Chlorates?

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AGRICULTURE AND FOOD DEVELOPMENT AUTHORITY

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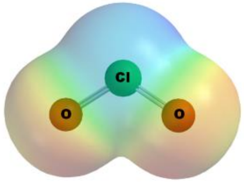
- Chemistry of Oxychloro anions
- Chloralkali industry
- Hypochlorite

- Decomposition Reactions & Conditions

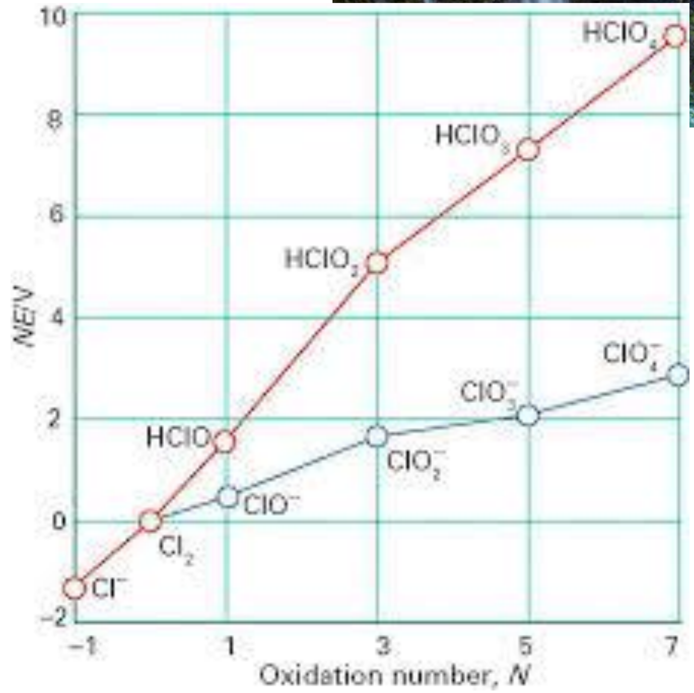
- Recommendations

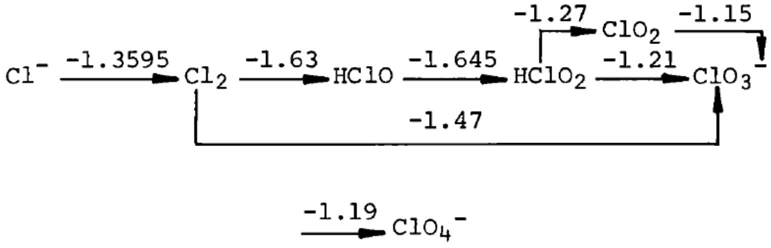
