Sustainable Advanced Oxidation Processes for Treating Refining and Petrochemical Wastewaters

Background

- *New Central Government requirements for reducing Chemical Oxidation Demand in Refining and Petrochemical wastewater effluents and controlling the use of fresh water sources has driven greater wastewater reuse by these industries and the need for more sophisticated treatment technology to achieve these new effluent standards.*

- *This presentation explores the use of advanced oxidation technologies coupled with conventional biological treatment technologies as a long-term sustainable, cost effective practice to achieve significant wastewater reuse objectives.*

The Challenge for Reuse –
How to Get to Effluent Quality Required?

Refinery Wastewater (Post Deoiling)

- COD 300 - 500 mg/L
- BOD 100 - 200 mg/L
- TDS <600 mg/L

90% CODr

Petrochemical Wastewater

- COD 600 - 1500 mg/L
- BOD 200 - 300 mg/L
- TDS 500 – 5,000 mg/L

96.7% CODr

Propylene Oxide-Styrene Monomer Wastewater (POSM)

- COD 30,000 – 50,000 mg/L
- BOD 10,000 – 15,000 mg/L
- TDS 30,000 – 50,000

99.9% CODr

Reuse/Effluent Discharge Quality

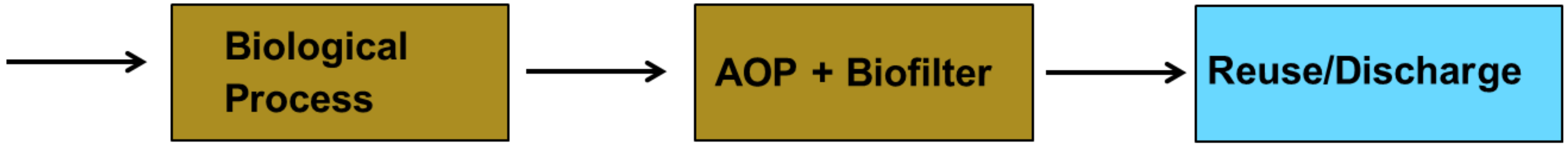
- COD 30 – 60 mg/L
- BOD 5 - 10 mg/L

- Bio-treatment alone yields 85 – 92% COD removal.

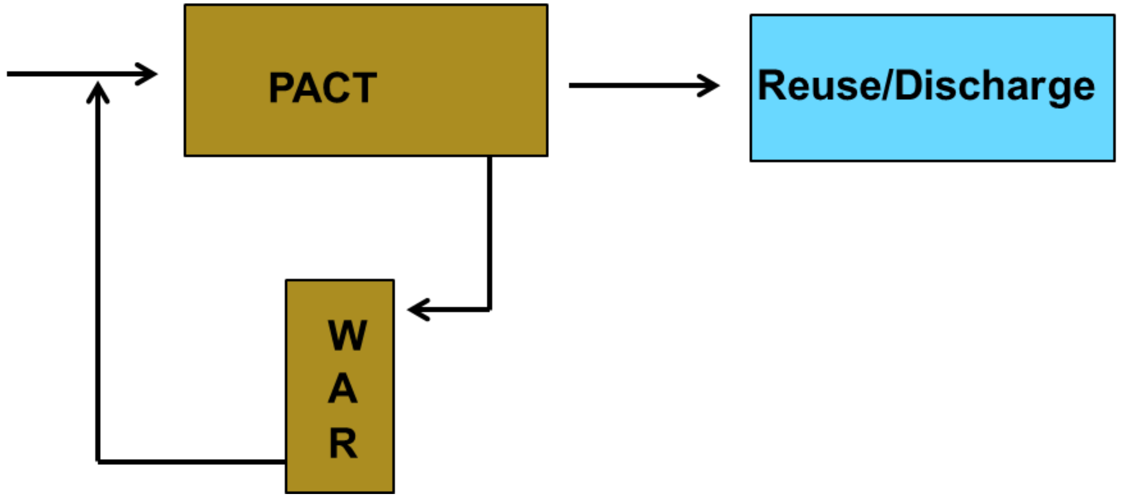
- How to decide on added technology for remaining COD removal?

