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AN ECONOMIC STUDY OF OXYGEN DIFLUORIDE

Final Report

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by Air Products and Chemicals, Inc.,
Allentown, Pennsylvania
F. L. Hyman and J. F. Tompkins, authors)

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FOREWORD

This is the final report on NASA Contract NASW 1911 "An Economic Study of Oxygen Difluoride". The work reported covers the period from June 4, 1969 to June 4, 1970. The objective of the contract is to investigate the economics of processes for the preparation of oxygen difluoride, and to specify a process or processes by which it may be supplied below the present market price. The oxygen difluoride will be needed at uneven rates with 2,000 to 4,000 lbs required per year. At the request of the NASA technical manager this final report presents economics for producing OF₂ at 4,000 to 50,000 lb/yr. This increased production is based on the possible use of OF₂ for engine testing as well as actual mission requirements.

The economics presented are based on literature yields except those for the fluorine-caustic process which are based on experimental work performed under this contract. Some limited experimental work was also performed on the porous anode electrolytic method.

The NASA Program Manager for this contract is Dr. Robert S. Levine, NASA Headquarters, Washington, D. C. and the Technical Manager is Mr. Wolfgang Simon, Jet Propulsion Laboratory, Pasadena, California.

ABSTRACT

The economics of oxygen difluoride production based on four processes described in the literature are presented. These four processes are: 1) fluorine-caustic 2) fluorine-water catalyzed by alkali fluorides 3) electrolysis of water in hydrogen fluoride, and 4) electrolysis of oxygen in hydrogen fluoride using a porous anode. The literature for these four processes and other potential processes are reviewed. It is concluded that at this time the fluorine-caustic offers the least expensive method for making OF_2 at rates at or below 10,000 lb/yr. The main reasons for this choice are the relatively low process development costs and reasonably well defined yields and investment costs.

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I. Summary

This report presents the economics of oxygen difluoride production based on four processes described in the literature. These four processes are: 1) fluorine-caustic 2) fluorine-water catalyzed by alkali fluorides 3) electrolysis of water in hydrogen fluoride, and 4) electrolysis of oxygen in hydrogen fluoride using a porous anode. The literature for these four processes and other potential processes are reviewed.

The economic advantages and disadvantages of the processes are discussed together with the important criteria to be considered in selecting a process. Investment, process development, shipping and storage costs are discussed for all processes at production rates of 4,000, 10,000 and 20,000 lb/yr, and at 50,000 lb/yr for the fluorine-caustic and electrolytic porous anode processes.

Experimental results are presented for the fluorine-caustic and the electrolytic porous anode process. Yields of 70% or better were obtained for the fluorine-caustic process at fluorine rates of 2 lb/hr.

It is concluded that at this time the fluorine-caustic offers the least expensive method for making OF_2 at rates at or below 10,000 lb/yr. The main reasons for this choice are the relatively low process development costs and reasonably defined investment costs. The more economical process for high production rates (50,000 lb/yr), appears to be the electrolytic oxygen porous anode process if the literature yields can be maintained on scale-up and estimated development costs prove realistic.

Estimated selling prices for OF_2 produced for all four processes are given in Figure I up to 20,000 lb/yr. In addition the selling price for the fluorine-caustic and electrolytic porous anode processes are given in the range of 4,000 to 50,000 lb/yr in Figure I. These prices are for a single 12 month continuous production contract and include writing off all process development and OF_2 production and purification investment costs over the 12 month contract. Estimated selling prices for OF_2 after process development and OF_2 production and purification equipment have been fully depreciated are shown in Figure II. For this depreciated investment case the lower operating costs of the porous anode electrolytic process become significant and result in a lower selling price. The estimated OF_2 selling prices do not include storage, transportation and working capital costs.

FIGURE I

Selling Price for OF_2 at Various Production Levels for Different Processes

Plant Depreciation and Development Cost Charged Over a Single 12 Month Contract

No Storage, Transportation or Working Capital Charges Included

OF_2 Stored in Government Owned Cylinders up to 20,000 Lbs.

OF_2 Stored in Government Owned Liquid Trailer Above 20,000 Lbs.

