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PRELIMINARY EVALUATION OF CHLORINE  
FOR USE AS A GAS COOLED REACTOR SAFEGUARD

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AUTHOR  
  
R. E. Dahl

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PRELIMINARY EVALUATION OF CHLORINE  
FOR USE AS A GAS COOLED REACTOR SAFEGUARD\*

By

R. E. Dahl

March 8, 1960

Hanford Laboratories Operation  
 Richland, Washington

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\*Material from this paper was presented at the US/UK Gas Coolant Compatibility Conference 1960.

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SUMMARY

A coolant line rupture during operation of a high temperature gas cooled graphite moderated reactor would present a serious hazard. The reactor would immediately depressurize and a great deal of air would be introduced into the coolant stream. As the air passed over the graphite moderator a runaway oxidation reaction would probably ensue unless an adequate safety system were available.

This investigation was designed to evaluate chlorine as a reactor safeguard to be used to control a runaway reaction. Throughout this study, a small amount of chlorine in an air stream has demonstrated the ability to substantially reduce the oxidation rate of graphite. This has been the case even where the principal oxidizing agent was molecular oxygen or ozone.

Testing will continue in the presence of ionizing radiation to evaluate the effectiveness of chlorine as an inhibitor under simulated in-reactor environment.

Chlorine appears to inhibit graphite oxidation by blocking active sites on the surface. On the basis of this mechanism a rate law was derived which is consistent with observed behavior.

## Introduction

Several investigations<sup>(1-5)</sup> have been conducted to evaluate inhibitors of carbon oxidation. These inhibitors can be categorized by phase. Solid phase inhibitors have been very effective in laboratory experiments with reactor graphite, but have failed to inhibit oxidation during in-reactor tests. Evaluation of gas phase inhibitors in the presence of ionizing radiation, or under reactor conditions is not reported in the literature. Of the gas phase inhibitors previously investigated, chlorine appeared to be the most suitable for use as a reactor safeguard since the quantity necessary to control oxidation is small. Day<sup>(5)</sup> illustrated the effectiveness of chlorine when he was able to extinguish burning graphite at 2200° C with the addition of 0.25 per cent chlorine to his oxygen stream.

This investigation has been designed to evaluate the effectiveness of chlorine as an inhibitor for controlling runaway oxidation in gas cooled reactors. In order to make a proper evaluation, chlorine will be tested first in the laboratory without ionizing radiation to determine mechanisms and rates. Effects of ionizing radiation upon the reactions will then be tested to insure the effectiveness of the inhibitor under reactor conditions. Testing in a neutron flux is not considered essential to the program since it can be reasonably assumed a reactor would scram if a coolant line ruptured and air was drawn into the system. Gas phase inhibitors would not have to withstand high neutron density for prolonged periods but would have to operate under intense gamma radiation, and be capable of reducing the oxidation rate of graphite at elevated temperatures to the point that a runaway oxidation could not occur.

Following these premises, this investigation was planned in three phases: (I) Laboratory experiments in the absence of radiation, (II) Experiments in the presence of gamma radiation, microwave, and high voltage discharge, and (III) Experiments to test the inhibitor during runaway conditions in a prototype unit which is a full scale mock-up of an EGCR channel. All experiments are to be oxidations of reactor grade graphite in flow systems with temperature and the  $\frac{Cl_2}{O_2}$  ratio as independent variables.

DiscussionPhase I--Experimental

Phase I experiments were conducted at four temperatures, (750, 700, 600, 550°C), and at chlorine to oxygen ratios varying from 0 to 114. Samples were of CSF graphite taken parallel to the extrusion axis of the bar. CSF is a reactor grade, gas purified graphite, and the density of the bar from which the samples were made was 1.67 g/cm<sup>3</sup>. Samples were made in the form of sleeves 2" in length, 0.426" O.D. and 0.25" I.D. to furnish a relatively high reaction surface. Samples were not outgassed prior to oxidation.

Air or oxygen was dried through silica gel to a measured moisture content of  $5.7 \times 10^{-4}$  g/l before passing over the samples. Heat was provided in the reaction zone by an electrical tube furnace. Temperature was controlled with a Wheelco Capicontrol indicator controller using a platinum vs. platinum - 13% rhodium thermocouple sensing system. The temperature variation during a run was approximately  $\pm 5^\circ$  C. At least one absolute temperature value appears to have been in error; however, the experiments in question will be rechecked after equipment recalibration.

