CEE 597T

Electrochemical Water and Wastewater Treatment

ELECTROCHEMICAL OXIDATION
of Inorganic Compounds

- Anodic oxidation of some inorganic compounds such as cyanides, thiocyanate, and sulfides known for their toxic properties allows complete transfer on these pollutants to a nontoxic compound.
- EO can be used for the treatment of wastewater from electroplating industries containing cyanides of iron, zinc, copper, and others.

Electrooxidation of Cyanide

- Anodic oxidation of cyanides leads to the formation of less toxic cyanates, ammonia, and nitrogen compounds along with CO_2 gas and carbonate ions and can be described through the following equations:

$$CN^- + 2OH^- - 2e^- \rightarrow CNO^- + H_2O$$

$$CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-}$$

$$2CNO^- + 4OH^- - 6e^- \rightarrow 2CO_2 + N_2 + 2H_2O$$

- Usually EO of cyanides is conducted in electrolyzers of continuous and bath mode using graphite, lead oxide or magnetite anodes, and steel cathode at applied current density laying in the range of 30-40 mA/cm^2 at pH of 8-9. The removal efficiency is nearly 100%.

with chlorine

- Cyanides can be also oxidized indirectly while interacting with the products of anodic chlorine decomposition through the following reactions:

$$2Cl^- - 2e^- \rightarrow Cl_2$$

$$CN^- + Cl_2 + 2OH^- \rightarrow CNO^- + 2Cl^- + H_2O$$

$$2CNO^- + 3Cl_2 + 4OH^- \rightarrow 2CO_2 + N_2 + 6Cl^- + 2H_2O$$

- Advantage of EO of cyanides comparing to conventional chemical neutralization methods is simultaneous recovery of metals deposited at the cathode.

Cyanide & Chlorine

$$HOCl + CN^- \xrightarrow{k_4} CNCl + OH^-$$

$k_4 = 1.22x10^9\ M^{-1}s^{-1}$

$pK_a = 7.47\ \ for\ HOCl$
$pK_a = 9.21\ \ for\ HCN$

- Reacts quickly
  - *Forming cyanogen chloride*
  - *Where*

$$\frac{d[CN]}{dt} = -k_4[HOCl][CN^-]$$

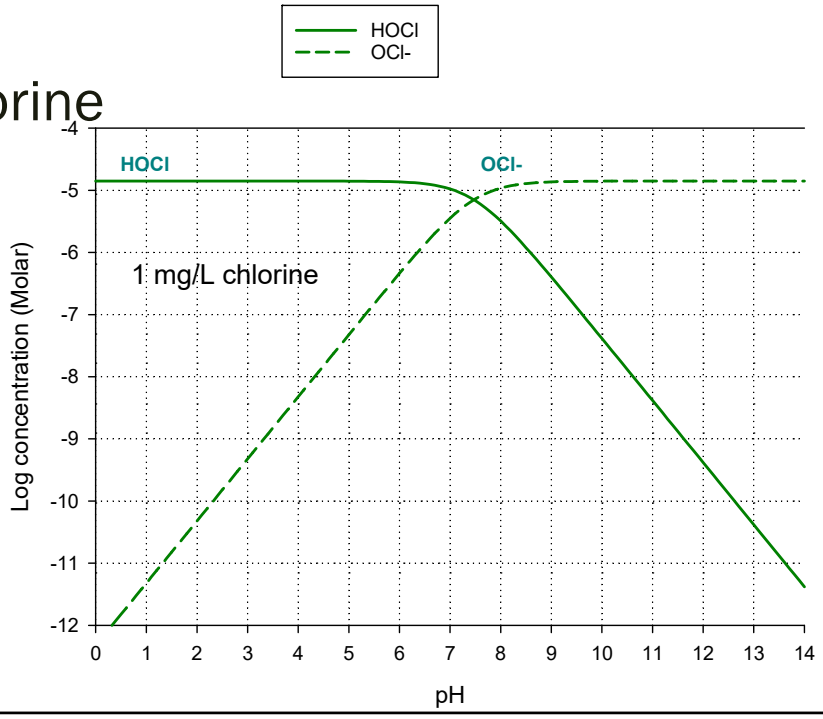
$$\frac{d[C_{T-CN}]}{dt} = -k_4\alpha_{0-OCl}C_{T-OCl}\alpha_{1-CN}C_{T-CN}$$

  - *Half life at pH 7 and 1 mg/L chlorine is 9 milliseconds*

Gerritsen CM, Margerum DW. NONMETAL REDOX KINETICS - HYPOCHLORITE AND HYPOCHLOROUS ACID REACTIONS WITH CYANIDE. Inorganic Chemistry. 1990;29(15):2757-62.