Prices Assume Continuous Production

Selling Price, \$/lb

Electrolysis of Water Process

F_2 Water Process

F_2 Caustic Process

Electrolysis of Oxygen in HF Process

OF_2 Produced, lb/12 Month Contract

80

70

60

50

40

30

20

10

0

0

10,000

20,000

30,000

40,000

50,000

FIGURE II

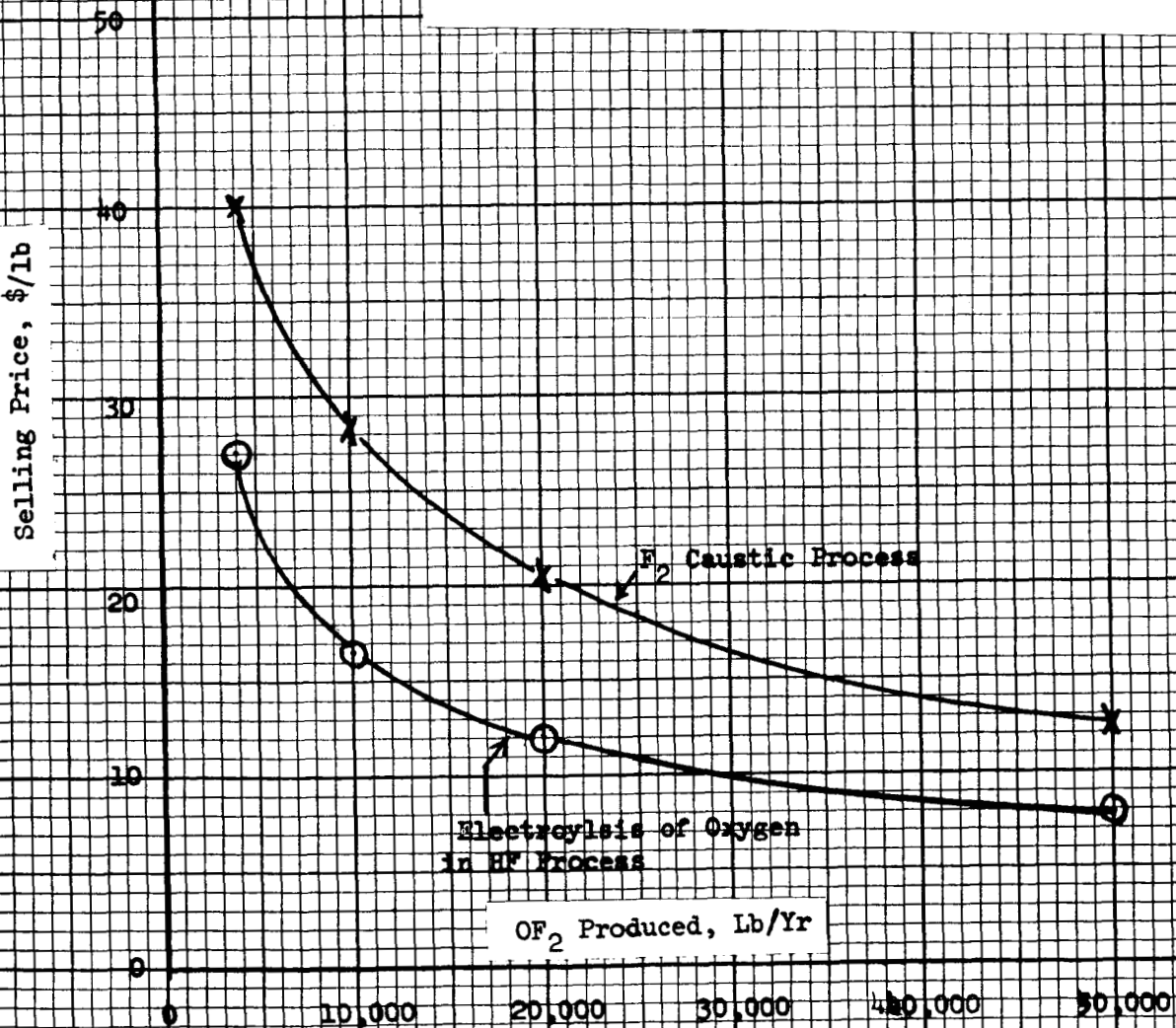
Selling Price for OF_2 at Various Production Levels by Fluorine-Caustic and Electrolysis of Oxygen in HF Processes for a Depreciated Plant with no Process Development Expense

No Storage, Transportation and Working Capital Charges Included.

OF_2 Stored in Government Owned Cylinders up to 20,000 lbs

OF_2 Stored in Government Owned Liquid Trailers Above 20,000 lbs

Prices Assume Continuous Production

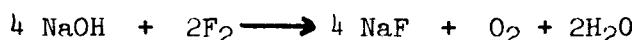
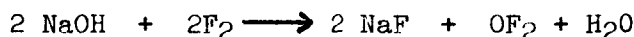


II. Introduction

The object of this contract was to find the most economical process for producing oxygen difluoride at uneven rates with 2,000 to 4,000 lbs required per year. At the request of the NASA Technical Manager the program objectives were broadened in September 1969 to include; accelerated experimental work on the most easily reduced to practice type process, and the investigation of the economics of all promising processes at production rates up to 50,000 lbs/yr. For this final report the Technical Manager requested that the three major production rates considered be 10,000 lb/yr, 4,000 lb/yr, and 20,000 lb/yr with fluorine-caustic and porous anode electrolytic processes investigated up to 50,000 lb/yr. The rates are given in order of decreasing importance.

