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The Challenges of Treating a Complex Pharmaceutical Wastewater

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THE CHALLENGES OF TREATING A COMPLEX PHARMACEUTICAL WASTEWATER

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INTRODUCTION

Newly mandated pharmaceutical pretreatment standards imposed by the USEPA and adopted by the city of Albany, Oregon, has led Synthetech, Inc., to install a wastewater treatment system. The new system, installed in the fall of 2001, is not only enabling Synthetech to meet the Federal and local pharmaceutical pretreatment standards, but is also saving Synthetech over $18,000/month in off-site disposal costs, sewer charges and POTW "site development charges".

BACKGROUND

Synthetech, Inc., of Albany, Oregon, produces peptide building blocks and specialty amino acids that are globally distributed to major pharmaceutical companies. Over 300 novel amino acids/alcohols/esters/amides are available from Synthetech for clinical development and commercial purposes. Products are offered in quantities ranging from grams to tons. Because of this, chemical manufacturing occurs in batches that contribute to large swings in waste production. Also, a wide range of chemicals is used within production to facilitate the synthesis of the various products, resulting in large fluctuations in variety and concentration of contaminants in the wastewater requiring treatment (see Table 1 and 2), generating wastes that represent a challenge to be treated safely and reliably.

Table 1 - Synthetech Wastewater Characteristics: Conventional

	Process	Non-Process
BOD_5, mg/L	14,000 – 24,000	
COD, mg/L	30,000 – 90,000	1,000 – 2,000
NPOC, mg/L	12,000 – 38,000	300 – 400
TKN, mg/L	1,500 – 14,000	6
NH_3-N, mg/L	1,200 – 13,000	1
TS, mg/L	70,000 – 115,000	3,000 – 4,000
TA, mg/L	47,000 – 65,000	2,000 – 3,000
Chloride, mg/L	14,000 – 25,000	300 – 500
SS, mg/L	10 – 100	60 – 80

Table 2 - Synthetech Wastewater Characteristics: VOCs, Semi-VOCs

	Process	Non-Process
Methylene Chloride, mg/l	120 – 380	0.3
Toluene, mg/l	15 – 50	0.03
Acetone, mg/l	20 – 65	10
Ethylacetate, mg/l	20 – 1,500	2
Tetrahydrofuran, mg/l	60 – 650	0.01
1,2 Dichloroethane, mg/l	1 – 8	0.6
MTBE, mg/l	600 – 1,300	0.2
Total Detected VOCs, mg/l	1,500 – 3,000	11

Synthetech discharges its wastewater stream to the Publicly Owned Treatment Works (POTW) of the City of Albany. The Albany POTW incorporated the Federal Pharmaceutical Pretreatment Standards into the local codes. These treatment standards include 23 Volatile Organic Compounds, pH and Ammonia Nitrogen. In addition to the contaminant limitations, the POTW levies a tolling charge on industrial wastewater dischargers tied to biochemical oxygen demand (BOD) loading and Total Suspended Solids (TSS) loading, and also a Site Development Charge (SDC) for increased quantities of BOD and/or TSS to the POTW. A large increase to the Synthetech SDC was intended for Synthetech based on increases of daily average BOD loading over 195 lbs/day, calculated monthly. Given the financial penalties alone, it behooved Synthetech to minimize the discharge of VOCs and organics to the sewer.

INITIAL DEVELOPMENT AND TESTING

The treatment of Synthetech wastewaters was investigated when waste minimization proved to be inadequate. Treatment approaches evaluated were UV/oxidation, GAC, evaporation, and biological treatment alternatives, including the PACT® system. And of these, the PACT system was chosen for testing and design development in 2000 because of the highly variable type and concentration of the wastes.

Bench scale testing was initiated on an equal mixture of process wastes and non-process wastewaters to assess performance and obtain insight into the challenges of treating the combined wastes. Results of the testing indicated that the treatment of the combined wastes' VOCs was not a problem, as shown in Table 3. Also, removal of BOD and COD was good, and there was assimilation of nitrogen in the production of biomass (see Table 4). However, ammonia removal via biological nitrification was problematic. Further analytical investigation noted that the sulfate concentration of the combined waste stream was 1,500 mg/L to 4,000 mg/L, well in excess of the inhibitory concentration for nitrification. Certain amines were present that could also inhibit nitrification. Based on this, it was apparent that sufficient ammonia could not be biologically nitrified to meet the required pretreatment standard of 29 mg/L.

