

Electrochemical Destruction of Cyanide in Water



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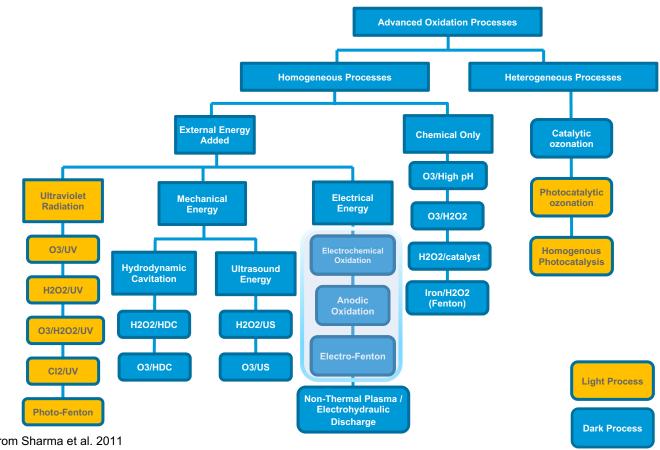
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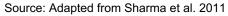
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Electrochemical Oxidation Background

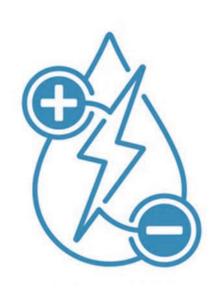
- Studied mostly at bench scale and currently emerging into commercial applications
- Significant amount of publications
- Fits into a continuum of advanced oxidation processes

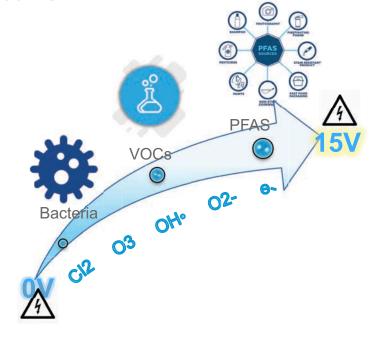


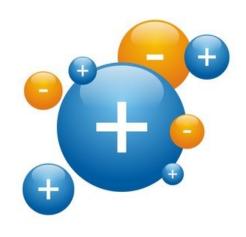




EAOPs 101 Fundamentals







Electrodes placed in water

Anode(+)/Cathode(–)

Electric potential above 1.23 V applied

 Surficial voltage at which water splits to O₂ and H₂

Mixed oxidant production with increasing voltage

Anodes with high overpotential are



Modes of Operation

Indirect oxidation

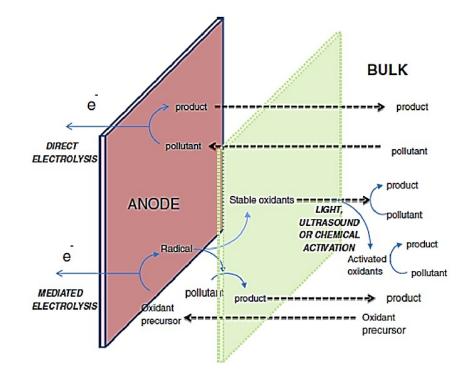
• Oxidants formed in-situ react in bulk solution (OCl-, HOOH, ClO₂, O₃, HO·, O₂-, S₂O₈²⁻)

Direct oxidation

- Adsorbed molecules react with electrons generated on surface of electrode
- Direct electron transfer reactions slower than indirect reactions and require adsorption of molecules to electrode surface

High degree of oxidation achieved

- Mineralization of organics to CO₂ and other trace gases
- Disinfection of microbes
- AOC produced by incomplete mineralization





Electrode Types

Noble metals

• Pt, Ti/Pt

Metal Oxides and Mixed Metal Oxides (MMO)

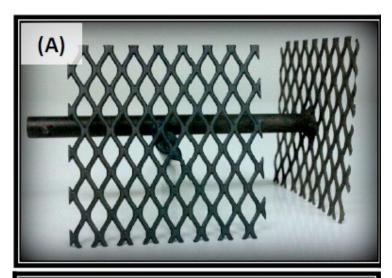
- PtO₂, PbO₂, IrO₂, TiO₂, SnO₂, RuO₂
- Substoichiometric titanium oxides

Boron Doped Diamond (BDD)

 BDD is claimed to have the largest electrochemical potential window in aqueous solutions compared to traditional electrode materials

Carbonaceous and Graphitic Materials

Carbon black, carbon fibers, carbon nanotubes, graphite







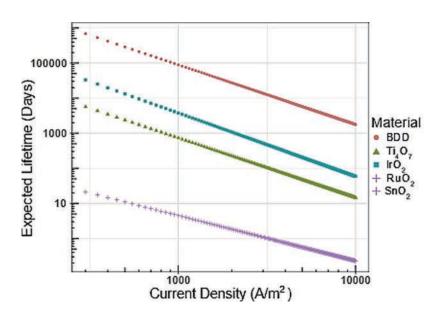
Ideal Electrode

- High oxidation potential
- Low cost
- Low energy (<0.5 kWh/gal)
- Long-lasting (years)
- Low maintenance
- Available in a variety of form factors



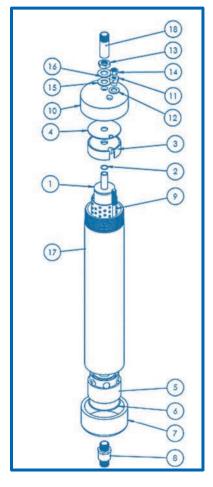


| Electrode Material | Overpotential (V) |
|---|-------------------|
| Aclarity | 2.5+ |
| BDD | 2.2-2.6+ |
| Ti/SnO ₂ -Sb ₂ O ₅ | 1.9-2.2 |
| Ti/Pt | 1.7-1.9 |
| IrO ₂ /Ta ₂ O ₅ | 1.5-1.8 |
| RuO ₂ /TiO ₂ | 1.4-1.7 |