Treatment Process Schemes

Post-Biological Treatment

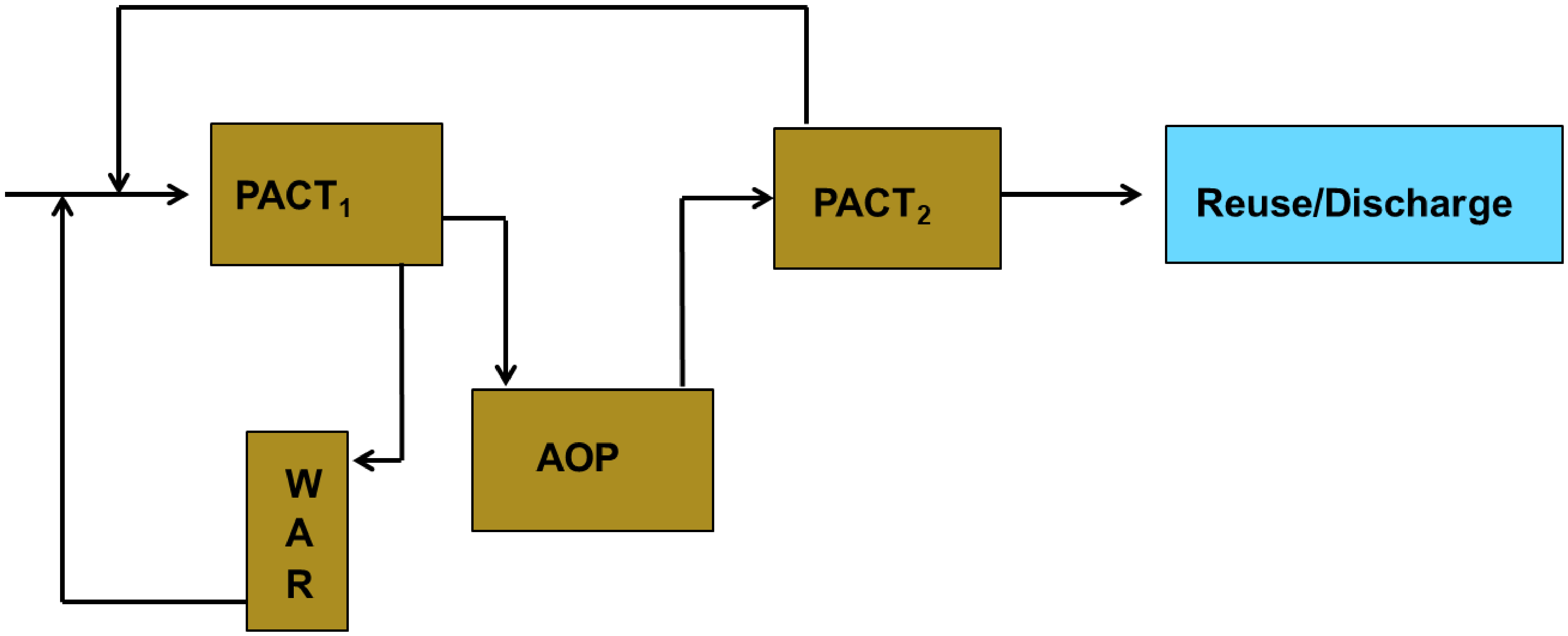


Powdered Activated Carbon/Wet Air Regeneration



Treatment Process Schemes

Combination PACT + AOP



Advanced Oxidation Processes

- Advanced oxidation processes (AOPs), are treatment processes designed to remove organic compounds in water and wastewater by oxidation through reactions with hydroxyl radicals (OH•).

- Originally developed for low-level TOC (COD) removal, now being applied to high strength industrial effluents.

- Hydroxyl radicals typically generated from hydrogen peroxide (H2O2), ozone, photo-catalysis (TiO_2), sometimes in combination with ultraviolet (UV) radiation.

- OH• reacts unselectively once formed and fragments and organic compounds into smaller organic and inorganic molecules.

