Overview of ClO$_2$ Generation Chemistry For Pulp and Paper Industry
ClO$_2$ Introduction

Chlorine dioxide (ClO$_2$) is a powerful oxidizing agent, used to bleach pulp. It is also used to sterilize drinking water and as a bactericide in general water treatment.

- The basic chemistry used in the Solvay process:
  - $4\text{NaClO}_3 + 4\text{H}_2\text{SO}_4 + \text{CH}_3\text{OH} \Rightarrow 4\text{ClO}_2 + 4\text{NaHSO}_4 + \text{CHOOH} + \text{H}_2\text{O}$

- ClO$_2$ is made as a gas and absorbed in chilled water to produce a solution concentration ranging from 8 to 10 g/L.
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Symbol</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chlorate</td>
<td>Na ClO₃</td>
<td>Chlorate</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>Na Cl</td>
<td>Salt</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Methyl Alcohol</td>
<td>CH₃OH</td>
<td>Methanol</td>
</tr>
<tr>
<td>Chlorine Dioxide</td>
<td>ClO₂</td>
<td>Chlorine dioxide, chlo\text{e}\text{ two}</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl₂</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Sodium sesqui sulfate</td>
<td>Na₃H(SO₄)₂</td>
<td>Saltcake</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>Na OH</td>
<td>Caustic</td>
</tr>
<tr>
<td>DEC</td>
<td>NaSH</td>
<td>DEC</td>
</tr>
</tbody>
</table>
Basic R8 Generation Chemistry

\[ 0.85\text{CH}_3\text{OH} + 3\text{NaClO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \]

\[ 3\text{ClO}_2 + \text{Na}_3\text{H(SO}_4)_2 + 0.6\text{CHOOH} + \]

\[ 2\text{H}_2\text{O} + 0.05\text{CH}_3\text{OH} + 0.2\text{CO}_2 \]
## General ClO$_2$ Chemical Usage

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Ton/ton of ClO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO$_3$</td>
<td>1.85</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.02</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>2.35</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>0.187</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>0.06</td>
</tr>
<tr>
<td>NaSO$_4$</td>
<td>1.2</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>1.68</td>
</tr>
</tbody>
</table>
## Properties of Sulfuric Acid

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility</td>
<td>100%</td>
</tr>
<tr>
<td>Sp.Gr. at 50°F</td>
<td>1.835</td>
</tr>
<tr>
<td>Density at 50°F lb./gal</td>
<td>15.3</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-31°F</td>
</tr>
<tr>
<td>Boiling Point 760 mm Hg</td>
<td>534°F</td>
</tr>
<tr>
<td>Viscosity cP @ 68°F</td>
<td>22</td>
</tr>
</tbody>
</table>

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Chemical Properties of \( \text{H}_2\text{SO}_4 \)

- Vigorous reactions occur with alkaline solutions; metals; metal powders; carbides; chlorates; strong oxidizer; reducing or combustible organic materials.

- Hazardous gases are evolved on contact with chemicals such as cyanides, sulfides and carbides.
Chemical Properties of $\text{H}_2\text{SO}_4$

- $\text{H}_2\text{SO}_4$ is stable but reacts violently with water and organic materials with evolution of heat.

- $\text{H}_2\text{SO}_4$ chars organic substances on contact which results in the formation of carbon.

- $\text{H}_2\text{SO}_4$ attacks most common metals.

- However, for acid at commercial strengths, carbon steel or stainless steel is generally satisfactory.
Sodium Chlorate NaClO₃

Physical properties
- White crystalline solid.
- Pale yellow solution.
- No odor

Health hazard
- Inhalation or contact with eyes or skin may cause irritation.
- Ingestion may cause nausea, vomiting, diarrhea.
General NaClO₃ Chemical Properties

• Sodium chlorate is a stable chemical.

• A strong oxidizer, it readily reacts with acids to form toxic and explosive gases.

• Reaction with combustibles normally occurs only after solution has dried out and the combustible is impregnated with chlorate.

• Such mixtures are likely to be ignited by heat, friction, contact with acid, or any other source of ignition.
Methanol - CH₃OH

Physical Data

- Boiling Point - 769 mm Hg 148.5°F
- Freezing Point -148.9°F
- Specific Gravity - 0.791 at 68°F
- Vapor Pressure - 138 mm Hg at 77°F
  200 mm Hg at 99.9 °F
- Vapor Density ~1.1 (Air = 1)
- Solubility in Water - 100%
**General Methanol Health Hazards**

- CH$_3$OH is a clear, colorless liquid with faint alcohol odor.

- Because it can readily enter the body by swallowing, skin absorption and inhalation, it should be handled as a poison.

- It cannot be made nonpoisonous.
Select Methanol Considerations

- Reacts vigorously with strong oxidizers, lead perchlorate, perchloric acids.

- Decomposition occurs from heat and reaction with above stated materials.