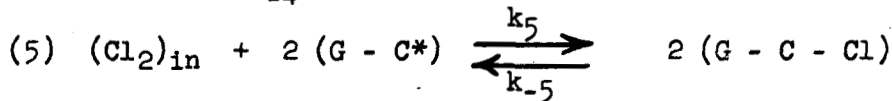
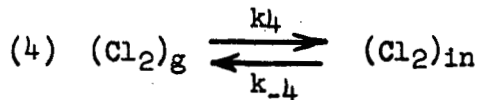
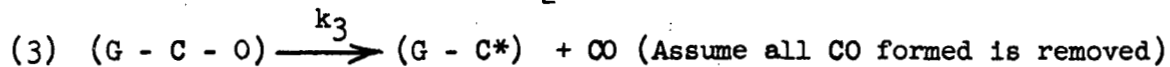
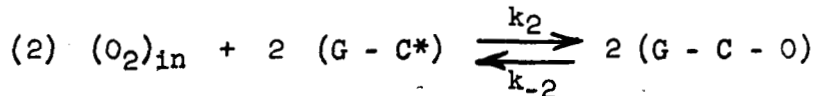
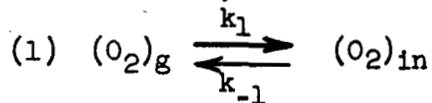
Helium was used to provide an inert atmosphere in the reaction zone before and after the oxidations. Oxidation was measured as a function of graphite weight loss and the rate expressed in units of gram/gram-hour. Several control runs were made during which the samples were brought to 750° C, held for 15 minutes, and then cooled to room temperature in helium. Weight loss was negligible. Similar runs were made with tank chlorine to test for impurities. The oxidation was again negligible.

Phase I--Data

Data from Phase I experiments agreed with previous investigations in establishing the ability of chlorine to inhibit oxidation of graphite. However, it was noted that at constant temperature the oxidation rate varied inversely with the chlorine to oxygen ratio. A power function relationship existed as long as a stoichiometric

excess of oxygen was maintained. A mechanism, consistent with observed data, would involve blocking of active sites on the graphite surface by chlorine, effectively reducing the active site concentration, thereby reducing the reaction rate. This mechanism is supported by the fact that activation energies remained constant over widely varying chlorine to oxygen ratios (See Figure 1). Values of activation energies were  $37.6 \pm .06$  kcal/mole at  $\frac{\text{Cl}_2}{\text{O}_2}$  ratios from 0 to 114. It may be concluded then, that the principle mechanism and the order of the reaction did not change in this range.

On this basis, the following reactions were assumed:



G - bound carbon atoms in the graphite lattice

C\* - available active sites

g - gas phase

in - diffused into reaction zone

It is assumed that the gas phase concentration remains constant.

From these reactions, the rate law:

$$\frac{d(\text{CO})}{dt} = k_3 \frac{A B}{\left[ \frac{\text{Cl}_2}{\text{O}_2} \right]^{1/2} + B}$$

is derived. (See Appendix I)



where A is the total number of active sites both occupied and unoccupied

$$B \text{ is } \left[ \frac{k_2}{k_{-2}} \frac{k_{-5}}{k_5} \frac{k_1}{k_{-1}} \frac{k_{-4}}{k_4} \right]^{1/2}$$

Data from Phase I experiments appearing in Table I are plotted against curves calculated from the rate law (see Figure 2). Correlation of observed and calculated values confirm the law. Nitrogen apparently does not enter into the reaction since similar experiments in oxygen showed the same behavior. Values and dimensions of  $k_3A$  for a specific temperature are identical to the oxidation rates with no chlorine present at that temperature. B remains essentially constant at  $0.1 \pm 0.03$ , is insensitive to variation in temperature and thus has a low net activation energy.

Figure 2 is very useful for predicting the oxidation rate at any chlorine to oxygen ratio, but because it is a log - log plot it distorts the picture of actual behavior. For this reason a linear plot of oxidation rate vs. per cent chlorine at  $700^\circ \text{C}$  is shown in Figure 3. With no chlorine, the oxidation rate was  $1.34 \times 10^{-1} \text{ g/g hr.}$  The rate was reduced by a factor of 8 to  $1.7 \times 10^{-2} \text{ g/g hr.}$  with 1.9% chlorine. A rate reduction of this magnitude would be equivalent to a temperature drop of  $93^\circ \text{C}$  in a reactor. Figure 3 illustrates the high initial rate reduction caused by a low percentage of chlorine, and then a quasi-saturation effect at about 2%. On this basis, approximately 2% would be the maximum chlorine concentration necessary to control a runaway reaction, and since the chlorine concentration would be relatively low, the corrosion and toxicity hazards would be diminished.

### Phase II

Experiments are currently being conducted to evaluate chlorine as an inhibitor in cases where ozone is the principle oxidant. Data from these experiments will be correlated with experiments conducted in a microwave glow discharge where oxygen atoms are the principle reactant species. Results should give a clearer insight into reactions which occur in the presence of intense gamma radiation.

