OxyChem®

Basic Chemicals

Sodium Chlorite
Chlorine Dioxide Generators

Introduction

Chlorine dioxide enjoys many different types of use particularly in water treatment; among these is disinfection, bleaching, and chemical oxidation. The chlorine dioxide used in these applications is always generated on-site, usually from sodium chlorite, as an aqueous solution.

Chlorine dioxide is a reactive oxidizing gas that is readily soluble in water. Even dilute solutions (10 ppm) of chlorine dioxide have a characteristic yellow color. The maximum chlorine dioxide concentration typically produced in commercial generators is approximately 4000 ppm. This is to minimize the concentration of chlorine dioxide gas in equilibrium with the solution. Gas phase chlorine dioxide concentrations in excess of 10%, like ozone, can decompose explosively. This is the reason that chlorine dioxide must be generated at its point-of-use. This document will cover the chemistry of chlorine dioxide generation, generator design and operation requirements, generator safety requirements, features of many chlorine dioxide generators presently available in the market.

Generation Chemistry

While chlorine dioxide may be produced from sodium chlorate ($NaClO_3$), most small-scale generators use sodium chlorite ($NaClO_2$) as their precursor chemical. The economic breakpoint between chlorite and chlorate generation is on the order of tons/day of chlorine dioxide. Three feed chemical combinations will be covered:

1) chlorine-sodium chlorite,
2) acid-sodium hypochlorite-sodium chlorite, and
3) acid-sodium chlorite.

Chlorine-Chlorite

This method, the most flexible and efficient method of generating chlorine dioxide, generates chlorine dioxide in a two step process. First, (equation 1), chlorine reacts with water to form hypochlorous acid (HOCl) and hydrochloric acid (HCl). These acids react (equation 2) with sodium chlorite to form chlorine dioxide, water, and sodium chloride (NaCl). The ratios of sodium chlorite and hypochlorous acid (chlorine) must be carefully controlled. Insufficient chlorine feed will result in a large amount of unreacted chlorite. Excess chlorine feed will result in the formation of sodium chlorate ($NaClO_3$), which is the oxidation product of chlorine dioxide. The typical operating conditions and yields for this method of generation are shown in Table 1.

(1) $$Cl_2 + H_2O \rightarrow HOCl + HCl$$

(2) $$2NaClO_2 + HOCl + HCl \rightarrow 2ClO_2 + H_2O + 2NaCl$$

Net:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

Acid-Hypochlorite-Chlorite

This is an alternative to chlorine-chlorite generation that is used when chlorine gas is not available. First (equation 3), sodium hypochlorite is combined with hydrochloric or other acid to form hypochlorous acid. Sodium chlorite is then added to this reaction mixture to produce chlorine dioxide (equation 4).

(3) $$NaOCl + HCl \rightarrow HOCl + NaCl$$

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(4) $NaClO_2 + HOCl + HCl \rightarrow 2ClO_2 + H_2O + 2NaCl$

Net: $2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + H_2O + 3NaCl$

Since equations 2 and 4 are identical, the chlorine dioxide generation step is the same. Consequently, the typical operating conditions, yield, and purity for this method of generation are the same as for chlorine-chlorite generation. This method also shares the requirement of carefully balancing sodium chlorite and hypochlorous acid feeds, which is made more difficult by poor storage characteristics (rapid degradation) of sodium hypochlorite solutions. The typical operating conditions, and yields for this method of generation are shown in Table 1.

Table 1		
	Minimum	Maximum
$NaClO_2$ (ppm)	1,340	5,360
HOCl (ppm as Cl_2)	526	2,100
pH	2.7	3.2
ClO_2, theory (ppm)	1,000	4,000
ClO_2, actual (ppm)	950	3,800

Acid-Chlorite
Acid-chlorite is the simplest and easiest to operate generation chemistry. This is a consequence of the use of only two feeds and its simple reaction chemistry (equation 5). Instead of having to balance the amounts of sodium chlorite and hypochlorous acid, one merely has to provide sufficient hydrochloric acid. Excess acid does form undesirable reaction products. Unfortunately, there is no such thing as a "free lunch." This ease of operation comes at the cost of chlorine dioxide yield. The theoretical conversion of sodium chlorite to chlorine dioxide is only 80%, while the chlorine-chlorite and acid-hypochlorite-chlorite reactions both have theoretical conversions of 100%.

