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PURELY CHEMICAL LASER BASED ON CHLORINE ATOM REACTIONS: C10 SUB 2 GENERATOR

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by

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RESUME

On a construit un appareil pour la production d'un débit de ClO_2 dilué avec He, en adaptant un modèle décrit dans la littérature. Cet appareil produit des concentrations de ClO_2 variant jusqu'à 4% en He (ou en autres gaz inertes) et ayant un débit de 0.18 mmol/s. Le Cl_2 est présent dans le gaz, mais non en concentration importante. Par ailleurs, le gaz effluent est humide à cause de l'eau dans le $NaClO_2$ qui est présent dans la colonne où la réaction se fait. (NC)

ABSTRACT

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A ClO_2 generator capable of producing a flow of ClO_2 in inert diluent gas has been constructed using an adaptation of a design appearing in the literature. This generator supplies ClO_2 in concentrations up to 4% in helium or other inert gases at a flow rate of 0.18 mmol/s. Cl_2 in important concentration is not present in the effluent gas; the effluent gas is, however, moist, due to water in the $NaClO_2$ charge in the column. (U)

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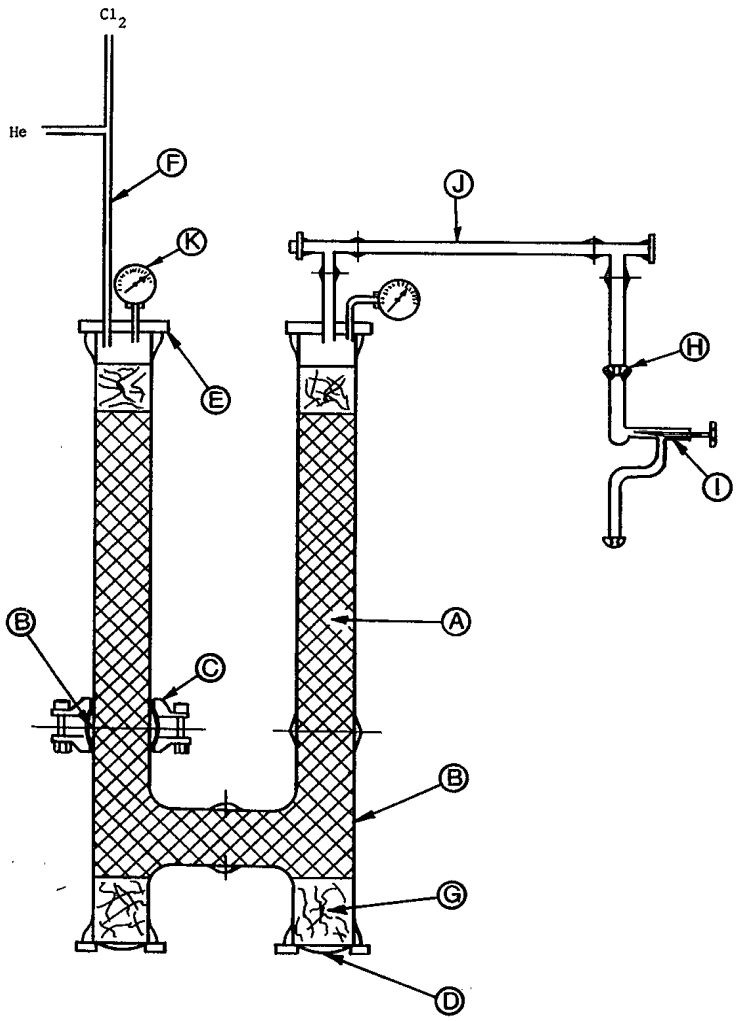

LEGEND

A: 7.7 Kg $NaClO_2$ PACKING; REAGENT GRADE, FLAKED

B: CORNING DOUBLE TOUGH TUBING SECTIONS, 4-IN ID

C: TYPICAL CLAMP FOR JOINING DOUBLE TOUGH SECTIONS

D: LEAD SHEET RUPTURE DISK; 1/16-IN THICK, SEALED WITH TEFLON PUTTY

E: TEFLON SEALING PLATE, FURNISHED WITH MACHINED BOSS TO MATE WITH O-RING GROOVE IN DOUBLE TOUGH GLASS SECTION; 3/4-IN THICK, SEALED WITH TEFLON PUTTY