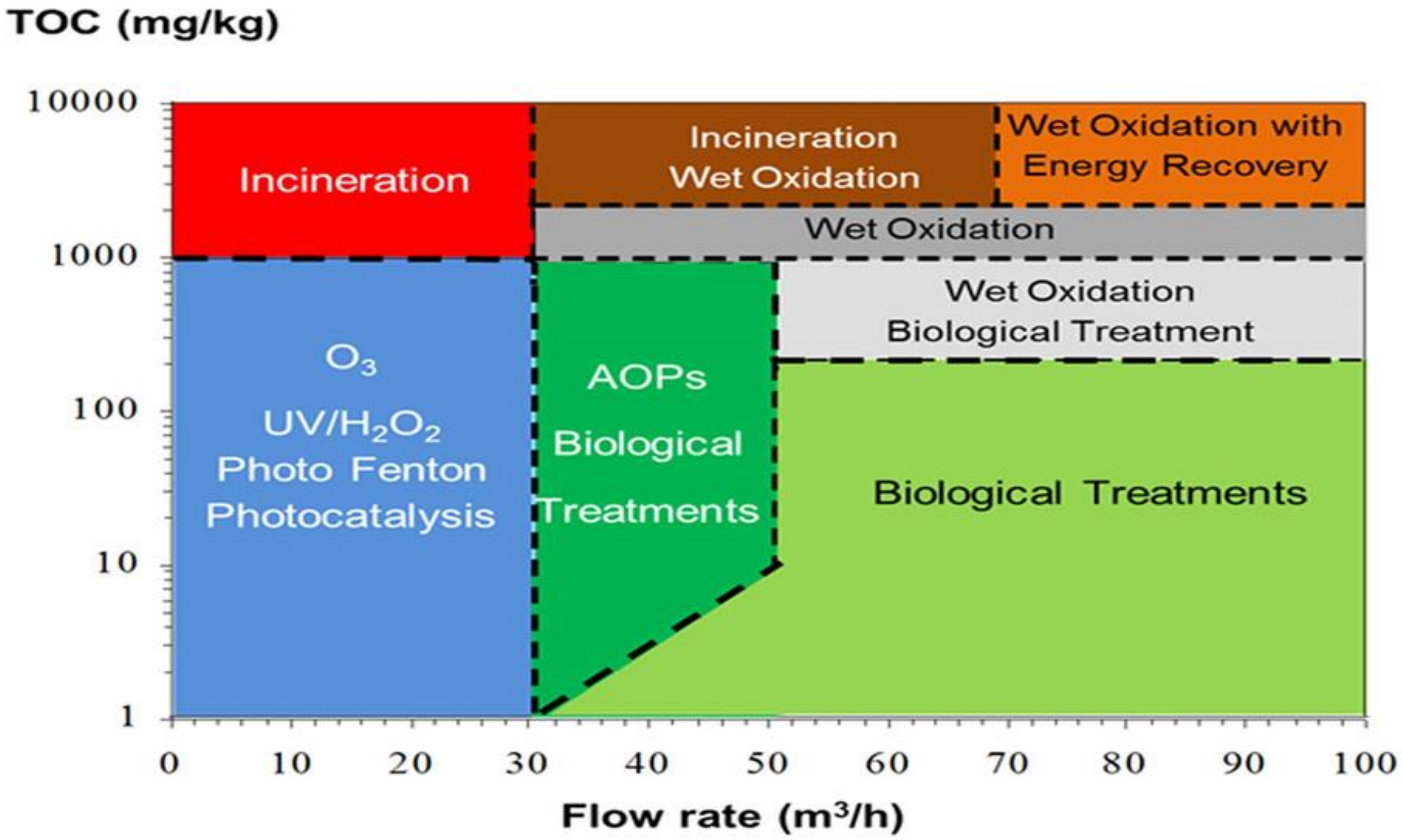
$$R-H + HO\cdot \rightarrow H2O + \cdot R$$

- Other processes, discussed herein, function similarly to transform difficult to treat organics and make up a critical part of an integrated treatment approach to produce high quality effluents.

Advanced Oxidation Processes

- AOPs are responsible for decreasing the toxicity and increasing the biodegradability of the effluents treated; for low level contaminant removal, complete mineralization of contaminants is possible.

