. 10. Liquid Phase Aniline Concentration versus Time (2-85)

TABLE 3. Aniline Predictions

PAC Dose (mg/L) (1)	Expected Liquid Phase Aniline (mg/L) (2)	Measured Aniline (mg/L) (3)
500	1.8	3.9
1,000	0.6	1.9
2,000	0.17	not detected
4,000	0.05	not detected

which 75% nitrification occurred was approximately 80 mg/L PAC. The corresponding liquid phase aniline concentration for this PAC dose, based on the isotherm parameters, is 7.2 mg/L. For comparative purposes, Tomlinson (35) observed, under similar experimental conditions, that the concentration of aniline causing 75% nitrification inhibition in nitrifying activated sludge is 7.7 mg/L. Thus, the foregoing discussion suggests, at least for aniline, that nitrification inhibition is caused by liquid phase inhibitor concentration, as opposed to total inhibitor concentration in the PAC-AS process.

To form a quantitative basis for comparing the degree of nitrification enhancement among different experiments, an inhibition coefficient (I) was calculated to express the degree of inhibition observed at each PAC dosage for each inhibitor tested. I is defined as the ratio of calculated reaction rate constant K in the presence of the added compound to K in the control (i.e., no added compound). Calculated I's for ammonia oxidation rate constants for all experiments are presented in Table 4. Inspection reveals that for nonadsorbable compounds such as cyanide, nitrification enhancement above that in the control assays with no PAC additions was 16 and 30%, respectively, for 0.7 and 1.4 mg CN/L, at the highest PAC dose tested (4,000 mg/L). For ethanol, the least adsorbable of the compounds tested, the degree of enhancement was only 3% at the highest PAC dose tested. In contrast, nitrification enhancements of 75%, 97%, and 94% over the corresponding controls with no PAC addition were observed for aniline, aniline, and phenol, respectively, at 4,000 mg/L PAC. These results provide strong evidence that adsorption is the major mechanism of nitrification enhancement in activated sludges.

Figure 11 shows inhibition constants, based upon ammonia oxidation rate, plotted against PAC dosage for adsorbable and nonadsorbable inhibitors. There is a general relationship, dependent on inhibitor adsorptivity, between the degree of nitrification enhancement and PAC concentration. For adsorbable inhibitors, at the initial concentrations used, the relationship can be characterized by an S-type curve. This indicates that nitrification is marginally enhanced at low PAC doses and that the degree of enhancement increases steadily with increasing PAC dose until a plateau is reached. For nonadsorbable inhibitors, the enhancement/PAC relationship is characterized by a relatively horizontal curve showing little or no enhancement. Thus, it appears that enhancement depends upon the lowering of inhibitor concentration, through adsorption, to some threshold value before nitrification can proceed at reasonable rates. Similar results were obtained for inhibition constants based upon nitrate production.

TABLE 4. Nitrification Inhibition Coefficients, I Based on Ammonia Reaction Constants for Carbon Dose Experiments

Spiked Compound (1)	Type (2)	Adsorption[c] Parameters (3)	Control A (No PAC) (4)	4,000 A mg/L (5)	2,000 A mg/L (6)	1,000 A mg/L (7)	500 A mg/L (8)
Aniline 10 mg/L (2-85)	AI[a]	12.2 mg/g 0.52	0.19	0.94	0.91	0.88	0.38
Aniline 10 mg/L (1-85)	AI	12.2 mg/g 0.52	0.02	0.99	0.93	0.88	0.3
Phenol 20 mg/L (1-85)	AI	21.0 mg/g 0.54	0.06	1.0	1.0	0.37	0.07
Cyanide 1.4 mg/L (2-85)	NAI[b]	2.0 mg/g	0.0	0.158	—[d]	—[d]	0.0
Cyanide 0.7 mg/L (1-85)	NAI	2.0 mg/g	0.22	0.52	—[d]	—[d]	0.37
Ethanol 2,500 mg/L (2-85)	NAI	0.0 mg/g	0.357	0.387	—[d]	—[d]	0.385

[a] AI = Adsorbable nitrification inhibitor.

[b] NAI = Nonadsorbable nitrification inhibitor.

[c] Adsorption parameters are Freunlich parameters K and l/n for aniline, phenol, and ethanol (based on C_e = 1.0 mg/L); for cyanide, the adsorption parameter represents the maximum adsorption observed at an initial concentration of 20 mg/L.

[d] Carbon doses not evaluated in these experiments.

It is important to note that in these experiments, unacclimated activated sludge and virgin PAC were used. For adsorbable inhibitors, the beneficial effects of PAC were observed almost immediately after the start of the experiments (i.e., 1–2 hr). These observations further support the adsorp-

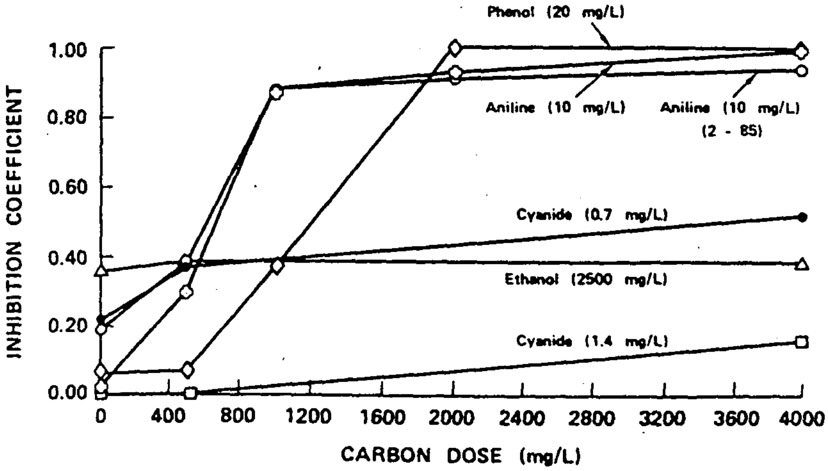

FIG. 11. Inhibition Coefficient, I (NH_4^+-N) versus Powdered Activated Carbon Dosage

tion of inhibitory compounds for nitrification enhancement. Other theories cannot account for the results since there was insufficient time for the following: (1) Enhanced nitrifier growth on the PAC surface, (2) biological acclimation; or (3) concentration of trace nutrients on the virgin PAC.

CONCLUSIONS

Based on the results in this study, the following conclusions are presented:

1. The addition of PAC in the proper amounts can completely nullify the toxic effects of an adsorbable nitrification inhibitor. For adsorbable inhibitors, the addition of PAC resulted in nitrification enhancements of 75%–97%. For relatively nonadsorbable inhibitors, nitrification enhancements of only 3%–30% were observed at the same PAC dosage. These results provide convincing evidence in support of the theory that PAC can adsorb inhibitory compounds, thereby enhancing nitrification rates.
2. Results of nitrification enhancement in this study cannot be accounted for by any of the following mechanisms: (1) Enhanced growth of nitrifiers on the PAC surfaces; (2) increased trace nutrient or substrate concentration on the PAC surfaces; or (3) heterotrophic acclimation and subsequent bioregeneration.
3. There appears to be an optimal dose of PAC required to negate the effects of an inhibitor, given that its concentration and adsorptive properties are known *a priori*.

ACKNOWLEDGMENTS

This work was supported in part by NSF Grant CEE 7911792. At the time the research was being performed, the writers were postgraduate engineer and associate professor, respectively, Dept. of Civil Engineering, University of California, Los Angeles, CA 90024.

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TECHNICAL REPORT NO. 023

THE INFLUENCE OF INDUSTRIAL WASTE ON NITRIFICATION

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Presented At:
32nd Purdue Industrial Wastewater Conference
May, 1978

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THE INFLUENCE OF INDUSTRIAL WASTE ON NITRIFICATION

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The City of Kalamazoo, Michigan has a population of about 80,000. The Metropolitan Area is highly industrialized with most of the industrial activity being generated by paper, pharmaceutical, and automotive parts manufacturing.

The area is served by a wastewater treatment plant that provides secondary treatment to domestic, commercial, and industrial wastewaters. Approximately half of the wastewater reaching the City's secondary treatment plant is of industrial origin. Most of the wastes from paper manufacturing receive primary treatment at the mills and are discharged directly to the plant's aeration tanks. Figure 1 is a diagram of the existing process.

The flows to the plant are expected to reach 53.3 mgd in the year 2000. The paper mill wastes are expected to contain about 250 mg/l SS and 300 mg/l BOD. The remaining wastes including domestic, commercial, pharmaceutical, and miscellaneous industries are expected to contain about 335 mg/l SS and 380 mg/l BOD. At the projected flow rate, daily total loading to the plant will average approximately 138,300 lbs SS and 158,900 lbs BOD. The existing plant does not have capacity for the projected loads and will necessitate substantial expansion and upgrading.

The NPDES Permit conditions require that the plant produce an effluent with 10 mg/l BOD and 2 mg/l NH_3-N during the summer months. During the winter the restriction is 30 mg/l BOD. The average suspended solids discharge is limited to 10 mg/l and 30 mg/l during the summer and winter, respectively. Phosphorus concentrations are not to exceed 1.0 mg/l throughout the year.

During the approximately two years that it took to complete the planning process, numerous studies covering physical-chemical treatment, disinfection, filtration, odor control, sludge dewatering, etc., were conducted. This paper covers a discussion of the nitrification studies, pilot investigations, the effects of industrial waste on nitrification, and the program findings. The selected treatment process is also presented.

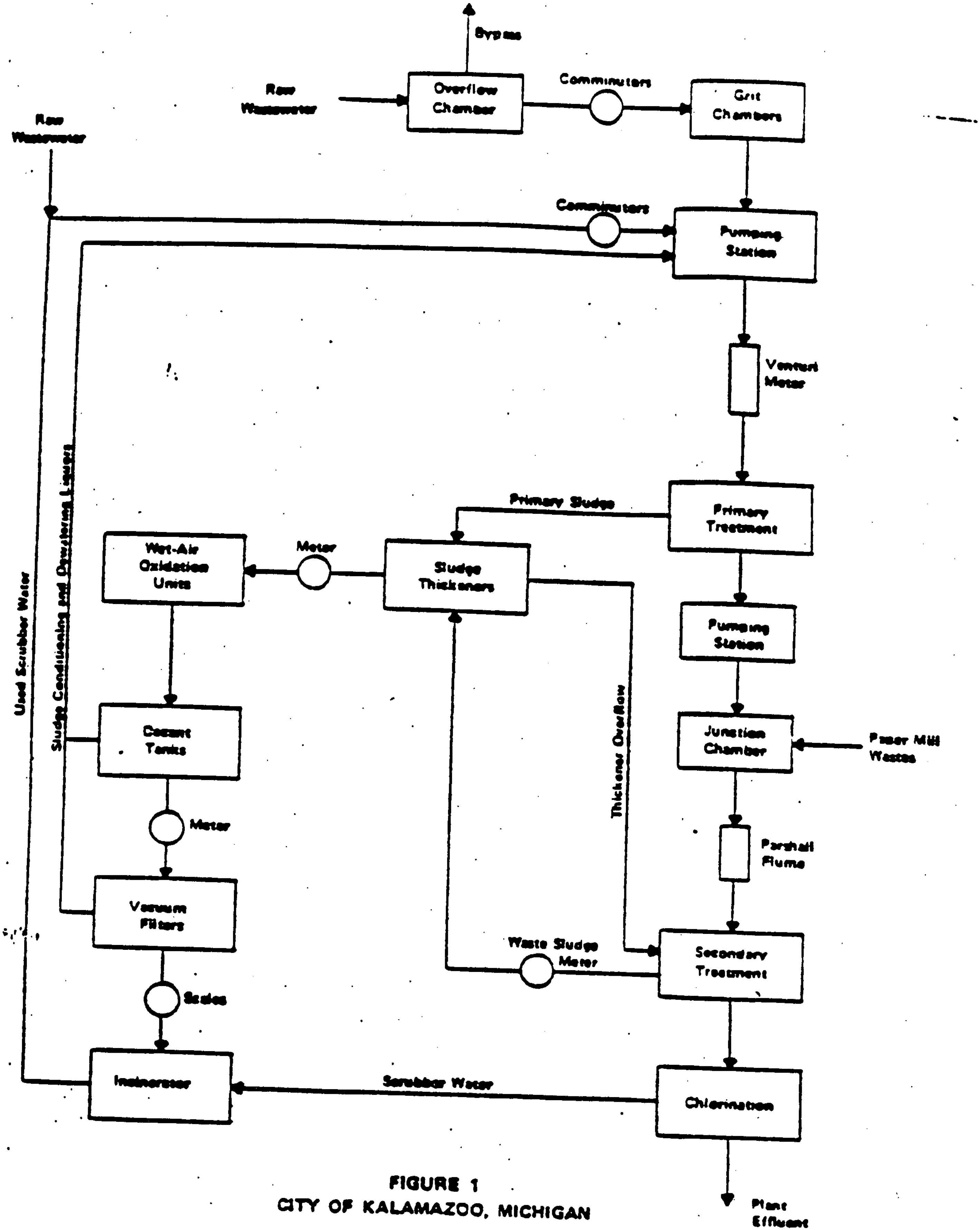


FIGURE 1
CITY OF KALAMAZOO, MICHIGAN
FLOW DIAGRAM OF
EXISTING TREATMENT PLANT

NITRIFICATION

Nitrification is the microbial mediated oxidation of ammonia to nitrites and finally to nitrates. The bacterial mediators are the aerobic autotrophs Nitrosomonas and Nitrobacter. Several researchers have recently discussed the stoichiometric relationships and kinetics of the process.[1,2,3,4]

Although the concept of nitrification is well understood, the process is often difficult to operate with any degree of consistency. The performance of a nitrification system is greatly dependent upon such things as temperature, pH, and the presence of toxins. Many substances which kill or inhibit the growth of nitrifiers have little or no effect on the heterotrophic bacteria responsible for carbonaceous removals. Among the most common inhibitors are heavy metals and many organic compounds such as amino acids and some benzene derivatives.[5]

Because of the type and quantity of industrial wastes discharged to the treatment plant, the potential presence of toxins was recognized. Several researchers have reported varying degrees of success in nitrifying wastewaters containing toxins. The two-stage activated sludge system has been found to be very effective in some conditions. Stover et al reported excellent results with a two-stage system containing a biodegradable toxin.[6] The organic toxin was oxidized in the first stage and the nitrifiers in the second stage were thus unaffected. The two-stage system is also effective in the presence of heavy metals, which are absorbed into the first stage biofloc and removed from the system.[4,6,7] The activated sludge process with the addition of powdered activated carbon has been reported to be effective in nitrifying wastewaters containing persistent organic toxins.[8]

It is apparent from the literature that the type of toxin present will greatly influence process selection. Also to be considered is the fact that in complex wastewaters, such as found in most industrialized areas, many synergisms and antagonisms are possible. In such instances, the amenability of the wastewater to nitrification can only be determined in pilot studies.

PILOT STUDIES

The pilot investigations were undertaken to evaluate various biological treatment techniques and their ability to produce an effluent of the required quality. The five processes studied were conventional activated sludge, sludge reaeration modification of the activated sludge process, rotating biological reactor, activated sludge using pure oxygen and biophysical treatment. The conventional activated sludge and sludge reaeration processes failed to produce effluents of the required quality and are not discussed in any detail. The effluent from the sludge reaeration process was used to feed other pilot plants.

The large pilot plant used for the investigation of conventional and sludge reaeration activated sludge was developed from existing tanks and equipment. The equipment used was as follows:

Aeration Tanks: number - 2
dimensions - 27' long x 26.67' wide x 11.2' deep
total capacity - 16,130 cubic feet

Aerators: 1 - Nells Surface Aerator 15 hp
1 - Roots-Connerville Blower 5 hp

Final Clarifier: dimensions - 54' long x 13.6' wide x 8.07' swd
surface area - 711 square feet/tank

Sludge Pump: 2 - Gorman-Rupp Model T3A3B - 3 hp

Rotating Biological Reactor

Equipment

The rotating biological reactor used in the study was manufactured by Autotrol Corporation and consisted of a 24-inch module containing 36 discs with a total area of 250 square feet arranged in four stages. The unit included a bucket feed mechanism but no final clarifier. The feed rate to the unit was varied by changing the number of buckets used. The peripheral velocity of the discs was varied by changing sprockets. The unit was housed to protect it from the weather.

Methodology

The unit operated from late August 1975 through the middle of April 1976. Influent to the reactor was the effluent from the sludge reaeration or from the first stage of the high purity oxygen pilot plant. The flow through the unit was approximately 0.1 gpm and resulted in a loading of about 0.58 gpd/sf of disc area. The temperature of the wastewater during the study averaged 66°F. Influent and effluent samples were collected seven days per week, one sample every hour. The effluent sample was allowed to settle for 30 minutes before drawing an aliquot of the supernatant for analysis. All analyses were made on composite samples. Parameters monitored were limited to NH_3-N and NO_3-N. The results are shown in Figure 2.

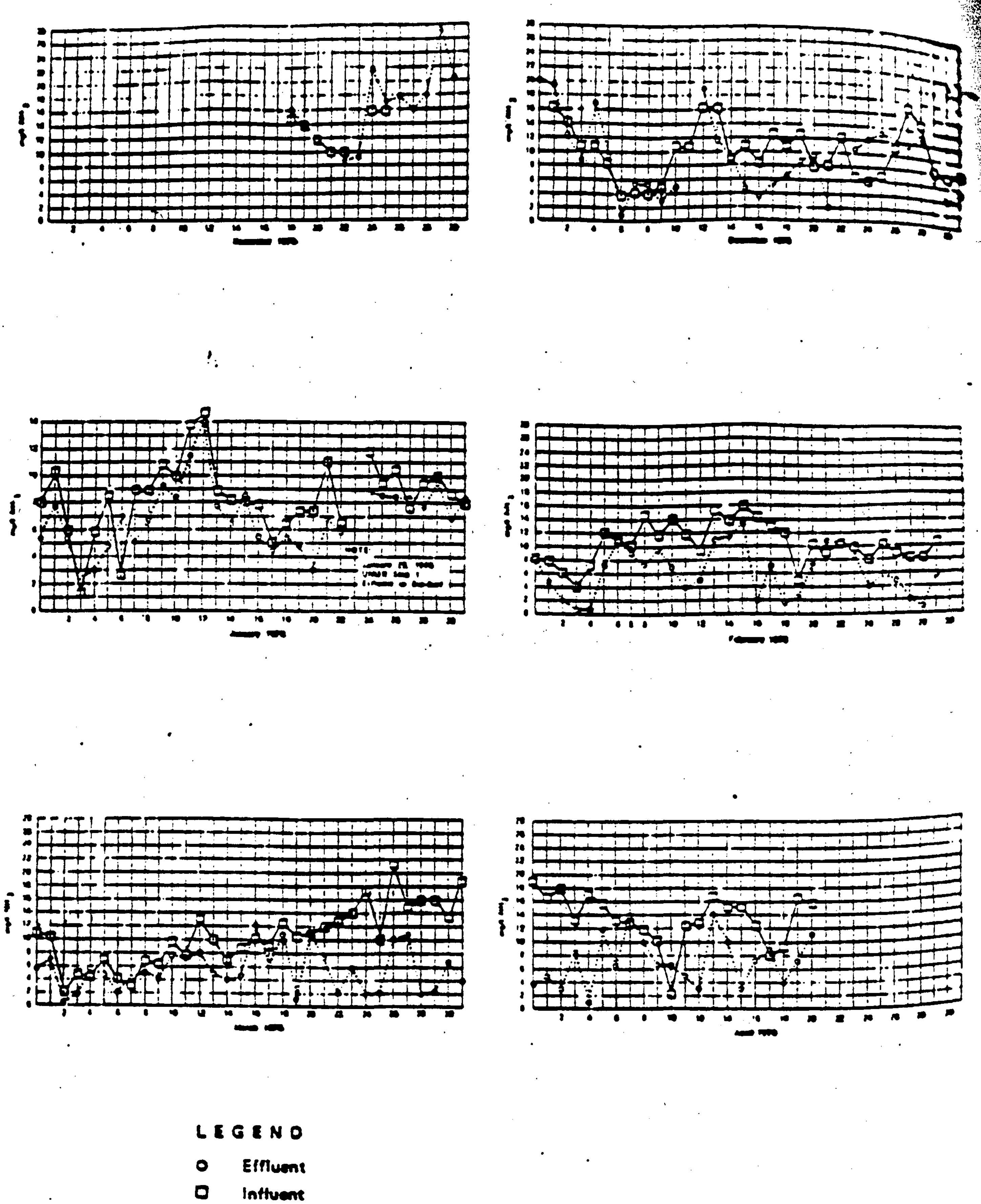


FIGURE 2
CITY OF KALAMAZOO, MICHIGAN
NITRIFICATION IN A ROTATING
BIOLOGICAL REACTOR

Discussion

The rotating biological reactor failed to provide consistent nitrification of either the sludge reaeration pilot plant effluent or the high purity oxygen first-stage effluent.

High Purity Oxygen Activated Sludge

The high purity oxygen activated sludge pilot study was run in cooperation with Union Carbide. The Company manufactures the Unox System. The objectives of the program, which ran from June 17, 1975 to October 8, 1976, were to evaluate the system's performance for carbonaceous removal and nitrification, and to obtain data useful in the design of a full-scale plant.

Equipment

The Pilot Plant contained two complete and separate oxygen activated sludge systems that were run in series as a two-step nitrification process. All liquid flow rates were controlled by volume-time calibration of variable speed pumps. The schematic of the high purity oxygen pilot plant is shown in Figure 3.

Methodology

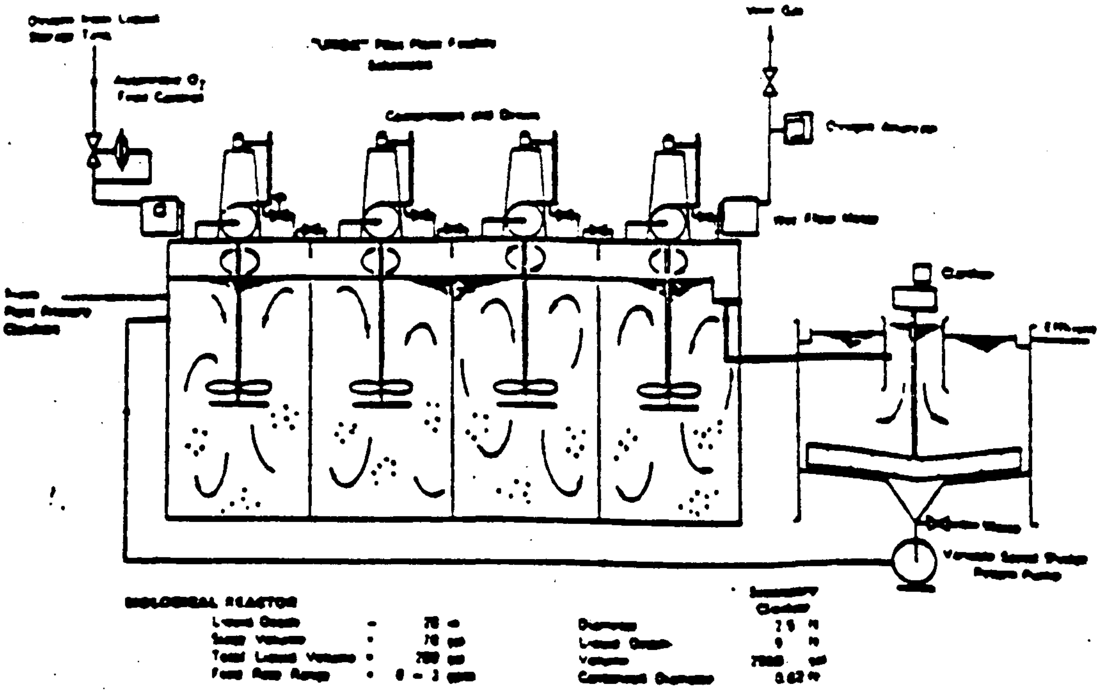
The analytical testing was done by City of Kalamazoo personnel. The pilot facility was monitored twenty-four hours per day, seven days per week, by personnel from the City of Kalamazoo, under the supervision of a Unox technician. Samples of the influent and effluent streams, first- and last-stage mixed liquors, and the recycle streams for each plant were taken every four hours and combined into 24-hour refrigerated composites for analysis.

Operational monitoring included liquid and gas flow meters, dissolved oxygen and pH meters, oxygen gas analyzers, and clarifier blanket level indicators. Readings were, in general, taken every four hours, except for influent and recycle flows, which were monitored every two hours during periods of diurnal flow variation.

Operation and Summary of Results

The two reactor-clarifier units were designated as "A" plant and "B" plant. During the study the "A" plant went through six phases of operation as follows:

Start-up Phase: Period used to bring system up to design conditions.



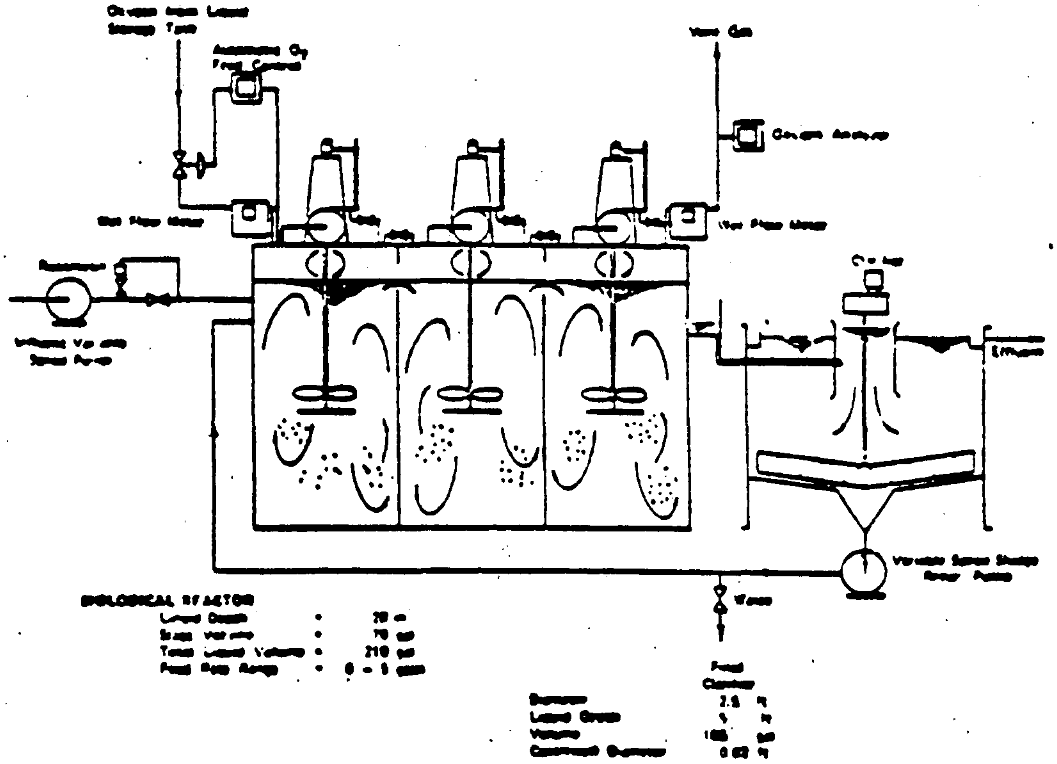


FIGURE 3

CITY OF KALAMAZOO, MICHIGAN

SCHEMATIC OF HIGH PURITY OXYGEN PILOT PLANT

Phase 1A: Operation at approximate design biomass loading.

Phase 2A: Operation at increased biomass loading.

Phase 3A: Operation under diurnal flow conditions at biomass loading greater than Phase 2A.

Phase 4A: Operation under steady flow conditions at biomass loading greater than Phase 2A.

Phase 5A: Operation at reduced biomass loading in an attempt to optimize carbonaceous removal.

During the same period the "B" plant went through five phases of operation as follows:

Phase 1B: Start-up and attempt to achieve nitrification under design conditions and plug-flow configuration.

Phase 2B: Operation in step-feed mode.

Phase 3B: Operation in plug-flow mode with a stripping stage preceding the Unox reactor at long sludge retention times.

Phase 4B: Operation in plug-flow stripping stage configuration at shorter sludge retention times than in Phase 3B.

Phase 5B: Operation as a high dissolved oxygen (high stripping level) air activated sludge system.

"A" Plant (Carbonaceous Step) Results

Operational results on a phase average basis are summarized in Table 1. Influent phase average BOD_5 ranged from 268 mg/l to 464 mg/l with a program average of 426 mg/l. BOD_5 removals ranged from 86% to 94% with effluent phase average BOD_5 ranging from 25 to 62 mg/l. With the exception of periods during which operational problems were encountered in the pilot plant (primarily during Phase 5A) effluent quality was found to improve with decreasing biomass loading.

Phase average total suspended solids removals ranged from 69% to 89% with effluent values ranging from 25 to 45 mg/l. The large fraction of industrial waste at Kalamazoo appeared to affect the effluent solids level from the plant.

TABLE 1
CITY OF KALAMAZOO, MICHIGAN
UNOX SYSTEM - "A" PLANT SYSTEM PERFORMANCE SUMMARY

Parameters						
Phase	Start-up	1A	2A	3A	4A	5A
Duration, Weeks	4	16	14	6	13	15
Oxygenation Time						
Q, Hrs	3.45	2.33	2.33	2.33	2.33	3.37
Recycle Fraction (R/Q), %	43	.30	30	30	.39	.86
Biomass Loading						
lb, BOD5/day/lb, MLVSS	0.45	0.91	1.08	1.20	1.16	0.84
Organic Loading						
lb, BOD5/day/1000 ft^3	126	256	286	299	263	218
Mixed Liquor SS, mg/l	5995	6575	6171	6009	4824	5329
Mixed Liquor VSS, mg/l	4146	4514	4215	3986	3619	3861
Clarifier Overflow Rate, gal/day/ft^2	440	626	626	626	626	475
Influent Concentrations:						
Biochemical Oxygen Demand						
Total, mg/l	268	397	444	464	409	457
Soluble, mg/l	219	323	343	344	345	389
Suspended Solids						
Total, mg/l	172	203	234	223	147	146
Volatile, mg/l	132	129	144	135	97	109
Effluent Concentrations:						
Biochemical Oxygen Demand						
Total, mg/l	23	25	40	62	51	51
Soluble, mg/l	14	21	27	48	38	38
Suspended Solids						
Total, mg/l	43	38	25	43	45	40
Volatile, mg/l	35	28	19	32	31	32
Removals:						
Biochemical Oxygen Demand						
Total	91	94	91	86	87	88
Soluble, %	94	95	94	89	91	91
Suspended Solids						
Total, %	72	77	88	79	69	69
Volatile, %	71	75	86	75	66	67
Oxygen Consumption						
lb, oxygen/lb, BOD5 Removed	--	72	53	55	68	68
Oxygen Utilization, %	63	75	85	78	89	84

"B" Plant (Nitrification Step) Results

Average results from operation are summarized in Table 2. The first four phases included numerous studies attempting to achieve reliable nitrification. Throughout the course of the program, special studies such as shaker bath analyses, treatability reactor studies, and special sample analyses of reactor gas and liquid phases were conducted in conjunction with the operation of the "B" plant nitrification step. Analysis conducted previously had shown that metal levels reaching the plant were not sufficiently high to inhibit nitrification.

The history of the nitrification studies using high purity oxygen is summarized in the material that follows.

Phase 1B (6/22/75 - 10/4/75)

Seeding of the nitrification plant was accomplished through wasting of excess sludge from the carbonaceous step during the week of June 22, 1975. On July 2, 1975, the nitrification step also received 50 gallons of nitrifier seed. No effluent stream ammonia nitrogen reduction was evident following the seeding. An apparent toxic shock was experienced over the July 4th, 1975 weekend. This shock was indicated by high effluent suspended solids and turbidity, low oxygen uptake rates, and very high dissolved oxygen concentrations. On July 10, 1975, a raw wastewater spike stream was initiated in an effort to bring the plant under control and increase the system solids concentration and SRT. On July 16, 1975, a grab sample of the pilot plant influent was analyzed for substances inhibitory to nitrification. The results of this test indicated some inhibition of the nitrifying process in the wastewater samples tested. Reseeding took place on July 25th, again without positive results. At that time, a drum was started on-site with synthetic feed to develop nitrifier seed.

An 8-litre treatability reactor was started on-site on August 14, 1975 to identify the effects of influent shocks to the nitrification system. The function of the treatability study was to provide additional flexibility to the investigative program. The treatability system was started with nitrifier seed.

