Available Methods of Wastewater Treatment

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The use of ever-dwindling natural resources in industry is a topic of great public interest. Many companies have developed right-to-operate philosophies as a result of this increasing awareness of the environment. These new policies often have zero emissions as their ultimate goal. Whether these lofty goals are achievable or not, the plant engineer will have to work toward them and hope that technology will fill any current voids of knowledge. However, all hope is not lost. There currently exists much of the technology needed to yield nearly zero emissions, but there exists no one, comprehensive source for engineers to refer to. This paper will define some of the uses of existing wastewater treatment operations and propose a few generic solutions for industrial conditions.

Water is probably the most needed natural resource besides air for the sustaining of life. Therefore, the wastewater effluent from chemical plants must be treated for one of two reasons. The first of these reasons is to release clean water that will not upset the operation of the natural environment. The second reason for wastewater treatment is to comply with the government's environmental regulations as they pertain to the plant's emissions. The most relevant legislation dealing with the chemical effluents is the Clean Water Act. This act sets limits on the toxic constituents in wastewater. These limits may be "technology based" or "water quality based." (Hall and Musterman, July/Aug. 1992) Technology based goals are achieved by using the best, most reasonable technology available, whereas water quality based goals are achieved by meeting regulated limits on specific toxic chemicals.

Wastewater Reuse

One method of circumventing wastewater discharge to the environment is to use partially treated wastewater as the makeup water source of other unit operations in the plant. One example of this method of dealing with contaminated wastewater is to use it as cooling tower makeup thereby reducing wastewater effluent and overall water intake. The following table lists some of the advantages of wastewater reuse.

Table 1 - Water Reuse Benefits

Water supply related

* Supplements regional water supply, eliminating need to develop additional supplies.
* Provides more reliability than the usual supply and is less affected by weather.
* Provides a locally controlled supply, reducing dependence on state or regional politics.
* Avoids the operating costs of water treatment and delivery.
* Eliminates social and environmental impacts of diverting water from natural drainageways.
* Eliminates impacts of constructing large-scale water storage and transmission facilities.

Wastewater related

* Avoids the capital and operating costs of disposal facilities.
* Avoids the costs of advanced treatment facilities needed to meet state and federal discharge requirements.

("Assessing the Benefits of Water Reuse" Lejano, Grant, et al. Water Environment & Technology, August 1992.)

Although there are many benefits to water reuse, there are special considerations to be made when considering this method. For one, metal precipitates such as calcium carbonate and calcium phosphate can cause pipe fouling within heat exchangers and cooling towers. Biological fouling can occur in cooling towers from the high nitrogen and organic content in reclaimed wastewater. Also, copper alloys can be corroded by ammonia, a typical factor in waste effluents. (Rebhun 341). Even though some of these negative factors can be removed to minimize cost, they may offset the economic benefits of water reuse. However, the social rewards of reusing valuable water may be of much greater value.

Typical Water Pollutants

Before one can set up a wastewater treatment system, the pollutants must be defined and classified. According to Noonan, there are three major classifications of water pollutants: chemical, biological, and physical. Some chemical pollutants are acids, alkalis, salts, detergents, dyes, dissolved gases, phenols, pesticides, hydrocarbons, organic chemicals, oxidizing agents, reducing agents, and hardness. (Some specific chemical pollutants are listed in Appendix A.) Of the biological type there are bacteria, fungi, algae, viruses, pathogens, and coliforms. Heat, color, odor, taste, radioactivity, suspended solids, and silt are examples of physical pollutants.

The effects of these pollutants are varied. For example, the biological activity in sewage can reduce the dissolved oxygen content of the water. Heat can lower the amount of dissolved oxygen by increasing bio-chemical reaction rates. Floating materials like grease can inhibit sunlight penetration and, therefore, reaeration of the water. Suspended matter can facilitate the production of microorganism-killing slime. On top of all of these detrimental effects of pollutants, many soluble compounds are poisonous and must be removed before discharge.

It is impossible to know the entire composition of the waste stream, but key pollutants can be measured, either directly or indirectly. A direct measurement could be the monitoring of a specific compound. Indirect measurements are more general descriptions of the water quality. These parameters are pH, electrolytic conductivity, dissolved oxygen, BOD, COD, TSS, temperature, and turbidity.

The reason for measuring the pH of wastewater is because of the dependency of microbial activity on alkalinity or acidity. Since biological systems are often used to reduce organics from the wastewater, pH must be at its optimum value at that stage. Electrolytic conductivity tells of the concentration of total ionizable solids. Dissolved oxygen must also be maintained at certain levels, or aquatic life will die. Five to six ppm dissolved oxygen is desired in the effluent. At three ppm, fish die.

BOD stands for biochemical oxygen demand or the milligrams of molecular oxygen in one liter of water used by microorganisms in the consumption of biodegradable organics. The analysis of BOD is slow, which can be a problem if the control of the treatment process is based on this parameter. A faster analysis can be performed for COD, the chemical oxygen demand. COD relates the amount of molecular oxygen required to oxidize both organic and inorganic compounds. TSS stands for total suspended solids, the effects of which have already been discussed.

Perhaps the easiest parameter to measure is the temperature which can be controlled to obtain the desired level of biological activity. Dissolved oxygen content is also dependent on temperature. Typically, more dissolved oxygen

exists in cold water than in warm water. Finally, turbidity is the amount of suspended matter present in a body of water. This measurement correlates to the clarity of the water. The measurements mentioned are often required to be at certain levels as defined by law. BOD and TSS are typically stipulated in government permits, as are others which are more specific to the particular process. (Cheremisinoff, March 1989) By using all of these measurements, one can monitor the three classifications of pollutants, the chemical, the biological, and the physical.

