Froth Reactor for Small-Scale Generation of Chlorine Dioxide

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Chlorine dioxide is an oxidizing gas which is consumed primary by the paper industry in the bleaching of wood pulp. Interest in chlorine dioxide is growing in smaller applications such as water treatment, disinfection, sterilization, and flour treatment. It is replacing chlorine because of environmental concerns.

Richardson et al. (1994) reported that chlorine dioxide is used in more than 300 drinking water treatment plants in the U.S. and several thousand plants in Europe. They cited several reasons for growing interest in chlorine dioxide: (1) concerns of the National Cancer Institute (1976) about trihalomethanes (THMs) in chlorinated drinking water; (2) EPA regulations establishing maximum levels of THMs (Symons et al., 1981; Lykins et al., 1990); (3) EPA establishment of chlorine dioxide treatment as a suitable alternative to chlorine treatment (Federal Register, 1983); (4) the biocidal nature of chlorine dioxide to a wide range of microorganisms; and (5) the ability of chlorine dioxide to reduce odor and color, probably because it readily oxidizes phenols and phenolic-type compounds, unlike chlorine (Gordon, 1993).

A potentially large user of chlorine dioxide is the environmental industry for the treatment of supply, boiler, process, cooling, and waste waters. Treatment equipment and chemicals revenues were $13.5 billion in 1994. Chlorine had been used in this industry to control microorganisms and destroy organic materials; its use is declining because of handling and environmental concerns. This industry is expected to grow at better than 10 percent per year through 1997 (Hoffman, 1995).

Chlorine dioxide is unstable and must be generated at the point of application and dissolved in water. Depending upon the scale of application, generation processes vary. At a paper mill, chlorine dioxide is produced at typically 10 to 40 ton/d by reacting sodium chlorate, sulfuric acid and a reducing agent—hydrogen peroxide or methanol. In small-scale systems [1 to 10 lb/h (0.45 to 4.5 kg/h)] it is generally produced by reacting sodium chlorite with chlorine or sodium hypochlorite.

There is economic incentive to produce chlorine dioxide using chlorate-based chemistry. Sodium chlorate is inherently less expensive than sodium chlorite because sodium chlorate is the raw material for making sodium chlorite. There is some environmental concern that has stimulated the exploration of small-scale production using chlorate-based chemistry. The chlorite-based process is about 95%-efficient, and some chlorine escapes the reactor with the chlorine dioxide product. High levels of unreacted chlorite and chlorate ions can appear in the effluent when improper ratios of feedstocks are used (Hoehn, 1993). Studies suggest that residual chlorite may pose health concerns (Abdel-Rahman et al., 1979).

Process Description

Hydrogen-peroxide-based chlorate chemistry

$$2NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + O_2 + 2H_2O + Na_2SO_4 \qquad (1)$$

is being considered for small-scale production of chlorine dioxide because: (1) the byproducts are nonhazardous; (2) chlorine cannot form if any excess hydrogen peroxide is present; (3) unconverted hydrogen peroxide in the reactor product stream would be beneficial in some applications since it is also an oxidant.

A hydrogen peroxide-based chlorate process was developed to supply pulp bleaching processes (Sokol and Conkle, 1993). Burke et al. (1993, 1995) studied rate behavior in stirred batch and constant flow stirred tank reactors at conditions that apply in large-scale processes. The operating ranges of

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this study were, 25–85°C, 0.75- to 4-M H_2SO_4, 0.05- to 2.9-M H_2O_2, and 0.5- to 3.2-M $NaClO_3$. They correlated the rate of chlorine dioxide, r_{ClO_2} (mol/L/min), by the power law expression

$$r_{ClO_2} = k[H_2SO_4]^{4.4}[H_2O_2]^{0.6}[NaClO_3]^{1.3} \qquad (2)$$

where

$$k = 4.4 \times 10^{12} \exp(-12{,}230/T) \qquad (3)$$

Chlorine dioxide generators for small-scale applications must be designed for safe and unattended operation with a minimum of processing steps. A flow reactor that is close-connected to a vacuum jet eductor is a design that has been used for water treatment and other applications. This type of reactor has been used to produce chlorine dioxide from sodium chlorite and chlorine (Anon., 1988) and from sodium chlorate, sodium chloride and sulfuric acid (Jenson and Eltomi, 1995).