The major industrial organic waste load to the Kalamazoo plant is pharmaceutical. Since this waste stream was suspected of potential nitrification inhibition, a series of 77, 2-hour composite waste samples over a seven-day period were analyzed using the Shaker Bath Technique to determine the existence of components inhibitory to nitrification. This study indicated that a minimum dilution of 14:1 was required for nitrification of one of the weekday samples. Under normal conditions, the dilution ratio of these wastes is about 30:1. Tests conducted on the paper mill wastes failed to show toxicity to nitrifiers.

CITY OF KALAMAZOO, MICHIGAN
UNOX SYSTEM - "B" PLANT
SYSTEM PERFORMANCE SUMMARY

Parameters					
Phase:	1B	2B	3B	4B	5B
Duration, Weeks	15	8	7	25	11
Oxygenation Time					
Q, Hrs	4.52	4.76	3.60	3.57	3.80
Recycle Fraction (R/Q) %	66	84	88	56	111
Biomass Loading*					
Lb, BOD_5/day/lb, MLVSS	0.13	0.05	0.09	0.11	0.08
Organic Loading					
Lb, BOD_5/day/1000 ft^3	31	19	41	38	25
Mixed Liquor SS, mg/l	5872	10047	10968	9070	7773
Mixed Liquor Volatile SS, mg/l	3798	6080	7596	5330	4697
Clarifier Overflow Rate, gal/day/ft^2	250	233	305	309	292
Influent Concentrations:					
Biochemical Oxygen Demand					
Total, mg/l	92	59	100	88	61
Soluble, mg/l	70	20	72	30	40
Suspended Solids					
Total, mg/l	61	26	54	70	39
Volatile, mg/l	48	17	33	44	29
Effluent Concentrations:					
Biochemical Oxygen Demand					
Total, mg/l	19	20	12	22	9
Soluble, mg/l	15	12	6	15	10
Suspended Solids					
Total, mg/l	45	41	17	21	18
Volatile, mg/l	32	21	14	14	13
Removals:					
Biochemical Oxygen Demand					
Total, %	73	63	85	72	83
Soluble, %	85	79	92	82	84
Suspended Solids					
Total, %	13	1	53	62	33
Volatile, %	23	7	50	62	37
Nitrification Parameters:					
Influent Concentrations					
Nitrogen, TKN, mg/l	19.9	16.4	15.5	18.0	19.3
NH_3, mg/l	17.0	13.5	7.9	9.9	9.7
Effluent Concentrations					
Nitrogen, TKN mg/l	18.6	8.0	5.1	7.5	6.1
NH_3, mg/l	19.3	4.4	1.56	4.1	2.55
Removals					
Nitrogen, TKN, %	7	51	67	58	68

The fact that the treatability reactor was successfully started and the pilot plant was not may have been related to toxicity. The nitrification step was modified to simulate complete mix on September 25, 1975 to investigate the potential of this method of operation for overcoming a toxicity threshold.

Phase 2B (10/5/75 - 11/29/75)

The second phase of operation ran from 10/5/75 to 11/29/75. During this phase, the plant was operated in a step feed mode as determined through Phase 1B investigations. Following the conversion to step feed operation and reseeding with acclimated nitrifier seed, successful nitrification commenced on 10/7/75. Nitrification proceeded throughout October with the effluent NH_3N concentration strongly a function of the irregular influent load patterns.

By late October 1975, the sludge quality had deteriorated resulting in substantial nitrifier population washout. This deterioration was attributed to the very low food level in the influent waste stream. To regain control of the system, a dextrose spike stream was initiated on 11/3/75. An almost immediate reduction in effluent suspended solids appeared to confirm food deficiency as the cause.

During the last week of November 1975, a recurrence of deterioration of plant performance was experienced. The presence of a volatile strippable toxic material was suspected since the open top treatability reactor functioned consistently and stably while the closed top pilot plant nitrification step experienced periodic deterioration in performance.

Phase 3B (11/30/75 - 1/17/76)

The third phase of operation ran from 11/30/75 to 1/17/76. During this period the system continued to operate on carbonaceous step effluent but returned to plug flow operation with an open "stripping" stage preceding the nitrification reactor. The synthetic food spike was replaced with paper mill wastewater. Following this seven week period of successful nitrification, it was decided to attempt optimization of the nitrification step and diurnal flow treatment in the next phase.

Phase 4B (1/18/76 - 7/10/76)

Phase 4B had a duration of approximately twenty-five weeks.

Following an upset during the week when a diurnal flow pattern study was initiated, it was decided to revert to a conservative SRT operation with maximum air stripping stage (D.O. > 6.0 mg/l). On 2/20/76, the nitrification step hydraulic retention time was increased to 4.0 hours and nitrification was reestablished by 2/24/76. The plant operated in this mode until 4/9/76 during which time the SRT and influent and effluent NH3N concentrations averaged 34 days, 10.8 and 2.3 mg/l, respectively. Increases in effluent NH3N occurred at the end of March when the system was adjusting to higher influent NH3N concentrations.

By April 9, 1976, it was felt that optimization of the air stripping stage should be investigated. The gas recirculation rate in the stripping stage was then cut back to maintain an average dissolved oxygen level of 4 mg/l. Within twelve days, effluent deterioration was evident and the stripping rate (D.O. level) returned to 6.0 mg/l. A brief recovery was experienced, but on 6/9/76 another upset occurred from which the system did not recover, although operating at long SRT, maximum stripping, and with the paper mill spike stream.

During this phase, numerous attempts were made to identify the volatile toxin through on-site gas tube analysis and aeration gas sample analyses at the UCC facilities in Tarrytown, New York. These analyses showed that six chlorinated hydrocarbon compounds were present. One, two dichloroethane was the major chlorinated compound identified with a concentration of less than 2 mg/M^3.

On July 6, 1976, it was decided that the closed top reactor system had proven unable to provide consistent nitrification. For this reason, a final phase of pilot plant operation was defined. This phase consisted of two-step operation with a high purity oxygen carbonaceous step and an air nitrification step.

Phase 5B (7/11/76 - 9/23/76)

The final phase of operation had a duration of approximately eleven weeks from 7/11/75 to 9/23/76. The objective of this phase was to demonstrate the nitrogen removal capability of a two-step system employing a high purity oxygen carbonaceous step and a high D.O. (high stripping) air nitrification step.

Of primary significance during this phase was the relationship between air stripping levels corresponding to D.O. levels greater than 5.0 mg/l and consistent nitrification. During the week of August 8, stripping was reduced to a level corresponding to an average D.O. level of 4.4 mg/l and system performance began to deteriorate on August 11. During the week of August 15, the stripping level was increased and the nitrification system recovered.

Discussion

High purity oxygen activated sludge operated as a two-step nitrification process failed to provide consistent nitrification. Some of the investigations indicated that strippable toxins caused failure of the process. When the second stage was operated as an open tank with high stripping rates, the system appeared to perform better.

Biophysical Treatment

A bench-scale study of the biophysical treatment system was initiated to evaluate the system's performance for carbonaceous removal and nitrification, and to obtain data for design of a full-scale plant. The results indicated that the system had the potential for success at Kalamazoo. Following completion of this study, a pilot and a second bench-scale investigation were undertaken. The studies were conducted in cooperation with Zimpro, Inc.

The individual bench-scale and pilot studies are presented in the material that follows.

Single-Stage Nitrification - Bench-Scale Pilot Study

Description of Process

A biophysical process pilot plant using powdered activated carbon enhanced activated sludge was operated in a single-stage mode for a period of four months. The process flow scheme was identical to that of a standard activated sludge system followed by rapid sand filtration. Excess biomass and carbon were removed from the system as required to maintain steady state conditions. This waste slurry was then subjected to wet air regeneration.

The wet air regeneration facility was a separate batch wet air oxidation unit. Waste spent carbon slurry and organic solids were subjected to thermal and pressure conditions to destroy adsorbed and associated organics and renovate the carbon for reuse.

Test Results

Operation of the pilot facility was maintained at aeration periods of 6-1/2 and 8 hours and at the ambient wastewater temperatures encountered. Also, diurnal flow variations were examined during the study.

The results are shown in Table 3. Analytical results from periods of system upset caused by mechanical failures (i.e., pump and tubing failures) are included in this summary.

TABLE 3

CITY OF KALAMAZOO, MICHIGAN

BIOPHYSICAL PROCESS
ANALYTICAL RESULTS - PHASE 1
OCTOBER 9, 1975 - FEBRUARY 4, 1976

	Influent Overall (mg/l)	Effluent From Sand Filter Overall (mg/l)
BOD	268.0	0.2
COD	680.0	76.0
SS	206.0	18.0
TKN	32.0	5.5
NH_3-N	17.9	2.0
NO_3-N	1.0	8.0
TN	33.6	15.6
P	7.6	2.2

A 54% total nitrogen reduction was achieved in the system without the addition of methanol or other oxygen acceptor. The capability of handling shock loads was demonstrated. Changes in effluent quality due to shock loading were not discernible in the analyses performed.

An additional period of single-stage nitrification was demonstrated with the bench-scale pilot system following the Phase 1 demonstration. The Phase 2 study was from August 27, 1976 to September 22, 1976 and was concurrent with the full-scale demonstration. The operational parameters and analytical results are presented in Table 4.

TABLE 4

CITY OF KALAMAZOO, MICHIGAN

BIOPHYSICAL PROCESS
OPERATIONAL PARAMETERS - PHASE 2

MLSS = 16,100 mg/l
Biomass = 5,080 mg/l
M.L. Volatile Carbon = 5,020 mg/l
Ash = 5,800 mg/l
Recycle SS = 30,600 mg/l
SRT = 28 days

TABLE 4
(continued)

ANALYTICAL RESULTS

	Influent	Effluent From Sand Filter
BOD	182.0	2.0
COD	466.0	50.2
TKN	29.6	4.5
NH_3-N	14.5	1.8

Conclusions

The bench-scale studies demonstrated the applicability of the process for organics removal and nitrification in a single-stage process. Nitrification was established quite rapidly, usually within 7 days of operation of the system.

Nitrification Stage - Bench-Scale Pilot Study

Description of Process

The same pilot plant was operated as a second-stage nitrification process from September 27 to October 27, 1976. The first-stage treatment (initially pure oxygen and later conventional activated sludge) was designed to provide BOD removal. The second stage was designed for nitrification and for additional organics removal. From September 27 to October 9, 1976, the first stage was a pure oxygen activated sludge pilot plant. Following this period until October 27, 1976, the first stage was the Kalamazoo activated sludge plant.

Regenerated carbon slurry was made available from the full-scale pilot study.

Test Results

The operational results are shown in Table 5.

Conclusions

The biophysical system used as a second-stage process for nitrification would meet the treatment objectives.

TABLE 5

CITY OF KALAMAZOO, MICHIGAN

BIOPHYSICAL PROCESS FOR NITRIFICATION STAGE ANALYTICAL RESULTS
SEPTEMBER 27, 1976 TO OCTOBER 27, 1976
(Average Values)

	Influent	Effluent From Sand Filter
BOD	--	4.6
COD	160.0	67.0
TKN	13.7	3.8
NH_3-N	4.5	1.06

Single-Stage Nitrification - Full-Scale Pilot Plant

Description of Process

A full-scale pilot plant was operated in a single-stage mode from April 22 to October 20, 1976. The plant treated a combination of approximately 60% municipal primary and 40% industrial primary wastewaters. The test was conducted at the previously described large pilot facility operated by the City. Excess biomass and carbon removed from the system were transported to a full-scale carbon regeneration facility at Rothschild, Wisconsin, for processing and subsequently returned to the full-scale pilot facility for reuse.

The raw wastewaters were combined, degritted, and settled. At the flow rates employed, a primary settler overflow rate of approximately 1000 gpd/ft^2 and a hydraulic detention period of 1.5 hours was obtained. A portion of the primary effluent was pumped to the aeration contact tank. The tank was equipped with a coarse bubble diffused air system. Additional oxygen transfer capabilities to meet peak demand requirements were provided by a surface aerator located in the center of the aeration contact tank.

Final settling was provided in a rectangular tank with a chain and flight collection mechanism. At the flow rates employed, clarifier overflow rates of 200-300 gpd/ft^2 and 6-12 hour hydraulic detention periods resulted. A portion of the final clarifier effluent was pumped to two effluent filters operated in parallel.

All waste streams were sampled continuously (5-minute intervals) with automatic samplers. Samples were refrigerated immediately upon collection.

Test Results

The following test results are reported for the period September 16 to October 20, 1976. Approximately 2.55 million gallons of wastewater were processed during this time.

The operational parameters are shown in Table 6. The data indicates that the aeration tank mixed liquor suspended solids and volatile carbon concentrations were low, and less than that recommended in full-scale design.

TABLE 6

CITY OF KALAMAZOO, MICHIGAN

BIOPHYSICAL PROCESS
FULL SCALE PILOT PLANT
OPERATIONAL PARAMETERS
SEPTEMBER 16, 1976 TO OCTOBER 20, 1976

MLSS = 11,800 mg/l
Biomass = 4,600 mg/l
ML Volatile Carbon = 3,100 mg/l
Ash = 4,100 mg/l
SRT = 35 days

The system achieved the results shown in Table 7. The results for October 5, 1976 are omitted due to the accidental emptying of the entire contents of the regenerated carbon storage tank into the pilot plant aeration tank.

TABLE 7

CITY OF KALAMAZOO, MICHIGAN

BIOPHYSICAL PROCESS
ANALYTICAL RESULTS
SEPTEMBER 16, 1976 TO OCTOBER 20, 1976
(Average Values)

	Primary Sewage	Clarifier Effluent	Sand Filter Effluent
BOD_5	200.0	5.2	3.3
COD	455.0	103.5	65.0
SS	110.0	43.0	9.3
TKN	29.7	6.1	5.8
NH_3-N	15.6		1.58
P	6.6		3.0

Conclusions

The use of a system including activated carbon appears to be required in Kalamazoo if the wastewater treatment plant is to provide consistent and reliable nitrification. None of the other biological treatment system, whether single- or dual-stage, gave the required results.

A single-stage activated sludge system enhanced with activated carbon and carbon regeneration will produce high quality product water and provide consistent and reliable nitrification. The effluent from such a treatment plant should meet the NPDES requirements consistently.

RECOMMENDED FACILITIES

The single-stage biophysical process was recommended since it provided the most reliable operation as well as the lowest total equivalent annual cost. Figure 4 is a diagram of the recommended process.

The existing primary facilities will be used to coagulate and settle paper mill wastes, while new primary tanks will treat the remaining wastes.

Raw wastewater and recycle streams will be pumped to two aerated grit chambers. These tanks will be covered and vented to the odor control system. Grit will be hauled to a sanitary landfill.

Alum will be fed in the aerated grit tanks for phosphorus removal. Because of the potentially critical nutrient balance in the system, this point of chemical addition will not be used if the resultant phosphorus levels in the aeration tanks are too low to maintain biological activity.

The degritted wastewater will flow through comminutors to primary settling tanks. These tanks will be covered and vented to the odor control system. The primary sludge will be pumped to gravity thickeners. The scum will be pumped to the sludge incinerator.

The primary effluent will be conveyed to the secondary influent junction chamber and combined with virgin powdered activated carbon, regenerated carbon slurry, and paper mill primary effluent.

Four aeration tanks will be constructed adjacent to the existing ones. The aeration basins will provide an average hydraulic detention time (based on Q) of 7.5 hours. The tanks will be partially covered to contain spray and mist.

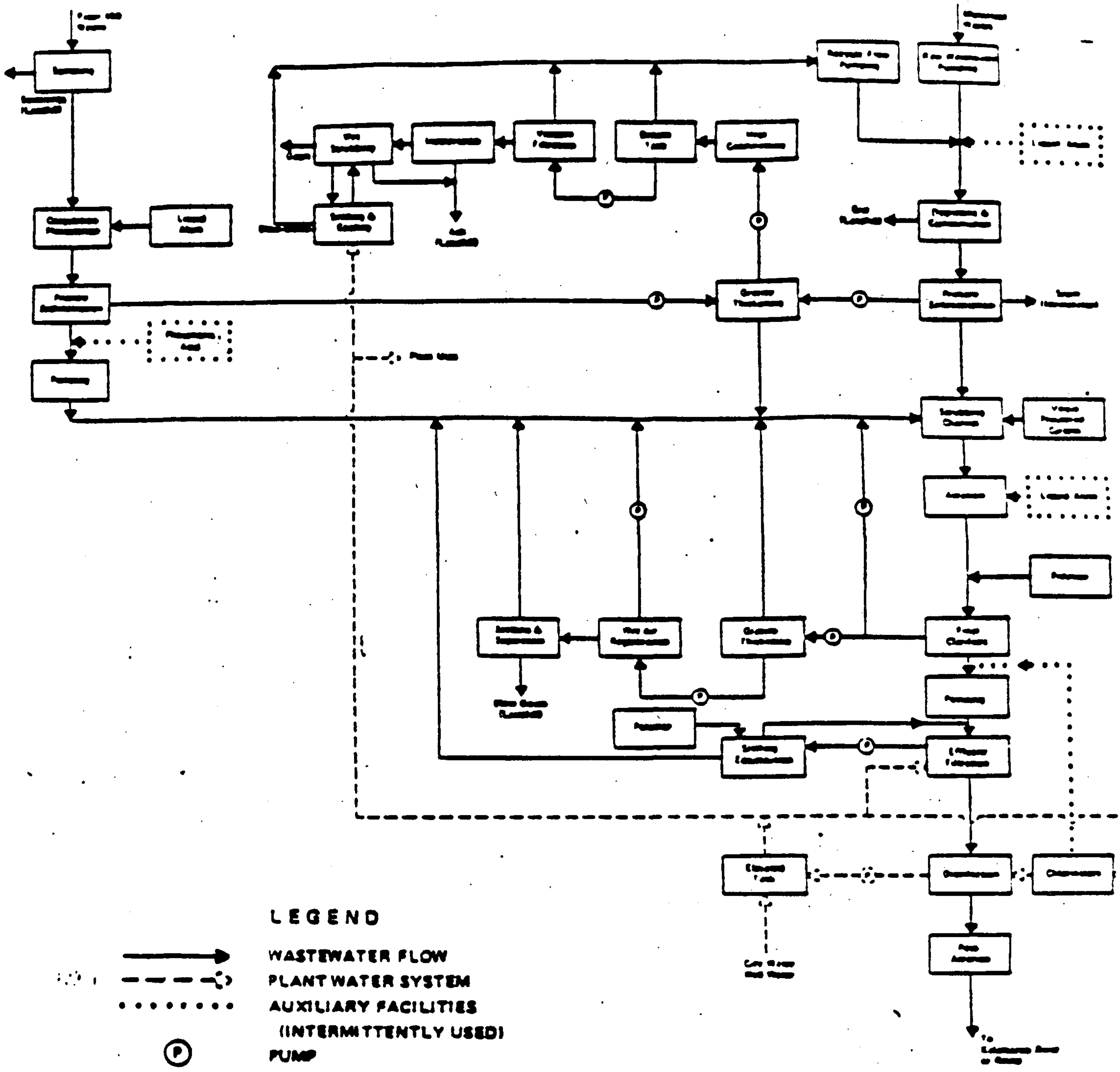


FIGURE 4
CITY OF KALAMAZOO, MICHIGAN
SCHEMATIC OF RECOMMENDED PROJECT

Provisions will be made to remove phosphorus in the secondary when removal in primary treatment would jeopardize the nutrient balance in the aeration tanks.

Liquid cationic polymer will be applied to the aeration tank effluent to aid in the coagulation and settling of the mixed liquor. The dosage will depend upon the clarifier denitrification-gasification rate as well as the biomass to carbon ratio in the mixed liquor.

The aeration tank effluent will flow to final clarifiers sized for a surface overflow rate of about 490 gpd/sf at average flow and 640 gpd/sf at peak sustained flow.

The return sludge pumps will be sized for a firm capacity of 80 mgd. The waste sludge pumps will have a firm capacity of 14 mgd.

The final clarifier overflow will be pumped to the effluent filters. The filters will be sized for a hydraulic rate of 4 gpm per square foot at average flow with one filter out of service. The filter effluent is expected to contain 5.0 mg/l of BOD, 73 mg/l of COD, 3.0 mg/l of SS, and 1.0 mg/l of NH_3-N.

The filtered effluent will flow to chlorine contact tanks sized for 15 minutes detention at the peak hourly flow rate of 95 mgd. A chlorine dose of 2.0 mg/l will be used for disinfection.

Since the plant effluent must contain a minimum dissolved oxygen concentration of 5.0 mg/l, aerators will be installed at the effluent end of the chlorine contact tank.

Sludge Treatment and Disposal

All primary sludges will be gravity thickened, heat conditioned in existing low pressure wet air oxidation units, and vacuum filtered. The filter cake at a solids concentration of 40% will be incinerated.

The vacuum pump exhaust will be vented to the incinerator. Filter hoods will be provided to collect process gases and convey them to the odor control system.

Waste sludge from the biophysical system will be discharged to spent carbon thickeners and then pumped to the carbon regeneration units. The ash and a quantity of the carbon that accumulates in the reactor must be removed in gravity separators, and the carbon returned to secondary treatment.

The recommended facilities have been approved by U.S. EPA and are currently under design.

SUMMARY

The findings of the investigations may be summarized as follows:

1. The presence of industrial wastes may greatly reduce the options available for nitrification.

2. Biological treatment processes, whether single- or dual-stage, failed to provide reliable nitrification at Kalamazoo.

3. Enhancement of the activated sludge process with powdered activated carbon appeared to eliminate or reduce toxicity problems and provided reliable nitrification.

4. Based on the findings of the study, a single-stage activated sludge system enhanced with activated carbon (bio-physical process) was recommended for use at Kalamazoo.

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APPENDIX D

TECHNICAL REPORT NO. 071

TREATMENT OF A HAZARDOUS LANDFILL LEACHATE

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Presented At:

51st Annual Meeting International Water Conference,

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BACKGROUND

Envirosafe Services of Ohio, Inc. (ESOI) manages a facility located in Oregon, Ohio (near Toledo) which operates as a Resource Conservation and Recovery Act (RCRA) landfill for disposal of hazardous and non-hazardous wastes on a 135.6 acre tract of land. Typical industrial wastes disposed at this landfill include electroplating sludges from metal finishing operations, soil and debris from Comprehensive Environmental Response and Compensation Liability Act (CERCLA) activities, wastewater treatment sludges from petroleum refining processes and other solid industrial wastes.

The landfill consists of engineered land disposal cells or units which typically range from 4 to 8 acres at the surface. The cells are constructed in what is described as lacustrine soils overlying glacial tills of low permeability. The cells are constructed of recompacted clay bottoms and sideslopes, dual flexible membrane liners with a primary leachate collection system overlying the top liner and a leak detection system between the liners. The primary leachate collection system consists of a network of pipes located within a zone of granular material which intercept and convey leachate (which is generated as rainwater percolates through the waste) to a removal sump. By the nature of the disposed material and associated precipitation, the landfill becomes a generator of waste by RCRA's "Derived From" rule which maintains that leachate generated in the disposal cells must be managed as a regulated waste.

Annual volumes of the waste leachate generated from the disposal units can exceed 1 million gallons per year. Presently, these leachates are treated and disposed off-site at permitted wastewater treatment facilities. The operation of hauling the leachate off-site for treatment and disposal has been expensive and transporting the leachate increases the potential for accidental releases and exposure to others. Sludges and effluent waters generated by the treatment and disposal of multi-source leachates from landfills are subject to the treatment standards for multi-source leachate contained in the RCRA land disposal restrictions.

ESOI desires to construct and operate a wastewater pretreatment system to treat the leachate and contaminated rainwater generated at the landfill before discharging to a local publicly owned treatment works (POTW). The purpose of this report is to present the results of a pilot plant operation to verify that the powdered activated carbon/activated sludge (PACT^R) process as manufactured by Zimpro/Passavant, Inc. could pretreat the leachate and produce an acceptable discharge to comply with the requirements of the POTW.

The objectives and goals of this study are to select a pretreatment system that would provide the following benefits:

1. Minimize space.
2. Easy to operate and maintain.
3. Not require highly skilled operators for supervision and operation.
4. Produce an effluent that would comply with the pretreatment limits and would minimize or eliminate the surcharge fees levied by the POTW.

WASTE CHARACTERISTICS AND TREATMENT REQUIRED - Table No. 1 summarizes the significant leachate characteristics and compares these values with the pretreatment standards required by the local POTW. The leachate data was obtained by analyzing grab samples collected during the period from December 1983 to November 1986. The leachate contains high concentrations of organic compounds that exhibit an average BOD$_5$ of 14,200 milligrams per liter (mg/l) and an average COD concentration of 27,100 mg/l. This data did not include any analyses for phosphorus and ammonia nitrogen. The COD/BOD ratio of 2 to 1 indicates that the leachate is biodegradable. The metals analyses indicate that heavy metals are present at low concentrations. The constituent removal requirements, calculated from the leachate data and pretreatment standards, are also presented in Table No. 1. The variability of the wastewater characteristics and the extremely high removal requirements mandate that a treatment process be conservatively designed and be capable to quickly adjust to changes in wastewater quality.

TABLE NO. 1

LEACHATE TREATMENT REQUIREMENTS

Constituent	Influent Leachate Average mg/l	Influent Leachate Maximum mg/l	POTW Pretreatment Standards mg/l	Maximum Percentage Removal Required
BOD$_5$	14,200	43,100	300	99+
COD	27,100	120,000	600	99+
SS	500	5,000	400	92
TOC	7,000	20,000	200	99
P	-	-	15	-
Oil/Grease	123	420	100	77
TTO	57	142	5	97
TOX		55	0.5	99+
Phenol	105	236	30.0	88
Cd	0.4	1.9	3.6	-
Cr	1.2	5.2	8.0	-
Cu	1.0	2.3	5.0	-
Pb	4.3	21.0	4.0	81
Hg	0.0	0.61	0.15	76
Ni	11.0	43.0	8.0	82
Ag	0.3	0.7	15.0	-
Zn	7.0	23.0	11.0	53
CN	9.7	47.0	2.0	96

WASTE VOLUME - The volume of wastewater flow from the landfill is related to weather conditions and the number of operating cells. ESOI's landfill is currently operating with two open cells and two closed cells. In the near future, one of the active cells will be closed and capped. The leachate from open cells is generated in greater volumes than leachate from closed cells. During rainfall events, the run-on of rainwater flows through the cells where it contacts hazardous waste and is collected by the leachate collection system. In a closed cell, leachate formed by seepage that contacts the hazardous waste, in addition to fluids leached from the waste, is collected by the underdrain system and discharged to a sump. The contents of the sumps are periodically pumped to a tanker truck for hauling off-site for treatment and disposal.

The average and maximum dry weather flow is 2700 gallons per day (gpd) and 11,000 gpd, respectively, and the peak wet weather flow is 165,000 gpd. After one operating cell is closed, the dry weather flows would remain at 2,700 and 11,000 gpd, but the peak wet weather flow would become 90,000 gpd.

The leachate wastewater pretreatment plant is to be designed for an average flow of 30,000 gpd and maximum of 50,000 gpd. The leachate pretreatment plant is to include an equalization tank to impound and store the excess flow until it can be treated. This study assumes ESOI could provide a service for the treatment of leachate from other landfills to use the excess dry weather capacity of the pretreatment plant.

Previous studies which included table top surveys and evaluations and bench scale laboratory tests have provided the following conclusions:

1. The use of the chemical-flocculation and settling process to remove insoluble and colloidal material from the leachate before subsequent treatment is not desired. The chemical sludge that is generated could be a regulated waste subject to land disposal restrictions and could not be economically disposed in the landfill.

2. Neither a conventional activated sludge biological treatment process nor an activated carbon physical adsorption process could treat the high concentration of wastewater constituents to acceptable levels as determined from a review of literature. A treatment system that included both the biological treatment and carbon adsorption processes could meet the pretreatment standards.

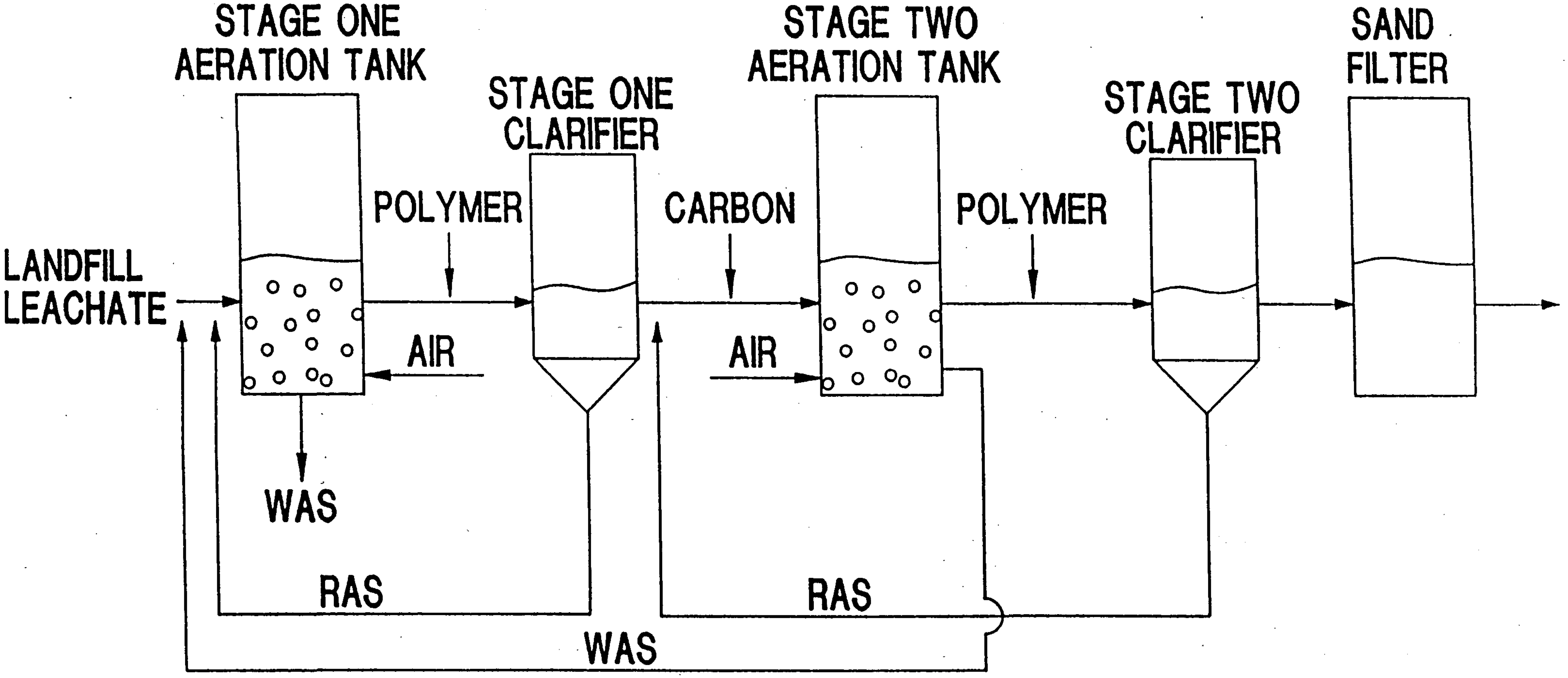
3. The UV/Ozone process could potentially be used as a polishing process to assure that the treated wastewater characteristics comply with the pretreatment standards or to provide additional treatment to comply with the recently promulgated RCRA Third-Third Land Disposal Restrictions.

4. A PACT^R process could treat the wastewater to comply with the pretreatment standards.

The PACT^R process was selected for further study over the other alternatives because the combined biological/physical adsorption functions offer the potential to remove a higher percentage of the priority pollutants from the leachate. The powdered activated carbon in the mixed liquor provides stability against shock loadings. Other inherent advantages of this process over the alternative treatment systems include enhanced removal of hazardous constituents and color bodies through physical adsorption and the suppression of volatilization of organics.

PILOT PLANT TEST

PROCESS DESCRIPTION - A flow diagram of the Two Stage PACT^R treatment system is shown in Figure 1. The influent wastewater (untreated leachate) was fed to the aeration tank of Stage One and mixed with the return activated sludge (RAS) from the Stage One clarifier and waste activated sludge (WAS) from Stage Two. The WAS in the PACT^R process actually consists of excess activated sludge and powdered carbon. The mixed liquor suspended solids (MLSS) consisting of wastewater, powdered carbon and biological solids were mixed and aerated for a sufficient period of time to effect biological oxidation and assimilation of the biodegradable substances of the wastewater. The mixed liquor flowed to the Stage One clarifier where the carbon and biological solids were settled and removed from the treated wastewater. The effluent from Stage One became the feed for Stage Two. Virgin carbon was added to the process at the influent to the Stage Two aeration tank.



ENVIROSAFE SERVICES OF OHIO, INC.

