Alternative Technologies - Chlorine Dioxide

Technology Overview-

- Chemistry of Disinfection
- Areas of Consideration
- Chlorine Dioxide Generation Technologies
- Potential Byproduct Formation
- Limitations of the Technology

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Introduction - Chlorine Dioxide

First used in beginning of 20th century, Ostend Belgium.

Known powerful water disinfectant, implemented to water disinfection in 1950’s

Approximately 700-900 installations in water treatment.

Does not react with organics in the same way chlorine does.

Introduction -Chlorine Dioxide

Major Uses -

Enhance CT Disinfection Credit.

Preoxidant for taste and odour control.

Control of Iron and Manganese

Control hydrogen sulfide and phenolic compounds

Introduction - Chlorine Dioxide

Chlorine Dioxide can not be stored as a gas or in liquid form, so it must be generated on site.

Chlorine Dioxide can be an explosive gas at concentrations above 10% by volume.

Chemistry of Disinfection - Chlorine Dioxide

Chlorine Dioxide disinfects by oxidation, and not substitution as with chlorine.

Thus chlorine dioxide does not form THM DBPs, or HAA5 compounds.

Chlorine Dioxide is very unstable at high concentrations, and reacts violently at concentrations above 30 g/l or 3%.

The molecule, oxidizes other compounds and forms the Chlorite ion which can subsequently reduce to Chlorate and Chloride.

Applications - Chlorine Dioxide

Chlorine Dioxide can be used as a primary or a secondary disinfectant as it does carry residual capabilities

- Effects of using Chlorine Dioxide
  - CT enhancement in primary disinfection.
  - Primary disinfection to prevent the formation of THMs and HAA5 compounds.
  - Taste and Odour control
  - Oxidation of Iron and Manganese

Applications - Chlorine Dioxide

Disinfection-

Consideration must be given to the overall demand of chlorine dioxide accounting for -

Seasonal Variability
Temperature
Application Point

Applications - Chlorine Dioxide

Limits are set for Chlorine Dioxide and for Chlorite Levels in drinking water.

Following the principal modes of disinfection, typically 70% of the initial dose of chlorine dioxide is converted to chlorite.

Thus the initial dosage of chlorine dioxide should not exceed 1.4 ppm to prevent exceeding DBP formation.

Guidelines for Chlorite formation - 1.0 ppm

Applications - Chlorine Dioxide

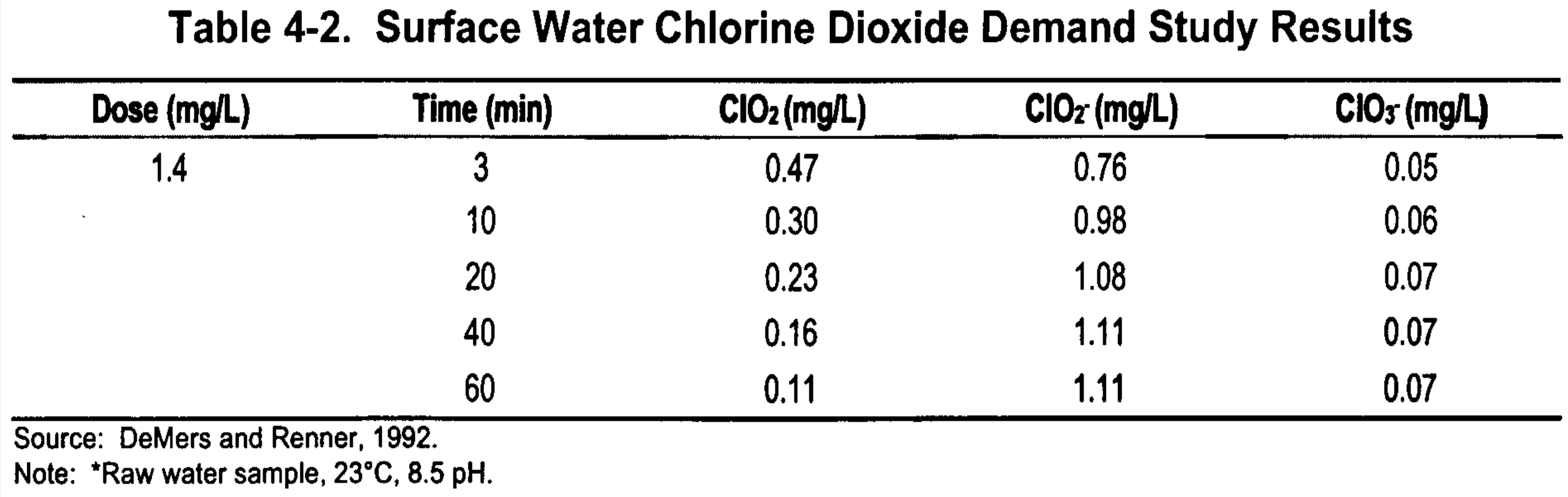


Table 4-2. Surface Water Chlorine Dioxide Demand Study Results

Dose (mg/L)	Time (min)	ClO_2 (mg/L)	ClO_2^- (mg/L)	ClO_3^- (mg/L)
1.4	3	0.47	0.76	0.05
	10	0.30	0.98	0.06
	20	0.23	1.08	0.07
	40	0.16	1.11	0.07
	60	0.11	1.11	0.07

Source: DeMers and Renner, 1992.
Note: *Raw water sample, 23°C, 8.5 pH.

Applications - Chlorine Dioxide

Taste and Odour Control-

Common application as taste and odours present from decaying plant material (algae) are destructed by chlorine dioxide.

Also capable of controlling the phenolic compounds that contribute to taste and odour problems

Taste and odour application points can typically be made after initial sedimentation or at the beginning of the plant is turbidity is low < 10 NTU.

Applications - Chlorine Dioxide

Oxidation of Iron and Manganese-

Chlorine Dioxide reduces to Chlorite when oxidizing iron and manganese.

Iron Oxidation - 1.2 mg / mg Iron

Manganese Oxidation - 2.5 mg / mg Manganese

Sulphite Reduction - 5.8 mg / mg H_2S

Important to realize the byproduct formation rules only allow for limited removal of these compounds without removing chlorite.

Applications - Chlorine Dioxide

Parameters effecting disinfection (pH)-

No effect of pH on disinfection ability, unlike chlorine.

Studies have demonstrated variations on the effectiveness of chlorine dioxide, but to what degree is still uncertain.

Studies done have shown as pH increases the relative strength increased against giardia, cryptosporidium and viruses.

Applications - Chlorine Dioxide

Parameters effecting disinfection (Temperature)-

Disinfection capability decreases with decrease of temperature.

Changes in temperature to below 4° C can have a great effect on the ability to disinfect as at this point chlorine dioxide exists as a dissolved liquid and diffusion through the fluid is slower.