Unit Operations of Wastewater Treatment

Once the nature of the pollutants is known, treatment can begin. There are many different ways to remove chemical, biological, and physical pollutants, and the order of treatment processes is important in that some unit operations affect the efficiencies of those downstream. In this paper, methods of removing biological contaminants are not dealt with as such. Instead, the removal of contaminants that catalyze the growth of undesired microorganisms will be discussed.

The unit operations of wastewater treatment are often split into a typical order of operation consisting of primary, secondary, and tertiary treatments. The primary and secondary steps are generally considered to be the steps which remove the bulk of the pollutants. The tertiary step is often used as a polishing step which removes undesired components from a significantly diluted waste stream. Examples of the primary step are screening and settling of suspended solids with a typical BOD_5 removal of 35%. (BOD_5 refers to five-day biochemical oxygen demand.) Secondary treatment usually consists of some sort of biological action i.e., *trickling filters*, *activated sludge*, or *stabilization lagoons*. Finally, tertiary treatment consists of an advanced treatment like adsorption of organics via *activated carbon* or *ion exchange*, and *reverse osmosis*. Tertiary treatments are usually the most expensive and sophisticated of all.

Filtration

Almost all treatment operations begin with filtration, of which there are many types. The purpose of filtration is to remove suspended solids which can block sunlight and inhibit reaeration of the water. Also, approximately 35% of BOD_5 can be removed through primary filtration and sedimentation processes. The most important reason for primary removal of solids is that the fewer the complications, the easier it is to deal with the waste remaining. In other words, any method that simplifies the downstream operations is desired. Filtration is often used to remove precipitated phosphorous, metal compounds, and organic compounds.

The driving force of filtration can be gravity or applied pressure. Pressurized filters are the most common in industrial applications where gravity cannot apply the force needed. To accomplish solids removal one could use *microscreening*, the simplest form of filtration. The particle size removed depends on the size opening in the screen or weave. *Deep bed filtration* involves passing wastewater through a bed of granular materials. This kind of filtration removes particles by trapping the particles and by particle adhesion to the filter media. Finer filtration can be accomplished with sand than with coarser materials. *Diatomaceous earth filtration* is a mechanical separation process using powdered filter aid and diatomaceous earth built upon a loose

septum which removes the suspended solids. Filters of this type are very efficient, but they do not have the capacity required to maintain filtration of an untreated wastewater stream. For this reason, diatomaceous earth filtration should be used mainly as a polishing step.

Ultrafiltration is a membrane separation process whereby suspended solids and large molecule (organic) colloidal solids measuring 0.002 to 10.0 microns are removed. (Cheremisinoff "Treating Wastewater" 63). Ultrafiltration uses coarse membranes at low pressures. Ultrafiltration differs from *reverse osmosis* in that R.O. operates with fine membranes at high pressures. Ultrafiltration's major asset is its relatively small size; however, it is a very expensive process. All of these filtration processes yield a filter cake

Table 2 - Some Unit Operations of Wastewater Treatment

Chemical Oxidation
- Alkaline chlorination
- Ozonation
- Electrochemical

Chemical Precipitation
(pH adjustment, flocculation/settling)
- Sodium hydroxide
- Soda ash
- Sulfide

Chemical Reduction
- Sodium bisulfite
- Sulfur dioxide
- Ferrous sulfate

Complexed metals treatment
- High pH precipitation
- Other complexed metals treatment

Emulsion breaking
- Thermal
- Chemical

Metals recovery
- Activated carbon
- Electrodialysis
- Electrolytic metal recovery
- Ion exchange
- Reverse osmosis
- Solvent extraction
- Ultrafiltration
- Chemical precipitation

Filtration
- Diatomaceous earth
- Sand
- Multimedia
- Mechanical

Air Flotation
- Dissolved air flotation

Oil Skimming
- Gravity separation
- Coalescing plate separation
- Mechanical oil skimming

Biological treatment
- Activated sludge
- Trickling filter
- Waste stabilization pond
- Nitrification
- Anaerobic treatment
- Denitrification

Adsorption
- Activated carbon
- Ion exchange
- Resin adsorption

Stripping
- Air stripping
- Steam stripping

Other
- Neutralization
- Wet air oxidation

(from "Water and Wastewater Treatment-Fundamentals and Innovations" by Paul N. Cheremisinoff, Pollution Engineering, March 1989.)

that must be dewatered and properly disposed. Also, filters must be cleaned periodically, requiring parallel systems if constant filtration is desired.

Clarification/Flotation

Not only is filtration used for primary removal of suspended solids, but clarification and flotation can be used as well. A definition of clarification and flotation could be separation by gravity. *Flotation* is often aided by bubbling fine air bubbles through the wastewater to buoy suspended particles to the top of a settling tank where the buoyed particles are skimmed off. Skimming can also remove some of the oils and greases from the waste stream. *Clarification* is usually accomplished by holding wastewater in holding tank with a residence time sufficient to allow the suspended particles to settle. With the outlet weirs placed correctly and the depth of the tank being deep enough to allow sedimentation thickening, the effluent from a clarification tank should be significantly cleaner. The use of *centrifuges* is another possibility for highly effective solid/liquid separation.

pH Adjustment

Once the suspended solids are removed, the primary unit operations have to incorporate pH control so that downstream processes, such as the biological operations, are not rendered inefficient. Ideally, pH should be held neutral. When dealing with acidic wastewater, the pH must be raised. There are four popular methods for doing this.