TWO-STAGE PACT® PILOT PLANT FLOW DIAGRAM

FIGURE 1

The clarifier overflow from the Stage Two clarifier was discharged from the PACT^R system. The underflow from each clarifier (RAS) was returned to the respective aeration tank on a continuous basis to maintain the desired MLSS concentration. Polymers were added to the influent to each clarifier to improve removal efficiency of carbon fines.

WAS was removed from the PACT^R process by removing a predetermined volume of mixed liquor from the Stage One aeration tank to maintain the desired solids residence time (SRT). This process of carbon addition to Stage Two aeration tank and the use of waste activated sludge (WAS) from Stage Two as the carbon source for Stage One is referred to as counter-current treatment. Counter-current treatment uses the adsorptive characteristics of the virgin carbon more efficiently than a single stage system.

TEST EQUIPMENT - The treatment of the ESOI leachate was performed in a laboratory pilot scale two-stage PACT^R system. The apparatus for each stage included stainless steel cylindrical aeration tanks, stainless steel conical clarifiers, peristaltic mixed liquor recycle pumps, mechanical mixers in each aeration tank and refrigerated effluent collection bottles. Mixed liquor dissolved oxygen levels were maintained above 2.0 mg/l by using air diffusers located at the bottom of the aeration tanks. Because pilot scale clarifiers do not provide the suspended solids removal that could be expected from a full scale clarifier,. a sand filter was used as a final polishing step.

OPERATION - The treatability study was conducted from September 21, 1989 through December 15, 1989. A 30-day period for biological acclimation ran from September 21 to October 20. Two steady state operating conditions were reviewed in this study. Condition 1 followed the acclimation period and ran from October 21 to November 21, 1989. Data obtained from observing the process operation in Condition 1 provided a basis for optimizing the process to assure increased levels of treatment while minimizing equipment requirements and purchase costs. Table No. 2 presents the operating data for Condition 1 and Table No. 3 presents data for Condition 2. Following a four day adjustment period, Condition 2 ran from November 26 to December 15, 1989. The changes that were made to the PACT^R system Condition 1 to develop Condition 2 operating parameters were:

1. SRT of Stage One increased from 20 days to 30 days.
2. SRT of Stage Two decreased from 20 days to 6.7 days.
3. HDT of Stage Two decreased from 3.8 days to 1.25 days.

OPERATING PARAMETERS - Operation of the PACT^R system was controlled by adjustment of specific process parameters which included hydraulic detention time (HDT), SRT, MLSS and carbon dose. Samples of the mixed liquor were analyzed three times per week throughout the duration of the study. Because there was not a significant decrease in performance by changing from Condition 1 to Condition 2, Condition 2 was preferred based upon anticipated lower capital costs.

The desired carbon dosage rate of 3,000 mg/l was provided by adding powdered activated carbon to the Stage Two aeration tank on a daily basis. Mixed liquor suspended solids levels in the range of 15,000 to 20,000 mg/l with a 1:1 ratio of carbon to biomass were maintained.

TABLE NO. 2

CONDITION 1 OPERATING DATA

Parameter	Stage One Target	Stage One Average	Stage Two Target	Stage Two Average
Solids Residence Time, days	20	18.5	20	19.6
Hydraulic Detention Time, days	8	8.3	3.8	3.9
Carbon Dose, mg/l	0	0	3,000	3,108
Mixed Liquor DO, mg/l	> 2	3.3	> 2	5.0
Mixed Liquor pH	6 - 9	8.1	6 - 9	7.7
Mixed Liquor Temperature, C	Ambient	22	Ambient	21.4
Mixed Liquor Volatile Carbon, mg/l	5,250	6,420	11,200	9,100
Mixed Liquor Suspended Solids, mg/l	15,000	15,530	15,000	15,270
Oxygen Uptake, mg/l/hr	-	101.9	-	6.6

TABLE NO. 3

CONDITION 2 OPERATING DATA

Parameter	Stage One Target	Stage One Average	Stage Two Target	Stage Two Average
Solids Residence Time, days	30	26.7	6.7	5.5
Hydraulic Detention Time, days	8	8.0	1.25	1.25
Carbon Dose, mg/l	0	0	3,000	3,000
Mixed Liquor DO, mg/l	> 2	2.7	> 2	8.7
Mixed Liquor pH	6 - 9	7.3	6 - 9	7.3
Mixed Liquor Temperature, C	Ambient	21.7	Ambient	21.3
Mixed Liquor Volatile Carbon, mg/l	7,900	8,600	11,200	3,900
Mixed Liquor Suspended Solids, mg/l	20,000	23,600	10,000	7,700
Oxygen Uptake, mg/l/hr	-	101.1	-	4.2

The leachate samples used in the study were nutrient deficient in phosphorus and borderline deficient in ammonia nitrogen. To compensate for this, 80 mg/l of phosphoric acid and 300 mg/l of ammonium chloride were added at the influent to the system. Chemicals were added for controlling reactor pH between values of 7.0 to 8.5 to enhance biological activity. Micronutrients which included copper at a concentration of 1.05 mg/l, iron at 40 mg/l, cobalt at 1.7 mg/l, potassium at 45 mg/l and manganese at 1.0 mg/l were added to increase the vitality of the biomass.

TEST WASTE CHARACTERISTICS - Representative samples of leachate were collected from the landfill site by ESOI personnel to provide a source of wastewater for the pilot plant study. Leachate was collected periodically and shipped to Zimpro/Passavant, Inc. for conducting the pilot study and providing analytical data. Data describing the quality of the untreated leachate indicated that the wastewater strength was changing as the study progressed. Initially the characteristics of the hazardous leachate from ESOI revealed a high strength wastewater with a COD of 29,290 mg/l and a BOD_5 of 10,150 mg/l. The leachate was highly colored (1,689 APHA) and had a high concentration of TKN (660 mg/l). Other characteristics of the leachate included a total solids concentration of 29,700 mg/l, a pH of 7.9 and an alkalinity of 4,900 mg/l. The data also indicated that heavy metals were present at relatively low concentrations. Some of these metals included zinc at 2.4 mg/l, arsenic at 8.1 mg/l and nickel at 4.6 mg/l. Cyanide was also present at 12.1 mg/l. Some of the organic constituents of primary concern included acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), phenols, methylene chloride and the cresols. Analytical results for the pilot plant test are shown in Table No. 4 which includes leachate feed characteristics and effluent concentrations for operating Conditions 1 and 2. The data of the untreated leachate for Conditions 1 and 2 in Table No. 4 follows the trend noted above that most constituent concentrations decreased during the study especially BOD and COD.

TABLE NO. 4

RESULTS OF PILOT SCALE PACT^{R} TREATABILITY STUDY FOR ESOI LEACHATE

(All values except pH reported in mg/l)

	CONDITION 1		CONDITION 2	
Constituent	Before Treatment	After Treatment	Before Treatment	After Treatment
BOD	11,861	9.92	9,636	6.0
COD	23,600	975	22,909	993
TOC	7,533	250	6,225	253
TKN	513	23.5	594	36.3
NH3-N	294	1.46	217	4.1
pH	7.7	8.3	8.7	7.7
SS	890	67	4,000	300
SA	403	20	2,400	100
Grease	580	0.48	283	0.42
Acetone	363	1.32	110	0.07
Methyl Ethyl Ketone	187	<0.05	103	<0.05
Silver	0.005	0.005	<0.005	0.007
Arsenic	2.9	1.69	1.55	1.33
Barium	0.36	0.35	0.34	0.26
Cadmium	0.08	0.07	0.016	0.015
Chromium	0.28	0.04	0.784	0.096
Lead	0.19	0.08	0.731	0.046
Mercury	0.026	0.002	0.003	<0.0008
Selenium	0.2	<0.2	<0.2	<0.2

DISCUSSION OF RESULTS - The carbon dosage for both conditions remained unchanged at 3,000 mg/l. Microbiological examination revealed that many organisms had moderate amounts of slime or capsule material outgrowth under Condition 1. The presence of the capsule material indicated that the microorganisms were in an environment where the availability of substrate is abundant. By lengthening the SRT in the first stage from 20 days to 30 days, the F/M (food to microorganism) ratio was subsequently decreased by increasing the number of organisms that the food source would be made available to. The net effect improved the biological efficiency of Stage One.

The SRT and HDT of Stage Two were reduced substantially for Condition 2. The results of isotherm analyses determined that the longer SRT and HDT being used for Condition 1 were not necessary to achieve the same level of pollutant removal. Oxygen uptake levels indicated low levels of microbial activity in Stage Two.

The removal rates for BOD_5 were greater than 99 percent for both Conditions 1 and 2, easily meeting the pretreatment limit of 300 mg/l. The COD removal efficiencies were quite similar from Condition 1 to Condition 2, 95.9 and 95.6 percent, respectively, which indicated that the changes to the operating parameters for Condition 2 did not impair COD removal. Total organic carbon (TOC) removals of 97 and 90 percent were obtained for Condition 1 and Condition 2, respectively. The average effluent concentrations from the pilot plant exceeded the pretreatment limits by 50 percent for COD and 10 percent for TOC. Wastewaters having COD values in excess of 600 mg/l are permitted to discharge to the POTW; however the sources are surcharged a fee for the excess quantity of COD.

A mass balance was calculated for Conditions 1 and 2 to determine the yield of solids produced by the biological treatment activity. The respective values for Condition 1 and Condition 2 are 0.11 and 0.08 mg biomass per day per milligram of COD removed per day. These yield values are typical for the $PACT^R$ process.

Sludge volume indexes (SVI's) were monitored regularly throughout the study. The SVI typically ranges from 50 to 150 milliliters per gram (ml/gm) for measuring the settleability of conventional activated sludges. Lower SVI values are preferred which indicate better removal efficiencies may be obtained by the settling process.

For Condition 2, the SVI for Stage One varied between 17 and 30 ml/gm and Stage Two varied between 11 and 18 ml/gm. The primary reasons for the relatively low SVI values, when compared to the typical range, is that the MLSS concentrations are significantly higher than those observed at activated sludge facilities. The other obvious reason is the additional settling velocity provided by the weight of the carbon which is an integral part of the floc particles.

The COD and TOC in the final effluent averaged 985 mg/l and 252 mg/l, respectively. This residual COD and TOC represented refractory compounds which resisted biological assimilation and carbon adsorption under the control parameters of the study. A noteworthy observation, however, is that the remaining COD and TOC yielded very low levels of BOD_5 and thus would present little oxygen demand on any downstream biological treatment unit employed by the POTW.

Additional studies on methods to reduce effluent COD from the $PACT^R$ system to levels below the 600 mg/l surcharge value were conducted to help determine the best treatment. Hydrogen peroxide addition studies indicated that the remaining COD and TOC were not oxidized by peroxide when added directly to the effluent. Carbon adsorption isotherm studies indicated that these residuals were still mildly adsorbable. Increased carbon dosages would reduce the COD to below the 600 mg/l pretreatment standard, however, dosages may be well in excess of the dosage piloted. If it is desirable to eliminate the surcharge, additional COD removals could be achieved by adding a physical chemical treatment process, such as a UV/Ozone process or a third stage $PACT^R$ process could be added to the leachate pretreatment system.

Recently promulgated federal RCRA legislation, the Third-Third Land Disposal Restrictions, has created a new waste category for multi-source leachates. The legislation sets treatment standards for over 200 chemical constituents in multi-source leachates. The leachate from ESOI's landfill, as well as the effluent and sludge from the treatment of the leachate, are subject to the new restrictions and must meet the treatment standards prior to land disposal or discharge to a POTW. Table No. 5 lists the chemical constituents found in the effluent from the pilot scale treatment unit and the treatment standards for each.

Samples of the pilot scale unit effluent were not analyzed for all chemicals which have treatment standards. Because the constituents for the multi-source leachate had not been defined, it is not known if the effluent would have met the treatment standards for those constituents. The table indicates that the treatment standards for benzyl butyl phthalate, methylene chloride, acetone, and arsenic were not achieved when the system operated under Condition 1. All of the listed treatment standards were met when operating under Condition 2, although arsenic barely met the limit. Since these constituents were undefined for a multi-source leachate, the data does not indicate if the treatment standards for methyl ethyl ketone and methyl isobutyl ketone were achieved.

The two-stage PACT^R system, when operated under the conditions modeled by the pilot scale system, may not be able to meet the treatment standards for multi-source leachate. The limited data suggests that Condition 2 is preferable to Condition 1, but variations in influent characteristics or other factors may account for the apparent better performance. Increasing the carbon dosage may help achieve the treatment standards. Ultimately, a third stage PACT^R system or additional physical chemical treatment may be required.

RECOMMENDED LEACHATE PRETREATMENT SYSTEM

The results of the bench scale treatability studies and the pilot scale study indicate that a two-stage PACT^R process is very effective in treating leachate from the ESOI landfill. The two stage system offers advantages such as greater operational flexibility, better ability to handle upset loadings, increased capability to comply with more stringent effluent limits, such as the RCRA Third-Third Land Disposal Restrictions for multi-source leachates and higher likelihood of achieving favorable bioassay results, if these tests are required in the future. A two stage PACT^R system is necessary to provide counter-current flow of powdered activated carbon to increase the efficient use of the activated carbon. For these reasons, it is felt that the installation of a two stage PACT^R system is preferred over a single stage system.

The pretreatment system should be designed based upon the following parameters:

Flow

Average	30,000 gpd (25 gpm)
Peak	50,000 gpd (35 gpm)

Treatment Requirements	Influent	Effluent
BOD_5	15,000 mg/l	300 mg/l
COD	30,000 mg/l	1,000 mg/l
Total Toxic Organics (TTO)	57 mg/l	5 mg/l
Total Halogenated Compounds (TOX)	55 mg/l	0.5 mg/l

TABLE NO. 5

EFFLUENT CONSTITUENTS SUBJECT TO TREATMENT STANDARDS FOR MULTI-SOURCE LEACHATES

(All values reported in mg/l)

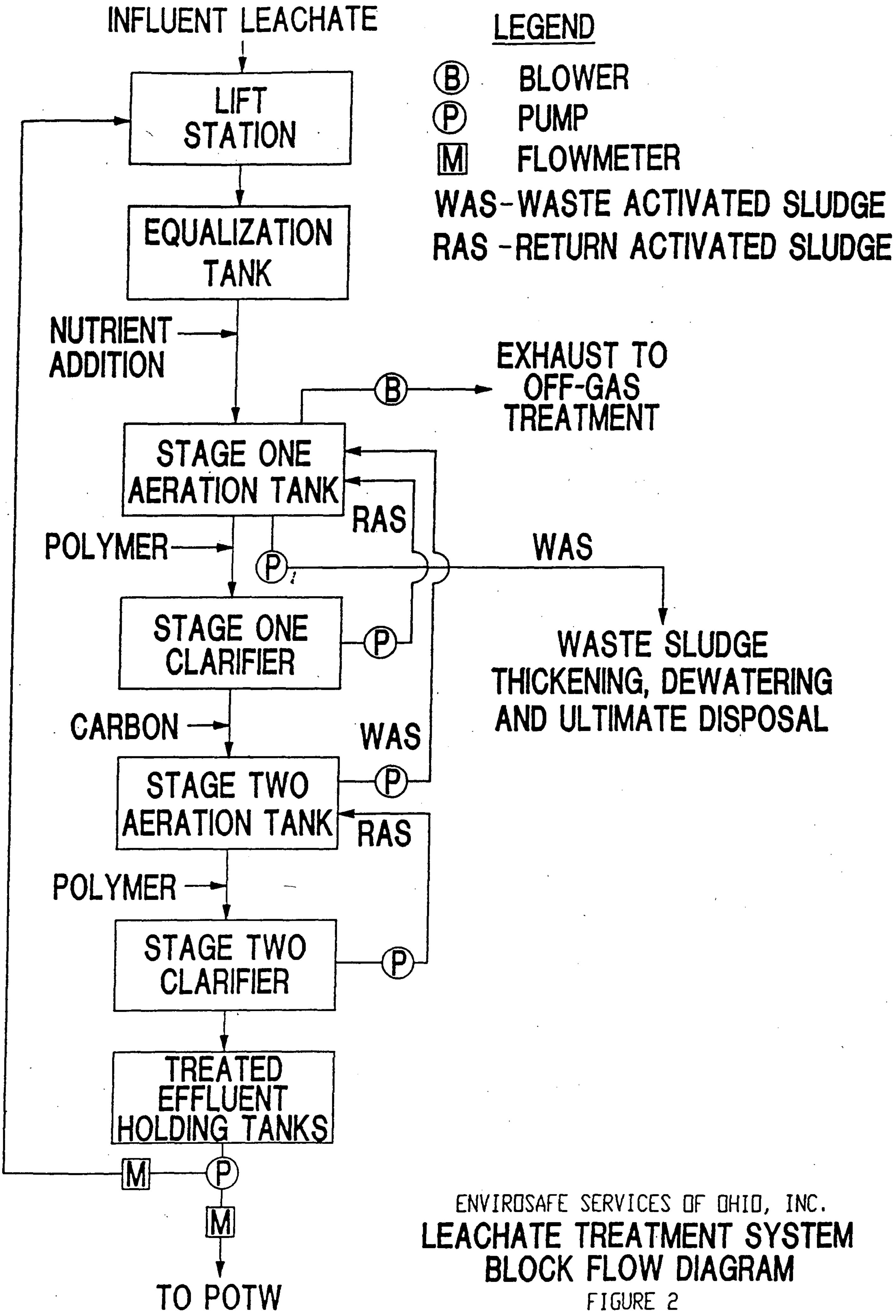
Constituent	Condition 1 Analysis 1	Condition 1 Analysis 2	Condition 2 Analysis 1	Treatment Standard
Benzyl Butyl Phthalate	0.014	0.003		0.012
BIS (2-Ethylhexyl) Phthalate	0.008		0.006	0.279
Di-n-Butyl Phthalate	0.003			0.057
Dimethyl Phthalate	0.001	0.004		0.047
Methylene Chloride	0.18	0.136	<0.025	0.089
Toluene	<0.013	<0.0125		0.080
Acetone	1.83	0.806	0.072	0.162
Methyl Ethyl Ketone	<0.05	<0.05	<0.05	0.016
Methyl Isobutyl Ketone	<0.05	<0.05	<0.05	0.032
Cyanide	0.29	0.014	0.016	1.9
Benzene		<0.012		0.136
1,1-Dichloroethane		<0.0125		0.059
Ethylbenzene		<0.025		0.032
Trichloroethylene		<0.005		0.054
Silver	0.007	<0.005	0.007	0.29
Arsenic	1.667	1.695	1.330	1.390
Barium	0.438	0.273	0.259	1.150
Cadmium	0.074	0.066	0.015	0.200
Chromium	0.026	0.050	0.096	0.370
Lead	0.083	0.073	0.046	0.280
Mercury	0.000464	<0.002	<0.0008	0.150
Selenium	<0.200	<0.200	<0.200	0.820

Figure 2 presents a simplified block flow diagram for the recommended full scale plant with a two stage PACT^R process. As shown on the block flow diagram, the treatment process should include a 50 gpm lift station; one 100,000 gallon mixed equalization tank with secondary containment; a PACT^R process with a 300,000 gallon first stage aeration tank; a 41,000 gallon second stage aeration tank with first and second stage clarifiers both sized at 12 feet diameter by 12 feet SWD and two nominal 200,000 gallon effluent holding tanks with secondary containment. The WAS would be thickened, chemically conditioned with lime and dewatered in preparation for ultimate disposal.

To confine odors, especially on start-up or during periods of process upset and to assure a safe environment around the pretreatment facility, all pretreatment tanks should be enclosed with removable covers. Air would be continually exhausted from above each process tank and connected by scrubbing or by some other form of treatment before exhausting to the atmosphere.

The pretreatment system using the PACT^R process for activated carbon/activated sludge treatment is capable of treating this high strength wastewater with a minimum number of treatment processes. The untreated, equalized leachate can be discharged directly to the PACT^R process without the need for upstream pretreatment processes, and the process conveniently provides biochemical treatment that is necessary to remove the total toxic organics to very low concentrations. The process operation is not complex and can be easily operated similar to a two-sludge activated sludge system. The pretreatment system reduces the cost for treatment and disposal of the leachate from $0.23 per gallon to approximately $0.13 per gallon but more importantly eliminates the concern for handling and hauling the leachate off-site for treatment and disposal.

All wastewater constituents with the exception of COD are removed to within acceptable concentrations of the pretreatment standards. Additional testing is necessary to determine if the PACT^R process should be modified in configuration and/or operation or the addition of other processes is necessary to comply with the recently promulgated RCRA legislation.



ENVIROSAFE SERVICES OF OHIO, INC.

LEACHATE TREATMENT SYSTEM
BLOCK FLOW DIAGRAM

FIGURE 2

TECHNICAL REPORT NO. 034

POWDERED CARBON-ACTIVATED SLUDGE TREATMENT OF MID-STATE DISPOSAL SITE LEACHATE

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POWDERED CARBON-ACTIVATED SLUDGE TREATMENT OF MID-STATE DISPOSAL SITE LEACHATE

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C.A. Hoffman(2)
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Abstract

The powdered carbon - activated sludge process, which incorporates the use of powdered activated carbon in a conventional activated sludge system, was used to treat leachate from the Mid-State disposal site, a superfund site in Marathon County, Wisconsin. Initial laboratory waste characterization testing indicated that this particular leachate contained a high percentage of biologically refractive organic constituents as well as aromatic and chlorinated aliphatic organic priority pollutants. Laboratory activated carbon isotherm testing indicated that this leachate was readily amenable to powdered carbon - activated sludge biophysical wastewater treatment.

Continuous bench scale powdered carbon - activated sludge testing has shown that the powdered carbon - activated sludge process is highly effective in removal of the organic pollutants including the priority pollutants. In addition, the powdered carbon - activated sludge process was capable of effecting complete nitrification of the leachate wastewater. It was also demonstrated that the powdered carbon - activated sludge treated leachate could be further treated, if required, by additional adsorptive techniques to provide a water clear effluent suitable for surface stream discharge.

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Introduction

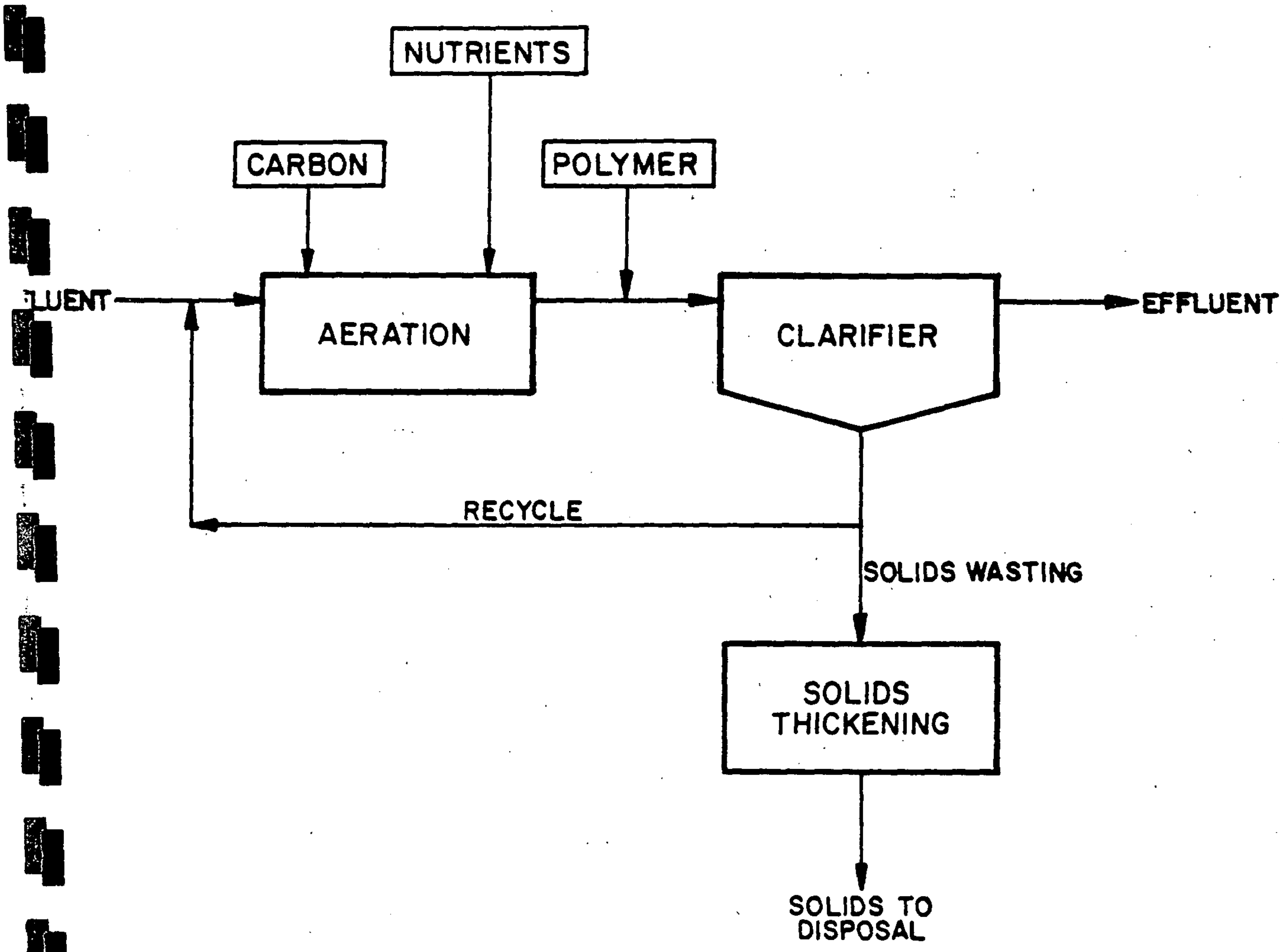
Leachate from landfills can seriously degrade the quality of both surface and groundwater. Treatment of leachate is a difficult problem because of its complex and often highly refractory organic content. The powdered carbon - activated sludge process has been recently applied to the treatment of hazardous and toxic wastewaters(1). This technology would appear to be highly suited for the treatment of landfill leachate.

The Mid-State Disposal Site, Marathon County, Wisconsin was operated as a landfill from 1973 to 1979. The landfill was used to dispose of municipal wastes, sludges, asbestos dust, fly ash, pesticides, solvents and various unknown materials. The Mid-State Disposal Site has been placed on the U.S. Environmental Protection Agency's National Priorities List due to contaminants found in the soils, sediments, and leachates at the location. The discharge of this leachate to surface waters or groundwater could result in extensive environmental damage. The present study was undertaken to assess the effectiveness of the powdered carbon - activated sludge process in treatment and detoxification of the Mid-State landfill leachate.

The Powdered Carbon - Activated Sludge Wastewater Treatment Process

The basic purpose of wastewater treatment is the removal of inorganic and organic pollutants from wastewater. Insoluble pollutants can be removed through sedimentation. After sedimentation, the remaining pollutants are colloidally dispersed or soluble in the aqueous waste stream. These constituents can usually be removed by adsorption, biological oxidation, and/or assimilation into biological cellular material. By combining adsorption on powdered activated carbon and biological oxidation into a single treatment step, a higher degree of wastewater treatment can be achieved than by either separate physical adsorption or biological treatment. The powdered carbon - activated sludge system process combines powdered activated carbon with the conventional biological activated sludge process. This combined process has proven to be effective in treating wastewaters that are highly colored, contain high concentrations of non-biodegradable compounds, or contain materials that are potentially toxic to biological growth. A flow diagram which illustrates the operation of the powdered carbon - activated sludge process is shown in Figure 1.

FIGURE I
POWDERED CARBON-ACTIVATED SLUDGE WASTEWATER TREATMENT SYSTEM FLOW DIAGRAM



Characterization of the Mid-State Landfill Leachate

The wastewater analyses which characterize the Mid-State landfill leachate are reported in Table I. These analyses indicated a high strength wastewater with a low BOD/COD ratio. This leachate is typically highly colored and contains a considerable amount of suspended and colloidal material. In addition to the highly refractory (non-biodegradable carbonaceous COD) content, this leachate contains a rather high concentration of ammonia (208 mg/l). The total and suspended solids analyses indicate that a considerable amount of dissolved material is present in this leachate. The inorganic fraction of this soluble material is probably present as inorganic biocarbonates (inorganic carbon dioxide concentration of 2160 mg/l and a pH of 7.1). The metals analyses indicate that heavy metals are present at low concentration levels.

The BOD/COD ratio of leachates, in general, has been shown to decrease as the age of the landfill increases(2). Since the Mid-State landfill site has been closed for several years, the BOD/COD relationship of this leachate is consistent with previous findings.

Laboratory Apparatus and Experimental Plan

The powdered carbon - activated sludge treatment of Mid-State landfill leachate was conducted in a laboratory bench scale unit. An illustration of the bench scale unit is shown in Figure II. The treatment apparatus consisted of a cylindrical aeration tank with a mechanical stirrer, a conical clarifier, peristaltic feed and recycle pumps, and an effluent collection bottle. In operation, leachate feed was transferred from a feed reservoir to the aeration tank by means of a peristaltic pump controlled by an interval timer. The powdered carbon - activated sludge mixed liquor flowed by gravity to the clarifier. Solids settling to the bottom of the clarifier cone were returned to the aeration tank using a timer controlled pump. The treated effluent overflow from the clarifier was collected in the effluent collection bottle. The dissolved oxygen level in the aeration tank was maintained at a concentration >4 mg/l by introducing compressed air through a diffuser near the bottom of the aeration tank.

On a daily basis, the required amount of powdered activated carbon (carbon dose) was added to the aeration tank to maintain carbon levels in the system. A fixed volume of mixed liquor was withdrawn from the aeration tank, on a daily basis, to maintain the desired solids retention time (SRT). Samples of mixed liquor and treated effluent were analyzed three times each week throughout the treatment study. Leachate feed samples were analyzed

Table I

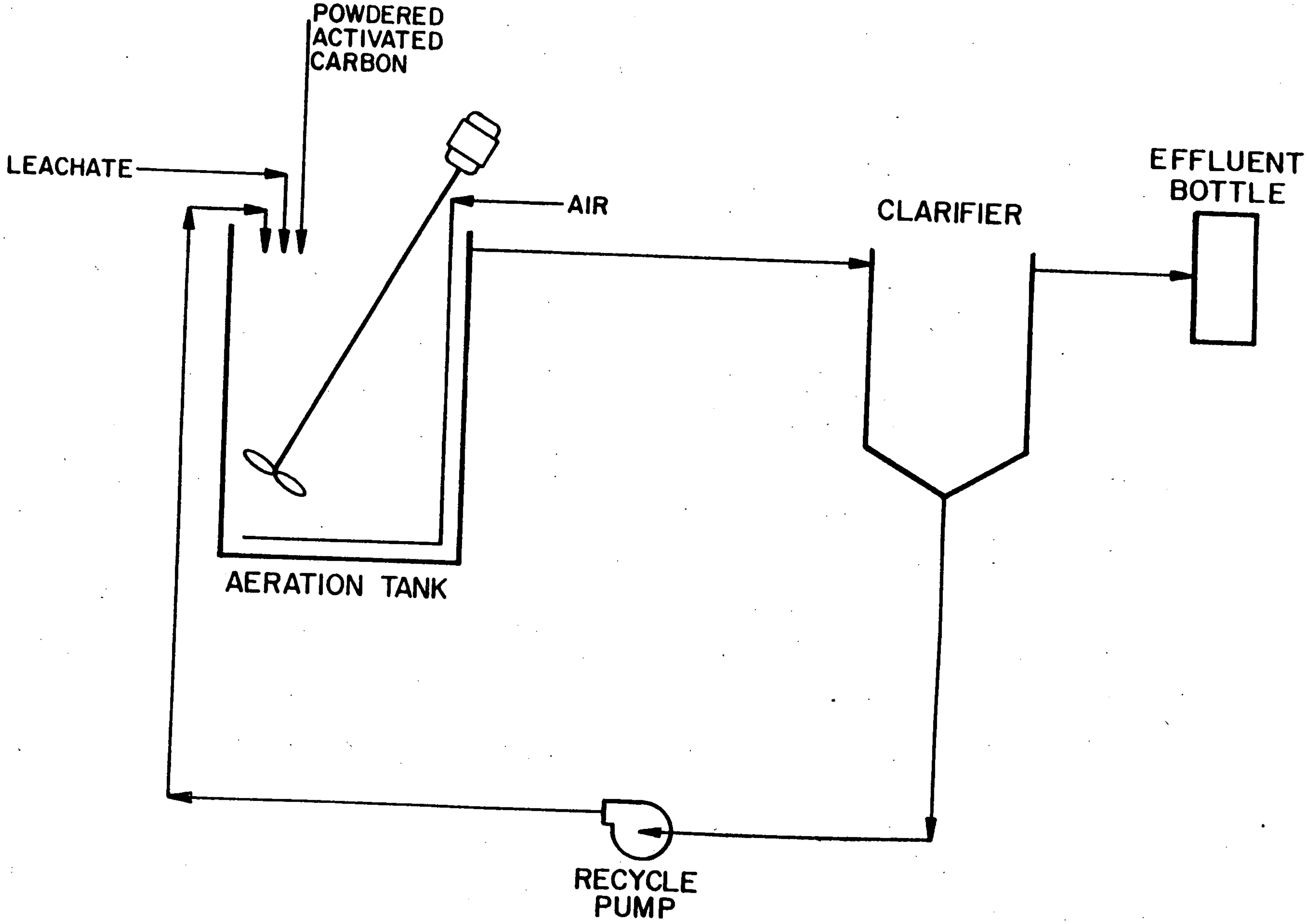
Average Characterization of Mid-State Disposal Site Leachate

(All Values in mg/l except color and pH)

Chemical Oxygen Demand	920
Soluble Chemical Oxygen Demand	821
Carbonaceous Biochemical Oxygen Demand (BOD_5)	48
Soluble Carbonaceous Biochemical Oxygen Demand (BOD_5)	30
Dissolved Organic Carbon	222
Total Kjeldahl Nitrogen	254
Ammonia Nitrogen	208
Nitrite Nitrogen	<0.5
Nitrate Nitrogen	1.4
Color	452 AHPA Units
pH	7.1
Inorganic Carbon Dioxide	2160
Total Solids	4450
Total Ash	2880
Volatile Solids	1570
Suspended Solids	212
Suspended Ash	109
Volatile Suspended Solids	103
Total Phosphorus	1.3
Cyanide	0.15
Phenols	0.22
Calcium	1.50
Magnesium	187
Aluminum	378
Iron	51.0
Sodium	489
Potassium	267
Chromium	<0.009
Copper	0.094
Nickel	0.057
Manganese	0.373
Cadmium	0.006
Lead	0.104
Mercury	<0.0004
Arsenic	0.005
Silver	<0.004
Barium	0.408
Berrylium	<0.001
Zinc	0.253
Selenium	0.002
Soluble Chlorides	595
Total Sulfur	16
Sulfate Sulfur	<14

FIGURE II

POWDERED CARBON-ACTIVATED SLUDGE LABORATORY UNIT



once per week. Feed and effluent samples were analyzed for BOD, COD, dissolved organic carbon (DOC), TKN, pH, ammonia, nitrate, and nitrite concentrations. All analyses were performed according to Standard Methods(3) and EPA Methods for Chemical Analyses of Water and Wastes(4). A phosphorus nutrient deficiency was indicated by the analyses of the leachate listed in Table I. To ensure that biotreatment was not limited by a phosphorus deficiency, dibasic sodium phosphate was added to the powdered carbon - activated sludge system feeds throughout this study.