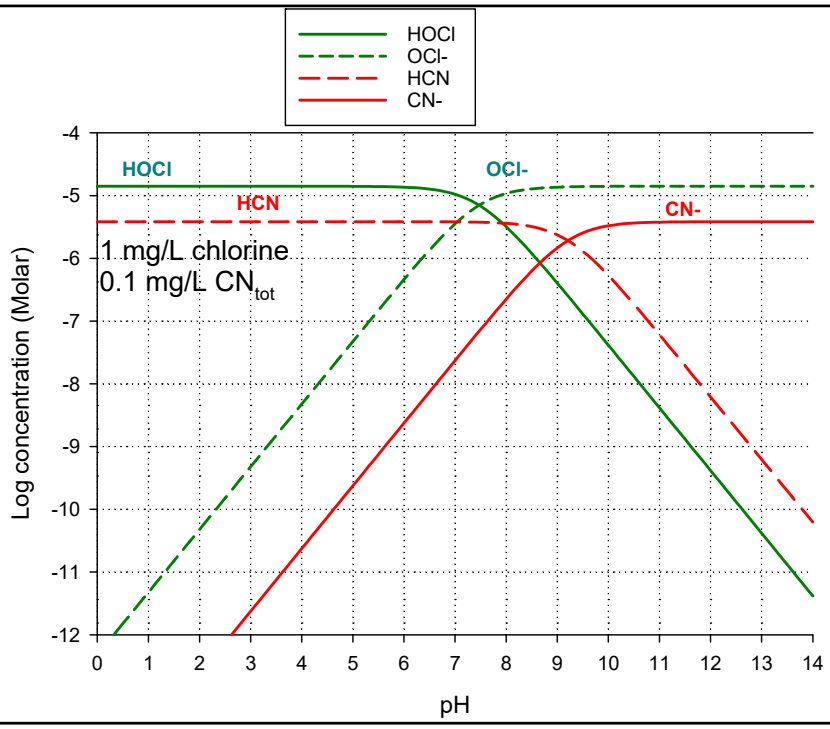
Free Chlorine

- pKa = 7.47



Cyanide

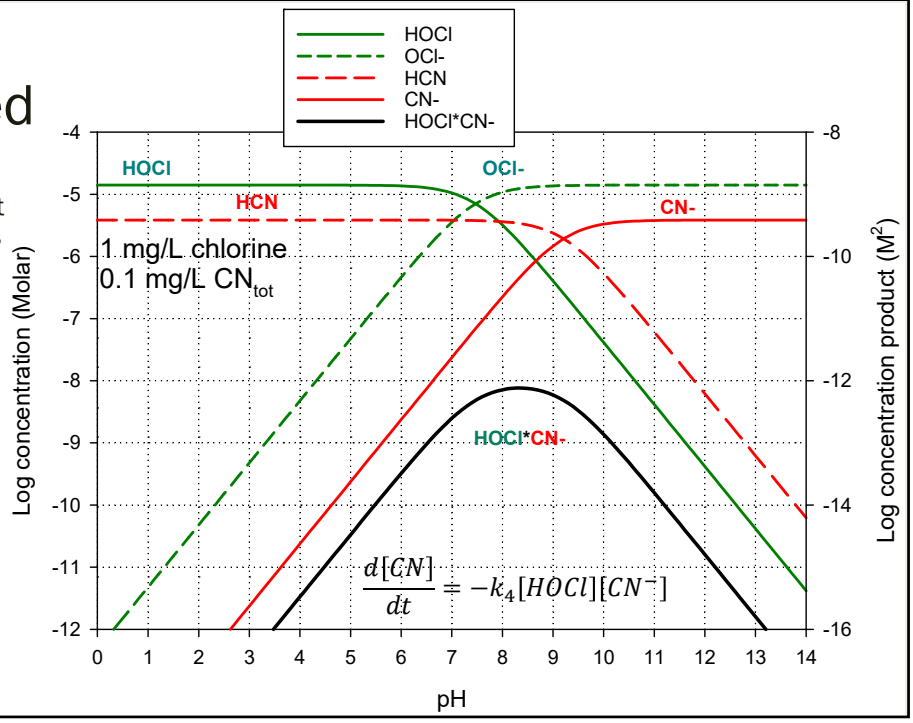
- pKa = 9.21



Combined

- Max rate is at midpoint between the two pKa's
  - *pH = 8.34*

$$HOCl + CN^- \xrightarrow{k_4} CNCl + OH^-$$



Cyanogen Chloride

$$CNCl + OH^- \xrightarrow{k'} OCN^- + Cl^- + H^+$$

- Hydrolysis
  - *Forming cyanate*
  - *Where* $k' = k_1 + k_2[OH^-]$

$$k_1 = 2.58x10^{-5}\ s^{-1} \qquad k_2 = 4.53\ M^{-1}s^{-1}$$

  - *Half life at pH 7 is 63 hours*

Bailey PL, Bishop E. HYDROLYSIS OF CYANOGEN CHLORIDE. Journal of the Chemical Society-Dalton Transactions. 1973(9):912-6.

Pedersen EJ, Marinas BJ. The hydroxide-assisted hydrolysis of cyanogen chloride in aqueous solution. Water Research. 2001;35(3):643-8.

Electrooxidation of thiocyanate

- EO of thiocyanate leads to the formation of less toxic cyanates that can be further oxidized to carbonates, CO_2, and N_2 gas.

$$SCN^- + 10OH^- - 8e^- \rightarrow CNO^- + SO_4^{2-} + 5H_2O$$

Electrooxidation of sulfide ions

- Sulfide ions can be electrochemically oxidized to sulfates at pH 7. The formation of elemental sulfur can occur at lower pH values.
- Formation of polysulfides, sulfites, and tetrathionates can be observed and are described by the following reactions:

$$S^{2-} - 2e^- \rightarrow S$$

$$S + 8OH^- - 6e^- \rightarrow SO_4^{2-} + 4H_2O$$

$$S^{2-} + 8OH^- - 8e^- \rightarrow SO_4^{2-} + 4H_2O$$

