

## Clo2 Generator

### Chlorine Dioxide Chemistry

- Chlorine dioxide (ClO<sub>2</sub>) is a neutral compound of chlorine in the +IV oxidation state.
- It disinfects by oxidation; however, it does not chlorinate.
- It is a relatively small, volatile, and highly energetic molecule, and a free radical even while in dilute aqueous solutions. At high concentrations, it reacts violently with reducing agents. However, it is stable in dilute solution in a closed container in the absence of light (AWWA, 1990).
- Chlorine dioxide functions as a highly selective oxidant due to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO<sub>2</sub><sup>-</sup>) (Hoehn et al., 1996).
- The pK<sub>a</sub> for the chlorite ion, chlorous acid equilibrium, is extremely low at pH 1.8. This is remarkably different from the hypochlorous acid/hypochlorite base ion pair equilibrium found near neutrality, and indicates the chlorite ion will exist as the dominant species in water
- The Oxidation Reduction reactions are as under;  
$$\text{ClO}_2(\text{aq}) + \text{e}^- = \text{ClO}_2^-$$
$$\text{ClO}_2^- + 2\text{H}_2\text{O} + 4\text{e}^- = \text{Cl}^- + 4\text{OH}^-$$
$$\text{ClO}_3^- + \text{H}_2\text{O} + 2\text{e}^- = \text{ClO}_2^- + 2\text{OH}^-$$
$$\text{ClO}_3^- + 2\text{H}^+ + \text{e}^- = \text{ClO}_2 + \text{H}_2\text{O}$$

### Physical Properties of ClO<sub>2</sub>

- Highly soluble in water
- In contrast to the hydrolysis of chlorine gas in water, chlorine dioxide in water does not hydrolyze to any appreciable extent but remains in solution as a dissolved gas.
- It is approximately 10 times more soluble than chlorine (above 11°C), while it is extremely volatile and can be easily removed from dilute aqueous solutions with minimal aeration or recarbonation with carbon dioxide.
- Chlorine dioxide cannot be compressed or stored commercially as a gas because it is explosive under pressure. Therefore, it is never shipped. Chlorine dioxide is considered explosive at higher concentrations which exceed 10 percent by volume in air, and its ignition temperature is about 130°C (266°F) at partial pressures (National Safety Council Data Sheet 525 – ClO<sub>2</sub>, 1967).

## CLO<sub>2</sub> Generation

- Chlorine dioxide can be formed by sodium chlorite reacting with gaseous chlorine (Cl<sub>2</sub>(g)), hypochlorous acid (HOCl), or hydrochloric acid (HCl).
- $2\text{NaClO}_2 + \text{Cl}_2(\text{g}) = 2\text{ClO}_2(\text{g}) + 2\text{NaCl}$
- $2\text{NaClO}_2 + \text{HOCl} = 2\text{ClO}_2(\text{g}) + \text{NaCl} + \text{NaOH}$
- $5\text{NaClO}_2 + 4\text{HCl} = 4\text{ClO}_2(\text{g}) + 5\text{NaCl} + 2\text{H}_2\text{O}$