- Chlorine Dioxide Chemistry

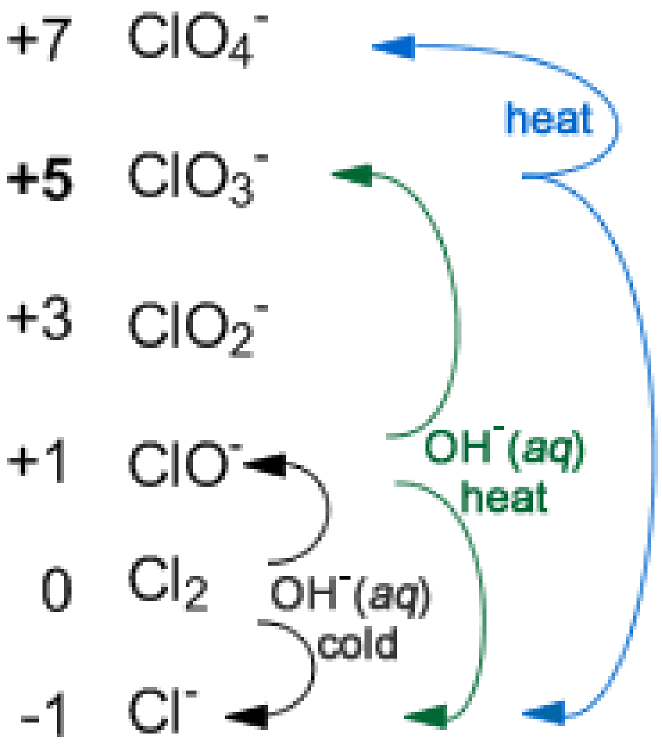


- Removal Options

Disproportionation

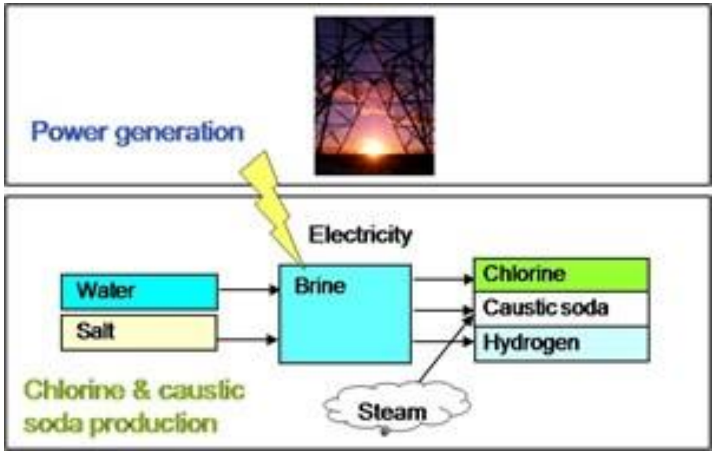


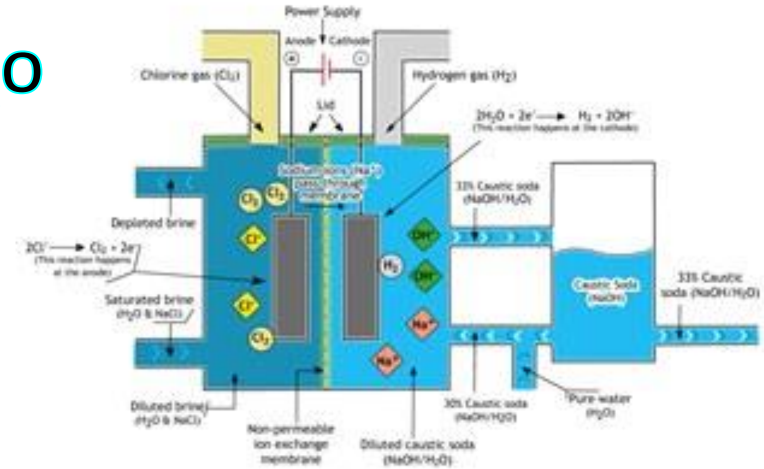




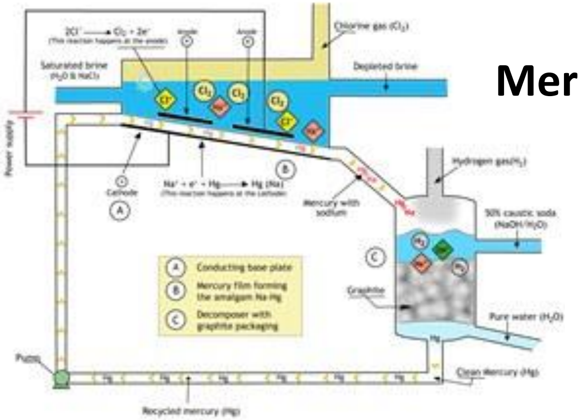
Chloroalkali Industry

$Cl_2 + 2\ NaOH \rightarrow NaCl + NaClO + H_2O$



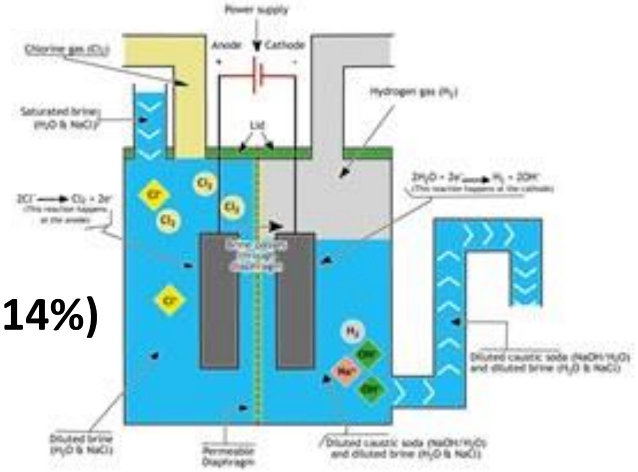


Membrane (52%)