$$2S^{2-} + 6OH^- - 8e^- \rightarrow S_2O_3^{2-} + 3H_2O$$

$$S^{2-} + 6OH^- - 6e^- \rightarrow SO_3^{2-} + 3H_2O$$

- There is a wide variety of intermediate products generated during the anodic oxidation of sulfides.

Catalytic Oxidation of sulfide ions

- The use of catalytic anodes such as Pt or BDD can significantly improve the selectivity of the process toward sulfate formation.
- With Pt anode:

$$Pt + HS^- + OH^- - 2e^- \rightarrow PtS + H_2O$$

$$PtS + HS_x^- \rightarrow Pt + HS_{x+1}^-$$

$$PtS + 8OH^- - 6e^- \rightarrow Pt + 4H_2O + SO_4^{2-}$$

- With BDD anode:

$$BDD + S^{2-} - 2e^- \rightarrow (BDD)S$$

$$(BDD)S + S_x^{2-} \rightarrow BDD + S_{x+1}^{2-}$$

$$(BDD)\,S + 8OH^- - 6e^- \rightarrow BDD + 4H_2O + SO_4^{2-}$$

Electrooxidation of ammonia nitrogen

- Ammonia nitrogen in wastewater could be eliminated efficiently by electrooxidation. The electro-oxidation mechanism of ammonia nitrogen included direct oxidation which happened on the anode surface, and indirect oxidation in which ammonia was oxidized by electrogenerated oxidants.
- Ammonia can be oxidized to N_2 with excellent chemical and current efficiency at noble metal anodes, but several factors make the approach impractical for the proposed application.
- These include the

high cost of noble metals,

the need for highly alkaline pH to convert NH4 + into the more easily oxidized NH3, and

careful control of the anode potential to avoid overoxidation to nitrate.