### Ozone Experiments

Temperatures in these experiments were necessarily low ( $< 350^{\circ} \text{C}$ ), because of ozone instability at higher ranges. Experiments are conducted at atmospheric pressure, with flow ranging from 2.0 cfh to 6.0 cfh of air or oxygen. The ozone concentration at the generator outlet was 6% by volume in an oxygen stream and 3% in air; however, the concentration was not measured at the sample position. Reacting gases were dried to about  $6.5 \times 10^{-5}$  g/l moisture content by passing through silica gel and then through a dry ice-acetone trap. In normal experimentation chlorine was added to the carrier gas between the ozone generator and the sample position to reduce damage to the generator. Control runs were made in which chlorine was passed through the generator, but since no significant difference was noted in oxidation rates this was discontinued.

### Results

Data from ozone oxidation experiments (see Table I) are preliminary but lead to interesting conclusions. Chlorine is a much more efficient ozone oxidation inhibitor in an oxygen stream than in an air stream. It may be noted that a  $\frac{\text{Cl}_2}{\text{O}_2}$  ratio of ca. 0.15 reduced the oxidation rate by a factor of 120 in an oxygen (ozone) system and by only a factor of 5 in an air (ozone) system. The rate reductions in an air stream are comparable in magnitude to those experienced in thermal work in the absence of ozone, and it would be reasonable to conclude the rate determining mechanism may be the same. Competition for active sites, however, will not explain the magnitude of reduction of ozone attack noted in an oxygen stream. Chlorine would be expected to compete less effectively for active sites with ozone than with oxygen, and the rate would be correspondingly higher rather than the lower values that were experienced.

Since competition for active sites does not seem to be rate determining in an oxygen (ozone) chlorine system, the mechanism may involve conversion of ozone to less active species by the chlorine.

One possibility would be recombination of ozone to form molecular oxygen in the presence of a third body. Another would be formation of chlorine-oxygen complexes which would either be less reactive with graphite than ozone, or would decompose rapidly to form molecular oxygen.

Third body recombination may be tentatively discounted. If third body recombination was significant the nitrogen in the air would also be expected to have some inhibiting effect on the oxidation by ozone. Within the accuracy with which the ozone concentration was known at the sample position, the oxidation rates in the absence of chlorine were proportional to the ozone concentration, whether the carrier gas was oxygen or air.

Formation of chlorine oxygen complexes could be considered the rate limiting mechanism. Species such as  $\text{ClO}$  and  $\text{OClO}$  have been observed to be formed under electrical discharge or flash photolysis conditions.<sup>(6-7)</sup>  $\text{OClO}$  is stable and would probably undergo little reaction with graphite.  $\text{ClO}$  rapidly decomposes into  $\text{Cl}_2$  and  $\text{O}_2$ . Analysis of effluent gas is expected to aid in determination of the correct mechanism.

#### Microwave and Gamma Experimentation

Oxidation experiments are in progress in both microwave glow discharge, and in the presence of high gamma radiation. Work to date is exploratory, however, and accurate evaluation of data is not possible at this time.

Microwave oxidation experiments are conducted either in or down stream of a glow produced by a Raytheon diathermy unit producing 112 watts at 2450 megacycles. Flows range from a maximum of 40 ml/min down. Pressure is ca. 500 and temperature approximately 250° C.

Experiments in the presence of gamma radiation are being conducted in a radiation field of  $1.2 \times 10^6$  R/hr. Temperature is varied from 750° C to 500° C and flow from 5.0 to 0.2 cfh.

Phase III

The prototype unit to be used in Phase III experiments is now being constructed. Design is essentially complete and is shown schematically in Figure 4. It has been designed to allow experiments similar to those of Robinson and Taylor<sup>(8)</sup> to determine conditions which would support a runaway oxidation reaction in the EGCR. It will also provide for testing corrosive inhibitors under these circumstances. Temperature of the graphite can be raised as high as 800° C, with air flow up to 100 cfm through the annular test zone.

Experimentation is planned between the flow limits of 63.1 cfm (119 #/hr) and 3.02 cfm (5.7 #/hr) through the test zone. These flows correspond respectively with air flow through the EGCR central channel annulus with full blower capacity and convective currents with the blowers off. Chlorine concentration up to 5% in the air stream can be safely tolerated.

Conclusions

The experimental program is incomplete at this time so no final evaluation of chlorine as a reactor safeguard can be made. Results to date are encouraging and certainly justify continuance of the investigation. Rate reductions in thermal work and ozone studies, and the correlation of data with models, makes the use of chlorine appear very favorable. If work in the gamma facility follows this trend, it will be possible to make accurate decisions on the amount of chlorine to be used in a reactor accident.

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7. Benson and Buss, J. Chem. Phys., 27, 1382 (1957).
8. Robinson, P. J., Taylor, J. C., Thermal Instability Due to Oxidation of A Graphite Channel Carrying An Air Flow, IGR-R-W-302 (1958).