- Spark free tools should be used for maintenance.
## Properties of Chlorine Dioxide

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name</td>
<td>Chlorine Dioxide</td>
</tr>
<tr>
<td>Synonyms</td>
<td>Chlorine Peroxide, “Chlo-2”</td>
</tr>
<tr>
<td>Formula</td>
<td>ClO₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>67.5</td>
</tr>
<tr>
<td>Gas</td>
<td>Yellow-green to orange gas</td>
</tr>
<tr>
<td>Aqueous solution</td>
<td>Yellow-deep green</td>
</tr>
<tr>
<td>Odor</td>
<td>Sharp, pungent, acrid at as low as 0.1ppm</td>
</tr>
<tr>
<td>Specific Gravity (gas)</td>
<td>2.4 at 52°F (air = 1)</td>
</tr>
</tbody>
</table>

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Select Health Hazards of ClO$_2$

- ClO$_2$ will cause irritation of the eyes, nose, throat, and lungs.
- ClO$_2$ can affect the body if it is inhaled or if it comes in contact with the eyes or skin.
- Repeated exposure may cause chronic bronchitis and delayed onset of pulmonary edema.
- It will produce coughing, wheezing, and severe breathing difficulties which may be delayed in onset.
- Severe body interactions if swallowed.
ClO$_2$ Puffs

ClO$_2$ gas is unstable and decomposes readily to chlorine and oxygen

ClO$_2$ $\Rightarrow$ $\frac{1}{2}$Cl$_2$ + O$_2$ + 26.3 kcal/mole
(heat and steam)

The decomposition or “puff”, is exothermic and propagates through the gas at a rate proportional to the concentration of ClO$_2$ in the vessel.
Initiators of ClO$_2$ Puff

Decomposition of chlorine dioxide at low concentrations can be initiated by:

- Reactive metals, such as iron.
- An electric spark or static electricity occurs.
- A temperature rise above 212$^\circ$F.
- Organic contaminants, especially hydrocarbon greases, oils, and rubber.
- Dust and rust particles.
- Sunlight.
- Sudden pressure fluctuations.
Violence of a ClO$_2$ Puff

- When the partial pressure of ClO$_2$ is at 91mm or less, “puffs” are generally mild.
- The force of the “puff” increases with increase in partial pressure.
- The decompositions become much more violent as the ClO$_2$ partial pressure increases.
- Potentially damaging detonations can result at ClO$_2$ partial pressure greater than 190 mm.
- R8’s typical ClO$_2$ partial pressure before the condenser is 8 mm, after the condenser it is 56mm
Chemical Feed Contamination

- Chemical feeds are a major source of these undesirable impurities.

- Parts per million (ppm) of most oxidizable substances, particularly insoluble compounds, lower the decomposition temperature of ClO$_2$.

- The ClO$_2$ system then becomes less stable and more sensitive to “puffs”.

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Removal of Contaminants

Filtration

- Improves yield of the ClO$_2$.
- Reduces the cost.
- Increases the plant’s availability.
- Prevents violent destruction of the equipment.
- Protects personnel and the environment.
Processing Sulfuric Acid

Tank Truck → Filter → Transfer Pump → Acid Storage tank → Filter → To Generator
Foaming

- Some chemicals form fine solid suspensions with a high surface area and create and stabilize foam.
- The foam interferes with the mixing of the H$_2$SO$_4$, and floats solids to the gas liquid interface, an active and responsive region.
- The foam impedes the reaction of CH$_3$OH and reduces its contact time in the generator.
- Foam is controlled by continuous addition of defoamer tri butyl phosphate in the CH$_3$OH.
R8 ClO₂ Process

- Operated under vacuum for safety reasons

Diagram of the process flow:

- Salt Cake Dissolver
- Filter Feed
- Filter Separator
- Generator Crystallizer
- Reboiler
- Condensate
- Recirculation Pump
- Dump Tank
- NaClO₃
- Ejectors
- Water
- Chilled H₂O
- HP steam
- Chilled
- Cl₂O₂ Absorption Tower
- Indirect Contact Cooler
- Barometric condenser
- Sewer
- Seal pot
- ClO₂ Storage Tank
- VP Steam
- VP Condensate
- VP Recycle
- VP Cooling
- VP Water
- VP Ejectors
- VP Seal Pot

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In the R8 Water Vapor is Essential

- The presence of water vapour is the significant factor in avoidance of a violent ClO$_2$ decomposition.

- The ClO$_2$/H$_2$O ratio determines the system sensitivity to decomposition.