Applications - Chlorine Dioxide

Parameters effecting disinfection (Suspended Material)-

Suspended and colloidal material greatly effects the disinfection ability of chlorine dioxide.

Particles can hide bacteria from disinfection.

Can increase the required CT by up to 3X depending on the micro-organism and the actual turbidity.

Applications - Chlorine Dioxide

Typical Dosages Required for Treatment-

Iron Removal - 1.2 mg / mg iron - immediate

Manganese Removal - 2.5 mg / mg manganese - immediate

Sulfide Removal - 5.8 mg / mg H_2S

Taste and Odour - 1 - 2.5 mg/L 10 minutes contact time

Bacteria Inactivation - 1 to 5 mg/L 5 minutes contact time

Giardia - 1.5 to 2.0 ppm 60 minutes contact time

Cryptosporidium - Approx 8-16 times giardia

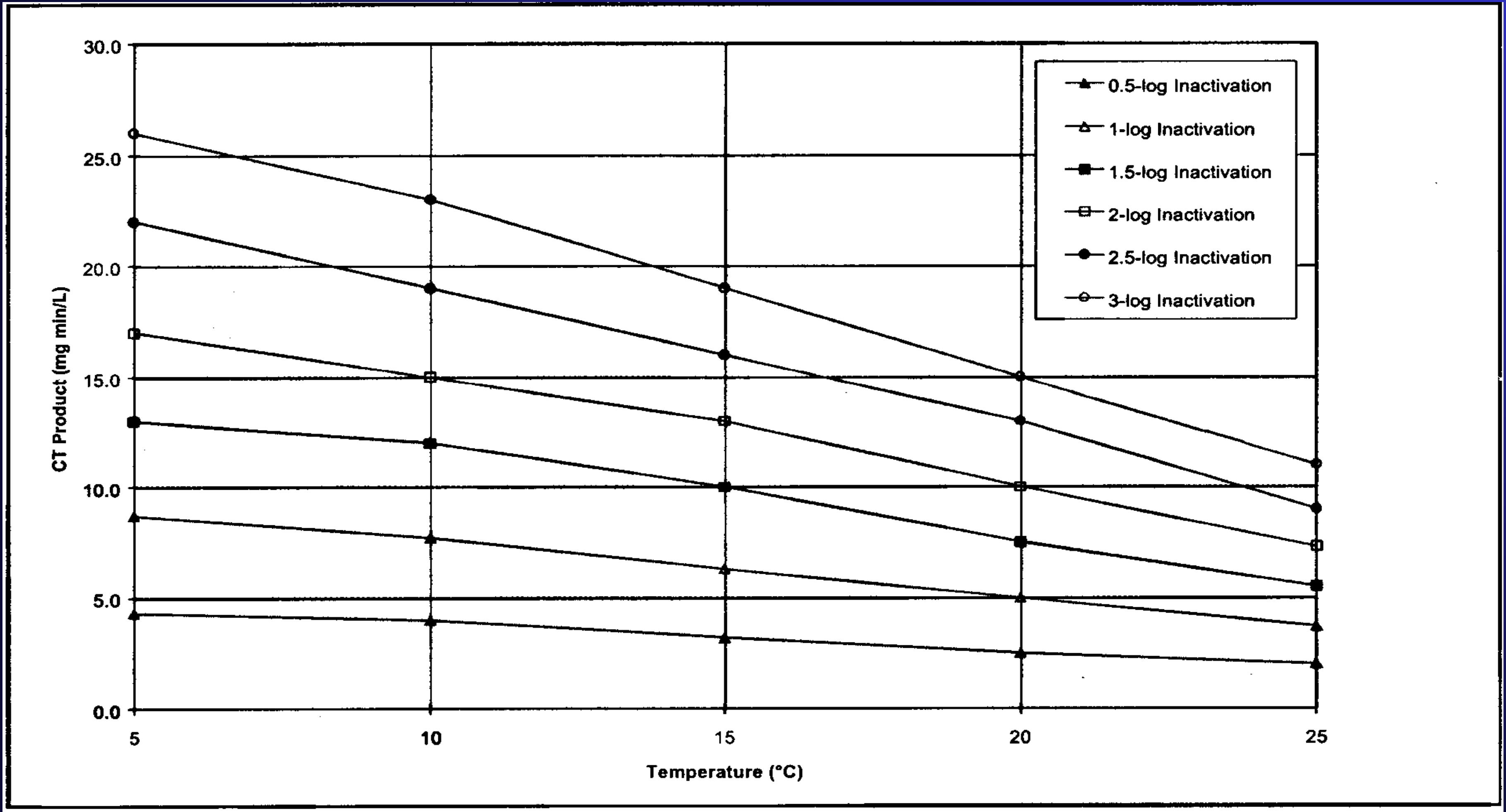
Applications - Chlorine Dioxide

CT Value Enhancement-

Chlorine Dioxide has been studied extensively to provide CT values for viral, bacterial and protozoan removal.

CT studies have shown proof that chlorine dioxide can be used to increase the credit given for removal of these pathogens.

Applications - Chlorine Dioxide



Source: AWWA, 1991.