Other reactor requirements include: stability under a wide range of operating conditions and high purity chlorine dioxide product at the near-complete conversion of sodium chlorate. For some uses, there may be a limit on unreacted sulfuric acid in the product. For design, it is important to understand the influence of sulfuric acid on rate and conversion, and to determine methods of reducing the acid dependence.

Experimental Studies

A vacuum eductor-type reactor has been designed and installed at Tiberian Technologies, Inc. as an initial step of a program that will explore and optimize alternative operational procedures and equipment configurations. A system is shown in Figure 1. It consists of the reactor, reactant feed vessels and diaphragm pumps, jet eductor, product treatment tank and analytical equipment.

The reactor is a 4 in. dia. × 12 in. (102 mm × 305 mm) Pyrex cylinder surrounded by a 6 in. (152 mm) dia. square polycarbonate safety shield. The feed mixing head consists of a perforated plate through which hydrogen peroxide and sodium chlorate solutions flow upward into the reactor. The plate contains a gasket that seals it against the reactor wall. Sulfuric acid flows through a vertical tube passing through the center of the perforated plate. The tube is capped at the end, but is perforated on the side so that acid jets out radially into the solution. The outlet end of the reactor is a movable disk that contains a central outlet tube that connects to the eductor. The edge of the disk contains a vacuum tight gasket that