(5) $5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$

Generator Design
Chlorine dioxide generators must feed and mix precursor chemicals and provide sufficient residence time for the generation reaction to go to completion. The required residence time varies from less than a minute for hypochlorous (Cl_2 or HCl-NaOCl) generation to 15 minutes for acid generation. Generators differ predominantly in the type of chemical feed systems they employ. Three types of designs are used: 1) vacuum feed systems, which pull fluids into the generator; 2) pressure feed systems, which push fluids into the generator; and 3) a combination of pressure and vacuum feed systems. While liquid chemicals (acid, sodium hypochlorite, and sodium chlorite solutions) can use any type of feed system, chlorine gas must be added by a vacuum (or combination) feed system.

Vacuum Feed Systems
A vacuum feed system is composed of a venturi and a rotameter. The venturi or eductor uses the flow of a fluid (water) to create the vacuum that pulls the precursor into the generator. The venturi cross-section shown in the figure below demonstrates how this vacuum is created.

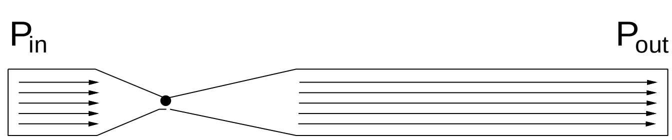

Figure 1 - Venturi

As water flows through the venturi, it passes through a narrow section where the increase in the water's velocity causes a vacuum. The amount of the vacuum formed depends upon the

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pressure drop (ΔP) across the venturi (the greater the pressure drop, the greater vacuum).

(6) $\Delta P = P_{in} - P_{out}$

The conditions required for proper venturi function define the limit of this type of feed system. First of all, those applications that have a low supply water pressure (P_{in}) or a high system back-pressure (P_{out}), will require a booster pump to provide a large enough ΔP. Second, the venturi feed system places a limit on the chlorine concentration that can be fed. As more and more chlorine is dissolved in water, the water pH decreases until it shifts the equilibrium (equation 7) to release chlorine gas. The pressure of this gas will prevent the venturi from operating. This occurs at chlorine concentrations around 4,000 ppm.

(7) $Cl_{2(g)} + H_2O \leftrightarrow HOCl + HCl$

The feed rate of the precursor chemicals are measured and controlled by rotameters (see figure below). The amount of chemical fed is controlled by a needle valve and measured by a ball supported by the flowing chemical. The venturi may be installed before, after, or at the point of chemical mixing and reaction.

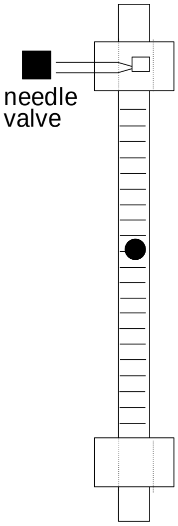

Figure 2 - Rotameter

Vacuum feed systems use venturi locations both at or after the mixing and reaction zone. Locating the venturi after the mixing and reaction zone mixes undiluted feed chemicals. This causes a very rapid reaction to form chlorine dioxide, but may also cause plugging of the mixing and reaction zone with sodium chlorite. Locating the venturi at the mixing and reaction site mixes and dilutes the feed chemical in the motive venturi water. This slows the reaction that forms chlorine dioxide but avoids plugging with sodium chloride. A venturi location before the mixing and reaction zone is typically used in combined feed systems to provide time for the hydrolysis of chlorine to form hypochlorous acid.

