Treatment Technologies for Frac and Produced Water

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ABSTRACT

This course briefly summarizes the general information about biochemical and chemical oxygen demand, the theory behind their definitions, methods of their determination, the US regulatory issues pertaining to them, and a brief theory and description of the technologies potentially capable of reducing these pollutants in wastewater resulting from oil and gas (O&G) exploration activities. The same or similar data and approaches can be successfully applied in treatment of various industrial wastewaters containing organic compounds.

Detailed analyses of these technologies were conducted to identify the most efficient and cost-effective technologies suitable for treatment of a variety of BOD and COD ranges in frac and produced water depending on their chemical, physical and biological composition. Since no data on the applications of these technologies specifically in frac & produced water treatment is readily available, some costs and the energy and efficiency data were inter- and extrapolated from other wastewater treatment applications of these technologies.

The author used his best professional judgment in rating and ranking the technologies with respect to frac and produced water treatment based on his personal experience with O&G and water and wastewater treatment industries in the US as well as oversees and the references sited in this paper. A further research into the cost and efficiencies of the proposed technologies is needed once this data has become available directly from the O&G field service operators and equipment manufacturers.

LIST OF ACRONYMS

ABR – Activated Bioreactor

ACT - Automated Chemostat Treatment

Alk – Alkalinity

AOP – Advanced Oxidation Process

APT - Applied Process Technology

ASP – Activated Sludge Process

BAF - Biological Aerated Filter

BC - BOD_5/COD Ratio

BOD – Biochemical Oxygen Demand

BTEX – Benzene, Toluene, Ethyl Benzene and Xylene

CAPEX – Capital Expenditures

CB - Conduction Band

CFR – Code of Federal Regulations

CO – Chemical Oxidation

COD – Chemical Oxygen Demand

CBOD – Carbonaceous Biochemical Oxygen Demand

DAF – Dissolved Air Flotation

DBR – Disinfection Byproducts Rule

DGF - Dissolved Gas Flotation

DO – Dissolved Oxygen

EC - Electrocoagulation

ED - Electrodialysis

EF – Electroflotation

FM – Formaldehyde

GAC - Granular Activated Carbon

GPM – Gallon per Minute

HAA_9 – Haloacetic Acid

HRL - Health Risk Level

HRTF - High-rate Trickling Filter

IGF - Induced Gas Flotation

ISO- International Organization for Standardization

LP – Low Pressure

MBR – Membrane Bioreactor

MCL – Maximum Contaminant Level

MGD – Mega Gallon per Day

MLSS - Mixed Liquor Suspended Solids

MP – Medium Pressure

MRL - Minimal Risk Level

MTBE - Methyl Tertiary Butyl Ether

NBOD - Nitrogenous Oxygen Demand

NOM – Natural Organic Matter

NPDES – National Pollutant Discharge Elimination System

NZLD – No Zero Liquid Discharge

O&G – Oil and Gas

O&M – Operation and Maintenance

OPEX – Operational Expenditures

OSHA – Occupational Safety and Health Organization

PEL – Permissible Exposure Level

POTW – Publicly Owned Treatment Works

PPM – Part Per Million

PPB – Part per Billion

PW – Produced Water

SBR – Sequencing Batch Reactor

SDWA – Safe Drinking Water Act

TDS – Total Dissolved Solids

TENORM – Technologically Enhances Normally Occurring Radioactive Material

TF – Trickling Filter

THM – Trihalomethane

TOC – Total Organic Carbon

TSS – Total Suspended Solids

USEPA – United States Environmental Protection Agency

UV – Ultraviolet

ZLD – Zero Liquid Discharge

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1. INTRODUCTION

During the process of lifting oil or gas from underground formations, trapped water is brought to the surface along with oil or gas. This water is known as frac and produced water (PW) which is high in salinity. The standards for produced water disposal are governed by state, national and international regulatory bodies and new technologies are constantly bringing new options to reduce environmental impact. Flowback water is what gets produced from the first 5% of water returned after a well is started. It's simple to recycle and sometimes can be done on-site for reuse.

The physical and chemical properties of PW water significantly depend on the geographic location of the oil or gas field, the geological contact materials of the water in the past, and the type of the products. In addition of oil and grease, salt content (referred to as TDS – total dissolved solids) is a primary constituent in produced water that is of much concern in onshore operations. Produced water contains many organic and inorganic compounds that result in elevated biochemical and chemical oxygen demands of the water (BOD and COD, respectively). The type and amount of these substances extensively vary from location to location and even over time in the same well. In addition to its natural components, produced waters from oil production may also contain groundwater or seawater (generally called "source" water) injected to maintain reservoir pressure, as well as miscellaneous solids and bacteria.

PW may contain some subset or mixture of dissolved inorganic salts, dispersed hydrocarbons, dissolved hydrocarbons, treatment, well operations, and work-over chemicals, dissolved gases (such as H_2S and CO_2), bacteria and other organisms, and dispersed solid particles. Quantities of these chemical compounds vary over a wide range. PW may also include chemical additives used in drilling and producing operations and in the oil/water separation process. The chemical additives are of different kinds for several purposes. They are used to act as corrosion inhibitors of the equipment, as oxygen scavengers, as scale inhibitors, as emulsion breakers and clarifiers in oil-water emulsions, to act as coagulants and flocculants to remove solids, as solvents to reduce paraffin deposits, etc. In produced water, these chemicals can affect the oil/water partition coefficient, toxicity, bioavailability, and biodegradability.

The chemical species present in PW are normally in the reduced form. As such, they react with oxygen when PW is in contact with air which results in highly elevated COD levels.

2. BOD

2.1 .DEFINITION

BOD is the amount of dissolved oxygen (DO) needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. The term also refers to a chemical procedure for determining this amount. This is not a precise quantitative test, although it is widely used as an indication of the organic quality of water. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample (or ppm) during 5 days of incubation at 20 °C (BOD_5) and is often used as a robust surrogate of the degree of organic pollution of water. Normally up to 99 percent of total BOD is exerted within 20 days, 90 percent within 10 days, and approximately 68 percent within 5 days.

An oxygen demand can also result from biological oxidation of ammonia. A 4.57 mg of oxygen is consumed per every mg of ammonia oxidized to nitrate (nitrification). The oxygen required for this conversion is known as the NBOD (nitrogenous oxygen demand). When nitrification occurs, the measured BOD value will be higher than its true value. The effect of nitrification on oxygen demand can be overcome either by using various chemicals to suppress the nitrification reactions or by treating the water to eliminate the nitrifying organisms (e.g. pasteurization and chlorination/dechlorination). When the nitrification reaction is suppressed, the resulting BOD is known as the carbonaceous BOD (CBOD), i.e. BOD = CBOD + NBOD.

The 5-day BOD test protocol with acceptably reproducible results emphasizing CBOD has been endorsed by the United States Environmental Protection Agency. This 5-day BOD test result may be described as the amount of oxygen required for aquatic microorganisms to stabilize decomposable organic matter under aerobic conditions. Stabilization may be perceived in general terms as the conversion of food to living aquatic fauna. Most natural waters contain dissolved oxygen and small quantities of organic compounds which aquatic microorganisms use as food and energy for growth and reproduction. Populations of these microorganisms tend to increase in proportion to the amount of food available. This microbial metabolism creates an oxygen demand proportional to the amount of organic compounds useful as food. Under some circumstances, microbial metabolism can consume dissolved oxygen faster than atmospheric oxygen can dissolve into the water. Fish and aquatic insects may die when oxygen is depleted by microbial metabolism.

BOD can be used as a gauge of the effectiveness of wastewater treatment plants. It is listed as a primary conventional pollutant in the U.S. Clean Water Act.

2.2. BOD MEASUREMENT

2.2.1. DILUTION METHOD

To ensure that all other conditions are equal, a very small amount of micro-organism seed is added to each sample being tested. This seed is typically generated by diluting organisms with buffered dilution water. The BOD test is carried out by diluting the sample with oxygen saturated dilution water, inoculating it with a fixed aliquot of seed, measuring the dissolved oxygen (DO) and then sealing the sample to prevent further oxygen dissolving in. The sample is kept at 20 °C in the dark to prevent photosynthesis (and thereby the addition of oxygen) for five days, and the dissolved oxygen is measured again. The difference between the final DO and initial DO is the BOD. The loss of dissolved oxygen in the sample, once corrections have been made for the degree of dilution, is called the BOD_5. For measurement of CBOD, a nitrification inhibitor is added after the dilution water has been added to the sample. The inhibitor hinders the oxidation of ammonia nitrogen. BOD is similar in function to COD as both measure the amount of organic compounds in water. However, COD is less specific, since it measures everything that can be chemically oxidized, rather than just levels of biologically active organic matter.

2.2.2. MAMOMETRIC METHOD

This method is limited to the measurement of the oxygen consumption due only to carbonaceous oxidation. Ammonia oxidation is inhibited. The sample is kept in a sealed container fitted with a pressure sensor. A substance that absorbs carbon dioxide (typically lithium hydroxide) is added in the container above the sample level. The sample is stored in conditions identical to the dilution method. Oxygen is consumed and, as ammonia oxidation is inhibited, carbon dioxide is released. The total amount of gas, and thus the pressure, decreases because carbon dioxide is absorbed. From the drop of pressure, the sensor electronics computes and displays the consumed quantity of oxygen.

2.2.3. DISSOLVED OXYGEN PROBES

Membrane: The development of an analytical instrument that utilizes the reduction-oxidation (redox) chemistry of oxygen in the presence of dissimilar metal electrodes was introduced during the 1950s. This redox electrode utilized an oxygen permeable membrane to allow the diffusion of the gas into an electrochemical cell and its concentration determined by polarographic or galvanic electrodes. This analytical method is sensitive and accurate to down to levels of ± 0.1 mg/l dissolved oxygen. Calibration of the redox electrode of this membrane electrode still requires the use of the Henry’s law table or the Winkler test for dissolved oxygen.

Luminescence: During the last two decades, a new form of electrode was developed based on the luminescence emission of a photo active chemical compound and the quenching of that emission by oxygen. This quenching photophysics mechanism is described by the Stern-Volmer equation for dissolved oxygen in a solution. The determination of oxygen concentration by luminescence quenching has a linear response over a broad range of oxygen concentrations and has excellent accuracy and reproducibility. There are several recognized USEPA methods for the measurement of Dissolved Oxygen for BOD, including the following methods:

1. Standard Methods for the Examination of Water and Wastewater, Method 4500-O
2. In-Situ Inc. Method 1003-8-2009 BOD Measurement by Optical Probe.

2.2.4. BOD BIOSENSORS

An alternative to measure BOD is the development of biosensors, which are devices for the detection of an analyte that combines a biological component with a physicochemical detector component. Biosensors can be used to indirectly measure BOD via a fast (usually <30 min) BOD substitute and a corresponding calibration curve method. Biosensors, both online and offline, are commercially available but they have several limitations such as high maintenance costs, limited run lengths due to the need for reactivation, and the inability to respond to changing quality characteristics as would normally occur in small wastewater treatment systems. Diffusion processes of the biodegradable organic matter into the membrane and different responses by different microbial species lead to problems with the reproducibility of results. Another, perhaps the most important limitation, is the uncertainty associated with the calibration function for translating the BOD substitute into the real BOD_5.

2.3. HISTORY OF THE USE OF BOD

The UK Royal Commission on River Pollution, which was established in 1865, and the formation of the Royal Commission on Sewage Disposal in 1898 led to the selection in 1908 of BOD_5 as the definitive test for organic pollution of rivers. Five days was chosen as an appropriate test period because this is supposedly the longest time that river water takes to travel from source to estuary in the U.K. The Royal Commission recommended that the standard should be 20 parts dissolved oxygen by weight per million of water and 30 parts per million of suspended solids. This was the cornerstone for the 20:30 concept (BOD: Suspended Solids) plus full nitrification standard which was used as a yardstick in the U.K. up to the 1970s for sewage works effluent quality.

The United States includes BOD_5 effluent limitations in its secondary treatment regulations. Secondary municipal sewage treatment is generally expected to remove 85 percent of the BOD_5 measured in sewage and produce effluent BOD_5 concentrations with a 30-day average of less than 30 mg/L and a 7-day average of less than 45 mg/L. The regulations also describe "treatment equivalent to secondary treatment" as removing 65 percent of the BOD_5 and producing effluent BOD_5 concentrations with a 30-day average less than 45 mg/L and a 7-day average less than 65 mg/L.

3. COD

3.1. DEFINITION

The chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water that can be oxidized chemically by potassium dichromate in an acidic solution. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers) or wastewater, making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. Some references express the units as parts per million (ppm) as in the current paper.

The basis for the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. The amount of oxygen required to oxidize an organic compound to carbon dioxide, ammonia, and water is given by:

$$\mathrm{C}_n\mathrm{H}_a\mathrm{O}_b\mathrm{N}_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right)\mathrm{O}_2 \rightarrow n\mathrm{CO}_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)\mathrm{H}_2\mathrm{O} + c\mathrm{NH}_3$$

The following equation defines nitrification:

$$\mathrm{NH}_3 + 2\mathrm{O}_2 \rightarrow \mathrm{NO}_3^- + \mathrm{H}_3\mathrm{O}^+$$

The amount of alkalinity required to completely nitrify (i.e. reduce oxygen demand) an effluent is 7.14 mg *Alk* as $CaCO_3$/mg N. Although it would be expected that the value of ultimate (long-term) CBOD would be as high as the COD, this is seldom the case. Some of the reasons for this are as follows:

1. Many organic compounds which are difficult to oxidize biologically (e.g. lignin) can be oxidized chemically.
2. Inorganic substances that are oxidized by the dichromate increase the apparent organic content of the sample.
3. Certain organic substances may be toxic to the microorganisms used in the BOD test.
4. High COD values may occur because of the presence of inorganic substances with which the dichromate can react.

The COD test can be completed in as little as 15 min (usually 2.5 hours for the regular test) compared to 5 or more days for the BOD test. Same as for BOD, online COD monitors have recently become available.

3.2. MEASUREMENT

The International Organization for Standardization describes a standard method for measuring chemical oxygen demand in ISO 6060. Several oxidizing agents such as ceric sulphate, potassium iodate, potassium permanganate and potassium dichromate have been used to determine COD. Of these, potassium dichromate ($K_2Cr_2O_7$) has been shown to be the most effective: it is relatively cheap, easy to purify, and is able to nearly completely oxidize almost all organic compounds. In this method, a fixed volume with a known excess amount of the oxidant is added to a sample of the solution being analyzed. After a refluxing digestion step, the initial concentration of organic substances in the sample is calculated from a titrimetric or spectrophotometric determination of the oxidant remaining in the sample.

Potassium dichromate is a strong oxidizing agent under acidic conditions. Acidity is usually achieved by the addition of sulfuric acid. In the process of oxidizing the organic substances found in the water sample, potassium dichromate is reduced (since in all redox reactions, one reagent is oxidized and the other is reduced), forming Cr^{3+}. The amount of Cr^{3+} is determined after oxidization is complete and is used as an indirect measure of the organic contents of the water sample.

For all organic matter to be completely oxidized, an excess amount of potassium dichromate (or any oxidizing agent) must be present. Once oxidation is complete, the amount of excess potassium dichromate must be measured to ensure that the amount of Cr^{3+} can be determined with accuracy. To do so, the excess potassium dichromate is titrated with ferrous ammonium sulfate until all of the excess oxidizing agent has been reduced to Cr^{3+}. Typically, the oxidation-reduction indicator Ferroin is added during this titration step as well. Once all the excess dichromate has been reduced, the Ferroin indicator changes from blue-green to reddish-brown. The amount of ferrous ammonium sulfate added is equivalent to the amount of excess potassium dichromate added to the original sample. Chlorides, nitrites, sulfides, ferrous ion are often the most serious source of interference in measuring COD.

3.3. GOVERNMENT REGULATIONS

Many governments impose strict regulations regarding the maximum COD allowed in wastewater before it can be returned to the environment. In some European countries, effluent COD must reach between 200 and 1000 ppmO_2 before domestic, industrial, commercial, etc. wastewater can be discharged.

COD and total organic carbon (TOC) laboratory tests can provide an accurate measure of the organic content of wastewater in a shorter time frame than a BOD_5 test (i.e., several hours versus 5 days). In the US, the effluent discharge permit (NPDES permit) for industrial and commercial wastewater treatment facilities often have COD below 500 ppm. Pursuant to 40

CFR §133.104(b), the NPDES permit writer may substitute COD or TOC monitoring for BOD_5 when a long-term BOD:COD or BOD:TOC correlation has been demonstrated.

4. BOD, COD AND TOC CORRELATION

The TOC test is used to measure the total organic carbon in an aqueous sample. The TOC of a wastewater can be used as a measure of its pollution characteristics. For domestic wastewater and some industrial wastewaters, it is possible to relate TOC to BOD and COD as indicated in the table below:

Type of Wastewater	BOD_5/COD	BOD_5/TOC
Untreated	0.3-0.8	1.2-2.0
After Primary Setting	0.4-0.6	0.8-1.2
Final Effluent	0.1-0.3	0.2-0.5

The typical average ratio of BOD_5/COD for untreated municipal wastewater is around 0.5. Above this value, the waste is considered easily treatable by biological means. If the ratio is below 0.3, either the waste may have some components that may be toxic to the microorganisms or acclimated microorganisms may be required in its stabilization.

