

**Overview of ClO_2
Generation Chemistry
For Pulp and Paper Industry**

ClO₂ Introduction

Chlorine dioxide (ClO₂) 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:**



➤ **ClO₂ is made as a gas and absorbed in chilled water to produce a solution concentration ranging from 8 to 10 g/L.**

ClO₂ Related Chemicals

Chemical	Symbol	Common Name
Sodium Chlorate	Na ClO₃	Chlorate
Sodium Chloride	Na Cl	Salt
Sulfuric Acid	H₂SO₄	Sulfuric acid
Methyl Alcohol	CH₃OH	Methanol
Chlorine Dioxide	ClO₂	Chlorine dioxide, chloe two
Chlorine	Cl₂	Chlorine
Sodium sesqui sulfate	Na₃H(SO₄)₂	Saltcake
Sodium Hydroxide	Na OH	Caustic
DEC	NaSH	DEC

Basic R8 Generation Chemistry



General ClO₂ Chemical Usage

Chemicals	Ton/ton of ClO ₂
NaClO ₃	1.85
NaCl	0.02
H ₂ SO ₄	2.35
CH ₃ OH	0.187
Cl ₂	0.06
NaSO ₄	1.2
H ₂ SO ₄	1.68

Properties of Sulfuric Acid

Solubility	100%
Sp.Gr. at 50°F	1.835
Density at 50°F lb./gal	15.3
Freezing Point	-31°F
Boiling Point 760 mm Hg	534°F
Viscosity cP @ 68°F	22

Chemical Properties of H₂SO₄

- **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 H₂SO₄

- **H₂SO₄ is stable but reacts violently with water and organic materials with evolution of heat.**
- **H₂SO₄ chars organic substances on contact which results in the formation of carbon.**
- **H₂SO₄ attacks most common metals.**
- **However, for acid at commercial strengths, carbon steel or stainless steel is generally satisfactory.**

Sodium Chlorate NaClO_3

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_3OH 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

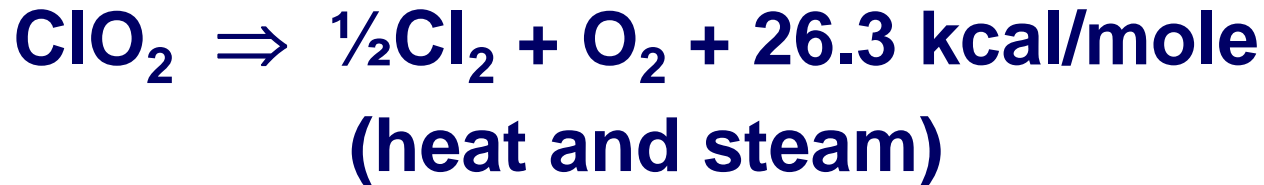
Chemical name:	Chlorine Dioxide
Synonyms:	Chlorine Peroxide, “Chlo-2”
Formula:	ClO₂
Molecular weight:	67.5
Gas:	Yellow-green to orange gas
Aqueous solution:	Yellow-deep green
Odor:	Sharp, pungent, acid at as low as 0.1ppm
Specific Gravity (gas):	2.4 at 52°F (air = 1)

Select Health Hazards of ClO₂

- ClO₂ will cause irritation of the eyes, nose, throat, and lungs.
- ClO₂ 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.

ClO₂ Puffs

ClO₂ gas is unstable and decomposes readily to chlorine and oxygen



The decomposition or “puff”, is exothermic and propagates through the gas at a rate proportional to the concentration of ClO₂ in the vessel.

Initiators of ClO₂ 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°F.
- Organic contaminants, especially hydrocarbon greases, oils, and rubber.
- Dust and rust particles.
- Sunlight.
- Sudden pressure fluctuations.

Violence of a ClO₂ Puff

- When the partial pressure of ClO₂ 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 ClO₂ partial pressure increases.
- Potentially damaging detonations can result at ClO₂ partial pressure greater than 190 mm.
- R8’s typical ClO₂ partial pressure before the condenser is 8 mm, after the condenser it is 56mm