APPENDIX IDerivation of the Rate Law

Basis: Chlorine inhibits graphite oxidation by blocking active sites.

- Assumptions: 1. Experiments are conducted in a flow system so that  $Cl_2$  and  $O_2$  concentrations in the gas phase remain constant.
2. Reaction is not diffusion limited, i.e., absorbed  $Cl_2$  and  $O_2$  are in equilibrium with gas phase  $Cl_2$  and  $O_2$  and their concentrations also remain constant.
3. Adsorption is accompanied by molecular dissociation.
4. Most active sites are occupied by chlorine or oxygen.

Nomenclature

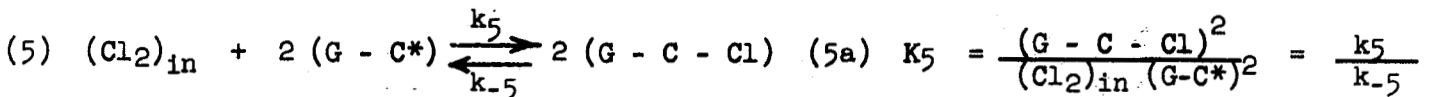
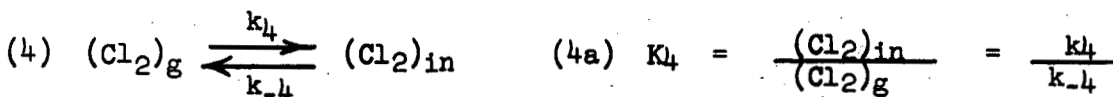
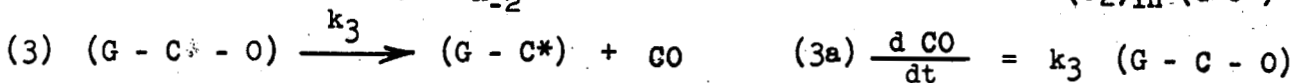
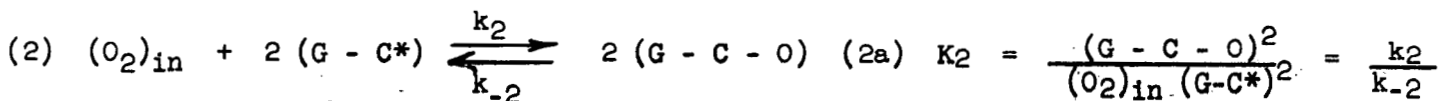
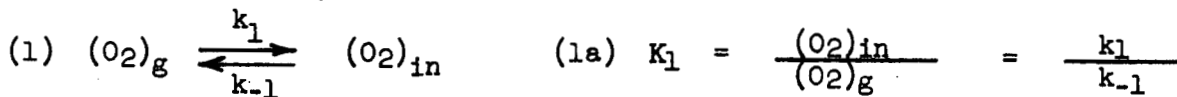
A = total number of active sites (occupied or unoccupied).

C\* = available active sites

G = bound carbons (graphite lattice)

in = into reaction zone

g = gas phase



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thus,

$$(6) \quad (G - C^*)^2 = \frac{(G - C - Cl)^2}{K_5 (Cl_2)_{in}}$$

and

$$(7) \quad (G - C - O)^2 = K_2 (O_2)_{in} (G - C^*)^2$$

Substituting equation 6 into equation 7:

$$(8) \quad (G - C - O)^2 = \frac{K_2 (O_2)_{in}}{K_5 (Cl_2)_{in}} (G - C - Cl)^2$$

At constant temperature,

$$A = (C^*) + (G - C - O) + (G - C - Cl)$$

and remains constant.

$$(9) \quad \text{If } C^* \ll A, \text{ then } (G - C - Cl) \approx A - (G - C - O)$$

$$(10) \quad (G - C - O) = \left[ \frac{K_2 (O_2)_{in} [A - (G - C - O)]^2}{K_5 (Cl_2)_{in}} \right]^{1/2}$$

$$\text{from equations 1 and 4} \quad (10a) \quad (G - C - O) = \left[ \frac{K_2 K_1 (O_2)_g}{K_5 K_4 (Cl_2)_g} (A - (G - C - O))^2 \right]^{1/2}$$

$$\text{Let } B^2 = \frac{K_2 K_1}{K_5 K_4}$$

and

$$(11) \quad (G - C - O) = B \left[ \frac{(O_2)_g}{(Cl_2)_g} \right]^{1/2} \left[ \frac{1}{1 + B \left( \frac{(O_2)_g}{(Cl_2)_g} \right)^{1/2}} \right]$$

from equation 3

$$\frac{dCO}{dt} = k_3 (G - C - O)$$

Then

$$\frac{dCO}{dt} = k_3 A B \left[ \frac{1}{\left( \frac{(Cl_2)_g}{(O_2)_g} \right)^{1/2} + B} \right]$$