- Optimal Operation of AOPs: (Advanced Technologies for Water Treatment and Reuse, Wiley Online Library, 2015)



Chemical Principles

Ozone Based AOP

- Molecular Ozone: a combination of reactions with molecular ozone and reactions with HO• causes the oxidation of organic compounds:

$$3O_3 + OH^- + H^+ \rightarrow 2HO\bullet + 4O_2$$

- Ozone/Peroxide: the decomposition cycle of ozone can be enhanced by the addition of hydrogen peroxide to result in the formation of HO•

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

- Ozone Photolysis: ozonation can be also be enhanced when ozone decomposes by readily absorbing UV radiation

$$O3 + H2O + UV \rightarrow O2 + H2O2$$

$$2\ O3 + H2O2 \rightarrow 2HO\bullet + 3O2$$

Chemical Principles

Hydrogen Peroxide Based AOP

- Hydroxyl radicals are formed by the photolytic dissociation of hydrogen peroxide in water by UV irradiation

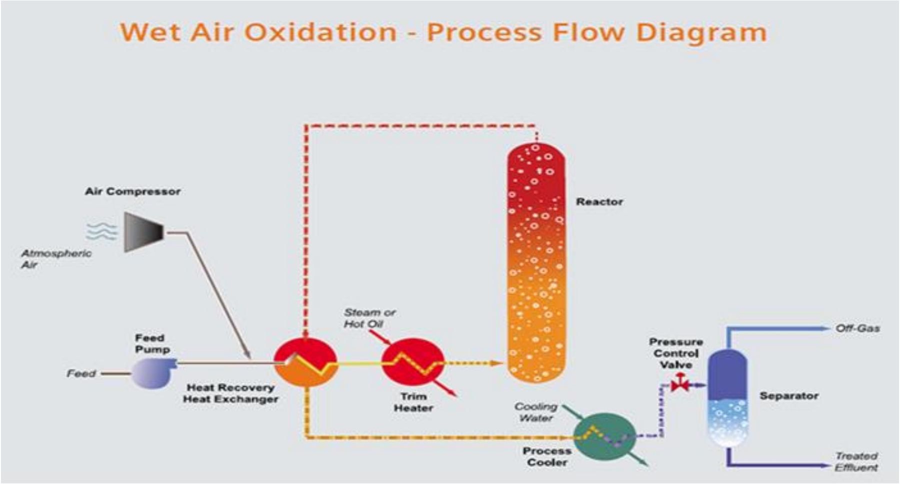
$$\mathbf{H_2O_2 + UV \rightarrow \underline{2HO} \bullet}$$

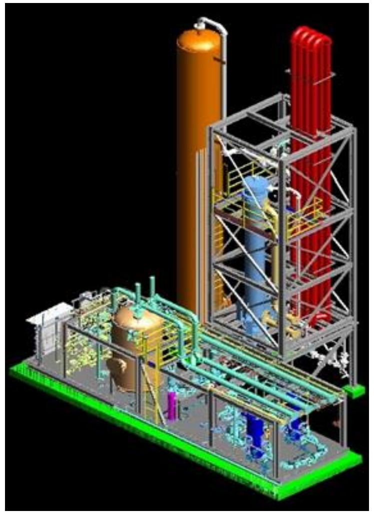
Fenton's Reagent Based AOP

- Radicals are produced when iron (II) reacts with hydrogen peroxide, where the Fe^{2+} ion acts as a catalyst for this reaction

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO\bullet}$$

Hydrothermal Systems – Wet Air Oxidation





Process

Wet Air Oxidation (WAO) systems are used for treatment of high strength industrial wastewater, including spent caustic streams generated by ethylene crackers and refineries.

Wet air oxidation is the oxidation of organic and inorganic compounds in water using oxygen as the oxidizing agent. The oxidation reactions occur at elevated temperature and pressure.

The wet oxidation process can pre-treat very high COD wastewater streams, making them treatable in a conventional biological treatment plant.