Table 3 - Testing: PACT Testing, VOCs (mg/L)

	Influent	Effluent	Discharge Standards
Methylene chloride	250	0.031	0.7
Toluene	35	< 0.004	0.2
Chloroform	< 1	< 0.0006	0.03
Acetone	52	< 0.050	8.2
Ethylacetate	750	< 0.500	8.2
Tetrahydrofuran	360	0.0337	3.4
n-Hexane	< 1	< 0.500	0.7
1,2-Dichloroethane	5	< 0.0015	8.2
Methyl –tert-butyl-ether (MTBE)	900	< 0.0014	
Total Detected VOCs	2,100	0.065	

Table 4 - Testing: PACT System, Conventional Analyses

	PACT Feed[1]	PACT Effluent
BOD, mg/l	10,600	480
COD, mg/l	25,000	4,000
TKN, mg/l	1,160	
NH_3-N, mg/l	906	200
TDS, mg/l	53,600	

[1] Mixture of process and non-process wastes

At this point, Synthetech and USFilter, Zimpro Products evaluated a number of alternatives to overcome the ammonia problems, those being sulfate elimination in production (not possible), use of breakpoint chlorination to remove NH_3 (not favored due to potential creation of additional complex chlorinated hydrocarbons), TDS removal by membrane (not recommended due to organics fouling potential) or evaporation means. Of these, it was determined by USFilter and Synthetech that evaporation using a small skid-mounted, factory-built evaporation unit would

best be applied since it was possible to eliminate TDS and control ammonia (see Table 5) without a fouling problem.

Table 5 – Pilot Evaporator Performance

Evaporator pH	Distillate NH_3-N, mg/L
< 2	20
2.5 – 4	30 – 70
> 4	> 80

Bench scale testing was conducted to confirm design conditions and performance characteristics of the proposed system, which is shown in Figure 1. The results of the test work are shown in Table 6 and Table 7.

Table 6 - Testing: Evaporation + PACT® System, Conventional (mg/L)

	High Salt Waste	Evaporator Distillate	Dilute Waste	PACT System Feed[1]	PACT System Effluent	Discharge Limits
COD	67,300	11,000	1,200	6,000	< 600	
BOD	22,400	3,700	--	3,200	< 50	480
Ammonia Nitrogen	8,640	34	1.1	25	< 20	29.4
Total Solids	103,000	40	2,700	1,370	4,130	--

[1] Combination of evaporator distillate + dilute waste

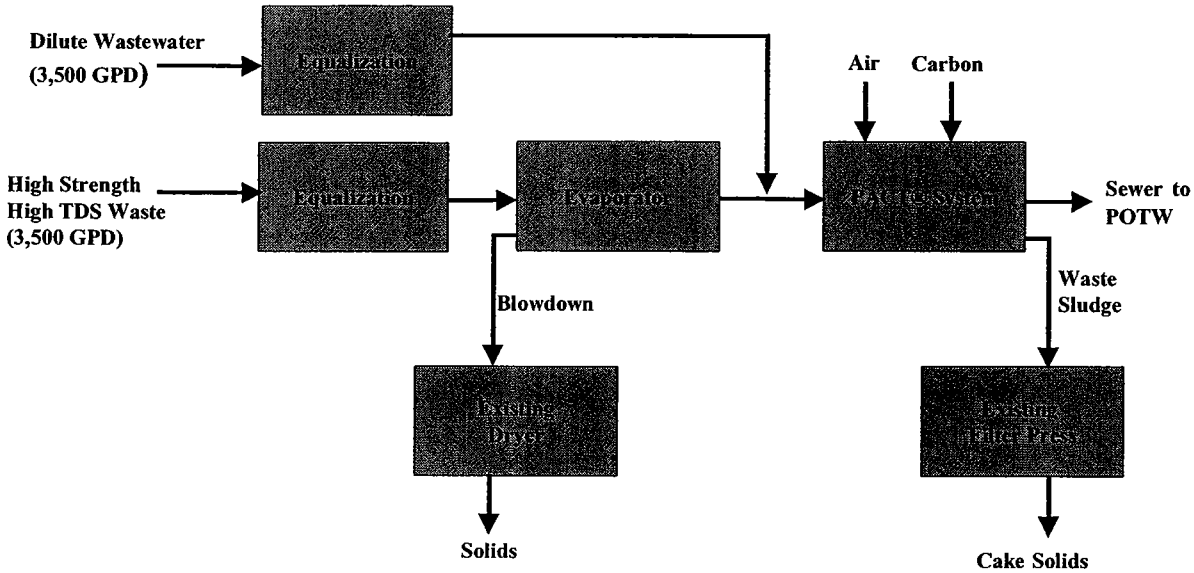
Table 7 – Phase 2 Testing: Evaporation + PACT® System, Effluent VOCs (mg/L)