- The electrochemical oxidation of ammonia can also be carried out indirectly in the presence of chloride ion, which is oxidized at the anode to hypochlorite (HOCl or OCl^-, depending on the pH). Hypochlorite oxidizes ammonia to N_2, with reduction back to chloride ion; hence, the reaction is the electrochemical analogue of "breakpoint chlorination" of drinking water.

- Electrolysis is applied in the suggested process directly on the rearing seawater, utilizing the inherently high Cl^- concentration for efficient Cl_2 generation near the anode.
- Simultaneously, H^+ is reduced to $H_{2(g)}$ near the cathode. Since the anodic reaction is acidic, low pH conditions (typically <pH2) develop close to the anode. NH_4^+, the dominant ammonia species at acidic conditions, reacts with Cl_2(and probably also with the species Cl_3^-, present in the water at low pH) in a complex set of reactions occurring in three distinct pH zones (low pH close to the anode, high pH close to the cathode and approximately neutral pH in the bulk water), resulting overall in oxidation of TAN(total ammonia nitrogen) to $N_{2(g)}$.
- $2Cl^- + 2H^+ \rightarrow Cl_2 + H_{2(g)}$
- $3Cl_2 + 2NH_4^+ \rightarrow N_{2(g)} + 6Cl^- + 8H^+$
- $2NH_4^+ \rightarrow N_{2(g)} + 3H_2 + 2H^+$
- Eq. results in the release of one mole of protons per each mole of NH_4^+ oxidized to $N_{2(g)}$. However, since the NH_3that is excreted from the fish gills contributes one mole of alkalinity as OH^- (per mole NH_3) to the rearing water upon completely transforming to NH_4^+ at pH < ~8 the alkalinity mass balance can almost be preserved if most of the treated water is returned back to the rearing tank.

Electrooxidation of Urea

- The pollutant can be removed from the solution by a chemical attack on the reactive species generated at the electrodes (indirect electrochemical oxidation). The electro-oxidation of urea in its simplest form should occur according to the following electrode half-reactions

$$\text{Anode}: CO(NH_2)_{2(aq)} + 6OH^-_{(aq)} \rightarrow N_{2(g)} + 5H_2O_{(l)} + CO_{2(g)} + 6e^-$$

$$\text{Cathode}: 6H_2O_{(l)} + 6e^- \rightarrow 3H_{2(g)} + 6OH^-_{(aq)}$$

$$\text{Overall}: CO(NH_2)_{2(aq)} + H_2O_{(l)} \rightarrow N_{2(g)} + 3H_{2(g)} + CO_{2(g)}.$$

- The first obvious advantage of the electrochemical approach to urea decomposition is the fact that the overall electrochemical process produces only gaseous products that are not harmful to the environment (perhaps with the exception to CO_2). However, the exact mechanism of urea decomposition on various electrode materials may differ, and the effluent from the treatment may contain some intermediate products.

Presence of Chloride ions

Due to their presence, additional reactions along with reactions may take place at the electrodes and in bulk of the solution

Anode:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

$$4OH^-_{(aq)} \rightarrow O_{2(g)} + 4e^-$$

$$\text{Cathode}: Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$$

Bulk of the solution:

$$Cl_{2(g)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + HCl_{(aq)}$$

$$CO(NH_2)_{2(aq)} + 3HOCl_{(aq)} \rightarrow N_{2(g)} + CO_{2(g)} + 3HCl_{(aq)} + 2H_2O_{(l)}.$$

References

- Mika Sillanpää, Marina Shestakova, Electrochemical Water Treatment Methods, 1st Ed., Elsevier, 2017
- Ewelina Urbańczyk, Maciej Sowa, ,Wojciech Simka, Urea removal from aqueous solutions—a review, Journal of Applied Electrochemistry 46(10) · August 2016
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- http://www.groundeffects.org/products/electrocatalytic-oxidation