The first method is done by passing the wastewater through a limestone bed. This is relatively inexpensive. The next process involves mixing the wastewater with lime slurries, but this method causes difficulty because of the clogging of the apparatus involved. Lime slurry addition is less expensive than the third possibility, which is to add caustic soda (NaOH). However, caustic soda is much easier to use than the lime slurry. Another negative aspect of using lime slurries is that up to thirty minutes may be needed even if it is introduced to a thoroughly mixed situation. Furthermore, lime slurries tend to form more sludge than neutralization with caustic soda. Lime must be stored dry. Caustic soda is more expensive, has a faster reaction time, and can be stored as a liquid. The fourth alternative is soda ash (Na_2CO_3).

When dealing with alkaline wastewater, the pH must be lowered. To accomplish this task, one can bubble CO_2 through the water or add a strong acid like hydrochloric or sulfuric acid. Unless CO_2 is available on site, the use of carbon dioxide is expensive.

Chemical precipitation/coagulation

Not only can pH be adjusted to a neutral condition, it can be used to precipitate metallic precipitates given that no strong chelating agents are present. Even if complexing agents are present, the hydroxide anion can overcome them if it exists in the right amounts. One useful tool that can predict when certain species will yield the hydroxide precipitate is the Pourbaix diagram. The Pourbaix diagram can be easily constructed if the aqueous species are known. The diagram is a plot of electrical potential versus pH with a set concentration of the species i.e.,$[Zn^{2+}] = 0.1$ Molar.

In constructing a Pourbaix for zinc, the major aqueous species are Zn^{2+}, $Zn(OH)_2$, and ZnO_2^{2-}. All of these species are stable in water. That is, their electrical potentials do not cause the oxidation or reduction of aqueous species into H_2 or O_2 gas. However, Zn metal lies below the H^+/H_2 couple line. Therefore, zinc is electrochemically unstable in water. As an example, the Pourbaix diagram for zinc will be constructed.

First, the major oxidation states should be defined. For zinc, these states are zero and +2. Since the +2 oxidation state forms a hydroxide precipitate, the regions for Zn^{2+}, $Zn(OH)_2$, and ZnO_2^{2-} must be defined. The first line to be drawn is that for the transition from Zn^{2+} to $Zn(OH)_2$. The reaction must be balanced to form the expression for the equilibrium constant, K.

$$Zn^{2+} + 2OH^- \text{ <--> } Zn(OH)_2 \qquad (1)$$

Equation (1) is simply the reverse of the solubility product constant which has a value of $10^{15.5}$. Now, an equation for the line of equilibrium can be written.

$$\frac{[Zn(OH)_2]}{[Zn^{2+}][OH^-]^2} = 10^{15.5} \qquad (2)$$

Since zinc hydroxide is a solid precipitate, it can be set equal to one.

$$\frac{1}{[Zn^{2+}][OH^-]^2} = 10^{15.5} \qquad (3)$$

The diagram is to be drawn for a $[Zn^{2+}]$ concentration equal to 0.1 molar . Therefore,

$$pH = 5.75 \qquad (4).$$

Equation (4) is the equation for the transition of 0.1 molar Zn^{2+} to $Zn(OH)_2$.

For the transition from $Zn(OH)_2$ to ZnO_2^{-2}, the balanced chemical equation is as follows.

$$Zn(OH)_2 + 2OH^- \text{ <--> } ZnO_2^{-2} + 2H_2O \qquad (5)$$

When an equilibrium constant is not tabulated, it can be approximated from its free energy of reaction by equation (6).

$$\Delta G_r^o = -5.7 \log (K) \qquad (6)$$

The free energy has units of kilojoules per mole. ΔG_r^o for the reaction is -20 kJ/mol; therefore, $K = 10^{3.51}$. This information yields the following expression.

$$\frac{[\ ZnO_2^{-2}\ ]}{[OH^-]^2} = 10^{3.51} \qquad (7)$$

Again, with substitution for a 0.1 molar solution, the pH is equal to 14.00.

$$pH = 14.00 \qquad (8)$$

This concludes the construction of the equilibrium lines for the +2 oxidation state of zinc.

Now, the Zn metal to Zn^{2+} equation must be derived. The balanced reduction equation is used.

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad (9)$$

The Nernst equation is now used. It relates the electrical potential in volts to the Q expression for initial conditions. Equation (10) is the general expression of the Nernst equation.

$$E = E^o - \frac{0.059}{n} \log(Q) \qquad (10)$$

Knowing that n, the number of electrons transferred, is two and that the E^o is -0.76v for the reduction, equation (11) is obtained.

$$E = -0.76 - 0.0295 \log [Zn^{2+}]^{-1} \qquad (11)$$

For a 0.1 molar solution,

$$E = -0.79 \text{ volts} \qquad (12)$$

The two species left have equilibrium equations to be derived. The ZnO_2^{2-}/Zn couple has a value of -1.22 volts at pH=14. The following derivations lead to the equation needed.

$$ZnO_2^{2-} + 2\ e^- + 2\ H_2O \rightarrow Zn + 4\ OH^- \qquad (13)$$

$$-1.22\ v = E^o - \frac{0.059}{2} \log \frac{[OH^-]^4}{[ZnO_2^{2-}]} \qquad (14)$$

