

Leachate Treatment Methods When Gas Wells Are Aggressively Pumped

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ABSTRACT

As landfills commence extracting and beneficially using landfill gas for energy, the quality of leachate and the associated condensate from gas treatment causes constituents in the wastewaters to increase, often significantly. BOD, COD, ammonia and other constituent concentrations, such as phenol, VOCs (both chlorinated and non-chlorinated) and PCBs may increase by up to an order of magnitude or more. Depending on the disposition of the leachate, these increased constituents may cause the leachate (with blending of the gas condensate) to cause effluent violations. This increase may cause landfill operators to retrofit leachate treatment systems to address these issues, and the problems are significant from both an operation and cost perspective. The constituent concentrations also exhibit a wide variability relating to which gas wells are in use and their balancing, gas withdrawn from active versus legacy cells, precipitation, temperature, and other factors. The gas wells serve as a vertical conduit for younger, stronger leachate to be collected compared with a mature leachate that has had more residence time before collection, and thus has further degraded. A number of technologies have been used to improve the quality of the leachate/condensate at landfills without gas well, and alternative technologies may be used at landfills employing gas well pumping and gas condensate compared to landfills without these uses. Alternatives for both off-site and on-site management alternatives include hauling to an off-site location; leachate recirculation; constructed wetland treatment;

phytoremediation; physical/chemical treatment such as precipitation, ion exchange, and reverse-osmosis membrane treatment; and leachate evaporation. Biological treatment may be a component of the previous technologies, or used as a stand-alone alternative. Cost implications for alternative technologies are site dependent, but guidelines are presented for generalized site alternative costs and a structured evaluation method for ranking alternatives is shown at the end of this paper.

Key Words: Leachate, Gas Well Condensate, Treatment, Evaluations

INTRODUCTION

As landfills increasingly extract and process gas, experience has shown that leachate constituents increase. Landfill operators are using more aggressive gas extraction techniques to increase gas supply by increasing pumping rates, extraction vacuum or other techniques. The resulting quality of gas well extraction liquids is showing higher constituents than leachate pumped from the bottom of a waste pile. If the extracted gas is treated to remove condensate, even further increases of constituents have been observed. The liquid must be treated before discharge, and these increasing concentrations require larger, more complex treatment processes that cost to install and operate,

An example of an east coast US landfill leachate BOD that has been impacted by landfill gas is shown below:

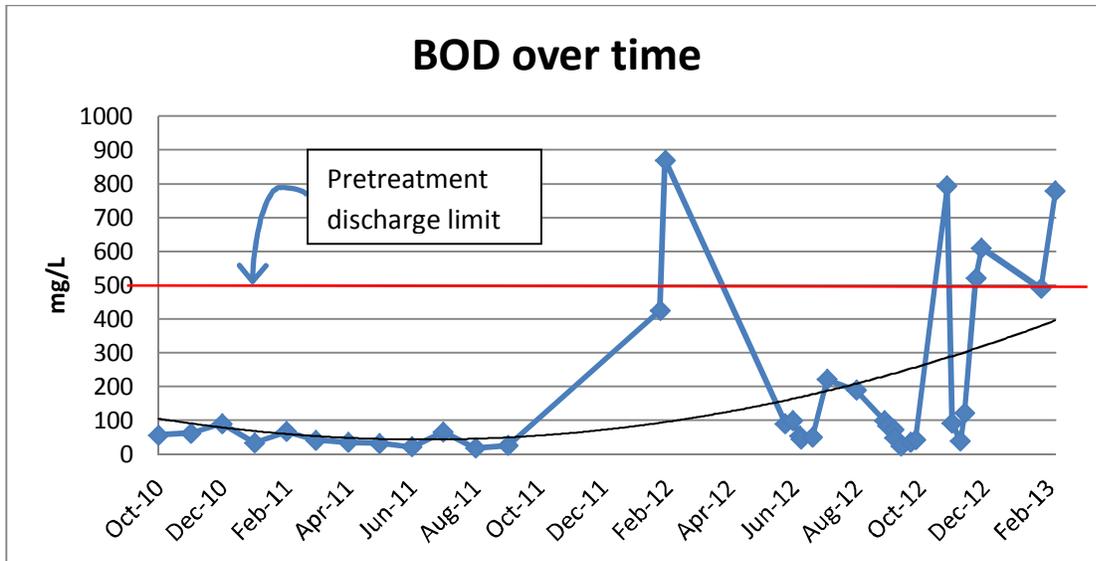


Figure 1. Comparison of Leachate BOD before and After Aggressive Gas Well Pumping

A number of technologies have been used to improve the quality of the leachate/condensate at landfills without gas well, and alternative technologies may be used at landfills employing gas well pumping and gas condensate compared to landfills without these uses. Alternatives identified for both off-site and on-site management alternatives include hauling to an off-site location; leachate recirculation; constructed wetland treatment; phytoremediation; physical/chemical treatment such as precipitation, ion exchange, and reverse-osmosis membrane treatment; and leachate evaporation. Biological treatment may be a component of the previous technologies, or used as a stand-alone alternative. Cost implications for alternative technologies are site dependent, but guidelines are presented for generalized site alternative costs and a structured evaluation method for ranking alternatives is shown at the end of this paper.