Chemical Feed Contamination

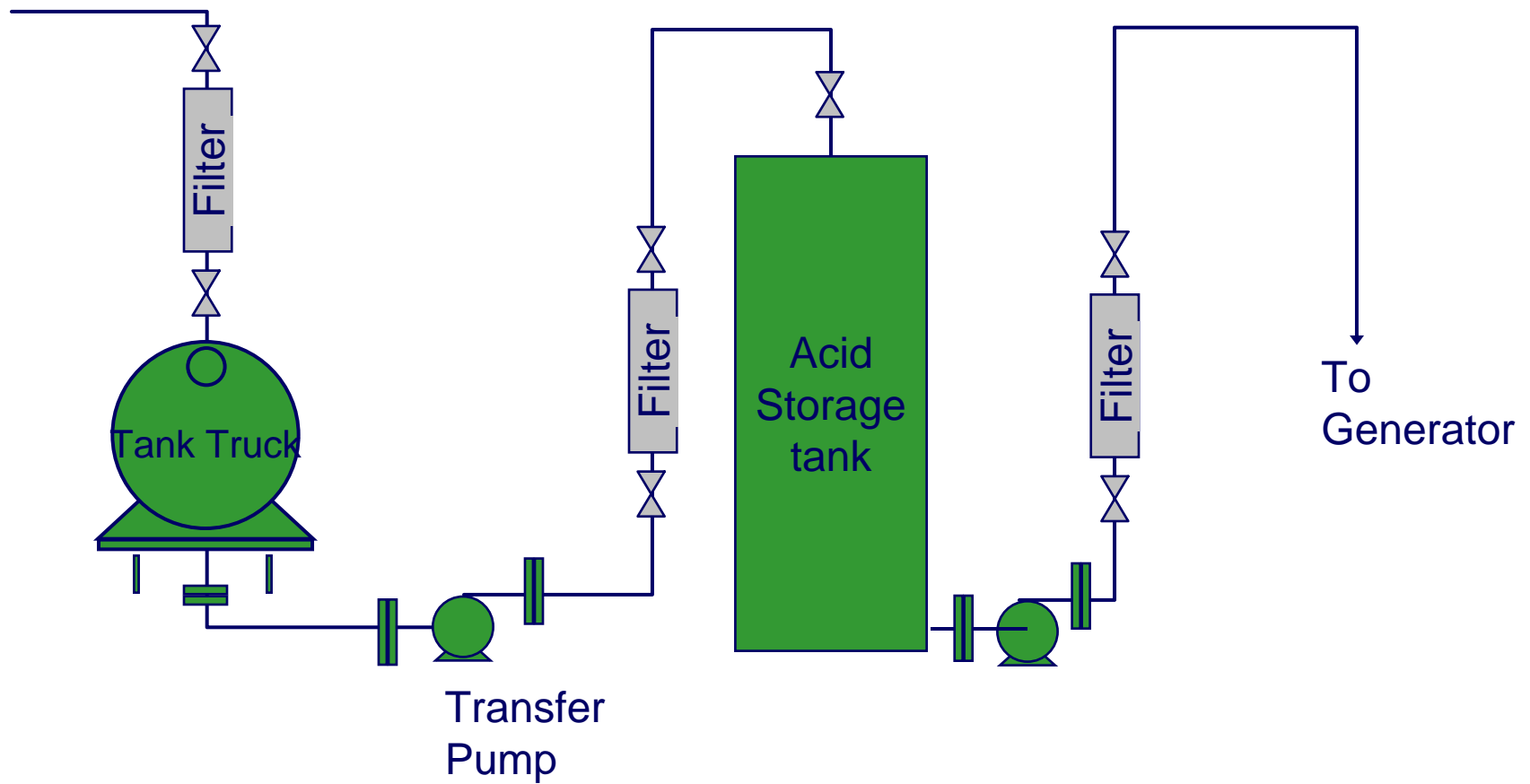
- Chemical feeds are a major source of these undesirable impurities.
- Parts per million (ppm) of most oxidizable substances, particularly insoluble compounds, lower the decomposition temperature of ClO_2 .
- The ClO_2 system then becomes less stable and more sensitive to “puffs”.