Figure 4-5. CT Values for Inactivation of *Giardia* Cysts by Chlorine Dioxide

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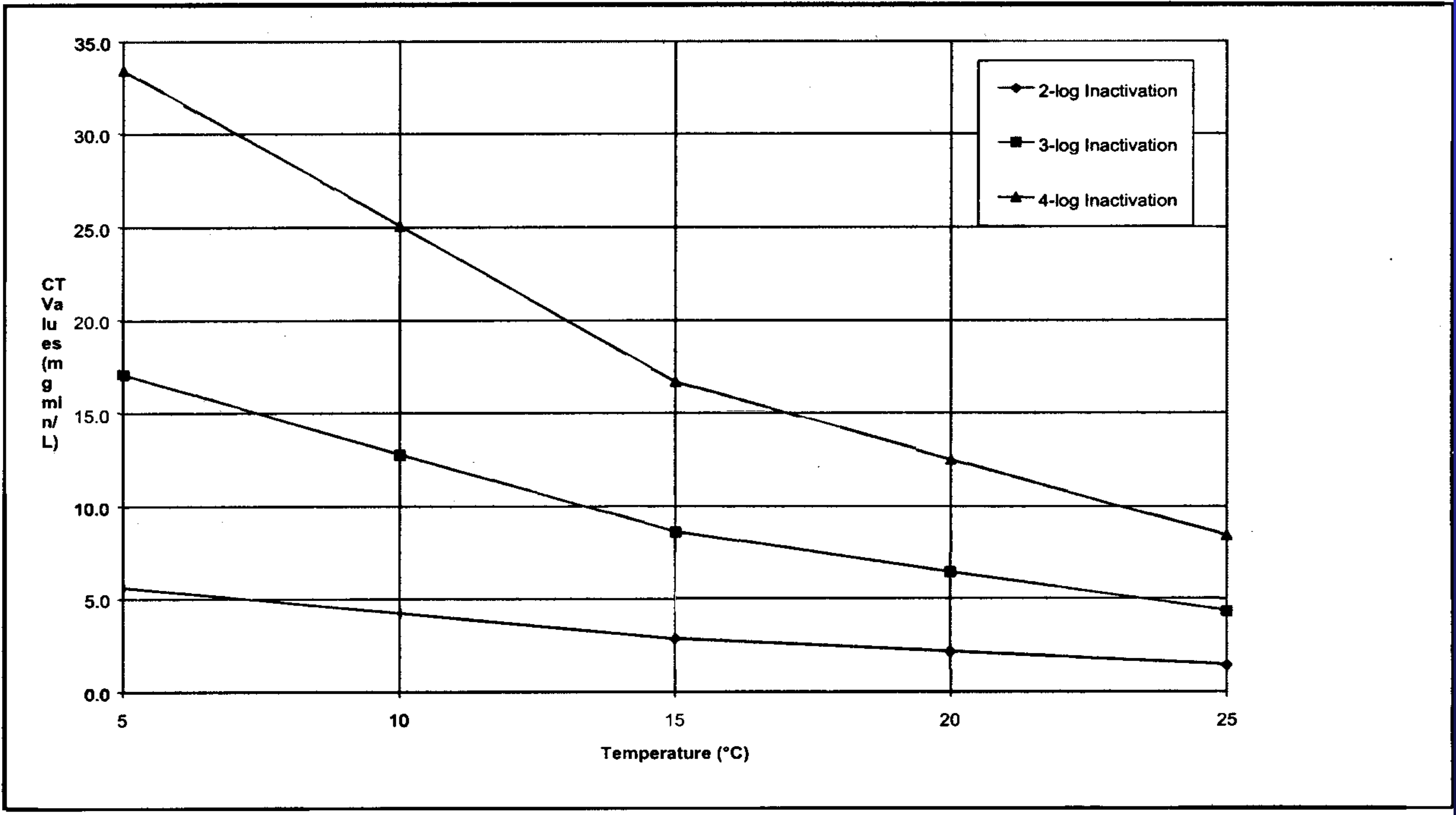
Applications - Chlorine Dioxide



Source: AWWA, 1991.

Figure 4-6. CT Values for Inactivation of Viruses by Chlorine Dioxide

Generation Technologies - Chlorine Dioxide

Chlorine Dioxide can not be stored for long periods of time and its reactivity when concentrated does not allow it to be transported.

Generation on site occurs through one of the following methods:

- Acid / Chlorite Combination - Two Chemical
- Electrolytic Membrane System - One Chemical
- Chlorine Gas Method - Three Chemical

Generation Technologies - Chlorine Dioxide

Acid / Chlorite Method.

The two chemical acid / chlorite method is commonly used for small to medium size requirements.

Feeds up to 10 kg / hour can be attained from this process. - 48 MLPD at 1.4 ppm.

The two chemicals used for generation are Sodium Chlorite and Hydrochloric Acid.

Generation Technologies - Chlorine Dioxide

Acid / Chlorite Method.

Sodium chlorite can be supplied in two concentrations. 25% and 7.5%, depending on the generation rate required.

Acid solution is also supplied at two concentrations, 32% and 9% to correspond to the sodium chlorite solution.

Generation Technologies - Chlorine Dioxide

Acid / Chlorite Method.

Sodium chlorite can be supplied in two concentrations. 25% and 7.5%, depending on the generation rate required.

Acid solution is also supplied at two concentrations, 32% and 9% to correspond to the sodium chlorite solution.

$$5\ NaClO_2 + 4\ HCl \text{ ---> } 4\ ClO_2 + 2\ H_2O + 5\ NaCl$$

Generation Technologies - Chlorine Dioxide

Acid / Chlorite Method.

Sodium chlorite can be supplied in two concentrations. 25% and 7.5%, depending on the generation rate required.

Acid solution is also supplied at two concentrations, 32% and 9% to correspond to the sodium chlorite solution.

No secondary storage is required - thus no intermediate decomposition of chlorine dioxide to chlorite.

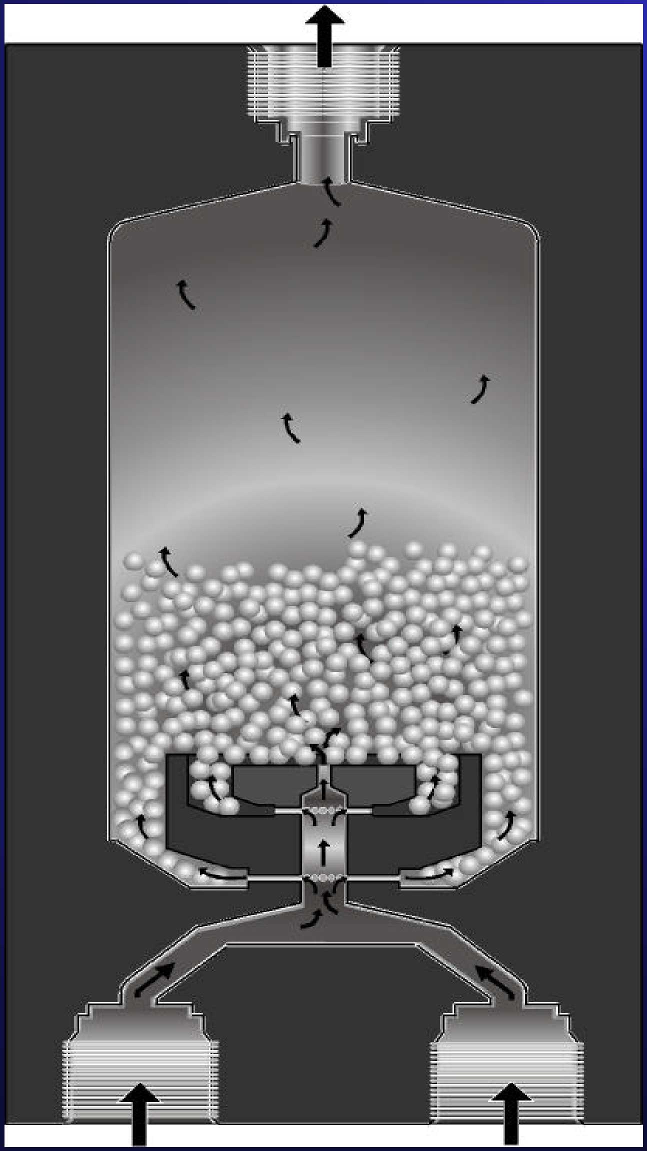
Generation Technologies - Chlorine Dioxide