TREATMENT TECHNOLOGIES

Physical / Chemical

Physical-chemical treatment systems for TKN removal include pH adjustment with air stripping, ion exchange, volatilization, chemical oxidation, evaporation and membrane processes. Most of these processes are not capable of reducing the excess BOD when that parameter exceeds the 300 mg/l concentration. Physical-chemical treatment systems

potentially applicable include chemical oxidation, evaporation, and membrane processes. Metals removal by chemical precipitation or other means is important to preclude interference with biological treatment, and to avoid discharge concerns with either pretreatment or direct discharge.

Anaerobic pretreatment is a commonly used technology to efficiently reduce high strength BOD/ammonia concentrations for subsequent aerobic biological treatment. Physical - chemical treatment systems for BOD include chemical oxidation, membrane processes and evaporation. Oxidation treatment may include breakpoint chlorination, membrane processes and evaporation. Higher concentrations than stoichiometric ratio of chlorine compound are usually required for breakpoint chlorination, typically about 8 parts chlorine to one part ammonia. This would require a significant concentration of chemicals to be added to many leachate streams for ammonia removal. Although breakpoint chlorination is a relatively simple operation, regulatory agencies discourage this practice due to the environmental impacts of the use of chlorine. BOD excesses are not removed by chlorination.

Membrane Technologies

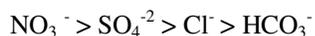
Membrane processes including Reverse Osmosis, Nano Filtration, and Ultrafiltration. Evaporation is a

commonly used land based technology in the drier Western US, but is not feasible in the wetter Eastern US. Deep well injection in acceptable geologic terranes may be an option to consider, but corrosion and regulatory constraints may also apply. Mechanical evaporation/crystallization systems are complex and have high CAPEX as well as OPEX. Additionally, the membrane processes are simply as separation technology, requiring 10 – 30% or more of the influent flow as a reject to be managed further, typically redistributed on the landfill surface. The redistributed leachate may undergo additional anaerobic treatment as it again flows through the waste material.

Ion Exchange

Two types of ion exchange systems may be employed for nitrogen removal: cation or anion exchange systems for ammonium or nitrate ion removal, respectively. Ammonium is readily sorbed using activated carbon and ion exchange media such as natural zeolites and resins, whereas nitrate is generally less readily exchanged except with modified zeolites or specific anion-exchange resins. In the ion exchange process, as the flow passes through the exchange media, the ammonium cation (or nitrate anion) is preferentially exchanged for an ion attached to the media's exchange site, for example ammonia may be exchanged for Na^+ or nitrate for Cl^- .

Natural zeolites are low cost ion exchange materials shown to remove ammonium from water and can be modified with surfactants for uptake of anions such as nitrate. Clinoptilolite, a common naturally occurring zeolite that has excellent selectivity for ammonium over most other cations in wastewater, can be used as an exchange medium. Nitrate is less strongly exchanged/sorbed due to its anionic nature and fewer positively charged exchange/sorption sites on the zeolite surface. Competition between nitrate and other common anions also reduces nitrate uptake with the affinity for the following ions in decreasing order of:



Zeolites are crystalline hydrated aluminum silicates with a framework structure containing pores that are occupied by water and various cations. Due to their high cation-exchange ability as well as molecular sieve properties, natural zeolites (cheap and easily available in large quantities in many parts of the world) are particularly suited to water and gas

purification, adsorption and catalysis. Zeolites also have an advantage over filter materials with significant permeability and are widely used for water purification by filtration. Clinoptilolite is considered one of the most suitable ion exchange materials for ammonium removal from drinking water and wastewater due to its ammonium-ion selectivity and performance in ammonium sorption under a range of temperatures. NH_4^+ removal rates from water using clinoptilolite have been reported in the range of 72 % to 86 % with concentrations in the 1 -10 mg/L range and with a pH less than 7. Approximately 5 percent of nitrate concentrations can be removed.

The ammonium cation-exchange capacity of clinoptilolite varies depending on the presence of other cations in the aqueous phase and initial ammonium concentrations. Amounts of NH_4^+ adsorbed by clinoptilolite increase with increasing initial concentration in an aqueous solution, and NH_4^+ adsorption and desorption by zeolite is a particle-diffusion controlled processes. For best performance the pH level of an aqueous solution must be at or below 7. The exchange efficiency is influenced significantly by chemical and physical pre-treatment techniques and loading or regeneration of the zeolite. Sodium chloride solution treatment seems to be the best method of clinoptilolite preparation and regeneration. The efficiency of ammonium removal increases with decreased zeolite particle size. While uptake of nitrate on clinoptilolite would be expected to be minimal, surfactant modified zeolites (SMZ) can be used to remove cations, anions (including nitrate) and nonpolar organic molecules from water. Strong-base anion resins can be employed as an exchange medium for nitrate, but their performance is typically strongly influenced by sulfate concentrations that compete with nitrate adsorption sites as well as with total dissolved solids, and are generally better suited for water polishing purposes.