For comparison, the following table shows the median, minimum and maximum concentrations of $BOD_{5,}$ TOC and COD in 29 Marcellus Shale well samples in West Virginia and Pennsylvania.

Parameter	Unit	Minimum	Median	Maximum
BOD_5	ppm	3	275	4450
COD	ppm	1480	5500	31900
TOC	ppm	70	449	1080

In should be noted that sometimes laboratories need to use different analytical methods depending on the consistency and quality of samples. Sometimes the laboratories are only required to provide a certain level of accuracy. Also, the quality and composition of flowback water (PW) from a single well can change within a few days soon after the well is fractured. As such, the treatment process is designed to achieve a minimum acceptable treatment efficiency for a range of expected variables.

Based on this data, the median-value BOD_5/COD (B/C) ratio is 0.05. According to the Penn State University research, the average BOD_5 and COD values in the Marcellus flowback water are 60 ppm and 4000 ppm, respectively (B/C = 0.015). For such a B/C ratio, none of the conventional biological treatment processes for the purpose of surface discharge is economically feasible due to extremely low bacterial metabolic rates, much larger reactor volumes and extensive hydraulic retention times.

5. PRODUCED WATER TREATMENT FOR BOD/COD REDUCTION

5.1. GENERAL OVERVIEW

Despite the costs and logistical challenges, companies in the oil industry are starting to explore more efficient and effective ways of wastewater treatment. This is due in large part to the combined effects of stricter governmental discharge standards, increasing environmental awareness, and a growing understanding of how re-using untreated water damages both drilling and pumping equipment as well as oil-well quality. There are a few technologies employed for the treatment of PW. These include phase separations, use of gravity oil/water separators, dissolved air floatation, thermal, freeze and membrane (for low salinity waters) distillation, chemical treatment, etc. Among electrochemical methods, electrofloatation (EF), electrocoagulation (EC) and electrodialysis (ED) are being used around the world. Some researchers found that ED can remove more than 95% of oil and grease and 89% of total dissolved solids, and EF can remove 72% water insoluble oil without addition of any flocculent. Arnold Zilverentant et *al* report that a pilot-scale membrane bioreactor used to treat high-COD produced water (up to 50,000 ppm) was able to achieve a 97% reduction in COD. The effluent COD concentration however was above the discharge limit of 250 ppm. Jewel Gomes, *et al* report an 83-percent reduction in produced water COD concentration using electrocoagulation (EC). Biological Aerated Filter (BAF) was reported to achieve a 70-80 % / 30-60% BOD/COD reduction, respectively, at TDS < 6,600 ppm. BiPetroClean reported a 94% COD reduction using

Automated Chemostat Treatment (ACT) method of bioremediation. Pendashteh, et al report the removal rate for COD above 81% by a sequencing batch reactor (SBR) using isolated halophilic bacteria. Linares- Hernandez *et al* report a 99% COD removal efficiency using EC with iron electrode and electrooxidation with a boron dipped diamond electrode. Augustin reports a 90-percent industrial wastewater effluent BOD/COD removal using aluminum electrodes and NaCl as electrolyte.

Asselin *et al* report also suggests that aluminum (Al) is the most effective electrode material for the purpose of petroleum refinery wastewater treatment. Khansorthong and Hunsom were able to reduce color and COD by 91% and 77%, respectively, with operating costs of \$0.29/m^3 wastewater when treating pulp and paper mill by EC in batch mode using iron electrodes. Using EC, Raju *et al. were able to reduce* COD in textile wastewater by 97% using titanium electrodes. Espinoza-Quniones *et al* report a complete COD and turbidity removal at neutral pH and 45 min of EC time. Zaied and Bellahkal report 98% COD removal at pH 7, electrolysis time of 50 min and the current density of 14 mA/cm^2. A 2-log COD removal in oil refinery wastewater using Al electrodes was reported for the current density of 35 mA/cm^2 and energy consumption of 42 kWh/kg COD. Sengil *et al* achieve an 82% COD reduction from tannery liming drum wastewater, again using EC. Merzouk *et al* report a 1-log reduction in BOD and an 80%-reduction in COD in textile wastewater using EC. Meas *et al* indicate a 95%-COD reduction in industrial wastewater using EC.

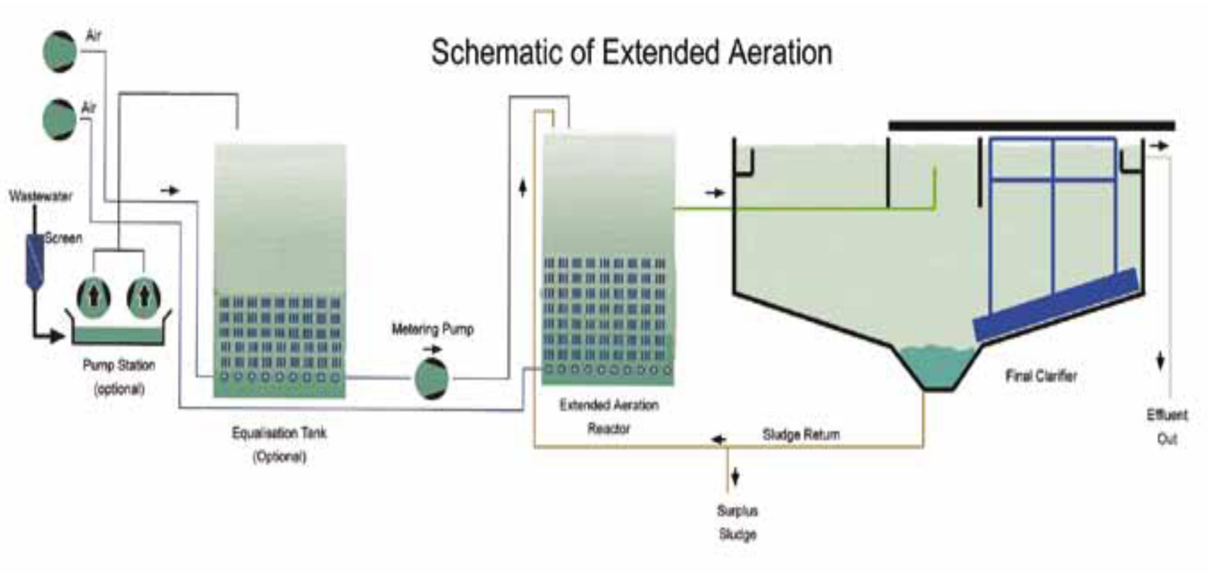
5.2. AEROBIC BIOLOGICAL TREATMENT

5.2.1. BRIEF PROCESS DESCRIPTION

Typically, physical and chemical methods for wastewater treatment are efficient in the elimination of suspended solids, dissolved metals as well as free and dispersed oil. These methods, however do not achieve a high level of efficiency for the elimination of dissolved solids. For steady domestic and medium-strength COD industrial wastewater streams, biological treatment is one of the most commonly used treatment technologies capable of reducing various types of dissolved organic molecules including petroleum hydrocarbons. As such, this technology is capable of lowering the organic contamination levels in low-salinity produced waters and consequently reducing BOD and COD.

The most common biological method for treating domestic sewage and some commercial and industrial wastewaters is known as the activated sludge process (ASP). There are multiple of variations of ASPs the descriptions of which are beyond the scope of this paper. The reader may refer to the standard wastewater engineering references for their descriptions and design details.

Treating domestic wastewater with ASP entails the consumption of the dissolved contaminants by the microorganisms within the tank (bioreactor) to form an additional bio-mass (activated sludge) in the presence of air, oxygen or ozone. As shown in the ASP diagram below, the effluent and sludge are washed out of the bioreactor into a clarifier. The solid waste (sludge) that settles on the bottom of the clarifier is composed of both live and dead bacteria. Normally 40-70% of this sludge is transported back to the bioreactor (recycled) in order to continually re-activate the biological process. The remainder of the sludge is fed into a de-watering system for removing additional water and is then disposed of in a landfill. The effluent from the clarifier passes through a sedimentation unit and in case of tertiary treatment through a filtration unit before discharge, recycle or re-use.



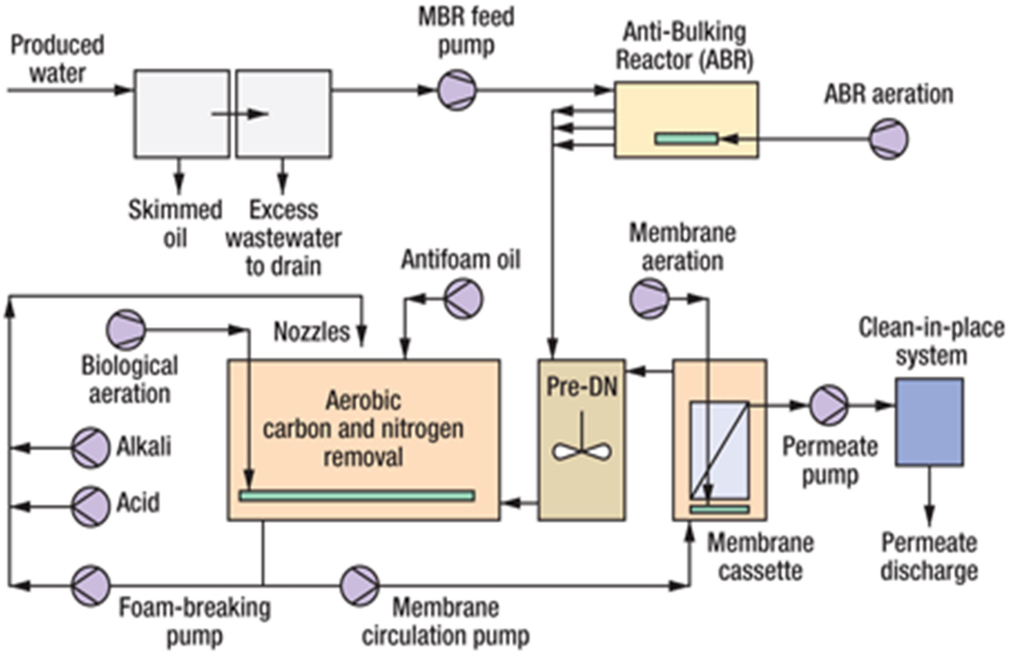
Common biological processes, such as ASP or membrane bioreactors (MBRs) are based on the concept of maintaining a high cell concentration throughout the process (3.5-10 g/L). This leads to high final sludge levels that translate directly into higher disposal costs. The infrastructure of the common biological methods is stationary, requiring a long time for assembly and operation such as those for ASP or trickling filters. Since biological treatment systems with capacities of 50 gpm and higher cannot be readily moved from one drilling site to another, the only option in these cases is to transport PW from the various wells (sometimes from a significant distance) to the stationary wastewater plant which is very costly as demonstrated on the example of Marcellus Shale where the PW is hauled to Ohio and West Virginia from Pennsylvania. For these reasons, biological treatment methods are not always ideal for cleaning produced water.

The second consideration in regard to choosing the most suitable treatment method or technology to reduce BOD/COD is that despite numerous claims, the ASP or attached growth processes are not efficient in treating produced waters due to potentially high concentrations of dissolved solids. For conventional wastewater treatment processes, high-TDS fluxes will cause the level of salinity in the biological reactor to increase over time. This is problematic because salinity levels between 0.8% and 1.0% (8,000 mg/L – 10,000 mg/L) will cease biological activity. At these salinity levels, the bacterial populations begin to undergo plasmolysis, a condition where the plasma membrane pulls away from the cell wall due to the loss of water through osmosis. This condition may cease the entire biological treatment process for several weeks and even months unless the halophilic bacterial populations such as those found in the Great Salt Lake are added to the biological reactor. The bacterial acclimation process however may take a while which would make the entire process cost prohibitive. It is clear now that at e.g. 10 % salinity which is e.g. the median salinity level for Marcellus, biological treatment would not be economically feasible. If the capital cost is not an issue, a combination of a stationary ASP/MBR treatment unit followed by a high-rate trickling filter (HRTF) for BOD/COD reduction theoretically would be the most reasonable process to try. No information however regarding the existence of such a treatment train for the purpose of treating PW was found. In general, there is very little or no data published about PW constituents and its treatment.

The contamination levels and composition in produced water can vary through time or from one oil well to another. This may cause upsets during the biological treatment process since bacterial populations are very sensitive to fluctuating conditions. Therefore, a flow and mass equalization facility large enough to accommodate a certain daily or weekly flow volume needs be installed at the headworks. The upsets can ultimately lead to complete site shut downs, costing exorbitant amounts of money and people resources to bring it back online. Furthermore, common biological systems such as ASP, MBR, or TF usually include very cumbersome systems that require highly skilled management. The figure below represents a configuration of the combined ASP/MBR process designed for COD reduction. In this design, PW passes through an oil-water separator after which it is pumped into a preconditioning reactor sometimes referred to as ABR. By removing easily broken-down compounds, ABR prevents the development of activated sludge with poor settling characteristics (bulking sludge). In addition, experience shows that substantial savings are made in aeration energy such as up to 30% of the sludge production can be saved. The use of ABRs allows wastewater treatment plants to be built more compactly. Also, odor emissions can be decreased significantly due to reduction in the hydrogen sulfide production.

After ABR, PW gravity-flows to a denitrification unit for ammonia removal and then passes into a biological reactor sized and equipped for both CBOD and NBOD removal. To maintain appropriate pH, acids and alkalis are usually added to the biological reactor. From here PW is pumped to an MBR there PW undergoes additional biological treatment and membrane filtration. The MBR reactor in this example is separate from the biological reactor so that the settled sludge is recirculated from the MBR back to the bioreactor to maintain a certain level (usually 3.5%-5%) of so-called mixed liquor suspended solids (MLSS) in the bioreactor.

Based on the number of functioning units shown in the diagram, such prefab treatment modules with capacities of 40,000 gal/day and above would have to be transported to drilling sites on a rail car or by multiple trucks. The aerobic ammonia-nitrogen removal unit is usually a separate air stripping column or tower preceding the ASP tank where the MBR can be physically placed in depending on the reactor's mixed liquor suspended solids (MLSS) concentration (up to 10%).



5.2.2. TECHNOLOGY EVALUATION

The table below briefly describes the major evaluation criteria.

Criteria	Description/Rationale
Industrial status	The technology such as ASP which exists since 1913 entails dozens of variations successfully used throughout the world for COD/BOD and other pollutants reduction in domestic, industrial and commercial wastewaters. It has limited applications in PW treatment.
Feed water quality bins	Not applicable to all TDS bins, is highly independent of salt and fracking constituents' type and concentration.
Product water quality	No data for PW. According to the discussion above, PW may simply bypass the treatment process.
Production efficiency (recovery)	98.5%-99% recovery. The 1%-1.5% contributes to the sludge water content.
Energy use	Energy usage depends on the influent COD/BOD concentrations and may account for 90% of the total O&M.
Chemical use	Chemical costs may be high.
Expected lifetime of critical components	Considering potentially high concentrations of TDS and corrosion issues, almost every unit process can be considered a critical component. For normal environments, the life span for most of the process units and equipment are 15-25 years.
Infrastructure considerations	Depending of discharge options, the primary, secondary, possibly tertiary, and solids train stationary processing and handling facilities are required. Mobile units may not be cost effective.
O&M considerations	Periodic calibration and maintenance of chemical meter pumps, valves, actuators, sensors and remote controls (for remote operations) is required. Two plant operators during 2 shifts and one maintenance worker can be sufficient for a 1-mgd plant.
Overall costs	For a 1-mgd plant, the capital costs can range from \$1500/1000 gal to \$8000/1000 gal depending on the

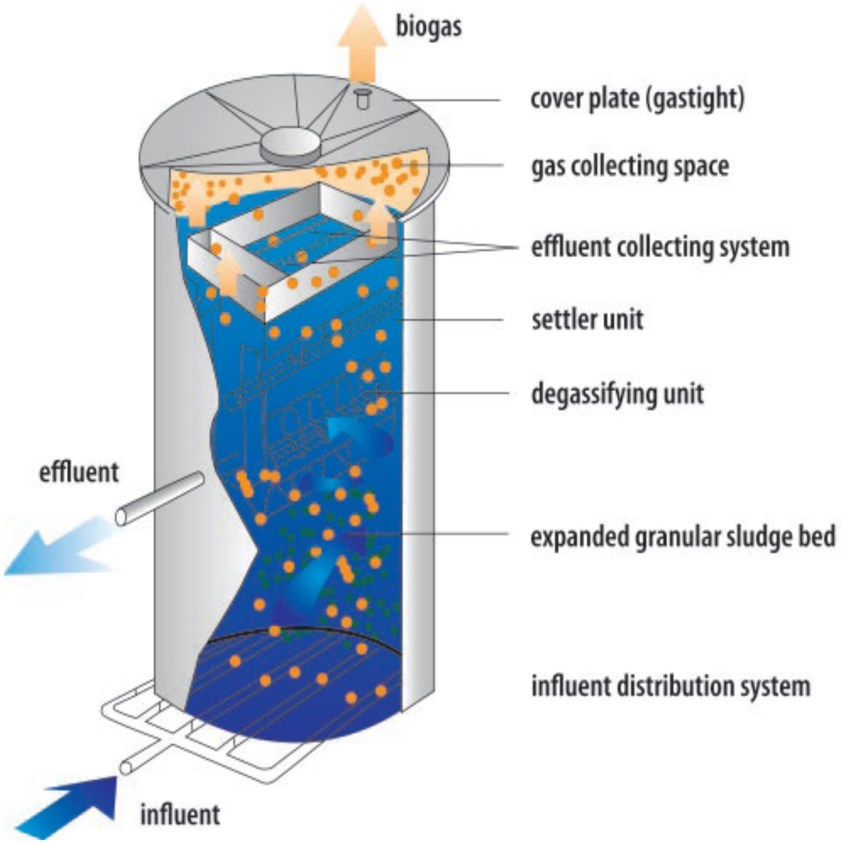
	process configuration and construction/equipment material options. In comparison with other treatment options described in this paper, the O&M costs can be as low as $0.12/1000 gal for dilute streams.
Pre- or post-treatment of feed water	Usually required and included in the overall cost.
Concentrate management or waste disposal	A 1-mgd plant can generate a few tons of sludge per day depending on the TSS and TOC. The average disposal cost is $220/ton (for none pathogenic waste).