In preparing an experimental plan for the powdered carbon - activated sludge treatment process, a wide range of operating parameters was desired, not only to assess treatment results but also to determine the biological kinetic constants associated with the treatment process. The hydraulic detention time (HDT), the solids residence time (SRT), and the powdered carbon dose rate were the process parameters that were varied throughout this study.

During the course of the study, some consideration was given to the addition of a granular activated carbon (GAC) adsorption step following the powdered carbon - activated sludge treatment process. This was accomplished in the laboratory by using two cylindrical columns, 1.75 inches in diameter and 12 inches in length, each containing 185 g of granular activated carbon (ICI Hydrodarco 4000). During the GAC portion of this study, the GAC columns were operated in series both in an upflow mode. Samples of treated leachate were obtained after passage through each GAC column and were analyzed for COD, DOC, BOD, and color. The feed material to the GAC columns, whether effluent from the powdered carbon - activated sludge treatment process or untreated leachate, was filtered through a sand filter (2.75 inches diameter, 10 inch sand bed depth, 0.35 mm sand) to remove suspended solids prior to GAC adsorption.

Results and Discussion

The bench scale powdered carbon - activated sludge treatment studies were conducted to assess the treatability of the Mid-State landfill leachate process. Operating conditions which were varied during the study included the hydraulic detention time (HDT), the solids residence time (SRT) and the powdered activated carbon dosage.

The performance summary for the powdered carbon - activated sludge treatment system under nine operating conditions is listed in Table II. The reported operational and analytical results are average values obtained over the duration of each experimental condition.

Best Available Copy

Table II

Average Performance Summary Bench Scale Powdered Carbon - Activated Sludge Systems

Solids Retention Time, Days	3.2	5.5	3.6	6.0	10	11	32	11	26
Hydraulic Detention Time, Hours	4	8	12	12	12	12	24	12	24
Volatile Activated Carbon Dose, ml/l Feed	400	400	400	400	400	400	400	800	800
Mixed Liqior									
Suspended Solids, mg/l	18000	19800	5500	11200	16600	20700	20800	25100	32300
Volatile Carbon, mg/l	8100	9700	2300	5200	8600	8200	9400	13300	16400
Volatile Biomass, mg/l	2400	2800	1100	1900	2700	3700	3900	2500	4200
COD									
Influent, mg/l	812	871	952	989	971	834	975	730	934
Effluent, mg/l	482	312	431	438	375	264	292	166	262
% Removal	40.6	64.2	54.7	55.7	61.4	68.3	70.2	77.3	72.0
BOD_5									
Influent, mg/l	38	38	40	40	38	51	41	41	48
Effluent, mg/l	<6	<6	<6	<9	<6	<6	<6	<6	<6
% Removal	>84	>84	>85	>78	>84	>88	>85	>85	>88
DOC									
Influent, mg/l	238	229	226	235	246	197	248	186	235
Effluent, mg/l	132	110	132	135	125	91.2	102	59.0	91.8
% Removal	44.5	52.0	41.6	42.6	49.2	53.7	58.9	68.3	60.9
TKN									
Influent, mg/l	260	249	277	268	258	238	252	232	262
Effluent, mg/l	52.1	9.4	13.9	27.0	10.9	9.6	8.8	5.8	8.4
% Removal	80.0	96.2	95.0	89.9	95.8	96.0	96.5	97.5	96.8
NH_3-N									
Influent, mg/l	212	200	214	226	217	184	223	187	222
Effluent, mg/l	36.4	1.0	<1.5	13.4	<0.5	<2.0	<0.5	1.6	<0.5
% Removal	82.8	99.5	>99.3	94.1	>99.8	>98.0	>99.8	99.1	>99.8
Nitrite-N									
Influent, mg/l	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Effluent, mg/l	71.6	8.0	33.2	7.4	<0.7	1.5	<0.5	1.2	<0.5
itrate-N									
Influent, mg/l	1.0	<0.7	1.7	2.9	1.2	<0.6	1.6	0.8	1.3
Effluent, mg/l	99.4	201	195	211	246	210	252	186	262
uspended Solids									
Influent, mg/l	108	113	230	167	287	330	241	106	162
Effluent, mg/l	116	74	85	410	552	89	34	86	313
olor									
Influent, APHA units	432	415	518	407	427	434	527	350	455
Effluent, APHA units	273	271	434	277	274	281	330	95	212

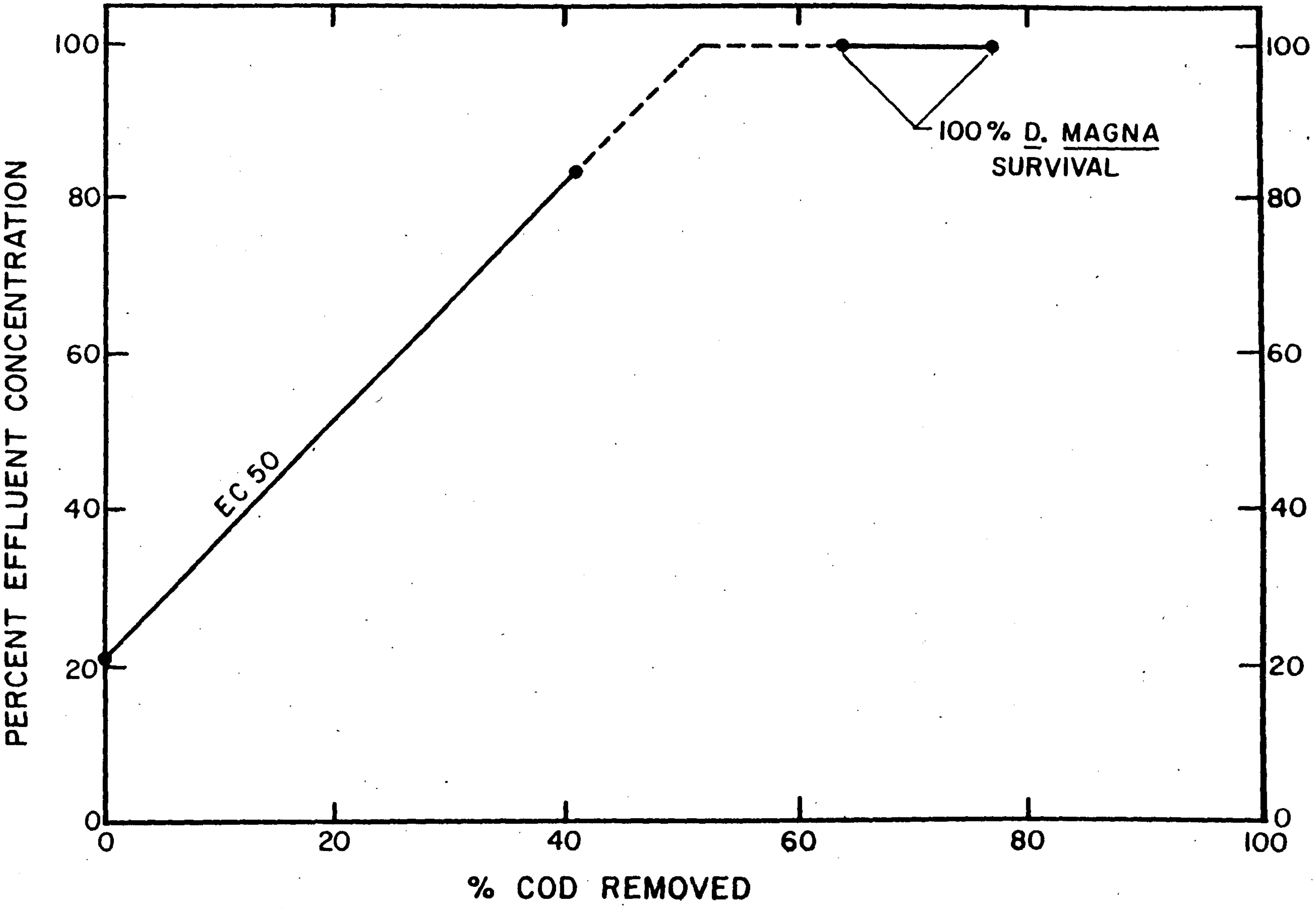
Results show that COD and DOC removal efficiencies up to 77 and 68%, respectively, were obtained in the treatment system. Under all conditions, carbonaceous BOD removal was essentially complete and the residual carbonaceous matter would appear to be nonbiodegradable.. However, further removal of carbonaceous matter was shown to be accomplished by adsorption processes which use additional powdered or granular activated carbon.

Analyses of the Mid-State leachate showed a total Kjeldahl nitrogen content of 254 mg/l with about 80% of the nitrogen present as ammonia nitrogen. Nitrification of the ammonia nitrogen and a portion of the non-ammonical nitrogen was readily achieved in this study. In the systems operated with a short SRT of 3.2 - 5.5 days, 82-99% of the ammonia was nitrified to nitrites and nitrates. In the experiments with a longer SRT, 99+% of the ammonia nitrogen was nitrified to nitrates.

Evaluation of the aquatic toxicity of the powdered carbon - activated sludge process effluents was performed with Daphnia magna test organisms(3). The static tests involve addition of <24 hour old organisms to several dilutions of untreated leachate and dilutions or full strength of powdered carbon - activated sludge effluents. On a regular basis, the number of dead or immobile organisms were noted. From the data obtained, the median effective concentration (EC_{50}) values were determined. Figure III shows the toxicity test results for the 48 hour exposure. The data show that powdered carbon - activated sludge treatment was greatly effective in removing leachate toxicity to Daphnia magna. Total organism survival was observed in one hundred percent effluent after treatment that resulted in >68 percent COD removal.

The powdered carbon - activated sludge treatment results were used to provide estimates of the various kinetic coefficients associated with the biological portion of the treatment process. Graphical techniques(5) are typically used to determine the kinetic coefficients, Y (the maximum cell yield coefficient), K_d (the endogenous decay coefficient), K_s (the substrate half-velocity constant), the k (the maximum rate of substrate utilization).

The kinetic coefficient values determined from the results of this study are listed as follows:



AQUATIC TOXICITY OF EFFLUENTS TO D. MAGNA

FIGURE III

[redacted]

Coefficient	Numerical Value
$Y, \frac{\text{mg biomass}}{\text{mg COD}_R}$	0.31
K_d, day^{-1}	0.02
K_s, mg/l	126
$k, \frac{\text{mg COD}}{\text{mg biomass-day}}$	0.35

Since the untreated leachate contained low concentrations of readily biodegradable substrate, the determination of all kinetic constants was based on COD removal.

Previously, it was shown that substantially all biodegradable organic materials could be removed from the Mid-State landfill leachate by the powdered carbon - activated sludge treatment process. Isotherm testing indicated that much of the residual organic content in the treated effluents can be adsorbed by further contact with activated carbon. An initial investigation showed that additional removal of organics could be accomplished by passing the effluent through a GAC bed. A flow diagram, along with an indication of overall average performance of the three step leachate treatment process is shown in Figure IV. The powdered carbon - activated sludge effluent that was treated in the GAC columns was obtained during the operating condition with a 12 hour HDT, a 11 day SRT, and 400 mg/l carbon dose. Initially the product water from the GAC columns contained very low levels of organics as was indicated by the COD, DOC, and color values. The concentration of organics in the product water slowly increased with continued use of the GAC columns. The average concentration values listed in Figure IV were obtained after passage of 104 liters of filtered effluent through the column. These results show that this combined treatment scheme is capable of producing a high quality water (COD <100 mg/l, DOC <25 mg/l, SS <10 mg/l and color >30 APHA units) suitable for discharge into surface water streams. These results also show that a granular carbon usage rate of 3462 mg/l (360 g carbon, 104 l cumulative flow) was required to obtain the high quality effluent water. Experimental work currently in progress indicates that this carbon usage can be substantially reduced while maintaining the same high quality effluent by employing a second stage powdered carbon process in place of the GAC column.

To estimate GAC requirements when treating leachate to the same level as the powdered carbon - activated sludge process, untreated leachate was passed through GAC

	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE	RANGE
COD, mg/L	869	844-882	285	263-303	278	252-293	103	88-134
DOC, mg/L	199	160-216	93	75-100	93	75-113	23	9-35
COLOR, APHA UNITS	404	345-459	277	244-305	266	248-304	16	1-27
SUSPENDED SOLIDS, mg/L	212	140-262	114	27-189	18	3-32	3	0-9
BOD_5, mg/L	53	36-77	<6		<6		<6	

DIAGRAM AND AVERAGE PERFORMANCE OF THREE STEP TREATMENT PROCESS

FIGURE IV

columns. Based on a COD breakthrough of 285 mg/l (the average value of the effluent from the powdered carbon - activated sludge treatment using comparable raw leachate), breakthrough occurred at 26 days which yields a carbon usage rate of 2564 mg/l (300 g carbon, 117 l cumulative flow).

Several organic chemicals which are listed as priority pollutants were identified in the landfill leachate. Analysis for the volatile organic fraction indicated the presence of benzene, chloroethane, ethylbenzene, toluene and 1,1,1-trichloroethane in concentrations of 3-54 ug/l (ppb). Three phthalate esters, dibutylphthalate, bis (2-ethylhexylphthalate) and diethylphthalate were present at concentrations of 1 to 16 ug/l (ppb). Significant levels of the latter compounds might be expected in landfill leachate since they are widely used as plasticizers in plastic products.

Effluents from the powdered carbon - activated sludge treatment of leachate (40.6, 64.2 and 72.0% COD reduction experiments) were analyzed for priority pollutants. None of the volatile organics were detected in the effluent indicating complete removal by the powdered carbon - activated sludge treatment. The concentration of phthalate esters was not substantially effected by the powdered carbon - activated sludge treatment or adsorption on granular activated carbon.

In the powdered carbon - activated sludge process, sand filtration, and GAC adsorption treatment steps, three process solids residuals were generated. These materials, wasted powdered activated carbon - activated sludge solids, sand filter backwash solids, and spent granular activated carbon were examined for Extraction Procedure (EP) metals toxicity(6). It should be noted that a solid exhibits the characteristic of EP toxicity when the aqueous extract (pH = 5 ± 0.2) equals or exceeds the heavy metals concentration limits promulgated by the EPA. The heavy metal concentrations of the extracts along with the EPA maximum metal concentrations are reported in Table III. These results show that all residual solids from a powdered carbon - activated sludge, sand filtration, and GAC treatment system would be classified as non-hazardous according to EP toxicity testing.

Table III

Concentration of Metals for Characteristic of EP Toxicity
(All concentrations in mg/l)

Metals	Maximum Allowable Concentration	Powdered Carbon - Activated Sludge Wasted Solids	Sand Filter Backwash Solids	Spent Granular Activated Carbon
Arsenic	5.0	<0.004	<0.004	<0.004
Barium	100	0.13	0.07	1.4
Cadmium	1.0	<0.004	<0.004	<0.004
Chromium	5.0	<0.01	<0.01	<0.01
Lead	5.0	0.05	<0.05	<0.05
Mercury	0.2	<0.001	<0.001	<0.001
Selenium	1.0	<0.004	<0.004	<0.004
Silver	5.0	<0.005	<0.005	<0.005

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TECHNICAL REPORT NO. 054

THE TREATMENT OF CONTAMINATED GROUNDWATER AND RCRA WASTEWATER AT BOFORS-NOBEL, INC.

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Presented At:
4th National RCRA Conference on
Hazardous Waste & Hazardous Materials (HMCRI)
Washington, D.C.
March 16-18, 1987

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ABSTRACT

Bofors-Nobel, Inc., a Michigan manufacturer of herbicides and organic chemicals, is using an innovative approach to treat production (RCRA) wastewaters as well as contaminated groundwater at its site. A powdered carbon/biological system (known commercially as PACT^R) and Wet Air Oxidation (WAO) are used to ensure that Bofors' discharge is acceptable to the Muskegon County wastewater system.

In PACT^R, powdered carbon is added to end-of-pipe activated sludge treatment, to remove a wide range of organic compounds not treatable solely by biological means. As demonstrated at Bofors, such addition also eliminates the need for end-of-pipe GAC adsorption. Currently, 1.8 million gallons per day of contaminated groundwater and RCRA production wastewaters are being treated.

When Bofors expanded organic chemicals manufacturing operations, the quantity of powdered carbon used in the PACT^R system justified regeneration. Wet air oxidation was selected as the technology to regenerate spent carbon from the PACT^R system. WAO also destroys toxics adsorbed on the carbon.

A second WAO unit has been installed at Bofors to detoxify certain process waste streams.

More than 100 different organic compounds have been effectively treated by the system since its start-up in March, 1983. Overall treatment results are shown, as well as information on system selection and economic comparisons of treatment alternatives.

INTRODUCTION AND SUMMARY

It is not often that wastes regulated by the Resource Conservation and Recovery Act (RCRA) and Superfund (CERCLA) are generated and treated at the same site.

But Bofors-Nobel, Inc., a manufacturer of herbicides and organic chemicals located near Muskegon, Michigan, presents a rare opportunity to observe successful technological solutions to both types of waste problems. A unique combination of treatment processes has been in use there since 1983, detoxifying process wastewater as well as contaminated groundwater emanating from an abandoned landfill.

The backbone treatment processes at Bofors are a powdered activated carbon/biological system (known commercially as PACT^R) and Wet Air Oxidation (WAO). Manufacturing wastewaters, containing several organics classified as toxic and hazardous under RCRA, are treated in the PACT^R system.

PACT^R is also used, however, to decontaminate 1.2 million gallons per day of groundwater that is pumped from beneath an abandoned landfill located on plant property.

Removals of orthochloroanaline (OCA) and dichlorobenzidene (DCB) are significant in the PACT^R system. COD reduction has averaged greater than 98 percent, even though the system must take heavy loads from on-going chemical production.

The wasted biomass and spent carbon from the PACT^R system are processed in a skid-mounted WAO unit; the biological sludge is oxidized, while the powdered carbon is regenerated and reused again in slurry form. Carbon recoveries of 97 percent or better have been common.

A second skid-mounted WAO unit is used to detoxify production wastes, providing roughing treatment of an acid waste stream prior to a crystallization process that produces fertilizer.

The PACT^R system was selected for cost-effectiveness and treatment capability following an engineering analysis of biological treatment, adsorption by granular carbon, combinations of biological and granular carbon treatment, chemical oxidation and sorption on such materials as bentonite and clay.

Actual capital and operating costs have confirmed the validity of the earlier review and selection; and in conjunction with the WAO units, PACT^R gives Bofors essentially total control of both its liquid and solid waste streams, cost effectively.

BACKGROUND

In 1977, the AB Bofors Group of Sweden bought Lakeway Chemical located just a few miles east of Muskegon's city limits. The purchase was part of a plan to increase the company's service level and participation in the U.S. specialty and fine chemical markets.

Shortly after the purchase, however, severe environmental problems—resulting from past disposal practices—surfaced at the site. More than 370 million pounds of sludge had been placed in on-site lagoons since 1971. Materials excavated from the lagoon area were used to form berms or dams to contain the sludges. Sludges consisted primarily of a watercalcium sulfate slurry containing several primary organic amine compounds—each with concentrations as high as 5,000 parts per million.

Due to the porous nature of surface and subsurface soils, groundwater beneath the site became contaminated with these organic compounds. This was a source of pollution of Black Creek—which ultimately flows to Lake Michigan.

In 1978, when the State of Michigan filed suit against Bofors-Nobel, the company voluntarily installed eight purge wells to intercept the contaminated groundwater and direct it to a public treatment plant.

In addition to the accumulated waste materials, continued chemical manufacturing at Bofors produced a variety of other waste streams. Many were too toxic for biological treatment and had required hauling by a commercial treater.

Bofors faces a difficult problem: how to expand production at its facility while at the same time resolving complex environmental issues. Together, these requirements would place heavy demands on capital resources.

A solution to the environmental problem could have involved creation of a burial vault to contain 170,000 cubic yards of primary sludges and 350,000 cubic yards of contaminated subsurface soils.

Some form of treatment of the contaminated groundwater, such as carbon adsorption units, would also be necessary.

However, Bofors felt that such a solution would not truly destroy the bulk of the contamination—thus leaving a legacy which might possibly have to be dealt with a second time.

Additionally, after investigation it became apparent that costs of destroying all toxic components through on-site treatment--while significant--were not so different than those for mere containment of the materials.

Thus, in 1982, Bofors joined with two other companies to form a separate company, Environmental Systems Corp. (ESC), to solve the environmental problems. Zimpro/Passavant Inc., of Rothschild, Wisconsin, and Chemical Waste Management, a Waste Management, Inc., subsidiary, were the other members.

ESC developed a combination of technologies and facilities which could be used to perform cleanup of the site and simultaneously process the wide variety of wastes from continuing and expanding chemical operations in an environmentally acceptable manner. The technologies are:

- Wet Air Oxidation;
- PACT^R system treatment;
- waste acid neutralization and detoxification
- secure landfill; and
- forced water-soil flushing.

Each technology or system can uniquely integrate with one another so as to permit the use of the lowest cost treatment or detoxification method for each of a wide variety of waste streams.

Ultimately, the environmental impact of ESC is to eliminate the discharge of any form of pollutant--gas, liquid or solids--from the plant site, and to completely rectify past disposal.

GROUNDWATER TREATMENT

Engineering Studies

The original site survey confirmed that a large volume of sludge existed south of the manufacturing facility. Acid wastes had been neutralized with calcium hydroxide, which precipitated calcium sulfate solids. This sludge was landfilled, and contained high levels of organics which were seeping into the groundwater.

As a first step, Bofors installed a purge well system to intercept the contaminated groundwater. About 1.3 million gallons of purge water per day were brought to the surface and discharged to the Muskegon County system. Table No. 1 indicates the results of a GCMS organic pollutant wide scan analysis of the purge water performed by the County Wastewater Authority in 1980. Fifteen different organic compounds are identified, the most concentrated being 2-chloroaniline, or OCA. The next most abundant organic in this analysis was benzene.

In response to an OCA minimization plan put forth by the County, Bofors began a series of treatment studies and pilot plant runs to determine the most cost-effective methods of reducing OCA and the other organic constituents such as benzidine and dichlorobenzidene (DCB), in the purge water.

The waste characterization strongly suggested that a combination of biological treatment and carbon adsorption would most likely be required to achieve the desire results.

Studies performed by the Ada, Michigan, engineering firm of Fishbeck, Thompson, Carr and Huber demonstrated that biological treatment (activated sludge) could accomplish reduction of the OCA, benzidine, chemical oxygen demand (COD) and total organic carbon (TOC). In addition, activated sludge treatment apparently reduced ethylenedichloride and toluene, likely from air stripping.

However, little consistency was observed for removal of DCB.

When physical adsorption on granular carbon columns was tested, DCB removals to levels near five parts per billion were achieves, but it was also apparent that considerably more carbon contact would be required to reduce DCB levels further.

These findings led Bofors and its consulting engineer to pursue additional testing of various combinations of carbon adsorption and biological treatment. Raw purge water was treated with carbon in one series of tests. Other tests attempted to answer questions relating to the use of carbon both prior to and after biological treatment (See Table 2).

It became obvious that the optimum system for the Bofors purge water would maximize hydraulic detention time, so that the OCA could be virtually eliminated, and would maximize carbon contact time so that the DCB could be reduced to less than 5 ppb. It was also obvious the conventional approach of using carbon columns in conjunction with activated sludge would be very costly under these conditions.

At this point, since both biotreatment and carbon adsorption appeared to be necessary, Bofors began experimenting by adding powdered activated carbon directly to the activated sludge system so that physical adsorption and biological treatment could occur simultaneously in the activated sludge reactor. Commercially, this treatment process is known as the PACT^R system, and is marketed by Zimpro/Passavant Inc. Such an approach increases the amount of time the waste constituents are in contact with both the carbon and the biological mass, and also exposes the wastes to treatment for the full solids residence time of the system, as opposed to only the hydraulic residence time occurs in a biological process. Testing indicated that this condition met the treatment objectives most cost effectively.

System Design

In the original plan, Bofors contemplated using a second stage for additional powdered carbon contact, following the PACT^R system, but results obtained in further pilot testing indicated the second stage was not necessary.

In the final design scheme, the purge water and process wastewater are to single-stage treatment, with wastewater aerated in the presence of a high concentration of powdered activated carbon (PAC) and volatile biological solids in the aeration basin.

Wastes are accumulated in an equalization basin. Phosphoric acid is added as a nutrient for the biomass.

In the aerator, the PAC concentration may range from 4,000 to 12,000 mg/l, depending on the influent wastewater characteristics and effluent quality required. Mixed liquor is composed of 50 percent PAC, 40 percent biomass, and 10 percent ash.

Due to the concentrations of PAC and biological solids maintained in the system, a high degree of reliable treatment is obtained. Toxic materials or shock loadings can be accommodated without upset; the carbon adsorbs materials which are non-biodegradable, and the biological organisms assimilate non-adsorbable pollutants.

The aerator, a circular, above-ground tank, is mixed by two, 100 horsepower downdraft turbine aerators. Two blowers are capable of providing 1,600 each. Aerator capacity is 1.5 million gallons.

Following aeration, treated wastewater is settled in a circular, above-ground, 1 million gallon skimmerless clarifier. Effluent is discharged to the Muskegon County Wastewater Treatment System.

Spent carbon and biomass are wasted from the system periodically, and treated in a separate titanium wet air oxidation process. This consists of a prefabricated skid-mounted unit, capable of processing 10 gallons of slurry per minute. At temperatures of 500°F and under pressures of 1,500 psig, the biological material associated with the carbon is oxidized to a small amount of inert ash, while the carbon is regenerated for use again.

The process operates autothermally on feed solids of 8 to 10 percent, utilizing double-pipe heat exchangers to conserve on fuel costs even further.

In addition to recovering virtually all of the carbon (Table 3), the process is cost effective since it eliminates the need to dispose of sludge from the PACT^R system—estimated at the onset of the project to be in the neighborhood of $350.00 per ton, or $600,000.00 per year.

Performance

The facility has been treating about 1.2 million gallons a day of contaminated groundwater pumped from beneath the old landfill site, and up to 600,000 gallons a day of process wastewater. A total of 780 million gallons has been processed since start-up.

More than 100 organic chemical components are received by the PACT system during a year; 90 are biodegradable and 10 are carbon adsorbable (see Table 4).

System effectiveness is shown on Table 5. COD reductions have averaged better than 98 percent, or from 6,000 ppm to well under 100 ppm. OCA and DCB in the effluent average less than 10 ppm and 2 ppm, respectively, despite influent levels that contain high concentrations and vary widely from day to day and hour to hour. The PACT^R system has also been nitrifying.

Annual operating costs budgeted for the PACT^R plus wet air regeneration systems for 1986, including solids disposal, neutralization, groundwater pumping, and county wastewater treatment charges, is less than $1.0 million a year, or less than 10¢ per pound COD treated. Regeneration of spent powdered activated carbon has proven to be cost effective as well. Some 2,500 pounds of carbon are recovered daily. Annual cost for regeneration, virgin carbon makeup and solids disposal is budgeted at less than $300,000 per year; without regeneration those same annual costs would exceed $1,000,000—and the problem of contaminated solids would not be eliminated.

RCRA WASTEWATERS

In addition to the accumulated waste materials, continued chemical manufacturing at Bofors-Nobel produces a variety of waste streams, some of which are too toxic for biological treatment and have required hauling by a commercial treater in the past. Expansion of manufacturing capacity, of course, produces more quantities of non-biodegradable wastes. A list of compounds contained in these production wastes is reported in Table 4.

Because these wastewaters are too dilute to incinerate economically, yet too toxic for even the PACT^R system, a second wet air oxidation unit is employed to reduce their toxicity before further treatment. This unit operates alongside the unit for carbon regeneration.

Wet air oxidation destroys toxics contained in aqueous solutions, or converts them to biologically degradable organics such as acetic acid.

The WAO unit is designed to operate at a temperature of 500°F. The unit has a capacity of 10 gpm with a design pressure rating of 2,000 psig.

Wastewater is pumped to the WAO system high pressure pumps from existing storage. The high pressure pumps raise the pressure of the wastewater to the 1,600-1,700 psig range. Following the high pressure pumps, a portion of the oxidizing gas—air—is added to the wastewater. The remainder of the air necessary for oxidation is added to the oxidation reactor downstream.

The wastewater-air feed is first preheated against hotter oxidation reactor effluent. Preheating is such that when the wastewater-air mixture is introduced into the downstream oxidation reactor, the heat oxidation will raise the mixture temperature to the desired maximum. Included in the pre-heating circuit is another heat exchanger using natural gas-fired hot oil which is used for start-up, and to sustain the process during periods when oxidation is not autothermal.

The reaction of oxygen-demanding components takes place in the oxidation reactor, which provides a 60 minute residence time.

The reactor effluent, comprised of oxidized liquor and spent air, is used to preheat the feed mixture in the feed heat exchanger prior to being cooled indirectly against plant cooling water in the cooler. Following cooling, the system pressure is released through a pressure control valve and the oxidized liquor-spent air mixture is separated in a separator vessel. A water spray in the scrubber-separator serves to cool the off-gases before discharge to a stack.

Like the other WAO unit at ESC, this one is also a prefabricated, portable package consisting of two 8′ x 35′ skids and a reactor vessel.

Performance

The wet air oxidation unit began operating at Bofors on process wastewater in April, 1983, and averaged 99.8 percent destruction for the toxic components in the feed stream (See Table 6). These components, produced during the manufacture of a pesticide product, were nonbiodegradable, ranging in concentration from 600 to 1,200 parts per million.

After wet oxidation, concentrations of the toxic components were less than 10 ppm, and often undetectable. The biodegradable effluent was pumped through the PACT^R system before discharge.

Currently, the WAO unit is used for another purpose. A 40 percent sulfuric acid wastestream is first neutralized with ammonia and then wet oxidized at 6 gpm. Organic contaminants are destroyed or reduced to short-chained compounds. The oxidized liquor is sent to a proprietary waste acid neutralization and detoxification plant--a continuous crystallization process that produces high nitrogen fertilizer which is sold for agricultural use.