When contaminated water flows over the resin beads, the chloride ion is exchanged for a nitrate ion because of its relatively higher affinity for the quaternary amine group. The chloride ion flows out with the effluent stream, while the exchanged ion remains bonded to the functional group. When all of the resin's functional groups have been bonded to contaminant anions, the resin is saturated. The resin is then regenerated with a saturated sodium chloride brine solution. Due to the regeneration solution's high concentration of chloride ions in relation to the contaminant ions on the resin, the chloride will displace the contaminant from the resin's functional

group. The resin is then rinsed with the process water and returned to service.

The USEPA has reported that the use of synthetic anionic exchange resins appears impractical at this time. Cation exchange of NH_4^+ with clinoptilolite is feasible but expensive because of the regeneration management costs. Exchange systems require either media disposal or resin/zeolite regeneration on-site or off-site. Further, media may be subject to fouling and clogging problems. Regeneration wastewater must be collected and disposed of as industrial wastewater. Thus, the regeneration of the media and treatment of the regenerant flow adds system complexity and cost. BOD will not be removed in an ion exchange process.

Air Stripping (for ammonia removal)

Air stripping to remove ammonia (NH_3) from water is possible. The high solubility of ammonia in water means that a very high air/water ratio must be used. For each unit volume of water treated, more than a thousand unit volumes of air must be contacted with the water to move the ammonia from solution into the passing gas phase. In the past this has had the consequence that ammonia air stripping towers must be sized very large due to the volume of air that must pass the tower and allow for a reasonable pressure drop across the packing. Ammonia removal is strongly affected by pH (typically most effective at a pH of 10 to 11) and temperature (the higher the better). The pH of the wastewater must be adjusted (raised) in order to enhance the change in speciation from the ammonium ion to ammonia to allow partitioning from the liquid phase to the gas phase with subsequent transfer to a gas stream. The pH must be readjusted prior to discharge or further treatment. Ammonia stripping performance is also highly dependent on air temperature and air/water ratios.

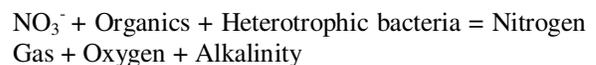
Nitrates will generally not be removed by the air stripping process. According to Henry's law, which describes the partitioning constants for various chemicals, but nitrates are not practically amenable to air stripping technology. Media must be employed that offer an extremely efficient contact between water and air in the stripping tower, and can also accommodate the large volume of air that must pass through the tower with minimal head loss. Therefore, if a biological BOD removal process precedes an ammonia stripping tower, the biological system can be operated in a manner not to convert ammonia to nitrate.

There are two variations of ammonia stripping towers, cross-flow and counter-current. In a cross-flow tower, the solvent gas (air) enters along the entire depth of fill and flows through the packing, as the alkaline leachate flows downward. A counter-current tower draws air through openings at the bottom, as leachate is pumped to the top of a packed tower. Free ammonia is stripped from falling water droplets into the air stream and then discharged to the atmosphere.

Elevated temperature can result in significantly increased ammonia removal rates, with ammonia removal typically doubling with every 6 °C rise in temperature. Similarly, efficiency decreases significantly as air temperature decreases. For example, at 20 °C, there is 90 to 95 % ammonia removal efficiency, while at 10 °C, efficiency decreases to 75 percent.

Biological Treatment

Biological BOD/TKN removal systems can include lagoon based treatment as well as mechanical treatment within tanks. These systems achieve carbonaceous and nitrogen removal through respiration and cell growth. Nitrification (microbial oxidation of ammonia and organic nitrogen to nitrate) and denitrification (microbial reduction of nitrate to nitrogen gas) along with biological oxygen demand (BOD) reduction can occur in bioreactors. The BOD is preferentially removed before ammonia conversion to nitrate occurs. Processes can be suspended growth, attached growth, or hybrid systems that use a combination of attached growth (biofilms) and suspended growth technologies. BOD/TKN removal can be partially achieved by means of volatilization, sedimentation and other mechanisms. Disposal of waste solids generated during treatment is required. Ammonia removal by nitrification utilizes autotrophic bacteria (nitrosomonas and nitrobacter) to oxidize ammonia to nitrate, requiring 4.6 parts oxygen and 7.1 parts alkalinity to convert one part ammonia. In those systems where denitrification is required (and serves as an energy conservation method in treatment), heterotrophic bacteria utilize nitrate as an electron source under anoxic conditions to break down organic substances and remove nitrates, with the reaction as follows:



Biological treatment that includes nitrification/denitrification is termed Biological

Nutrient Removal (BNR) systems. Many treatment systems/configurations are proprietary, though they are generally based on common fundamental treatment principals.