5.3. ANAEROBIC BIOLOGICAL TREATMENT

5.3.1. BRIEF PROCESS DESCRIPTION

In general, the anaerobic treatment of wastewaters (i.e. in the absence of oxygen) usually requires higher hydraulic detention times (HRTs) and therefore larger treatment unit volumes. The anaerobic processes perform extremely well and usually achieve very high BOD/COD removal efficiencies for domestic and some industrial wastewaters. During the process, the biomass and organic compounds are metabolized to methane, carbon dioxide and water. However, the range of HRTs in regard to mobility and the ease of installation can easily make the use of this technology unfavorable in the field of O&G exploration. For this reason, no technical evaluation of the technology is offered in this paper. No single application of this technology for BOD/COD reduction in PW was found.

It's worth mentioning here of the BIOBED® EGSB Technology by Veolia from the treatment volume perspective because it is claimed to be the most compact units of its kind capable of operating at a COD loading of 15-30 kg COD/m^3/day. This approximately corresponds to the COD concentrations in the upper Marcellus range (15,000-30,000 mg COD/L). The BIOBED package plants can be extended to up to 6 package modules (50 m^3 or 120 m^3) as 40-ft container-framed modules for transportation. The maximum COD load that can be treated per module is 1,000-2,000 kg/day or up to 100,000 gal/day (at COD = 5,000 mg/L). To prepare the PW anaerobic treatment, the pH value and temperature are regulated in a conditioning tank there it is mixed with recycled effluent. Nutrients are added if necessary to achieve optimal growth conditions for the anaerobic biomass. Then the PW is pumped into the reactor at a constant flow rate where it would pass through a dense and expanded anaerobic granular biomass bed converting the COD into biogas. The gas which is mostly methane can be flared or served as an energy source. The biomass would settle back to the bottom of the reactor whilst part of the treated effluent is recycled and returned to the conditioning tank for dilution. The following picture depicts the major details of this process.



5.3.2. TECHNICAL ASSESSMENT

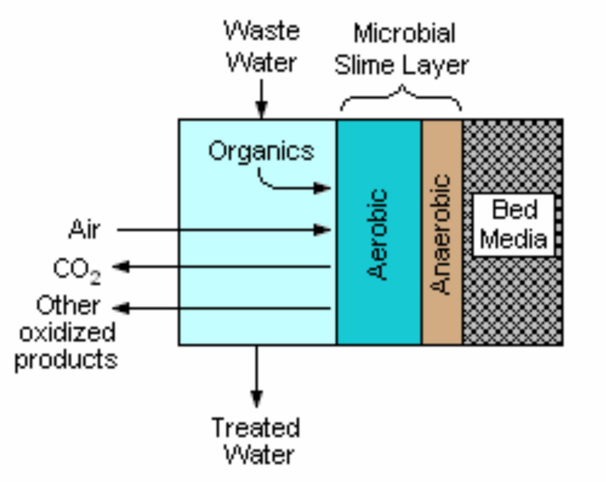
No data are available on the CAPEX, OPEX, dimensions, operating parameters or efficiency of this unit until a formal RFP entailing the exact composition of the PW is provided to Veolia.

5.4. BIOLOGICAL AERATED FILTER PROCESSES

5.4.1. BRIEF PROCESS DESCRIPTION

In this context, the biological treatment systems including MBRs that are not fully or partially based on the suspended growth processes such as the ASP are referred to as Biological Aerated Filters (BAF). The term biological aerated filter refers to a class of technologies, including fixed film and attached growth processes, roughing filters, intermittent filters, packed bed media filters, and conventional TFs. A BAF can remove oil, suspended solids, ammonia, and nitrogen, chemical oxygen demand (COD), biological oxygen demand (BOD), iron, manganese, heavy metals, soluble organics, trace organics, and hydrogen sulfide. Iron and manganese removal in BAFs is mainly due to chemical oxidation rather, not a biological process.

Since BAFs do not remove dissolved constituents, however, high concentrations of salts can decrease the effectiveness of this technology due to salt toxicity effects. At chloride levels below 6,600 mg/L, there is no diminished contaminant removal with BAFs and at 20,000 mg/L chloride levels there will be a reduction in slime growth and BOD removal. This technology can be used to treat water with much greater organic contaminant concentrations than typically found in regular domestic wastewater. The schematic drawing of a biological aerated filter is shown above.



BAF is a well-established technology and has been used for produced water treatment for many years. Because of this technology’s ability to remove oil and grease, it has been primarily used for oil-field produced water treatment. Informal versions of BAFs require minimal equipment, can be made by flowing water over rock beds. These types of BAFs have also been used in coal bed methane produced water treatment for iron and suspended solids removal.

Removal capability of BAFs is dependent on the hydraulic loading rate on the filter and the raw water quality. The following are approximate removal capabilities of this technology: 60 to 90% nitrification, and 50 to 70% total nitrogen, 70 to 80% oil, 30 to 60% COD, 85 to 95% BOD, and 75 to 85% suspended solids.

There is nearly 100% water recovery from this process. The residuals generated are from the settling of the microbial layer that sloughs off of the media. The residuals generation, which is highly dependent on the water quality, is approximately 0.4 to 0.7 pounds of dry solids per 1000 gallons of water treated.

Primary sedimentation should be employed upstream from BAFs to allow the full bed of the filter to be used for removal of non-settling, colloidal, and dissolved particles if the water requires a large degree of contaminant removal. Sedimentation should also follow BAFs to remove the microbial layer that sloughs off of the filter. Other equipment that may be used includes pumps and fans for aeration, and distribution nozzles. The estimated energy demand for BAFs is 1 to 4 kWh/day. No chemicals are necessary.

5.4.2. TECHNICAL ASSESSMENT

A summary of the BAF assessment is provided in the following table.

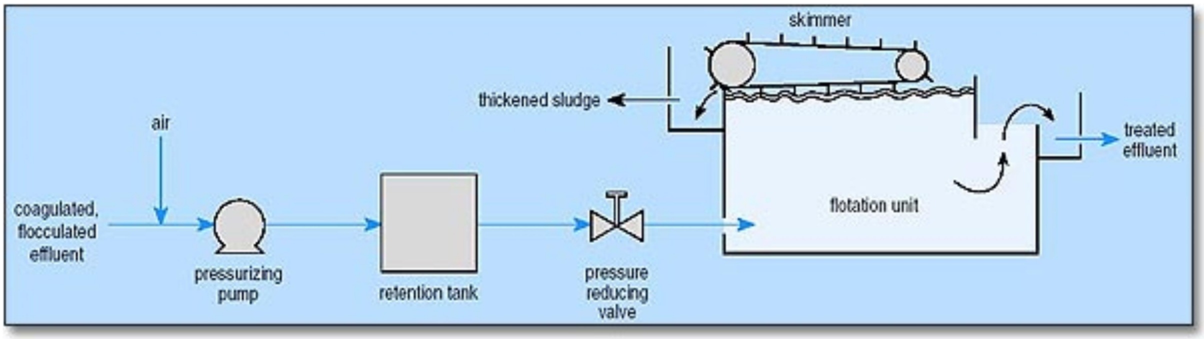
Criteria	Description/Rationale
Industrial status	Well established technology for domestic and industrial wastewaters but not for produced water. Numerous vendors.
Feed water quality bins	Not effective for brackish, saline and oily waters.
Product water quality	60 to 70% total nitrogen. 70 to 80% oil 50 to 60% COD 85 to 95% BOD
Production efficiency (recovery)	Waste from this process is removed as a solid, therefore, water recovery is nearly 100%
Energy use	The power requirement for BAFs is 1 to 4 kWh

Chemical use	No chemicals are required for BAFs during normal operation, no cleaning is required
Expected lifetime of critical components	Long expected lifespan. Some types of BAFs consist only of rock beds hand holding ponds and do not require any equipment.
Infrastructure considerations	BAFs require upstream and downstream sedimentation, therefore, they have a large footprint and are not very mobile or modular
O&M considerations	Very little monitoring required. Occasional emptying of sedimentation ponds required. Does not require skilled operators. Easy to adapt to highly varying water quantity and quality. Little down time or need for maintenance. TF do require substantial maintenance due to cleaning and media replacement.
Overall costs	The majority of the overall cost of this technology is capital. CAPEX $2000/1000 gal. O&M costs are very low, < $0.10/1000 gal.
Pretreatment of feed water	Sedimentation may be required upstream of BAFs and is required downstream of BAFs
Post-treatment of product water	Typically none required.
Concentrate management or waste disposal	Solids disposal is required for the sludge that accumulates in the sedimentation basins. Can account for up to 40% of total cost of technology. TFs require filter media disposal (at $1000/ton).

5.5. FLOTATION

5.5.1. BRIEF PROCESS DESCRIPTION

Flotation is a process in which fine gas bubbles are used to separate small, suspended particles that are difficult to separate by settling or sedimentation (refer to figure below).



Gas is injected into the water to be treated and particulates and oil droplets suspended in the water are attached to the air bubbles and they both rise to the surface. As a result, foam develops on the surface, which is commonly removed by skimming. The dissolved gas can be air, nitrogen, or another type of inert gas. Dissolved air/gas flotation can also be used to remove volatile organics and oil and grease. Dissolved air flotation units have been widely used for treatment of produced water.

Gas flotation technology is subdivided into dissolved gas flotation (DGF) and induced gas flotation (IGF). The two technologies differ by the method used to generate gas bubbles and the resultant bubble sizes. In DGF units, gas (usually air) is fed into the flotation chamber, which is filled with a fully saturated solution. Inside the chamber, the gas is released by applying a vacuum or by creating a rapid pressure drop. IGF technology uses mechanical shear or propellers to create bubbles that are introduced into the bottom of the flotation chamber. Coagulation can be used as a pretreatment to flotation.

The efficiency of the flotation process depends on the density differences of liquid and contaminants to be removed. It also depends on the oil droplet size and temperature. Minimizing gas bubble size and achieving an even gas bubble distribution are critical to removal efficiency. Flotation works well in cold temperatures and can be used for waters with both high and low TOC concentrations. It is excellent for removing natural organic matter (NOM). Dissolved air flotation (DAF) can remove particles as small as 25 µm. If coagulation is added as pretreatment, DAF can remove contaminants 3 to 5 µm in size. In one reported study, flotation achieved an oil removal of 93%. Flotation cannot remove soluble oil constituents from water. Treatment costs are estimated to be \$0.60/m^3.

Because flotation involves dissolving a gas into the water stream, flotation works best at low temperatures. If high temperatures are present, a higher pressure is required to dissolve the gas in the water.

5.5.2. TECHNICAL ASSESSMENT

A summary of the flotation assessment is provided in the following table.

Criteria	Description/Rationale
Industrial status	Widely used for produced water treatment, primarily for conventional oil and gas produced water
Feed water quality bins	High TOC, oil and grease, particulates < 7% solids Not ideal for high temperature feed streams
Product water quality	93% oil removal 75% COD removal 90% removal of H_2S
Production efficiency (recovery)	High water recovery, nearly 100%
Energy use	Energy is required to pressurize the system to dissolve gas in the feed stream.
Chemical use	Coagulant chemical may be added to enhance removal of target contaminants.
Expected lifetime of critical components	No information available.
Infrastructure considerations	Dissolved air flotation requires an external pressurized tank
O&M considerations	Chemical coagulant and pumping costs are the major components of O&M costs for flotation
Overall costs	The majority of the overall cost of this technology is capital. CAPEX $2700/1000 gal. O&M costs are around $0.80/1000 gal.
Pretreatment of feed water	Coagulation may be used as a pretreatment for flotation
Post-treatment of product water	Typically none required.

Concentrate management or waste disposal	Solids disposal will be required for the sludge generated from flotation

5.6. ADSORPTION

5.6.1. BRIEF PROCESS DESCRIPTION

Adsorption is a widely accepted technology for the removal of soluble hydrocarbons from the produced water. Adsorption columns are packed with porous solid material known as adsorbent. The hydrocarbons contributing to COD in the PW present in the produced water adhere onto the surface of adsorbent and are eventually retained within the porous structure. The effluent from the adsorption column contains little or no hydrocarbons. Highly porous adsorbents with higher surface area offer better performance. The major concern of adsorption operation is the requirement of retention time which limits the throughput capacity.

Adsorption can be accomplished using a variety of materials, including zeolites, organoclays, activated alumina, and activated carbon. Chemicals are not required for normal operation of adsorptive processes. Chemicals may be used to regenerate media when all active sites are occupied. Periodically the media is backwashed to remove large particulates trapped between the voids in the media. Typically, these processes can be gravity fed and do not require an energy supply, except during backwash.

Adsorbents are capable of removing iron, manganese, total organic carbon, BOD/COD, BTEX compounds, heavy metals, and oil from produced water. Adsorption is generally utilized as a unit process in a treatment train rather than as a stand-alone process. The adsorbent can be easily overloaded with large concentrations of organics, so this process is best used as a polishing step rather than as a primary treatment process.

The most common adsorbent for TOC removal is granular activated carbon (GAC). Coagulation processes, as a pretreatment to GAC, can both reduce influent TOC concentration and decrease the influent pH to the adsorber, thus leading to improved GAC performance. Several investigators have reported better GAC performance for TOC control after coagulation or after increasing the coagulant dose (i.e., enhanced coagulation). Parallel GAC contactors are operated in a staggered mode wherein each contactor has been in operation for different lengths of time. In this mode of operation, one contactor at a time is taken off-line when the blended effluent exceeds the target effluent concentration, and a column with fresh or reactivated GAC is then placed on-line. The effluent from the contactor in operation the longest can be higher than the target breakthrough concentration, as it is blended with water from the contactors that have effluent concentrations much lower than the target concentrations. Consequently, the effluent of parallel contactors is blended prior to disinfection. Thus, parallel operation in a multiple contactor configuration will result in longer GAC bed-life and the time between reactivation will be longer. Under ideal conditions, staged blending with multiple parallel contactors leads to near steady-state effluent concentration and increases the run time for TOC by an average of 150 percent.

Media usage rate is one of the main operational costs for adsorptive processes. When all active sites of the adsorptive material have been consumed, the material must either be regenerated or disposed of. Regenerating the materials will result in a liquid waste for disposal. Solid waste disposal is necessary when the material needs to be replaced entirely.

5.6.2. TECHNICAL ASSESSMENT

A summary of the adsorption assessment is provided in table below.

Criteria	Description/Rationale
Industrial status	Adsorption is commonly used for treatment of produced water
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration. Can remove iron, manganese, TOC, BTEX, and oil. Zeolites can also be used to exchange calcium for sodium to reduce SAR
Product water quality	> 80% removal of heavy metals COD removal – 10-60% BOD removal – 30-75%

Production efficiency (recovery)	High water recovery, nearly 100%
Energy use	Minimal
Chemical use	Chemicals may be required for media regeneration.
Expected lifetime of critical components	Media may require frequent replacement or regeneration depending on media type and feed water quality.
Infrastructure considerations	Adsorption processes require a vessel to contain the media (usually GAC) and pumps and plumbing to implement backwashes.
O&M considerations	There will be a pressure loss incurred across the filter, however, depending on the plant configuration; this may not require any additional pumps. Pumps will be necessary to backwash the filters. GAC needs to be periodically regenerated or disposed of which significantly contributes to OPEX.
Overall costs	CAPEX - $404/1000 gal, OPEX - $68/1000 gal
Pretreatment of feed water	GAC systems may require some kind of pretreatment to prevent build-up of solids in the GAC bed, to minimize the organic loading on the GAC, and to improve cost effectiveness.
Post-treatment of product water	Adsorption is best used as a polishing step to avoid rapid usage of adsorbent material.
Concentrate management or waste disposal	Waste disposal is required for spent media or the waste produced during regeneration of the media.

5.7. ADVANCED OXIDATION TECHNOLOGIES

5.7.1. OVERVIEW

Oxidants commonly used in water treatment applications include chlorine, hydrogen peroxide, chlorine dioxide, permanganate, oxygen, and ozone. The appropriate oxidant for a given application depends on many factors including raw water quality, specific contaminants present in the water, and local chemical and power costs. Chemical oxidation (CO) is well established, reliable, and requires minimal equipment. CO is often used in conjunction with nonchemical oxidation technologies. Section 5.7.2. describes the design criteria and costs of CO.

Oxidation of soluble organics and contaminants (bacteria, nitrate, etc.) is an effective produced water treatment. Ozone and hydrogen peroxide are strong oxidizers. Oxidation process produce dissolved carbon dioxide which can be removed by air stripping. Ultraviolet (UV) light has also been used for oxidation, which de-ionizes water into hydrogen and hydroxyl ions. The UV effectiveness however is strongly dependent on the turbidity. To increase the UV lamps efficiency, PW must be practically free of turbidity, i.e. in addition to a conventional suspended solids removal, undergo a polishing step which results in higher treatment costs. Provided that a tertiary treatment of PW is needed, any combination of the treatment technologies entailing UV will not be cost effective.

