

# THE USE OF EVAPORATION AND BIOLOGICAL TREATMENT TO MEET PHARMACEUTICAL PRETREATMENT STANDARDS

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## INTRODUCTION

Pharmaceutical pretreatment standards imposed by the USEPA in 2001 and adopted by the city of Albany, Oregon, triggered Synthetech, Inc., to install a wastewater treatment system. In addition, the City of Albany planned to dramatically increase their System Development Charge (SDC) – a levy used by the City to fund expansion of their wastewater treatment system – making Synthetech’s new wastewater treatment system even more important.

The new system has enabled Synthetech to meet the Federal and local pharmaceutical pretreatment standards and to avoid exceeding the BOD loading limits that would have triggered the SDC increase. The system matches the plant batch operations profile while minimizing operational support staff

## 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/chiral intermediates and peptide fragments are available from Synthetech for clinical development and commercial purposes. Because products are offered in quantities ranging from grams to tons, chemical manufacturing occurs in batches that contribute to large swings in waste production. Also, a wide range of chemicals is used in production to facilitate the synthesis of the various products. This results in large fluctuations in variety and concentration of contaminants in the wastewater requiring treatment (see Tables 1 and 2), and generating wastes that are a challenge to treat safely and reliably.

**Table 1 - Synthetech Wastewater Characteristics: Conventional**

	Process	Non-Process
BOD <sub>5</sub> , 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 <sub>3</sub> -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. In 2001, the Albany POTW incorporated Federal Pharmaceutical Pretreatment Standards into the local codes. These treatment standards include limitations for 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 SDC was intended for Synthetech based on increases of daily average BOD loading over 195 lbs/day, calculated monthly. The plant could not continue to operate without a reliable means of controlling VOCs. Also, it made sense for Synthetech to minimize the discharge of BODs in order to avoid the additional, one-time added SDC charge, estimated at \$386,000- \$1,000,000.

As will be shown, the treatment performance of the new wastewater treatment system has been exceptional. However, some challenges arose that needed to be overcome. This paper will summarize those developments.

## **INITIAL DEVELOPMENT AND TESTING**

The treatment of Synthetech wastewaters was investigated when waste minimization and solvent recovery proved to be inadequate. UV/oxidation, GAC, evaporation, and biological treatment alternatives, including the PACT® system, were the treatment approaches evaluated. Of these, the PACT system was chosen for testing and design development because of the highly variable type and concentration of the wastes. There have been a series of papers produced about this system since it was commissioned in the fall of 2001. A list of these is provided in the bibliography at the end.

Bench scale testing was initiated in early 2000 using an equal mixture of process wastes and non-process wastewaters as feed. The testing aimed to assess performance and gain insight into the challenges of treating the combined wastes. Results of the testing indicated simultaneous reduction of VOCs was not a problem. Also, removal of BOD and COD was good, and there was assimilation of nitrogen in the production of biomass. However, ammonia removal via biological nitrification was problematic. Also, the sulfate concentration of the combined waste stream was 1,500 mg/L to 4,000 mg/L – a level detrimental to nitrification. Certain amines were present that could also inhibit nitrification. It was apparent that sufficient ammonia could not be biologically nitrified to meet the required pretreatment standard of 29 mg/L. Ultimately, this issue was to surface during operation.