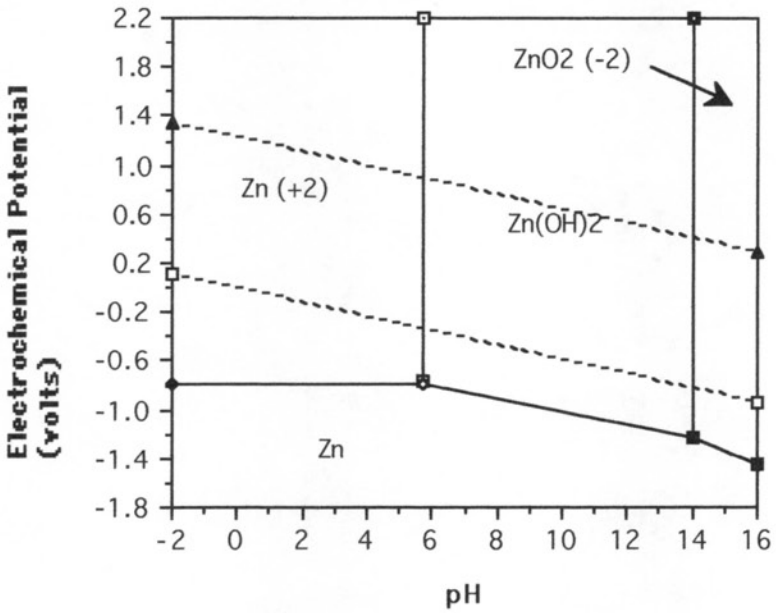
$$E = -1.191 - 0.0295 \log \frac{[OH^-]^4}{[ZnO_2^{2-}]} \qquad (15)$$

For a 0.1 molar solution,

$$E = -1.22 - 0.118 \log [OH^-] \qquad (16)$$

Equation (16) is the final equation needed to complete the zinc Pourbaix diagram because a line can be drawn between the existing points to form the diagram.

Figure 1 -- The Pourbaix Diagram for 0.1 Molar Zinc Species



The two dotted lines on the Pourbaix diagram are for water. The lower dotted line refers to the H^+/H_2 couple, and the upper dotted line refers to the OH^-/O_2 couple. The equations used to produce these lines are based on the Nernst equation and balanced chemical equations. Their derivation follows.

For the lower line:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (17)$$

$$E = -(0.059)(pH) \qquad (18)$$

For the upper line:

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \qquad (19)$$

$$E = 1.23 - (0.059)(pH) \qquad (20)$$

All of the E^O values used are obtained from standard chemistry texts, as are all free energies and equilibrium constants. Depending on the quality and quantity of information available about the aqueous characteristics of an element, a reasonably accurate Pourbaix diagram can be constructed. Also, one should always consider the possible complexation with other anions in the

wastewater. The principles used in constructing this Pourbaix diagram can be applied to complexation diagrams as well.

Like zinc, some metals redissolve at high and low levels of pH. If the pH can be manipulated, alkaline precipitation is a safe bet because once the precipitates are removed, pH can be neutralized without producing hazardous materials. Chemical precipitation with lime typically yields inorganic metals removal of 90% or greater. Sometimes simple pH manipulation is not enough to precipitate contaminants. When this situation occurs, many alternatives exist. For one, many metals will precipitate as a sulfide. If the metal exists in an oxidation state that will not precipitate, oxidation or reduction can be used to bring the metal to a state that will precipitate. However, if precipitation can be brought about without the addition of contaminating chemicals like sulfide, that method should be used. If a chemical is added, chances are that it will have to be removed downstream.

Once the waste is precipitated, it must be concentrated. If sedimentation occurs too slowly, *coagulation* and *flocculation* can be used to enhance the sedimentation process. For example, particles the size of bacteria can take 55 hours to settle one foot. (Nyer, 1985) Therefore, coagulation and flocculation are very common unit operations of wastewater treatment. Coagulation is facilitated by the rapid mixing of a coagulant that neutralizes the charges on the particles and collapses colloids to facilitate agglomeration and settling. Colloids often need coagulation to increase particle size when sedimentation time is at a premium. Flocculation is the more gentle mixing of particles to allow them to link into large settleable flocs. Typical coagulants are lime, aluminum salts, and iron salts. Polyelectrolytes, large, water soluble organic molecules, may be used as coagulants because they both neutralize the charges and grow the particles to form flocs (large settleable groups of particles). These processes of precipitation and sedimentation are fairly economical and effective and should be used as a secondary treatment after primary filtration and sedimentation is used to remove the bulk of already existing particles.

Oxidation/Reduction

The goal of chemical oxidation and reduction is to convert hazardous chemicals to less hazardous forms and to forms which can be safely removed by precipitation processes. As an example, hexavalent chromium compounds can be reduced by zinc metal to its trivalent state. At the same time, zinc metal is oxidized to its divalent state, and both the trivalent chromium and the divalent zinc can be precipitated as a hydroxide. Cyanide compounds can be oxidized by chlorination to cyanate, which is less toxic, and then to carbon dioxide and nitrogen. Cyanide can also be oxidized with hypochlorite solutions with hydrogen peroxide and by ozonation to completely destroy the cyanide. Wet air oxidation, which is discussed later, is also used to treat wastewater. (Cheremisinoff, Sept. 1990)

Oxidation and reduction can also be used to treat organic pollutants. These processes typically convert organic species into carbon dioxide, water, oxides of nitrogen, and other less harmful oxides. Chemical components used in this capacity are ozone, hydrogen peroxide, hydroxyl free radical, molecular oxygen, catalytic oxidation, chlorine, oxy-acids, potassium permanganate, and electrochemical treatment. (Cheremisinoff, March 1989) Wet air oxidation is also an accepted method for oxidizing inorganics and organics.

Removal of Organics

Although chemical oxidation can be used to remove organics, biological treatment via *activated sludge, trickling filters, waste-stabilization lagoons,* and *aerated lagoons* is usually less expensive than chemical processes. *Carbon adsorption* is a non-biological method of organic removal that is also widely accepted.

Activated carbon adsorption

The carbon adsorption process concentrates waste by adsorbing the material onto the carbon adsorbent. Activated carbon is the most commonly used adsorbent. Its surface area and activity make it an attractive choice as an adsorbent. It comes in two forms, either granulated or powdered. The adsorption rate of powdered carbon is faster than granular carbon processes, but granular activated carbon has the ability to use countercurrent flow to make the most use of the carbon.