Hydroxyl ions are also strong oxidizers. UV light also kills bacteria and other microorganisms to disinfect the water. Oxidation is able to reduce COD, BOD, organics, iron, nitrite, manganese, cyanides, pesticides, hydrogen sulfide and aromatic hydrocarbons. Biological decomposition (combined oxidation and reduction) of produced water in a constructed wetland is also useful for treating raw produced water and treating post-treatment water after it has been through other treatment

Advanced oxidation processes (AOPs) have been shown to destroy organic compounds in different waters and significantly reduce both BOD and COD. The compounds are completely oxidized into water, carbon dioxide and mineral acids such as HCl. In general, the effectiveness of an AOP is proportional to its ability to generate hydroxyl radicals. The following AOPs are available commercially for full-scale installations:

- Ozone + hydrogen peroxide
- UV + Ozone
- UV + hydrogen peroxide
- Titanium dioxide + UV
- Fenton’s reagent
- Cavitation (requires O_3 or H_2O_2 to supplement the process, for not reviewed here)

- Combinations of the above
- E-beam (not reviewed here, limited applications due to safety/public perception).

As with the other treatment technologies discussed in this report, the design of an AOP is governed by the influent contaminant concentration, target effluent contaminant concentration, desired flow rate, and background water quality parameters such as pH, bromide concentration, and alkalinity. The key design parameters for AOPs include: chemical dosages and ratios with other chemicals, reactor contact time, and reactor configuration. The optimum dosages, ratios, and contact time are water-specific and treatment scenario-specific and are often determined through pilot studies using the water matrix of interest. As can be expected, higher oxidant dosages and contact times are typically expected to result in higher removal rates; however, increasing dosages results in higher O&M costs and possible by-product formation. In some cases, the formation of by-products can be limited by higher chemical ratios.

The hydroxyl radical is nonselective and, thus, can be exhausted by the presence of organic or inorganic compounds other than the contaminants of concern. Alkalinity and TOC, nitrates, nitrites, phosphates and sulfates compounds have the potential to scavenge hydroxyl radicals, i.e. increase the oxidants dosages. For example, both carbonate and bicarbonate will scavenge hydroxyl radicals to create carbonate radicals which, in turn, react with other organic or inorganic compounds present. The reaction for the scavenging of hydroxyl radicals by bicarbonate ions is shown below:

$$\bullet OH + HCO_3^- \rightarrow CO_3\bullet + H_2O$$

Likewise, nitrates and nitrites adsorb UV light in the range of 230 to 240 nm and 300 to 310 nm and, consequently, high nitrate (>1 mg/L) or high nitrite (>1 mg/L) concentrations have been shown to limit the effectiveness of UV technologies. While phosphates and sulfates are commonly present in low concentrations in PW, these compounds have the potential to scavenge hydroxyl radicals. However, they are extremely slow in reacting with •OH, and their scavenging effect can usually be neglected for ozone/peroxide/UV systems. For TiO_2 systems, sulfates have been noted to significantly decrease the destruction rate of organic contaminants at concentrations above approximately 100 mg/L.

E-beam systems are used widely in the food and drug industry for disinfection. Over the past several years, a large number of pilot-scale studies have been completed at drinking water facilities. Due to the nature of the reducing and oxidizing species created in an E-beam reactor, COD concentrations can be reduced to well below any action levels with minimal to none by-product formation. Despite this fact, the negative public perception resulting from the use of radiation combined with the requirement for skilled operators and the expected high capital and O&M costs for E-beam systems results in their limited application. However, because this technology has been used in the past, there may be some treatment or remediation scenarios where E-beam will be selected because it may provide advantages relative to other treatment options. There are no known applications of the E-beam systems in PW treatment for BOD/COD reduction.

5.7.2. CHEMICAL OXIDATION

5.7.2.1. BRIEF PROCESS DESCRIPTION

Chemical Oxidation (CO) treatment can be used to remove iron, manganese, sulfur, color, tastes, odor, organics and some inorganic compounds. CO relies on oxidation/reduction reactions, which consist of two half-reactions: the oxidation reaction in which a substance loses or donates electrons, and a reduction reaction in which a substance accepts or gains electrons. Oxidation and reduction reactions will always occur together since free electrons cannot exist in solution and electrons must be conserved. Chemical oxidants commonly used in water treatment applications include chlorine, chlorine dioxide and permanganate. The appropriate oxidant for a given application depends on many factors including raw water quality, specific contaminants present in the water, and local chemical and power costs. The removal or oxidation rate may be controlled by applied chemical dose and contact time between oxidants and water.

No pretreatment is required for oxidation. Solid separation post-treatment might be required to remove oxidized particles. Chemical metering pumps are required for dosing. Some equipment may be required to generate the oxidant on-site. Chemical costs may be high.

5.7.2.2. TECHNICAL ASSESSMENT

A summary of the oxidation assessment is provided in table below.

Criteria	Description/Rationale
Industrial status	Chemical oxidation is well established, reliable, and requires minimal equipment. For potable water treatment, ozone, chlorine, hydrogen peroxide, chlorine dioxide and permanganate are used to remove COD, BOD, organic, pathogens, and some inorganic compounds like iron and manganese. The application of CO on PW is limited to disinfection only.
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration.
Product water quality	Depends on the type of oxidant used.
Production efficiency (recovery)	100% recovery.
Energy use	Energy usage usually accounts for approximately 18% of the total O&M for oxidation processes.
Chemical use	Chemical costs may be high.
Expected lifetime of critical components	Critical components of the oxidation process are the chemical metering pumps. Chemical metering equipment can have a life expectancy of 10 years or greater.
Infrastructure considerations	Chemical metering equipment/controls are required.
O&M considerations	Periodic calibration and maintenance of chemical meter pumps is required.
Overall costs	For the purpose of BOD/COD reduction in PW, the capital costs can be near $3000/1000 gal, O&M costs can be as low as $0.25/1000 gal for dilute streams and as high as $4/1000 gal for high-TOC waters. For disinfection only, these costs can be between 25%-

	40% of the above costs.
Pre- or post-treatment of feed water	Pretreatment for high organics-laden streams may be required. No post-treatment is usually required for oxidation processes.
Concentrate management or waste disposal	No solid waste is generated from oxidation processes.

5.7.3. HYDROGEN PEROXIDE/OZONE (H_2O_2/O_3)

5.7.3.1. H_2O_2/O_3 PROCESS DESCRIPTION

When O_3 is added to water, it participates in a complex chain of reactions that result in the formation of radicals such as the hydroxyl radical (•OH) and the superoxide radical (O_2•). Like O_3, these radical products (•OH and O_2•) are oxidants capable of COD destruction. Of the radical intermediates formed in ozonated water, •OH is the most powerful COD oxidant, even more powerful than O_3 itself. Direct oxidation of ethers by O_3 is known to occur very slowly; this reaction's second-order kinetic rate constant is less than 1/M·s. By contrast, oxidation of ethers by radical oxidants is extremely rapid. Hydroxyl radicals react with TOC according to a rate constant of 1.6×10^9 1/M·s. H_2O_2 can be combined with ozone to enhance the transformation of O_3 to •OH in solution. H_2O_2 is a weak acid, which partially dissociates into the hydroperoxide ion (HO_2^-) in water. H_2O_2 reacts slowly with O_3, whereas the HO_2^- ion can rapidly react with O_3 to form •OH:

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O+$$

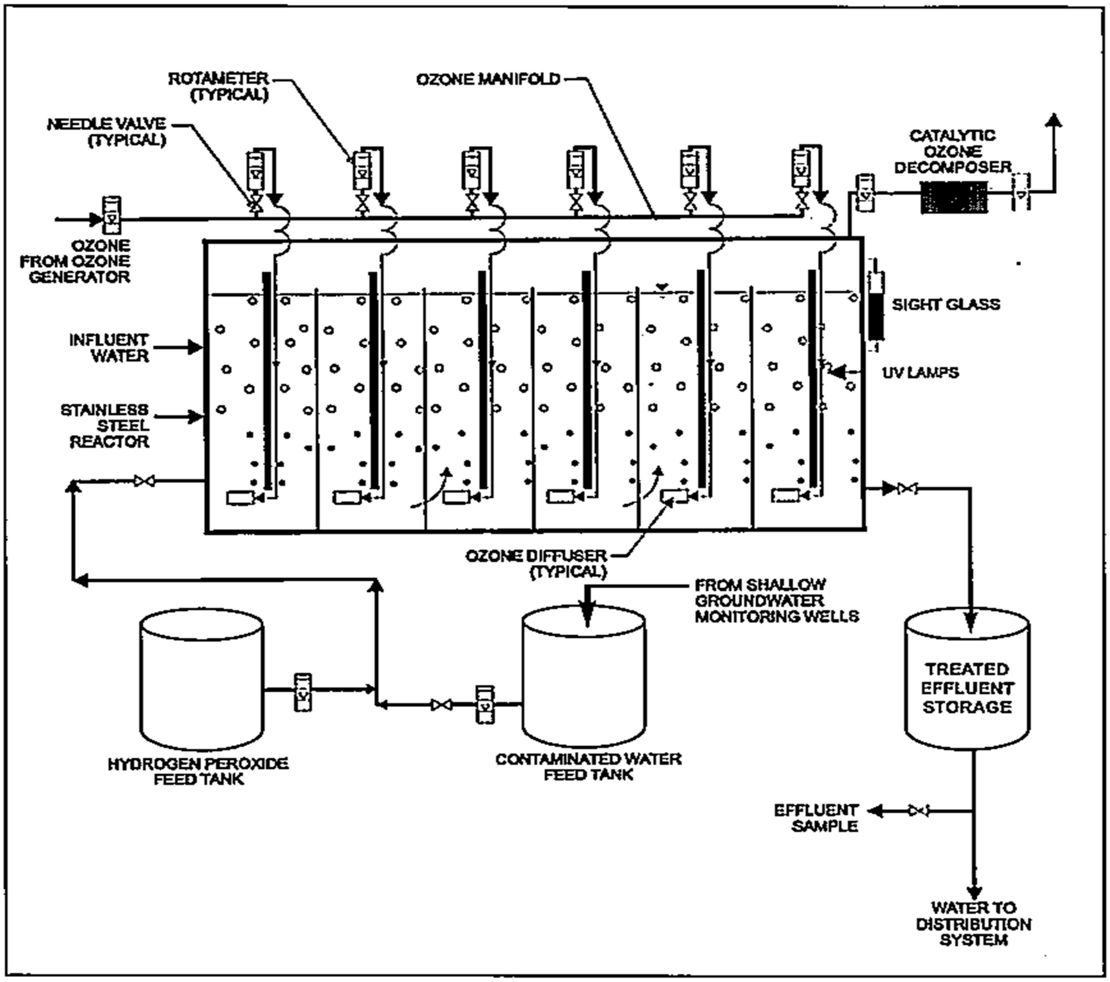
$$O_3 + HO_2^- \rightarrow \bullet OH + O_2^- + O_2$$

5.7.3.2. H_2O_2/O_3 SYSTEM DESCRIPTION/DESIGN PARAMETERS

H_2O_2 is used in conjunction with O_3 to enhance the formation of hydroxyl radicals. Since O_3 decomposes rapidly, it is typically produced on-site using a generator fed with dried compressed air or oxygen. The gas mixtures produced from air and oxygen by an ozone generator usually consist of 0.5 to 1.5 percent and 1 to 2 percent by volume O_3, respectively. The use of air to generate ozone requires dehumidification, which may be cost prohibitive relative to the use of pure liquid oxygen. In addition, larger quantities of ozone can be produced from a unit of liquid oxygen (14 percent O_2 by weight) compared to a unit of compressed air (2 percent O_2 by weight), which facilitates greater mass transfer of the ozone into the source water. Finally, ozone can be generated from liquid oxygen using less energy relative to compressed air.

For AOPs, O_3 gas is fed through spargers, porous piping or plates, or Venturi-type injectors at dosages equivalent to 1 to 2 mg/L ozone per mg/L DOC (dissolved organic carbon, part of TOC); however, higher dosages are recommended for source waters with high alkalinity (>100 mg/L as $CaCO_3$). O_3 transfer efficiencies from the gas to the water of up to 90 to 95 percent can be achieved. H_2O_2 is fed from an aqueous solution, at peroxide to ozone ratios ranging from 0.3:1 to 3:1. This ratio will be a function of disinfection requirements (if performed), bromide concentration, contaminant concentration, and other water quality parameters. Since ozone residual can provide disinfection credit, a lower peroxide to ozone ratio is typically applied to source waters requiring disinfection (e.g., surface waters) in order to leave some ozone residual. However, researchers have shown that bromate formation is a strong function of the H_2O_2/O_3 ratio, and that H_2O_2/O_3 ratios can effectively reduce the concentration of bromate generated. These counter-acting effects should be considered when trying to determine the optimal peroxide to ozone dosage ratio to apply for a specific water source with significant influent bromide concentrations (>1 mg/L). The median bromide concentration in e.g. Marcellus PW is 616 mg/L and can be as high as 3070 mg/L.

Two types of ozone contact configurations exist for application: 1) conventional 3 to 5-meter-deep continuously stirred reactor basins, and 2) long (up to 30 meters) plug flow reactors. In a conventional ozone reactor, ozone is bubbled through the base of the reactor and allowed to diffuse through the reactor until it either escapes through the top or is completely reacted. This results in high ozone concentrations at the base of the reactor, independent of the contaminant concentrations, which promote the reaction of ozone with other chemical constituents to form regulated by-products (e.g., bromate). These reactors are typically covered so that excess O_3 can be collected and directed to an off-gas decomposer. Automatic monitoring and control systems are used to regulate chemical feed rates, pH, and other parameters. In addition, a variety of safety, monitoring, and control systems are included to facilitate operation. A process flow diagram of a conventional H_2O_2/O_3 system is shown in the figure below.



The second type of H_2O_2/O_3 contact system, referred to as HiPOx, has been commercialized by Applied Process Technology, Inc. (APT) (San Francisco, CA). HiPOx is a continuous, inline plug flow reactor where H_2O_2 and O_3 are injected into the water stream in precisely controlled ratios at multiple ports along the flow reactor. The primary advantage of this system is that high dosages can be applied at the beginning of the flow reactor, where contaminant concentrations are high. As contaminant concentrations are reduced along the line, decreasing dosages can be applied, thereby controlling formation of regulated by-products (e.g., bromate). Using multiple injection ports, the concentration of molecular ozone in solution can be maintained at a lower concentration, typically below 0.5 mg/L, than in a large continuously stirred reactor. This keeps the H_2O_2/O_3 ratio high which, in turn, increases the rate of molecular ozone being converted to the hydroxyl radical (and also increases the rate of hypobromite reduction to bromide). In addition, this system can be operated without the loss of pressure experienced by bringing the source water in contact with the atmosphere, thereby reduce pumping costs.

5.7.3.3. ADVANTAGES AND DISADVANTAGES OF THE H_2O_2/O_3 PROCESS

The benefits of using an H_2O_2/O_3 system are:

- The combined H_2O_2/O_3 process has been demonstrated to be more effective at removing TOC and other natural and synthetic organics than O_3 or H_2O_2 alone. In addition, using a combination of O_3 and H_2O_2 to produce hydroxyl radicals, rather than just O_3, allows a lower dosage of O_3 to be used. This is desirable for reducing costs and bromate formation potential.
- The theoretical yield of hydroxyl radicals via H_2O_2/O_3 technology is less than that of the H_2O_2/UV technology; however, the yield is less affected by water quality (i.e., turbidity, iron, and nitrates lower the yield for UV processes but not H_2O_2/O_3 processes). Once the hydroxyl radicals are formed, however, the chemical destruction and interferences are the same for both technologies.
- According to a literature review, H_2O_2/O_3 systems appear to be the most tested and applied AOP in remediation applications for groundwaters, relative to the other AOPs. Thus, the implementation of H_2O_2/O_3 systems has a field-proven history of operation and regulatory acceptance.
- The H_2O_2/O_3 process seems to be the preferred USEPA technology choice for destruction of several groundwater pollutants including MTBE, dioxins and para-dioxane.
- The H_2O_2/O_3 process receives the highest rating for mechanically reliability and requires less frequent maintenance than the other AOP processes.