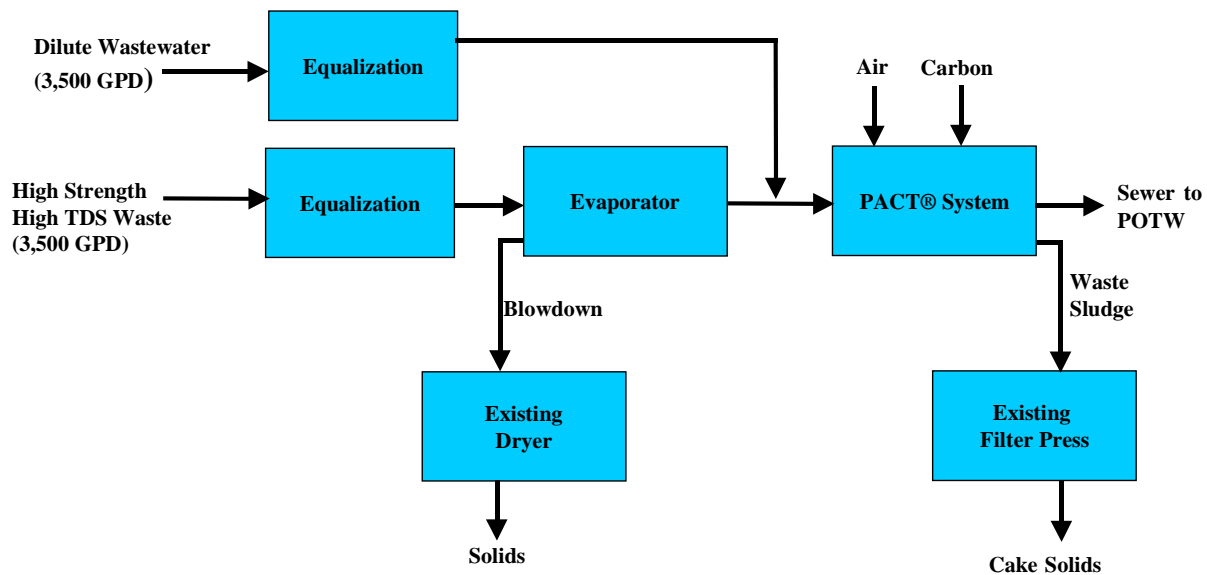
At this point in the development process, Synthetech and USFilter, Zimpro Products evaluated a number of alternatives to overcome the ammonia problems. For several reasons, the method chosen to deal with

this issue was pretreatment using evaporation. A small, skid-mounted, factory-built evaporation unit was chosen to eliminate TDS and control ammonia. Note that distillation in existing equipment continued for certain process waste streams to reduce, and where possible, recover solvents prior to wastewater treatment in the evaporator/PACT system.

### THE FULL SCALE SYSTEM

Using the information learned from the bench-scale testing program, a full-scale system was configured and designed to treat the Synthetech waste streams. The system consisted of an evaporator to pretreat the process stream and a PACT treatment system to further treat the evaporator distillate after combining it with the non-process wastewater. This equipment was installed at Synthetech in September, 2001. A flow diagram is provided (Figure 1).

**Figure 1 – Synthetech, Inc., Flow Diagram**



The evaporator is a factory built system that exploits the combined effect of vacuum and heat pump technology to obtain 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.

The PACT system is the heart of the treatment process – it 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 (Figure 2).

**Figure 2 – Installed and Operating PACT® System**



The 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 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 system measures 14 ft. by 12 ft. by 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. 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, such as tankage for wastewater storage/equalization, a sludge dryer for the evaporator concentrate, and a plate filter press for minimizing sludge to disposal. Synthetech uses an existing distillation column to recover solvents from particularly concentrated waste streams prior to treatment in the evaporator/PACT system. Also, some production equipment is used as back-up to the evaporator.

The concentrated process wastewaters are sent to the evaporator where the high levels of TDS and problematic nitrogen compounds are reduced to levels that the system can handle. This results in efficient biological treatment in the downstream PACT system.

Synthetech monitors COD in and out of the system. Data indicates that BOD levels (monitored by the City of Albany) are two-thirds to a fraction of the COD level. It is crucial that we limit effluent BOD loading to less than 195 lbs/day to avoid stiff penalties. The COD is a simple test that provides us assurance that the BOD level meets the limit prior to discharge. It has proven to be a reliable surrogate for

Synthetech to use to assure that BOD targets are met. Synthetech also conducts daily screening for the 23 VOCs on the Pharmaceutical Pretreatment list as well as for the level of residual ammonia.

These tests are conducted on the PACT effluent prior to discharge (Figure 3). If a batch exceeds limits for any of the key parameters, Synthetech maintains sufficient tankage to hold the batch for further digestion by the PACT system. To date, only one batch – out of over 700 – has been returned for further processing. This batch was returned for high ammonia and was successfully treated for discharge the next day.

The City of Albany also monitors Synthetech effluent for BOD and Suspended Solids on a bi-monthly basis, and for 64 VOCs on a monthly basis at unannounced sampling times determined by the City.