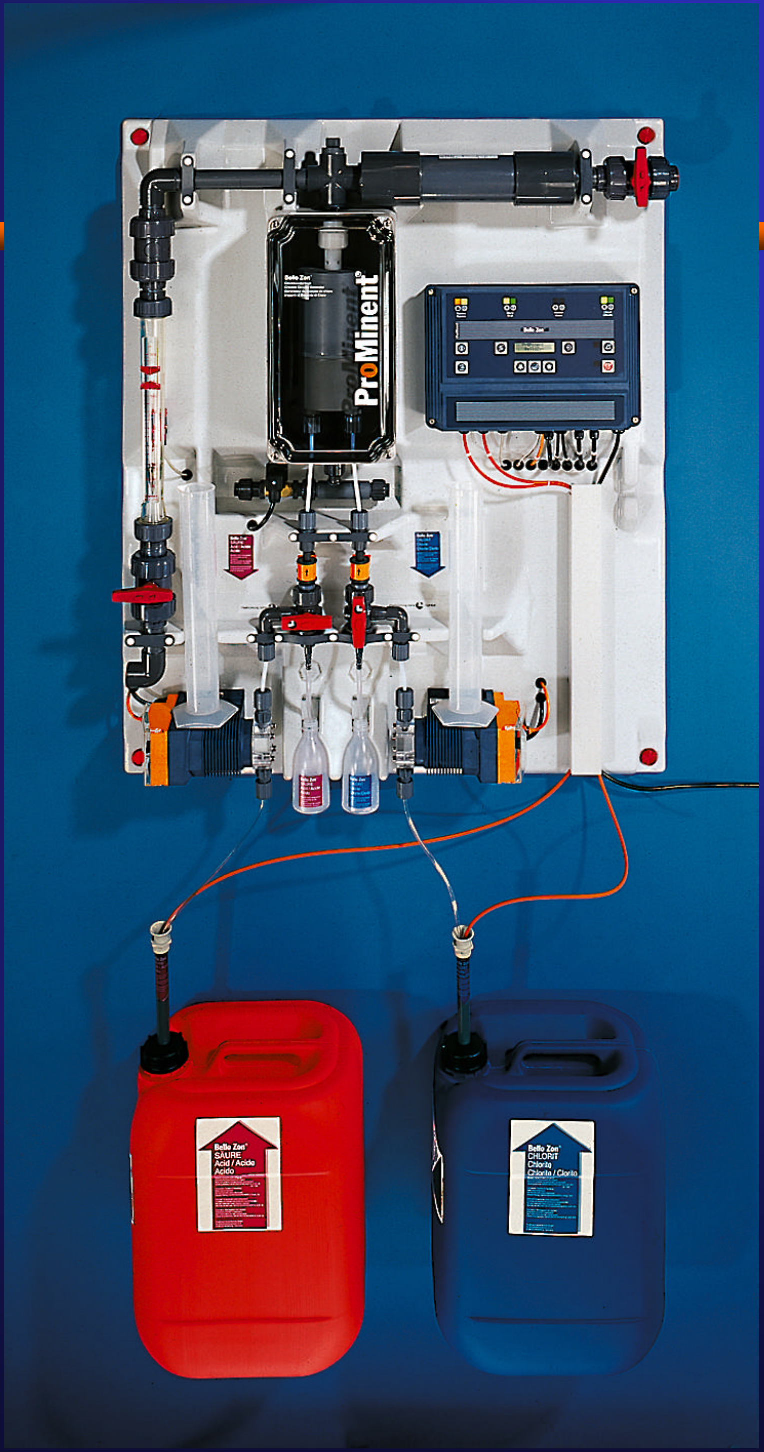
Acid / Chlorite Method.

System reaction is easy to control. The mechanism for feeding the stock solutions to the process are monitored to maintain a consistent ratio of chemicals.

This ratio guarantees a production rate of a 2% solution in liquid form. This liquid is below explosive strengths.

Generation Technologies - Chlorine Dioxide




ProMinent
Bello Zon
SÄURE
Acid / Acide
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Bello Zon
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Chlorite
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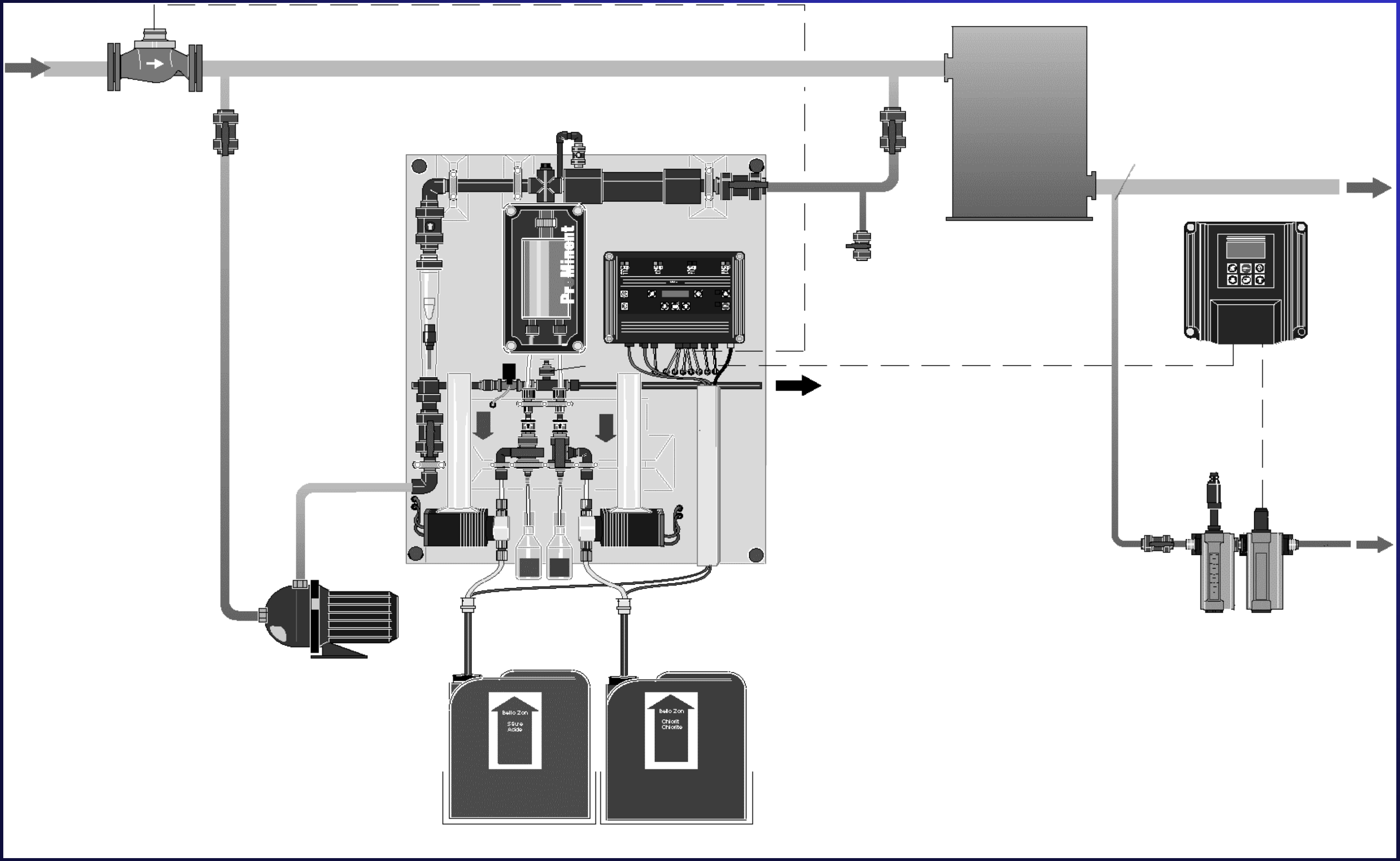
Generation Technologies - Chlorine Dioxide