Electrode materials

Unique profile of inherent power, low-cost anodes; pairing right cathodes increase this further



Geometry

Radial, porous shape with small band gap optimizes efficiency and speciation



Reactor flow

Flow-through path, mixing, and detention time ensure oxidants are used



Cyanide Uses and Occurrence



Widely used in industry

 Market for NaCN alone expected to be \$3B in us by 2027



Recovery of metals from mining

 Metal processing and plating from 2500 metal plating shops in US



Salt manufacturing and processing

Sodium ferrocyanide decahydrate (YPS) used as anti-caking agent



Cyanide Chemistry

Hypochlorite

$$CN^- + OCl^- \rightarrow CNCl + Cl^-$$

 $CNCl + H_2O \rightarrow OCN^- + 2H^+ + Cl^-$
 $OCN^- + H_2O + OH^- \rightarrow NH_3 + CO_3^{-2}$

Ozone

$$CN^{-} + O_{3} \rightarrow OCN^{-} + O_{2}$$

 $2OCN^{-} + 3O_{3} + H_{2}O \rightarrow 2HCO_{3}^{-} + N_{2} + 3O_{2}$

Chlorine Dioxide

$$CN^{-} + 2CIO_{2} + 2OH^{-} \rightarrow OCN^{-} + 2CIO_{2}^{-} + H_{2}O$$

 $OCN^{-} + H_{2}O + OH^{-} \rightarrow NH_{3} + CO_{3}^{-2}$

Hydrogen Peroxide

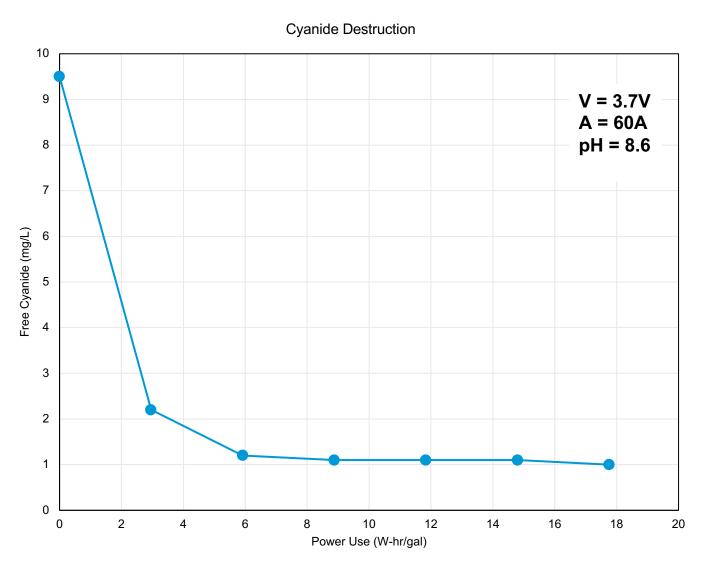
$$CN^- + H_2O_2 \rightarrow OCN^- + H_2O$$

 $OCN^- + H_2O + OH^- \rightarrow NH_3 + CO_3^{-2}$





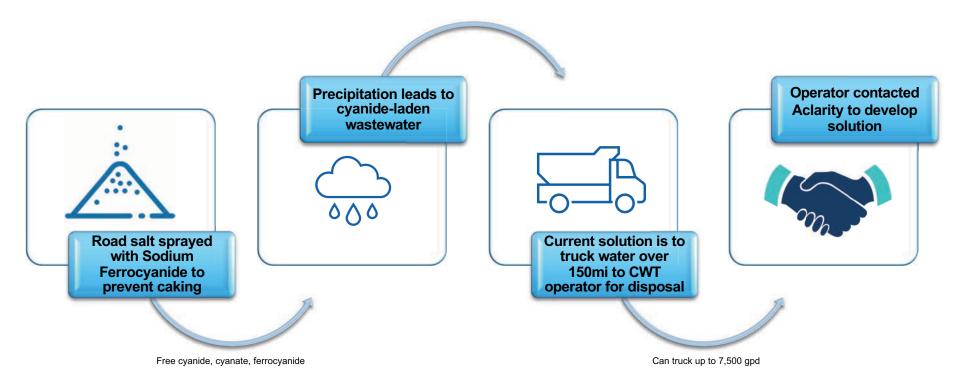
Cyanide Bench Results





Case Study – Cyanide Destruction Road Salt Depot





- Conducted bench and on-site pilot testing
- Designed, constructed and installed system in less than 6 months (Capacity 16,000 gpd)
- Working with local POTW to accept treated water



Aclarity Skid-mounted reactors





Cyanide Destruction Economics

Existing Costs

Trucking wastewater

- •Time/labor
- Mileage/tolls
- Disposal Fees
- •\$286,000/yr



Aclarity Costs

CAPEX

- Construction of shed
- Reactor(s)/Skid(s)
- Engineering
- Installation
- •\$130,000.00

OPEX

- Power \$1,600/yr
- Disposal \$91,000/yr

ROI

•~ 7 months



Conclusions



Free cyanide readily destroyed by electrochemical generation of hypochlorite at power

Achieving <1 mg/L cyanide limit



Complexed cyanide requires higher power to create hydroxyl radicals

Reactions are pH dependent



Economics are favorable

ROI < 1 year



Acknowledgements



- Julie Bliss Mullen
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Questions





Thank you!



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