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

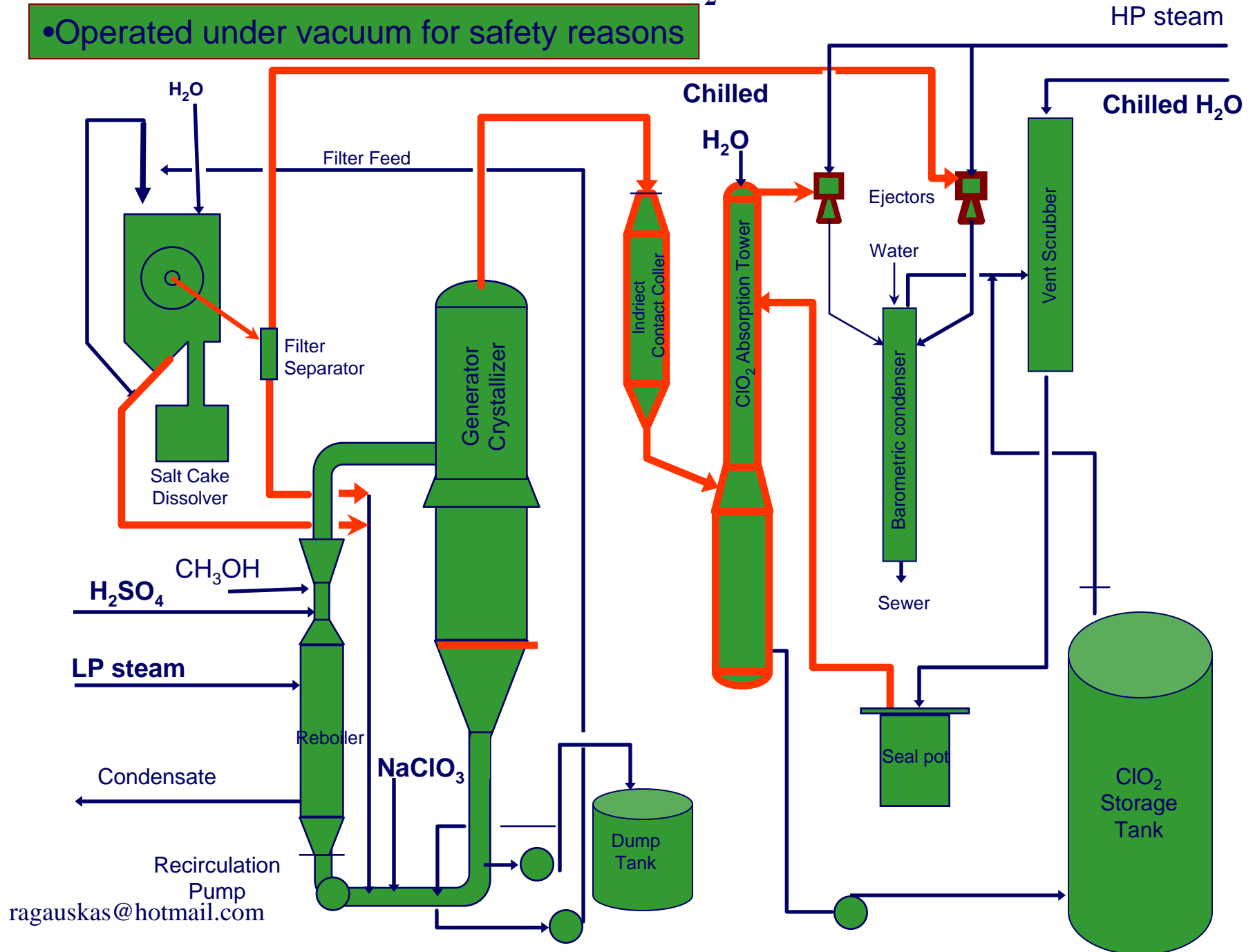


Foaming

- **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_2SO_4 , and floats solids to the gas liquid interface, an active and responsive region.**
- **The foam impedes the reaction of CH_3OH and reduces its contact time in the generator**
- **Foam is controlled by continuous addition of defoamer tri butyl phosphate in the CH_3OH .**

R8 ClO₂ Process

• Operated under vacuum for safety reasons

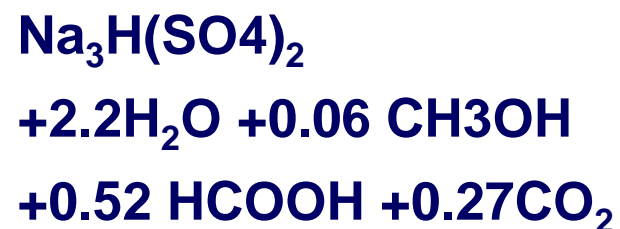


In the R8 Water Vapor is Essential

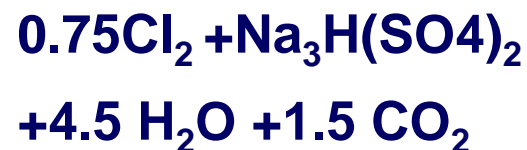
- The presence of water vapour is the significant factor in avoidance of a violent ClO_2 decomposition.
- The $\text{ClO}_2/\text{H}_2\text{O}$ ratio determines the system sensitivity to decomposition.
- The generator must be boiling prior to the addition of methanol and other chemicals.