Generation Technologies - Chlorine Dioxide

Acid / Chlorite / Sodium Hypo Method.

Utilizes similar reaction as Acid / Chlorite method, however also introduces liquid chlorine to the process.

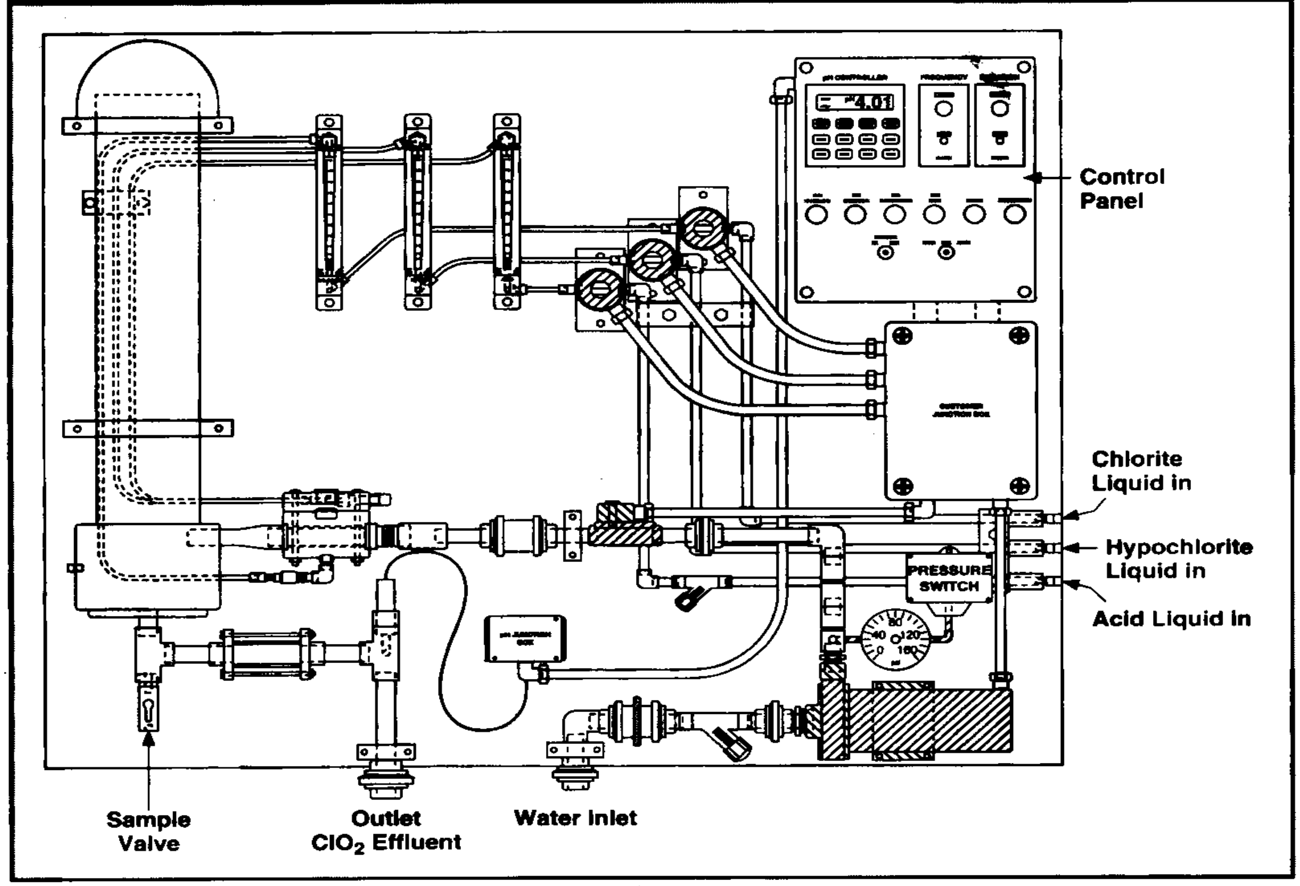
This liquid chlorine, if fed in excess can leave unreacted and as a result form THM and HAA5 compounds in the treatment process.

Reaction difficult to control to prevent byproduct formation.

Secondary Storage typically required.

Generation Technologies - Chlorine Dioxide

Figure 11
Three-Chemical System Generator



Generation Technologies - Chlorine Dioxide

Gaseous Chlorine Method

Stock chemicals are Sodium Chlorite and Chlorine Gas.

Chlorine reacts with the sodium chlorite under vacuum.

Chlorine Dioxide in concentration of 0.2 to 0.3 g/l leaves the generation system.

Generation Technologies - Chlorine Dioxide

Gaseous Chlorine Method

Method also prone to over feed of chlorine to the process, resulting in DBP formation.

$$2ClO_2^- + Cl_2 \text{ -----> } 2ClO_2 + 2Cl^-$$

Typically used in large applications for pulp and paper bleaching process.