TABLE I

THERMAL OXIDATION EXPERIMENTS.  
PRESSURE 1 ATM FLOW, 2.0 cfm AIR.

| <u>T °C</u> | <u><math>\frac{Cl_2}{O_2}</math></u> | <u>Oxidation Rate</u><br><u>g/g hr</u> |
|-------------|--------------------------------------|--|
| 750         | 0.                                   | $3.8 \times 10^{-1}$                   |
|             | 0.009                                | $2.1 \times 10^{-1}$                   |
|             | 0.21                                 | $7.15 \times 10^{-2}$                  |
|             | 5                                    | $1.55 \times 10^{-2}$                  |
|             | 106                                  | $3.9 \times 10^{-3}$                   |
| 700         | 0                                    | $1.34 \times 10^{-1}$                  |
|             | 0.009                                | $5.3 \times 10^{-2}$                   |
|             | 0.025                                | $4.05 \times 10^{-2}$                  |
|             | 0.095                                | $1.70 \times 10^{-2}$                  |
|             | 0.21                                 | $1.55 \times 10^{-2}$                  |
|             | 0.30                                 | $1.30 \times 10^{-2}$                  |
|             | 5                                    | $4.35 \times 10^{-3}$                  |
| 106         | $9.30 \times 10^{-4}$                |  |
| 600         | 0                                    | $1.19 \times 10^{-2}$                  |
|             | 0.009                                | $1.05 \times 10^{-2}$                  |
|             | 0.055                                | $4.5 \times 10^{-3}$                   |
|             | 0.21                                 | $3.2 \times 10^{-3}$                   |
|             | 5                                    | $6.4 \times 10^{-4}$                   |
|             | 106                                  | $1.87 \times 10^{-4}$                  |
| 550         | 0                                    | $3.8 \times 10^{-3}$                   |
|             | 0.009                                | $2.78 \times 10^{-3}$                  |
|             | 0.052                                | $1.55 \times 10^{-3}$                  |
|             | 114                                  | $7.0 \times 10^{-5}$                   |



TABLE II

DATA FROM OZONE EXPERIMENTS  
TEMPERATURE--300°C PRESSURE--1 ATM--AIR OR OXYGEN FLOW--2.0 cfh  
EXPERIMENTS IN OXYGEN (NOMINAL 6% OZONE)

| <u>Cl<sub>2</sub></u><br><u>O<sub>3</sub></u> | <u>Rate</u>           |
|---|-----------------------|
| 0   | $7.2 \times 10^{-3}$  |
| 0   | $7.2 \times 10^{-3}$  |
| $9.0 \times 10^{-4}$                          | $5.69 \times 10^{-3}$ |
| $1.8 \times 10^{-3}$                          | $4.15 \times 10^{-4}$ |
| .0106   | $6.0 \times 10^{-5}$  |
| .0565   | $6.35 \times 10^{-5}$ |

EXPERIMENTS IN AIR (NOMINAL 3% OZONE)

|      |                       |
|------|-----------------------|
| 0    | $2.03 \times 10^{-3}$ |
| 0    | $2.24 \times 10^{-3}$ |
| .21  | $4.42 \times 10^{-4}$ |
| 0.21 | $4.81 \times 10^{-4}$ |

