# American Institute of Chemical Engineers

# STUDENT CONTEST PROBLEM

## 1968

345 East 47 Street • New York, New York 10017

# CONTEST PROBLEM

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# AMERICAN INSTITUTE OF CHEMICAL ENGINEERS STUDENT CHAPTERS

Open Only to Undergraduates or Those
Without a Degree in Chemical Engineering

## DEADLINE FOR MAILING

Solution must be postmarked not later than midnight, June 15, 1968

## RULES OF THE CONTEST

Solutions will be graded on (a) substantial correctness of results and soundness of conclusions, (b) ingenuity and logic employed, (c) accuracy of computations, and (d) form of presentation. Accuracy of computations is intended to mean primarily freedom from mistakes; extreme precision is not necessary.

It is to be assumed that the statement of the problem contains all the pertinent data except for those readily available in handbooks and similar reference works. The use of textbooks, handbooks, journal articles, and lecture notes is permitted. In cases where there is disagreement in the data reported in the literature, the values given in the statement of the problem have been chosen as being most nearly applicable.

The problem is not to be discussed with any person whatever until June 15, 1968. This is particularly important in cases where neighboring institutions may not begin the problem until after its completion by another chapter. Submission of a solution for the competition implies adherence to the foregoing condition.

A period of not more than 30 consecutive days is allowed for completion of the solution. This period may be selected at the discretion of the individual counselor, but in order to be eligible for an award a solution must be postmarked not later than midnight, June 15, 1968.

The finished report should be submitted to the chapter counselor within the thirty-day period. There should not be any variation in form or content between the solution submitted to the chapter counselor and that sent to the A.I.Ch.E. office. The report should be neat and legible, but no part need be typewritten.

The solution should be accompanied by a letter of transmittal giving only the contestant's name, school address, home address, and student chapter, lightly attached to the report. This letter will be retained for identification by the Secretary of the Institute. The solution itself must bear no reference to the student's name or institution by which it might be identified. In this connection, graph paper bearing the name of the institution should be avoided.

Each counselor should select the best solution or solutions, not to exceed two, from his chapter and send these by registered mail to

Mr. F. J. Van Antwerpen, Secretary
American Institute of Chemical Engineers
345 East 47 Street
New York, New York 10017

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## STATEMENT OF PROBLEM

A proposed expansion program for a kraft pulp mill in Western Kentucky requires the design of a 7 tons/day chlorine dioxide ($ClO_2$) generation system. (Chlorine dioxide has been selected as the final bleaching agent for the preparation of high-brightness pulp.)

Of the several processes that have been developed for the commercial production of $ClO_2$ from sodium chlorate, preliminary calculations have restricted the design to the process wherein sulfur dioxide, sodium chlorate, and sodium chloride are the primary reactants. With the exception of a sodium sulfate recovery system, new facilities must be provided for each operation in the chlorine dioxide system. Your final report should include the following items:

1. A detailed process flow sheet.
2. A discussion of optimum operating conditions.
3. The estimated production cost, dollars/ton $ClO_2$.
4. A recommended startup procedure.

Please submit your solution within thirty days.

## INTRODUCTION

Numerous reagents are available for the delignification and bleaching of wood pulp in the paper industry. Each pulp must be treated according to its individual requirements to ensure bright and stable color at a minimum loss in strength. Moderate brightness is commonly obtained by a three-stage sequence of chlorination, caustic extraction, and hypochlorite bleaching. When the hypochlorite bleaching reaction is carried to the high-brightness level required for fine papers, however, cellulose degradation is excessive. In the production of extremely high-brightness pulp a final chlorine dioxide stage has been adopted.

The exceptional ability of chlorine dioxide to react with chromophoric groups in lignin without degrading cellulose has been recognized for many years, but general acceptance of the bleaching agent has been retarded by its toxicity, its corrosiveness, and its tendency to explode. The development of safe and economical continuous methods of generating chlorine dioxide vapor has produced a tremendous growth in the annual production of sodium chlorate and chlorine dioxide. (Sodium chlorate is the raw material in all commercial $ClO_2$ generating schemes employed in this country.) Chlorine dioxide generating capacity has been estimated to exceed 360 tons a day in 1968.