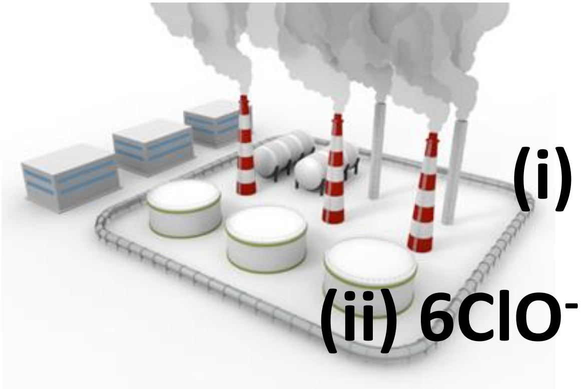
Mercury (31%)

Diaphragm (14%)



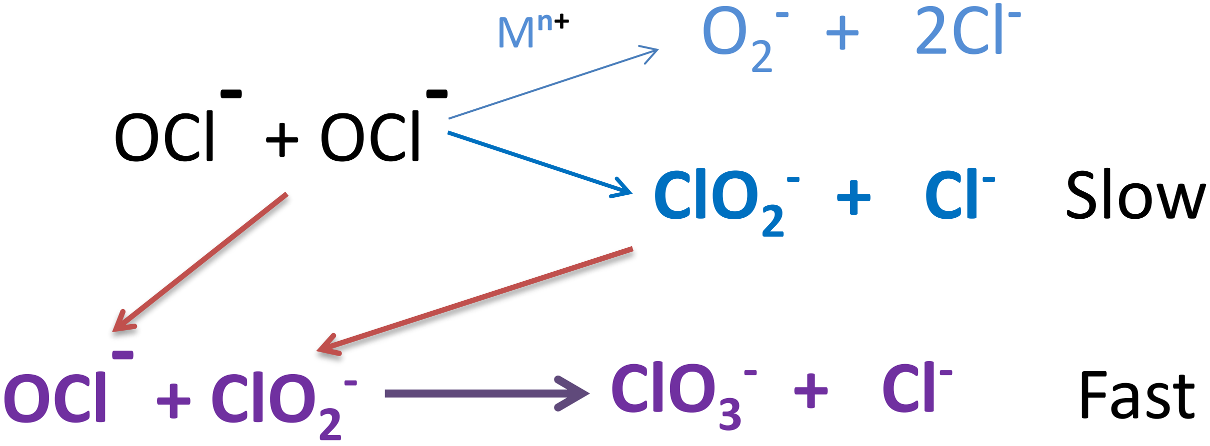
Decomposition Reactions

Two decomposition pathways in competition, one to form chlorate the other to form oxygen.