The disadvantages and limitations of the H_2O_2/O_3 system are:

- No full-scale applications for COD/BOD reduction in PW exist for this technology.
- The use of O_3 can result in the potential formation of bromate; however, bromate formation can be mitigated by lowering the pH to <6.5, increasing the H_2O_2/O_3 ratio, or adding another radical scavenger that will react with hydroxyl radicals prior to the bromide (e.g., ammonia which in PW can be as high as 90 mg/L).
- The H_2O_2/O_3 process typically requires an air permit for ozone emissions in addition to an off-gas treatment system for ozone destruction. The hydrogen peroxide reacts rapidly with most of the applied ozone and, thus, the air exiting the contactor has been observed to typically contain ozone concentrations less than 1 mg/L. This concentration is significantly higher than the US 1-hour Clean Air Act standard of 0.12 ppm_v (US CFR Title 40, Part 50). Current methods for removal of ozone in the off-gas include thermal destruction, catalytic reduction, or a combination of the two. Thermal destruction takes advantage of the fact that ozone decomposes rapidly at high temperatures. Catalytic reduction involves passing the ozone off-gas across a surface (commonly iron or manganese oxide) that catalyzes the decomposition of ozone to elemental oxygen. These controls will add to the operational and capital cost of the system).
- Residual H_2O_2 can serve as an oxygen source for microorganisms and can promote biological re-growth in the distribution system. Although there are currently no federal or state standards for residual H_2O_2/O_3 in treated drinking water, any detectable levels of H_2O_2 in treated PW in a surface discharge (detection limits range from 1 µg/L to 100 µg/L depending on the method and concentration) may not be appreciated by the numerous environmental groups because of concerns over biological growth. Thus, depending on the effluent concentration, post treatment of excess H_2O_2 may be required to limit downstream biological fouling. However, if residual H_2O_2 concentrations are limited to less than a few mg/L, treatment systems already in place for the removal of oxidation by-products from the H_2O_2/O_3 system effluent will also remove the residual H_2O_2. In cases where residual H_2O_2/O_3

generally exceeds a few mg/L, a treatment system specifically for H_2O_2 removal (e.g., catalytic activated carbon) may need to be employed.

5.7.3.4. SUMMARY OF H_2O_2/O_3 PROCESS ASSESSMENT

H_2O_2/O_3 systems have been extremely well studied at the bench-, pilot-, field-, and full-scale levels for the removal of variety organic contaminants such as BTEX, TCE, PCE, etc. in groundwater and TOC and COD reduction. There are currently hundreds of full-scale H_2O_2/O_3 systems in use for MTBE, dioxane, etc. remediation. According to APT Water and Purifics, Inc., the use of this technology for PW or frac water applications has only been performed at the pilot scale. Even though the process can achieve a 2- 3-log removal efficiency for COD, there is no data relating the COD removal efficiency to the TOC or TDS concentrations in PW. Whilst the effect of TOC and particular pollutants concentrations on the overall performance and operating cost of the H_2O_2/O_3 process have been well studied and reported, no indication of such studies with respect to TDS concentrations have been found. Nor are there legitimate data reported that would shed light on the oxidants' effect on the slicking agents in PW and friction.

While concerns have been raised about the formation of bromate with drinking water systems, this concern can be mitigated by increasing the peroxide to ozone ratio, decreasing the pH, or raising the concentration of other radical scavengers. The chemistry behind H_2O_2/O_3 systems in regard to drinking and ground waters is well understood. However, as with all PW BOD/COD proposed treatment technologies, bench-, pilot- and field-scale experiments and demonstration sites under a variety of PW water quality matrices are needed prior to general acceptance. The table below summarizes the most important H_2O_2/O_3 process criteria.

Criteria	Description/Rationale
Industrial status	H_2O_2/O_3 oxidation is well established in regard to groundwater and industrial wastewater but not for PW. Can be successfully used to remove COD, BOD and TOC.
Feed water quality bins	May not be applicable to all TDS bins since the ozone propagation in PW may be retarded by high-TDS concentrations
Product water quality	No data for PW is available

Production efficiency (recovery)	100% recovery
Energy use	Energy usage may account for up to 25% of the total O&M for oxidation processes depending on the TOC concentration. Up to 8% of annual O&M cost for low TOC.
Chemical use	Chemical costs may be high depending on the TOC. For low TOC, this cost is 7% of the annual O&M cost.
Expected lifetime of critical components	Critical components of the oxidation process are the chemical metering pumps. Chemical metering equipment can have a life expectancy of 15-20 years depending on the TDS concentration.
Infrastructure considerations	Chemical metering equipment/controls are required.
O&M considerations	Periodic calibration and maintenance of chemical meter pumps is required.
Overall costs	O&M costs can vary widely depending on TOC; for low TOC O&M cost < $1.00/1000 gal; for TOC = 450 mg/L, the O&M cost is $5.40/1000 gal. CAPEX is not usually a function of TOC but rather the design flow, on the average is $3077/1000 gal PW treated.
Pre- and post-treatment of feed water	Depending on the TOC concentration, pretreatment may be required to reduce the oxidants generation/dosages. Post-treatment may be required depending on reuse/discharge options.
Waste disposal	No solid waste is generated from oxidation processes.

5.7.4. O_3/UV AND H_2O_2/UV

5.7.4.1. PROCESS DESCRIPTION

Due to the relatively high molar extinction coefficient of ozone, LP-UV or MP-UV radiation can be applied to ozonated water to form highly reactive hydroxyl radicals. The use of UV irradiation — whether MP-UV, LP-UV, or P-UV — to produce hydroxyl radicals with ozone and peroxide occurs by the following reactions:

$O_3 + H_2O \rightarrow O_2 + H_2O_2$ (l <300 nm)

$2O_3 + H_2O_2 \rightarrow 2 \bullet OH + 3O_2$

H_2O_2 → 2 •OH (l <300 nm)

•OH + TDOC → Oxidation by-products

As the above reactions illustrate, photolysis of ozone generates hydrogen peroxide and, thus, O_3/UV involves all of the organic destruction mechanisms present in H_2O_2/O_3 and H_2O_2/UV. These mechanisms include direct reaction with ozone, direct photolysis by UV irradiation, or reaction with hydroxyl radicals. In most past applications of O_3/UV, LP-UV lamps have been used.

5.7.4.2. SYSTEM DESCRIPTION/DESIGN PARAMETERS

Two basic UV reactor design configurations are used for the removal of organic contaminants from water. For large scale applications (>500 gpm), a tower design is typically utilized. In the tower configuration, multiple UV lamps are arranged horizontally within a single large reactor vessel with the contaminated water flowing perpendicularly past the UV lamps. For example, a tower system may consist of 12 20-kW UV lamps arranged horizontally throughout the tower. Heat transfer for MP-UV lamps is typically <1°C for every 4 kWh/1,000 gallons. Therefore, no cooling systems are needed for the large-scale tower configuration. For small-scale systems (<500 gpm), reactors where a single UV lamp per reactor vessel is arranged vertically can be employed. For example, a small-scale system may consist of three individual reactor vessels in series, each containing one 30-kW UV lamp in a vertical position. For very small systems (<50 gpm), these higher watt lamps operate at a higher temperature and, thus, require a cooling fan to effect heat transfer. Many of such systems can use either ozone, peroxide, or a combination of both as supplemental oxidants. A typical oxidation system can consist of a combination of the following four components: 1) a stainless steel reaction chamber with LP-UV lamps; 2) an air compressor/ozone generator; 3) a hydrogen peroxide feed system; and 4) a catalytic ozone decomposition unit. As a first step in the treatment process, the contaminated source water is mixed with peroxide and then fed into the reaction chamber where ozone is added, if necessary. The reaction chamber ranges in size from 300 to 5000 gallons and is divided into a series of parallel sub-chambers, each housing a bank of LP-UV mercury vapor lamps. As the water flows through each sub-chamber, it passes in front of each bank of UV lamps (the number of sub-chambers and the number of lamps depend on the size of the system and type of contaminant being destroyed). For low intensity UV lamps, the surface temperatures of the quartz sheath surrounding each lamp rarely exceed 90°F.

For O_3/UV applications, ozone is introduced into the system at the bottom of each chamber by a stainless steel sparger. The ozone generator employed by most systems can electrically generate ozone from either air or liquid oxygen. Any ozone that is present in the off-gas is put through a fixed bed catalytic scavenger. This ozone decomposition unit typically operates at 150°F and uses a proprietary nickel-based catalyst to convert ozone to oxygen. Some systems can operate from flow ranges of 5 gpm to 1,500 gpm. Higher flowrates are attainable with multiple treatment trains.

All of the reactor configurations discussed for the O_3/UV process are applicable for the H_2O_2/UV process. H_2O_2/UV systems are equipped with hydrogen peroxide storage and injection systems in place of an ozone generator and diffuser system. Hydrogen peroxide is injected upstream of the reactor using metering pumps and mixed by in-line static mixers. Hydrogen peroxide can be added either as a single slug dose or at multiple points in the system. The optimum dose of H_2O_2 should be determined for each water source based on bench and pilot-scale testing, but is commonly estimated at twice the TOC and not less than
1 to 2 mg/L for drinking water (e.g., TOC for drinking water ranges from less than 0.1 mg/L to greater than 7 mg/L, which would suggest a peroxide concentration of up to 14 mg/L). Consequently, the H_2O_2 concentration generated by the reactor for the purpose of treating Marcellus Shale PW should be in the range from 1000 mg/L to 4000 mg/L, i.e. the reactor capacity should be about an order of magnitude higher than that for the conventional drinking water applications. It is clear the H_2O_2/UV process will not be a cost effective BOD/COD treatment alternative for a high-turbidity PW having elevated TOC concentrations.

To minimize problems associated with potential fouling of the UV lamp sleeves in cases where the influent water has high concentrations of fouling agents (e.g., iron, calcium, and magnesium), UV systems are equipped with automated cleaning devices. Quartz sleeves that separate the water from the UV lamps are periodically cleaned by pneumatically driven wipers. Quartz sleeve cleaning devices are common in UV oxidation technologies, and the costs are generally included in the total costs of the system. The frequency of UV lamp cleaning is a function of the presence of iron and other scaling agents in the water.

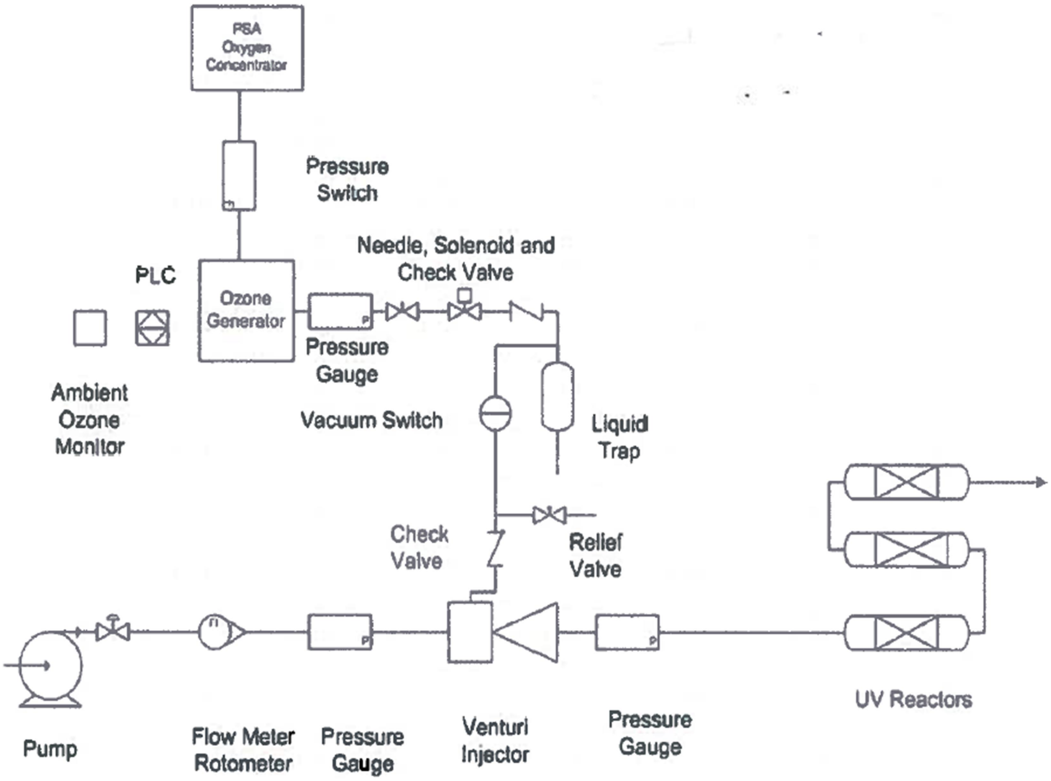
The two primary design variables that must be optimized in sizing a UV AOP system are the UV power radiation per unit volume of water treated — more commonly referred to as UV dose — and the concentration of hydrogen peroxide or ozone. UV dose, when applied to AOP, is a measure of the total lamp electrical energy applied to a fixed volume of water. The units are measured in kWh/1,000 gallons treated. This parameter combines flowrate, residence time and light intensity into a single term. The dose of UV light and peroxide/ozone required per unit volume of water treated may vary from one type of water to another.

Design tests are typically performed to measure the UV dosage required to achieve the desired effluent BOD/COD concentration. The dosage to be applied is determined in an iterative manner by examining the effect on treatment of selected process variables such as pH, oxidant concentration and retention time.

The major components of an O_3/UV or H_2O_2/UV system include:

- UV lamps, lamp sleeves, and lamp cleaning system
- Ozone generator and diffusers or H_2O_2 storage and reactor chamber
- Ozone contactor
- Ozone off-gas decomposer
- Liquid oxygen or compressed air tank
- Supply and discharge pumps and piping
- Monitoring and control systems

The process flow diagram below depicts the major components of the O_3/UV process.



5.7.4.3. ADVANTAGES AND DISADVANTAGES

The advantages and disadvantages of the O_3/UV and H_2O_2/UV systems are briefly summarized below.

There are certain benefits of using the systems for certain applications such as:

- The removal efficiency of the combined O_3/UV or H_2O_2/UV process is typically higher than the additive removal efficiencies of ozone and UV alone. The magnitude of this synergistic effect varies depending on the contaminant of interest.
- There is no potential for bromate formation in the H_2O_2/UV process because the system does not rely on ozone for organic destruction.
- The combined O_3/UV process is more efficient at generating hydroxyl radicals than the combined H_2O_2/UV process for equal oxidant concentrations using LP-UV. This is because the molar extinction coefficient of O_3 at 254 nm is two orders of magnitude

greater than that of H_2O_2, indicating that a lower UV intensity or a higher H_2O_2 dose is required to generate the same number of hydroxyl radicals for these two processes. However, for MP-UV lamps, H_2O_2/UV processes can generate more hydroxyl radicals than O_3/UV processes, assuming the peroxide absorbs greater than 17percent of irradiated light (200 nm to 300 nm).

- According to the literature review, H_2O_2/UV systems appear to be the most tested and applied AOP in drinking water applications relative to the other AOPs, although not for BOD/COD reduction in PW. Thus, the implementation of H_2O_2/UV systems for drinking water applications has a history of operation and regulatory acceptance.
- The theoretical yield of hydroxyl radicals via the H_2O_2/UV process is greater than that for the H_2O_2/O_3 process; however, due to turbidity and interfering compounds in the PW water, this theoretical yield can be decreased to below that of the H_2O_2/O_3 process. Once the hydroxyl radicals are formed, however, the chemical destruction and interferences are the same for both technologies.

The disadvantages of the O_3/UV and H_2O_2/UV systems are:

- No full-scale applications for BOD/COD reduction in PW exist for these two technologies.
- UV light penetration into the source water and, thus, process efficiency is adversely affected by turbidity which makes any combination of UV cost prohibitive in regard to COD reduction in PW.
- Elevated TOC concentrations in PW dictates the employment of much larger oxidant reactors so that these processes most likely be cost prohibitive for BOD/COD reduction in PW.
- The use of ozone for source waters with high bromide concentrations (>0.1 mg/L) can result in the formation of bromate.
- The O_3/UV process typically requires an air permit for ozone emissions in addition to an off-gas treatment system for ozone destruction. These controls will add to the operational and capital cost of the system).

- Despite the fact that O_3/UV is more stoichiometrically efficient at generating hydroxyl radicals than H_2O_2/UV or H_2O_2/O_3, the O_3/UV process is less energetically efficient than H_2O_2/UV or H_2O_2/O_3 for generating large quantities of hydroxyl radicals due to the low solubility of O_3 in water compared to H_2O_2. Thus, operational costs are expected to be much higher than these comparative processes. The hydroxyl radical yield can be decreased further by the presence of interfering parameters (e.g., nitrates, turbidity, or iron) in the source water.
- Gaseous O_3 must be diffused into the source water, resulting in potential mass transfer limitations relative to H_2O_2, which is fed as a liquid solution.
- There are many interference compounds that absorb UV light (e.g., nitrate and iron) and, thus, reduce process efficiency.
- UV lamp and sleeve failures can potentially contaminate treated water with mercury (although there is no evidence that all lamp failures to date have resulted in aqueous Hg concentrations above drinking water standards).
- Research suggests that the use of UV combined with pre- and/or post-chlorination can potentially result in the increased formation of THM and HAA_9 at UV dosages >100 mJ/cm^2.
- The presence of residual hydrogen peroxide in the treated effluent will promote biological growth in the storage pits and perhaps water distribution systems. Thus, post-treatment of excess H_2O_2 (using catalytic activated carbon) may be required.
- All of the UV-based AOP technologies discussed in this paper receive a medium rating for mechanical reliability since they require periodic replacement and inspection of UV lamps and quartz sleeves to prevent leakage and scaling.

5.7.4.4. SUMMARY OF H_2O_2/UV and O_3/UV PROCESSES ASSESSMENT

The applications of ozone and UV are energy intensive processes and, hence, a combined O_3/UV or H_2O_2/UV process will not be cost effective for treating waters with high TOC/COD and potentially high TSS concentrations such as PW. In general, O_3/UV process requires the expending of significantly more electrical energy than H_2O_2/UV or H_2O_2/O_3 processes. Due to highly elevated TOC concentrations in PW however, the H_2O_2/UV process will require even more energy that the O_3/UV process. The use of ozone in any water treatment applications including PW can result in the generation of bromate at concentrations above the Stage 1D/DBP Rule of 10 µg/L. Also, due to sometimes elevated concentrations of suspended solids (up to 2 g/L), the influent to the UV reactors may need to be polished. In conclusion, due to these economic and practical constraints, any combination of UV technology cannot be considered a viable alternative to BOD and/or COD reduction in PW. Consequently, an extensive literature research could not locate a single pilot- or full-scale application of these technologies for BOD/COD reduction in PW or frac waters. The table below summarizes the most common H_2O_2/UV and O_3/UV processes criteria.