The four processes considered in this report as having potential for producing OF₂ in commercial quantities are:

1. Fluorine-Caustic: Defined by Ruff and Menzel (A-14) in 1930 later refined by others and most recently studied by Brown (A-2) in 1968. The process consists of bubbling fluorine through 2% caustic solution. The fluorine is converted to OF₂ and an alkali fluoride as defined by the following equations:



2. Fluorine + Water: Borning and Pullen (A-3) modified the fluorine-water reaction by running it in the presence of an alkali fluoride.
3. Direct electrolysis of Water in Hydrogen Fluoride: This process was studied in detail by J. A. Donohue et al at American Oil Co. (C-6,8) under contract DA-31-124-ARO(D)-78. Original discovery of the method was made by Engelbrecht and Nachbauer in 1959 (C-10).
4. Direct Electrolysis of Oxygen in hydrogen fluoride using a Porous Anode: This method recently patented by W. V. Childs at Phillips Petroleum (C-5) involves passing air or oxygen into a porous carbon anode where it reacts with fluorine to liberate OF₂.

The fluorine-caustic process was chosen for the initial experimental work for several reasons; the process is the most extensively investigated and required the least investment and development cost of the four considered. Experiments performed with the fluorine-caustic system at fluorine rates up to 2 lb/hr show no reduction in yields from literature values. Some experiments have also been done on the porous anode process.

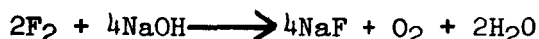
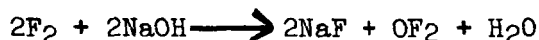
III. Literature Review

Methods for making OF₂ can be divided into three main classes. These include (1) reactions of fluorine with inorganic compounds (2) reactions of fluorine and oxygen and (3) direct electrolysis.

A. Reactions of Fluorine with Inorganics

A-1. Fluorine-Caustic

Historically OF₂ was first observed in the off gas of fluorine cells containing small amounts of water in the electrolyte by Lebeau and Damiens (C-13). Soon after their discovery they were able to prepare OF₂ by reacting fluorine with 2% caustic (A-9). A year later Ruff and Menzel (A-13) prepared OF₂ by the caustic method and further characterized it. During the next fifteen years several authors reported yields of OF₂ using variations of the caustic-fluorine process (A-4, 5, 8, 15, 16, 19). Early reactions with caustic-fluorine involved bubbling excess fluorine through a thin layer of 2% caustic. This technique was used so that the competing oxygen producing reaction would be minimized. The two reactions of fluorine and caustic are:



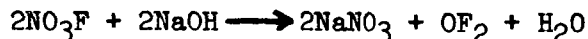
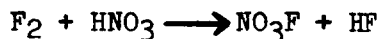
In the early 1960's Harshaw (A-18) and Thiokol (A-7) prepared OF₂ in laboratory quantities by contacting fluorine with a thin film of 2% NaOH in wetted wall columns. In both cases an excess of fluorine was used. The Harshaw workers obtained a 70% yield. Experimenters at Thiokol were only able to obtain a 45% yield using a 100 cm column giving a 25.5 sec. residence time. By decreasing the column length to 50 cm workers at Thiokol obtained yields over 70% at a 10.5 sec. residence time.

In a recent patent of Brown (A-2), yields up to 85% are claimed using large excesses of caustic. His claim is that the main source of oxygen is really the decomposition of OF₂.



This decomposition reaction is accelerated by the heat generated in OF_2 reaction. By using excesses of caustic and keeping the temperature between 0 to 25°C , he has obtained yields between 70 and 85%. The fluorine caustic literature results are summarized in Table I.

Ruff and Kwasnik (A-13) prepared OF_2 in a two step fluorine-caustic reaction with NO_3F as an intermediate by the following reaction sequence.



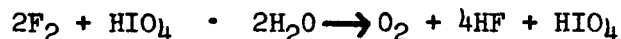
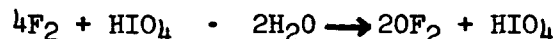
Yields for this reaction were not reported. The authors do mention that explosions with NO_3F were common if the proper reaction conditions for the nitric acid reaction were not maintained.

A-2. Fluorine-Water Reactions

Several other reactions of fluorine with inorganic compounds have been reported. The basis for several of these is the reaction of fluorine and water.