Generator Type	Reactants, byproducts, key reactions and chemistry notes	Special Attributes
ACID-CHLORITE: (Direct Acid System)	$4\text{HCl} + 5\text{NaClO}_2 \rightarrow 4\text{ClO}_2(\text{aq}) + \text{ClO}_3^-$ <ul style="list-style-type: none"> <li>○ Low pH</li> <li>○ ClO<sub>3</sub><sup>-</sup> possible</li> <li>○ Slow reaction rates</li> </ul>	<ul style="list-style-type: none"> <li>○ Chemical feed pump interlocks required.</li> <li>○ Production limit ~ 25-30 lb/day.</li> <li>○ Maximum yield at ~ 80% efficiency.</li> </ul>
AQUEOUS CHLORINE CHLORITE: (Cl <sub>2</sub> gas ejectors with chemical pumps for liquids or booster pump for ejector water).	$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow [\text{HOCl}/\text{HCl}]$ $[\text{HOCl}/\text{HCl}] + \text{NaClO}_2 \rightarrow \text{ClO}_2(\text{g}) + \text{H}/\text{OCl}^- + \text{NaOH} + \text{ClO}_3^-$ <ul style="list-style-type: none"> <li>○ Low pH</li> <li>○ ClO<sub>3</sub><sup>-</sup> possible</li> <li>○ Relatively slow reaction rates</li> </ul>	<ul style="list-style-type: none"> <li>○ Excess Cl<sub>2</sub> or acid to neutralize NaOH.</li> <li>○ Production rates limited to ~ 1000 lb/day.</li> <li>○ High conversion but yield only 80-92%</li> <li>○ More corrosive effluent due to low pH (~2.8-3.5).</li> <li>○ Three chemical systems pump HCl, hypochlorite, chlorite, and dilution water to reaction chamber.</li> </ul>
GASEOUS CHLORINE CHLORITE: (Gaseous Cl <sub>2</sub> and 25% solution of sodium chlorite; pulled by ejector into the reaction column.)	$\text{Cl}_2(\text{g}) + \text{NaClO}_2(\text{aq}) \rightarrow \text{ClO}_2(\text{aq})$ <ul style="list-style-type: none"> <li>○ Neutral pH</li> <li>○ Rapid reaction</li> <li>○ Potential scaling in reactor under vacuum due to hardness of feedstock.</li> </ul>	<ul style="list-style-type: none"> <li>○ Production rates 5-120,000 lb/day.</li> <li>○ Ejector-based, with no pumps. Motive water is dilution water. Near neutral pH effluent. No excess Cl<sub>2</sub>. Turndown rated at 5-10X with yield of 95-99%. Less than 2% excess Cl<sub>2</sub>. Highly calibrated flow meters with min. line pressure ~ 40 psig needed.</li> </ul>

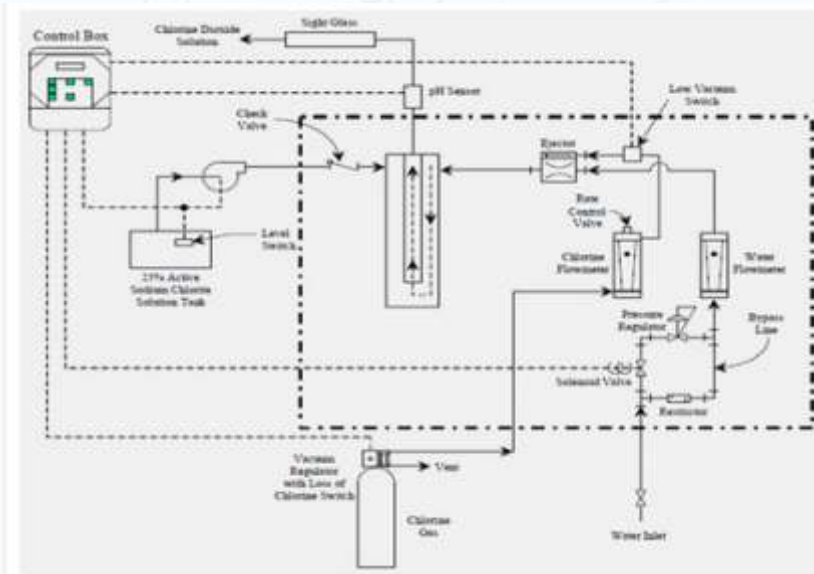
## Proposals

- Sodium Chlorite Solution-31% + HCL – 33% (2 Chemical based system)
- Chlorine Gas + Sodium Chlorite Solution (25%)

## Base

- 25 Kg/hr Capacity – 2 nos. (1W + 1 S)
- Required dose: - 2 ppm of ClO<sub>2</sub>
- Residual ClO<sub>2</sub> – 0.8 ppm

## Option 1:- Conventional ClO<sub>2</sub> Generator (Chlorine – Chlorite Method)



**Base: - 25 Kg/hr Capacity of ClO<sub>2</sub> generation**

**Chemicals (input) requirement:-**

- NaClO<sub>2</sub> (25% Conc.) – 134 Kg/hr  
or
- NaClO<sub>2</sub> (31% Conc.) – 108.12 Kg/hr
- Chlorine gas – 13.15 Kg/hr

**Major Components**

- Chlorinator (Chlorine gas based vacuum feed chlorinator)
- Chlorine gas handling system
- Sodium Chlorite Storage and handling system
- ClO<sub>2</sub> generator
- ClO<sub>2</sub> feeding piping and dispersion equipment's

**Capital Cost (in Rs.) - Tentative**

**Recurring Cost (in Rs.) - Tentative**