WAO Process Reactions

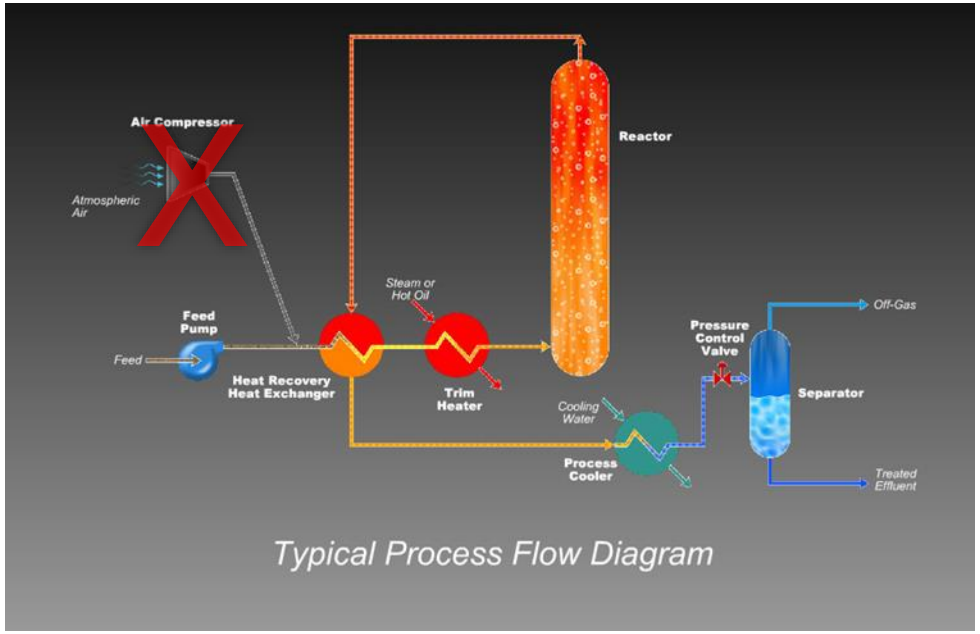
WAO converts organic contaminants to carbon dioxide (CO_2), water, and biodegradable short chain organic acids. Inorganic constituents such as sulfides and cyanides can also be oxidized. The wet air oxidation process can involve any or all of the following process reactions:

Organics + O_2	$CO_2 + H_2O + RCOOH^*$
Sulfur Species + O_2	SO_4^{-2}
Organic Cl + O_2	$Cl^- + CO_2 + RCOOH^*$
Organic N + O_2	$NH_3 + CO_2 + RCOOH^*$
Phosphorus + O_2	PO_4^{-3}

**Short chain organic acids such as acetic acid make-up the major fraction of residual organic compounds.*

Catalytic Hydrolysis

- Uses heterogeneous catalyst for treatment reactions
- Catalytic hydrolysis achieves greater COD destruction at lower temperatures for very high strength COD wastewater
- Produces methane which can be used for fuel
- Does not require high pressure air compressor or pure oxygen for high strength COD