An added benefit of carbon adsorption is on-the-spot clarification of small suspended particles. Usually, branched-chain organic compounds are more sorbable than straight-chained ones. Also, many inorganics are highly sorbable. Mercuric chloride and ferric chloride are relatively sorbable, but potassium chloride and polar molecules adsorb poorly. (Lankford, et al. 78) Some removal efficiencies are as follows: carbon tetrachloride, 97.3%; hexachloroethane, 99.8%; chloroform, 98.1%; napthalene, >99.4%; and toluene, >99.9%.

As with any removal process, a point occurs when the activated carbon must be replaced or regenerated. Regeneration by high temperature combustion of removed organics is the most economical method for replacement of granular activated carbon, and wet air regeneration is the most commonly used regeneration method for the powdered form. However, regeneration is not one-hundred percent effective. One problem with carbon adsorption is that organics with a boiling point of more than 150 degrees Celsius inhibit regeneration of spent activated carbon. The loss of the ability to adsorb pollutants varies with the type of carbon and the nature of the adsorbed chemicals.

Activated-sludge

Kenneth Bush states that "activated-sludge procedures are used extensively for coagulating and removing nonsettleable colloidal solids, as well as to stabilize organic matter." From EPA reports, 80-99% of BOD, 50-95% of COD, 60-85% of suspended solids, 80-99% of oils, 95-99+% of phenols, 33-99% of ammonia, and 97-100% of sulfides are removed by the activated sludge process. (Bush 115) When properly designed, activated-sludge is a highly effective method for the removal of organics and some inorganic pollutants.

Activated-sludge is an aerobic biological process containing a high concentration of microorganisms within a reaction tank. Nutrients required by the microorganisms are nitrogen and phosphorus which are generally found in wastewater, but if these nutrients are missing, they must be supplied by some other means. The microorganisms acquire air from mechanical aerators or diffused-air systems. In the sludge they convert the waste by chemical synthesis and oxidation reactions, and the converted waste must be removed by sedimentation.

Trickling filters

Another aerobic biological unit operation is the trickling filter. This particular process is not an economical polishing step and is, therefore, recommended as a secondary treatment only. Trickling filters typically remove 60-85% of BOD, 30-70% of COD, 60-85% of suspended solids, and 50-80% of oils. (115) A trickling filter consists of a filter bed, a wastewater distributor, and a sedimentation tank for clarification of the biologic growth that sloughs from the filter bed. The filter consists of broken rock, coarse aggregate, plastic sheets, or other standard industrial packings.

Waste-stabilization lagoons

Stabilization ponds are large, shallow ponds containing oxidizing bacteria to break down the pollutants in the wastewater. Typically, aerobic, rather than anaerobic, bacteria is used. Aerobic bacteria is the oxidizing agent in the pond, and removal efficiencies of 40-95% of BOD, 30-65% of COD, 20-70% of suspended solids, and 50-90% of oils are observed. The key to the efficiency lies in the retention time. Long retention times result in high pollutant removal efficiencies. Likewise, short retention times yield poor efficiencies. Unless land is inexpensive, this method is impractical. In colder climates where seasonal shifts are experienced, much lower efficiencies will be observed in the winter. Furthermore, these lagoons often release undesirable gases which will probably translate to poor relations with the community unless the lagoons are covered.

Aerated lagoons

Land requirements for aerated lagoons are much lower due to the greater concentration of bacteria that can be maintained in an aerated environment. Mechanical aeration equipment provides the air, resulting in lower retention times of approximately three to five days. The removal efficiencies are as follows: 75-95% of BOD, 60-85% of COD, 40-65% of suspended solids, 70-90% of oils, 90-99% of phenols, and 95-100% of sulfides. One drawback to the aeration process is that it keeps the solids in suspension. Therefore, a sedimentation process should be included. Aerated lagoons suffer the same climatic and community problems as stabilization lagoons.

Advanced Treatments

Advanced treatments are often used as polishing tertiary wastewater treatments. Some of these treatments have already been mentioned such as filtration, carbon adsorption, and chemical oxidation. Air stripping is a common polishing step, as is wet air oxidation. Newer technologies like ion exchange, reverse osmosis, and ozonation are also used for the polishing of wastewater effluent.

Air stripping

Air stripping is the mass transfer of volatile wastewater components into the gas phase. These volatile compounds are most often organic, and air stripping can remove up to 99% of them from the waste stream. The process

usually consists of the countercurrent flow of wastewater to a forced air stream in a packed tower which maximizes the transfer. The major disadvantage to air stripping is that the pollution is transfered to a gas phase that must oftentimes be scrubbed before being released to the atmosphere.

Wet air oxidation

Wet air oxidation is a proven, reliable technology for the oxidation of organics and inorganics. This technology has existed for thirty-five years, and much is known about specific operations performed by the process. This research is a definite plus. The process itself is the aqueous phase oxidation of organic and inorganic materials at high temperatures and pressures. The solubility of molecular oxygen at elevated temperatures is high and is the driving force of the oxidation process. Compressed air or high pressure pure oxygen is the source of oxygen.

The high pressures keep the water in the liquid state thereby allowing the liquid water to catalyze the oxidation of toxics at lower temperatures than flame combustion would allow. The water also serves as a heat transfer fluid which moderates oxidation and removes excess heat. Wet oxidation can use the heat released by the oxidation process to elevate the temperature of the incoming oxygenated water. This procedure conserves energy and is its major advantage over other processes. Another benefit of wet air oxidation is that it can process wastewater which is too toxic for biological processes. The products of wet air oxidation are relatively harmless, but biological processes are often necessary to convert the remaining pollutants to carbon dioxide and water.