Criteria	Description/Rationale
Industrial status	H_2O_2/UV and O_3/UV processes are well established in the fields of groundwater remediation and for some industrial wastewater treatment applications but not for PW. Without pretreatment for TOC and TSS, their costs for COD, BOD and TOC reduction in PW will be prohibitive.
Feed water quality bins	Theoretically applicable to all TDS bins, independent of salt type and concentration. The effect of TDS on the process efficiency needs to be evaluated.
Product water quality	No data exists for PW
Production efficiency (recovery)	100% recovery
Energy use	Energy usage may account for up to 25% of the total O&M for oxidation processes depending on the TOC concentration.
Chemical use	Chemical costs may be high depending on the TOC. For low TOC, this cost is 5% of the annual O&M cost.
Expected lifetime of critical components	Critical components of the oxidation process are the UV lamps and chemical metering pumps. The average lamp life ranges from 8,760 to 14,000 working hours, and the lamps are usually replaced after 12,000 hours of use. Chemical metering equipment can have a life expectancy of 10-15 years depending on the TDS concentration.
Infrastructure considerations	Chemical metering equipment/dose controls are required.

O&M considerations	Periodic calibration and maintenance of chemical meter pumps is required. Although the life cycle of ballasts is approximately 10 to 15 years, they are usually replaced every 10 years. Quartz sleeves will last about 5 to 8 years but are generally replaced every 5 years.
Overall costs	O&M costs can vary widely depending on TOC; for low TOC O&M cost is \$1.00/1000 gal; for TOC = 450 mg/L, the O&M cost can be as high as \$20/1000 gal. CAPEX is not usually a function of TOC but rather the design flow, on the average is \$2120/1000 gal PW treated.
Pre- and post-treatment of feed water	Pretreatment such as AC adsorption will be required to reduce the oxidants generation/dosages for high TOC PWs. Post-treatment may be required depending on reuse/discharge options.
Concentrate management or waste disposal	No solid waste is generated from oxidation processes.

5.7.5. FENTON'S REACTION

5.7.5.1. PROCESS DESCRIPTION

Hydrogen peroxide reacts with iron (II) to form Fenton's reagent (an unstable iron-oxide complex) that subsequently reacts to form hydroxyl radicals. The net reaction is shown below:

$Fe^{2++} + H_2O_2 \rightarrow Fe^{3++} + OH^- + \bullet OH \quad k = 76\ M^{-1} \cdot s^{-1}$

This reaction can occur either in homogeneous systems with dissolved ferrous iron or in heterogeneous systems in the presence of complexed iron such as goethite (FeO-OH). The by-product, ferric iron, in turn reacts with peroxide or superoxide (O_2^-) radical to reproduce ferrous iron as shown below:

$Fe^{3++} + H_2O_2 \rightarrow Fe^{2+} + \bullet O_2^- + 2H+$

$\bullet O_2^- + - + Fe^{3+} \rightarrow Fe^{2+} + O_2$

The above three reactions cycle iron between the ferrous and ferric oxidation states until the H_2O_2 is fully consumed, producing •OH in the process. If the pH is less than 5, the iron (III) is reconverted to iron (II), via a side cyclic reaction, and the iron remains in solution to sustain the initiation of hydroxyl radical production. As in other AOPs, the destruction of TOC/COD is primarily due to oxidation reactions initiated by the hydroxyl radical. Similar reactions can occur with copper (II) in place of iron (II).

An important side reaction also occurs resulting in the formation of precipitates—it involves the reaction of two end products of this chain reaction, hydroxide ions and Fe (III): $Fe^{3+} + nOH^- \rightarrow$ amorphous iron oxides (precipitate). Therefore, it is necessary to either lower the pH or use chelating agents to maximize the available iron (II). The optimal pH for non-chelated iron is acidic, ranging 3.5–5. Typical acids used to alter the subsurface pH include HCl, H_2SO_4, and acetic acid. However, organic acids have a tendency to increase side reactions that are undesirable in high-organic soils. Alternatively, iron solubility can be increased using chelating agents. It should be noted that inorganic metal compounds present in the subsurface, manganese, for example, may exert a demand on the hydrogen peroxide and decrease the efficacy of radical initiation.

A classical Fenton's system cannot be readily created in-situ, as it is generally too difficult to maintain a well-mixed, low-peroxide concentration in the subsurface. In practice, more concentrated solutions of hydrogen peroxide are injected, ranging 4%–20%, and either followed or preceded by an injection of acidic iron solution. Any deviation from the traditional low-concentration hydrogen peroxide/iron mixture is known as a "Modified Fenton's System." This includes the use of higher concentrations of H_2O_2 or calcium peroxide (CaO_2), with or without chelating agents. This type of system is more complicated than traditional Fenton's chemistry, and the generation of other radical species has been proposed. Hydroxyl radicals are very strong oxidizing agents. When hydrogen peroxide is present in excess, radical-initiation and propagating reactions are supported, and more radicals are available to react with the contamination. In almost all cases, the intermediates that are produced in these reactions are more biodegradable than and less toxic than the parent compound.

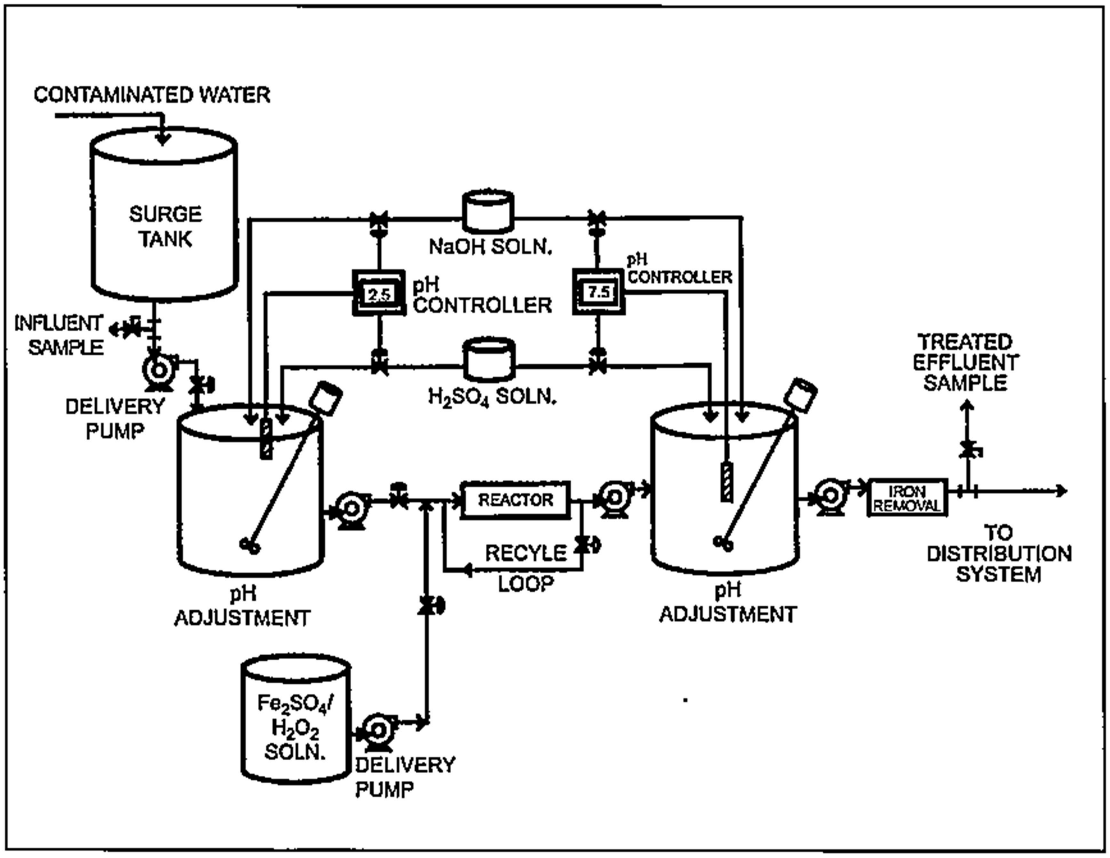
5.7.5.2. SYSTEM DESCRIPTION/DESIGN PARAMETERS

The use of Fenton's chemistry to destroy COD in PW requires the addition of iron and H_2O_2 to PW. The dosages of Fe(II) and H_2O_2 are determined based on the organic contaminant removals required. The reactor must be configured to provide adequate mixing of Fe(II) and H_2O_2 in order to optimize hydroxyl radical formation and destruction of TOC. To keep iron in solution in case of the conventional Fenton's, a very low pH (~2.5) is required. For the purpose of barium, radium and other metals precipitation from PW where pH needs to be maintained above 9 s.u., the conventional Fenton's process may not be cost effective. For NZLD applications, an iron removal system may be required prior to discharge. Based on the Marcellus Shale analytical lab results on iron, there is not enough naturally occurring iron in PW sufficient to provide the metal catalyst needed for the Fenton's reaction. Otherwise, stoichiometrically over-dosing hydrogen peroxide would decrease treatment residence-time necessary for achieving BOD/COD reduction goals and compensate for hydrogen peroxide dissipating side-competition reactions.

The major components of a system utilizing Fenton's reaction usually include:

- Fe(II) and hydrogen peroxide storage and injection systems
- Completely stirred tank reactor
- pH controllers
- Iron removal system
- Supply and discharge pumps and piping
- Monitoring and control systems.

The diagram of the conventional Fenton's reagent process is presented in the figure below.



5.7.5.3. AVANTAGES AND DISADVANTAGES

The advantages of the Fenton's reagent process are:

- Modified Fenton's processes do not always require pH adjustment. For example, the ISOTEC's process utilizes specially developed catalysts composed of active components that chelate the iron and keep it in the dissolved form as an organometallic complex that functions effectively in the circum-neutral pH range (i.e. pH 7) for contaminant destruction.
- This process requires very little energy compared to other oxidation technologies that utilize O_3 or UV.
- The COD reduction of over 90% is reported.

- This process produces no vapor emissions and, therefore, requires no off-gas treatment or air permits.
- The oxidizing power of the Fenton's reagent is 2.8 eV i.e. almost 3 times higher than that of chlorine gas and 2 times higher than chlorine dioxide.
- The modified Fenton's does not require iron removal.

The disadvantages of the classical Fenton's process are:

- No full-scale PW BOD/COD treatment applications exist for this technology.
- May not be cost effective if pH reduction to 5 (by using e.g. H_2SO_4) is necessary.
- Not cost effective if metal removal from PW is required.
- An iron extraction system is needed to remove residual iron from the treated water prior to discharge (in case of NZLD), which may increase the cost of the system.
- In the case of the conventional process, sludge disposal may be costly because the precipitated iron hydroxide may precipitate other metals and organic substances.
- Excessive heat may be generated if strong solutions of hydrogen peroxide (>10%) are used.
- There is potential gas generation/volatilization of contaminants.
- Carbonate ions capture hydroxyl radicals and exert a strong demand on acids (H+ ions).
- As with all oxidants, the optimal oxidant loading, including both target and non-target compounds should be determined before application through a treatability study.
- In the conventional process, the addition of ferrous sulfate ($FeSO_4$) or sulfuric acid as the reagent will precipitate barium, radium, calcium, magnesium and strontium. These particular salts are usually disposed of as a regular solid waste (which may be an advantage rather than a disadvantage) or sold in bulk. The discussion on the use of these salts is however beyond the scope of this paper.

The photo below shows Isotec's mobile equipment during site installation (Ref. USEPA).

5.7.5.4. SUMMARY OF TECHNOLOGY EVALUATION

The table below offers a brief summary of the major criteria.

Criteria	Description/Rationale
Industrial status	The process has been successfully used for groundwater remediation and treatment of some industrial wastewaters. No precedence with PW.
Feed water quality bins	Theoretically applicable to all TDS bins, independent of salt type and concentration. The effect of TDS on the process efficiency needs to be evaluated.
Product water quality	No data exists for PW.
Production efficiency (recovery)	100% recovery
Energy use	This process requires very little energy compared to other oxidation technologies that utilize O_3 or UV.
Chemical use	Chemical costs may be up to $3.30/1000 gal for high-COD PWs.
Expected lifetime of critical components	Critical components of the oxidation process chemical metering pumps. Chemical metering equipment can have a life expectancy of 10-15 years depending on the TDS concentration.
Infrastructure considerations	Chemical metering equipment/dose controls are required.
O&M considerations	Periodic calibration and maintenance of chemical meter pumps is required.
Overall costs	O&M costs can vary widely depending on TOC; for low TOC

	O&M cost is \$1.43/1000 gal; for TOC = 450 mg/L, the O&M cost can be \$3.30/1000 gal (including Fe-reagent and peroxide). CAPEX is not usually a function of TOC but rather the design flow, on the average is \$945/1000 gal PW treated.
Pre- and post-treatment of feed water	Pretreatment such as AC adsorption will be required to reduce the oxidants generation/dosages for high-TOC PWs. Post-treatment may be required depending on reuse/discharge options.
Concentrate management or waste disposal	No solid waste is generated from oxidation processes.

5.7.6. TiO_2-CATALYZED UV OXIDATION (TiO_2/UV)

5.7.6.1. PROCESS DESCRIPTION

When TiO_2, a solid metal catalyst, is illuminated by UV light at $\lambda = 380$ nm, valence band electrons are excited to the conduction band and electron vacancies, or holes, are created. This combination of excited-state electrons is capable of initiating a wide range of chemical reactions. However, hydroxyl radical oxidation is the primary mechanism for organic contaminant destruction. The production of hydroxyl radicals can occur via several pathways but, as with many of the other AOPs analyzed, is readily formed from hydrogen peroxide.
The production of hydrogen peroxide primarily occurs through the following three reaction mechanisms. In the first mechanism, peroxide is created by the reduction of oxygen with two conduction band (CB) electrons. As the concentration of oxygen is increased in solution, the yield of these CB electrons is increased, thereby increasing the yield of hydrogen peroxide. The presence of electron acceptors decreases the combination of excited electrons with holes and, thus, increases the formation of hydrogen peroxide or other radicals:

$$O_2 + 2H^+ + 2e^-_{CB} \rightarrow H_2O_2$$

Hydrogen peroxide is produced via the second mechanism through the oxidation of water by holes in the valence band (h_{VB}). This mechanism is thought to occur only in the absence of electron acceptors and the presence of electron donors (e.g., H_2O, OH^-, and HCO_3^-):

$2\ H_2O + 2h_{VB}+ \rightarrow H_2O_2 + 2H^+$

Finally, hydrogen peroxide can be produced by secondary reactions between oxidized organic matter. These reactions are thought to be important at high TOC concentrations or after long illumination periods. Once hydrogen peroxide is formed, it can dissociate in the presence of UV radiation to form hydroxyl radicals (see H_2O_2/UV discussion) or react with other radicals (e.g., hydroperoxyl or superoxide radical) to form hydroxyl radicals. The hydroperoxyl radical is formed when oxygen is reduced by a CB electron:

$O_2 + H^+ + e^-_{CB} \rightarrow HO_2\bullet$

Deprotonation of the hydroperoxyl radical at neutral pH results in the formation of a superoxide radical ($\bullet O_2$) which, in turn, reacts with hydrogen peroxide:

$HO_2\bullet \rightarrow H^+ + \bullet O_2^-$

$H_2O_2 + \bullet O_2^- \rightarrow OH^- + O_2 + \bullet OH$

Finally, hydroxyl radicals can be formed from the direct reduction of TiO_2-absorbed H_2O_2 by a CB electron or by the reaction of a hole with a hydroxide ion:

$H_2O_2 + e_{CB}^- \rightarrow OH- + \bullet OH$

$OH^- + h^+_{VB} \rightarrow OH\bullet$

5.7.6.2. SYSTEM DESCRIPTION/DESIGN PARAMETERS

TiO_2/UV systems experience interference due to the same radical scavengers that affect the other AOPs; however, TiO_2/UV systems are also fouled by the presence of anions (e.g., chloride, phosphate, and bicarbonate), cations, and neutral molecules, which compete with the contaminant for reactive sites on the surface of the TiO_2 particles. The effect of cations and anions is strongly pH dependent. Any acidic PW would need to be neutralized since the pH of zero charge for TiO_2 is approximately pH 6. At low pH (pH 3 to 4), reaction rates are significantly retarded due to anion adsorption onto the positively charged TiO_2 surface. At higher pH (pH

>7), the TiO_2 particles are negatively charged and there is negligible anion adsorption; however, the presence of cations was shown to decrease the reaction rate. As a result of this decreased activity, TiO_2 systems usually require ion-exchange pre-treatment to remove both anions and cations (based on personal experience with several groundwater remediation projects).