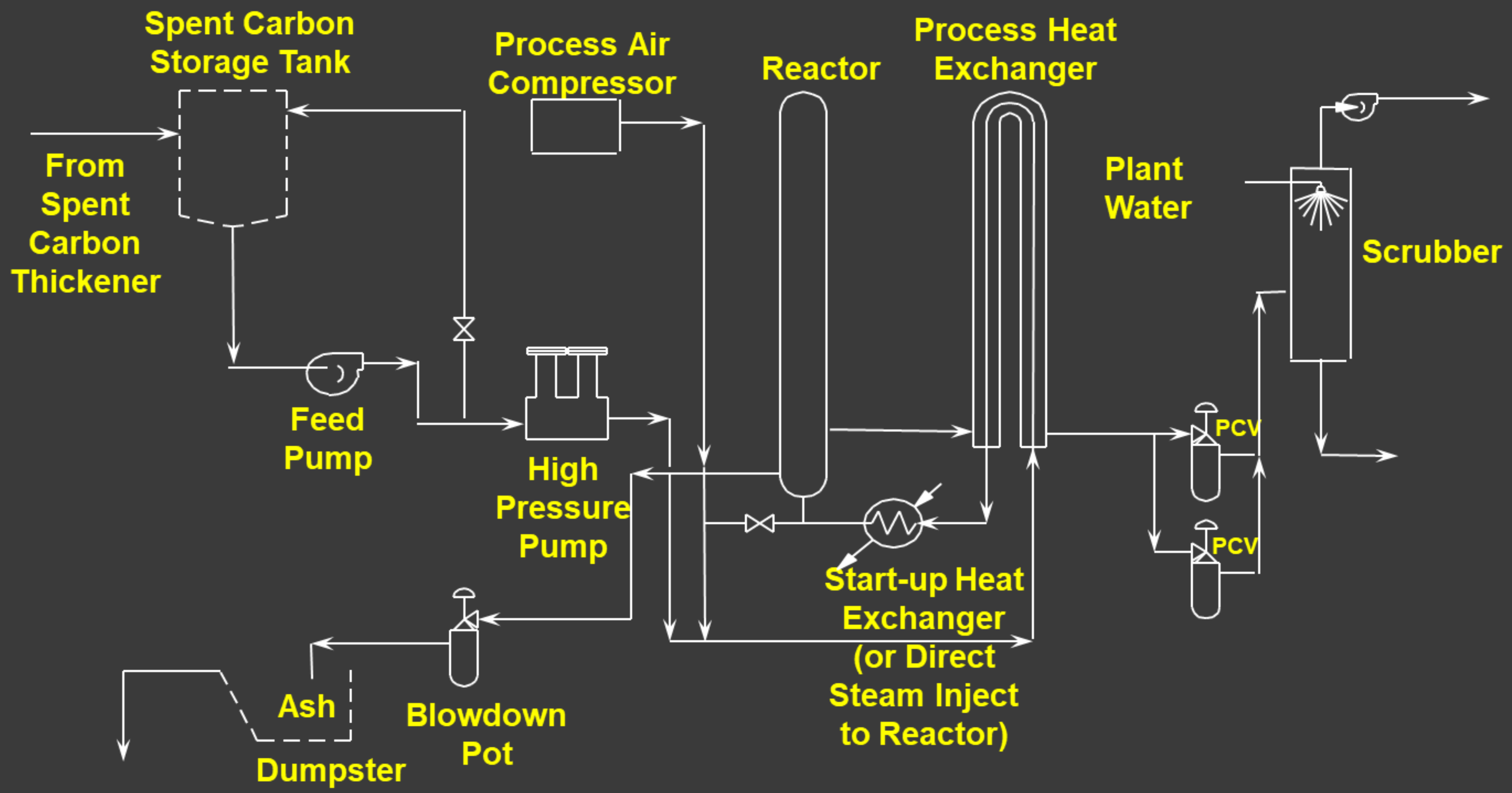
Wet Air Regeneration (WAR) of Spent Powdered Activated Carbon

- Converts adsorbed non-biodegradable COD to degradable organic acids and alcohols
- Destroys the biomass – no biomass sludge to dispose
- More than 40 years of technology implementation of Wet Air Regeneration (WAR) of Powdered Activated Carbon (PAC)