Because the explosive characteristics of $ClO_2$ preclude safe and economical transportation, it must be manufactured close to its point of application. Several economical processes are available for chlorine dioxide production in the United States, the primary reaction in each process being the redox combination of sodium chlorate and sodium chloride. The processes may be modified through the selection of methanol or sulfur dioxide as a second reductant. The choice of a particular reaction system is dictated by local chemical costs and potential byproduct recovery.

The 1968 AIChE student problem requires the design and optimization of a 7 tons/day $ClO_2$ generation system wherein sodium chlorate, sodium chloride, and sulfur dioxide are the primary reagents.

## PROCESS DESCRIPTION

A schematic representation of the proposed chlorine generation system is presented in Figure 1.

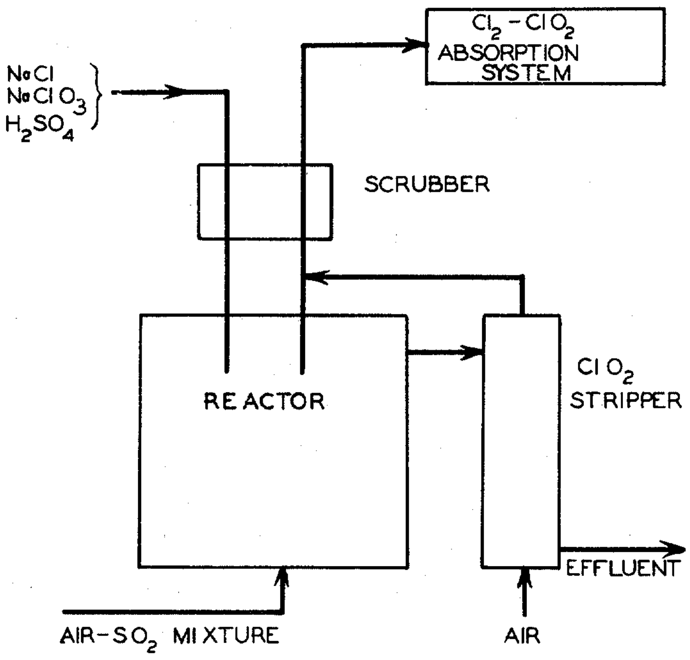


Figure 1. Chlorine Dioxide System.

In the $SO_2$ reduction process an acid solution of sodium chlorate and sodium chloride is charged continuously at the top of the reaction vessel. Sulfur dioxide diluted with air is introduced through porous ceramic plates in the bottom of the reactor. The rising gas bubbles produce sufficient turbulence to maintain uniform temperature and composition throughout the reactor. Chlorine dioxide is stripped from the reaction solution by the air stream. Liquid effluent is passed to a small stripping tower for the recovery of dissolved chlorine dioxide. The vapor products from the stripping column and the reactor are combined and passed through a scrubber to reclaim entrained liquid and unreacted $SO_2$. The vapor product passes from the scrubber to the absorption system.

Higher chlorine dioxide yields are obtainable with a two-stage reaction system, but although secondary generators are capable of efficiently reducing effluent chlorate concentrations to approximately 4 grams/liter, the reaction mechanism in the secondary reactor is complicated by this low chlorate concentration. Do not include a secondary generator in this design problem.

## REACTIONS

Chlorine dioxide is produced by the action of sulfur dioxide on sodium chlorate in an acid medium according to the overall reaction

$$2NaClO_3 + SO_2 \xrightarrow{H_2SO_4} 2ClO_2 + Na_2SO_4 \tag{1}$$

Laboratory investigations of the sodium chlorate–sulfur dioxide reaction indicated that chloride ion was essential to the production of $ClO_2$. Equation (1) does not provide a complete picture of the process.