F: STAINLESS STEEL 1/4-IN OD SUPPLY LINE, FIT WITH SWAGELOK FITTINGS

G: GLASS WOOL END PACKING

H: BALL AND SOCKET GLASS JOINT, LUBRICATED WITH HALOCARBON GREASE

I: TEFLON AND GLASS NEEDLE VALVE TO REGULATE OUTPUT

J: CORNING DOUBLE TOUGH TUBING, 4-IN ID

K: PRESSURE GAUGE AT ENTRANCE AND EXIT TO COLUMN

FIGURE 1 - Schematic - ClO_2 generator

1.0 INTRODUCTION

We are presently constructing a continuous wave chemical flow laser at DREV based on the reactions of Cl atoms. Details of this device will appear separately (Ref. 1,2) and need not be repeated here. In brief, however, this laser depends on the vibrationally excited HCl formed during the reaction of Cl atoms with HI:

$$Cl + HI \rightarrow HCl\dagger + I + 31.7 \text{ kcal/mol} \qquad (1)$$

Chlorine atoms are formed in the laser flow tube by the addition of NO to a flow of ClO_2 in inert gas, generally He, according to the overall equation:

$$ClO_2 + 2NO \rightarrow Cl + 2NO_2 + 23.5 \text{ kcal/mol} \qquad (2)$$

The necessary ClO_2 is generated on demand in a $NaClO_2$ packed column when Cl_2 in He is flowed through the column. The following reaction occurs between the gaseous Cl_2 and the solid $NaClO_2$ packing material.

$$Cl_2 + 2NaClO_2 \rightarrow 2NaCl + 2ClO_2 \qquad (3)$$

This process is the basis of a patent (Ref. 3) for ClO_2 production, generally used for industrial in situ bleaching applications; designs for the generator itself have been published (Refs. 4, 5) and the device described in this communication is an adaption of those designs. We shall describe our design and present some measurements of its performance.

This work was done during the first quarter of 1974 under project PCC 97-01-39; "Research on Chemically Excited Lasers".

2.0 DESCRIPTION OF THE APPARATUS

2.1 ClO_2 Generator

The ClO_2 generator tube itself was constructed of Corning Double Tough glass plumbing with a 4-in inside diameter. A schematic drawing of this is shown in Fig 1. The entry and exit to the columns were sealed by means of 3/4-in thick Teflon plates sealed to the glass surface by means of a perfluorocarbon putty (Ref 6). This putty was made by heating fine Teflon powder and fluorocarbon wax together in methylene chloride to form a heavy malleable paste. This paste has been found to be generally useful for sealing joints of relatively smooth mating surfaces that are to be exposed to highly reactive halogen compounds.

All the Double Tough glass sections were held together with standard bolts and collars; the seals were made with Teflon gaskets as supplied by the manufacturer. The bottoms of the vertical columns on each side were closed with sheets of 1/16-in thick lead which were sealed with the putty. These lead sheets served as rupture discs in the case of explosion or over-pressure in the column.

2.2 Gas Feed

The feed of gas to the column consisted of a stainless-steel gas handling system, employing 1/4-in OD stainless steel tubing and stainless steel 1/4-in Swagelok fittings. Bottled He and Cl_2 were employed. The He was handled in the usual way with standard regulators and pressure gauges. The flow was measured with a Hastings Model ALL-5K flowmeter at a pressure of 1200 torr absolute. The Cl_2 was metered into the column using a Monel needle valve manufactured by the Nupro Corp. The flow was measured at 1200 torr absolute pressure using a Hastings Model ALL 500 flowmeter made of Monel. The two flows were combined and fed directly into the column which was controlled at the desired operating pressure with a glass and Teflon needle valve at the effluent end. The flowmeters were calibrated from measured filling times of a known volume.

2.3 Column Filling

The column was filled with 7.7 kg of reagent grade "flaked" sodium chlorite ($NaClO_2$) supplied by Matheson, Coleman and Bell Company. With this packing, no measurable pressure drop, within ± 5 torr, was detected when a helium flow rate of 7000 standard cm^3 per minute (SCCM) was passed through the column.

3.0 EXPERIMENTAL

3.1 Operating Conditions

The ClO_2 column was required, in these experiments, to supply a flow of ClO_2 highly diluted in He gas (~ 4%) at a flow rate of about 100 μmol s^{-1} of ClO_2. The column itself was always run at a pressure of 970 torr and the flow was regulated by the needle valve at the effluent end of the column. By means of this needle valve, the gas pressure was broken down to that required in the laser; about 10 torr.