Pressure Feed System

Pressure feed systems use chemical dosing pumps to push the precursor chemicals into the reaction chamber. Usually diaphragm positive displacement pumps are used (see figure below). A piston moves the diaphragm into (to the left) and out of (to the right) the pump head. During the outward piston stroke, solution is pulled into the pump head through the inlet check valve. During the inward piston stroke, solution is pushed out of the pump head through the outlet check valve and into the reaction chamber. The amount of chemical fed is controlled by the stroke length and stroke frequency. This type of feed system, while the most accurate, can be used only with liquid feed chemicals, such as used in acid-chlorite and in acid-hypochlorite-chlorite feed systems.

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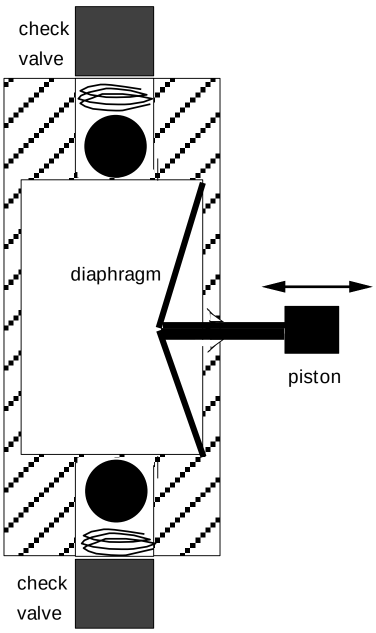

Figure 3 - Diaphragm Pump

Combination Feed Systems

Combination feed systems are used only in chlorine-chlorite generators. The chlorine feed rate is controlled by a venturi and rotameter. The sodium chlorite feed rate is controlled by a chemical dosing pump.

Safety Requirements

Numerous types of interlocks are usually built into chlorine dioxide generators. These serve two purposes: first, they prevent hazardous reaction conditions in the generator; and second, they ensure that only chlorine dioxide is being applied by shutting the system down when a precursor chemical is absent.

Hazardous Conditions

Hazardous reaction conditions are the result of too high a concentration of chlorine dioxide in solution. If a gas phase forms above this solution, the chlorine dioxide in this gas phase can reach a level (10% v/v) where spontaneous, explosive decomposition can occur. Even if a gas phase can not form, decomposition can occur in solution from the "red complex," $Cl_2O_4^-$, a species that can form in very concentrated solutions of chlorine dioxide and sodium chlorite. Its decomposition releases oxygen gas, which causes pressure increases. Consequently, it is critical to keep the chlorine dioxide in solution diluted with water. The minimum safety requirements are to 1) design the reaction chamber so that a gas phase can not form, and 2) provide a flow switch (safety interlock) that shuts the generator off in the event of loss of dilution water flow.

Out of Chemical

To ensure the application of only chlorine dioxide, many generators incorporate "out of chemical" sensors that shut the generator down when a feed chemical is absent. These may be level switches in tanks, vacuum-pressure sensors for gas cylinders, or liquid displacement devices for pumps.

Generator Automation

Chlorine dioxide generators are automated to provide modulation of chlorine dioxide feed rates based upon changes in flow (flow paced control) and chlorine dioxide demand of the water being treated (residual control). Theoretically, the chlorine dioxide feed rate may be varied by either modulating the precursor chemical feed rates to the generator or by turning the generator on and off. In practice, only pressure feed system generators can inexpensively modulate precursor chemical feed rates. Vacuum and combination systems are limited by the hydraulic requirements of their venturi and the optimum reaction conditions (concentration) for chlorine dioxide generation. Consequently, to achieve automatic operation, manufacturers of vacuum or combination feed system generators

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use a batch tank with a level switch to turn the generator on and off. A chemical dosing pump is used to feed chlorine dioxide solution. This allows the generator to operate at the optimum reaction conditions for good chlorine dioxide yield and purity.

Further Information

More information on sodium chlorite is available on request through the OxyChem Technical Service Department. Call or write to:

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