Fate of Organics in Wet Air Regeneration

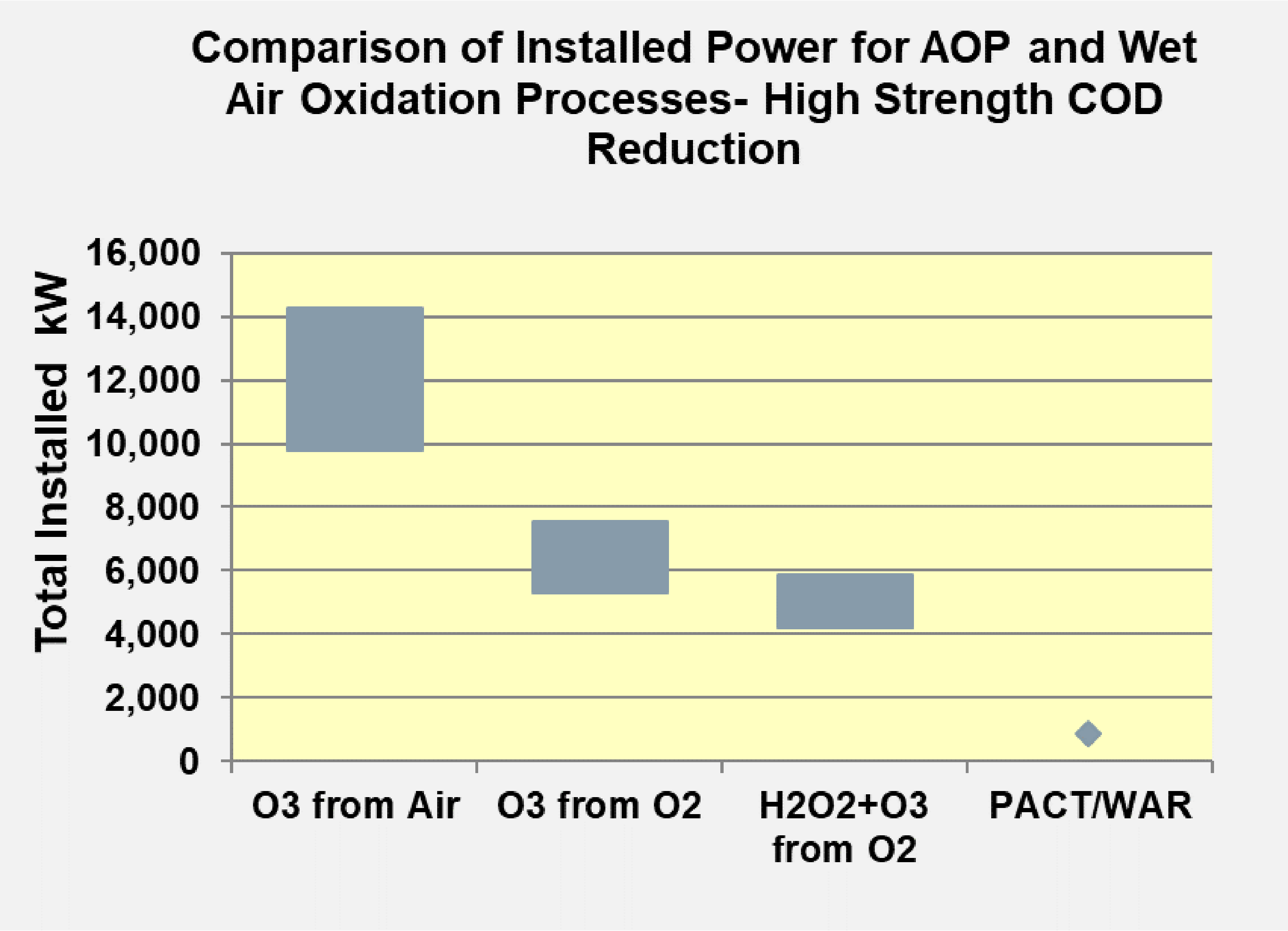
Feed	Effluent
Spent Carbon (WAS)	Regenerated Carbon + Ash
Adsorbed Refractory Organics + Biomass + O_2	CO_2 + H_2O + RCOOH*
Sulfur Species + O_2	SO_4^{-2}
Organic CL + O_2	Cl^-
Organic N + O_2	NH_4^{+1}
Phosphorus + O_2	PO_4^{-3}
* Short chain organic acids such as acetic acid make up the major fraction of residual oxidation intermediates in a typical WAR effluent. These acids are easily biodegraded.	