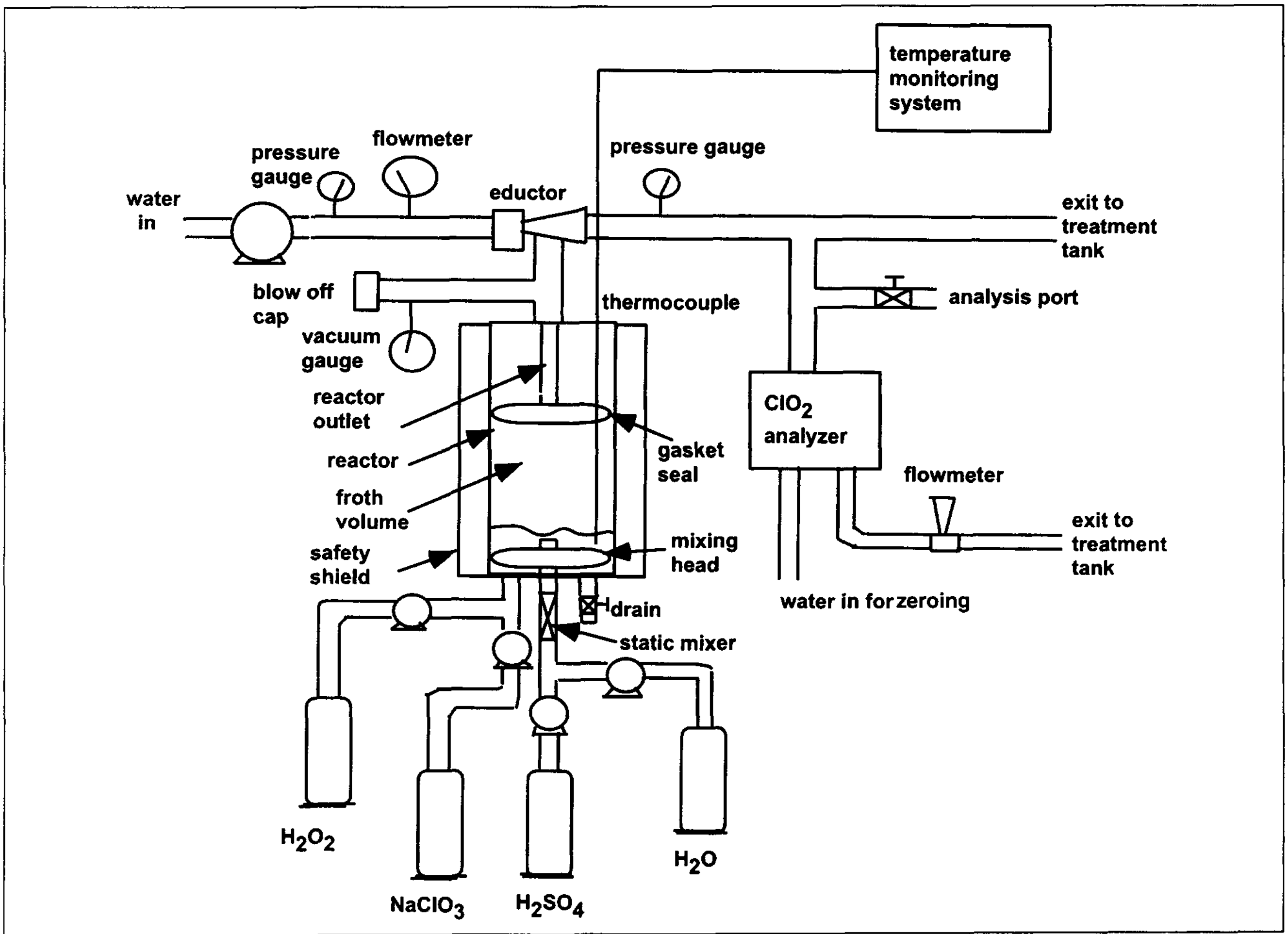

Figure 1. Experimental reaction system.

seals it to the reactor wall. The volume of the reactor can be modified by positioning the disk in relation to the mixing head.

Product gases form as the reaction takes place. The gas-liquid reaction mixture (froth) flows vertically and exits into the eductor, where the effluent mixes with a high velocity stream of water, which is the motive fluid for the eductor. In a water treatment application, the motive fluid would be recycled from the body of water that is being treated. In the experimental program, the reactor was operated under a vacuum to maintain chlorine dioxide partial pressures low enough to avoid chlorine dioxide decomposition. The vacuum level ranged from about 15 to 20 in. Hg (51 to 68 kPa). Production rate was determined from measurements of flow rate and dissolved chlorine dioxide concentration in the water flowing from the eductor. The concentration was measured on-line with a Spectra-Tec Model 4000 Chlorine Dioxide On-Line Analyzer.

There was some cyclic fluctuation in the vacuum during runs, presumably because the eductor withdraws a two-phase mixture rather than a single phase from the reactor, and because the cycling of the diaphragm feed pumps causes the foam level at the top of the reactor to intermittently drop below the entrance to the eductor.

Results

At steady state, the reactor contained a small pool of liquid on top of the mixing head. The pool was agitated by the jets of acid and by rising bubbles of product gases. From the top of the pool to the outlet disk, the reactor was filled with a gas-liquid mixture of products and unreacted reagents. The mixture was a froth, colored yellow by the chlorine dioxide, that appeared stable and similar in texture to suds of laundry detergent. The bubble size of the froth was relatively uniform, but varied from run to run from about 2 to 4 mm in diameter. The froth was very sensitive to the vacuum in the reactor. The froth collapsed to a liquid within 1 or 2 s if the vacuum was suddenly broken. In most experiments, the reaction at the mixing head was so violent that no pool of liquid could be observed and the entire length of the reactor was filled with froth.

A total of 157 experiments were conducted using four different disk placements, representing volumes of 350, 750, 1,375, and 1,575 mL. Solutions of the reactants were fed separately to the mixing head including 14-M sulfuric acid, 4-M sodium chlorate, and 16.7-M hydrogen peroxide. No dilution water was fed. The mixed inlet concentrations were varied by adjusting the rates of individual reactant solutions, and ranged from 4- to 8-M sulfuric acid, 1- to 3-M sodium chlorate, and 0.8- to 5-M hydrogen peroxide. The feed mixing process was exothermic. Temperature in the liquid pool was measured by a thermocouple, but was not controlled. The system was studied at production rates of 0.1 to 0.63 mol/min (0.8 to 5.6 lb/h) ClO_2.

Various data were recorded including: inlet volumetric flow rates of reactants, dynamic volume (volume of liquid pool during steady-state operation), settled liquid volume (total volume of liquid at the end of an experiment after vacuum was broken and froth collapsed), steady-state liquid temperature (for runs in which a liquid pool formed), and chlorine dioxide production rate. Various parameters were calculated from these data, including mixed inlet concentrations of reactants, effluent concentrations of reactants (calculated from chlorine dioxide rate, inlet reactant rates and reaction stoichiometry), and molar ratios of reactants.