The process can oxidize a wide variety of components which makes it very versatile. Examples include the following: inorganic and organic cyanide compounds; aliphatic and chlorinated aliphatic compounds; aromatic hydrocarbons; and aromatic and halogenated aromatic compounds containing non-halogen functional groups e.g., phenols and anilines. Removal efficiencies of 95 to 99% can be achieved for these examples. (Dietrich, et al. 173)

SUPERCRITICAL WET OXIDATION

Supercritical wet oxidation is similar to wet air oxidation in that the waste stream is brought up to high temperatures and pressures along with a similarly treated air stream which flow together into a reactor for oxidation. The advantage to this stream treatment is that the waste is oxidized in a more efficient manner, generally speaking, than would occur at more mundane physical conditions. In both processes, the waste is converted to carbon dioxide and nitrogen. However, since supercritical oxidation occurs at temperatures and pressures in excess of the critical point of water, the overall process is more efficient than wet air oxidation and requires less compressed air.

The technology of supercritical wet oxidation was originated by Dr. Mike Modell at the MIT approximately 14 years ago. His process involves compressing the waste stream to pressures in excess of 22.1 MPa and then heating it beyond 374.2°C. Once beyond the critical point of water, a single-phase fluid exists with vastly altered characteristics. This fluid creates a highly favorable reaction environment. Both the density and viscosity of supercritical water are gas-like. The dielectric constant drops to values similar to non-polar organic solvents at ambient conditions, and hydrogen bonding

becomes considerably less extensive. These properties allow for great nitrogen and oxygen solubility, hydrocarbon solubility, and salt precipitation.

The two streams, air and wastewater, can be fed into an isothermal plug-flow reactor with residence times of less than five minutes. However, for most waste streams this setup is unrealistic since any inorganics present in the waste stream are precipitated at supercritical conditions thereby plugging typically configured reactors. MODAR, Inc. of Natick, MA and ABB Lummus Crest Inc. of Bloomfield, NJ have developed bench and pilot-scale reactors which use cooled water at approximately 200°C to redissolve precipitating inorganic salts. The reactor is vertically configured with the caustically treated waste stream entering the top of the reactor at 265°C and exiting into the reactor via a spray-type nozzle with typical injection conditions of 600°C and 23 MPa.

Gaseous effluent exits the top of the reactor in the form of N2, CO2, H2O, and trace quantities of dissolved salts. In general, the equation of the chemical reaction is as follows:

$$C_xH_yN_zO_a + O_2 \longrightarrow CO_2 + N_2 + H_2$$

More specifically, for carbon monoxide (Helling and Tester, 1988):

$$CO + {}^1/_2O_2 \longrightarrow CO_2$$

$$CO + H_2O \longrightarrow H_2 + CO_2$$

Approximately 75% of carbon dioxide production can occur via the latter pathway. One should keep in mind that carbon monoxide is often an intermediate product of some of the other organic oxidation reactions. Specific reaction pathways have been worked out for phenol (Thornton and Savage, 1992), alcohols and acetic acid (Boock and Klein, 1993), and pyridine (Tebbal, et al, 1993). Salt is washed down the side of the reactor vessel and is also directly precipitated to the bottom of the vessel into the 200°C bath where it flows out as concentrated brine.

The typical residence time for the above configuration is approximately ten seconds. Comparable residence times of wet air oxidation are from 15 to 120 minutes. Supercritical oxidation is also more efficient in terms of COD removal. Supercritical oxidation yields COD removals of greater than 99.99%, whereas wet air oxidation yields COD removals of 75 to 90%. Ammonia removal in the supercritical wet oxidation process is upwards of 99.71%. The increased solubility of oxygen in supercritical water may explain this greater efficiency. In terms of energy usage, supercritical oxidation is less demanding than ordinary wet air oxidation. The supercritical oxidation process can be enclosed in one building.

According to Webley and Tester, "Any pumpable stream including slurries of biomass of soil can be fed to the [oxidation] reactor." According to Barner, et al, supercritical oxidation processes are applicable to waste stream loadings of "10 to 20 m3 per day in the lower range, and 100 to 150 m3/day in the upper range." Supercritical oxidation yields complete conversion to nitrogen and carbon dioxide while forming noxious byproducts such as NOx

and SO2 in quantities of less than one mg/m3 of effluent. Carbon monoxide yield is typically under 50 mg/m3 of total effluent. For aqueous wastes with 1 to 20% organics, supercritical oxidation is less costly than controlled incineration or activated carbon and is more efficient than wet air oxidation at temperatures less than 200° C and pressures less than 150 atm.

However, when one considers supercritical wet oxidation for use in an industrial setting, he must realize that at supercritical conditions corrosion is severe with respect to all components involved. Barner tested several different alloys for use in the supercritical reactor. All of the metallic alloys including those containing nickel, chromium, and titanium were easily corroded in the supercritical environment. Several different ceramics were tested as well, with only one ceramic material performing well. Also, there is an extreme temperature gradient along the vertical axis of the reactor which poses a potential problem to long-term stress and fatigue. Again, only one ceramic material proved suitable for all conditions, mechanical and otherwise. It is also recommended that all supporting process lines be composed of titanium alloy. The high fixed capital investment required may yet be offset by the resultant energy savings of the process.

Ion exchange

Ion exchange is a method of wastewater treatment that is often applied to the demineralization of water. The ion exchange media is insoluble and exchanges ions with the ions to be removed, thereby eliminating them from the waste stream. Both cation and anion resins exist. They are regenerated by acid or base, respectively. Regeneration of the ion exchange resin is very efficient, but the ion exchange process itself is susceptible to fouling by organics. Therefore, the ion exchange should occur after biological or some other type of organic removal. For these reasons, ion exchange is an excellent polishing step. When conditions of placement are met, ion exchange is a highly efficient means of removing metals and cyanides. Despite its ability to clean water, it is a very expensive process.