Chemical Reactions

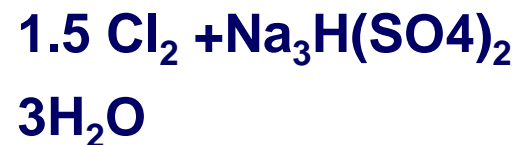
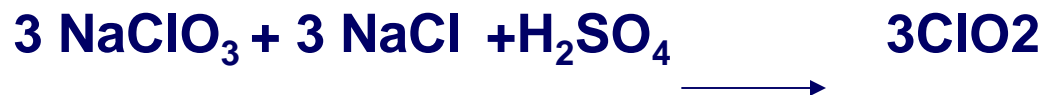
Reaction 1



Reaction 2



Reaction 3



Chlorine Dioxide Rates of Reaction

The process reaction rate:

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

$$[\text{Acid}]^{2.15}[\text{Chlorate}]^{1.14}[\text{Methanol}]^{1.12}$$

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

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

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

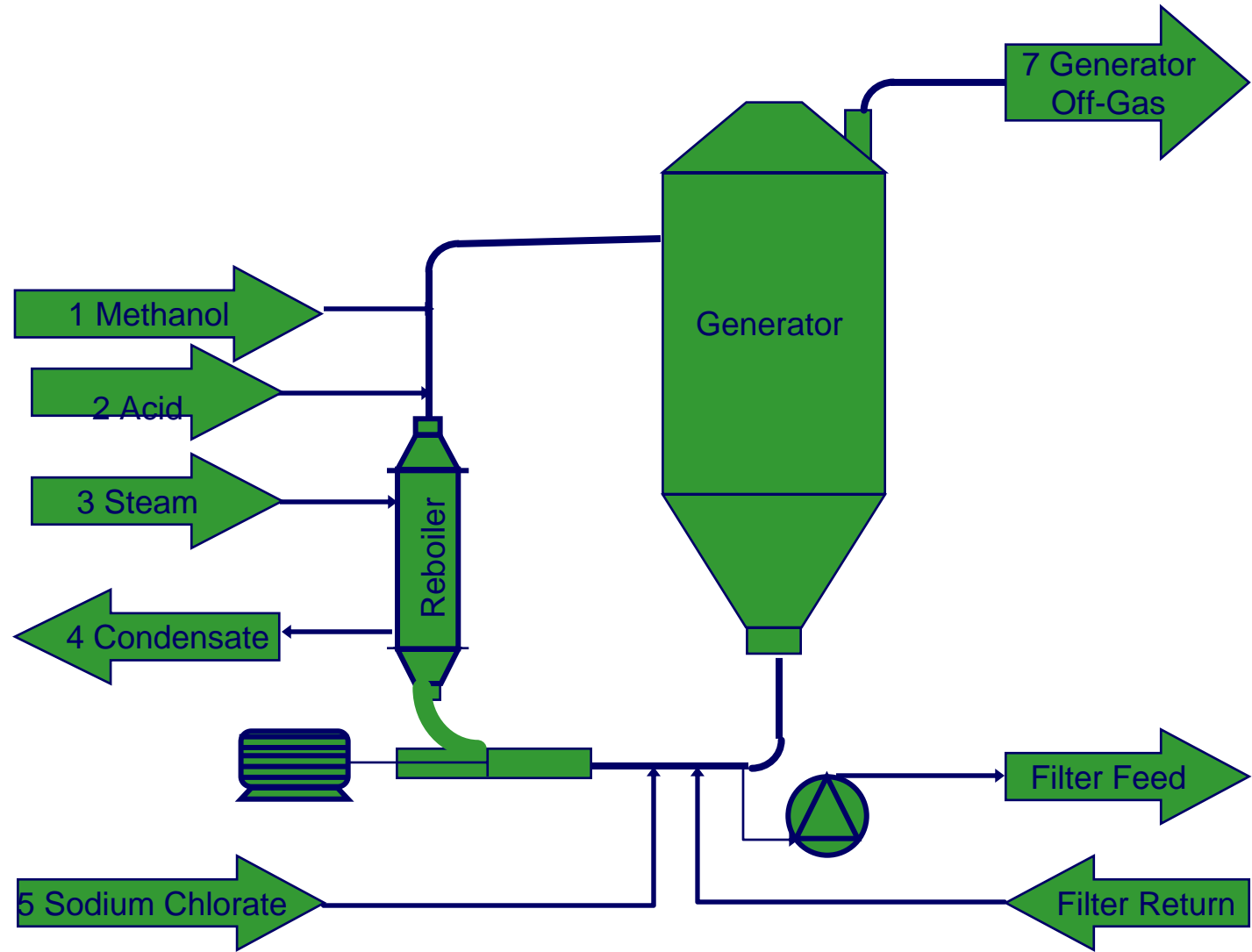
White Out

- At a combined normality and molarity >11 , the chloride will be consumed faster than it can be produced.
- As a result, the ClO_2 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