Both WAO units at Bofors are operated around the clock. Solvent washes with caustic or nitric acid have proven effective for scale control. The frequency of washings is higher for the carbon regeneration unit, about once every two to three weeks.

In addition, hydro-carbon emissions from the wet air oxidation unit have averaged 0.63 pounds per hour, and are well within prescribed emission limits of 3.0 pounds per hour.

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(2) Meidl, John A. and Wilhelmi, Allen R., "PACT: An Economical Solution in Treating Contaminated Groundwater and Leachate", New England Water Pollution Control Association, January, 1986.

(3) Fishbeck, Thompson, Carr & Huber, Consulting Engineers, Ada, MI, "Treatability Studies for Groundwater Treatment", 1981.

(4) Bofors-Nobel, Inc., Presidents Council on Environmental Quality Entry Award, 1983.

(5) Environmental Systems Corp., Plant Operating Records, 1986-87.

Table 1

G.C./M.S. ORGANIC POLLUTANT WIDE SCAN ANALYSIS OF PURGE WATER

Compound	Concentration (ppb)
2-Chlorophenol	4
Phenol	6
Cresol	5
2-Chloroaniline	13,000
1,2 Dichloroethane	420
Benzene	4,900
Perchloroethylene	5
Toluene	1,500
Chlorobenzene	150
Ethyl Benzene	220
Dichlorobenzene Isomer	2,500
3,3-Dichlorobenzidene	86
Bis (Ethyl Hexyl) Phthalate	100
3-Chloroaniline	68
Benzidine Isomer*	65

* Mass spectrum is very similar but retention time is two minutes earlier.

Table 2

ANTICIPATED WATER QUALITY
(mg/l Unless Otherwise Indicated)

Parameter	Raw Waste Concentration	Separate Biological Treatment	Separate GAC Treatment	Biological and Carbon
BOD	30 to 40	0 to 5	N.E.	0 to 5
COD	70 to 80	5 to 10	N.E.	5 to 10
SS	25	5 to 10	N.E.	5
TOC	20 to 30	5	N.E.	<5
DCB	100 ppb	75 ppb	5 ppb*	5 ppb*
OCA	30	N.D.	300 ppb	N.D.
Benzidine	90 ppb	N.D.	15 ppb	N.D.
EDC	24 ppb	7 ppb	80 ppb	3 ppb
Toluene	130 ppb	12 ppb	30 ppb	12 ppb

* Detectability Limit
N.D. = Non-Detectable
N.E. = No Estimate or Data

Table 3

BOFORS-NOBEL

Powdered Carbon Usage
PACT^R/Wet Air Regeneration Systems

Carbon Dose, lb/d

Regenerated	2,500*
Virgin	50
Total	2,550

Virgin Carbon Makeup = 2.0%

* Quality check against virgin carbon using DCB standards shows 90% adsorption recovery efficiency.

Table 4

PARTIAL LIST OF PERMITTED COMPOUNDS
BOFORS-NOBEL INC., MUSKEGON, MICHIGAN

Acetone
Aliphatic Amine
Allyl Alcohol
Ammonium Dithiocarbamate
Ammonium Thiocyanate
Aniline
B-Chloroaniline
B-Napthylamine
Benzene
Benzidine
Benzoic Acid
Biphenyl-OL
Biphyridene
Bis (ethyl hexyl) pthalate
Chloroaniline
Chlorobenzene
Chlorophenol
Cresol
Dichlorobenzene
Dichlorobenzidene
Dimethylaminexylanol
Dinitrotoluene
Di-N-Propylformamide
Diphenylether
1,2-Dichloroethane
Chlorobiphenyls
Ethyl Acetate
Ethyl Benzene
Formaldehyde
Isophorone
Methylene Chloride
Methylpyridine
Nitrocresol
Nitropthalic Acid
Perchloroethylene
Phenol
Phenoxybiphenyl
Phenylnaphthalene
Pthalic Acid
2-Propanol
Sodium Acetate
Tetrachloroethylene
Toluene

Table 5

WASTE TREATMENT PERFORMANCE
BOFORS-NOBEL, INC.

PACT^R Wastewater Treatment

	Influent	Effluent	Percent Removal
Flow, MGD	1.8	-	-
COD, ppm	6,000	< 100*	98.33
Orthochloroanaline, ppb	53,000	< 10	99.98
Dichlorobenzidene, ppb	12,000**	< 2	99.83
Suspended Solids, ppm	-	< 10	-
Ammonia Nitrogen, ppm	150-200	< 10	94.29

* Recent 7-day composite samples, ppm:

8/12/86	63
8/26/86	72
9/09/86	34
9/23/86	64
10/14/86	42

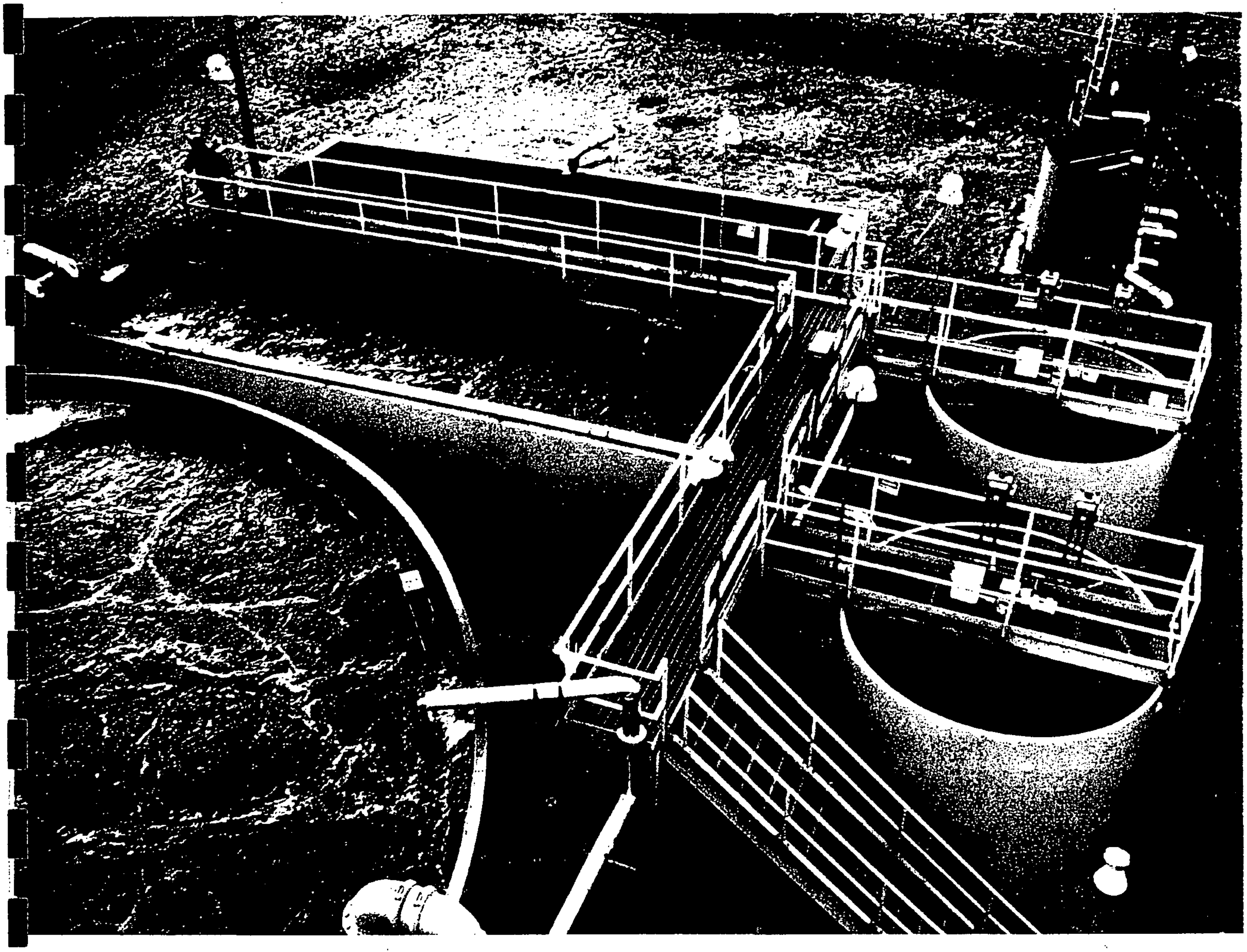
** Measured as soluble DCB. Actuals higher since DCB often received in high solid state.

Table 6

WET AIR OXIDATION UNIT
(Results on Original Waste Stream)

Design Flows: 10 Gallons/Minute, or 14,400 Gallons/Day

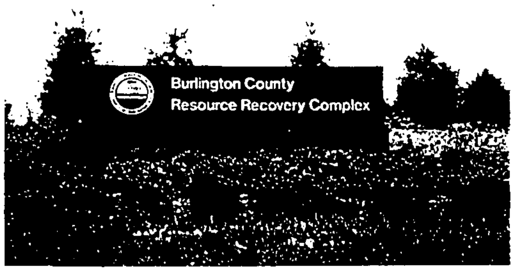
	Feed	Effluent	Percent Reduction
Toxic Component	600-1,200 ppm	2-9 ppm	99.8%
COD	70-80 g/l	30-40 g/l	50+%
Actual Flows	4,500-7,500 gpd		



Landfill leachate treatment

Innovations in South Jersey

Burlington County Resource Recovery Complex uses PACT® system to meet direct discharge requirements for leachate.

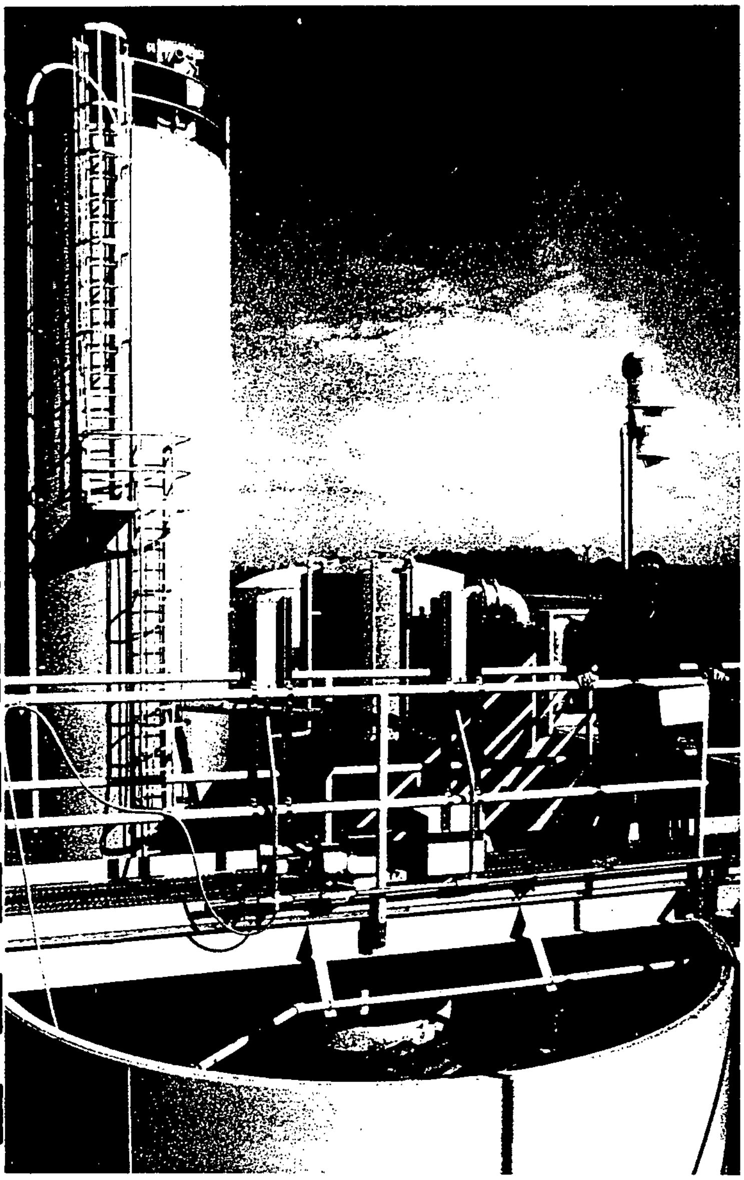


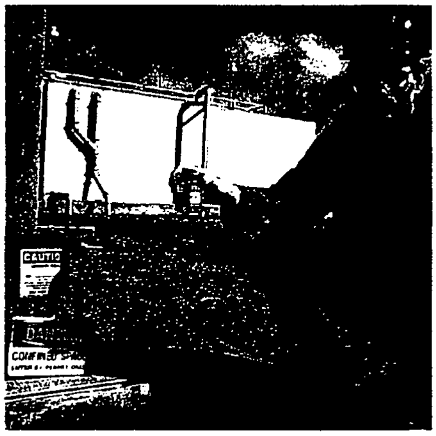
The new Burlington County, NJ, Resource Recovery Complex near Columbus, northeast of Philadelphia, is implementing many of the latest technologies for solid waste management. Among them is a PACT® system, supplied by Zimpro Passavant Environmental Systems, Inc., for on-site treatment of landfill leachates.

The PACT system was chosen for its ability to handle changing leachate characteristics, including toxic shock loadings. In the system, powdered activated carbon is added to biological treatment, so that physical adsorption and biological assimilation occur simultaneously. The carbon adsorbs contaminants that cannot be treated biologically. The carbon dose can be easily changed as waste concentrations change.

The Burlington County Facility began accepting waste in early 1989. It is situated on a 482-acre site over a major clay aquiclude. Fifty-four acres are permitted for secure non-hazardous solid waste cells. The facility serves a population base of some 400,000 people.

Reprinted from the Reactor.
No. 71. August. 1991.





Innovative treatment. Opposite page, two-stage aerobic PACT system at work on Burlington County landfill leachate. This page, clarifiers with carbon silo in background; effluent samples illustrate good performance.

Data:

Facility: Burlington County Resource Recovery Complex.

Zimpro Passavant equipment: PACT system, two-stage, aerobic.

Capacity: 50,000 gal/d.

Application: Landfill leachate.

Startup: April, 1989.

Owner: Burlington County, NJ, Board of Chosen Freeholders.

District Solid Waste Manager: Bob Simkins.

Design consultant: Richard A. Alaimo Engineering Co., Mt. Holly, NJ.

Zimpro Passavant representative: Riordan Materials Corp., Blue Bell, PA.

SI units: 50,000 gal/d = 190 m^3/d
482 acres = 193 ha
45 ft = 13.7 m
12 ft = 3.7 m

As Bob Simkins, District Solid Waste Coordinator, explains, the facility design includes a number of innovations to capitalize on recycling potential, and to minimize adverse environmental impact.

Included are a materials recovery facility for processing wood waste, corrugated, newsprint, plastics, and tires; a refuse-derived fuel and co-composting facility for solid waste and sewage sludge; a permanent household hazardous waste facility; a wood waste processing center; and two planned greenhouses, one in conjunction with the composting operation and the other with the landfill.

The PACT system.

The leachate treatment system at Burlington County has a treatment capacity of 50,000 gallons per day. It includes storage and flow equalization tanks which permit a regulated flow to the treatment processes. Then, leachate is pumped to a flash mix tank for pH control, and then to a flocculation tank where polymer is added to enhance settling of heavy metals.

After clarification, the leachate is directed to the PACT system – consisting of two aerobic stages, operated in series. In the first aeration chamber (45-feet in diameter) powdered activated carbon is added to the biomass so that physical adsorption and biological treatment occur simultaneously. In the second aeration chamber, the mixed liquor contains primarily powdered activated carbon to polish the effluent further.

Following treatment, flow passes to two 12-foot diameter clarifiers, and then to a chlorination tank. Following that, sulfur dioxide is used for dechlorination and the product water is discharged to a tributary of the Delaware River.

Bottom line.

Typical results for removal of COD (chemical oxygen demand) and ammonia nitrogen are shown in the following data:

Burlington County (NJ) Leachate Treatment Results (mg/L)

	COD		NH_3	
	in	out	in	out
1.91	2115	59.5	29.6	2.04
2.91	3003	101.5	47.4	0.132
3/91	988	48.0	23.5	0.135
4/91	3856	36.5	80.0	7.2

In addition to treating leachate from current operations, the PACT system will also treat leachate from an adjacent closed municipal waste landfill that is on the Superfund list.

"That future operation – made possible by the leachate treatment process in place – will represent a unique use of public infrastructure to help solve additional environmental problems," says Simkins.

APPENDIX E

TECHNICAL REPORT NO. 011

CONJUNCTIVE USE OF POWDERED ACTIVATED CARBON IN A SEQUENCING BATCH REACTOR

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CONJUNCTIVE USE OF POWDERED ACTIVATED CARBON IN A SEQUENCING BATCH REACTOR

by

JAMES H. KYLES, KENNETH C. MALINOWSKI,
A. SCOTT WEBER, and MARK R. MATSUMOTO

INTRODUCTION

Sequencing Batch Reactor (SBR) and Powdered Activated Carbon (PAC) treatment have each been proven to be useful and effective methods for the treatment of municipal and industrial waterwater[1]. The addition of PAC to a continuous flow activated sludge system has been shown to enhance organic carbon removal, enhance nitrification at low temperatures, dampen shock loads, remove priority pollutants, and improve sludge settleability[2]. The SBR has inherent advantages over continuous flow activated sludge systems in that its time oriented design offers decreased capital costs, greatly reduces filamentous bulking of biomass, improves clarification, reduces energy requirements, and allows flexibility to enact various treatment schemes, depending on treatment needs[3].

This paper presents research performed to determine the operating benefit of supplementing an SBR with PAC to provide stability from COD load variations and from toxic shocks. The research has direct applicability to the SBR system owned and operated by CECOS International, Inc. in Niagara Falls, NY.

BACKGROUND

CECOS International owns and operates a major treatment, storage, and disposal facility (TSDF) for industrial and hazardous wastes in Niagara Falls, New York. This facility utilizes an SBR for the biological oxidation of soluble organics present in the aqueous hazardous waste received from outside clients, and from leachates generated on-site from the Secure Chemical Management Facilities (SCMFs). Leachates are received in tank L-6, identifiable from Figure 1, while customer receipts are received and stored in Tank L-5. These tanks each have an equalization capacity of 1,140 m^3.

The received wastewaters are combined and the pH of the solution is adjusted to 7.0 in tank L-8, a 170 m^3 agitated reactor. Neutralized fluid is stored in the 1,140 m^3 SBR feed tank, L-7. Wastewaters are fed on a batch basis to the SBR, an 1,890 m^3 reactor containing a Jet-Tech aeration system, and controlled by a programmable control system.

After biological treatment, the treated wastewater is discharged through a floating decanter to a pre-carbon surge tank, L-12, having a capacity of 1,440 m^3. Treated wastewater is polished through multi-media filters and granular activated carbon (GAC) beds, prior to subsequent batch discharge to the City of Niagara Falls municipal treatment plant.

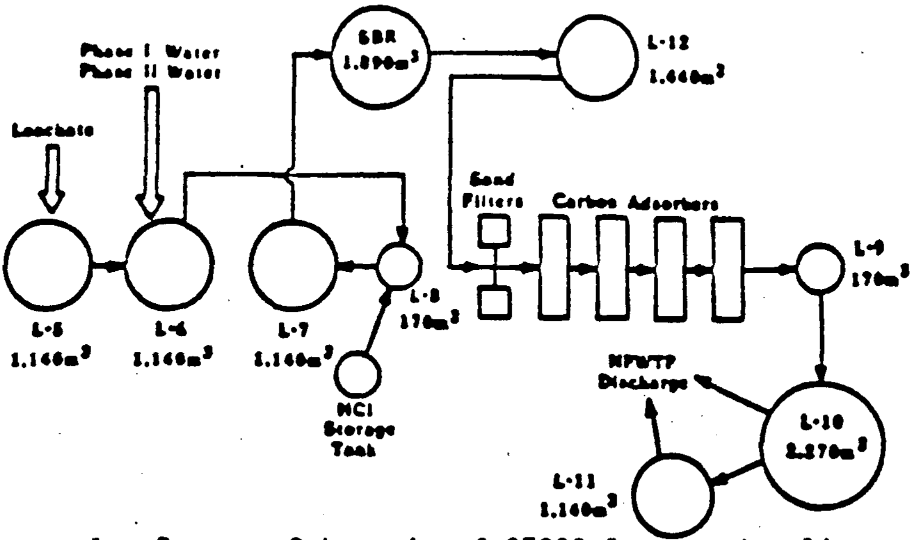


Figure 1: Process Schematic of CECOS International's Wastewater Treatment Plant, Niagara Falls, NY

The wastewaters treated through the SBR have been noted to vary in chemical composition, primarily due to the varying receipts from customers. This variation has, at times, resulted in temporary process upsets in the SBR, leading to a utilization of the GAC system to supply primary removal of aqueous organics. This shift from the typical role of a polishing mechanism has negative cost impacts on the wastewater treatment plant.

Although reasonably complete descriptions of SBR and PAC/activated sludge processes have been presented by Herzbrun et al[4] and Meidl and Wilhelmi[5], respectively, an overview of the technologies is provided below for the readers convenience.

SBR Process Description

The SBR is a modified activated sludge system which operates on time-based orientation as opposed to the space-orientation of the conventional activated sludge system. Typical operation of an SBR involves five cycles: FILL, REACT, SETTLE, DRAW, and IDLE. During the FILL cycle, wastewater is fed to the SBR which is experiencing either completely mixed, aerated, or anoxic conditions, depending on treatment needs. Wastewater may be added to the SBR quiescently, thus delaying biodegradation until the REACT cycle. During the REACT cycle, biological degradation reactions are initiated, and/or completed.

Following the REACT cycle, mixing and aeration activities are stopped and the solids within the reactor are allowed to settle. The clarified effluent is decanted from the SBR during the DRAW cycle. After DRAW, the tank may either receive additional wastewater for processing or a final IDLE cycle may be utilized for equipment maintenance, wasting of biomass, etc., as desired.

Figure 2 provides a pictorial description of the SBR process.

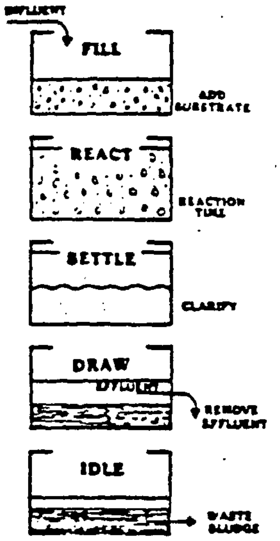


Figure 2: SBR Process Description

PAC/Activated Sludge Process Description

The addition of PAC to activated sludge provides an extension of the activated sludge system, particularly enhancing the system's ability to function in the treatment of industrial wastewaters. The addition of PAC allows chemisorption of non-biodegradable or bio-toxic contaminants, and provides teritary treatment quality to the effluent. Depending on waste characteristics, mixed liquor carbon levels in the aeration basin of the activated sludge system may range from 1000 mg/L upwards to 10,000 mg/L. Figure 3 illustrates the PAC/activated sludge process.

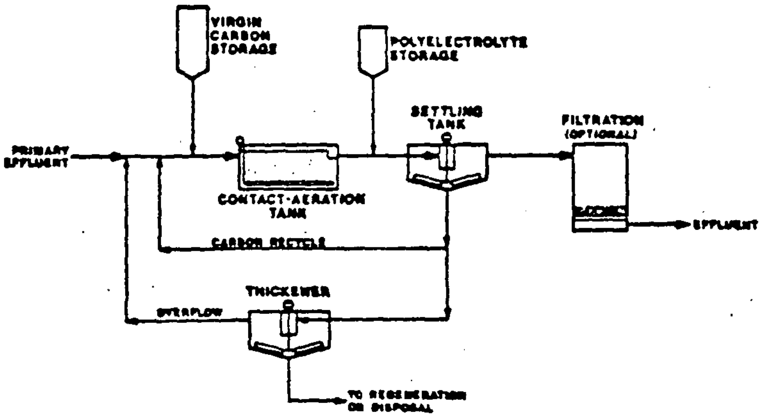


Figure 3: Typical PAC/Activated Sludge Process Flow Diagram

As wastewater enters the aeration chamber of the system, a slurry of virgin and/or recycled PAC is added to the reactor at a rate required to maintain the desired carbon dosage. In the aeration tank the PAC and biomass combine to form a dark sludge having good settling characteristics.

Wastewater mixed liquor typically overflows from the aeration tank to a secondary clarifier where sludge settles. Underflow clarifier solids are pumped in concentrations typically ranging from 3% to 5% back to the inlet of the aeration tank. Wasting of excess solids, which is a mixture of PAC, biomass, adsorbed organics, and inerts, may occur from the recycled activated sludge (RAS) line, or from the clarifier itself. Typically, waste sludge is dewatered and subsequently transferred for high temperature oxidation. Organics are incinerated and PAC is regenerated for recycle/reuse.

Process kinetics may be enhanced in the PAC/activated sludge system through three possible mechanisms: (1) enhanced bioactivity; (2) bioregeneration of the PAC; and (3) metabolic end product (MEP) adsorption[6].

Enhanced bioactivity is the ability of the PAC to increase the biological assimilation of organics by an activated sludge system. This phenomenon may be caused by a number of mechanisms, including: increased organic concentrations at the PAC surface; extended contact time between the biomass and adsorbed organic compounds; increased oxygen concentrations at the PAC surface; adsorption of compounds that are toxic to the biomass, and alterations of the microbial population by adsorption of non-flocculating bacteria. Of these, the only mechanism shown, to date, to be operative is protection of the microbial population by adsorption of toxic compounds[7].

Bioregeneration is the process by which adsorbed organics become available for biodegradation, thereby renewing the PAC site for further adsorption. Adsorbed organics may be removed either by de-adsorption, by bacterial assimilation, or by enzymatic attack.

A major portion of the soluble organics in the effluent of activated sludge systems is not the original substrate, but is MEP synthesized by the biomass[8]. MEP may be highly adsorbable; therefore, coupled PAC/activated sludge system may provide an ideal solution for the removal of MEP.

An interesting extension of current SBR research involves the addition of PAC to a functioning SBR system. As was identified previously, the use of PAC in a conventional activated sludge plant improves process kinetics. However, the need for flow equalization and effluent clarification still exists. By using the SBR's ability to function as equalization, aeration, and clarification tanks in one reactor, the PAC/SBR process may offer a simplified solution to industrial wastewater treatment problems.

EXPERIMENTAL DESIGN AND OPERATION

The experimental procedures were conducted in the Water Resources and Environmental Engineering laboratories at the State University of New York at Buffalo, Department of Civil Engineering. The reactors utilized consisted of four (4) 4-liter polycarbonate containers. Each container was covered and vented for the removal of any volatile organic compounds (VOCs) which may have been present in the wastewater. Wastewater was delivered to and withdrawn from the SBRs through peristaltic pumps. Pumps were adjusted to allow continuous feeding and withdrawal throughout the FEED and DRAW cycles.

Air was provided to each reactor by plant air available at the University, and controlled through automatic solenoid valves. Mechanical mixers provided additional agitation to the reactor during FILL and REACT cycles. All operational parameters, including pumping, aeration, agitation and discharge were microprocessor controlled.

During the study, the SBRs were subjected to a program of "normal" operations, mimicking the full scale SBR at Niagara Falls. In addition, a series of experiments investigating PAC types and dosage requirements was conducted. The experimental operating procedures for each phase of the study are discussed below.

Carbon Utilization Study

Prior to the actual start-up procedure for the reactor studies, an investigation of carbon utilization rates was conducted. This study was performed to provide an assessment of various PAC types and dosages, and to develop a database from which the PAC/SBR reactor experimental design criteria could be based.

Samples of neutralized wastewater were obtained from tank L-7 at the CECOS International, Niagara Falls Facility. Various grades and types of PAC were obtained from manufacturers. Adsorption isotherm studies were performed on: (1) raw wastewater; and (2) wastewater after 24 hours of intimate aeration with biosludge from a local POTW (public owned treatment works). Initial isotherms performed on raw wastewater indicated extremely high PAC dosages were needed to achieve effective treatment (ie., 200,000 mg/L). As a result, it was determined that subjecting the raw wastewater to aerobic bio-oxidation to remove biodegradable organics that were competing with target biostatic and biotoxic pollutants would prepare the sample so that isotherm results would be meaningful.

The methodology utilized for the isotherm tests consisted of a modification of the Freundlich isotherms proposed by Cheremisinoff and Ellenbusch[9], in that three screening dosages were evaluated as compared to the recommended 8 or 9. Results of the isotherm tests were converted to carbon utilization rates (mass of adsorbent needed per volume of influent wastewater) for various effluent COD concentrations. For the purposes of this study, a 500 mg/L effluent COD concentration was selected as a process goal, and carbon dosages necessary to obtain that target were calculated for all test carbons.

The PAC used in the study was selected based on process economics. The unit costs associated with each PAC tested were applied to the dosage necessary to obtain an effluent quality of 500 mg/L COD. Any operational concerns (i.e., poor PAC settling characteristics, etc.) were also considered prior to a selection of a PAC for use in the SBR study.

Normal Operations

At the CECOS SBR operation in Niagara Falls, New York, an average of 304,000 liters of wastewater are processed daily through the 1,890 m^3 SBR, equating to a hydraulic retention time of approximately six (6) days. Although flows have reached a peak of 685,000 l/day for short durations, the typical peak flowrate during wet weather (high leachate generation) averages 475,000 l/day. For the PAC/SBR study, a five-day hydraulic retention time was selected for all test reactors. This represented a mean between the observed average and peak full-scale flowrates.

The four (4) test reactors contained a maximum operating volume of 2.5 l during the study, each receiving 0.5 l of feed daily. Target PAC dosages in reactors #1-3 were 500, 1000, and 2000 mg/L, respectively. Reactor #4 served as a control reactor and received no PAC supplement.

During the study, a 2-hour FILL cycle was utilized, during which the SBR was under completely mixed and aerated conditions. An 18 hr. REACT cycle was used, followed by 2 hr. SETTLE and 2 hr. DRAW phases. One hour of IDLE time was provided at the end of the SBR cycles to provide for reactor maintenance.

After an initial start-up period, the SBRs were supplied wastewater that was periodically obtained from the CECOS facility. During storage, all wastewater samples were stored at $4 \pm {}^{0}C$. Initial sludge was obtained from the Town of Amherst, NY, Wastewater Treatment Plant.

RESULTS AND DISCUSSION

Carbon Utilization Study

As noted previously, ten (10) different PAC samples were screened prior to the initiation of reactor studies. The results of this study are summarized in Figure 4.

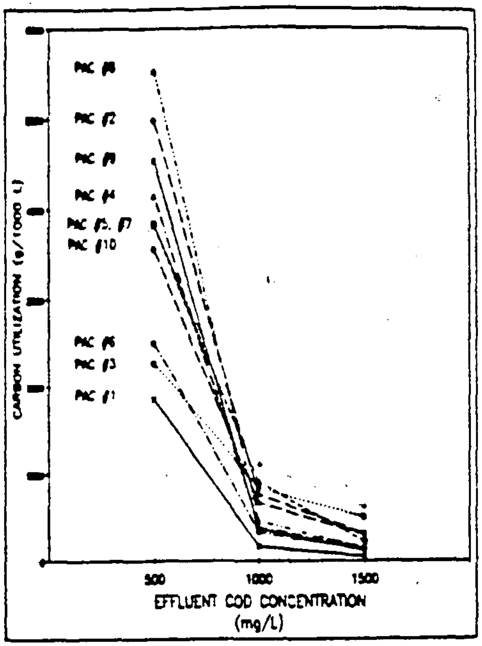


Figure 4: Powdered Activated Carbon Utilization Comparison Study

Although a wide disparity in utilization curves was noted, the spread of the curves at an effluent COD concentration of 500 mg/L was particularly useful in selecting the PAC desired. PAC nos. 1, 3 and 6 clearly had superior utilization rates when lower effluent COD concentrations were desired. PAC nos. 1 and 6, however, were samples of two virgin PACs, while PAC #3 contained a regenerated carbon which was blended with virgin PAC. All three PACs were comparable in physical characteristics (i.e., particle size).

The cost of the carbons tested ranged from $1.10/kg to a high of $6.61/kg. A cost comparison of PAC nos. 1, 3, and 6, for effluent COD concentrations of 1500, 1000, and 500 mg/L is provided in Table I.