This has been studied in detail by Ruff (A-15) and Cady (A-5). Although both reported obtaining quantities of OF_2 , yields were very low with large amounts of oxygen being formed. The oxygen was probably formed by the decomposition of OF_2 . Cady reported a 5% yield using fluorine and ice-water (A-5). Cady also made OF_2 from periodic acid (A-12) and solid hydroxides of sodium, barium, potassium and calcium (A-5). The periodic acid reaction is actually the water fluorine reaction.



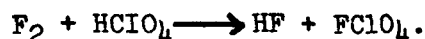
OF_2 accounted for 27% of the gaseous products of the reaction.

Rohrbach and Cady reported (A-11) OF_2 and O_2 in the off gas from the reaction of 60% perchloric acid with fluorine. Oxygen difluoride comprised 45 mole % of the off gas. The OF_2 and O_2 were probably formed from the water-fluoride reaction. The reaction desired was

TABLE I

COMPARISON OF LITERATURE DATA FOR OF₂ BY FLUORINE-CAUSTIC REACTIONS

Author (Ref)	Date	F ₂ Rate (lit/hr)	Caustic Type	Caustic Conc, %	lit/hr	Yield or Rate of Formation	Reactor Comments
Lebeau (A-9)	1929	1.0	NaOH	2	--	70% of off gas	F ₂ bubbled through 1.0 cm of NaOH in 0.2 cm tube
Ruff (A-14)	1930	1.0	NaOH	2	0.5	45% yield ~0.5 g/hr	same reactor as Lebeau
Cady (A-5)	1935	--	NaOH	2	--	60% yield	
Cady & Yost (D-10)	--	1-3	NaOH	2	1.0	50% OF ₂ + 50% O ₂ in off gas	F ₂ bubbled through 0.5 to 2.0 cm of NaOH
∞							
Schnizlein (A-16)	1952	2-6	NaOH	3	1-2		F ₂ bubbled through 1.5 cm of caustic
Swinehart (A-18)	--	--	NaOH	--	--	70% yield	Used 5:1 F ₂ to NaOH ratio in a wetted wall column
Holzmann (A-7)	1961	12	NaOH	2	50	45-70% yield	Used wetted wall column (50-100 cm long), yield varied inversely with column length
Brown (A-2)	1968	42	KOH	2	38	70-85% yield	Bubbled F ₂ through 10 to 20 inches of 2% KOH



The reaction of a 31% solution H_2O_2 with fluorine diluted with nitrogen has also been reported (A-7). The reaction was conducted at -18°C with nitrogen to prevent explosions and fires. Although some OF_2 was obtained no yields were reported and it is uncertain whether H_2O_2 or water reacting with the fluorine actually gave OF_2 . At the yields given in the literature these reactions can not compete with the fluorine-caustic process.

The most recent fluorine water reaction is the catalyzed reaction using an alkali fluoride catalyst. This process was disclosed in 1969 by Borning and Pullen (A-3).

Borning and Pullen passed fluorine into a glass vial containing an alkali fluoride and water. The water was condensed on the surface of CsF or NaF anhydrous powder or added as a hydrate when potassium fluoride was used as the alkali fluoride.

The yield for the reaction varied between 55 and 80%. The authors claim better yields with $\text{KF}\cdot 2\text{H}_2\text{O}$ and KF (70%+) than with NaF (60%). The fluoride mixture tended to lump during the reaction and agitation of the alkali fluoride was necessary.

Mr. Pullen was contacted regarding the experiments. He stated that no additional work had been done and that no other reports were available. The work had been conducted in a few weeks and that more things would have been done if time permitted. He thought that by diluting the fluorine with nitrogen so as to decrease the heat of reaction that better yields could be obtained. He also stated that even though their experiments showed better yields with KF than NaF , that NaF would be better on a larger scale reaction because of cost, ease of regeneration, and lessening of the caking problem. He attributed the caking to HF since none occurred until the reaction started.

In general the process appears to offer no concrete advantage over the fluorine-caustic method. It would probably require a more expensive reactor, plus the regeneration of alkali fluoride would be an additional processing step.

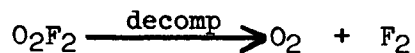
A-3. Other Fluorine-Inorganic Reactions

Brief mention has been found of three other reactions of this type of reaction although no yields have been obtained. Oxygen difluoride was found as a by-product of the cesium fluoride catalyzed reaction of fluorine and potassium carbonate (A-10) and from the reaction of fluorine and potassium chlorate (A-17). Chlorine pentafluoride as the fluorinating agent has been reported to react with ozone to give ClF_3 and OF_2 (A-1). These reactions are regarded as laboratory curiosities, and will not be considered further.