Some of the more common BNR treatment systems include recirculating sand filters (RSFs) with enhanced anoxic modifications, sequencing batch reactors (SBR), and an array of aerobic nitrification processes combined with an anoxic/anaerobic process to perform denitrification. Fixed-film or suspended-growth aerobic reactors can perform the aerobic nitrification when properly loaded and oxygenated. A variety of upflow (AUF), downflow, and horizontal-flow anoxic or anaerobic reactors can perform denitrification if oxygen is absent, including the availability of a degradable carbon source (for heterotrophic nitrification), and other conditions (e.g. temperature and pH). For the purposes of this Preliminary Feasibility Study, sequencing batch reactors (SBR), and attached growth systems will be considered.

Biological treatment may include systems in lagoon treatment, within tanks in mechanical systems, or passive treatment systems such as constructed wetlands and phytoremediation systems. Aerobic biological treatment systems may be installed as a component of the pretreatment prior to, or as an integral portion of the proposed new aeration tank. The proposed new leachate storage tank may be used as a biological treatment unit for the removal of ammonia, organic nitrogen, BOD, or other constituents to meet the permit limits. It may be possible to reconfigure the proposed leachate storage tank to a sequencing batch reactor (SBR), but construction of a separate SBR unit using the proposed leachate storage tank as an equalization and storage unit may prove more reliable and robust for treatment and operation.

In general, biological nitrogen removal systems can be designed to achieve nitrification, along with phosphorous and BOD reduction, in bioreactors followed by or incorporating clarification. Processes can be suspended growth, attached growth, or hybrid systems that use a combination of attached growth (biofilms) and suspended growth technologies.

SBR

Sequencing batch reactors (SBRs) are fill and draw batch systems in which treatment steps are performed in sequence for a discreet volume of water in a single

or set of reactor basins. SBRs use four basic phases for most systems:

- 1) Fill: wastewater is added to the basin and is aerated and mixed;
- 2) React: Biological processes are performed;
- 3) Settle: All aeration and mixing is turned off and the biomass is allowed to settle; and
- 4) Decant: Clarified effluent is removed and biomass is wasted as necessary. Solids removal may occur during the idle decant period or may occur during the react step.

The length of time that each phase occurs is controlled by a programmable logic controller (PLC), which allows the system to be controlled from remote locations. Process stages include the following descriptions:

- In the fill phase, raw leachate enters the basin, where it is mixed with settled biomass from the previous cycle. Some aeration may occur during this phase. Then, in the react phase, the basin is aerated, allowing oxidation and nitrification to occur. During the settling phase, aeration and mixing are suspended and the solids are allowed to settle.
- Wastewater fills the tank, mixing with biomass that settles during the previous cycle
- Air is added to the tank to aid biological growth and facilitate subsequent waste reduction. Corrosion resistant components should be considered. Aeration devices can include non-clog coarse bubble for consistent air flow.
- Mixing and aeration stop during this stage to allow solids to settle to the bottom of the tank. The baffled influent screening compartment prevents short circuiting and simplifies cleaning of treatment systems
- Clarified effluent is discharged. Some manufacturer's proprietary floating decant system excludes solids while remaining accessible in the event of pump failure. No need for confined space entry. If necessary, sludge removal occurs during this stage. Sludge production is minimized, which

means greater savings in the cost of sludge disposal

Denitrification can be programmed into this stage to reduce alkalinity needs and serve as an energy conservation technique. The created wastewater is then discharged from the basin in the decant phase. In the final phase, the basin is idle as it waits for the start of the next cycle. During this time, part of the solids are removed from the basin and disposed of as waste sludge. Sludge wasting is an important control in the SBR process and largely affects system performance, as the quantity and rate of wasting determines the system performance. Generally 0.65 lbs. of sludge are wasted per pound of BOD introduced to the system. An SBR system does not require return activated sludge piping, as both aeration and settling occur in the same tank, saving complexity and cost.

The SBR system mimics other suspended growth processes. It typically completes four to six cycles per day per tank for leachate. If properly designed and operated, SBRs can achieve about 90 percent removal of nitrogen. SBR design for nitrogen and phosphorus removal is essentially similar, but the amount of available carbon required is greater (6 to 8 mg/L COD per mg/L of TKN to be denitrified). If sufficient hydraulic retention time (HRT) is provided to permit nitrification during the "react" phase of the SBR cycle and if the fill stage is anoxic for a sufficient HRT, the system can remove significant amounts of ammonia and nitrate, and phosphorus.

As with any biological treatment system, oxygen requirements, blower design for oxygen required, and other issues should be determined by bench scale tests, which are recommended to be conducted prior to system design.

Attached Growth Systems

Attached growth processes will also provide nitrification and denitrification of wastewater. Trickling filters and rotating biological contactors (RBCs) have historically been used for biological treatment of leachate wastewater and can achieve nitrification with a low organic loading and a relatively high media volume. Typically, nitrification is achieved on the media after most of the BOD is removed since the heterotrophic population competes with the nitrifying organisms for oxygen and space on the media.

Typical nitrogen removal ranges from 40 – 80 % or more. To attain greater (>85 percent) nitrification, fixed-film systems cannot be loaded above 3 to 6 g BOD/m³ per day or 6 to 12 g BOD/m³ per day for rock and plastic media, respectively. Denitrification requires the addition of a supplemental carbon source. Suspended growth processes can be designed to denitrify 80 percent or more of nitrate using the incoming BOD as the carbon source.