	PACT System	Discharge Limits
Methylene Chloride	0.004	0.7
Toluene	< 0.0004	0.2
Acetone	0.093	8.2
Ethylacetate	< 0.050	8.2
Tetrahydrofuran	0.214	3.4
1,2-Dichloroethane	0.00051	8.2
Methyl-tert-butyl-ether	< 0.00014	

THE FULL SCALE SYSTEM

Using the information learned in the bench scale testing program, a full-scale system was configured and designed to treat the Synthetech waste streams, i.e. an evaporator for the process stream and a PACT treatment system for the evaporator distillate plus the non-process wastewater, was installed at Synthetech in September, 2001, having the same flow diagram as tested (Figure 1).

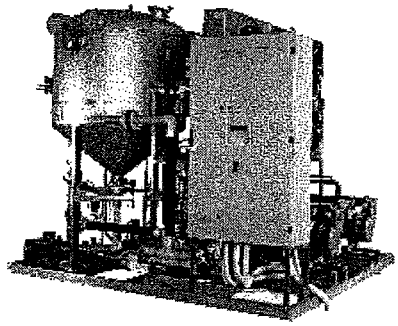
Figure 1 – Synthetech, Inc., Flow Diagram, Full Scale System



The concentrated process wastewaters are sent to the evaporator where the high levels of TDS and problematic nitrogen compounds are removed from the wastewater stream. This results in efficient biological treatment in the downstream PACT system. Originally, the pH of the concentrated waste was kept low to retain the ammonia in solution in the evaporator concentrate. However, the low pH feed resulted in some corrosion problems in the evaporator. Consequently, pH of the feed was raised. Although ammonia levels rose in the PACT system's influent as a result, effluent concentrations remained at acceptable levels. Approximately 3,500 GPD dilute wastewater is combined with the evaporator distillate and treated in the batch PACT system.

The evaporator, a factory built system as shown in Figure 2, exploits the combined effect of vacuum and heat pump technology to obtain a distillation at low temperatures. The heat pump, by means of a refrigerating circuit, expands and compresses the refrigerant which supplies both the heat necessary for the evaporation of the waste and the cooling for the condensation of its distillate. Heat transfer to the unit is accomplished using multiple tube and shell heat exchangers. The heating of compression is dissipated using finned air exchangers and variable speed fans.