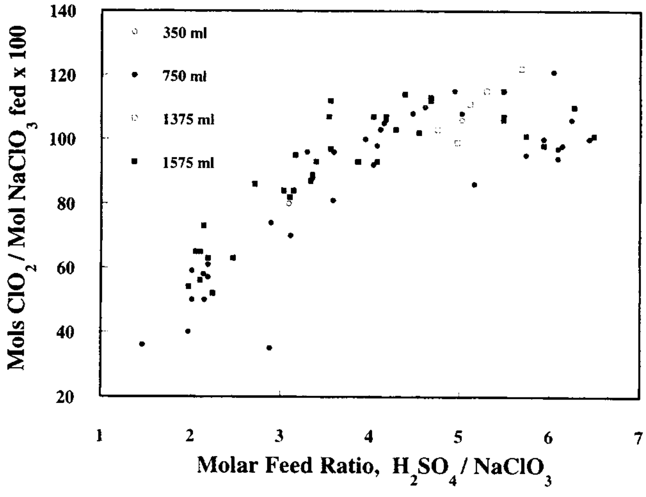

Figure 2. Influence of reactant feed ratio and reactor volume on reactor performance.

Figure 2 shows the ratio of mols of chlorine dioxide per 100 mol of sodium chlorate fed, which in theory is percent conversion of sodium chlorate. The ratio increased as molar ratio of sulfuric acid to sodium chlorate in the feed was increased for four different reactor volumes. The ratio of inlet hydrogen peroxide to sodium chlorate was varied from 1 to 6 times stoichiometric; however, there appeared to be no influence on the reactor performance. Dynamic volume, settled volume, and liquid pool temperature were constant during each run; however, the value of each varied from run to run. Dynamic volume varied from 0 to 30% of the total reactor volume, settled volume varied from 6 to 65% of the total reactor volume, and the liquid pool temperature varied from 38 to 74°C. None of these variables appeared to influence the correlation. Figure 2 shows data points at conversions greater than 100%, which is reflective of uncontrolled variation in the experiments.

To test more rigorously for influences of temperature, dynamic and settled volume, and hydrogen peroxide concentration, the data were statistically analyzed using the software, Minitab (Version 8). This method attempted to correlate chlorine dioxide rate, R_{ClO_2} (mol/min), by multilinear regression, first with all system parameters, and then with subsets of system parameters.

Stepwise regression and best subsets algorithms determined that the best linear correlating equation is

$$R_{ClO_2} = 0.0024 + 0.132 F_{H_2SO_4} + 0.4 F_{NaClO_3} \qquad (4)$$

where F_i are molar feed rates. Figure 3 is a parity plot of measured and calculated R_{ClO_2}, with the 45° line representing a perfect fit. Although the regression contained 157 data points, the generated equation accounts for 92.4% of the scatter (that is, $R^2 = 0.924$). Student t-ratios were high, 14 and 11.8, respectively, for the variables, $F_{H_2SO_4}$ and F_{NaClO_3},

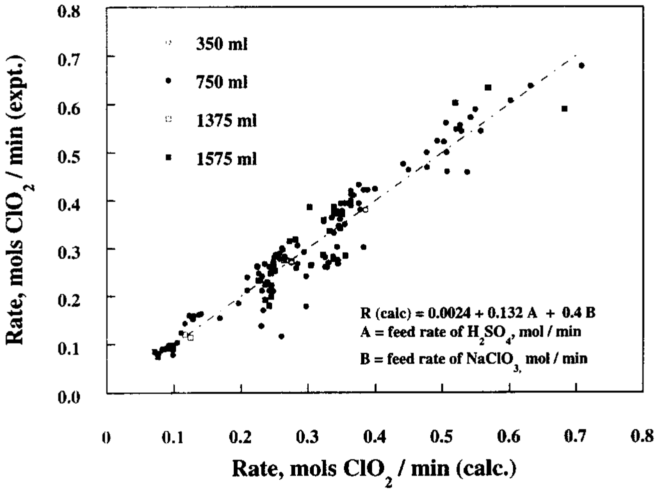

Figure 3. Correlation of production rate.