Other problems with fixed-film bioreactor systems are rotating system shaft failure, plugging, and limited mass transfer and distribution of air and water through systems using packed bed. Consequently, trickling filters and RBCs are less frequently used/designed for nutrient removal applications. Recent improvements to attached growth systems have overcome many of these limitations, including Immobilized Cell Bioreactors (IBC), Integrated Fixed Film Activated Sludge Systems (IFAS), Moving Bed Bioreactor Systems (MBBR), and others. Suspended growth biological systems were considered but not recommended due to lower efficiency and more susceptibility to shock loads than attached growth systems.

Passive Treatment

Constructed Wetlands offer nitrogen removal capabilities in a combination of physical-chemical and biological removal processes. The several variations of wetlands treatment are described in the following sections. Phytotechnology treatment is the conversion of organic matter and nutrient to vascular plant material, but is usually reserved for treatment with trees, usually hybrid poplars in the US. Several landfills have used this technology successfully in treating leachate, but a significant land area is required. In colder regions, a subsurface drip irrigation system is used to prevent freezing in winter conditions.

Constructed wetlands are a treatment technology where the primary pollutant treatment mechanisms are facilitated by plants. A wide variety of pollutant removal occurs in wetlands such as; biodegradation of organics, nitrification, volatilization, and precipitation. Constructed wetlands use vascular plants to remove and control contaminants, or to encourage contaminant breakdown by microorganisms in the root structure and degrade and bio-accumulate the contaminants in roots, branches or leaves. Constructed wetlands also trap particles and reduce suspended solids concentrations,

subsequently absorbing the contaminants in the rhizosphere.

In general, constructed wetlands have demonstrated good success with BOD, COD, ammonia concentration less than about 300 mg/l average, TSS, and trace metals. Constructed wetlands are not effective for treatment of total dissolved solids, chloride, or high ammonia concentrations. For leachate with high ammonia concentration, pretreatment is typically performed ahead of the constructed wetland to reduce the concentration of ammonia to a level that is not detrimental to the vegetation. Should adequate land become available, a “constructed wetlands” treatment may also include:

- Facultative aerated pond, designed to provide BOD and ammonia nitrogen removal,
- Intermittent sand filter for a portion of the recycled constructed wetland effluent designed for additional treatment of the BOD and ammonia nitrogen components.

Constructed Wetlands

Constructed wetlands are wastewater treatment systems that combine biological, chemical, and physical treatment mechanisms for water quality improvement. The mechanisms for water quality improvement in wetlands include biological nitrification/denitrification and other metabolic processes, adsorption, complexing characteristics, chemical precipitation, and plant uptake. A constructed wetland system commonly has two components: an upstream pond with relatively deep water and littoral macrophytes, and a downstream wetland system of one or more cells with extensive macrophyte vegetation.

Constructed wetlands are generally categorized by their configuration. The “Free Water Surface” (FWS) cells have been used as a polishing technology and have been used to treat mild leachate and other suitable wastestreams. In addition, Vegetated Submerged Bed and Vertical Flow wetland cells are design alternatives and have been used in combination. The Vegetated Submerged Beds (VSB) cells distribute flow under a soil structure and account oxygen transfer from the plant root structure to the subsurface. Both aerobic and anaerobic degradation occurs with VSB units. The Vertical Flow cells (pictured below) distribute flow on the top of a soil surface and include an underdrain system which collected the treated water as it flows

downward throughout the cell. These cells do not transfer oxygen well, and account for contaminant degradation mostly by anaerobic means. The combination of these types of cells has been shown to be effective in landfill leachate at high organic (BOD/COD) loadings and high initial ammonia concentration. Each type of cell generally includes a liner system to prevent groundwater impacts. Plants in wetland cells are chosen for their potential to tolerate and assimilate toxic substances, high growing rates, and characteristic deep roots and the ability.

FWS systems outnumber VSB and VF systems in the United States by over two to one though in Europe the reverse is true. In general, FWS wetlands require more land than the more efficient VSB and VF wetlands for the same pollution reduction but are easier and cheaper to design and build. VSB wetlands have several advantages, particularly in regard to the limited exposure pathway of pathogenic microbes and other contaminants. Treatment systems often use a combination of these alternative designs.

Nitrogen removal in a variety of wetlands types have been successfully used for landfill leachate treatment, as well as municipal, industrial, and stormwater treatment. Many researchers have reported that constructed wetlands can be an alternative for nitrogen removal from water and wastewater via the mechanisms of microbial denitrification and direct uptake by plants and microbes. Denitrification occurs in anoxic zones of sediments beneath an aerobic water surface layer or in anoxic microsites of biofilms attached to plant tissue or substrata. Bacteria in constructed wetlands tend to use plant productivity, either from biomass litter or root release, as the source of organic carbon to fuel denitrification, thus, external carbon sources may not be required. However, most literature reflects influents with substantial available carbon, but testing would be required for effluents, especially those with high mineral content and low carbon.