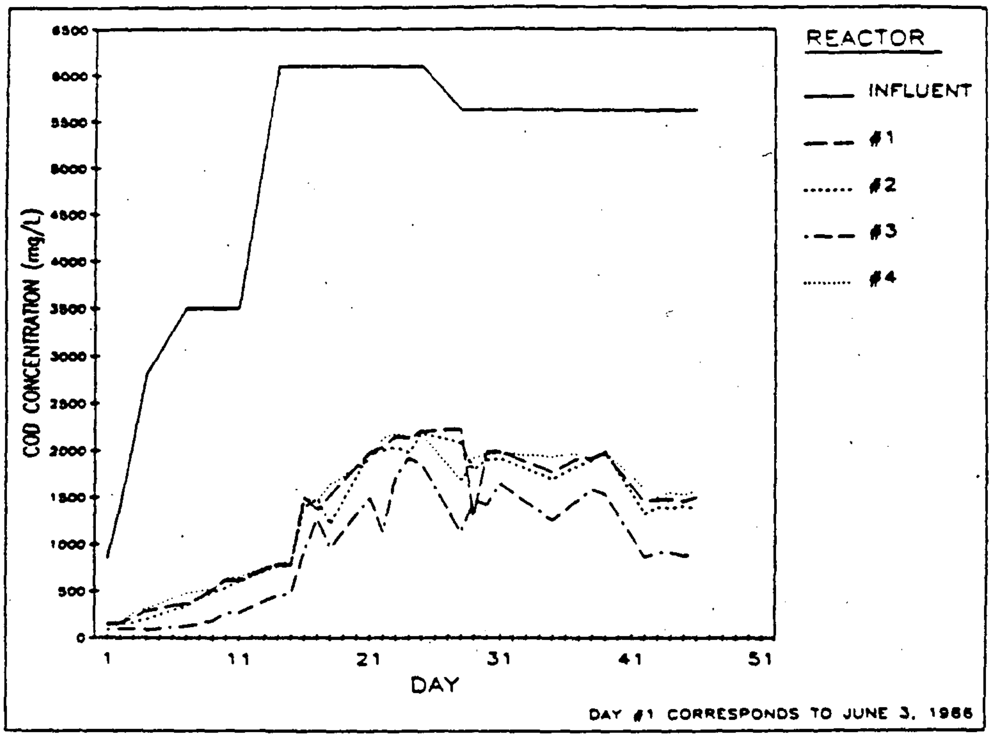
Table I: Cost Comparison of PACs Nos. 1, 3 and 6

		Cost ($/1000 l wastewater)		
PAC #	Cost ($/kg)	500 mg/L	1000 mg/L	1500 mg/L
1	6.61	12.24	1.10	0.33
3	2.20	4.99	1.84	1.10
6	5.51	13.82	1.85	0.72

As can be seen, the cost of carbons nos. 1 and 6 increase dramatically as effluent COD concentrations decrease. In a full scale SBR operation, the control of the PAC concentration in the reactor will, most likely, be difficult to control. It is expected that overdosing the reactor to compensate for PAC lost during DRAW will be common. As a result, the lower cost of PAC #3, coupled with the good removal characteristics noted in Figure 4 clearly identified PAC #3 as the carbon of choice for the remainder of the study.

Reactor Study

All four reactors were started by slowly introducing wastewater, on a diluted basis, in the normal SBR operating mode. The results of this phase of the program are tabulated in Table II. The variations in influent and effluent COD for the reactors is presented in Figure 5.



DAY #1 CORRESPONDS TO JUNE 3, 1986

Figure 5: Reactor Influent and Effluent COD Concentrations

During the time period of this study, MLVSS and PAC concentrations in the reactor were periodically determined using nitric acid digestion procedure[10]. Figures 6 and 7 illustrate a graphical history of these values, respectively.

From Figure 5, it can be noted that the addition of PAC to the SBR enhanced the removal of COD from the reactor. By comparing the effluent quality of reactor #4, the control reactor, to reactor #3 which had a target PAC dose of 2000 mg/L, it can be seen that substantial levels of COD were removed that, under the current system, would have been passed on to the GAC system. Figure 8 provides a clearer comparison of the effluent quality (COD) for reactors #3 and #4.

Table II: Summary of Reactor Performance

Day	Influent COD (mg/L)	Effluent COD mg/L			
		Reactor 1	Reactor 2	Reactor 3	Reactor 4
1	850	147	147	88	140
2	1400	162	148	100	151
3	2100	211	161	96	269
4	2800	289	205	91	319
5					
6					
7	3500	373	342	129	479
8	3500	425	429	150	499
9	3500	517	484	184	523
10	3500	615	537	269	630
11	3500	615	600	272	655
12					
13					
14	6100	780	765	456	791
15	6100	769	765	471	802
16	6100	1498	1382	922	1478
17	6100	1363	1478	1267	1459
18	6100	1512	1210	959	1636
19					
20					
21	6100	1974	1955	1485	1899
22	6100	2030	1993	1123	2124
23	6100	2143	2030	1730	2181
24	6100	2124	1974	1918	2143
25	6100	2200	2181	1842	2162
26					
27					
28	5630	2226	2079	1122	1674
29	5630	1877	1785	1454	1941
30	5630	1987	1895	1417	1951
31	5630	1987	1914	1638	1967
32					
33					
34					
35	5630	1766	1693	1251	1932
36					
37	5630	1914	1840	1472	1969
38	5630	1914	1895	1582	1895
39	5630	1969	1987	1527	1987
40					
41					
42	5630	1454	1325	897	1591
43	5630	1469	1390	907	1498
44	5630	1479	1384	913	1553
45	5630	1450	1406	876	1524
46	5630	1496	1373	892	1568

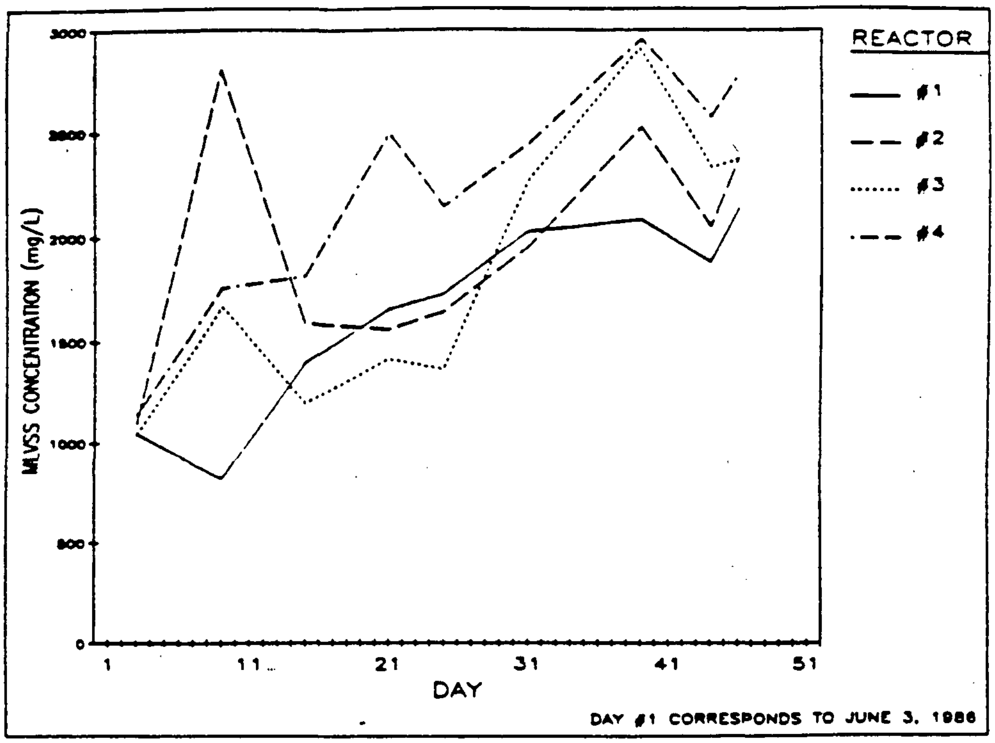


Figure 6: MLVSS Concentrations for Reactors

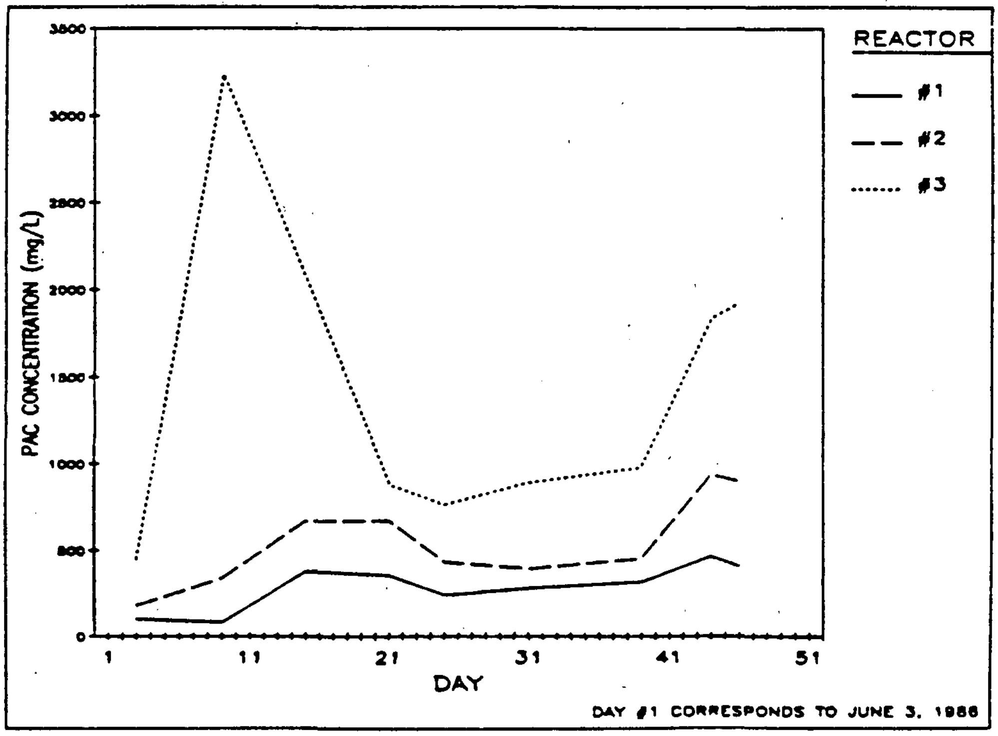


Figure 7: PAC Concentrations for Reactors

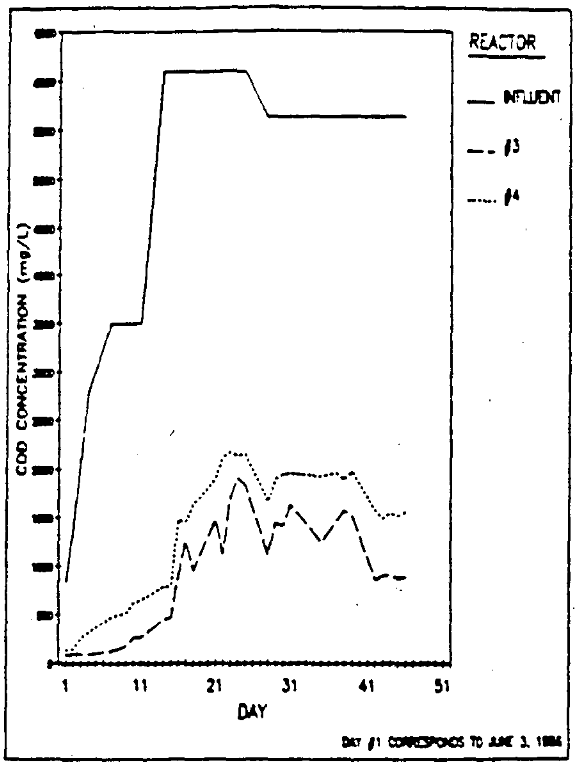


Figure 8: Comparison of Effluent Quality for Reactors #3 and #4

It is often desireable to identify the removal efficiency of a unit operation. For steady-state systems with no accumulation, the mass balance for the system is simplified to:

Output-Input = Generation (1)
where, in the case of a biological treatment process

Generation = removal of substrate by biooxidation (2).

To determine if this simple mass balance could accurately describe the SBR systems investigated and, subsequently, to determine if a removal efficiency for COD could be determined based on influent and effluent COD concentration, plots of the reactor COD mass were prepared. The COD contents of each reactor were calculated immediately after the introduction of substrate to the reactor and immediately prior to the removal of treated wastewater from the reactor. Figures 9 through 12 are provided as illustrations of the reactors' COD content over time.

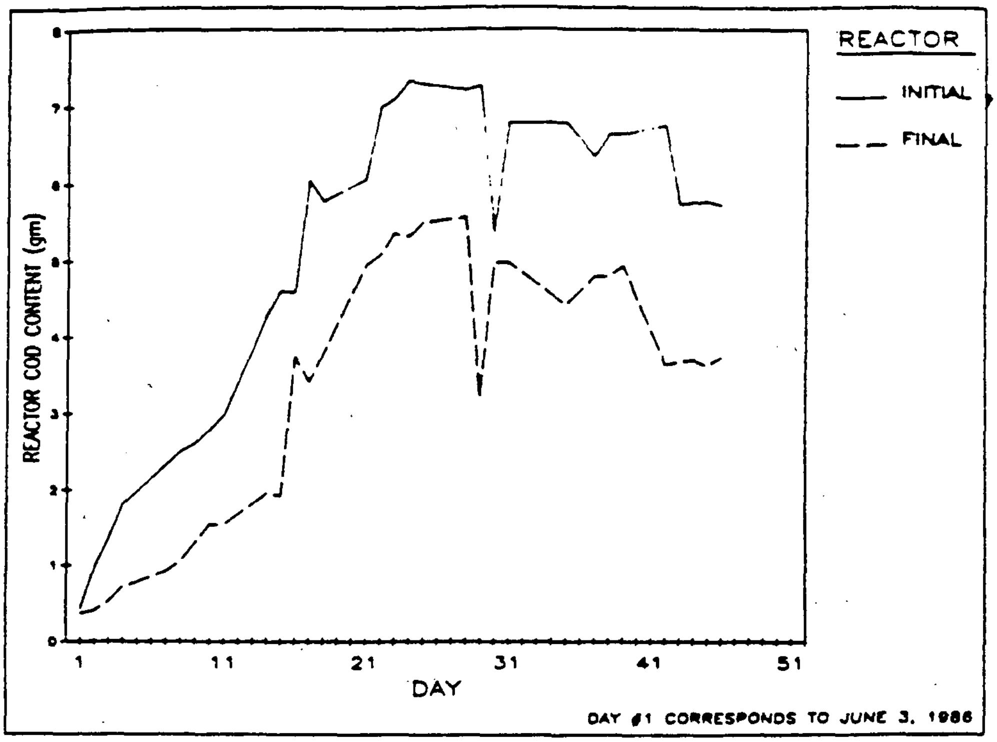


Figure 9: Reactor #1 - COD Content History

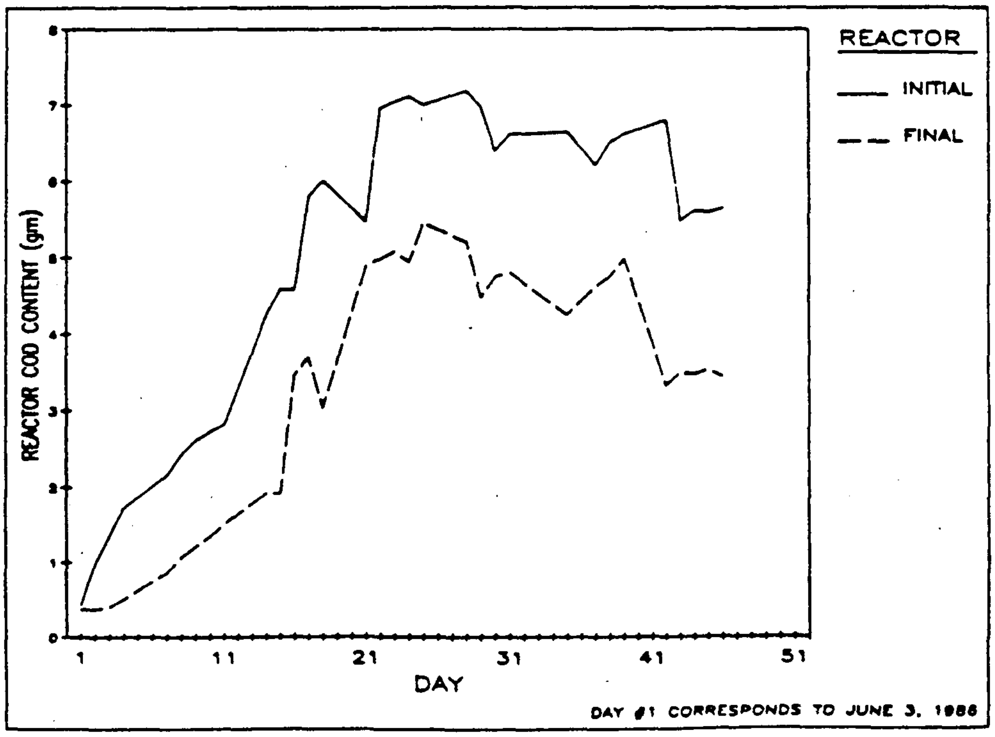


Figure 10: Reactor #2 - COD Content History

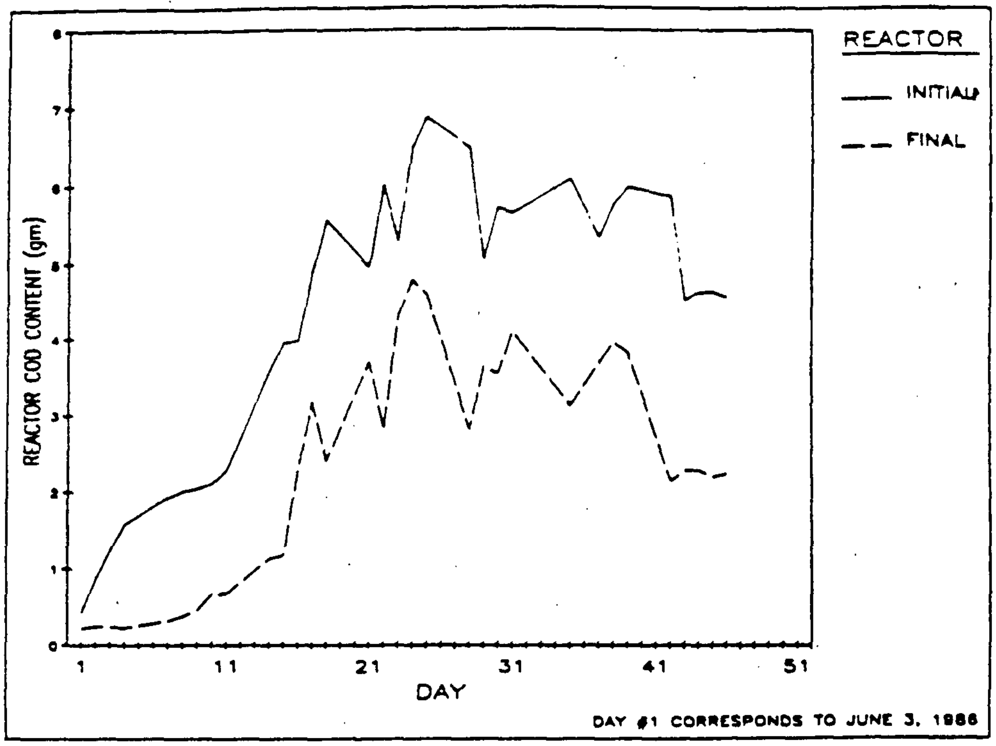


Figure 11: Reactor #3 - COD Content History

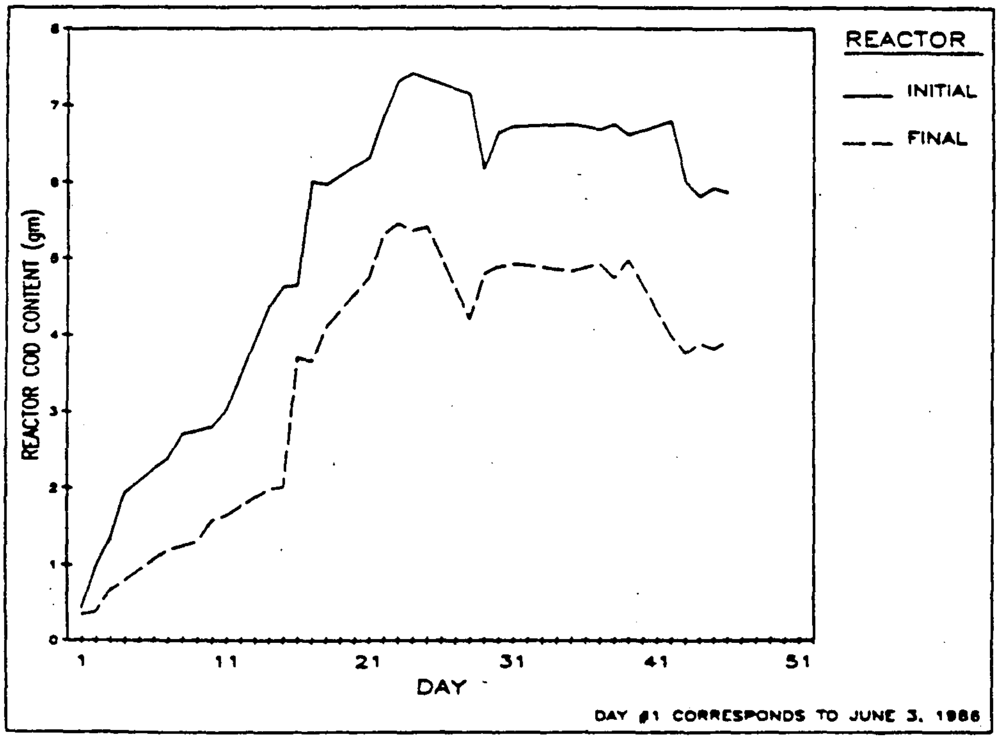


Figure 12: Reactor #4 - COD Content History

> As can be seen, the COD content of each reactor varied with time. The calculation of a COD removal efficiency based solely on concentration would, therefore, be erroneous due to the accumulation of COD within the reactor. The calculation of a removal efficiency based on the mass difference in the reactor before and after the REACT cycle would yield a more meaningful value.

An area of interest during this study involved the PAC addition requirements throughout the reactor studies. As may be noted by reviewing Figure 7, the PAC level within each reactor dropped occassionally. This was noted for periods of the study when no supplemental PAC was added. Although early data is suspect due to unfamiliarity with the nitric acid digestion procedure for determining PAC concentrations, it was observed, through effluent filtration, that some quantity of PAC did exit the reactor as suspended solids. The quantification of this PAC loss and a subsequent economic analysis of the PAC/SBR as compared to CECOS' existing SBR/GAC system is the subject of ongoing investigations.

As discussed earlier, one of the expected advantages of using the PAC/SBR as compared to the standard SBR system is the ability of PAC to buffer a biological system from shock loadings. A review of Figures 9-12 provides insight on the PAC/SBR's ability to buffer the system to the variabilities common to a commercial hazardous waste treatment facility. By comparing reactors #3 and #4, it can be seen that the addition of PAC facilitates the removal of COD from the wastewater and lowers the probability of accumulating COD to the extent seen in Figure 12. Planned research activities in the near future include shocking the four reactor systems with selected pesticide and herbicide priority pollutants to determine the resilience of each system to shocks.

CONCLUSIONS

The following conclusions may be drawn from the results available to date:

1. The addition of powdered activated carbon to an SBR increases the system's ability to remove soluble organic compounds from a wastewater;

2. Mass removal efficiencies for the systems, based on reactor COD content, should be used as compared to typical concentration based removal efficiences;

3. PAC dosages required for the PAC/SBR are expected to be economically competitive as compared to the existing PAC/GAC system, although not quantified by current research; and

4. The results of the current study support the theory that the PAC/SBR has an increased resistance to toxic shock as compared to a standard SBR. This conclusion is based on a qualitative review of the current results and will be quantified through upcoming research.

ACKNOWLEDGEMENTS

Credits. Laboratory testing was performed at the Water Resources and Environmental Engineering laboratories at the State University of New York at Buffalo, Department of Civil Engineering. The reactor systems were constructed and operated by Harpreet S. Nayyar. This project was wholly funded by CECOS International, Inc.

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APPENDIX F

TECHNICAL REPORT NO. 059

WASTEWATER TREATMENT AND GROUNDWATER RECHARGE: A LEARNING EXPERIENCE AT EL PASO, TEXAS

By:
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Parkhill, Smith & Cooper, Inc.

Javier Hernandez, Superintendent;
Fred Hervey Water Reclamation Plant, and

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Presented At:
1987 AWWA Conference
Denver, Colorado

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WASTEWATER TREATMENT AND GROUNDWATER RECHARGE: A LEARNING EXPERIENCE AT EL PASO, TX

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I. INTRODUCTION

A unique wastewater reclamation and groundwater recharge project has been in operation since June, 1985, at El Paso, Texas. At the 10 million gallon per day Fred Hervey Water Reclamation Plant, domestic sewage is treated in a state-of-the-art system consisting of ten separate steps before effluent is returned to the aquifer via a system of 10, 800-foot deep recharge wells. Ultimately, the treated wastewater returns to the city's potable water system.

Recharge was chosen for El Paso because: a) It solves existing wastewater problems; b) it adds to the steady-state drinking water supply; c) It is a prototype for larger-scale recycling which would provide more than one-fourth of El Paso's water needs over the next 70 years; d) The water supply benefits of recycling are judged by the public to warrant increased dollar costs, resource use and environmental impacts; e) Alternative wastewater recycling projects do not address municipal water supply concerns; and f) Alternative water supply projects, such as importation, are even more expensive and will result in significant resource use and environmental impact.

Since the recharge water is being added to a protected raw water supply, meeting drinking water standards is a criteria. For these reasons, the treatment process must have a high factor of safety for removal of those pollutants which are difficult to identify, particularly toxic materials, trace organics, and viruses. Chosen to accomplish these objectives were a multistage PACT^{TM} system in conjunction with lime treatment, recarbonation, sand filtration, ozone disinfection, and GAC adsorption. Primary solids are anaerobically digested, dewatered and composted. All secondary/treatment solids (PACT^{TM}) are regenerated in a wet oxidation unit. Waste ash from the wet oxidation unit plus chemical solids from lime treatment are taken to drying beds. Performance and operating costs of the overall system are detailed herein.

II. DESCRIPTION OF PROCESSES

A. Primary Treatment

Treatment begins with primary screening, degritting, sedimentation and flow equilization. Primary sludge is anaerobically digested and dewatered on sand drying beds prior to composting. Digester gas is used for fuel.

B. PACT^TM/Wet Air Regeneration Systems

Primary effluent then enters a two-stage biophysical process which combines activated sludge with powdered activated carbon adsorption (PACT^TM system). This portion of the system is designed for organic removal as well as nitrification and denitrification. Methanol is added to the second stage to provide a carbon source for the denitrifiers. Waste secondary sludge and spent carbon are passed through a wet oxidation unit which destroys the sludge while regenerating the carbon for use again.

The PACT wastewater treatment system was designed to process 10 MGD. The primary effluent and PACT effluent design concentrations are given in Table 1. The system is designed to also treat the recycle stream from the wet air regeneration unit. The major design sizings are given in Table 2. The PACT system was selected for its ability to achieve much lower effluent COD levels than the conventional activated sludge process, thus minimizing GAC use and the need for a GAC regeneration furnace. An added benefit is that nitrification in a PACT system is more stable than in many non-carbon processes. Further, partial denitrification can take place in the nitrification stage without upset of that treatment step.

The waste sludge and powdered carbon are processed in a wet air oxidation unit which oxidizes that sludge and regenerates the carbon. The solids are processed in slurry form at 6 to 10 percent at solids. The wet air regeneration unit was selected for its low carbon losses upon regeneration. Thermal regeneration processes would have carbon losses in the 25 to 40 percent range. The wet air regeneration system carbon losses are in the 5 to 10 percent range. The wet air regeneration unit at El Paso has a nominal capacity of 58 gallons per minute of waste PACT sludge thickened to 6 percent solids.

C. Remaining Processes

Following PACT, treatment wastewater advances to high lime treatment for virus kill, phosphorus and heavy metal removal, and softening. Two stage recarbonation utilizing CO2 follows the lime treatment. Turbidity removal is provided by sand filtration and ozonation follows for disinfection. The final product water is passed through a granular activated carbon polishing filter before release to storage prior to injection.

DESIGN WASTEWATER COMPOSITION

		Primary Effluent	PACT Effluent	(Soluble except for S.S.)
Flow	(MGD)	10	10	
COD	mg/l	364	20	
C. BOD	mg/l	143	3	
TKN	mg/l	28	2	
NH_3-N	mg/l	25	1	
SS	mg/l	88	20	
Vol. SS	mg/l	70	15	
NO_3-N	mg/l	0	3	
TOC	mg/l	50	4	

TABLE 1

PACT SYSTEM DESIGN PARAMETERS

	First Stage	Second Stage
HDT, Hr.	6.5	1.5 + 0.9*
SRT, Days	12	20
Carbon Dose, mg/l	160	20
MLSS, mg/l	17500	15000
Clarifier loading, GPD/ft^2	385	385

*re-aeration section

TABLE 2

D. Redundancy and Quality Control

Reliability is very important in a project of this type since there is no ultimate discharge other than to the potable water aquifer. Because of this, water must be properly treated or it will require the expense of retreatment. The process design provides duplicity of units and the unit processes selected provide some overlapping capabilities.

Plant control is provided by a direct digital control system using distributed control units. Forty process control loops are provided for the control of most process units. The control system was developed on the basis of a "control room" philosophy in which most process changes can be implemented by the chief plant operator at one location. Water samples from most process units are piped to the control room area for visual inspection as well.

Ultimate quality control is provided through the use of three 3.3 MG reservoirs which store "batches" of product water. These "batches" are tested by the laboratory before they are released for injection.

III. PLANT PERFORMANCE

A. Primary System, Sludge Digestion

The raw wastewater is processed through convention grit and primary solids removal systems. The primary effluent flow, about 6.6. MGD, is more than can be processed through the aeration system at the present time. Because of this limitation, the PACT system is fed a constant 4.3 MGD. The balance is collected in oxidation ponds and will be held until process modifications are made to the aeration system which will enable the plant to process 10 MGD.

Primary treatment performance matches that of a conventional system and is not discussed in detail.

B. Secondary System--PACT

1. Performance

In 1986, the PACT system was operated at an average 4.3 MGD. The reduced hydraulic throughput was due to mixing and oxygen transfer limitations of the aeration devices installed in the first stage tankage.

Organic removal across the PACT system is monitored by analyzing for BOD, TOC, and COD. As would be expected, nearly all of the organic removal occurs in the first stage. Primary effluent, first and second stage PACT effluent BODs averaged 85 mg/l, 3 mg/l and 1/mg/l for 1986, respectively. Overall removal of BOD is greater than 98 percent. BOD removal was stable throughout the year, without exception.

Average TOC concentrations through the PACT system as above were 29 mg/l, 2.9 mg/l, and 2.4 mg/l, respectively. Overall removal was greater than 90 percent. Figure 1 shows primary and first stage effluent TOC concentrations throughout the year. The peak in September was caused by a leaking, partially open valve in the line that allows the wet air regeneration unit reactor to be bypassed. This line is normally used when the heat exchangers are cleaned.

The leaking, partially open valve went unnoticed for some time causing unoxidized organics to be returned to the aeration tank without proper processing in the regeneration unit. The rise in the monthly average value was caused by much higher concentration occurring on only a few days.