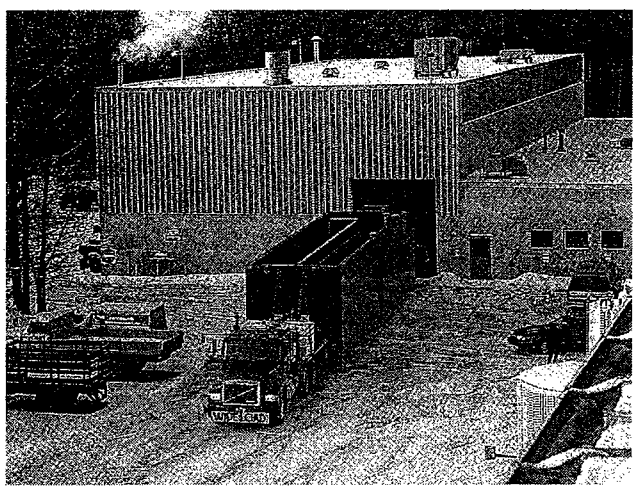
Figure 2 – Photo of Skid Evaporator



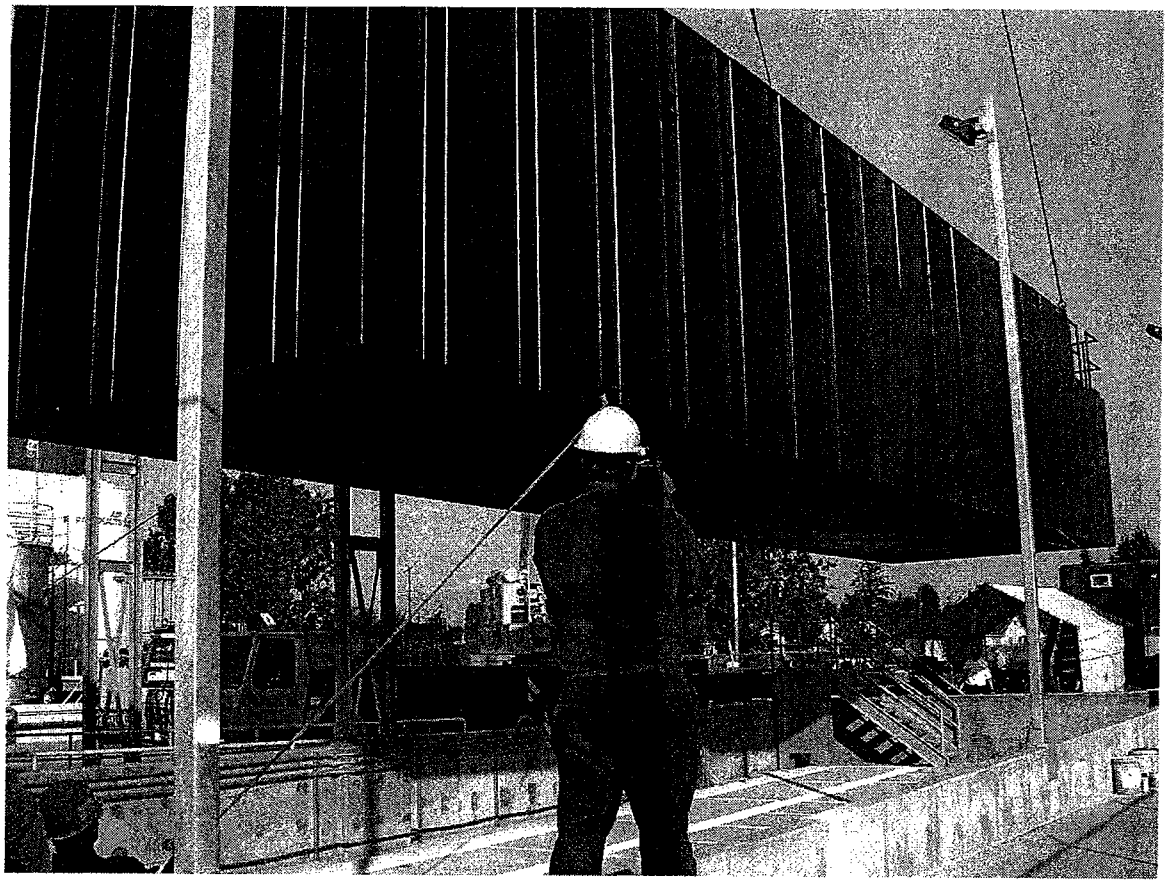
The PACT system is the heart of the treatment process. The PACT system treats the wastewater using powdered activated carbon in combination with microorganisms in a water matrix, and uses diffused air to ensure that the mixture remains homogeneous. The diffused air also ensures that the microorganisms in the system are given sufficient oxygen so that biodegradable organics are biologically stabilized. The activated carbon initially adsorbs much of the contaminants like VOCs and other organics, the VOCs/organics becoming the substrate upon which the microorganisms live. This allows the microorganisms to have opportunistic access to the contaminants, making them far more efficient in the process of oxidizing/destroying the sorbed organics.

The PACT system supplied at Synthetech is a factory-built, sequencing batch reactor (SBR) unit consisting of an aeration/settling tank, aeration blower, air distribution system, and delivery systems for various other inputs.

Full Scale PACT® System Leaving Manufacturing Plant



Full Scale PACT® Unit Being Lowered at Synthetech Site



The PACT system was designed to handle a waste stream of approximately 3,500 gallons of non-process water and 3,500 gallons of evaporator condensate from the process water. The PACT system measures 14 ft. x 12 ft. x 60 ft. and is outfitted with a cover, pH probe and continuous pH adjustment system. It has feed lines for addition of the wastewater, liquid polymer, and microorganism nutrients, and a vent discharge line that is connected to Synthetech's existing vent control system. Activated carbon is charged through a port on top. There is also a pump for removing sludge and a decant system for removal of treated wastewater.