B. Direct Combination of Oxygen and Fluorine

Combination of oxygen and fluorine was first performed by Kuff and Menzel (B-10, B-11). By using an electric arc at liquid air temperature Ruff and Menzel were able to make O_2F_2 . The reaction was performed in the gas phase at low pressures. Later by varying the ratio of O_2 to F_2 , the current and voltage O_3F_2 (B-1, 2, 7, 8, 12) and O_4F_2 (B-4) were prepared using the same basic low temperature and low pressure technique. Streng and Grosse (B-13) later prepared oxygen fluorides by the same technology in the liquid phase. No details or yields are given and which oxygen fluorides were obtained is not reported.

In 1966 Goetschel (B-3) obtained mass spectra data for OF_2 in the vapors distilling off a mixture assumed to be higher order oxygen fluoride. This material was prepared by low temperature irradiation of the elements. The previously reported decomposition series for oxygen fluoride had not included OF_2 .



In 1969 Kirshenbaum (B-6) reported a 20% conversion of OF_2 from ultraviolet irradiation of ozone and fluorine at 120°K using approximately a 2:1 ozone to fluorine ratio. The remaining gas included O_2F_2 (36% conversion) O_2 and F_2 . An equimolar mixture of O_3 and F_2 irradiated at 195°K resulted in only a 3 to 5% conversion to OF_2 .

No report has been found where O_2 and F_2 were combined without irradiation or direct electrolysis. A Pennsalt report states that O_2 and F_2 reacted for 16 hours at $375^\circ C$ and 2100 psig yielded only F_2 and O_2 (B-9).

The lack of any positive results for OF_2 production from oxygen-fluorine reactions preclude any economic calculations for this type. The work Goetschel (B-3) indicates that it may be possible to prepare OF_2 by low temperature irradiations but definite yields in excess of 35% will be needed before it can compete with the fluorine caustic published yield of 70% in raw material price alone. Since the reactions are carried out at low temperature with UV and/or high voltage equipment, a higher capital investment is inevitable. Therefore, further yield improvements would be necessary in order to make fluorine-oxygen reactions practical.

The work of Kirshenbaum (B-6) with ozone and fluorine represents the only quantitative results for this type of reaction. He found that 56% of the fluorine was converted with a 20% conversion to OF_2 . If the fluorine could be recycled the yield would be equivalent to the base case 70% yield for the fluorine-caustic process (since all the fluorine goes to product only one half the yield is necessary). Goetschel reports no yields for any of his oxygen fluoride work.

C. Direct Electrolysis

C-1. Water in HF

Although OF_2 was first discovered in the anode gas of a fluorine cell by Lebeau and Damiens (C-13), no work was done to optimize the production of OF_2 by electrolysis of wet HF until the last ten years. Several authors discussed the possibility of producing OF_2 electrolytically (C-11, 16) but no experimental yields were reported until Engelbrecht and Nachbauer published their work in 1959 (C-10). They reported OF_2 yields of 55 to 60% over a water concentration range of 1 to 20% using 10% NaF as a conductivity additive. The OF_2 yields were reported as % OF_2 in the anode gas with the only impurity given as oxygen. Since both OF_2 and

oxygen require four Faradays per mole, the electrical yield would be the same as the % OF_2 in the off gas at 100% anode efficiency. Engelbrecht, however, does not mention what anode efficiency was obtained.

A detailed study of the electrolysis of wet HF was conducted at Americal Oil Company under contract DA-31-124-ARO (D) - 78. The work was reported in several contract reports, patents, and journal articles (C-2, 3, 4, 6, 7, 8) by J. A. Donohue et al. Donohue reported that maximum yields (current efficiencies) of 45% could be obtained over a much narrower range than that reported by Engelbrecht. Donohue found that maximum yields could be obtained with water concentrations of from 0.2 to 2.0% mole and with alkali fluorides present in about 0.2 to 0.5 mole %. By increasing the water content ozone began forming in preference to OF_2 up to about 6% water content when the ozone production fell off. In this water range the OF_2 yield was about 10-15% and the current density fell off. Donohue suggests that above 8% water and 2% alkali fluoride the main product would be oxygen although no data are given in the 8 to 20% water range and at 10% alkali fluoride metal where Engelbrecht reports high yields.

Donohue's final contract report (C-6) and his OF_2 patent (C-8) present somewhat contrasting data. These are compared in the following table:

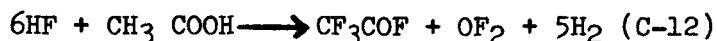
	Contract Reports	U.S. Pat. 3,276,981
Water Content, mole %	0.1 to 1.0	0.1 to 1.0
Metal Alkali, mole %	1.0	0.2 to 0.5
Interrupting current	Yes	No mention
Current density, Amp/ft ²	10-20	50-70
Maximum yield (current eff.), %	45	64
Water content @ max. yield, mole %	0.56	0.26
Fluorine present	None	10% Max.
Temperature, °C	10-15	-30 to +50
Voltage, Volts	5-7.5	6.4-8.3

The patent makes no mention of the interrupting current feature stressed in the contract report. The patent also gives higher yields by operating near the threshold voltage of 8 volts for fluorine production. At voltages between 7.0 and 8.3 volts Donohue reports in his patent up to 10% fluorine in the effluent gas. The contract report also mentions that a water content less than 0.2% gave severe anode corrosion.