**Figure 3 – Synthetech Conducts Daily Tests for Ammonia**



## **RESULTS**

The PACT /evaporator system has performed well. The most recent year of data demonstrates how well and how reliably the system is performing despite some problems, discussed further in the next section.

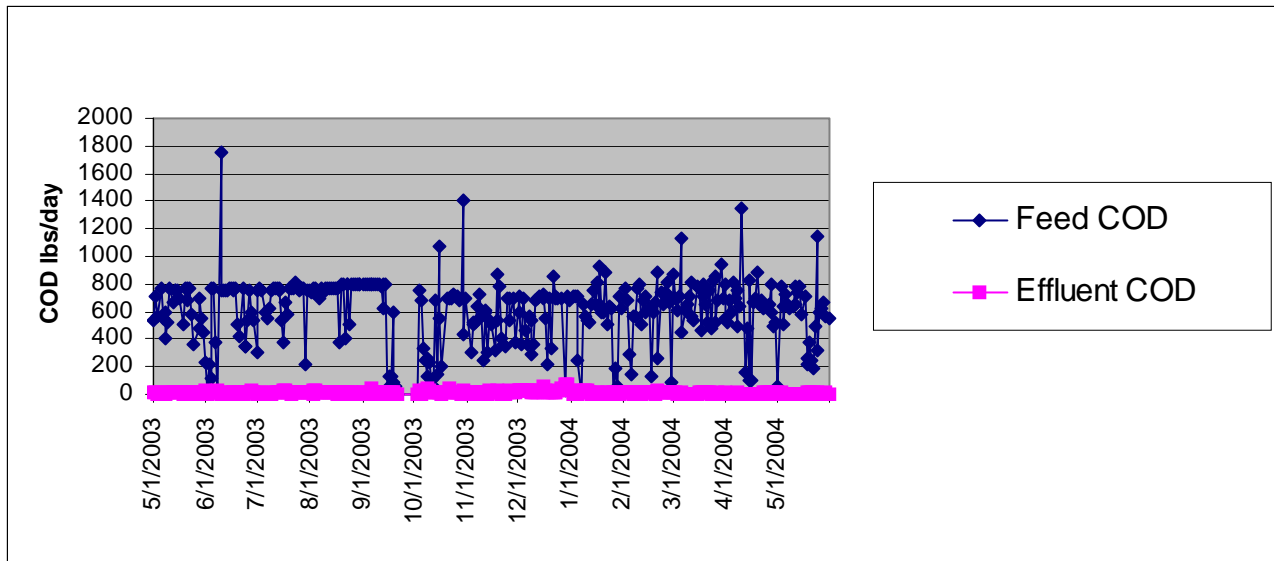
The overall system is meeting planned objectives. The data reported here encompasses the 13 months from May.2003 through May 2004. Effluent limit goals (ELGs) and local standards have been consistently met.

The system has treated an average of 3,560 gallons of non-process water and 597 gallons of process water during each operational day during this monitored period. Operations typically included six days/week. Counting all days, this equals 3,111 gal/day and 516 gal/day respectfully. During this time, the PACT system was fed an average of 607 lbs/day of COD frequently exceeding 800 lbs/day. Over the year, this amounted to 531 lbs/day. (Note that the latter number includes a two-week, plant-wide shutdown period, during which 20,000 gallons of the culture were stored in two, 10,000-gallon aerated tanks and fed only sparingly.)

COD removal for the period was 98 percent, effluent to sewer averaging about 12.0 lb/d or 261 mg/l (Figure 4). This equated to an effluent BOD on average of 2 lbs/day or about 44 mg/l. This is obviously well within the targeted 195 lbs/day BOD that the City of Albany had specified. Prior to installation of the

PACT system, Synthetech effluent discharges frequently surpassed 1000 lbs/day, which necessitated the process wastewater be treated offsite. No wastewater has been treated offsite since the PACT system was installed.

**Figure 4 – COD Feed vs. COD Effluent**



Wastewater TDS values to the PACT system averaged 12371 mg/l (1.2%) and ranged from 3600 mg/l (0.3%) to 22400 mg/l (2.2 %). MLSS maintained within the PACT system averaged 20438 mg/l and ranged from 15200 to 28800 mg/l.