The overall wastewater treatment system also uses existing equipment, i.e. tankage for wastewater storage/equalization, a sludge dryer for the evaporator concentrate, and a plate filter press for minimizing sludge to disposal. Synthetech also uses some production equipment as back up to the evaporator and dryer including a reactor and/or distillation column.

RESULTS

The overall system has performed in accordance with, and, in ways, than planned objectives. Effluent limit goals (ELGs) and local standards have been consistently met. Sewer surcharges are reduced. BOD and TSS levels have been maintained such that Synthetech has avoided the excessive SDC charges that it would have otherwise incurred. Residuals are consistently well within standards. Table 8 compares Synthetech discharges of non-process (dilute) wastes to the POTW for July, 2001, against treatment of all wastes when the overall system was installed.

Table 8 - Discharges to Albany POTW

Treatment System	Approx. Flow, GPD	BOD, lbs/mo	DCM, ppb	Toluene, ppb	Acetone, ppb	MIBK, ppb	Total Other VOCs, ppb
Prior to PACT® System Installation (Jul-01)	2,600	5,600	153	196	34,800	549	682
After PACT® System Installation	4,000	10	ND	< 5	< 2	ND	< 5

ND – non-detectable

It is notable that about 10 months into its operation, a problem occurred with the evaporator that required it to be off-line for an extended time. During this time, a TDS and organic load was placed on the PACT system not originally intended. Discussions between Synthetech and USFilter focused on the past bench scale pilot work to help determine a path forward. Synthetech began by gradually increasing the TDS concentration and organic load to the PACT system by carefully adjusting the amount of process waste to the PACT system. Synthetech was also careful in monitoring the high TDS wastewater to the PACT system. Synthetech maintained the load on the PACT system under about 750 lb/d COD. The program was successful in continuing treatment and maintaining a superior effluent quality despite the unavailability of the evaporator. Table 9 data shows what was originally expected as load to the PACT system and performance, and what was actually observed when the evaporator was on-line and when the evaporator was off-line. Carbon dose was held constant during this period.

Table 9 – PACT System (Full Scale)

	Anticipated (Evaporator On-line)	Actual (Evaporator On-line)	Actual (Evaporator Off-line)
Feed COD, lb/d	360	600 – 650	700 – 750
TDS, mg/L	5,000	< 10,000	30,000 – 35,000
Effluent BOD, mg/L	< 50	< 10	25
Effluent COD, mg/L	< 600	150	400
Effluent TSS, mg/L	< 50	120	250
Acetone, ppb	< 5	< 2	28
MTBE, ppb	ND	ND	< 1.5
MEK, ppb	ND	ND	< 1
Total Other VOCs, ppb	< 5	< 5	12

ND – non-detectable

As expected TDS concentration increased in the PACT with the evaporator off-line. The levels reached were higher than recommended for PACT system tolerances. None-the-less, the PACT system performed well.

These were some of the observations when PACT aeration TDS concentration went from < 1% to > 3%:

1. Effluent COD will increase when there is a significant increase in wastewater TDS.
2. Effluent SS will increase when there is significant increase in wastewater TDS.
3. Temperature has little impact on performance at a constant aeration TDS concentration within the temperature range of 70° - 90°F (20° – 32°C).
4. The PACT system as supplied has greater capacity to treat BOD, COD, and VOCs than originally designed.
5. The measured COD loading method used by Synthetech to feed the PACT system appears to be a reasonable approach to optimize system performance.

FINAL CONCLUSIONS

1. Synthetech has demonstrated that a PACT system is a reliable and effective means for treating waste streams with high VOC and COD levels as would be typical of the pharmaceutical chemical synthesis manufacturing sector.
2. The PACT system provides flexibility in handling batch type deliveries with contaminants that vary in type and strength.
3. VOCs have been treated consistently, and easily comply with the Federal Pretreatment Standards that went into effect September 21, 2001.
4. Total COD loading is a quick and reliable parameter to use for predicting the correct feed for a PACT system. For our case, COD data can be used to reliably predict BOD.