In a TiO_2/UV reaction system, catalysts can be either injected or dispersed (i.e., slurry design) into the system or attached to a support medium. For slurry design, rigorous bench and pilot-scale testing is required for each source water to determine the optimum TiO_2 dose. A low TiO_2 dose can result in a surface site limiting reaction and insufficient radical generation whereas a high TiO_2 dose can reduce the transmittance of the UV light. A suspension of 500 mg/L TiO_2 allowed the absorption of greater than

95 percent of the UV light at 330 nm. TiO_2 particles can vary in size and shape. Bubbling air through the system results in higher dissolved oxygen (DO) concentrations, which yield faster reaction rates. Significant change (from 6.8 to 4.2) in pH was observed under TiO_2-catalyzed UV treatment.

When TiO_2 is attached to a support substrate such as silica-based material, cobalt [II]-based material, or synthetic resins sorbents, it eliminates the need for a post-treatment separation system, which is required for slurry designs. In one fixed TiO_2, TiO_2 was mixed into a silica gel, which was subsequently hardened. The silica gel had 9-nm pore sizes with a total surface area of 480 m^2/g. The UV light penetrates this porous silica gel to activate the catalyst, which in-turn oxidizes contaminants in the source water as it is run through the TiO_2 impregnated silica gel.

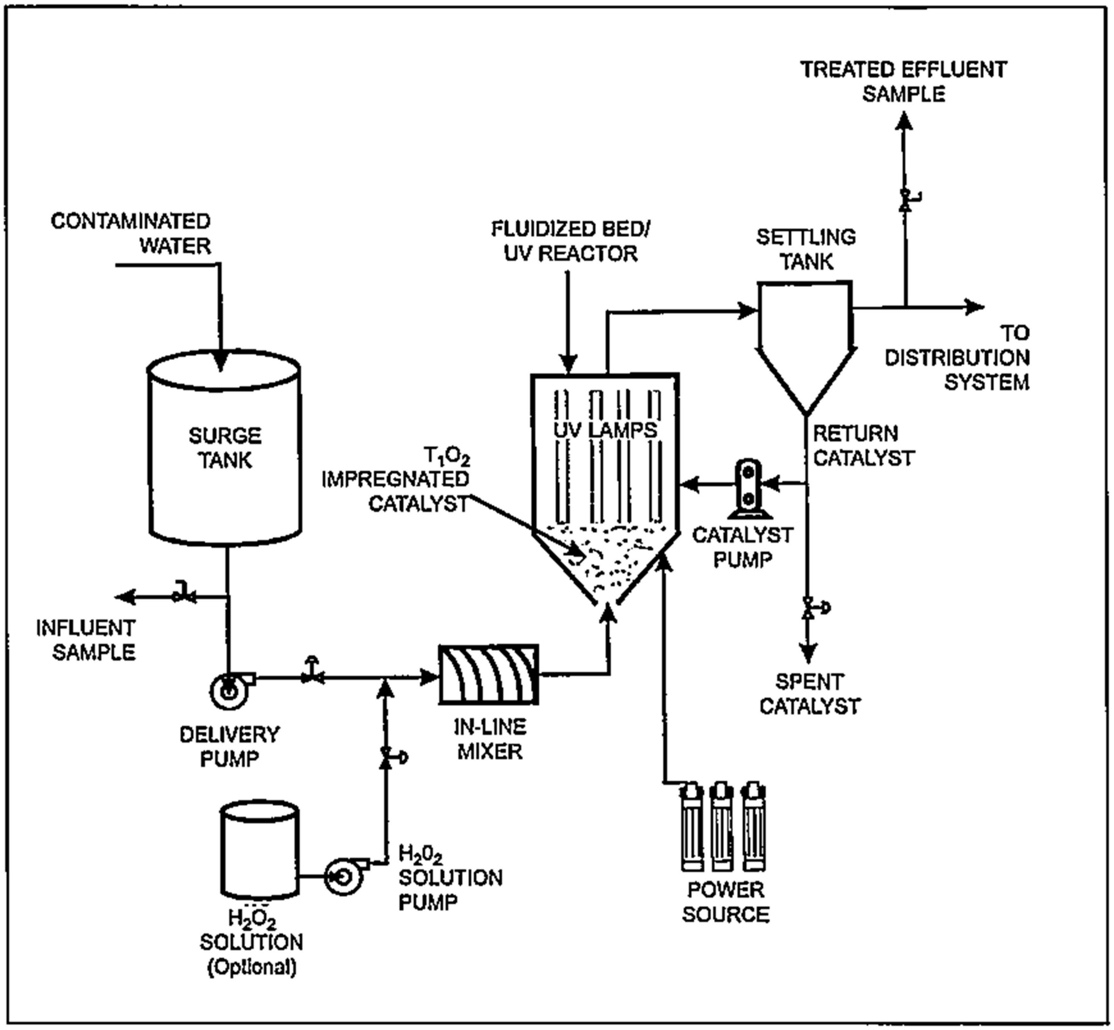
The catalytic activity of imbedded TiO_2 is improved by the addition of metals such as silver or platinum to the TiO_2 surface. Research has shown that destruction of BTEX compounds (2 mg/L) was slow when DO levels were below 3 mg/L and very rapid as DO levels increased to above 15 mg/L.

The major components of a TiO_2/UV system include:

- TiO_2 slurry injection and extraction system
- TiO_2 impregnated resin fluidized bed reactor
- UV lamps, lamp sleeves, and lamp cleaning system
- Static mixing device

- Supply and discharge pumps and piping
- Monitoring and control systems.

The process flow diagram below (Ref. USEPA) depicts these details.



5.7.6.3. ADVANTAGES AND DISADVANTAGES

The advantages and disadvantages of the UV/TiO_2 system are briefly summarized below.

The advantages are:

- TiO_2 assisted photocatalysis can be performed at higher (300 to 380 nm) wavelengths than the other UV oxidation processes.

- The TiO_2 oxidation process has been studied for many organic compounds, including MTBE, under a variety of water qualities.
- Process efficiency is highly dependent on the PW pH which is mostly neutral so no significant pH adjustment will be necessary.

The disadvantages of the TiO_2 system are:

- Currently, no full-scale applications exist for this emerging technology.
- In attached TiO_2 systems, pre-treatment is required to avoid fouling of the active TiO_2 sites and destructive inhibition of the TiO_2 catalyst. Significant fouling was observed due to deposition of NOM, inorganic particulates, photoreduced metal cations and, to a lesser extent, prolonged exposure to UV radiation. Inhibition was observed to occur due to the presence of increased alkalinity and other anionic species (e.g., sulfates [>100 mg/L] and chlorides). Based on the Marcellus Shale data, whilst the sulfates (as SO_4^{2-}) concentration is usually low (3 mg/L unless affected by acid mine drainage), the median concentration of the chlorides is 56900 mg/L and can be as high as 228000 mg/L. This range of concentrations most likely will be cost prohibitive for using the TiO_2/UV process for the purpose of BOD or COD reduction in PW.
- If TiO_2 is added to the system as a slurry, then a separation step is required to remove the solid TiO_2 from the treated water.
- There is a potential for rapid loss of TiO_2 photocatalytic activity, resulting in the need for a large volume of replacement catalyst on-site or a catalytic regeneration process.
- Since DO concentrations in the PW water are usually low, oxygen sparging may be required to increase the rate of contaminant destruction.
- Process efficiency is highly dependent on the PW pH, resulting in the need for close monitoring and control.

5.7.6.4. SUMMARY OF TiO_2/UV PROCESSES ASSESSMENT

TiO_2 catalyzed UV oxidation is a process recommended for use in ultra-pure water applications such as semi-conductor industry and for treating waters with low contaminant concentrations.

Based on the author's personal experience with the Purifics (one of the N. America's leading TiO_2/UV equipment vendors) equipment on multiple industrial- and ground-water treatment/remediation projects, SBRs, TFs, ASPs, GAC columns usually precede this process. Since none of the conventional biological treatment processes can sustain salinities above 7%, the application of the TiO_2/UV process may be limited to low-strength highly diluted frac waters only. The literature research could not locate a single pilot- or full-scale application of this process for BOD/COD reduction in PW or frac waters. The table below summarizes the most common TiO_2/UV process criteria.

Criteria	Description/Rationale
Industrial status	TiO_2/UV process is well established in the fields of groundwater remediation and for some industrial wastewater treatment applications but not for PW. Without pretreatment for TOC, TDS and TSS, its cost for COD, BOD and TOC reduction in PW will be prohibitive.
Feed water quality bins	Theoretically applicable to very low TDS bins.
Product water quality	No data exists for PW
Production efficiency (recovery)	100% recovery
Energy use	Energy usage may account for up to 20% of the total O&M for oxidation processes depending on the TOC concentration.
Chemical use	Chemical costs may be high depending on the TOC. For low TOC, this cost is < 5% of the annual O&M cost.
Expected lifetime of critical components	Critical components of the oxidation process are the UV. The average MP lamp life ranges from 9,000 to 14,000 working hours, and the lamps are usually replaced after 12,000 hours of use.
Infrastructure considerations	Controls are required. The equipment itself is very compact.
O&M considerations	Ballasts are usually replaced every 10 years. Quartz sleeves are generally replaced every 5 years. No catalyst replacement is required.
Overall costs	O&M costs can vary widely depending on TOC and TDS; for low TOC O&M cost is \$3.00/1000 gal; for TOC = 450 mg/L, the O&M cost can be as high as \$14.76/1000 gal. CAPEX is not usually a function of TOC but rather the design flow, on the average is \$5,042/1000 gal PW treated.

Pre- and post-treatment of feed water	Pretreatment such as AC adsorption (GAC), sand filter, ASP, TF, etc. will be required to reduce the oxidants generation/dosages for high TOC PWs. Capacitive deionization, membrane distillation or perhaps EC may be required to reduce TDS. Post-treatment may be required depending on reuse/discharge options.
Concentrate management or waste disposal	No solid waste is generated from oxidation processes.

5.7.7. AOP- PERMITTING

As with all wastewater none zero-liquid discharge (NZLD) treatment systems, the installation and operation of an AOP system will require multiple US state and local construction permits, operating (NPDES) permits, and air discharge permits. A detailed discussion of all necessary permits is beyond the scope of this document; however, the key permitting issue that may differentiate AOPs from other NPDES permits is the formation of oxidation by-products. Numerous researchers showed that AOP oxidation of organic compounds significantly increases the levels of aldehydes (besides nitrosoamines), in particular formaldehyde (FA) which amounts to 56% of total aldehydes. Some researchers found this level to be a linear function of the TOC (total organic carbon) concentration. The reference values can be averaged to approximately 4.3 µg FA/mg TOC. The research recently conducted by the URS Corporation indicated the median TOC value of 449 mg which according to the conversion above may result in approximately 2 mg FA/L treated water.

Obviously, with no primary reduction in the TOC level, the probable process effluent FA concentrations may exceed several action levels unless it's a ZLD. If the treated water is reused for fracking, the concentration of FA in PW will increase unless the FA decays in the strata due to friction, microbial metabolism, adsorption, etc. The reaction of FA with ammonia will probably produce hexamethylenetetramine or hexamine, $(CH_2)_6N_4$, which is also unwanted in any treated water.

It should be noted that many US jurisdictions have action levels set for FA in regard to both water and air. For example, the New York state's Ambient Water Quality Value for FA is only 8

µg/L (ppb); the HRL (Health Risk Level) in Minnesota for FA is 1 mg/L for groundwater, etc. The OSHA FA PEL is 0.75 ppm.
The USEPA Chronic Reference Dose for FA is 0.2 milligrams per kilogram body weight per day (mg/kg/d) (if simply stored, attainable at the specified concentration in 636 days at 8-hr of daily exposure).

The Agency for Toxic Substances and Disease Registry (ATSDR) has established a chronic inhalation minimal risk level (MRL) of 0.003 ppm_v (0.004 milligrams per cubic meter, mg/m^3) based on respiratory effects in humans. The MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure. At 20ºC, the FA vapor pressure is 3268 ppm (for a 100% solution) which at the specified above aqueous FA concentrations translates to 0.006 ppm_v. This value entailing a single oxidation pass is twice the MRL Value.

The combination of AOPs with pre- or post-chlorination may increase the formation of THMs or HAA9s, which are regulated under the Stage 1 D/DBP Rule. Consequently, whether the regulated compounds are THMs, HAA_9s, or an oxidation breakdown product of ethers, strict monitoring requirements may be enforced by the governing regulatory agency. To mitigate these concerns, a GAC filter will likely be required to polish the effluent from AOPs. However, it is likely that most polishing filters will sustain biological growth (due to the biodegradability of oxidation by-products).

Other relevant permitting considerations for AOPs include meeting the following standards:

- A 1-hour ozone effluent gas concentration of less than 0.12 ppm_v according to the US Clean Air Act (CFR Title 40, Part 50) and less than 0.09 ppm_v according to the California Code of Regulations Title 17, Section 70200 (H_2O_2/O_3, O_3/UV).
- H_2O_2 concentrations below 1 mg/L (1.4 mg/m^3) according to an OSHA permissible exposure limit (PEL).
- Iron concentrations below 0.3 mg/L according to the SDWA Secondary MCL (Fenton's reaction).
- pH level between 6.6 and 8.5 according to SDWA Secondary MCL (all AOPs).

- THMs below 80 µg/L according to Stage 1 D/DBP Rule (all AOPs).
- HAA5 below 60 µg/L according to Stage 1 D/DBP Rule (all AOPs).
- Bromate below 10 µg/L according to Stage 1 D/DBP Rule (H_2O_2/O_3, O_3/UV).

In summary, control of AOP by-products in the treated PW would require a comprehensive technical and regulatory study for NZLD cases the scope of which would be a function of the influent, effluent, and receiving water qualities when these data become available.

5.8. ELECTROCOAGULATION

5.8.1. BACKGROUND

Electrocoagulation (EC) is rapidly emerging and has a great potential to be successfully used in PW treatment. It effectively removes suspended solids to sub-micron levels, breaks emulsions such as oil and grease or latex, and oxidizes and eradicates heavy metals from water without the use of filters or the addition of separation chemicals. Numerous researchers reported the COD removal efficiencies in the range of 60-99 percent. It appears that EC can address any size of suspended solids and completely eliminates bacterial populations in treated waters.

In North America EC has been used primarily to treat wastewater from pulp and paper industries, mining and metal-processing industries. A large 1000 gpm cooling tower application in El Paso, TX illustrates EC growing recognition and acceptance to the industrial community. In addition, EC has been applied to treat water containing foodstuff waste, oil wastes, dyes, marinas, public transit, wash water, ink, suspended particles, chemical and mechanical polishing waste, organic matter from landfill leachates, defluorination of water, synthetic detergent effluents, and solutions containing heavy metals.

5.8.2. BRIEF DESCRIPTION OF THE EC TECHNOLOGY

In its simplest form, an EC reactor is made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation.

An EC system essentially consists of pairs of conductive metal plates in parallel, which act as monopolar electrodes. It furthermore requires a direct current power source, a resistance box to regulate the current density and a multimeter to read the current values. The conductive metal plates are commonly known as "sacrificial electrodes." The sacrificial anode lowers the dissolution potential of the anode and minimizes the passivation of the cathode. The sacrificial anodes and cathodes can be of the same or of different materials.

The arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections. In series cell arrangement, a higher potential difference is required for a given current to flow because the cells connected in series have higher resistance. The same current would, however, flow through all the electrodes. On the other hand, in parallel or bipolar arrangement the electric current is divided between all the electrodes in relation to the resistance of the individual cells, and each face on the electrode has a different polarity.

During electrolysis, the positive side undergoes anodic reactions, while on the negative side, cathodic reactions are encountered. Consumable metal plates, such as iron or aluminum, are usually used as sacrificial electrodes to continuously produce ions in the water.

Several oxidation processes occur in steps during EC: (i) anode dissolution, (ii) formation of OH^- ions and H_2 at the cathode, (iii) electrolytic reactions at electrode surfaces, (iv) adsorption of coagulant on colloidal pollutants, and (v) removal by sedimentation or flotation.

When aluminum is used, Al_3^+ ions are produced in water, which forms soluble monomeric and polymeric hydroxo-metal complexes. The main reactions occurring at electrodes during electrolysis are as follows:

At the anode, aluminum oxidation occurs,

$Al_{(s)} \rightarrow Al_3^+{}_{(aq)} + 3e^-$

At the cathode, water reduction occurs,

$3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^-$

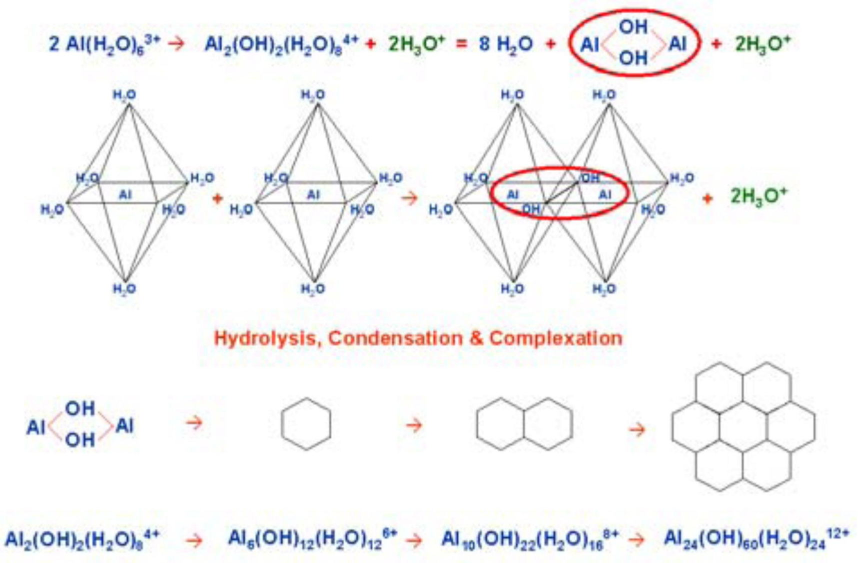
In alkaline waters,

$Al_3^+ + 3OH^- \rightarrow Al(OH)_3$

And in acidic waters,

$Al_3^+ + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

The following figure demonstrates these reactions.