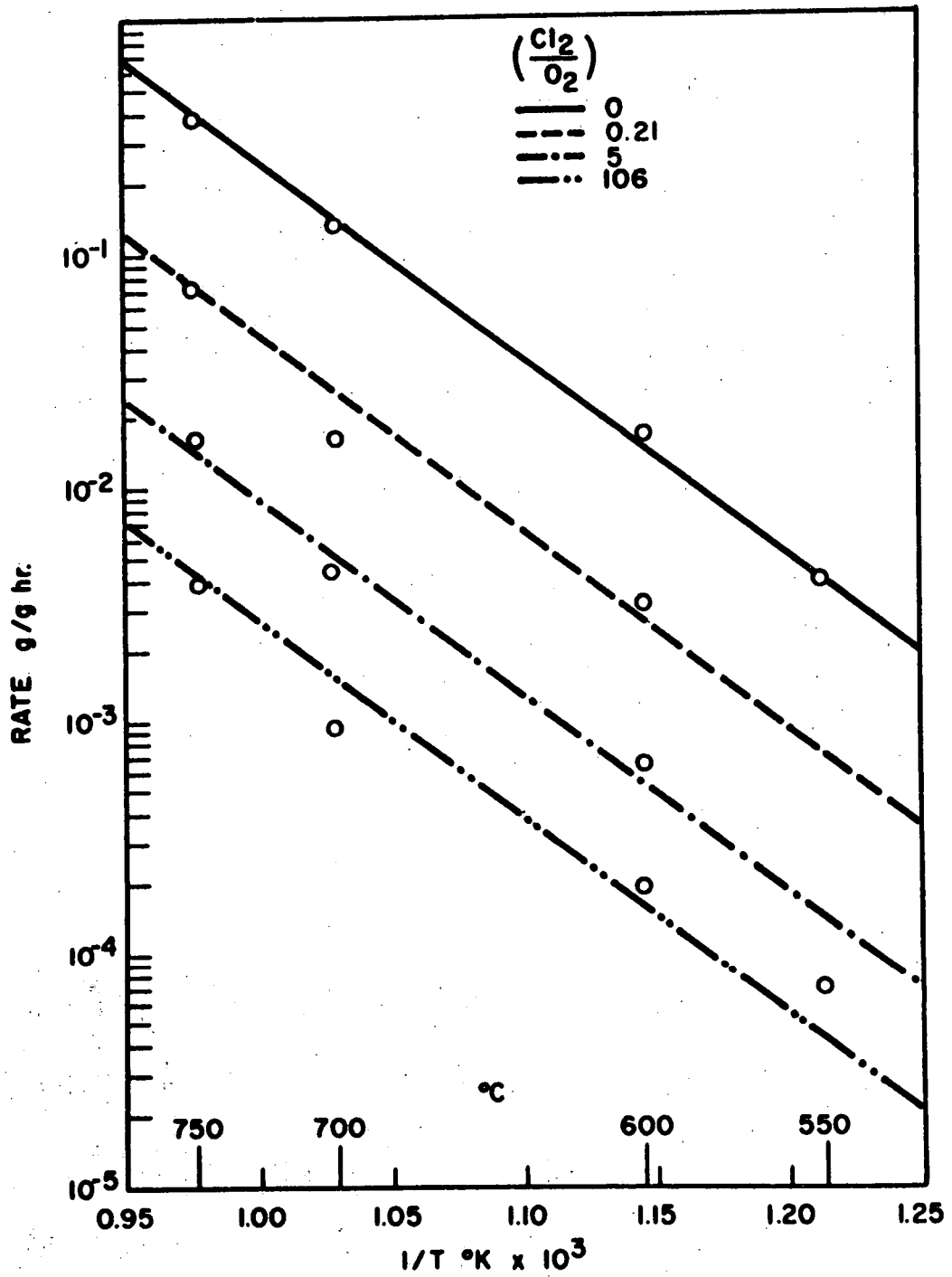


FIGURE 1

Rate vs.  $\frac{1}{T}$

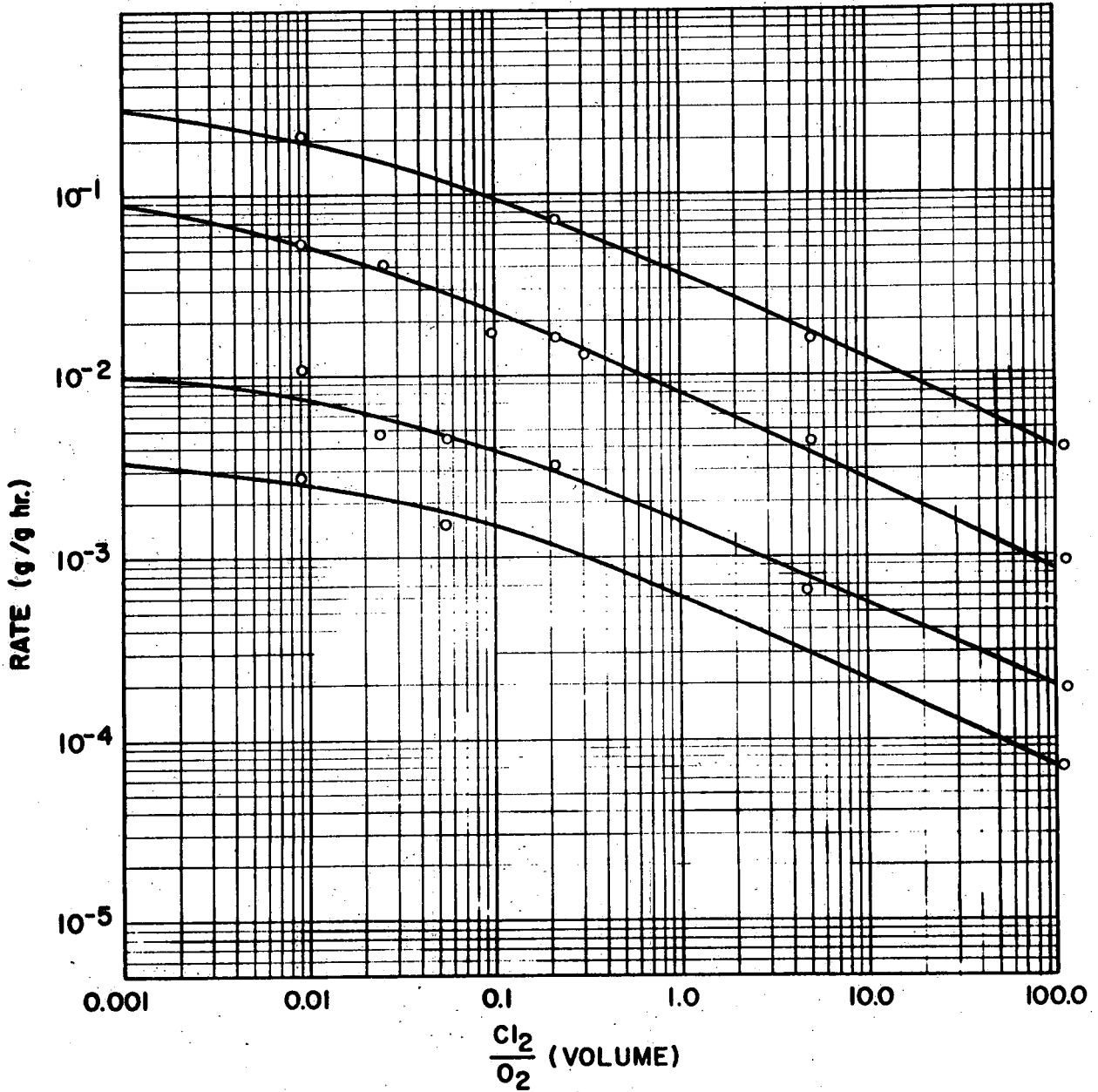