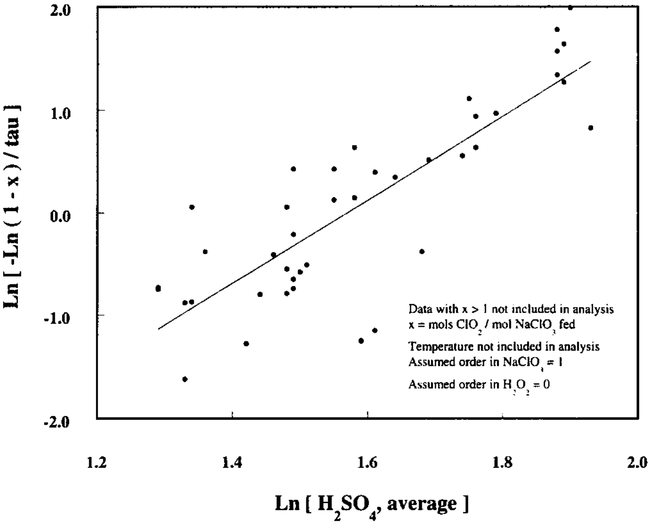

Figure 4. Reactor data plotted according to PFR model.

indicating that each is highly significant in fitting R_{ClO_2}. Dynamic volume, settled volume, total reactor volume, temperature, and reactant concentrations (inlet, outlet and average) correlated poorly. When these and any other variables, except $F_{H_2SO_4}$ and F_{NaClO_3}, were included in the correlation, the student t-ratio for each variable was below the criterion of 1.96, indicating that its influence was not significant.

The most puzzling result is the apparent lack of temperature dependence on rate. Although we have no clear explanation, we suspect that the temperature of the liquid pool may not have been uniform—a result of rapid heat release upon contact of the 14-M sulfuric acid feed as it jetted from the central tube into the liquid pool, and insufficient mixing within the pool. Nonuniformity of temperature would not have been detected since liquid temperature was measured by a single thermocouple positioned at a stationary location in each run.

An attempt was made to correlate the data using simple reactor models, but assuming no dependence on temperature and hydrogen peroxide as suggested by the statistical analysis. Figure 4 shows a plot developed by assuming a global rate expression of the form

$$r_{ClO_2} = k'[NaClO_3][H_2SO_4]^n \tag{5}$$

where the rate r is in units of mols ClO_2/min/L of settled volume, and assuming the reactor behaves as a plug-flow reactor (PFR). Further assumptions include: (i) reaction occurs throughout all liquid (in the pool and froth) (the differential volume on which the PFR material balance is based was the liquid volume); (ii) acid conversion was small, and acid concentration $[H_2SO_4]$ relatively constant and uniform throughout the reactor at the linear average of inlet and effluent concentrations; and (iii) space time (tau_0) is defined as the ratio of settled volume to the total volumetric flow rate of feed.

The PFR equation, in terms of fractional conversion x is

$$dx/dtau_0 = k[H_2SO_4]^n_{ave}(1-x) \tag{6}$$

The solution is

$$-\mathrm{Ln}(1-x)/tau_0 = k[H_2SO_4]^n_{ave} \tag{7}$$

The log of both sides leads to a straight line expression with a slope of n.

Figure 4, a plot based on this expression, shows considerable scatter. The correlation coefficient was $R^2 = 0.84$. The interesting feature, however, is that acid order (slope) is 4.1, which perhaps by coincidence agrees with the acid dependence found by Burke et al. (1993) in their work at much milder acidic conditions.

Future studies will focus on acquiring a better understanding of physical and chemical processes involved in reactor operation, and determining how these processes interact to influence performance. An important objective is to explain what physical effects mask the influences of temperature, hydrogen peroxide concentration, and other variables. To develop a model of the process, it will be necessary to determine to what extent mixing effects at the feed inlets influence performance, and to better understand the characteristics of the froth and the extent to which reaction occurs in the froth. The primary objective is to optimize equipment configuration and operation to yield a reactor effluent that contains a high concentration of chlorine dioxide, but minimum concentrations of unreacted sodium chlorate and sulfuric acid.

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