Several mechanisms have been proposed for the formation of $ClO_2$ from chlorates in acid media. A convenient representation of the process is presented below. Since the reactions take place in an acid medium, the reactants are expressed as acids.

$$HClO_3 + HCl \longrightarrow HClO_2 + HClO \tag{2}$$

$$HClO + HCl \longrightarrow Cl_2 + H_2O \tag{3}$$

$$HClO_3 + HClO_2 \longrightarrow 2ClO_2 + H_2O \tag{4}$$

$$Cl_2 + SO_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4 \tag{5}$$

$$2ClO_2 + 5SO_2 + 6H_2O \longrightarrow 2HCl + 5H_2SO_4 \tag{6}$$

$$HClO_3 + SO_2 + H_2O \longrightarrow HClO_2 + H_2SO_4 \tag{7}$$

$$HClO_2 + SO_2 + H_2O \longrightarrow HClO + H_2SO_4 \tag{8}$$

$$HClO + SO_2 + H_2O \longrightarrow HCl + H_2SO_4 \tag{9}$$

$$HClO_3 + 5HCl \longrightarrow 3Cl_2 + 3H_2O \tag{10}$$

When sodium chloride is not supplied in the feed solution, chloride ion must be produced at the expense of chlorate, according to Equations (7), (8), and (9). Continuous salt addition suppresses the undesired side reaction and decreases normal operation transients. Chloride to chlorate concentration ratios greater than one favor the reduction of chlorate according to reaction 10. A chloride to chlorate mole ratio of 0.1 is sufficient to negate the effect of Equation (10).

The reaction capabilities of $SO_2$ are demonstrated in Equations (5) through (9). Experimental studies of vapor-phase reaction rates indicate that reaction (5) proceeds much faster than reaction (6). The experimental vapor-phase results have been generalized to the conclusion that $SO_2$ will selectively react with chlorine in liquid and vapor mixtures which contain chlorine and chlorine dioxide.

The rate of formation of $ClO_2$ from chlorate and chloride is approximately ten times faster than the equivalent chlorate-sulfur dioxide reaction.

An investigation of reaction (3) in a batch reactor demonstrated that the reaction rate was so high that concentration transients could not be established. All the hypochlorous acid rapidly reacted with hydrochloric acid to form chlorine and negligible amounts of chlorine dioxide.

The results of several experimental investigations of the chlorate-chloride reaction in the production of $ClO_2$ without sulfur dioxide are presented in Figures 2 and 3. All studies were conducted in a batch reactor maintained at 25°C. The initial rate of chlorine dioxide production was observed to increase approximately sixfold when the reactor temperature was increased from 25° to 45°C. The overall rate of formation of chlorine dioxide was approximately proportional to the second power of the chloride ion concentration. Data on the chlorate-chlorite reaction are presented in Figure 4.

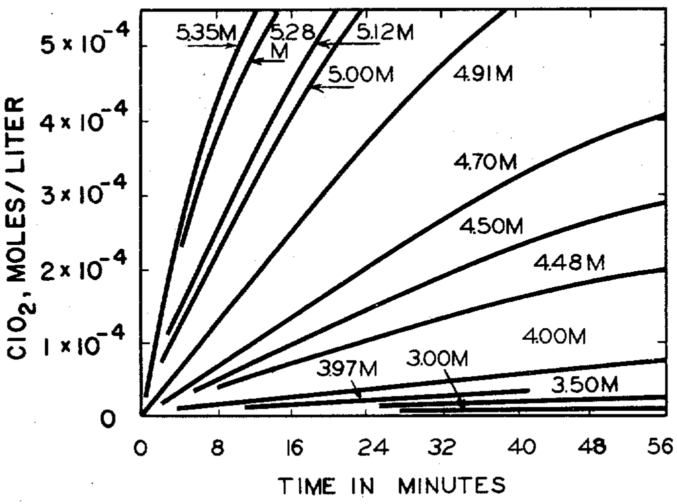
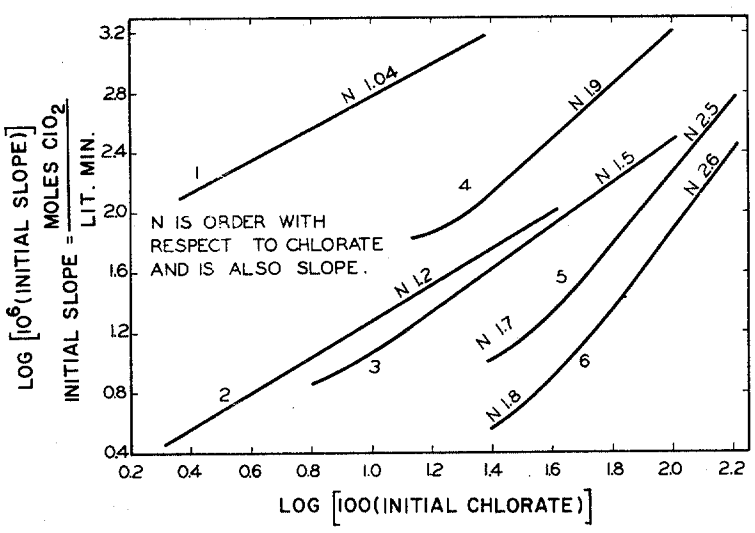