(i) $2HClO + ClO^- \rightarrow Cl^- + ClO_3^- + H^+$

(ii) $6ClO^- + 3H_2O \rightarrow 4Cl^- + 6H^+ + {}^{3}/_{2}\, O_2 + 2\, ClO_3^-$

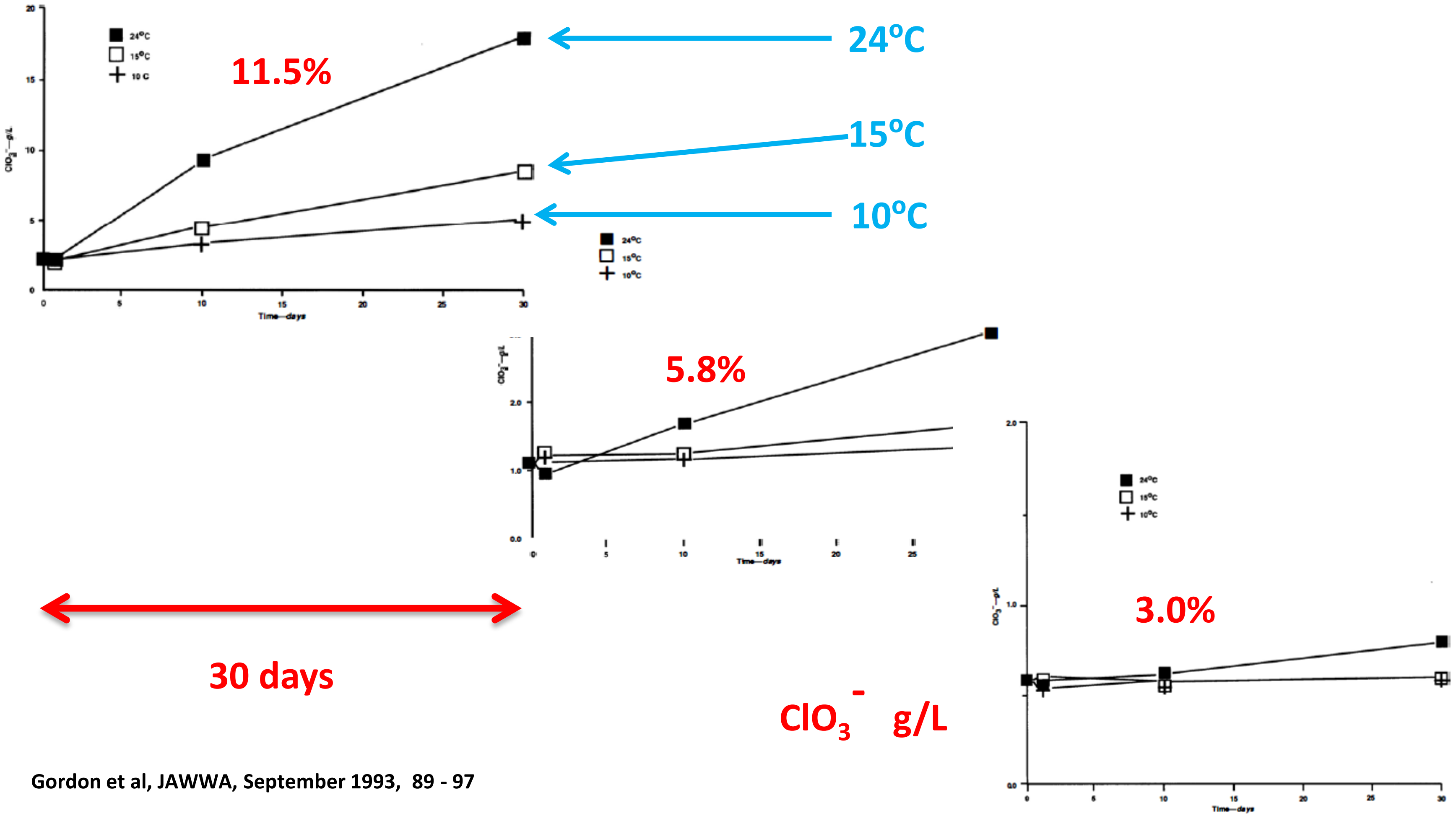


$OCl^- + OCl^- \xrightarrow{M^{n+}} O_2^- + 2Cl^-$

$OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$ Slow

$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$ Fast

Chlorate Formation v Temperature wrt Initial Hypochlorite Conc.