C-2. Water and Organic Compounds

In his early work on electrofluorination of organic compounds, J. H. Simons reported OF_2 present in the off gases when water was added for conductivity or if oxygen containing compounds (eg organic acids) were electrofluorinated (C-19). In 1966 Kasaki et al (C-12) in trying to find which type of compound gave the best perfluoroalkyl carbonyl fluoride (R_fCOF) yield also presented yield data for OF_2 and COF_2 . The best OF_2 yields are 20% for acids and 35% for aldehydes. Kasaki data for acetic and Simons for butyric both give 20% yields for OF_2 .

The electrolysis of acetic acid is shown by the following reaction:



The 10 Faradays needed to complete this reaction make it more expensive (operating and capital investment) than the electrolysis of water which requires only 4 Faradays per mole unless much higher yield could be obtained. Since only 6 Faradays would be required per mole for formic acid it would be better than acetic if the same yields could be obtained.

Kasaki showed a 35% yield of OF_2 from acetaldehyde. However, Nagase (C-14) found a great deal of polymeric residue when electrofluorinating aldehydes. This was caused by the decomposition of fluorinated aldehydes in the cell. Polymers in the cell would produce shorts which would result in increased maintenance costs. For these reasons aldehydes would be less desirable than acids.

Nagase et al (C-15) added water to ethyl and propyl esters and alcohols. He concluded that since the amount of electricity needed to produce any perfluorinated compound varied directly with the water added that water was electrolyzed preferentially over the organic alcohols and esters.

C-3. Direct Electrolysis of Inorganic Compounds

Oxygen difluoride has been reported as an anode product of inorganic compounds by Rogers (C-16, 17) and Engelbrecht (C-9). Rogers reported OF_2 and NF_3 to be the major anode products of the electrolysis of nitrogen oxides. When yields were calculated only a 2% yield of OF_2 was reported with large amounts of current going anode losses.

Engelbrecht electrofluorinated a number of sulfur, oxygen and nitrogen containing inorganics. Potassium and ammonium sulfates and persulfates yielded OF_2 , SO_2F_2 , N_2 , O_2 and various other compounds including CO_2 from the polyvinyl chloride diaphragm. Explosions were common in the piping of the divided cell. Some explosions were attributed to NO_3F . The best yields of OF_2 were obtained for potassium and ammonium persulfate. Early in one $\text{K}_2\text{S}_2\text{O}_8$ run the percent OF_2 in the anode gas ran as high as 60%. Later in the same experiment comparable amounts of SO_2F_2 were obtained. From the data presented it was impossible to calculate the amount of charge consumed during OF_2 formation. It is probable that OF_2 was formed mainly from water present in the HF since using $\text{KF}\cdot 2\text{HF}$ as the electrolyte at a higher temperature gave initially only 12% OF_2 in the anode gas.

C-4. Direct Electrolysis Using Oxygen

In a very recent patent (C-5) Childs at Phillips Petroleum has claimed that it is possible to produce OF_2 at 78% current efficiency by adding oxygen through a porous anode. He claims that oxygen and fluorine react in the pores of the electrode to form OF_2 . He states that electrodes may be made from porous metals (eg. nickel, steel) or with porous carbon which are desired. This route to OF_2 appears to have economic advantages over the water route if moderate current efficiencies can be maintained.

The process involves adding oxygen or air into a porous carbon anode. As the oxygen passes through the anode it reacts with fluorine being liberated from HF. The cell with the exception of the anode construction and small electrolyte modifications is essentially a typical fluorine cell.

The use of a porous anode for producing OF_2 has been reported in the literature. Allen (C-1) mentioned that OF_2 was produced by passing water through a porous carbon anode in a typical medium temperature fluorine cell. No experimental data or yields were presented. Donohue (C-2) tried to introduce oxygen into his electrolytic cell containing HF through a porous nickel anode. He reported that when the addition was attempted that the pores plugged and no oxygen passed into the cell. He then added oxygen through a porous nickel cathode and was able to regenerate water necessary for the electrolysis.

The literature data for the direct electrolytic methods are compared in Table II.