In addition, prior to installing the PACT system, Synthetech had a recurring problem with exceeding VOC limits imposed on the plant by the City of Albany. This was in spite of the fact that only the non-process wastewater was being discharged to the City. During this monitoring period, the average of the sum total VOC population monitored by the City of Albany was 0.17 mg/l. The offsite laboratory performing the VOC analyses monitors for 64 VOCs. It is a common occurrence to find ND for all these values.

The system at Synthetech does have its “Achilles heel” parameter that we have to monitor carefully. This parameter is the nitrogenous compounds involved. . Since the waste stream has considerable exposure to amino acids, this is expected, and was not a surprise as evidenced by early bench-scale testing, provided by USFilter. Accordingly, there is enough flexibility built into the design that a little operating experience is all that is needed.

Synthetech has experienced no compliance problems. Ammonia values discharged to the City average 5.5 mg/l with a high of 25 mg/l against the City of Albany limit of 30 mg/l. In one instance, ammonia in the decant prior to a planned discharge did exceed the limits. Synthetech deferred the discharge using existing tankage to hold material while that batch was returned to the PACT system for further processing. After one more day of processing, the PACT system reduced the levels within range.

Review of the performance to date indicates that Synthetech should be able to rely on the existing PACT tank system to handle higher loading of waste streams before the system reaches capacity. This may be limited by two factors: nitrifying bacteria and suspended solids.

## **Nitrification**

The system has experienced a brief bout with nitrification/denitrification and nitrifying/denitrifying bacteria. During late summer and early fall of 2003, the system developed a population of nitrifying and denitrifying bacteria, first noted when Synthetech experienced difficulty getting the sludge to settle for decant. During this part of the cycle, the aeration blower is shut down and a coagulant polymer added to consolidate the sludge. The clear supernatant that develops is then decanted off for discharge to the City of Albany.

Unfortunately, during this time, the sludge would settle and then quickly float back to the surface before it was clear enough to decant. After consultation with USFilter, we recognized that our “bug” population had developed a group of nitrifying and denitrifying bacteria. While the aeration system is on, these bugs convert nitrogenous compounds to nitrates. When the air is shut off, the system quickly goes anoxic. In this type of culture, denitrifying bacteria then metabolize the oxygen from the nitrate, liberating nitrogen gas in the process. This gas release floats the sludge. Nitrate levels reflected this scenario. They existed prior to decant and then disappeared. The floating sludge was noted to be full of tiny gas bubbles.

This issue appeared in September, 2003, about the time Synthetech scheduled the PACT system to be down for repairs due to corrosion damage. To continue operating the system until the shutdown, Synthetech and USFilter developed a procedure to do so. The normal decant cycle was conducted until the sludge floated, allowing time for the bugs to use up most of the nitrate. Then the system was aerated, stirring up the sludge and releasing the entrapped nitrogen gas. At that point, the sludge was allowed to settle again. By this time, nitrate levels had been reduced so that no more was available to produce nitrogen, and the decant cycle could be successfully completed. While not the most efficient way to operate, it allowed the plant to continue processing site water until the scheduled shutdown.

During shutdown, we discovered that corrosion issues had compromised some of the air diffusers in the PACT system. The resulting dead zones in the system may have contributed to an “aged” sludge that helped develop the denitrifying population. Considerable additional sludge was wasted as part of the shutdown, which led to a more normal sludge age after the shutdown.

After the shutdown, the system returned to normal, largely on it’s own. We did experience high suspended solids for a time, but the increased fees for discharging the higher SS to the City are marginal and did not pose a burden while the system returned to equilibrium. Synthetech did learn the hard way that generated wastes are particularly corrosive due to high salt (chlorides) loading, despite neutralization steps prior to the PACT tank to ensure neutral pHs going into that system. Because of these corrosive conditions, frequent (annual) inspections of the PACT system are warranted.

## **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 or fine chemical manufacturing sectors.
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.
5. Nitrification can occur in PACT systems that are handling wastewaters rich in nitrogenous compounds such as amino acids.
6. The decant cycle of a PACT system can be manipulated to mitigate the impact of denitrification on sludge settling.
7. Wastewater treatment systems with known corrosive fluids should be regularly inspected to ensure that corrosion is not an issue.

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