To establish the flow, the desired feeds of He and Cl_2 were set up in the gas feed system to the column, and the operating pressure was maintained at 970 torr with the needle valve. In this way, a steady feed of ClO_2/He to the laser could easily be maintained.

Typical flow rates of He plus Cl_2 were on the order of 5000 SCCM (5 ℓ/min); the total volume of the empty column was 27 ℓ. If the free volume of the column packed with $NaClO_2$ is ~ 3 ℓ, then the residence time of the gas in the column is on the order of 36 s. The free volume was not measured.

3.2 Analysis of the Column Effluent Gas

The method of Woodward et al (Ref 4) was used with some modification as follows. The flows in the column were stabilised and, after about 15 min of operation, the flow was switched into a gas bubbler charged with 200 ml of a solution of KI in water (2.5% by wt) for a precisely timed period, typically 60 s. As the gas bubbled through the solution, the following reactions occurred:

$$1/2\ Cl_2 + I^- \rightarrow Cl^- + 1/2\ I_2$$

$$ClO_2 + I^- \rightarrow ClO_2^- + 1/2\ I_2.$$

A known fraction of the resultant solution was titrated with 0.1 N $Na_2S_2O_3$ solution. This gives a measure of the total of Cl_2 and ClO_2 since each I_2 molecule liberated consumes two equivalents of $Na_2S_2O_3$ as:

$$I_2 + 2S_2O_3^{=} \rightarrow 2I^- + S_4O_6^{=}.$$

Following this titration, the ClO_2^- remaining can be estimated by acidification of the same aliquot used above with acetic acid and titration of the liberated iodine, again with the $Na_2S_2O_3$. The reaction

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O$$

describes the liberation of four equivalents of I_2 for each equivalent of ClO_2 present in the original aliquot. By subtraction, the ClO_2 determined in the acid titration can be taken from the sum of the Cl_2 carried with the ClO_2 in the gas system. In this way, the efficiency of conversion of Cl_2 in the column was determined.