TABLE II

COMPARISON OF LITERATURE DATA FOR OF₂ BY DIRECT ELECTROLYSIS

<u>Author</u>	<u>Date</u>	<u>% H₂O</u>	<u>Additives</u> <u>% F salt</u>	<u>Yields</u>	<u>Cell Conditions</u>
Lebeau (C-13)	1927	?	50 KF	3 to 27% of anode gas rest O ₂	---
Engelbrecht (C-10)]	1959	1-30	10 NaF	50-60% of anode gas rest O ₂	6 volts in divided cell with PVC screen
Donohue (C-6,8)	1966	0.1-1.0	0.2-2.0 KF	45% electrical yield 20-40% O ₂ 0-30% O ₃	0-15°C., 6-8 volts, undivided cell
Childs (C-5)	1969	Trace	40-60 KF	78% conversion	O ₂ added at a porous anode in divided cell @ 60-105°C.

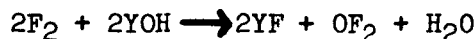
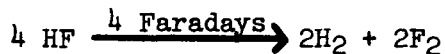
IV. OF₂ Production Economics

A-1. Basic Assumptions

Yields

The methods of OF₂ production considered in this report have been divided into three classes. These processes are (1) fluorine reactions with inorganics (2) fluorine reactions with oxygen and (3) direct electrolysis. These processes all involve directly or indirectly an electrolysis reaction since the only commercial source of fluorine is electrolytic. For fluorine reactions with inorganics and direct electrolysis 100% yield would result in 1.11 lb OF₂ produced per 1000 Amp-hr of electricity as shown by the following equations.

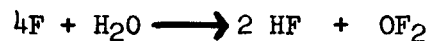
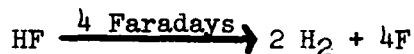
Fluorine production:



where Y is usually H, K, or Na

4 Faradays of electricity produce 1 mole OF₂

Direct Electrolysis: (H₂O as an example)



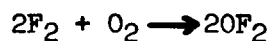
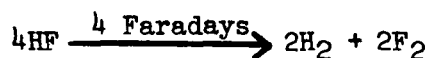
4 Faradays of electricity produce 1 mole OF₂

$$\left(\frac{1 \text{ mole OF}_2}{4 \text{ Fara}} \right) \left(\frac{\text{Fara}}{26.8 \text{ Amp-hr}} \right) \left(\frac{54 \text{ g}}{\text{g mole}} \right) \left(\frac{1 \text{ lb}}{454 \text{ g}} \right) = 1.11 \times 10^{-3} \text{ lb/Amp-hr}$$

or 1.11 lb/1000 Amp-hr

Since operating costs and capital investment are directly proportional to cell ampere rating, the lbs obtained per 1000 Amp-hr is the most meaningful way to express yields for electrolytic processes.

In the direct combination of oxygen and fluorine 100% yield would give 2.22 lb of OF₂ per 1000 Amp-hr.



2 Faradays of electricity yield 1 mole of OF_2

Therefore the direct combination has an inherent advantage over the other two processes at equal yields.

The electrolytic method using oxygen in a porous electrode has the same advantages, since it is the direct combination of oxygen and fluorine with all the fluorine going to OF_2 . This method then gives 2.22 lb of OF_2 per 1000 Amp-hr at 100% yield.

B. Process Comparisons

Based on the literature review of OF_2 production methods, four processes would seem plausible on a commercial scale. These processes are 1) fluorine-caustic 2) fluoride-water using an alkali fluoride catalyst 3) electrolysis of water in HF and 4) electrolysis using oxygen in a porous electrode. The advantages and disadvantages of these processes are given below.

B-1. Fluorine-Caustic

The fluorine-caustic is the oldest and best known process for preparing OF_2 . During this contract the fluorine-caustic process has been developed and operated at fluorine rates up to 2 lb/hr. A commercial unit using the output of a fluorine cell would be 7 lb F_2 /hr. Further development costs to get the process to a commercial size would be minimal which is the biggest advantage of the fluorine-caustic process. The main disadvantages of this process is that the mixture of moisture, caustic and fluorine is a very corrosive and reactive system. This results in high maintenance costs for equipment, in high labor costs and in low on-stream efficiencies. The reaction mixture can explode or burn if precise conditions are not maintained. For this reason labor costs may be higher than for the other processes considered.

B-2. Fluorine-Water (Alkali Fluoride Catalyzed)

This process is based on a brief article by Borning and Pullen using about 0.5 grams of fluorine in a 500 cc glass bulb. There has been no scale up of this reaction toward a 7 lb F₂/hr unit. Problems with this reaction would probably be similar to those in the fluorine-caustic in respect to corrosion. The problem of caking of the reactants when HF is formed would have to be solved. The reaction equipment, either a corrosion resistant stirred autoclave or fluidized bed, would be more expensive than the fluorine-caustic reaction system. In summary, the process offers no yield or other advantages over the fluorine-caustic system and would cost significantly more to develop to a commercial unit.