24°C

15°C

10°C

11.5%

5.8%

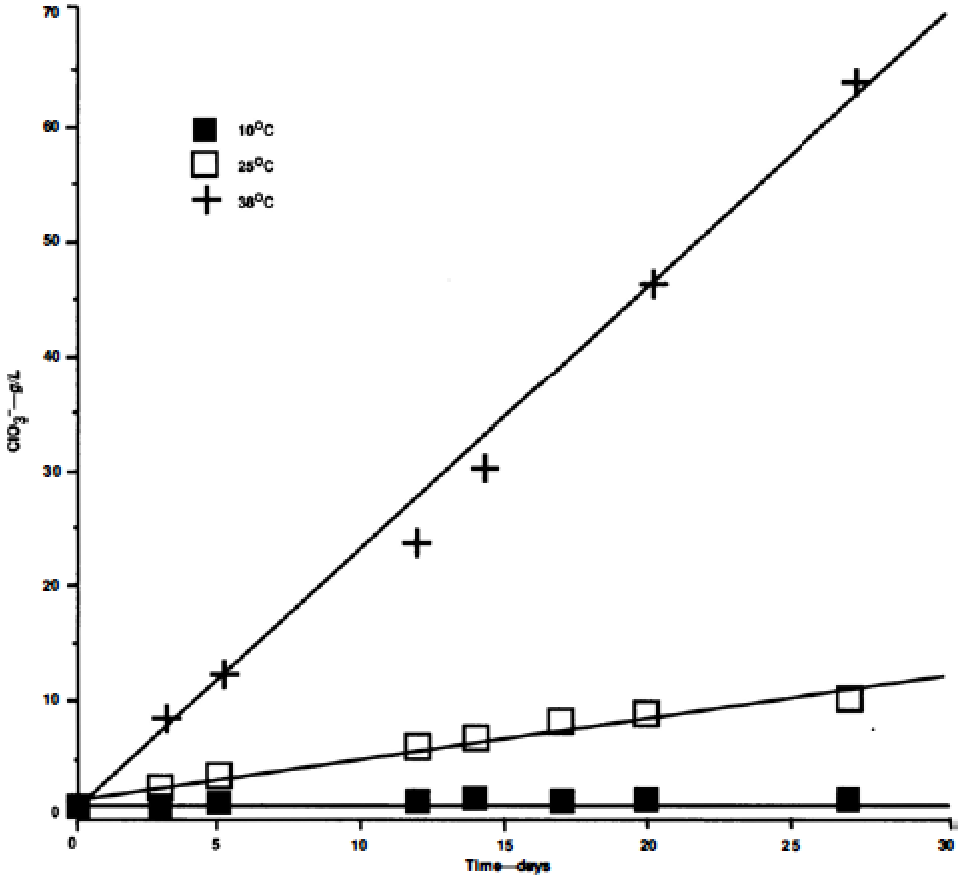
3.0%

30 days

ClO_3^- g/L

Gordon et al, JAWWA, September 1993, 89 - 97

Dilution



Diluting the hypochlorite solution by a factor of 2 is more effective than decreasing the temperature from 24°C to 10°C.

Gordon et al, JAWWA, September 1993, 89 - 97

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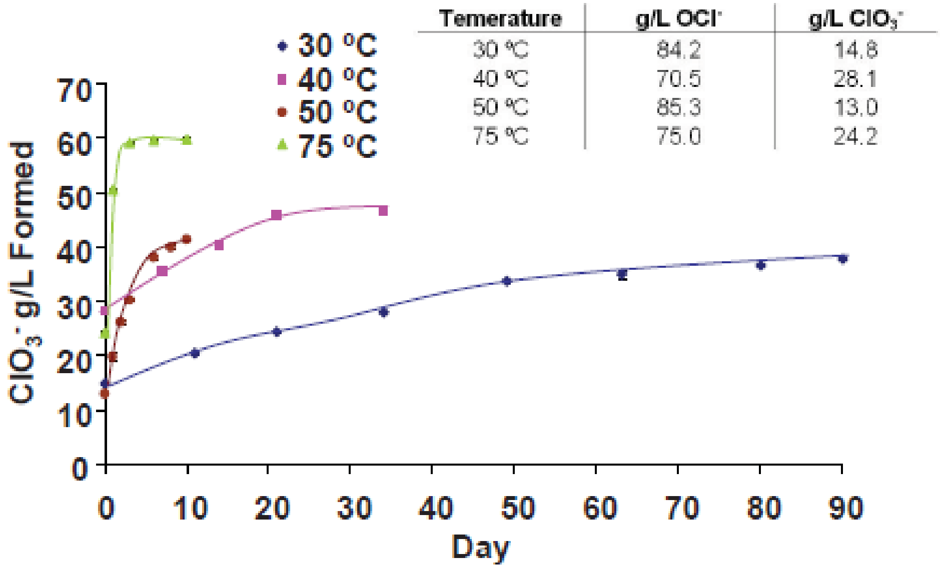
Decomposition of OCl$^-$ & formation of ClO$_3^-$
Influence of Temp ^oC

(i) $Cl_2 + OH^- \rightarrow Cl^- + ClO^- + H^+$ **(ii) $2HClO + ClO^- \rightarrow Cl^- + ClO_3^- + H^+$**

(iii) $6ClO^- + 3H_2O \rightarrow 4Cl^- + 6H^+ + {}^3/_2\,O_2 + 2\,ClO_3^-$

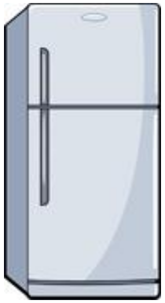


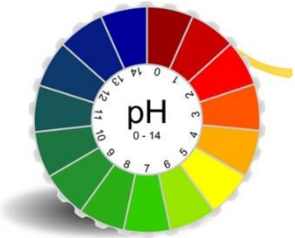
Temerature	g/L OCl$^-$	g/L ClO$_3^-$
30 °C	84.2	14.8
40 °C	70.5	28.1
50 °C	85.3	13.0
75 °C	75.0	24.2