FIGURE 2

Experimental Values and Calculated Curves

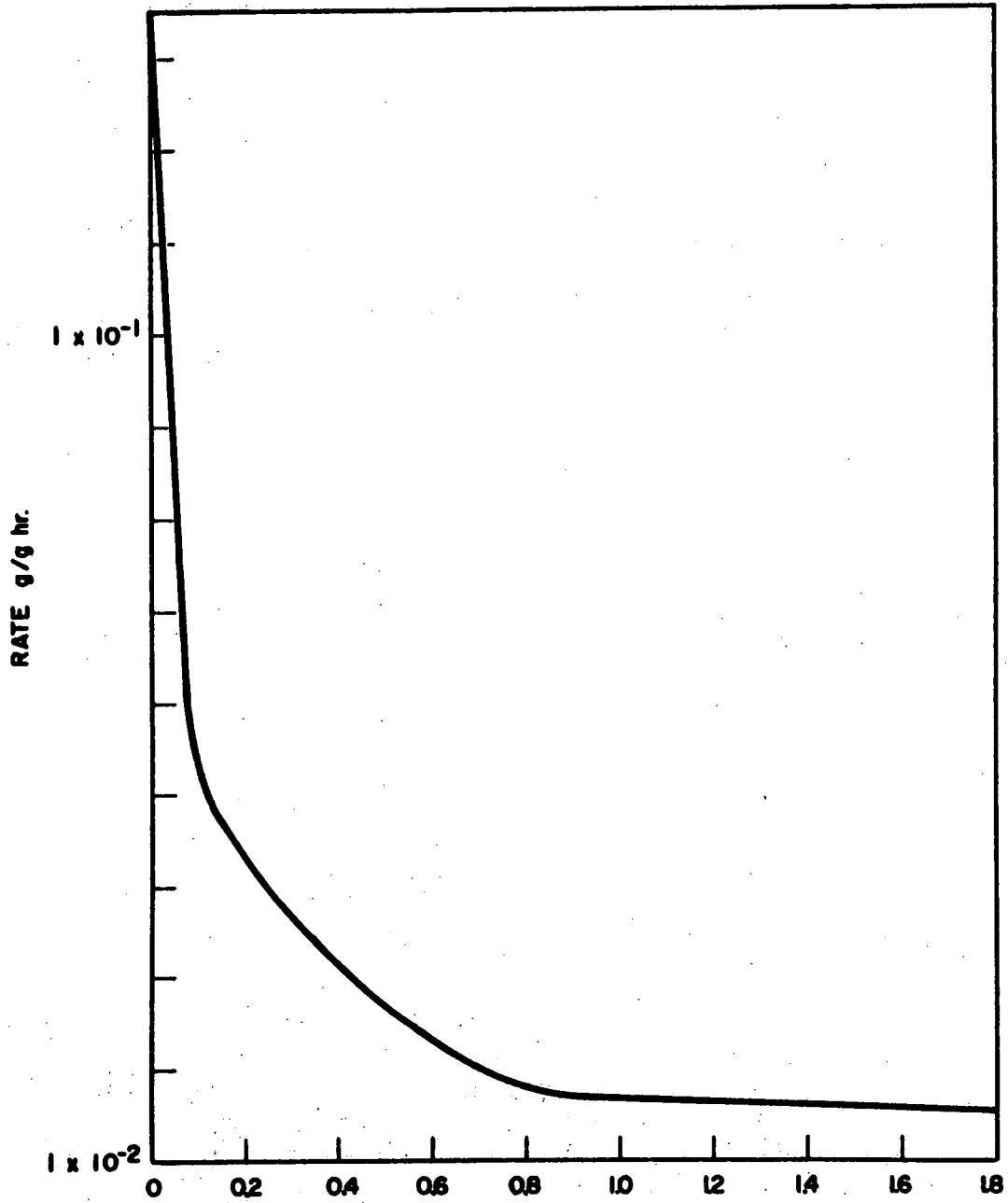