Phytoremediation

Phytoremediation is a form of passive treatment by plant structures in wetlands, or by grasses or trees in a land application disposal approach. Using either trees (including hybrid poplars or short rotation coppice) or grassland, phytoremediation of leachate has been successful; however, there are a significant number of examples where phytoremediation has failed. Typically, this failure can be ascribed to excessive leachate application and poor management due to a fundamental lack of understanding of critical

plant-soil system interactions. Careful management of a phytoremediation system can be a sustainable, cost effective and environmentally sound option.

For this section, the term “Phytoremediation” will be used to describe landfill leachate treatment in a tree environment as opposed to a constructed wetland described above. Landfill leachate has been treated by phytoremediation techniques at a number of landfills, such as the Jeffco Landfill near St Louis; South Barrington Landfill in South Barrington, Ill; and the Watts Road Landfill in Atlanta. Other tree based treatment and disposal systems have been documented at the Oneida County Landfill in Rhinelander Wisconsin. These sites have documented nutrient uptake without detriment to tree health, and have proven landfill leachate as an irrigation and fertilization technique.

The tree based system typically includes an initial aerated holding pond, and a distribution of the pretreated leachate by a surface drip system in warmer temperatures, and distribution of leachate by subsurface drip irrigation during periods when the ground is frozen.

Hybrid poplars have been utilized in a variety of phytoremediation projects. Some poplar species are ideal for remediation due to their ability to establish quickly after planting and produce large plant biomass, produce extensive root systems, use large volumes of water, can be propagated easily and inexpensively from hardwood cuttings, and grow on marginal lands. The lateral rooting in a Poplar tree is important for nutrient and contaminant uptake (organic carbon, nitrogen and phosphorous) when irrigated with highly variable or specific contaminants found in leachate, as it appears that phytoremediation is a robust treatment technology.

As a guideline, constructed wetland treatment for a 16,000 gpd flow may require between 5 to 15 acres of land, including post-treatment storage. Phytotechnology treatment by trees requires even more land area. Distribution of the leachate influent is critical to provide an even flow to a wetland, such that a typical configuration may be twice the length as the width. Narrow channels should be avoided to prevent clogging with growth, impeding hydraulic capacity. Startup with reduced concentration leachate or blending leachate with fresh water is important to help establish vegetation.

Lagoons Systems

Lagoon systems can remove BOD and ammonia nitrogen if properly designed and maintained. They are generally relatively inexpensive and easier to operate than mechanical wastewater treatment systems. The components use little aboveground infrastructure except for influent and effluent structures and aeration devices, and are built through excavation. Solids removal must occur periodically. Land area must be available for this technology.

Nitrogen removal has been documented to occur in aerobic/aerated lagoons. Both total nitrogen and ammonia concentrations can be significantly reduced in long detention time lagoon systems. Nitrogen removal mechanisms in lagoons include assimilation in biomass, sludge deposition, adsorption and absorption in the biomass, adsorption by bottom soils, nitrification/denitrification, and volatilization of ammonia to the atmosphere. Nitrification-denitrification and algal uptake of ammonium, nitrate and nitrite as nutrient sources are the major nitrogen removal pathways in leachate or wastewater stabilization lagoons.

Ammonia and nitrate removal is affected by temperature, pH, organic load, detention time, mixing conditions, inhibitions, and wastewater characteristics. For example, alkaline pH promotes ammonia speciation in the gaseous phase and strong mixing conditions affect the magnitude of mass transfer coefficient and volatilization of ammonia. Temperature affects both the equilibrium constant and mass transfer coefficient.

INNOVATIVE TECHNOLOGIES

Advanced Oxidation Processes (AOP)

Landfill leachate may contain constituents that may not be removed by conventional treatment. These constituents may include pharmaceutical and personal care products (PPCP) PCBs, pesticides, or other recalcitrant toxic organics. Advanced oxidation processes utilize highly reactive hydroxyl radicals to transform organic contaminants to stable inorganic compounds such as water, carbon dioxide and salts. There are several processes that can generate hydroxyl radicals by utilizing catalysts or reagents. Common reagents are:

- Ozone;
- Hydrogen peroxide; and

- Ultraviolet (UV) light.

Specialized AOP systems include the following and are described below.

- AOP by Photolysis
- Fenton's Reagent;
- PhotoCat System; and
- Titanium Dioxide AOP

For the purposes of this evaluation, a brief description of the more frequently used AOP systems is presented below; however the evaluation considerations are similar, so the technologies are combined in the subsequent evaluation step below.

AOP by Photolysis

Hydroxyl forming reagents can be utilized in different combinations (i.e. ozone and hydrogen peroxide, UV light and hydrogen peroxide, etc.) to obtain the removal efficiency. Ozone and hydrogen peroxide oxidation may not completely oxidize the organic contaminants. Enhanced oxidation can be achieved by adding UV radiation. Photolytic technologies generate hydroxyl radicals by using high energy photons to cleave the peroxide molecule to form hydroxyl radicals. UV radiation can also decompose organic contaminants by direct photolysis. The optimum reagent combination will depend on the target contaminants and the background water matrix. High turbidity or high metals concentration, mainly iron, could reduce the effective transmissivity of the UV light; therefore pretreatment may be required. AOP systems are in commercial use throughout the world.