Hypochlorite – An Assessment of factors that influence the formation of Perchlorate and other Organic Contaminants ; AWWA/WRF , 2009

Recommendations

- **Dilute OCl$^-$ upon delivery.**
  - High ionic strength produces ClO$_3^-$
  - Dilution by f x 2 results in 5-fold decrease in decomposition.
- **Store at low temperature.**
  - Every 5^{o}C reduction in storage yields reduction by factor of 2.
- **Control pH.**
  - Minimized at pH 11.86 to 13.00.
  - pH14, OH- increases by f x 1.5
- **Control transition metals.**
  - Ni (factor of 10), Co, Cu, (less so Fe & Mn)
- **Use fresh.**





ClO_2 Generation

Reacts by 1 e^- oxidative pathway,
Low THMs,
0.1 – 2.0 ppm

$$2NaClO_2 + Cl_{2(g)} = 2ClO_{2(g)} + 2NaCl$$

$$2NaClO_2 + HOCl = 2ClO_{2(g)} + NaCl + NaOH$$

$$5NaClO_2 + 4HCl = 4ClO_{2(g)} + 5NaCl + 2H_2O$$

Generator Type	Reactants	Products
Acid- Chlorite	$4HCl + 5NaClO_2$	$4ClO_2 + ClO_3^-$
Aq. Chlorine Chlorite	$Cl_2 + H_2O + NaClO_2$	$ClO_2 + HOCl + NaOH + ClO_3^-$
French Loop	$2HOCl + 2NaClO_2$	$2ClO_2 + Cl_2 + NaOH$
Gas. Chlorine-Chlorite	$Cl_2 + NaClO_{2(l)}$	ClO_2
Gas. Chlorine-Chlorite(s)	$Cl_2 + NaClO_{2(l)}$	$ClO_2 + NaCl$
Electrochemical	$NaClO_2$	$ClO2 + e^-$
Acid/Perox/Chloride	$2NaClO_3 + H_2O_2 + H_2SO_4$	$2ClO_2 + O_2 + NaSO_4 + H_2O$

$\{Cl^{-}\text{-}ClO_2\}$

$$Cl_2 + ClO_2^{-} = \{Cl\text{-}ClO_2\} + Cl^{-}$$

In generators that operate at low initial reactant concentrations, a significant amount of chlorate is formed by reactants with $\{Cl_2O_2\}$.

At low reactant concentrations or excess HOCl

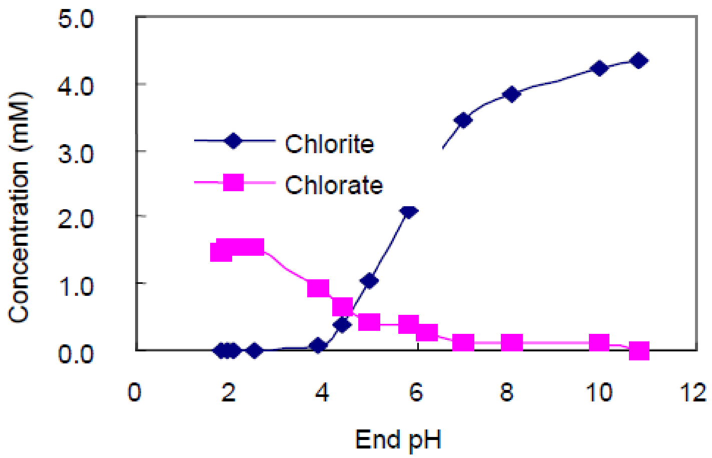
$$\{Cl_2O_2\} + H_2O = ClO_3^{-} = Cl^{-} + 2H^{+}$$

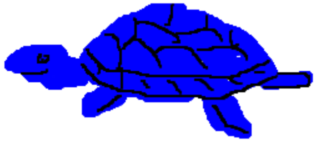
$$\{Cl_2O_2\} + HOCl = ClO_3^{-} + Cl^{-} + H^{+}$$

$$\{Cl_2O_2\} + 3HOCl + H_2O = 2ClO_3^{-} + 5H^{+} + 3Cl^{-}$$

$ClO_2\ (aq) + e^{-} = ClO_2^{-}$

Influence of pH





- **High pH slows the formation of ClO_2**
- **Generates less efficient chlorate forming reactions.**