Ozonation

Ozone can be used as a powerful oxidant or as a biocide. Unfortunately, there lacks a great deal of science of ozone's use in industrial wastewater treatment. It is generally felt to be beneficial in the destruction of some organics, and some industries do use it for this purpose.

Reverse osmosis

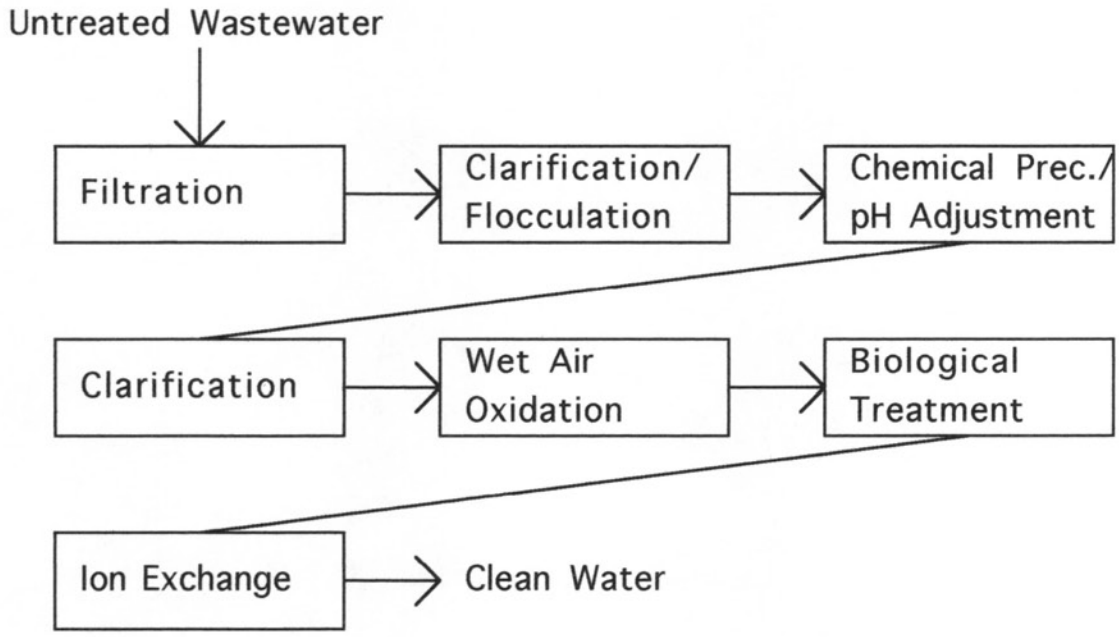
Reverse osmosis is an expensive method of demineralizing concentrated wastewater. It is efficient and simple. Reverse osmosis is a membrane process. The membrane allows the passage of clean water from the wastewater while preventing the flow of molecules with molecular weights greater than 120 g/mole. Ionic species are also removed by this process. The operation occurs when the osmotic pressure is greatly exceeded. Reverse osmosis is most efficient with dilute waste streams, making this process applicable to tertiary wastewater treatment.

There are many different types of R.O. apparatus. Tubular types are good at destroying suspensions because of their small area to volume ratio. Spiral-wound types have higher membrane area to volume ratios which makes them more sensitive for suspensions. Plate and frame types are prohibitively expensive due to their low membrane area to unit volume ratio.

Application of Wastewater Treatment Technology

Now that the general methods of industrial wastewater treatment are known, a generic flow chart for wastewater treatment can be constructed using the principles of primary, secondary, and tertiary treatments.

Figure 2 -- Wastewater Treatment for a Stream Containing Inorganic Organic Species



Economics of Wastewater Treatment

The ultimate goal of wastewater treatment is the purification of water, but for the industrial user, these methods can be so expensive that they cut into the profitability of the operation. Adams has set the following processes out as being expensive to operate: ozonation, macroreticular resins, ion exchange, solvent extraction, reverse osmosis, incineration, freeze crystallization, evaporation/crystallization, and chemical fixation. He also states that sludge handling and off-gas control should considered when checking the economic feasibility of a process. Any treatment process should be designed with future considerations in mind. After all, government environmental regulations have changed dramatically in the past twenty years and will continue to do so.

Conclusions

Considering the importance of water to everyday life, the needs for water protection and conservation are evident. The goal of zero emissions can be met if all of the treatment processes discussed could be used in concert. Unfortunately, some of these processes have costs which can cripple a plant's efficiency. Some of the unit operations in this paper can be used in combinations that are highly effective without being outrageously expensive. A great deal of emphasis should be placed on those systems which remove visible and odorous chemicals because these pollutants are the ones the community observes. Even though the treated wastewater may surpass government regulations, it is difficult to convince a public of their safety when their judgement of industry as a whole is based more on past shortcomings than on present achievements.

Appendix A

Priority Pollutants

Pollutant	Type of chemical
Acenaphthene	Aromatic
Acenaphthylene	Aromatic
Acrolein	Organic
Acrylonitrile	Organic
Aldrin	Pesticide
Anthracene	Aromatic
Antimony	Metal
Arsenic	Metal
Asbestos	Mineral
Beryllium	Metal
Benzene	Aromatic
Benzidine	Substitute aromatic
Benzo[a]anthracene	Aromatic
3,4-Benzofluoranthane	Aromatic
Benzo[k]fluoranthane	Aromatic
Benzo[ghi]perylene	Aromatic
Benzo[e]pyrene	Aromatic
e-BHC-α	Pesticide
b-BHC-β	Pesticide
r-BHC-(lindane)-γ	Pesticide
g-BHC-Δ	Pesticide
bis(2-chloroethoxy)methane	Chlorinated ether
bis(2-chloromethyl)ether	Chlorinated ether
bis(Chloromethyl)ether	Chlorinated ether
bis(2-Chloroisopropyl)ether	Chlorinated ether
bis(2-Ethylhexyl)phthalate	Phthalate ester
Bromoform	Chlorinated alkane
4-Bromophenyl phenyl ether	Chlorinated ether
Butyl benzyl phthalate	Phthalate ester
Cadmium	Metal
Carbon tetrachloride	Chlorinated alkane
Chlordane	Pesticide
Chlorobenzene	Chlorinated aromatic
Chlorodibromonethane	Chlorinated alkane
Chloroethane	Chlorinated alkane
2-Chloroethyl vinyl ether	Chlorinated ether
Chloroform	Chlorinated alkane
2-Chlorophenol	Phenol
4-Chlorophenyl phenyl ether	Chlorinated esther
2-Chlorophythalene	Chlorinated aromatic
Chromium	Metal
Chrysene	Aromatic
Copper	Metal
Cyanide	Miscellaneous
4,4-DDD	Pesticide
4,4-DDE	Pesticide
4,4-DDT	Pesticide