Generation Technologies - Chlorine Dioxide

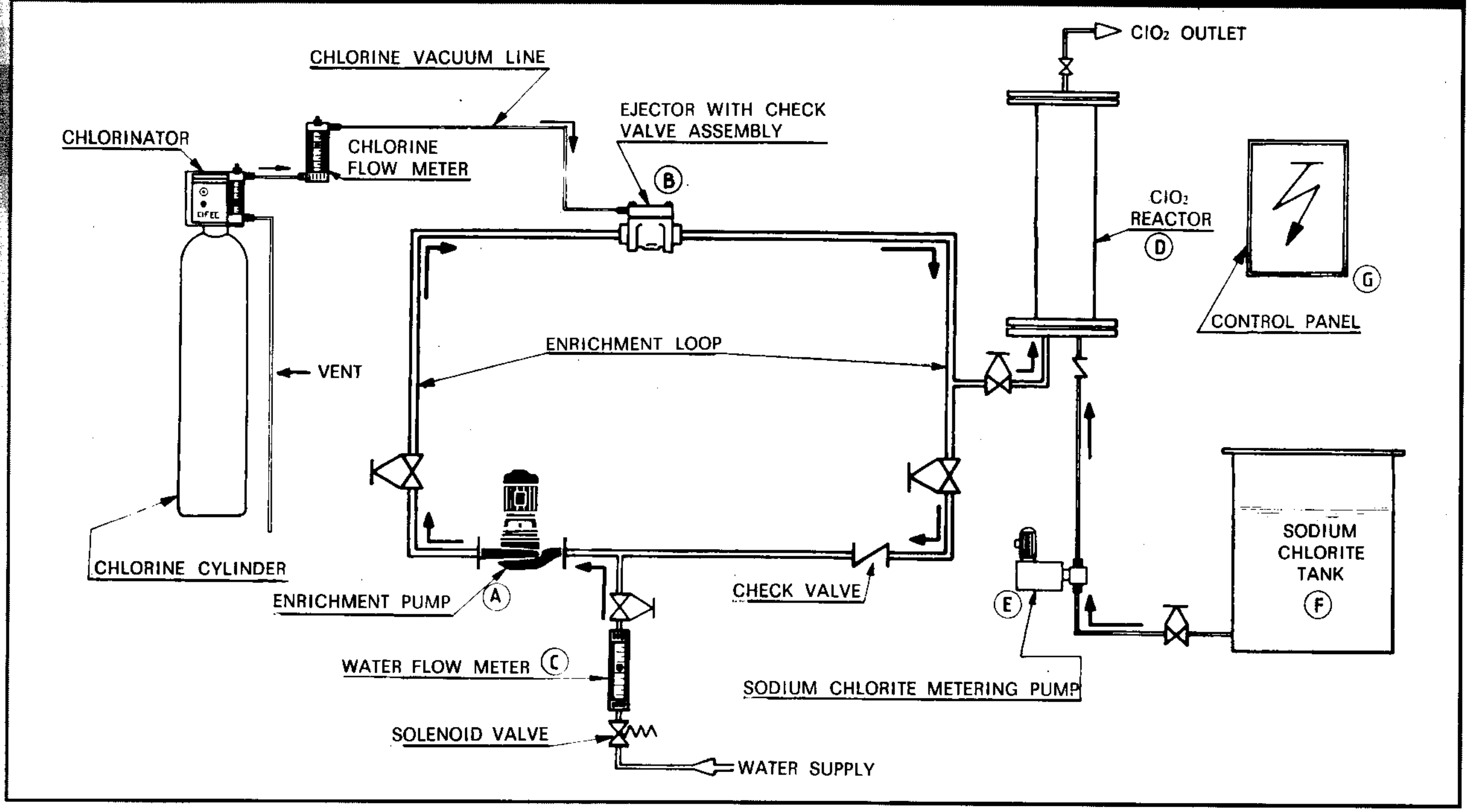


Figure 10
Aqueous Chlorine - Sodium Chlorite Generator

Generation Technologies - Chlorine Dioxide

Electrochemical Membrane System-

Uses one chemical as stock material - sodium chlorite.

Sodium chlorite is fed into a electrochemical cell with softened water.

Once hit with the energy from the cell chlorine dioxide is formed in low concentrations.

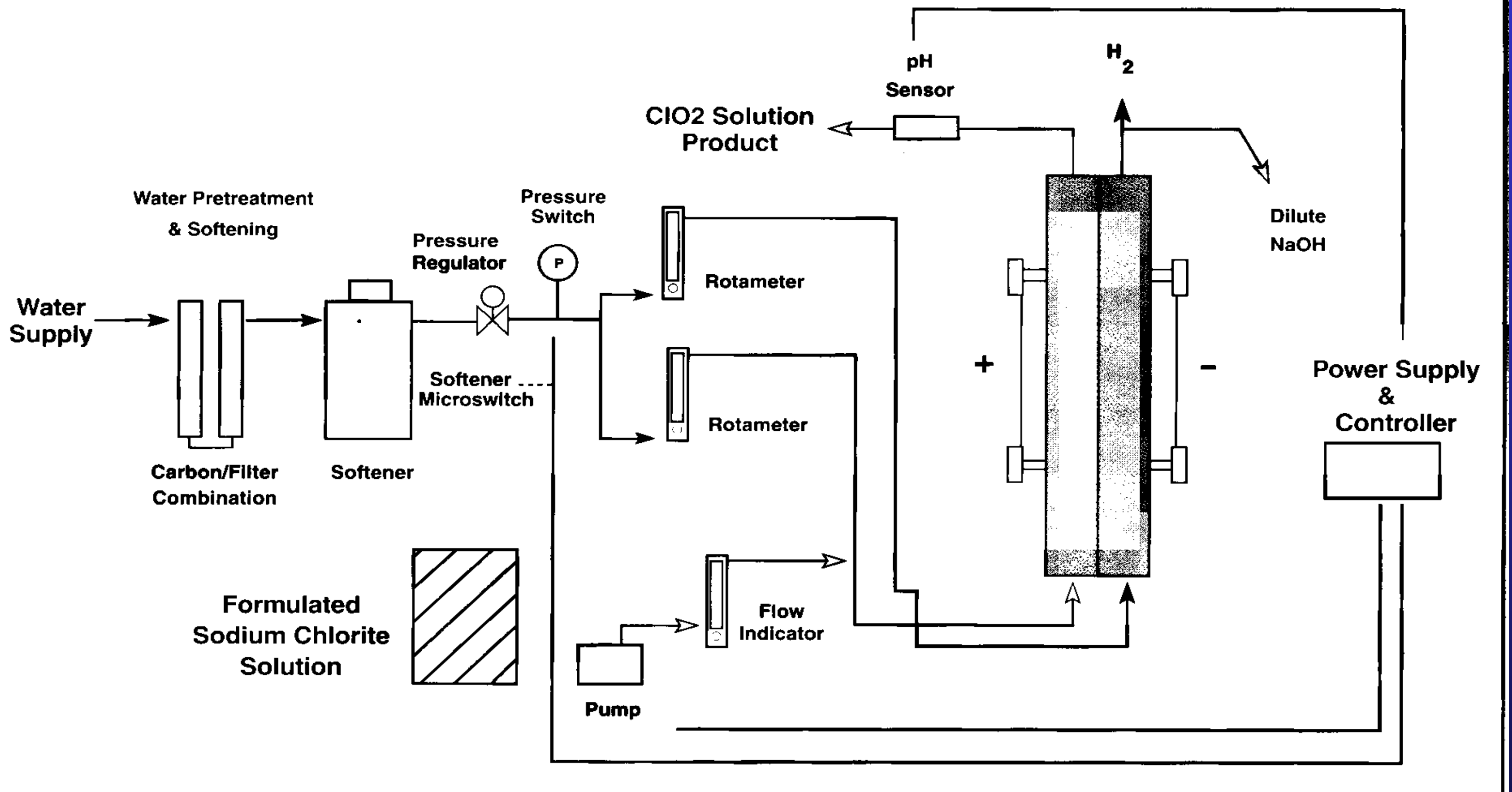
Generation Technologies - Chlorine Dioxide

Electrochemical Membrane System-

Chlorine dioxide is transported across a hydrolytic membrane and fed to storage tank.