At low pH: Chlorous acid (not chlorite) is oxidized to ClO_2.

$$2HClO_2 + HOCl = HCl + H_2O + 2ClO_2$$

However highly acidic (<pH 3) reaction mixtures force the degradation of $\{Cl_2O_2\}$ to chlorate rather than chlorine dioxide, as well as oxidation of chlorite to chlorate.

$$ClO_2^- + HOCl = ClO_3^- + Cl^- + H^+$$

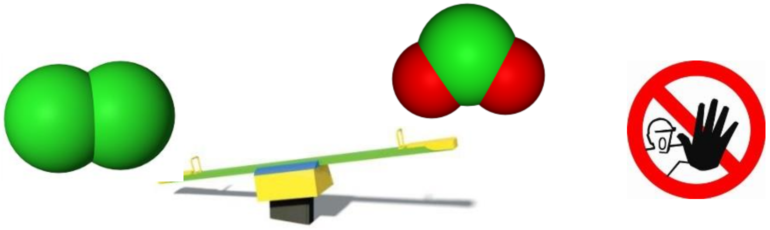
And

$$ClO_2^- + Cl_2 + H_2O = ClO_3^- + 2\,Cl^- + H^+$$

Avoid

The following conditions may also produce the chlorate ion.

- Excessively **high ratios of Cl_2 gas** : **ClO_2^-**
- Presence of **high conc. of free chlorine** at low pH in aq. Soln.
- **Dilute chlorite** soln. at low pH
- Base catalysed disproportionation of ClO_2 at high pH (**pH > 11**).
- Reaction mixtures that are highly acidic (**pH < 3**).
- An **excess of HOCl** will oxidize ClO_2^- to ClO_3^- rather than ClO_2, independently of $\{Cl_2O_2\}$ intermediate.

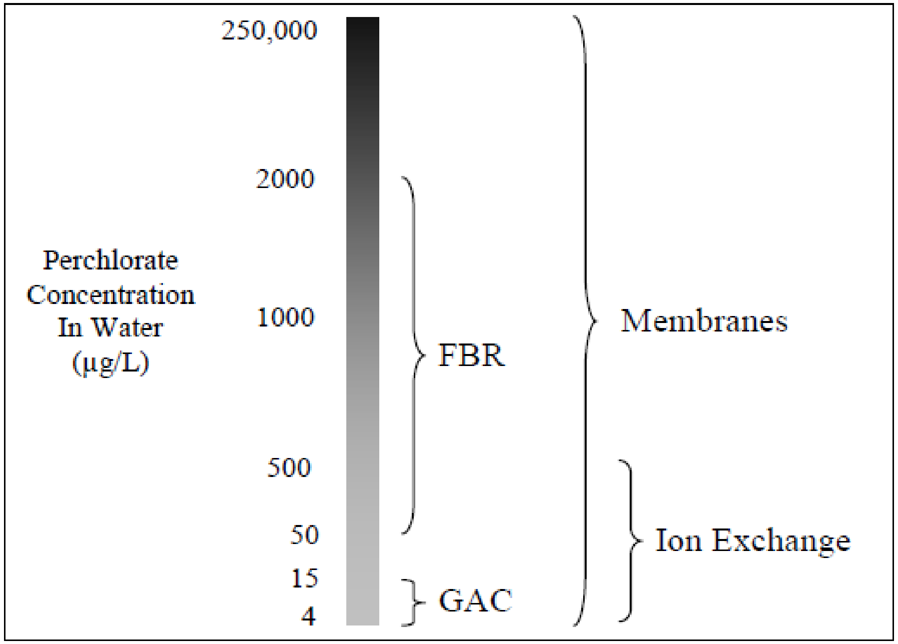


Treatment Technologies

(Mostly developed for Perchlorate in USA)

- Ozone
- Reduction, M^{n+}, e^-
- Sulphur Dioxide
  - SO_2 / SO_3^{2-}
- Activated Carbon
  - (GAC/BAC)
- Ion Exchange
  - Interferences from NO^{3-} & SO_4^{2-}
- Membrane
  - **P**oly**E**lectrolyte**UF**, **C**olloid **E**nhanced**UF**, UF, NF, ED
- **Reject streams??**

- "There is not a standardised treatment process for removal of chlorate once formed."
- Control of ClO_3^- formation preferable.
  - AWWA, 2014



THANKS FOR WATCHING!