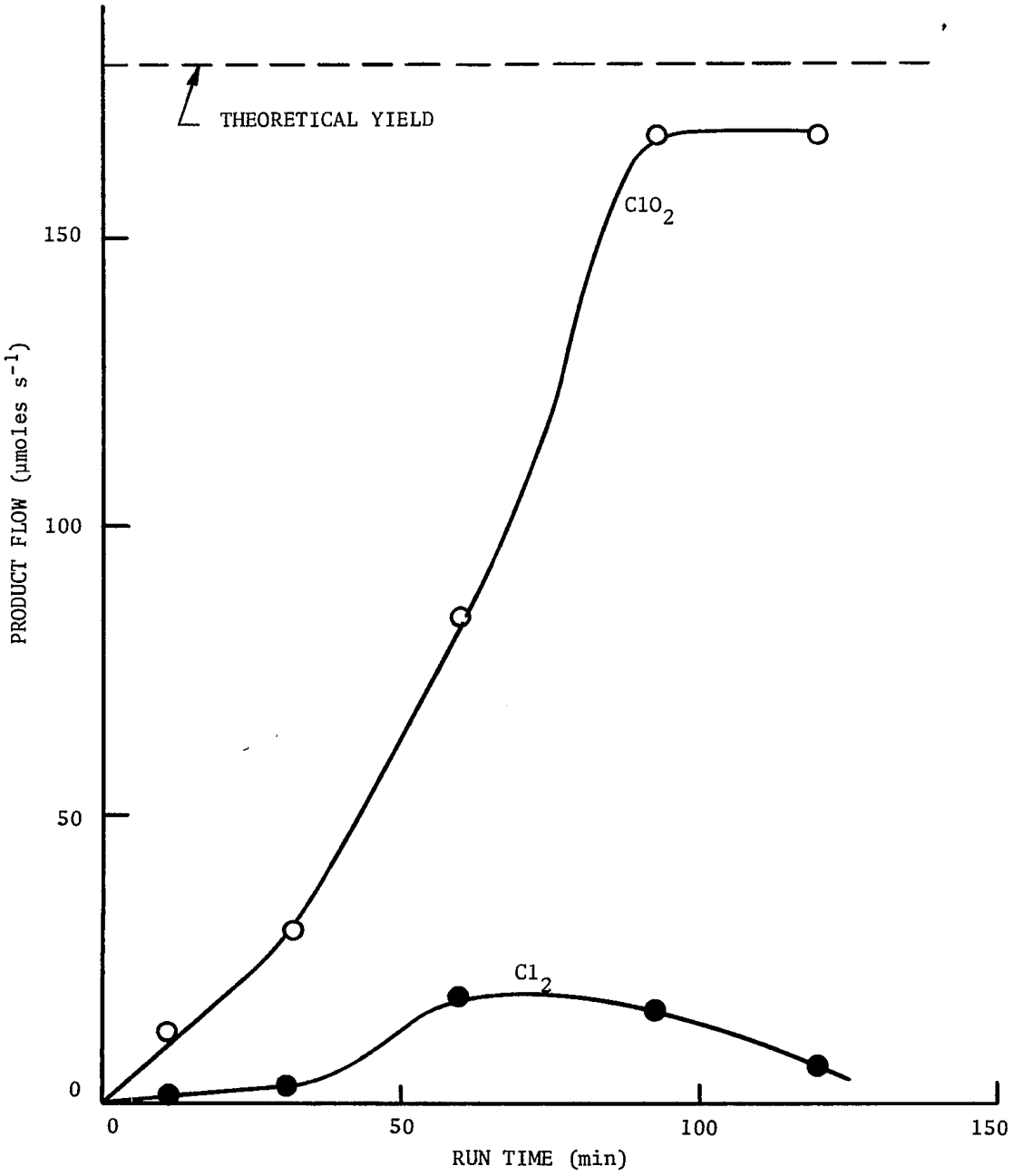

FIGURE 2 - Generator output at start-up for fresh column packing

4.0 RESULTS AND DISCUSSION

4.1 ClO_2 Yield

With a fresh charge of $NaClO_2$ in the column, a flow of 121 SCCM Cl_2 and 5000 SCCM He was admitted continuously to the column. The effluent gas was analysed periodically for Cl_2 and ClO_2, using the method described in Section 3.2.

A flow of 121 SCCM Cl_2 corresponds to 90 μmol s^{-1} which theoretically should be converted into 180 μmol s^{-1} ClO_2 after passing through the column according to the equation

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

The results of these measurements are shown in Fig. 2. Here we see that the ClO_2 yield starts out very low and increases steadily to a value near the theoretically expected yield. The flow of chlorine out of the column is never very great, but is always measurable, nonetheless. The induction period is similar to that already observed by Woodward, et al (Ref 4). During this induction period when there is less than the expected amount of ClO_2 produced, the shortfall is not accountable in terms of unreacted chlorine passing through the column. We conclude that the absorption of the equivalent of ~17 g of Cl_2 occurs during this conditioning period.

The maximum possible ClO_2 production has not been determined as yet. We know that ClO_2 flows sufficient for the flow laser under construction (Ref 2) are attainable without difficulty; subsequent laser designs embodying transverse flow will require higher flows and more complete characterisation will be carried out at that time. Reports in the literature (Ref 4) indicate, however, that flows up to 1000 μmol s^{-1} ClO_2 can be realised in a similar design to the present one. This is 5.9 times greater than the flow shown in Fig. 2.

4.2 Column Exhaustion

After several weeks of intermittent use, the columns ceased to provide a reliable stream of ClO_2. Analysis of the column packing material did not reveal any detectable depletion of the $NaClO_2$ charge. An error of about 5% could be imagined in this analysis, which embodies iodimetric titration of the $NaClO_2$ material. The error arises because there is probably $NaClO_3$ in the starting material, and, also, $NaClO_3$ can be formed during the reaction. However, it is certain that the evolution of ClO_2 stopped far in advance of the complete exhaustion of the $NaClO_2$ packing material. This problem is not, as yet, resolved. The total useful life of the column packing was not measured precisely, but is on the order of 20 h using flows on the order of 50-100 SCCM Cl_2, as required for the laser experiments.

5.0 CONCLUSIONS

The ClO_2 generator, constructed as shown in Fig. 1, is a reliable and convenient device for the supply of ClO_2-He mixtures as required for longitudinal flow lasers based on the reactions of Cl atoms.

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