Pollutant	Type of Chemical
Dibenzo[a,h]anthracene	Chlorinated aromatic
1,3-Dichlorobenzene	Chlorinated aromatic
1,4-Dichlorobenzene	Chlorinated aromatic
3,3-Dichlorobenzidene	Substituted aromatic
Dichlorbromothane	Chlorinated alkane
Dichlorodifluromethane	Chlorinated alkane
1,1-Dichloroethane	Chlorinated alkane
1,2-Dichloroethane	Chlorinated alkane
1,1-Dichloroethylene	Chlorinated alkane
2,4-Dechloro phenol	Phenol
1,2-Dichloropropane	Chlorinated alkane
1,2-Dichloropropylene	Chlorinated alkane
Dieldrin	Pesticide
Diethyl phthalate	Phthalate ester
2,4-Dimethyl phenol	Phenol
Dimethyl phthalate	Phthalate ester
Di-n-Butyl phthalate	Phthalate ester
4,6-Dinitro-o-cresol	Phenol
2,4-Dinitrophenol	Phenol
2,4-Dinitrotoluene	Substituted aromatic
2,6-Dinitrotoluene	Substituted aromatic
Di-N-Octyl phthalate	Phthalate ester
1,2-Diphenyl hydrazine	Substituted aromatic
A-Endosulfan-α	Pesticide
B-Endosulfan-β	Pesticide
Endosulfan sulfate	Pesticide
Endrin	Pesticide
Endrin aldegyde	Pesticide
Ethylbenzene	Aromatic
Fluoranthene	Aromatic
Fluorene	Aromatic
Haphthalene	Aromatic
Heptachlor	Pesticide
Heptachlor epoxide	Pesticide
Hexachlorobenzene	Chlorinated aromatic
Hexachlorobutadiene	Chlorinated alkane
Hexachlorocyclopentadiene	Chlorinated alkane
Hexachloroethane	Chlorinated alkane
Indeno[1,2,3-c,d]pyrene	Aromatic
Isophorone	Organic
Lead	Metal
Mercury	Metal
Methyl bromide	Chlorinated alkane
Methyl chloride	Chlorinated alkane
Methylene chloride	Chlorinated alkane
Nickel	Metal
Nitrobenzene	Substituted aromatic
2-Nitrophenol	Phenol
4-Nitrophenol	Phenol
n-Nitrosodimethylamine	Organic
n-Nitrosodi-N-propylamine	Organic

Pollutant	Type of Chemical
n-Nitrosodiphenylamine	Organic
Para-chlor-meta-cresol	Phenol
PCB-1016	Chlorinated biphenol
PCB-1221	Chlorinated biphenol
PCB-1232	Chlorinated biphenol
PCB-1242	Chlorinated biphenol
PCB-1248	Chlorinated biphenol
PCB-1254	Chlorinated biphenol
PCB-1260	Chlorinated biphenol
Pentachlorophenol	Phenol
Phenanthane	Aromatic
Phenol	Phenol
Pyrene	Aromatic
Selenium	Metal
Silver	Metal
2,3,7,8-Tetrachlorodlbenzo-p-dioxin	Chlorinated organic
1,1,2,2-Tetrachloroethane	Chlorinated alkane
Tetrachloroethylene	Chlorinated alkane
Thallium	Metal
Toluene	Aromatic
1,2-trans-Dichloraoethylene	Chlorinated alkane
1,2,4-Trichlorobenzene	Chlorinated aromatic
1,1-Trichloroethane	Chlorinated alkane
1,1,2-Trichloroethane	Chlorinated alkane
Trichloroethylene	Chlorinated alkane
Trichlorofluoromethane	Chlorinated alkane
2,4,6-Trichlorophenol	Phenol
Vinyl chloride	Chlorinated phenol
Zinc	Metal

(Appendix taken from page 426 of Hazardous Waste Management by C.A. Wentz)

Appendix B

Relative Biodegradability of Certain Organic Compounds

Biodegradable	Generally resistant to biodegradation
Acrylic acid	Ethers
Aliphatic acids	Ethylene chlorohydrin
Aliphatic alcohols	Isoprene
Aliphatic aldehydes	Methyl vinyl ketone
Aliphatic esters	Morpholine
Alkyl benzene sulfonates	Oil
Aromatic amines	Polymeric compounds
Dichlorophenols	Polypropylene benzene sulfonates
Ethanolamines	Tertiary aliphatic alcohols
Glycols	Tertiary aliphatic sulfonates
Ketones	Trichlorophenols
Methacrylic acid	Certain other hydrocarbons (aliphatics, aromatics, and those containing alkyl-aryl groups)
Methyl methacrylate	
Monochlorophenols	
Nitriles	
Phenols	
Primary aliphatic amines	
Styrene	
Vinyl acetate	

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