- The generator must be boiling prior to the addition of methanol and other chemicals.
## Chemical Reactions

**Reaction 1**

\[
3 \text{NaClO}_3 + \text{H}_2\text{SO}_4 + 0.85 \text{CH}_3\text{OH} \rightarrow 3\text{ClO}_2 \\
\text{Na}_3\text{H(SO}_4\text{)}_2 + 2.2\text{H}_2\text{O} + 0.06 \text{CH}_3\text{OH} + 0.52 \text{HCOOH} + 0.27\text{CO}_2
\]

**Reaction 2**

\[
3 \text{NaClO}_3 + 2 \text{H}_2\text{SO}_4 + 1.50 \text{CH}_3\text{OH} \rightarrow 1.5\text{ClO}_2 \\
0.75\text{Cl}_2 + \text{Na}_3\text{H(SO}_4\text{)}_2 + 4.5 \text{H}_2\text{O} + 1.5 \text{CO}_2
\]

**Reaction 3**

\[
3 \text{NaClO}_3 + 3 \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow 3\text{ClO}_2 \\
1.5 \text{Cl}_2 + \text{Na}_3\text{H(SO}_4\text{)}_2 + 3\text{H}_2\text{O}
\]
Chlorine Dioxide Rates of Reaction

The process reaction rate:

Rate of reaction $\propto [H^+]^{2.15}[\text{ClO}_3^-]^{1.14}[\text{CH}_3\text{OH}]^{1.12}$

Rate of reaction $\propto \text{Temperature}$

Methanol is the rate limiting step

➢ So no significant ClO$_2$ can be generated, if methanol is not added.
Impact of Acid and Chlorate on ClO2 Production

- Lower acidity and higher chlorate increase the conversion efficiency

- The reaction rates can be compared with
  \[
  \text{Rate of reaction } \propto [H^+]^{2.15} [\text{ClO}_3^-]^{1.14} [\text{CH}_3\text{OH}]^{1.12}
  \]
White Out

- At a combined normality and molarity >11, the chloride will be consumed faster than it can be produced.

- As a result, the ClO₂ generation will cease and "white smoke" will be produced.

- The reaction is restored when concentrations are restored by dilution with water.
Water Vapour Strips and Dilutes ClO₂

- Water vapour strips ClO₂ from the liquor and dilutes it to a safe concentration.

- The presence of water vapour is the factor in avoidance of a violent chlorine dioxide explosion.

- The generator must be boiling prior to the addition of methanol and other chemicals.
R8 Chlorine Dioxide Generation

1 Methanol
2 Acid
3 Steam
4 Condensate
5 Sodium Chlorate

Generator

Reboiler

Filter Feed
Filter Return

7 Generator Off-Gas
ClO$_2$ Explosion Relief

All chlorine dioxide generators and storage tanks are equipped with explosion lids, which will raise and relieve the pressure resulting from a puff.

For R8 chlorine dioxide plants:

- The chemical feeds are shut off at the first indication of a decomposition i.e. high gas pressure and or high gas temperature.

- Water is added to the generator liquor and air dilution is supplied to the generator gas space to quench, cool and dilute the decomposing chlorine dioxide.
Water Vapor Needs to Be Present

- The system pressure and chemical concentrations control the liquor boiling temperature.
- The presence of chemicals dissolved in the generator liquor elevates the boiling point of the liquor.
- The largest and most significant chemical concentration in the liquor is $\text{H}_2\text{SO}_4$. 
General Generator Operating Parameters

Generator Pressure: 105 mm Hg Abs.
Generator liquor temperature: 161°F
Level: 2-3 ft below return inlet
Percent Solids: 20-25%
Acid concentration: 8.1N +0.1N (390 g/L)
Chlorate concentration: 2.0M (235 g/L)
Chloride concentration: 0.2 M (1.2 g/L)
ClO₂ solution concentration: 11.0 ClO₂ g/L
# Impact of Condensing Water Vapour

<table>
<thead>
<tr>
<th>Exit temperature °F</th>
<th>Water partial pressure</th>
<th>ClO₂ partial pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>66</td>
<td>54</td>
</tr>
<tr>
<td>90</td>
<td>36</td>
<td>84</td>
</tr>
<tr>
<td>60</td>
<td>13</td>
<td>107</td>
</tr>
</tbody>
</table>

- As the exit temperature is lowered there is a significant increase in the ClO₂ partial pressure.
- The sensitivity to decomposition increases with increasing ClO₂ partial pressure.
- It is important that the water spray is clean.
Chlorine Dioxide Storage Tank

Safe storage of ClO₂ solution

- Sweep Air reduces ClO₂ gas concentration to vent scrubber
- Seal Water prevents ClO₂ gas escape and air leaking in
- Tank is insulated
- Sealed Sewer
- Explosion Hatch
- Vent gases to Scrubber
- From ClO₂ Dioxide Absorber
- To Bleach Plant

11g/L ClO₂ @52 °F

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# ClO₂ Chemical Usage

## Chemical usage for R8 ClO₂ processes

<table>
<thead>
<tr>
<th>Feeds</th>
<th>ton/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₃</td>
<td>1.66</td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.15</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>1.05</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>By-products</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>0.04</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.15</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1.26</td>
</tr>
</tbody>
</table>
ClO$_2$