Chlorine dioxide solution is then fed from the tank to the process by means of chemical feed device.

Generation Technologies - Chlorine Dioxide

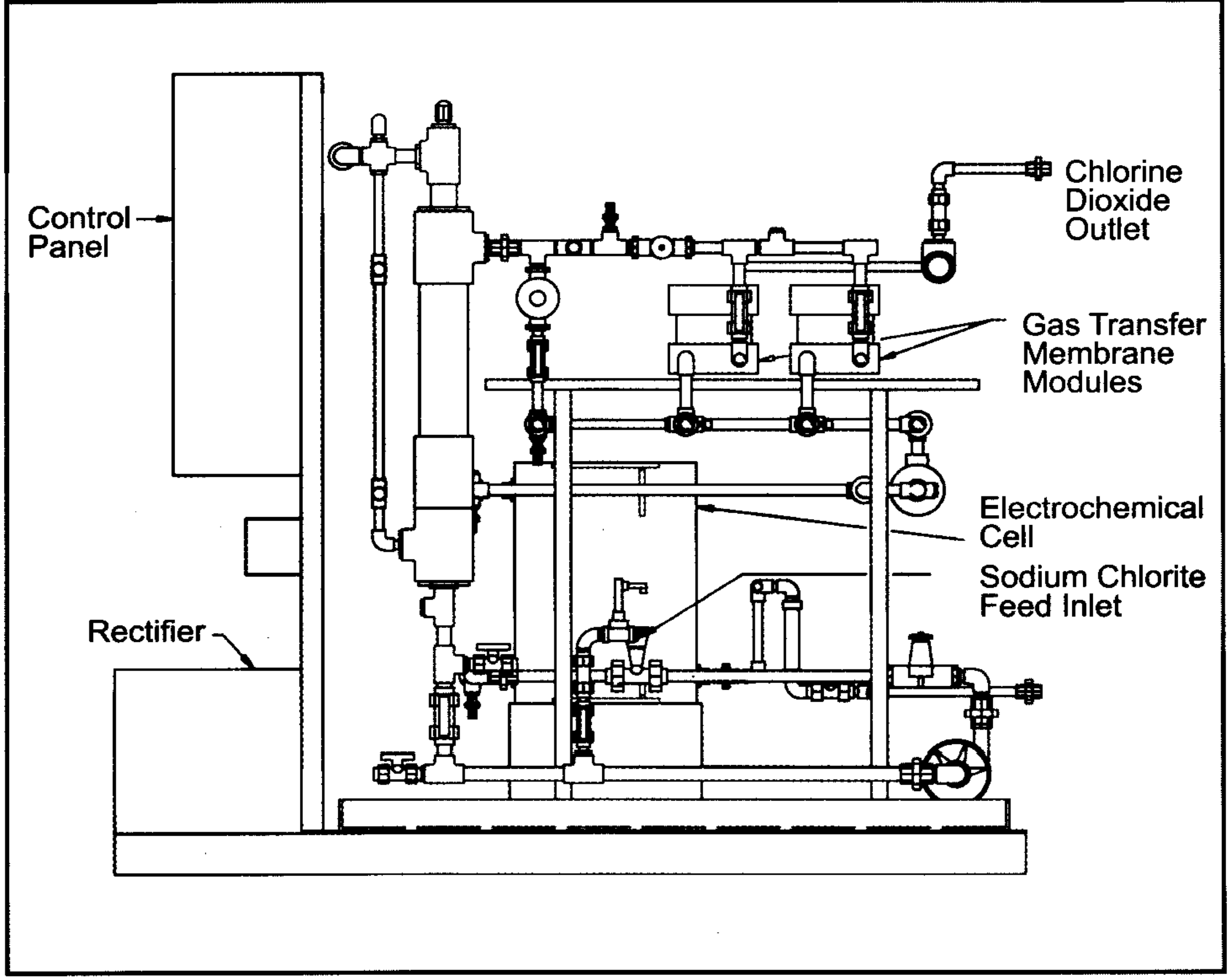


$NaClO_2 + H_2O + ENERGY \longrightarrow ClO_2 + Na\,OH + 1/2\,H_2$

urce: Olin Corporation, Published by Permission)