Figure 2. Chlorine Dioxide Production. The production rate of chlorine dioxide at different sulfuric acid concentrations. Initial $NaClO_3$, 0.100 molar; initial NaCl, 0.005 molar.



INITIAL CHLORATE = $\frac{\text{MOLES CHLORATE}}{\text{LITER}}$

Figure 3. Initial Production Rates of $ClO_2$.

| Curve | M $H_2SO_4$ | M NaCl |
|---|---|---|
| 1 | 6.07 | 0.0056 |
| 2 | 4.99 | 0.005 |
| 3 | 4.39 | 0.010 |
| 4 | 3.80 | 0.075 |
| 5 | 2.53 | 0.150 |
| 6 | 2.03 | 0.255 |

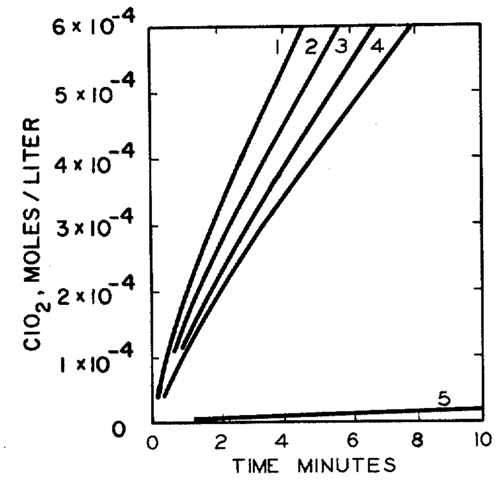


Figure 4. Comparison between Chlorate-Chlorite and Chlorate-Chloride Reactions. The effect of chloride on the chlorate-chlorite reaction and a comparison with the chlorate-chloride reaction, 0.0025 $NaClO_3$, 5 M $H_2SO_4$ for all runs.

| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| M NaCl | 0.001 | 0.0003 | 0.0001 | 0.00005 | 0.0025 |
| M $NaClO_2$ | 0.0025 | 0.0025 | 0.0025 | 0.0025 | |

0.0025 M $NaClO_3$ and 0.0025 M $NaClO_2$ without chloride gave no detectable chlorine dioxide.

Sulfur dioxide is employed primarily to regenerate chloride ions from chlorine produced in the reactor. The effectiveness of the chlorine-$SO_2$ reaction strongly depends upon $SO_2$-air dispersion and temperature. The addition of sulfur dioxide must be controlled to ensure maximum reaction before the gas bubbles reach the liquid surface. Excess sulfur dioxide will pass through the reactor and reduce chlorine dioxide [Equation (6)]. An $SO_2$ deficiency results in high chlorine concentrations and low reaction rates. Mass transfer coefficients, liquid- and vapor-phase reaction-rate data, and gas-dispersion characteristics are necessary for the complete design of the chlorine dioxide generator. The required calculations are too involved for this contest problem. The effect of temperature on the composition of gas evolved from a batch reactor with optimum $SO_2$ addition is illus-

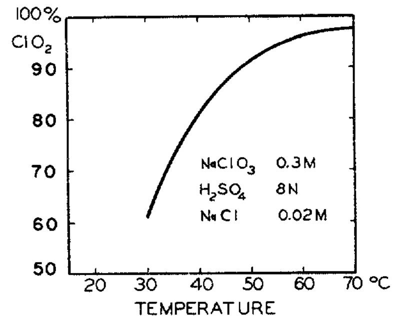


Figure 5. Effect of Temperature on the Ratio of $Cl_2$ and $ClO_2$ in a Laboratory Reactor.