FIGURE 3

Rate vs. % Chlorine

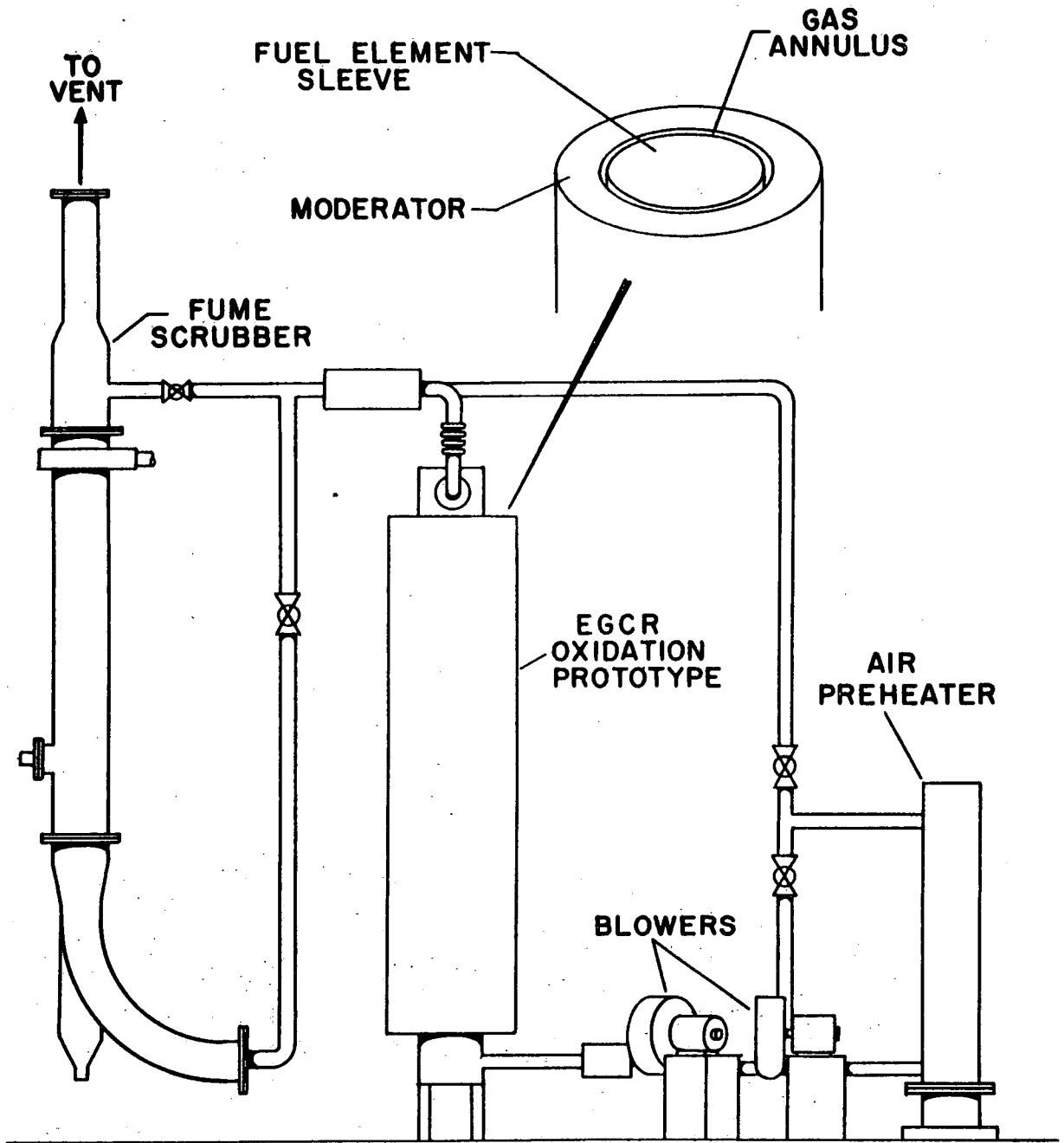


FIGURE 4

Engineering Scale Prototype Unit