Wet Air Regeneration Process Flow Diagram

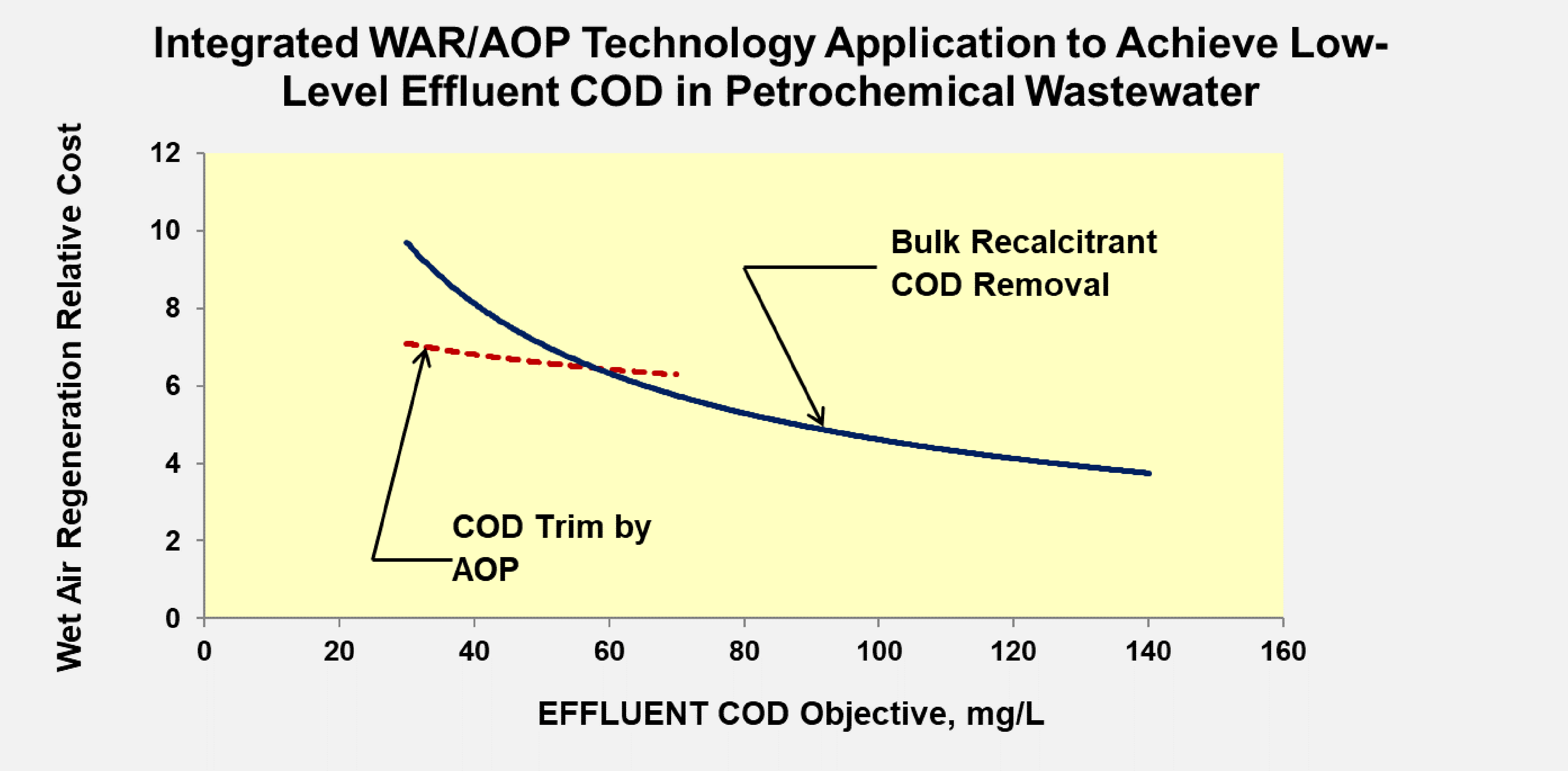


Example Energy Cost for High Strength COD Reduction by AOP

AOP Design Basis	
Parameter	**Value**
Flow	800 m^3/h
Feed COD to Bio-treatment	2,200 mg/L
Non-biodegradable Effluent COD	185 mg/L
Effluent COD Required	<50 mg/L
COD Removed By AOP	>135 mg/L



Relative Cost of Wet Air Regeneration vs. Effluent COD Objective



Conclusions

- Many treatment options exist for meeting the current and future challenging effluent limits and reuse mandates applied to Refinery and Petrochemical effluents

- AOPs, traditionally applied to drinking water and low-level TOC and COD, is now being applied to high strength wastewater for high concentration COD removal

- These are relatively simple system designs with moderate CAPEX; OPEX costs however can be significant due to huge power needs for ozone generation or chemical supply

- Careful examination of both CAPEX and OPEX is needed to best optimize lifecycle costs

- In many instances, an Integrated Systems approach will offer the optimum solution for applications where removal of non-biodegradable (recalcitrant) COD exceeds 50 mg/L, and final effluent COD quality is <50 mg/L.

Thank You

WJ Cunningham & Associates

6387 Irving Drive
Sun Prairie, WI 53790
Tel: +1 715 571 9652

William J. Cunningham P.E.
william.cunningham@wjcwatersolutions.com

www.wjcwatersolutions.com