Fenton's Reagent

The Fenton System utilizes iron to catalyze the decomposition of hydrogen peroxide to produce highly reactive hydroxyl radicals. The optimal reaction pH is between 3 and 5 in order to prevent the iron from precipitating. After pH adjustment and iron addition, hydrogen peroxide is slowly added. The optimal iron to hydrogen peroxide ratio is in the range of 1:5 to 1:25 by weight percent depending on water quality. The Fenton System is a low energy

process that can effectively destroy different phenols, nitrobenzene and other constituents generically characterized as "chemical oxygen demand" (COD).

Photo-Cat System

Purifics' photocatalytic technology (PhotoCat) utilizes a suspension of light-activated titanium dioxide catalyst slurry in combination with hydrogen peroxide. A ceramic ultrafiltration membrane removes suspended solids (titanium dioxide) for recycle. The Purifics treatment system has been shown to require pre-acidification for optimal treatment and post-treatment neutralization may be required dependent on downstream usage and associated quality requirements. Instead of a UV source with sufficient energy to break the chemical bonds to create radicals, the PhotoCat system uses UV light to activate the TiO₂ catalyst resulting in four claimed organic destruction pathways. These include oxygen reduction to form a superoxide radical, the electron-hole pair formation at the catalyst results in hydroxyl radical formation, direct oxidation of the adsorbed organic contaminants; and reduction by the conduction band electron. The four pathways occur at the surface of the TiO₂. PhotoCat system is fully automated and does not generate air emissions (regulated pollutants). Polishing treatment following photo-catalytic AOP may be required depending on the effluent water quality desired. GAC adsorption can be utilized to further remove volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs) and microfiltration/reverse osmosis (RO) can be utilized to remove inorganic contaminants. Additional process unit operations will add to the operating costs since the GAC requires replacement or regeneration and RO produces a brine stream that will require offsite disposal or treatment. Photo-catalytic AOP technology can achieve removal efficiencies greater than 99.9 percent for some organic constituents.

Titanium Dioxide AOP

Titanium dioxide AOP technology is a chemical free process that utilizes UV radiation. The titanium dioxide coated vessels catalyze the decomposition of organic contaminants. This technology requires less power than conventional UV systems. This process is fully automated and commercialized. Titanium dioxide AOP can achieve removal efficiencies greater than 99.9 percent some organic contaminants

of interest, but these process do not remove ammonia, and ammonia concentrations can increase as ammonia may be formed from the organic destruction.

Advanced AOP

There are several innovative advanced AOP processes that also have the capability of removing recalcitrant organics and ammonia. These three emerging oxidation processes may be considered a new generation of technologies for leachate treatment. There are two technologies that use sulfate radical-induced advanced oxidation processes (SR-AOPs); including thermally activated persulfate (TAP) and ultraviolet (UV) activated persulfate (UV-P). These two technologies function by creating persulfate to produce an active SO_4^- by heat and UV, respectively. The energy to create these two oxidation approaches is cost-effective since the heat and UV are catalysts and do not function as reactants with wastes.

There is another advanced oxidation technology using a non-energized ferrate (V and VI) oxidation. Iron (VI) and iron (V) are ferrates, which are powerful oxidants. These ions react with pollutants in a fast process, forming non-toxic by-products. Oxidations performed by Fe (VI) and Fe (V) are faster at lower pH. The Fe (VI) technology shows excellent functional properties and can inactivate a wide variety of constituents at low Fe (VI) doses. Additionally, the Fe (VI) ion functions as a preoxidant coagulant. While both ions react rapidly with trace constituents, Fe (V) is approximately 3–5 orders of magnitude faster than that of Fe (VI). The result of the oxidation with Fe (VI) and Fe (V) is Fe (III), a non-toxic compound. Commercial application is yet to be demonstrated.

EVALUATION PROCEDURE

In general, evaluations of alternatives should be performed to determine the wastewater treatment facility configuration and processes that will most cost effectively meet the requirements identified in the design basis. The analysis to determine cost effectiveness is integrated with consideration of subjective parameters in this section. Along with an evaluation of the treatment alternatives to meet effluent and considers solids treatment processes for handling and disposing of residuals. Residuals

handling can account for as much as 50% of capital and operational costs. The tank based options may have significant residuals handling costs, or may increase TSS concentrations in the effluent if discharged. In addition, recycle flows from solids handling and treatment processes can significantly affect liquid treatment processes and should be further evaluated.

In general, alternatives should be evaluated using a cost analysis that considers both life-cycle costs and other non-monetary evaluation criteria (including construction and operation of the proposed facilities).