Generation Technologies - Chlorine Dioxide

Figure 14
Electrochemical ClO_2 Generator with Membrane Contactor



(Source: EBCO R101 Electrochemical Generator, Sterling Pulp Chemicals

DBP Formation Potential - Chlorine Dioxide

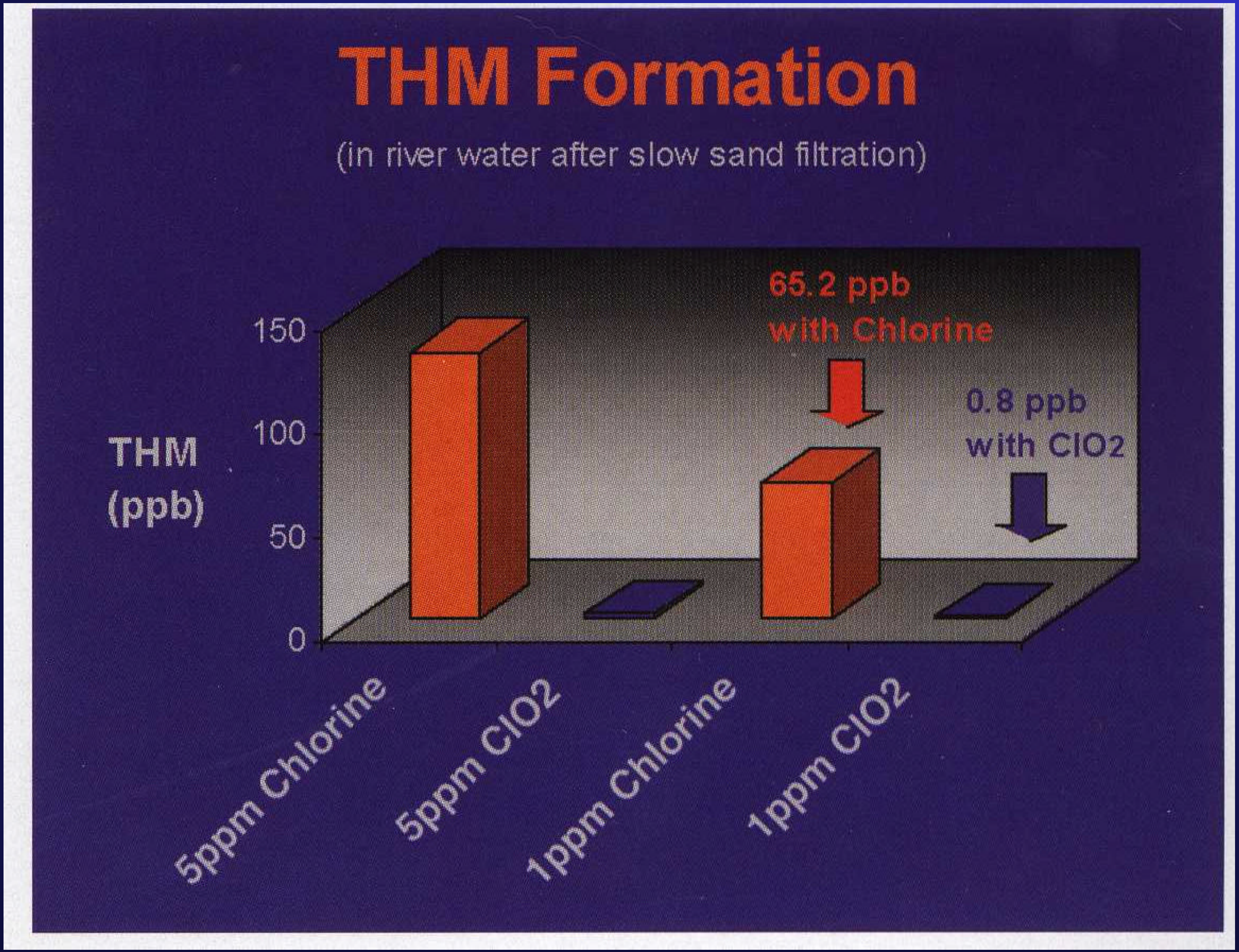
Chlorine Dioxide does not form halogenated byproducts, THM and HAA5 constituents when it interacts with NOM, as long as no excess chlorine is present from generation.

Chlorine Dioxide does form Chlorite and Chlorate, both have limits, however chlorate is not as problematic as chlorite.

Chlorate can be considerable if it is present in feedstock materials

Guideline for chlorite formation : 1.0 ppm

DBP Formation Potential - Chlorine Dioxide



DBP Formation Potential - Chlorine Dioxide

Considerations for chlorine dioxide DBP Formation:

1. Initial Dosage / Oxidation Demand
2. Blending Ratios of Sodium Chlorite and Chlorine in generation.
3. Exposure of chlorine dioxide to sunlight.
4. Reaction between chlorine and chlorite, if chlorine is used as a secondary disinfectant.
5. Levels of chlorate in feedstock solutions

DBP Formation Potential - Chlorine Dioxide

Generation of chlorine dioxide can be a source of DBP.

Incomplete reactions in chlorine based technologies can lead to chlorinated DBPs and chlorate as a result of the reaction between chlorite and chlorine.

Interaction / Oxidation of biological material increases overall demand and as a result increases DBP formation potential.

DBP Formation Potential - Chlorine Dioxide

Generation methods that require subsequent storage of chlorine dioxide also produce DBP in form of chlorite and chlorate under influence of sunlight.

Typically 50 - 70% of all chlorine dioxide applied to the water for disinfection will be reduced to chlorite, the remaining 30% will reduce to chlorate by means of other reactions.

Other reactions with chlorine, pH dependence, and sunlight.

DBP Formation Potential - Chlorine Dioxide

DBP must be monitored on a basis determined by exceedance of set guideline limits.

Chlorine Dioxide levels must also be monitored in the water leaving the plant by prescribed methodologies.

DBP Formation Prevention - Chlorine Dioxide

As previously noted, if initial demand and dosage is kept below 1.4 ppm, then no DBP formation over the set guidelines will be experienced.

If a system does have a problem with chlorite formation, the level of chlorite in the system can be reduced.

DBP Formation Prevention - Chlorine Dioxide

Chlorite Removal-

1. GAC or PAC Application
2. Adding reducing salts - ferrous chloride and ferrous sulfate.
3. Adding reduced sulfur compounds Sulfur Dioxide or sodium sulfite.

Option #3 is not prescribed as the process is effective at lower pH levels, thus the formation of chlorate can be a problem

DBP Formation Prevention - Chlorine Dioxide

Addition of Iron Salts for Chlorite control-

Reaction is very quick at pH of 5-7.

Forms Chloride, with the excess iron reacts with dissolved oxygen in the water, however lower pH conditions < 6.5 problems can exist with iron staining.

Adding iron salts should not occur if limits for iron levels can be exceeded.

DBP Formation Prevention - Chlorine Dioxide

PAC and GAC Addition-

Control by PAC can be achieved with high dosages (10-20 ppm) and low pH 5.5 to 6.5. As a result this can be costly.

GAC acts as a receptor for the chlorite molecule - interaction with the GAC and further interaction with available chlorine in the treatment process can lead to the formation of chlorate.

It is recommended that if GAC is used, minimize production run times and have no chlorine present in the filter.

Limitations and Considerations - Chlorine Dioxide

Chlorine Dioxide presents a number of advantages to other forms of Alternative disinfection methodologies,

Chlorine dioxide is more effective than chlorine and chloramine for inactivation of viruses and protozoan.

Oxidizes Iron, Manganese and Sulfides

Can enhance clarification process

Limitations and Considerations - Chlorine Dioxide

Advantages-

Control of taste and odour problems from algae and decaying plant material can be achieved.

Halogenated byproducts - THM formation is prevented as long as the generation system does not allow for the release of free chlorine.

Chlorine dioxide is easy to generate.

Limitations and Considerations - Chlorine Dioxide

Advantages-

Biocidal effectiveness is not effected by pH.

Chlorine dioxide provides residual disinfection.

Limitations and Considerations - Chlorine Dioxide

Disadvantages-

Chlorine dioxide forms DBPs of chlorite and chlorate.

Some generation technologies are difficult to maintain optimum yield and prevent excess chlorine from escaping unreacted.

Costs associated with chlorite, chlorate and training can be high.

Sodium chlorite costs are high.

Limitations and Considerations - Chlorine Dioxide

Disadvantages-

Chlorine dioxide must be generated on site.

Chlorine dioxide decomposes in sunlight.

Extended storage of chlorine dioxide solution can contribute to byproduct formation.

Chlorine dioxide can product noxious odours in some systems.