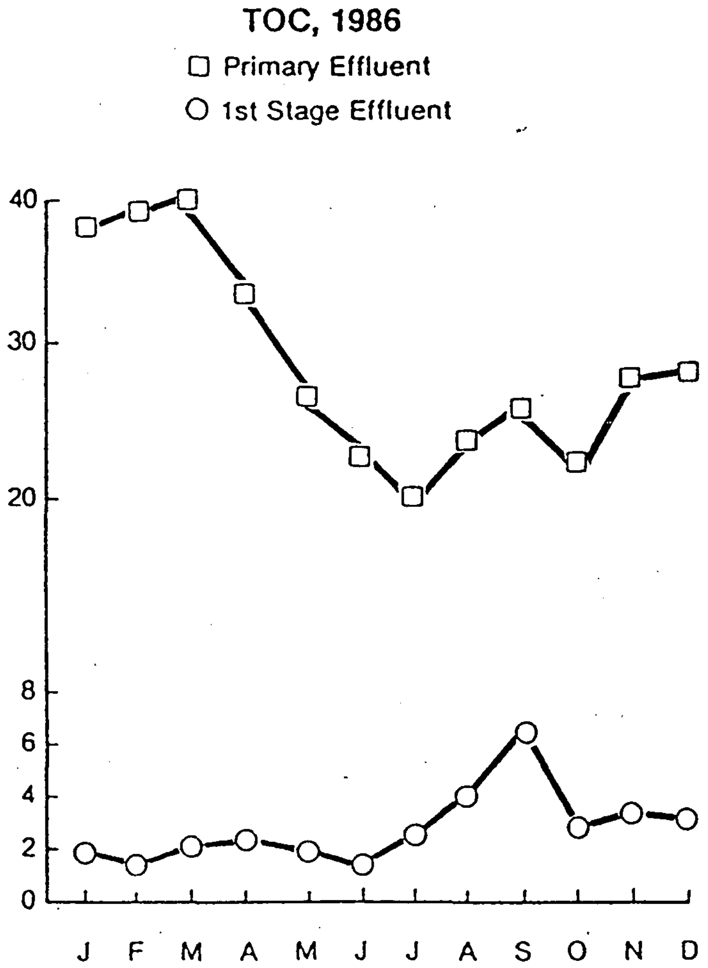
Soluble COD is also monitored. Yearly average values were 155 mg/l, 36 mg/l, and 31 mg/l for the sample points mentioned above. The COD concentration in the first stage effluent for the year is plotted in Figure 2, along with TOC. Both show the increase in concentration in August and September. The lack of a peak in the BOD concentration indicates that the recycled unoxidized organics are not as biodegradable as those from properly processed carbon sludges. This has been demonstrated as other PACT/wet air regeneration installations as well.

Nitrogen removal across the PACT system was very stable throughout the year. TKN removal in the first stage ran 96 percent. Figure 3 shows primary effluent and first stage effluent TKN monthly average concentrations. The primary, first, and second stages averaged 25.4 mg/l, 1.0 mg/l and 0.6 mg/l, respectively.

Ammonia nitrogen removals mirrored this performance (Figure 4) with primary, first and second stage concentrations of 20.4 mg/l, 0.4 mg/l, and 0.2 mg/l, respectively, for a 99 percent overall removal.

Nitrate removal overall was relatively stable across the process as a whole. Figure 5 shows first and second stage effluent nitrate concentrations for the year. The first stage nitrate concentration ranged from 22 mg/l to 5 mg/l. The yearly average was 11.6 mg/l. The second stage nitrate averaged 1.6 mg/l.

Table 3 shows nitrogen removal across the plant. Primary effluent TKN varied quite a bit during the year as did first stage denitrification. The very high levels of first stage denitrification seen during May, June, and July may be primarily due to a very long first stage sludge age carried during those months. The warm wastewater temperature during those months likely aided the denitrification as well.



TOC, 1986
□ Primary Effluent
○ 1st Stage Effluent
40
30
20
8
6
4
2
0
J
F
M
A
M
J
J
A
S
O
N
D

FIGURE 1

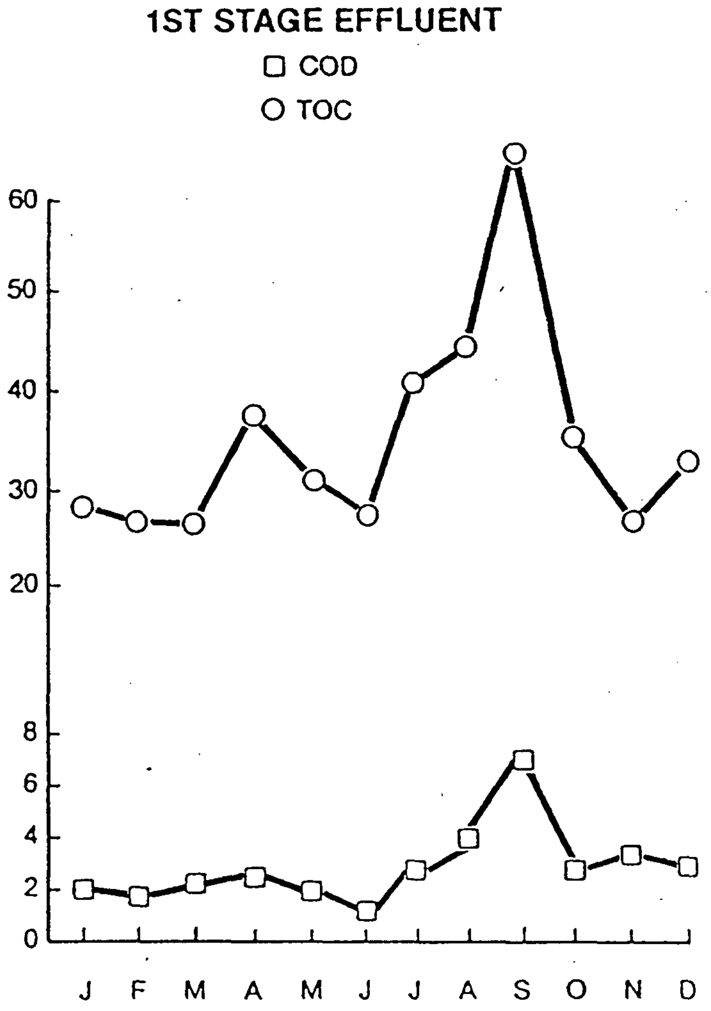
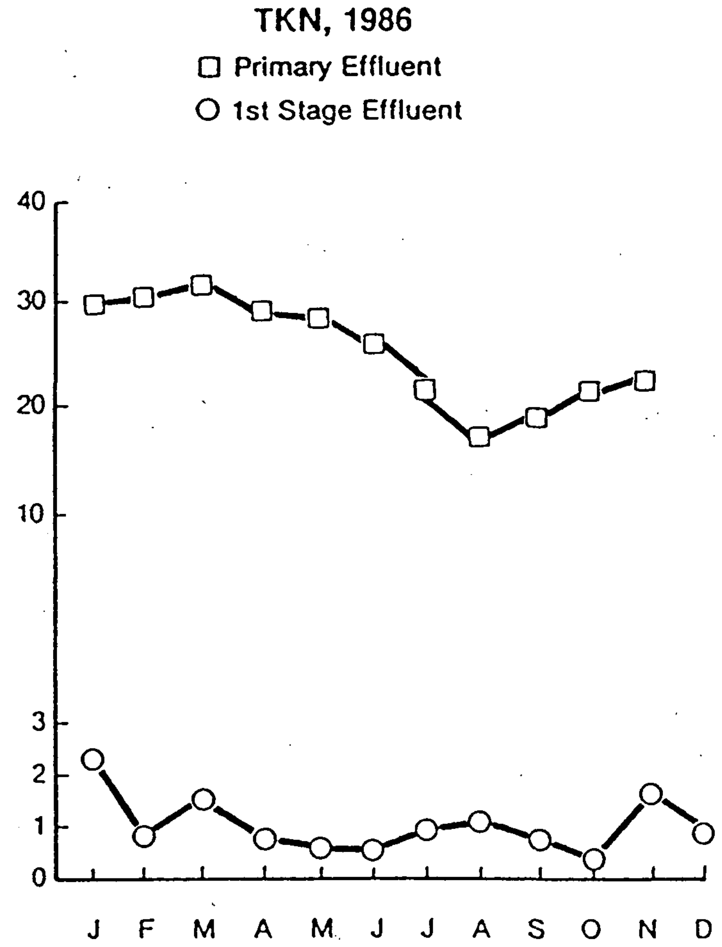
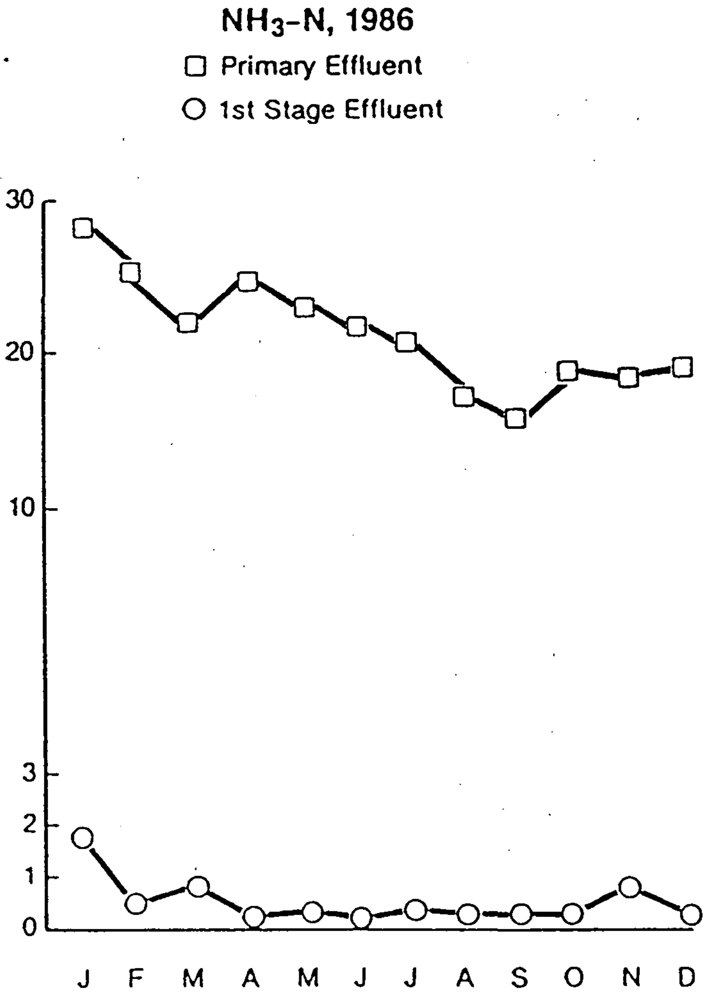


FIGURE 2



TKN, 1986
□ Primary Effluent
○ 1st Stage Effluent
40
30
20
10
3
2
1
0
J
F
M
A
M
J
J
A
S
O
N
D

FIGURE 3



NH_3-N, 1986
☐ Primary Effluent
○ 1st Stage Effluent
30
20
10
3
2
1
0
J
F
M
A
M
J
J
A
S
O
N
D

FIGURE 4

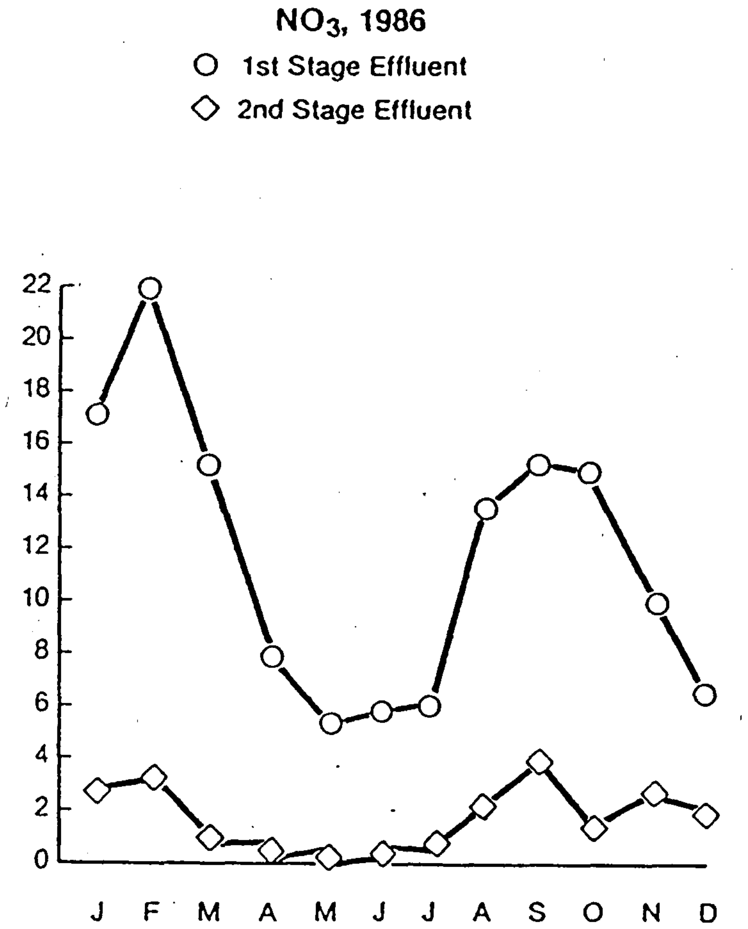

NO_3, 1986
○ 1st Stage Effluent
◇ 2nd Stage Effluent
22
20
18
16
14
12
10
8
6
4
2
0
J
F
M
A
M
J
J
A
S
O
N
D

FIGURE 5

1986 EL PASO TOTAL NITROGEN DATA
(TKN + NO_3)

	Primary Effluent mg/l	First Stage Effluent mg/l	Second Stage Effluent mg/l	Overall % Removal
Jan.	29.6	19.7	3.5	88.2
Febr.	30.3	22.7	3.6	88.1
Mar.	31.7	16.5	1.2	96.2
April	27.8	8.8	1.0	96.4
May	27.3	5.6	0.6	97.8
June	25.2	6.3	1.0	96.0
July	22.3	7.0	1.3	94.2
Aug.	17.7	14.7	2.6	85.3
Sept.	19.4	16.2	4.3	77.8
Oct.	20.8	15.7	1.7	91.8
Nov.	24.7	11.3	3.8	84.6
	25.2	13.1	2.2	90.5

TABLE 3

During August and September, the sludge age was lowered. And coupled with this was an "incomplete" wet air regeneration due to that units leaking bypass valve mentioned earlier. These conditions resulted in an increased nitrate load to the secondary stage.

Over the course of 1986, the first stage averaged 48 percent total nitrogen removal which exceed the expectations based on design. Overall, the plant achieved a 90.5 percent total nitrogen removal in 1986 with an average effluent total nitrogen concentration of 2.2 mg/l.

Methanol is added to the denitrification (second) stage as a carbon source. Because of sensing control problems in the NO_3-MeOH loop, methanol is fed manually. As a result, methanol is generally overfed. Even though this occurs, based on total nitrogen removed across the PACT system, methanol consumption is 2.1 lb per pound of nitrogen removed.

The plant staff is satisfied with the performance of the nitrification-denitrification aspects of the PACT system citing much greater stability than has been their experience with other nitrification processes.

2. Aeration

Since start-up, the plant has been able to produce design quality effluent water but not at the design flow rate of 10 MGD. The primary limitation is that the aerators cannot provide adequate dissolved oxygen to meet the demand in the aeration basins. The system was able to meet the demand in the aeration basins. The system was able to operate at approximately 60 percent of the design flow or at 6 MGD. As the feed rate is increased above 6 MGD, the dissolved oxygen concentration in the aeration basin decreases to zero resulting in reduced treatment performance. Following several investigations by the consulting engineer, the aerator manufacturer, and Zimpro/Passavant, it became clear that there was no certain answer to the question of supply versus demand. Either the true oxygen demand was higher than the original design, or the aerators were not able to supply the design amount of dissolved oxygen.

A test program was initiated in early 1986 to answer the supply versus demand question as well as to determine the best way to solve the problem. The test program was sponsored by the City of El Paso, the aerator manufacturer, and Zimpro/Passavent. During May and June, 1986, a pilot scale PACT^{TM} system was operated at El Paso in parallel with the full-scale PACT^{TM} system. The pilot scale system could be operated at the full scale system design hydraulic residence time and sludge age. An independent engineering firm was retained to monitor oxygen transfer efficiency in both the pilot as well as the full-scale PACT^{TM} systems using an aeration tank oxygen off-gas method of analysis.

Test results from the pilot system demonstrated that the true oxygen demand as the same as the original design equations would predict, and, therefore, the design demand was correct. The ultimate conclusion from the study was that the aeration system design parameter "alpha" used for the equipment supplied was incorrect. A value of 1.0 had been used for design. Field measurements using current techniques indicated alpha is between 0.5 and 0.6. This means that additional aerator capacity would be required in the aeration basins before the system could meet the design hydraulic capacity.

Current plans are to replace the existing aeration system with a higher capacity system.

3. Suspended Ash Removal

Since carbon from the PACT system is regenerated, ash that is associated with the spent carbon solids will pass through regeneration nearly untouched. Ash accumulation is contributed primarily by the ash in the influent wastewater. A second less significant source of ash is that contained in the virgin powdered activated carbon makeup. American Norit Hydrodarco C powdered activated carbon is used in the PACT system.

To keep this ash material from accumulating to unacceptable levels in the PACT system, some ash in the regenerated stream must be removed. The original design included a reactor blowdown step followed by gravity separation of carbon and ash.

The majority of the ash material, however, was found to have settling characteristics similar to that of powdered carbon.

Figure 6 shows that mixed liquor ash concentration of the first and second stage basins. The first stage mixed liquor ash concentration rose from roughly 3,600 mg/l to 5,800 mg/l (38 percent to 48 percent) while the second stage mixed liquor rose from 1,300 mg/l to 3,800 mg/l (26 percent to 40 percent).

To control this accumulation, several methods were evaluated. A separation technique was piloted whereby the sedimentation potential of the regenerated carbon/ash is altered to "float" the ash and settle the carbon. While the pilot testing was successful, it was decided to simply waste a portion of the spent carbon to the anaerobic digesters of the primary system since it will result in the carbon loss equal to about 5 mg/l. Put another way, to compensate for the additional carbon losses resulting from wasting these solids, the makeup carbon rate will increase about 5 mg/l.

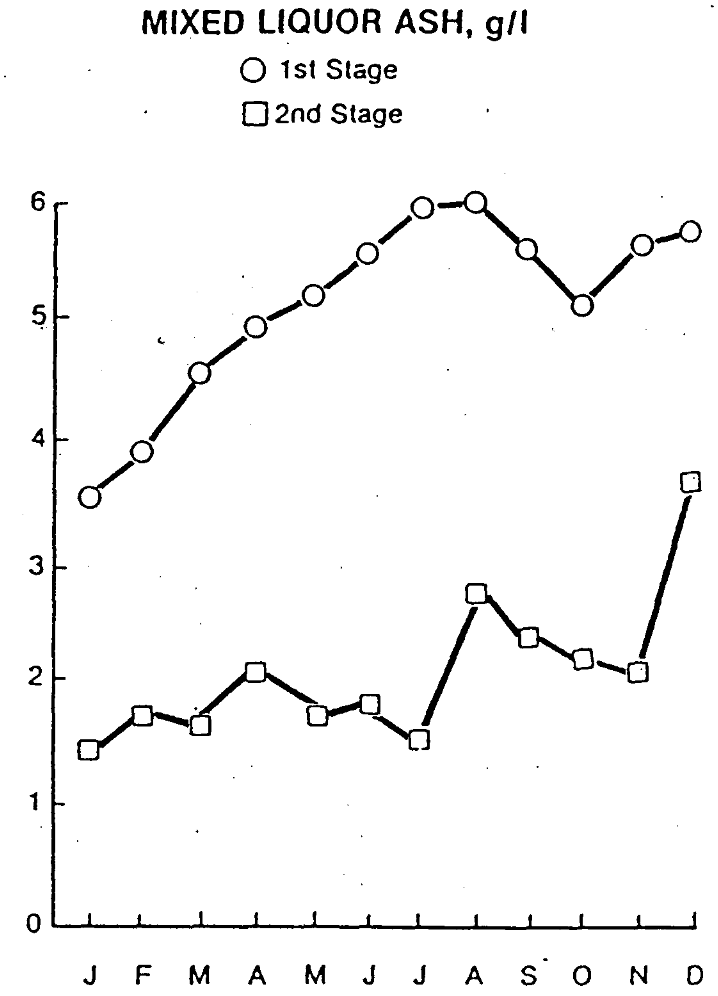

MIXED LIQUOR ASH, g/l
○ 1st Stage
☐ 2nd Stage
6
5
4
3
2
1
0
J
F
M
A
M
J
J
A
S
O
N
D

FIGURE 6

C. Secondary Solids Processing - Wet Air Regeneration

Solids wasted from the PACT™ system to control solids residence time are processed through a wet air regeneration unit as shown in Figure 7.

The unit regenerates the spent powdered carbon for reuse in the PACT process. In addition to carbon regeneration, the process destroys the spent sludges' biomass and oxidizes about 85% of all organics submitted to it. Because of conditions maintained therein, the balance of the organics exit the process in the form of low molecular weight oxygenated organics, mainly acetic acid.

Proper operation of the wet air regeneration unit requires an adequate temperature (greater than 440°F to drive the reaction to proper completion), adequate pressure (greater than 700 psig to control evaporation of water), and adequate residual oxygen in the off-gas (2-3% to assure a minimum recycle of COD to the PACT system).

The wet air regeneration unit allows some flexibility in the feed solids composition the unit can process. For instance solids to regeneration have ranged from 5.7% to 12.4%. As long as the unit's residual O_2 content is sufficient, the slurry feed rate can be matched to the air compressor rate.

The soluble characteristics of the regenerated stream are fairly consistent (summarized in Table 4) since regeneration conditions have remained fairly stable. Soluble COD, BOD_5, TKN, and NH_3-N values are about 4,000 mg/l, 2500 mg/l, 1,000 mg/l and 900 mg/l, respectively. Variability in concentration in this case is dependent on level of organics (noted as biomass) to the unit. In this case, the soluble COD/biomass value is 0.3 g/g. Respective values for BOD/biomass and TKN/biomass are 0.17 and 0.075.

The percent oxidation achieved by the regeneration unit averaged 81%, within an acceptable range for the PACT™/wet air regeneration systems.

There have been some problems associated with the regeneration system.

Process air is supplied by one of two large reciprocating air compressors. Initially these compressors both suffered from lubrication problems which ultimately lead to the need to rebuild various stages of the machine. The supplier and manufacturer worked together to locate the cause of the problem and to resolve it.

Another problem has been heat exchanger scaling. In wet air regeneration, scales are removed by recirculating a solution of dilute nitric acid, HNO_3.

WET AIR OXIDATION FLOW SCHEME

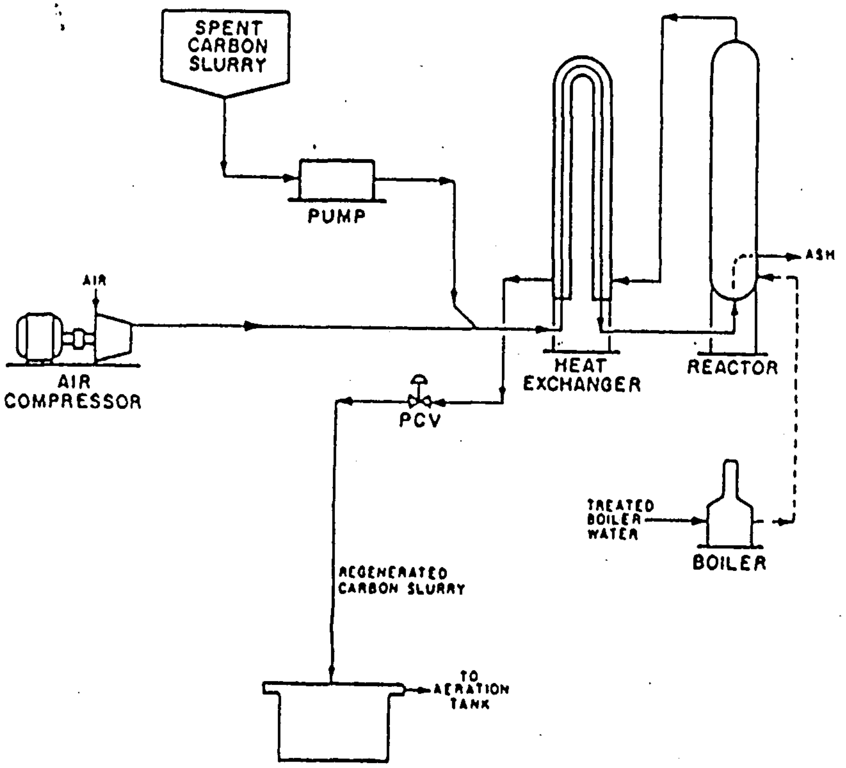


FIGURE 7

SOLUBLE CHARACTERISTICS
Wet Air Regeneration Unit
El Paso, Texas

	Concentration, mg/l	Value/Biomass, g/g
COD	4000	0.30
BOD_5	2500	0.17
TKN	1000	0.075
NH_3-N	900	0.065

TABLE 4

The amount of descaling acid (HNO_3) used was far more than expected. Analysis of the scaling problem appeared to be related to the method of operation. Daily startup-shutdown with heat exchange surfaces being washed with effluent water appeared to be the major culprit. Analysis of the scaling potential of the plant product water, however, indicated little potential. Soluble calcium and sulfate, hardness and langelier index were determined and evaluated.

In the fall, as mentioned previously, it was discovered that a reactor bypass valve was leaking/partially open. Since this is an integral valve in the cleaning cycle, it also may have played a role in the frequency of scale cleaning.

Presently, the regeneration unit is operated 24 hours per day, 7 days per week until descaling is necessary. Acid washes were originally performed once per week. After a continuous operation was adopted, acid washes have been reduced to less than one per month. Chemical consumption has dropped to one third of the initial rate.

D. Lime - Recarbonation

The lime treatment step is used for removing phosphorus, heavy metals and killing virus. Lime is added for pH control to pH 11.1. Average lime dose for 1986 was 265 mg/l as CaO. Phosphorus removal is shown in Figure 8. Metals have not been a problem in the plant product water.

Virus analyses have been run on plant product water annually and no virus have been detected. Additionally, virus analyses were run on internal plant streams with no virus detected except in the primary clarifier effluent.

The lime reactor and first stage recarbonation tank require descaling about every four months. This is not considered unusual for such a process.

The recarbonation process drops the pH to 7.5 in two stages, by dissolving carbon dioxide in the water. Chemical consumption for the lime processes are about as anticipated.

E. Sand Filtration

Sand filtration is done with traveling bridge type sand filters. Effluent turbidity has averaged 1.05 NTU during 1986. During the summer an algae film develops on the surface of the water above the sand. It poses only an appearance problem and does not effect performance. The algae film is skimmed off manually about once per week.

F. Ozone Disinfection

Disinfection is provided by one of two ozone units. Operation has been very good with no coliform detected in the effluent. Ozone dose has average 1.75 mg/l in 1986. Control of

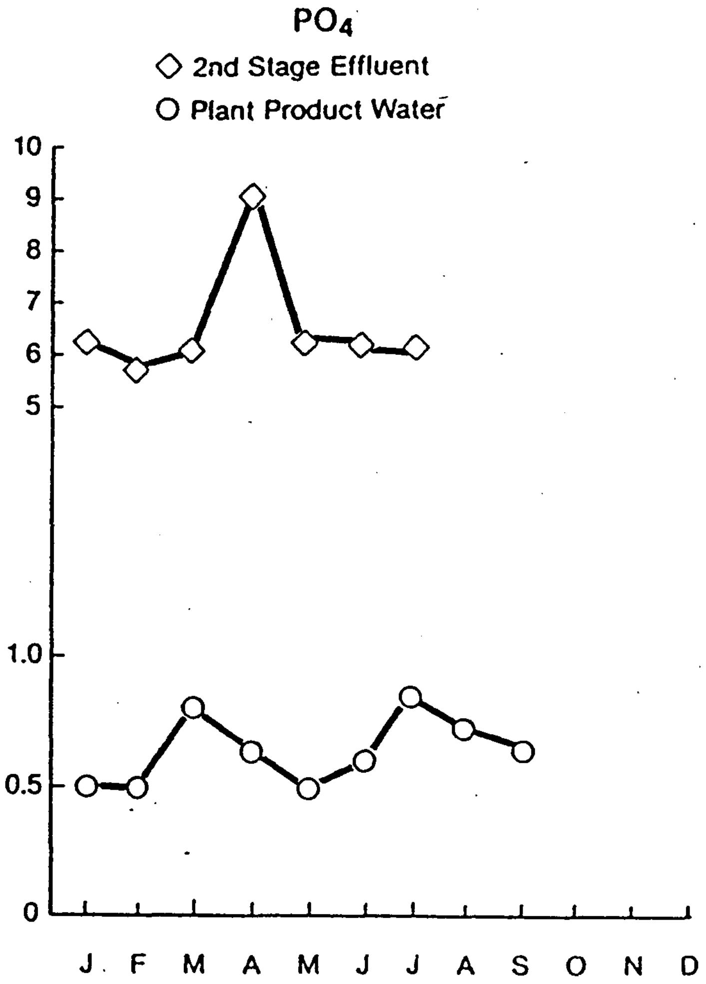

PO4
◇ 2nd Stage Effluent
○ Plant Product Water
10
9
8
7
6
5
1.0
0.5
0
J
F
M
A
M
J
J
A
S
O
N
D

FIGURE 8

the dose is based upon contactor efficiency rather than ozone residual. High pH to the contactor has resulted in loss of ozone residual due to the conversion of ozone to the ·OH radical. Disinfection capability remains high during this situation but control on residual is not feasible.

Pitting corrosion of the cooling water jackets was experienced and was apparently due to chloride pitting of the 304 SS. The problem was resolved by installing a closed loop cooling system for the ozone units.

G. Granular Carbon Filter

The granular carbon filter was installed to provide a final polishing removal or organic compounds. The 1986 average loading to the GAC filter was 1.84 mg/l TOC with only four occasions exceeding 5 mg/l. The average loading for 1986 was 0.00023 pounds of TOC per pound of carbon. No granular activated carbon has been regenerated or replaced.

Since adsorption on activated carbon (Calgon Filtersorb 300) is an equilibrium process, the carbon bed acts very much as a peak leveler. Adsorption occurs when either high feed organic concentrations or very low levels of adsorbed materials on the carbon are encountered. When the feed organics drop off or the carbon bed becomes saturated, organics desorb according to the equilibrium of the process. Table 5 shows this phenomenom occurring where the influent Trihalomethane Formation Potential (THMFP) in nanomoles is sometimes less than the effluent value. This nanomole value can be multiplied by 20% to approximate the concentration in micrograms per liter. Initial indications are that reduced regeneration of PACT carbon caused the higher influent THMFP values in late 1985. For the dates sampled, several show negative removals, but during these period product water remained within standards. Plant personnel are currently concerned that the procedure used to determine THMFP may not be accurately representing the influent THMFP concentrations. Other methods of analysis are being considered.

H. Injection Wells

There are 10 injection wells in the project. The water bearing strata is a fine grained alluvium under water table conditions. Each well is approximately 800 feet deep and is completed about 450 feet into the water table. Normal static water levels are about 350 feet below the surface. A 16" casing is used and is perforated (wire wrap screen) from the water table to total depth.

To date all of the wells have been used for injection on a routine basis. Water is injected down a 3.5" tubing sized to dissipate the hydrostatic head and eliminate freefall into the well. It has been found that the wells will operate at an injection rate of between 500 and 800 gpm. Injection rates are held constant by a rate of flow controller. Hydrostatic buildup

EL PASO GAC FILTER THMFP

Month	GAC Inf. (Nanomole)	GAC Eff.	Removal Eff.
Oct. 85	76	41	35
Nov. 85	26	19	7
Dec. 85	3	15	– 12
Jan. 86	1	5	– 4
Mar. 86	1	7	– 6
Jan. 87	7	12	– 5
Mar. 87	0	0	
May 87	3	14	– 11

TABLE 5

under injection conditions ranges from 100 feet to 150 feet initially and builds to approximately 250 feet before the well is backwashed with a pump installed in the well.

Backwashing procedures are initiated when the water table rises to within 100 feet of the surface. Each well is continuously monitored electronically with a downhole pressure transducer to indicate the water level in the well. Backwashing consists of pumping the well at a rate of 1000 gpm for several 30 minute periods so the well is surged. After the well blown-down clears up, usually after 3 or 4 cycles, the well is allowed to pump continuously for about two hours. This procedure is usually done on a three month frequency although the range is from 2 months to 4 months. After backwashing, the hydrostatic buildup after injection is resumed will be about the same as it was initially. Figure 9 shows the buildup experience on recharge well number 1 during 1986 and shows the effect of backwashing.

There are six observation wells in use. These wells are clustered in groups of two around two of the injection wells and are located 300' and 700' downgradient from the injection well. Two more observation wells are each located 300 feet upgradient from different injection wells. These wells are monitored quarterly with fluid resistivity logs and samples are taken at points indicated by the logs.

To date the only significant change in the water, based upon sampling results, has been an indication of trihalomethanes (THM) in the observation wells. The THMs have been detected at depths of 400 to 450 feet with the maximum value being 6.1 micrograms per liter. Dibromochloromethane and bromoform are the predominant forms detected. There have been no THMs detected in the produced water. The THMs could be formed as a result of the 0.1 miligram per liter free chlorine residual carried in the injected water and the organic material in the aquifer.

I. Reliability

Reliability has been high in that no "off spec" material has been injected based upon laboratory analysis of water in the holding basins. The treatment plant has the capability of "wasting" after most process units, thus an upset in one process will not propogate through the plant. This sytem has been used on occasions where ammonia bleed through, loss of methanol feed, or electrical problems were encountered.