Evaluation using non-monetary evaluation criteria is largely subjective, and non-monetary criteria can be weighted, and each alternative can be ranked for a total non-monetary ranking can then be established for each alternative. The following presents a list of Non-Monetary Evaluation Criteria:

- Operability - Ease of operation minimizes operator attention/expertise required to ensure successful process performance;
- Ease of maintenance - Maintenance requirements not excessive and do not require special expertise; facilities and equipment readily accessible;
- Operator familiarity - Staff familiarity and ability to use staff experience from existing facilities;
- Reliability – Demonstrated performance; Proven process/technology to meet treatment criteria reliably;
- Hydraulic sensitivity - Capability to handle variations in hydraulic loads with minimal process impacts;
- Waste loading sensitivity - Capability to handle variations in waste loads with minimal process impacts;
- Process control stability - Not subject to upset from inadvertent operational changes, toxic slugs;
- Flexibility - Capability for changes in process operations to handle differing waste load conditions and to meet differing treatment objectives for different effluent requirements;
- Environmental Effects - Minimize potential for odors; Sustainability
- Noise - Minimize potential for noise;

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- Visual impacts - Minimizes negative visual impact of facility;
- Hydrological Impact – Either relates to recirculation of effluent/reject to the landfill or Minimizes changes to floodplain/runoff (if applicable);
- Footprint - Minimizes footprint and disruption to site, including removal of trees;
- Expandability - Footprint maximizes area available for expansion;
- Flexibility - Easily modified to meet differing future loads, effluent requirements, and/or treatment objectives; and
- Implementability – Time to implement facility, including permit, design, construction, commissioning.

Table 1 - Screening Matrix

	Effluent Reliability/ Consistency	Operability	Construction Cost	Maintenance Cost	Operator Friendliness	Hydraulic Sensitivity	Load Sensitivity	Flexibility	Odor/ Offsite Enviro. Impacts	Noise	Visual Impacts	Hydrological Impact	Footprint	Expandability	Construction Timing
No Action	F	L	L	L	L	L	H	L	H	L	L	L	L	L	L
New Storage Tank Construction	M	L	M	M	M	M	H	L	L	L	M	M	M	H	M
pH Adjust, Air Stripping, Package Biological	M	M	H	H	M	M	H	L	H	M	H	M	M	H	M
Lagoon	M	M	M	L	L	L	M	H	H	L	M	H	F	M	M
SBR/Equalization Tank	H	H	H	M	H	M	H	M	M	M	M	M	M	H	M
Breakpoint Chlorination	F	H	M	M	M	M	H	H	M	L	M	M	M	H	M
Package Biological/ Nitrification/EQ Tank	H	H	M	L	M	M	H	L	M	L	H	M	M	M	M
Reverse Osmosis	H	H	H	H	M	F	M	L	L	M	M	F	L	H	M
Evaporation	M	M	F	L	H	M	H	M	H	L	M	F	H	M	M
Constructed Wetlands	M	M	M	L	H	L	M	H	H	L	H	H	F	L	M
Phytoremediation	M	M	M	L	H	L	M	H	H	L	H	H	F	L	M

L – Low

M – Moderate

H – High

F - Fatal Flaw

As most of these criteria are subjective and there are a large number of systems described above, a simplification of the analysis is critical. The above table presents a screening evaluation in order to eliminate unlikely or inadequate treatment options/technologies. In this example, eight of the treatment options have fatal flaws that would preclude them from being a potential option. The no action and breakpoint chlorination options do not satisfy the effluent discharge requirements. The evaporation technology was eliminated because of the substantial construction costs associated with a large evaporation system and the lack of an on-site

landfill gas fuel source. The lagoon, constructed wetlands, and the phytoremediation technologies are not viable because of the footprint requirements of the treatment options and the lack of space on-site.

To provide comparison of remaining treatment options, the treatment options were subjectively compared using a Pair-Wise Comparison. For the Pair-wise Comparison method, each candidate alternative is matched head-to-head with each other candidate alternative. Each alternative gets one point for a one-on-one win on the appropriate row and no points for a loss. Candidates with the most points are preferable.

Table 2 - Pair-Wise Comparison of Landfill Leachate Treatment

Pair-Wise Comparison of Nitrification Alternatives						
	No Action	SBR & AOP Process	EQ/ Package Biological /pH Adjust/ Air Stripping/ pH adjust	Equalization Tank/SBR	EQ Tank/ Package Biological/ Nitrification	Total Score
No Action		0	0	0	0	0
SBR & AOP Process	1		0	0	0	1
EQ/ Package Biological /pH Adjust/ Air Stripping/ pH adjust	1	1		0	0	2
Equalization Tank/SBR	1	1	1		1	4
EQ Tank/ Package Biological/ Nitrification	1	1	1	0		3

CONCLUSIONS

Leachate containing significant volumes of gas well pumping and gas well condensate from gas flow treatment contain significantly higher concentrations of constituents such as BOD, COD, ammonia, metals and other organics. Treatment is required prior to discharge to a POTW, direct discharge, or other disposal alternatives. Obtaining quality data on flow and concentrations is critical and should be obtained over a theater of seasons. Selection of potential

technologies can be narrowed by a structured evaluation process described in this paper. Additionally, there are a number of technologies that should be verified by treatability testing. As treatment alternatives may be comprised of a number of individual technologies, treatability should include the various technologies to confirm a robust and cost effective approach to treating the more concentrated leachate that is found with gas well pumping and condensate from gas processing.

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