ClO₂ 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 H_2SO_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

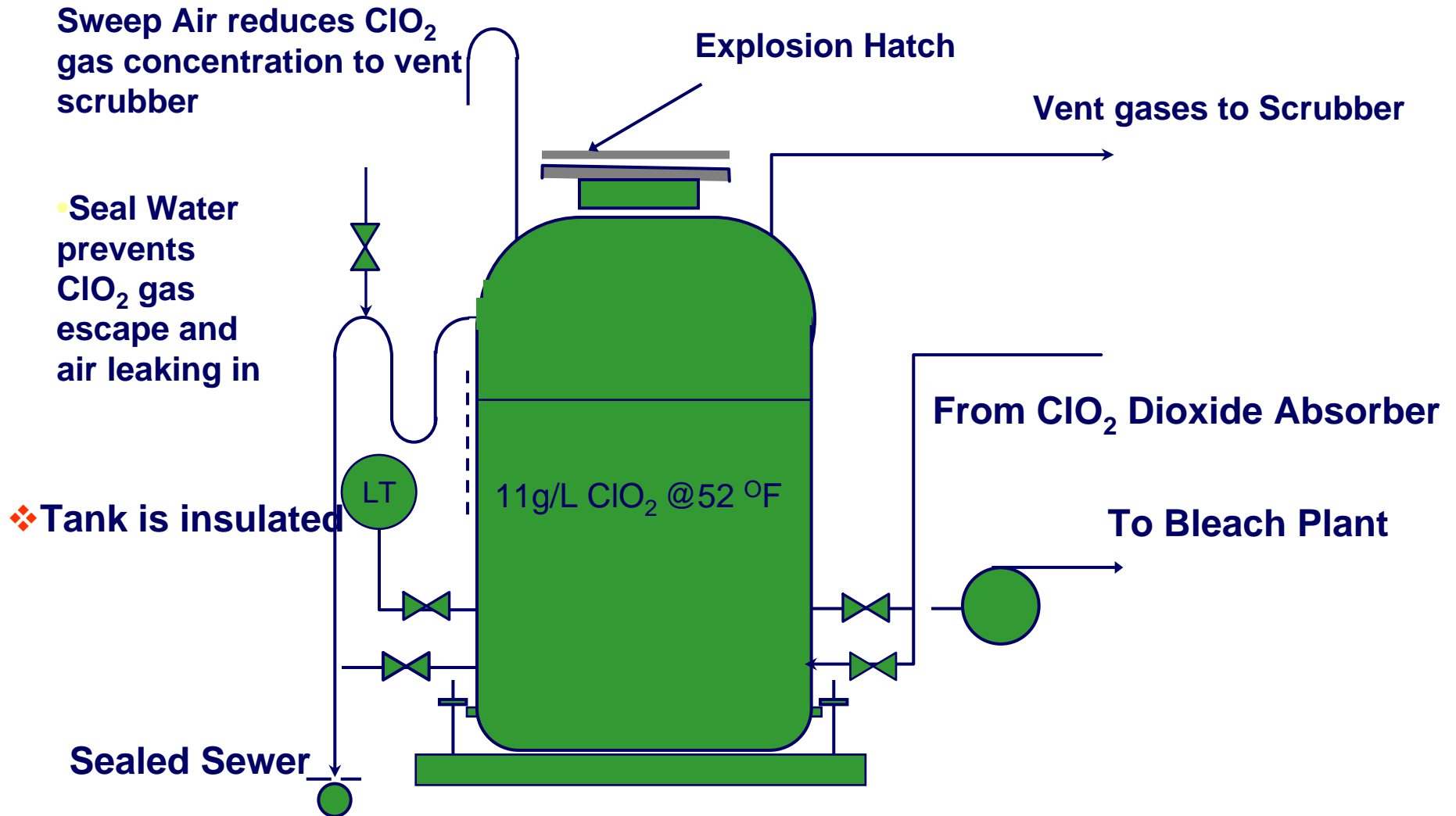
Impact of Condensing Water Vapour

Exit temperature °F	Water partial pressure	ClO ₂ partial pressure
110	66	54
90	36	84
60	13	107

- 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 ClO_2 solution



ClO₂ Chemical Usage

~Chemical usage for R8 ClO ₂ processes	
Feeds	ton/ton
NaClO ₃	1.66
NaCl	
CH ₃ OH	0.15
H ₂ SO ₄	1.05
NaOH	0.20
By-products	
Cl ₂	0.04
H ₂ SO ₄	0.15
Na ₂ SO ₄	1.26