J. Costs

In 1986 a total of 1.4 billion gallons of drinking quality water was returned to the Hueco Bolson reservoir by the Fred Hervey Water Reclamation Plant. The cost of this ater was approximately $1.55/1000 gallons. Table 6 shows the breakdown of costs into the major categories. Power and labor costs were nearly equal and made up a total of 65% of the overall costs.

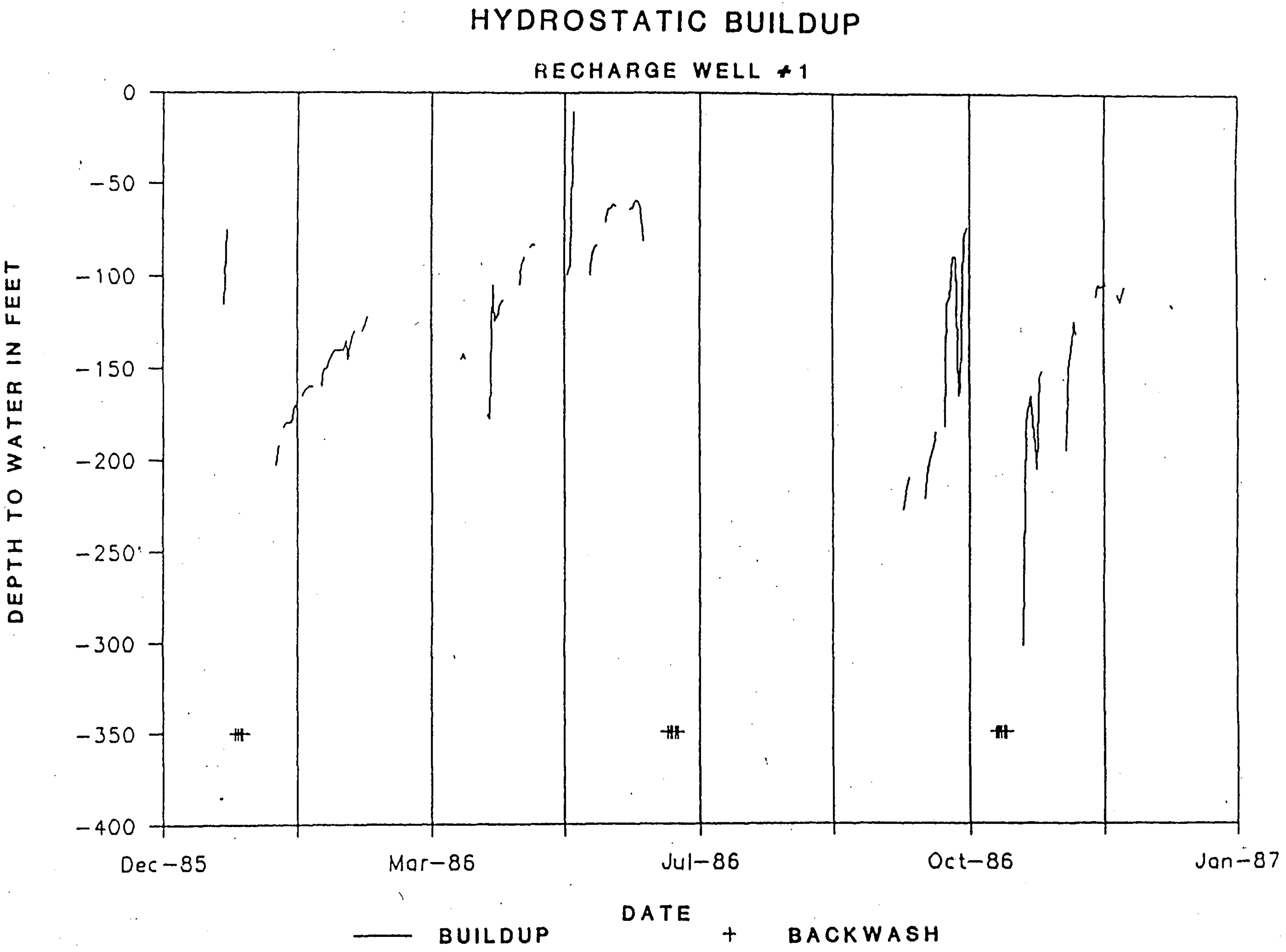

HYDROSTATIC BUILDUP
RECHARGE WELL #1
DEPTH TO WATER IN FEET
0
-50
-100
-150
-200
-250
-300
-350
-400
Dec-85
Mar-86
Jul-86
Oct-86
Jan-87
DATE
BUILDUP
+ BACKWASH

FIGURE 9

1986 COST BREAKDOWN

	$/1000 gal.	%
Labor	0.49	32
Power	0.51	33
Chemicals	0.28	18
Maintenance	0.12	8
Miscellaneous	0.13	9

TABLE 6

Chemical costs made up another 18%, with powdered carbon being only 5% of the chemical costs.

The chemical costs are broken down in Table 7. The major chemical costs are lime, carbon dioxide and methanol. The other major miscellaneous cost item was largely contribute by liquid oxygen fed to the force main to help reduce sulfides entering the plant.

No granular carbon was purchased in 1986 as the product water never failed to meet the effluent organic requirement.

The operating costs have increased over the first two years of operation as shown in Table 8. During the first roughly five months of operation the costs were reported to be $1.00/1000 gallons. The records show that the second half of 1985 ran at $1.17/1000 gallons and 1986 ran at $1.55/1000 gallons.

The major areas of cost increases have been power, chemicals and maintenance. Chemicals, alone, rose 10¢/1000 gallons. Another 4.5¢/1000 gallons is attributed to miscellaneous with most of the remainder associated with power.

It is reasonable to expect some increase in maintenance costs as equipment warranties expire and the costs are shifted from the supplier to the owner.

K. Conclusion

Since the Fred Hervey Water Reclamation Plant was placed in service in 1985, the facility has consistently met priority established aquifer recharge goals. The amounts of water recycled to the potable water system to date are felt to be minor based upon injected volumes and the displacement volumes involved in traveling to the production wells.

The processes in the train have proven their ability to accomplish the required treatment reliably and at a cost that is reasonable when the tough discharge standards are considered.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Dave Buela of Zimpro/Passavant, and Messrs. John Balliew and Tom Cliett of the El Paso Water Utilities for their help in the preparation of this paper.

CHEMICAL COST, 1986

Chemical	Cost, $/1000 gal.	%
CO_2	0.063	22
Lime	0.083	30
HNO_3	0.012	4
Methanol	0.035	13
Powdered Carbon	0.016	5
Granular Carbon	0.000	0
Polymer	0.015	5
Miscellaneous	0.055	20
TOTAL	0.280	

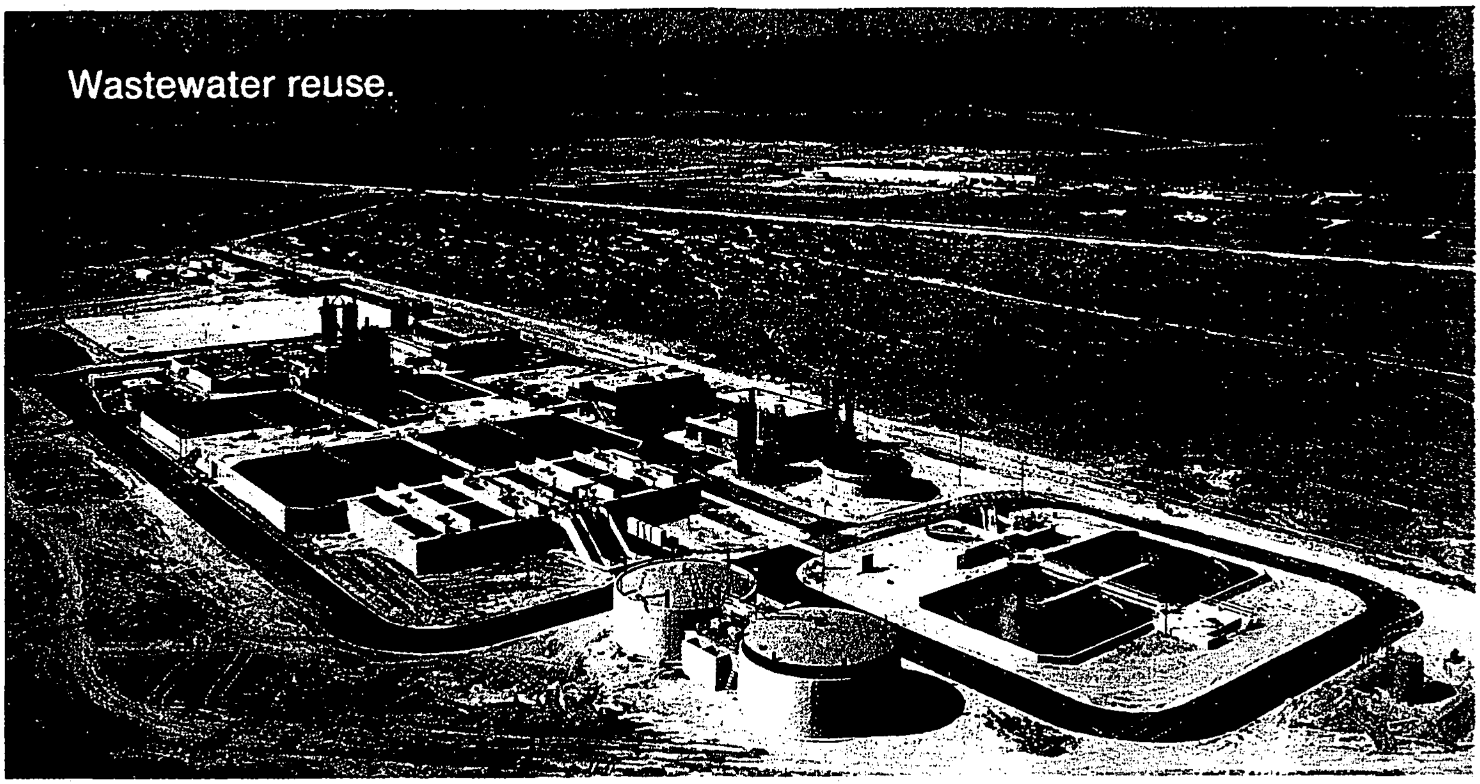
TABLE 7

TOTAL OPERATING COSTS

	3-6/85	8-12/85	1986
Cost, $ / 1000 gal.	1.00	1.17	1.55

TABLE 8

Reprinted from
the Reactor magazine
No. 56. December, 1985



Wastewater reuse.

El Paso closes the loop.

Leon Metz remembers the first time he came to El Paso, TX, and went down to see the Rio Grande River.

"I expected to find it wide and flowing," recalls the El Paso historian and river expert. "Instead, I found a trickle of water that I could almost jump across."

That scarcity of fresh water in the El Paso area has led to construction of the state-of-the-art treatment plant that converts raw sewage to high quality effluent that meets drinking water standards and is pumped back into the aquifier. The plant was commissioned last June; Metz was the keynote speaker.

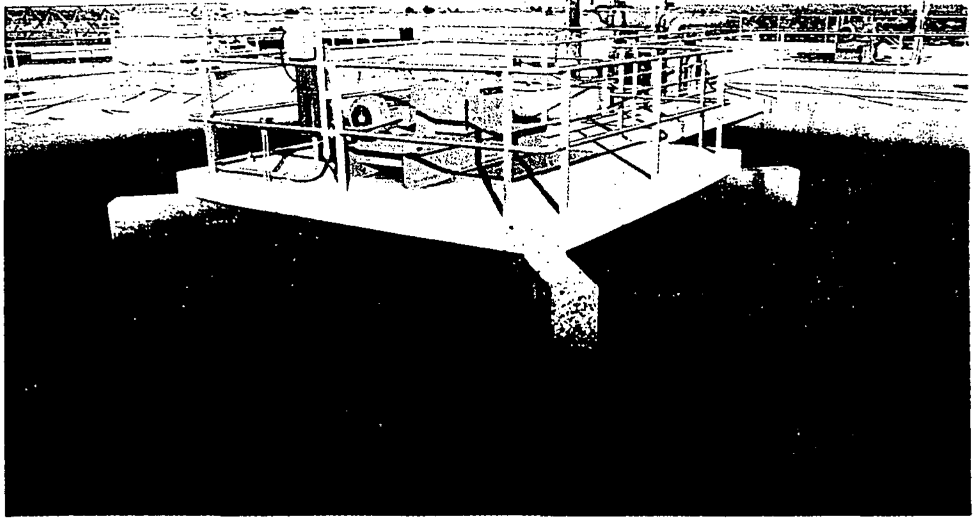
Designed by the El Paso firm of Parkhill, Smith and Cooper, Inc., and built by the M.A. Mortenson Co. of Minneapolis, MN, the new facility can treat up to 10 million gallons a day (current average flow is about half that). Wastewater passes through ten separate treatment steps—including a two-stage PACT™ system licensed by Zimpro Inc. of Rothschild, WI.

The treated water is returned to the Hueco Bolson aquifer through a system of 10 recharge wells, each reaching down some 800 feet. Over a period of two years, it will migrate back to the potable water wellheads.

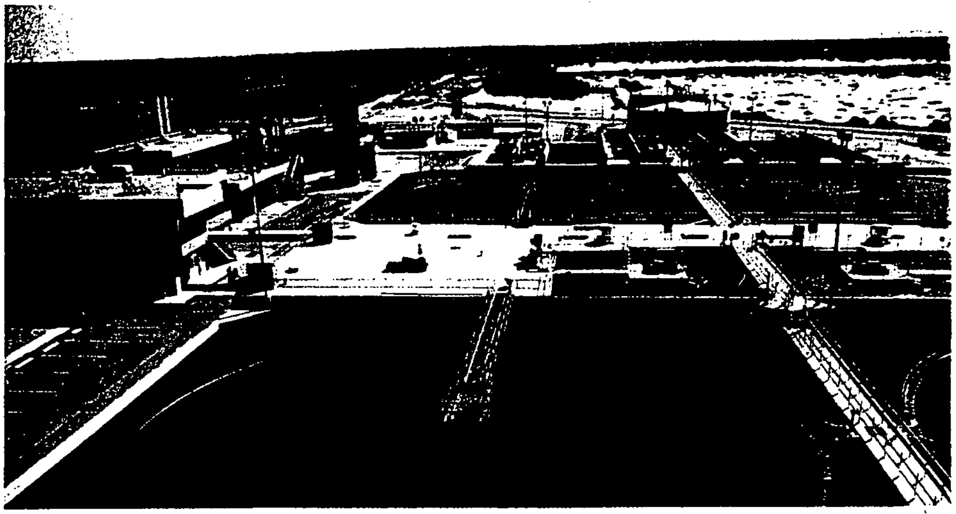
Steps to save water.
The plant is named for Fred Hervey, who founded the El Paso Public Service Board and championed water resources 30 years ago. It is just one of a number of steps this arid area of the Southwestern United States has taken to guarantee a constant supply of fresh water in the years ahead.

According to John Hickerson, general manager of the Public Service Board, these efforts include an aggressive water conservation

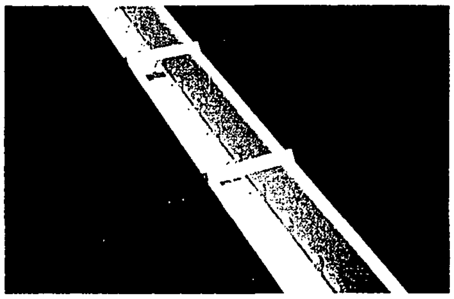
(continued)



Above, Fred Hervey Treatment Plant surrounded by arid land. Center, crystal clear effluent is returned to aquifer. Right, aerator of PACT™ system.



Above, two-stage PACT™ system clarifiers loom in foreground. Carbon regeneration unit is at upper left. Below, effluent from PACT system goes to lime treatment and looks "swimming pool" clear.



El Paso, cont.

program, acquisition of private land over the Hueco Bolson, leasing of surface water rights to the Rio Grande, and attempts to obtain rights to groundwater deposited beneath Federal lands near El Paso in New Mexico.

"Our objective is to employ a combination of methods to assure El Paso of an adequate supply of water over the next 100 years, even though our population may reach 2 million," he says.

The Fred Hervey plant will help meet that goal by returning water to the Hueco Bolson—source of about 65 percent of El Paso's fresh water, but being depleted about 20 times faster than the natural recharge rate.

Purification processes.

Wastewater begins the road to recovery by entering the plant from a collection system that serves about 50,000 residents in the northeast part of El Paso, near Fort Bliss. Primary treatment includes screens, degritting, and settling basins. Primary sludge is anaerobically digested and dewatered on drying beds before being composted. Digester gas is used for plant fuel.

After flow equalization, the purification process continues as primary effluent enters the two-stage PACT system, which accomplishes the bulk of the organic removal, including all of the nitrogen removal.

Large amounts of powdered activated carbon are carried in the PACT system aeration basins, allowing physical adsorption and biological treatment to occur simultaneously. The carbon adsorbs what the biomass can't handle; the biomass assimilates pollutants that aren't adsorbed.

Aided by the PACT system's long SRT (solids residence time), nitrification occurs in the first stage; denitrification in the second, Methanol—in smaller amounts than those required by conventional systems—is added to the second stage to provide carbon for the denitrifiers, assuring nitrogen levels of less than five parts per million.

After aeration, the treated wastewater moves on to secondary clarifiers. The waste sludge and spent carbon are withdrawn and pumped to a wet air regeneration unit—supplied by Zimpro. Here, at temperatures of 450 degrees F and pressures of 950 pounds per square inch, the organic material is wet oxidized. The carbon is regenerated for return to the PACT system.

Clarifier overflow advances to high lime treatment for virus kill, removal of phosphorus and heavy metals, and softening.

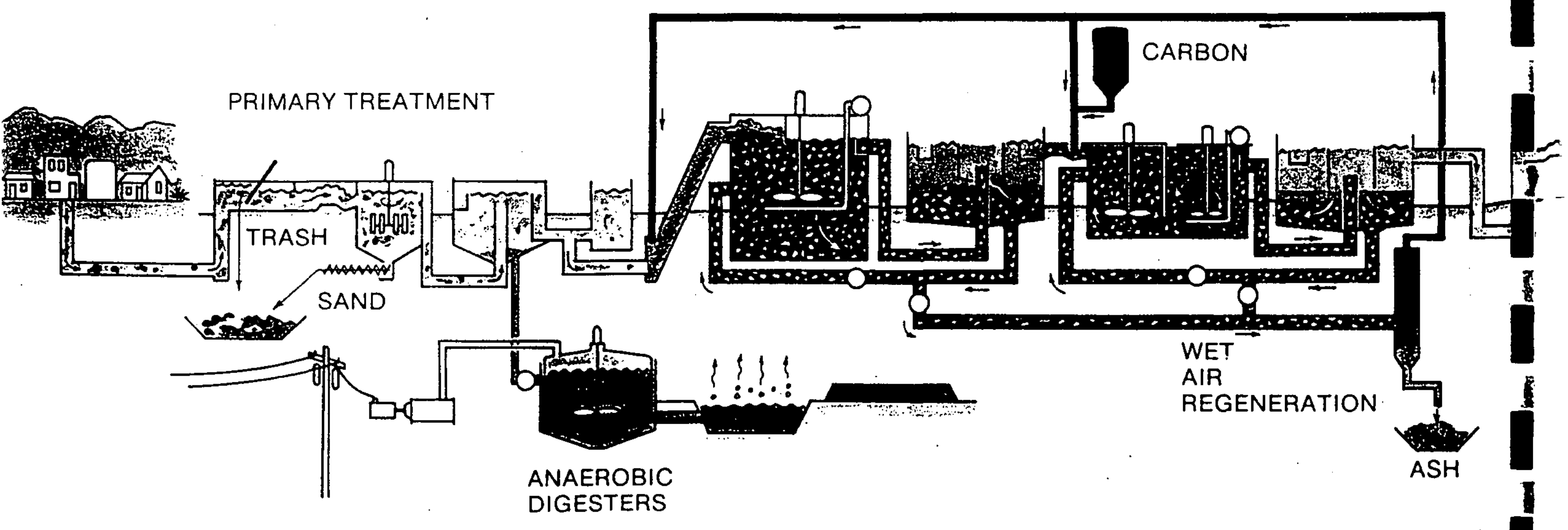
Sand filtration is next for turbidity removal, followed by ozonation for disinfection and granular activated carbon.

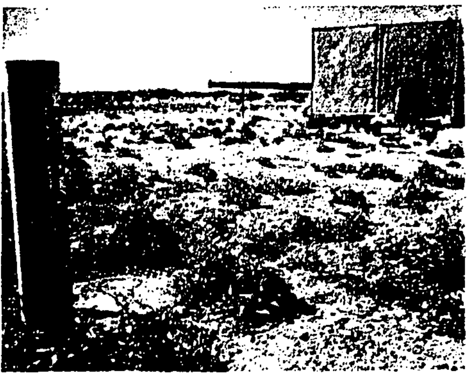
The product water is stored and tested for purity in one of the most

PACT system performance El Paso, TX

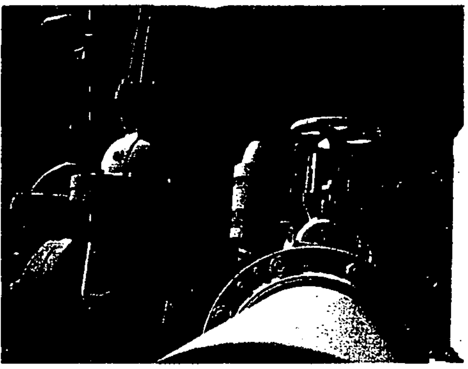
	In (mg/l)	Out (mg/l)
BOD	—	less than 3
TOC	—	less than 2
COD	180	less than 10
TKN	25	less than 1
NO_3	less than 1	less than 5
TN	25	less than 5
SS	56	less than 5

FRED HERVEY WATER RECLAMATION PLANT





Plant effluent is pumped to well-field (above) near the treatment plant, and recharged to aquifier through ten 800-foot wells (below).



Data:

Plant: Wastewater reclamation, recharge.

Flow: 10 million gallons per day (0.4 m^3/s).

Zimpro processes: 2-stage PACT system; wet air regeneration unit (capacity 60 gallons per minute or 3.8 L/s; operating conditions 450°F, or 230°C, at 950 psig, or 66 kgf/cm^2).

Other processes:: Primary, equalization, sludge digestion, high lime, 2-stage recarbonation, sand filtration, ozonation, GAC filtration.

Recharge: 10 wells, 800 feet (243 m) deep.

Designer: Parkhill, Smith and Cooper, Inc., El Paso, TX.

General contractor: M.A. Mortenson Co., Minneapolis, MN.

Owner: El Paso Public Service Board, John Hickerson, general manager; Robert Bustamante, assistant general manager.

Plant superintendent: Javier Hernandez.

sophisticated laboratories in the wastewater industry. Some 23 parameters are measured, including alkalinity, heavy metals, and trihalomethanes, before the water is released to the recharge wells.

Performance report.

The PACT system, and the treatment plant as a whole, have been performing well since startup (see chart).

"We selected this system for its reliability and capacity to handle toxic shocks and other extraordinary loads without upset, "says Dan Knorr, project manager with Parkhill, Smith and Cooper.

"To date, the product water has met or exceeded expectations."

The effluent **is** impressive.

At the open house in June, members of the public sampled it on the rocks or mixed with fruit punch, and gave it high marks.

One visitor confirmed the wisdom of reuse and even suggested the El Paso project was a model for others to follow.

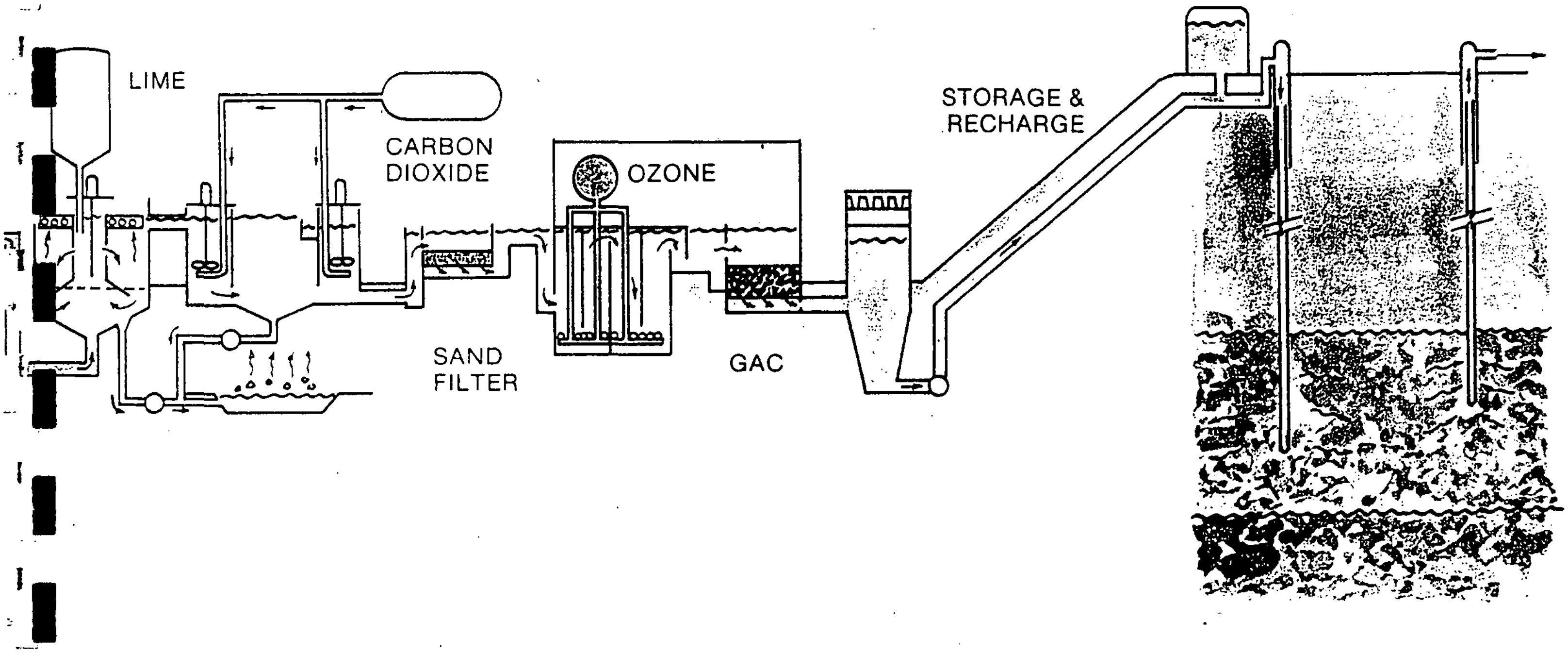
"It makes good sense," he told the El Paso Times, "With population increasing all over the Southwest, we're going to need this. More people have been killed over water than over women."

To landscape the new treatment works, El Paso uses and identifies trees and bushes that require little water.

Discharge Parameters El Paso, TX (established by Texas Water Commission)

Chlorides	300 mg/l
Sulfates	300 mg/l
Nitrates as N	10 mg/l
Turbidity	1 NTU
Arsenic	0.05 mg/l
Barium	1.0 mg/l
Cadmium	0.010 mg/l
Hexavalent Chromium	0.05 mg/l
Copper	1.0 mg/l
Iron	0.3 mg/l
Lead	0.05 mg/l
Manganese	0.05 mg/l
Mercury	0.002 mg/l
Selenium	0.01 mg/l
Silver	0.05 mg/l
Zinc	5.0 mg/l
Total dissolved solids	1000 mg/l
Endrin	0.0002* mg/l
Lindane	0.004* mg/l
Methoxychlor	0.1* mg/l
Toxaphene	0.005* mg/l
Chlorophenoxys	
2,4-D	0.1* mg/l
2,4,5-TP Silvex	0.01* mg/l

*annual average



A DYNAMIC MODEL OF NITRIFICATION-DENITRIFICATION IN THE ACTIVATED SLUDGE SYSTEM WITH POWDERED ACTIVATED CARBON

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL

OF THE UNIVERSITY OF MINNESOTA

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

DECEMBER, 1977

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VII. SUMMARY AND CONCLUSIONS

A number of batch tests were conducted with and without PAC to examine the kinetics of various substrates and the interaction of PAC with biological cells in activated-sludge systems. Also, dynamic flow tests were conducted of nitrification and denitrification activated-sludge processes with PAC and without PAC. Finally computer simulations were made with a dynamic model and compared with dynamic test data. Conclusions from these studies are summarized as follows.

1. Adsorption batch test results with PAC:

a. A dry milk solids solution and a settled municipal wastewater (primary effluent) were tested for adsorption and both were found to be highly adsorbable.

b. Glucose, glutamic acid, and lactose were only slightly adsorbable.

c. Methanol and nitrogen compounds including ammonia, nitrite and nitrate were found not to be adsorbable.

d. More than 90% of the adsorption of organics took place within 10 minutes.

e. Langmuir isotherm was the best applicable adsorption isotherm for the dry milk solution.

f. DO was highly adsorbable. PAC may act as a DO reservoir via adsorption-desorption of DO.

2. Tests of PAC adsorption with cell growth showed increased growth rates and removal of organics through adsorption-biooxidation.

3. PAC-sludge settling tests showed a marked improvement in settling characteristics when the PAC exceeded MLVSS concentrations by weight.

4. Qualitative examinations with a scanning electron microscope demonstrated the interaction of PAC, biomass and colloidal organics. Electronmicrographs exhibited numerous pores on the surface of fresh PAC particles. If PAC particles were aged in an activated-sludge aeration tank most of the pores became covered with adsorbed organics and cell debris. When PAC particles were associated with filamentous organisms they produced more compact flocs.

5. Dynamic flow nitrification:

a. The PAC unit was generally operated with continuous nitrification, but the non-PAC unit had chronic sludge bulking and a very low degree of nitrification.

b. Alum, sodium aluminate and high doses of polyelectrolyte were all effective in relieving sludge bulking, but each suppressed nitrification. Although nitrification reappeared a short time after the addition of polyelectrolyte ceased, the addition of alum or sodium aluminate gave a long-term inhibition to nitrification.

c. The effluent pattern of the nitrification corresponded precisely to that of the dynamic loading, but the nitrification pattern was delayed 2 to 4 hours from the dynamic loading.

d. Effluent DOC's did not vary sharply regardless of dynamic loadings with high peaking factors, because NB-DOC content increased as the LF decreased.

6. Dynamic flow denitrification:

a. Significant denitrification was obtained within a week from the initiation of the tests, and although no sludge bulking problems were observed, the heavy loss of solids due to gas-lifting was the most serious problem in operation. Gas-lifting was minimized for the PAC unit by applying a degasification device. Polyelectrolyte for the PAC unit was not needed. Although gas-lifting was reduced somewhat for the non-PAC unit by using the degasification device along with the addition of polyelectrolyte, a heavy loss of solids still persisted.

b. In the denitrification tests, particularly from test DN-7, it was concluded that denitrification was carried out by two different groups of denitrifiers, Denit I and Denit II.

c. The gas-lifting problems were believed to be caused by the reaction of the Denit II group of denitrifiers.

d. Various amounts of excess methanol were used as a carbon source and the results show that different amounts of excess methanol did not alter the pattern of denitrification, but the M/N ratio increased as the excess decreased.

e. Two different buffer systems, bicarbonate and phosphate, were used to control the pH. pH variations from 7.2 to 8.8 did not inhibit denitrification.

7. Model predictions and simulations:

a. Using the computer program as described, model simulations were made for all the test data from the nitrification and denitrification experiments, and the results of the simulations corresponded closely to the test data.

b. One of the major benefits from the use of PAC in activated sludge comes from more complete and rapid substrate removal. NB-DOC's became negligible during high loading and increased as the LF decreased to 0.25

or less.

c. Temperature dependency of nitrification and denitrification was demonstrated to show the relative changes in nitrogen concentrations and microbial concentrations with temperature.

d. The addition of PAC did not alter the kinetics of nitrification and only slightly affected that of denitrification. If a highly adsorbable organic substrate other than methanol is chosen as a carbon source for denitrification, it would alter the kinetics of denitrification significantly.

e. From sensitivity studies of the kinetic coefficients, it was found that the maximum growth rate coefficients have the greatest influence on the kinetics of both nitrification and denitrification. The process sensitivity to the various coefficients was found to decrease in the following order: maximum growth rate, yield, saturation coefficient, and decay coefficient. For the nitrification unit, kinetic coefficients of heterotrophs influence the degree of nitrification very little, and the kinetic coefficients of nitrifiers did not affect the organic substrate removal.