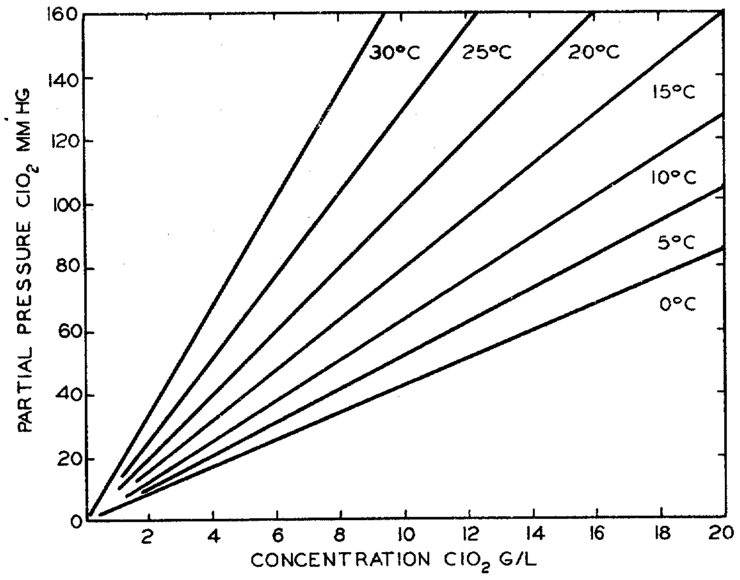


Figure 6. Solubility of $ClO_2$ in Water.

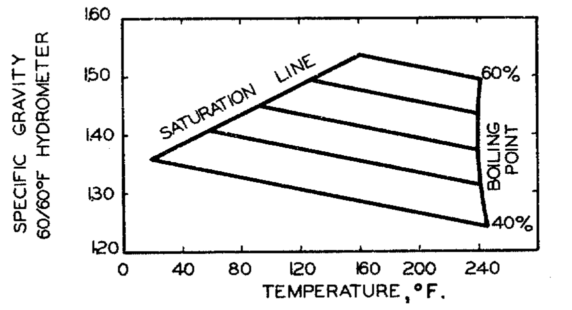


Figure 7. Specific Gravity of Sodium Chlorate Solutions.

trated in Figure 5. The reactor solution was 0.3 molar in sodium chlorate, 8 normal in sulfuric acid, and 0.02 molar in chloride ion. Figure 5 may be used to approximate the product composition for a chlorine dioxide generator with optimum $SO_2$ addition.

An investigation of a commercial 3 tons/day $ClO_2$ production system indicated excessive sulfur dioxide losses for effluent sodium chlorate concentrations below 10 grams/liter.

BIBLIOGRAPHY

Seidell, Atherton, "Seidell's Solubilities of Inorganic and Metal-Organic Compounds," American Chemical Society, Washington (vol. I, 1958; vol. II, 1965).

## NOTES

1. Various investigators have reported that gaseous chlorine dioxide is spontaneously explosive at concentrations of 12% and above (volume basis).

2. Chlorine dioxide is absorbed in water to produce the desired bleach solution—8 grams $ClO_2$/liter.

3. A system is available for the recovery of by-product sodium sulfate. Ninety-two percent of the sulfate product can be credited to the $ClO_2$ process at $17.50/ton sodium sulfate.

4. A synergistic effect has been observed for chlorine–chlorine dioxide bleach solutions. Chlorine concentrations up to 5% total chlorine content are acceptable in chlorine dioxide bleach solutions.

5. The following relation was obtained from a pilot-plant $ClO_2$ absorption column packed with 1-in. Berl saddles:

$$\frac{V}{K_G a P_T} = 3.39 \text{ ft.}$$

where $a$ = transfer area, sq. ft./cu. ft. column
$K_G$ = overall mass transfer coefficient, lb.-moles/(hr.) (sq. ft.) (mm. Hg)
$P_T$ = total pressure, mm. Hg
$V$ = vapor flow rate, lb.-moles/(hr.) (sq. ft.)

6. The acid concentration in the chlorine dioxide generator affects the chlorine content of the product. The reaction solution acid concentration should be in the range of 7 to 10.5 normal.

7. Your report should follow the format outlined below.

Letter of Transmittal

Abstract

Present a concise summary of the report.

Introduction

State the subject of the report and indicate your approach.

Summarize your conclusions.

Text

Discuss the details of your analysis.

Indicate simplifying assumptions.

Literature Cited

Appendix

Present detailed data and computations.