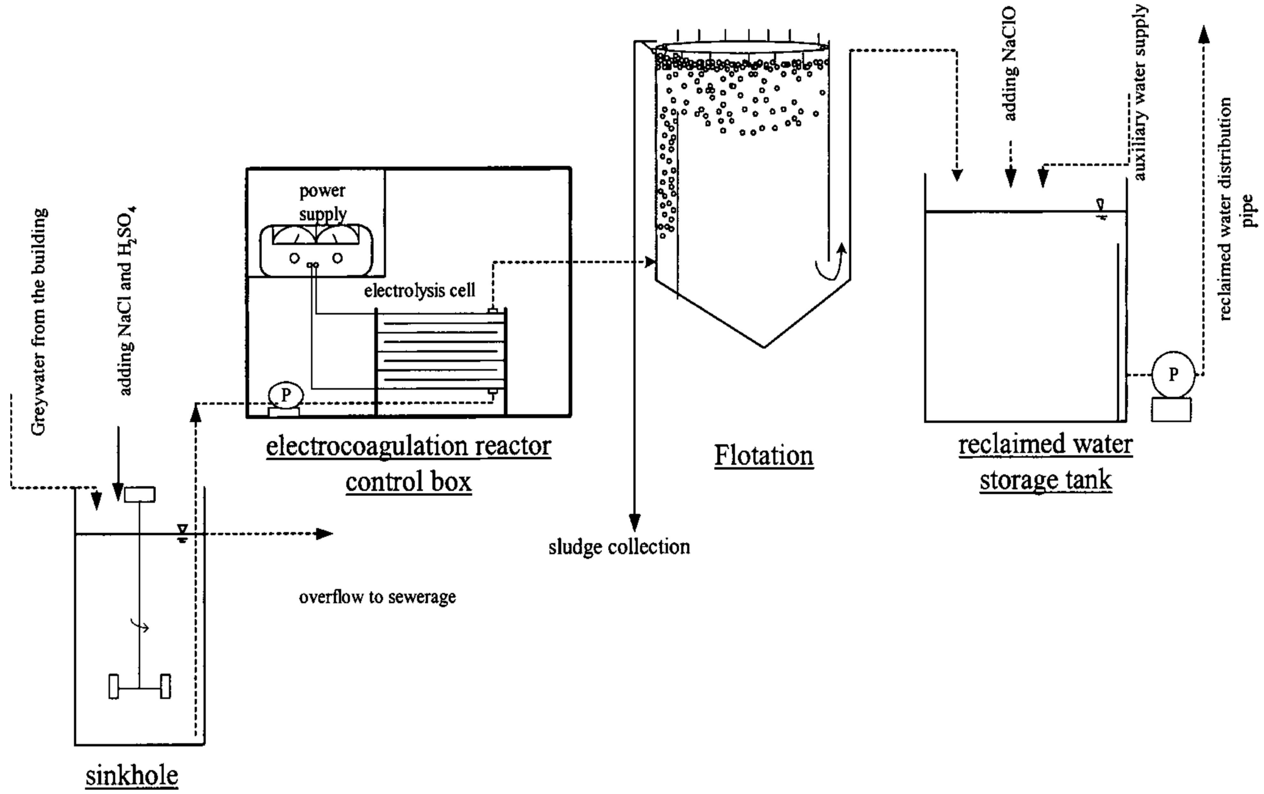


The standard potential of aluminum dissolution is lower (-1.662 V) than the standard potential of hydrogen evolution (-0.828 V), i.e. the dissolution of aluminum is thermodynamically favored and should proceed spontaneously. Aluminum ions (Al3+) are produced by electrolytic dissolution of the anode which generates various monomeric and polymeric species. Al3+(aq) and OH- ions generated by electrode reactions above react to form various monomeric species such as Al(OH)2+, Al(OH)2+, Al(OH)4-, and polymeric species such as Al6(OH)153+, Al7(OH)174+, etc.

The released ions neutralize the charges of the particles and thereby initiate coagulation. The released ions remove undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce, which can then be removed by flotation. In addition, as water containing colloidal particulates, oils, or other contaminants move through the applied electric field, there may be ionization, electrolysis, hydrolysis, and free-radical formation which can alter the physical and chemical properties of water and contaminants. As a result, the reactive and excited state causes contaminants to be released from the water and destroyed or made less soluble.

It is important to note that the EC technology cannot remove infinitely soluble matter. Therefore, ions with molecular weights smaller than Ca+2 or Mg+2 cannot be dissociated from the aqueous medium.

In the EC process the water-contaminant mixture separates into a floating layer, a mineral-rich sediment, and clear water. The floating layer is removed by means of a patented overflow/removal method and moved to a sludge collection tank. The aggregated mass settles down due to gravitational force and is subsequently removed through a drainage valve at the bottom of the EC reaction tank and moved to a sludge collection tank. The clear, treated water is pumped to a buffer tank for later disposal and/or reuse in the plant's designated process. The flow diagram of a pilot-scale EC process is shown below.



The photo below shows a 30 gpm portable EC unit (Ref. USEPA).

30 Gallon Per Minute System

Daily Capacity of
43,200 Gallons or
163.02 Cubic Meters

System Size -
66" Wide x 76" Long
x 70" High

5.8.3. ADVANTAGES AND DISADVANTAGES OF EC

The following advantages of EC have been reported:

- EC requires equipment that is easy to operate with sufficient operational latitude to handle most problems encountered on running.
- Wastewater treated by EC gives palatable, clear, colorless and odorless water.
- Sludge formed by EC tends to be readily settable and easy to de-water because it is composed of mainly metallic oxides/hydroxides.
- Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
- EC produces effluent with less TDS content as compared to chemical treatments. TA literature review indicates a significant reduction in TDS concentrations in low-TDS waste streams. As with all proposed here technologies, the effect of elevated TDS concentration in PW on the process efficiency needs to be evaluated through treatability studies.

- The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
- The EC process uses no chemicals so there is no need for pH adjustment.
- The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed by a motorized skimmer.
- The electrolytic processes in the EC cell are controlled electrically and with no moving parts, thus requiring less maintenance.
- Dosing the PW with chlorine dioxide would result in tremendous reduction of bacterial counts (besides BOD and COD). This technology as a stand-alone process was reported to be capable of achieving up to 3-log reduction in bacterial counts.
- The process is flexible in regard to pH such as whether Al or steel electrodes can be used at acidic and alkaline pH values, respectively, to enhance the COD reduction.

Based on very limited data for PW, the following are processes disadvantages:

- High operating cost which can be as high as $67/1000 gal.
- Is not widely accepted by the O&G industry with respect to PW treatment. Contrary to other references, the best COD removal with EC in PW was 56% which occurred at a dose of 20.6 mg/L of iron at pH 5.
- High sludge generation 1 ft^3/1000 gal.
- Energy use – 69 KWh/1000 gal.
- The sludge cake may contain metals including barium, radium and strontium which may render it toxic and/or TENORM. This however can be learnt of only after a comprehensive treatability study has been conducted.
- The percentage COD removal is influenced by applied current density electrolyte pH and effluent concentration.

5.8.4. SUMMARY OF EC ASSESSMENT

Criteria	Description/Rationale
Industrial status	Whilst the EC process is well established in certain industries such as textile, tannery, electroplating, etc. and rapidly expanding, only one application of this process with respect to COD/BOD removal in PW was found. The maximum COD removal was 56%.
Feed water quality bins	Theoretically applicable to all TDS bins.
Product water quality	Based on limited data, incomplete COD removal
Production efficiency (recovery)	100% recovery of the liquid phase
Energy use	69 KWh/1000 gal. May not depend on the TOC concentration.
Chemical use	Polymer - $0.26/1000 gal; steel plates - $3.13/1000 gal.
Expected lifetime of critical components	The most critical component of this process is electrode plates and associated controls. The electrode material (Fe or Al) is spent depending on the pollutant levels to be oxidation. The expected life span of the equipment is up to 15 years.
Infrastructure considerations	Controls are required. The equipment itself is very compact.
O&M considerations	Controls associated with electrodes and sludge handling
Overall costs	O&M costs can vary depending on influent and required effluent concentrations, between $3/1000 gal to $67/1000 gal. Capex for Fe electrodes is $1500/1000 gal, for Al electrodes - $3000/1000 gal.
Pre- and post-treatment of feed water	Pretreatment with GAC units may be required to reduce influent TOC. Post-treatment may be required depending on reuse/discharge options.
Concentrate management or waste disposal	Sludge generated by the process is disposed at the rate of $12.72/1000 gal.

6. DISCUSSION OF RESULTS OF FINDINGS

While numerous BOD/COD treatment technologies exist for domestic and industrial wastewaters, there are no specific BOD/COD reduction technologies or methodologies applied to treat PW or frac water. If PW is not hauled to adjacent states (such as Ohio and West Virginia in the case of Marcellus) for underground injection or treatment at brine processing facilities, the following simple pretreatment steps without treatment are usually performed on-site:

1. Adjust PW to a pH that is optimal for specific divalent metal precipitation
2. Use a divalent cation (Ca, Mg) additive to complex soluble ions to settle the resulting particle
3. Remove iron by converting soluble iron Fe_2+ to Fe_3^+ oxide/hydroxide particulate iron mechanically and chemically
4. Use gravity settling process to enhance removal
5. Perform a microbiological disinfection as needed
6. Conduct a final filtration step to remove any remaining suspended solids and dead microbial biomass.

All fracking experts and operators agree that freshwater meets the water quality needs for fracturing fluids. They also agree that somewhat lower quality water would be usable for fracturing operations. But there is no consensus on the minimum allowable water quality for a fracturing operation: different experts suggest different limits for TDS, chloride, calcium, suspended solids, dissolved organics contributing to COD, etc. Some experts suggest BOD/COD and bacterial counts should be below 25 mg/L and 100 CFU/100 mL, respectively. For comparison, BOD concentrations reported for Marcellus Shale were as high as 4,500 mg/L. Both BOD and COD are the sources of microbial metabolism that results in bacterial growth and consequently the need for disinfection.

This paper examined the most common BOD/COD reduction technologies potentially capable of reducing both BOD and COD in frac and dilute PW. Whilst some of these technologies can be used successfully alone to significantly reduce and even completely eliminate the oxygen demand in PW, the others may need to be used in conjunction with other technologies, increasing the capital cost (Capex) to reduce the operating cost (Opex). The table below summarizes the Capex and Opex costs for these technologies. The costs were inter- and extrapolated based on the data publicly available on the Internet and Tellus for other types of waste streams such as those from tannery, domestic sewage, landfill leachate, meat processing, electric power plans, boilers, soft beverage WWTP, etc. The costs need to be adjusted using an annual inflation factor of 0.06 for a hypothetical 1-mgd PW treatment facility with high TOC, BOD and COD.

2013 Cost of Treatment in USD/1000 gal, 1-MGD PW Treatment Plant

Process	ASP	BAF	DAF	GAC	CO	H_2O_2/O_3	O_3/UV	Fenton	TiO_2/UV	EC
CAPEX	1500-8000	2000	2700	404	3000	3077	2120	945	5042	1500-3000
OPEX	0.12	0.10	0.80	68	4	5.40	20	3.3	14.76	3-67

As expected, the capital cost for stationary facilities such as ASP would be higher than that for compact and mobile processes, but the operating costs would be much lower. For low TDS streams, however, the ASP would be the preferred choice of treatment. Biological treatment processes such as ASP and BAF due to their size, mobility and operational complexity are not usually a preferred field method. This would also be true for the dissolved air or oxygen flotation (DAF). In general, DAF can be considered one of the ASP variations. The equipment entailing ion exchange, membranes and/or surface adsorption for this type of operations may do the job but would require extensive maintenance (such as for GAC columns) due to very frequent media replacement or regeneration. CO, even though successfully used in PW disinfection, would require very sophisticated process control systems, skilled operators and most importantly may not be efficient at high TOC. Among the AOPs including EC, the Fenton's reagent and ozone/peroxide processes have the highest potential among the examined processes to be successfully applied to reduce BOC/COD in PW. The oxidizing power of the Fenton's reagent is almost 2 and 3 times higher than that of chlorine gas and chlorine dioxide, respectively. The two processes however have the following common disadvantage: a pretreatment step will be necessary to remove suspended solids. In addition, the ozone saturation is a direct function of the TDS concentration meaning that high-TDS-laden PWs probably will require more ozone. APT Water, the leading ozone/peroxide oxidation process equipment manufacturer in the US, cannot provide the process performance data as a function of TDS concentrations. As a general issue, any ozonation process entails ozone that is a more serious health and safety concern than peroxide which would make the Fenton's process more attractive. The classic Fenton's reagent process will precipitate dissolved divalent metals such as barium, radium, calcium, magnesium and strontium. This can be both advantage and disadvantage depending on the treatment goal such as reuse, recycle or discharge and its options. For instance, an operator who reuses PW for fracking may not be concerned about the presence of barium or radium in their PW as much as an operator whose PW discharges to a POTW that has a stringent industrial waste program. The former may want to use a modified Fenton's then whilst the latter would suit the classic Fenton's better. As discussed previously, the classic Fenton's -based processes function only under acidic conditions because of the inability of iron catalyst to remain dissolved in the natural subsurface pH range of 6-7. A modified Fenton's process (such as that by ISOTEC) utilizes specially developed catalysts composed of active components that chelate the iron and keep it in dissolved form as an organometallic complex that functions effectively in the circum-neutral pH range This pH and the lack of sulfate theoretically should not result in metal precipitation.

The following table evaluates the proposed technologies based on the commonly used in the field of wastewater treatment acceptance criteria. The scores assigned to the criteria are based on the author's opinion on the technologies and knowledge of the subject matter. The overall ranking, therefore, will vary depending on the reader's personal experience with and perception of these technologies.

BOD/COD Treatment Process Criteria for PW

Evaluation Criteria	ASP	BAF	DAF	GAC	CO	H_2O_2/O_3	O_3/UV	Modified Fenton’s	TiO_2/UV	EC
Mechanical Reliability	5	5	5	5	4	4	3	2	2	3
Process Reliability (PW)	5	5	5	3	5	5	4	3	4	3
Flexibility (mobile or stationary)	1	2	2	5	4	5	5	5	5	4
Process Flexibility (PW)	4	3	4	5	5	4	4	5	4	5
Adaptability to different PWs	3	2	4	2	1	4	2	5	2	3
Modification Potential	3	1	2	1	4	3	3	1	3	3
Energy Efficiency	2	4	3	5	3	3	1	5	3	2
O&G Industry Experience	1	1	2	3	5	1	1	2	1	1
Public Acceptance	5	5	5	5	4	3	3	3	3	4
Ease of Installation	1	2	1	5	3	5	4	4	4	4
Ease of Operations	2	4	4	5	1	4	4	4	4	4
Ease of Maintenance	3	2	3	1	2	4	3	5	4	3
CAPEX	1	3	3	5	3	4	3	5	2	2
OPEX	5	5	4	1	2	3	3	4	3	2
Overall Rating	41	43	47	51	50	52	43	53	44	43
Rank	*10*	*9*	*5*	*3*	*4*	*2*	*7*	*1*	*6*	*8*

*Rating is based on the following scores: pure – 1, below satisfactory – 2; satisfactory or no data – 3; good – 4; excellent – 5.

7.SUMMARY AND RECOMMENDATIONS

This course compiles much of the information publicly available in 2013 on biochemical and chemical oxygen demands (BOC and COD, respectively) treatment of frac and produced waters. The following technologies were identified and evaluated for the purpose of BOD/COD reduction in frac and produced waters: aerobic biological treatment based on the activated sludge process; anaerobic biological treatment; activated biofilters based on the example of trickling filter; chemical precipitation (in this context as part of oxidation technologies); dissolved air flotation; adsorption using granular activated carbon; some of the advanced oxidation technologies such as titanium oxide with ultraviolet radiation, ozone with ultraviolet radiation, a combination of ozone and hydrogen peroxide with ultraviolet radiation, electrocoagulation and the Fenton's reagent with hydrogen peroxide. The latter process and the combination process of ozone and hydrogen peroxide were identified as the most potentially feasible mobile treatment technologies for this application. The activated sludge process (ASP) with membrane bioreactors (MBR) in the aerated basins preceded with a proper pretreatment for suspended solids and followed by a trickling filter (TF) would be the most reliable BOD/COD treatment choice for stationary applications (e.g. centralized treatment facility) for low- to medium TDS-laden waste streams for purpose of surface water discharge. The ozone/peroxide process doesn't leave residues nor does it generate sludge. The technology has a great potential to be one of the leading technologies in industrial wastewater treatment and groundwater remediation.

Unlike the Modified Fenton's, the conventional Fenton's process has a potential of generating excessive amount of sludge consisting of oxidized biological matter and some metals. For onshore and offshore rigs, due to health and safety concerns related to oxygen and ozone on-site generation, the Modified Fenton's Process may be the best option. A comprehensive treatability study entailing a range of physical, chemical and biological characteristics of frac- or produced waters from various formation is required to explore its full COD reduction potential.

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