B-3. Electrolysis of Water in HF

The process is based on the work of Donohue, done at American Oil under government contract DA-31-124-ARO (D)-78 and patented in U.S. Patent 3,276,981. One possible advantage of the process is that the handling of fluorine may be avoided. A second advantage is that the amount of HF used for electrolytic processes is less than that for the fluorine reaction processes. The disadvantages are: 1) the process has not been scaled up past a 10 amp cell. A commercial cell for OF₂ production by this method would probably be between 4,000 and 6,000 amps. 2) The yields given in government reports are below those of the fluorine process, since 100% yields for the fluorine processes and the electrolysis of water are both 1.11 lb OF₂/1000 amp-hr. Yields reported for the electrolysis of water are 45 to 64% compared to 70% for fluorine processes. This means that the labor costs or the investment costs will be greater unless a greater on-stream factor can be obtained.

B-4. Electrolysis Using Oxygen in HF with a Porous Anode

The biggest advantage is that this process at 100% yield gives 2.22 lb OF₂/1000 amp-hr. This means substantially reduced labor costs in equivalent rated cells at equal yields. It also has the other advantage, listed above for electrolytic processes. The yield reported is also as good as the fluorine processes. The disadvantage is the process also has

not been scaled up. The work reported in the patent (U.S. Patent 3,461,049) was done with a 3 amp cell with a 30 cm² surface area anode. Again a commercial cell would operate at 4,000 to 6,000 amps.

C. Factors Affecting the Selling Price

C-1. Design Criteria

The design criteria by which 10,000 lb/yr. could be made by each process are listed in Table III. The electrical efficiency of each cell is assumed to be 90% (1.4 lb F₂/1000 Amp-hr. or 2.00 lb OF₂/1000 Amp-hr. for porous anode). The maximum number of operating weeks/yr is assumed to be 40. An additional 12 weeks for process maintenance are included in the labor man-hour figures. The on-stream factor for all processes considered was 66%. For processes involving fluorine this figure would appear to be realistic and perhaps higher than what could be realized in the initial stages of operation. The electrolytic processes should be able to operate at or above the 66% on-stream factor used.

The table also lists the labor requirements used in the calculations. The estimates for the fluorine-caustic process are based on the experiments carried out during this contract. The operator man-hours for the other fluorine process should be the same. Electrolytic processes should require less manpower since the OF₂ reactor has been eliminated. One less man/day for the electrolytic process was assumed although further work on scale up of the process may indicate that even less manpower is needed. In any case, three men/day (1 per shift) would be a minimum unit.

C-2. Investment Factors

The estimated investments for 10,000 and 20,000 lb/yr plants are given in Tables IV and V. The 10,000 lb/yr plant would be used part time for a 4,000 lb/yr commitment. At production rates above 10,000 lb/yr the plant would have to be operated 7 days/wk for rates up to about 14,000 lb/hr, or additional investment for more fluorine capacity and larger production and purification equipment would be needed. The point where additional investment is necessary would create a discontinuity in the selling price curve given in Figure I.

A schematic breakdown of the OF₂ processes is shown in Figure III. The figure shows eight components which make up a typical OF₂ process. These eight components also represent eight areas of capital investment. These areas are plant site, fluorine generation, OF₂ generation, OF₂

Table III

Design Criteria for Various OF₂ Processes

Process	F ₂ -Caustic		F ₂ -Water		Electrolysis of Water in HF		Electrolysis Using O ₂	
	Production Rate lb/yr	10,000	10,000	10,000	10,000	10,000	10,000	10,000
<u>Electrolyzer</u>								
Type	F ₂ Cell	F ₂ Cell	F ₂ Cell	F ₂ Cell	OF ₂ Cell	OF ₂ Cell	OF ₂ Cell	OF ₂ Cell
Amps	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000
On-Stream Factor, %	66	66	66	66	66	66	66	66
Production, lb/hr	7 of F ₂	7 of F ₂	7 of F ₂	7 of F ₂	2.5 OF ₂	2.5 OF ₂	7 of OF ₂	7 of OF ₂
Operating Time								
Wks/yr	40	40	40	40	40	40	20	20
Hrs/wk	120	120	120	120	168	168	120	120
<u>OF₂ Production</u>								
Crude Yield, %	70	70	70	70	50	50	70	70
Purification Eff., %	90	90	90	90	90	90	90	90
Overall Yield, %	63	63	63	63	45	45	63	63
Crude OF ₂ Rate lb/hr	3.5	3.5	3.5	3.5	2.5	2.5	7.0	7.0
<u>Labor</u>								
Man-hr/yr Oper.	10,400	10,400	10,400	10,400	10,400	10,400	5,120	5,120
Man-hr/yr Sup.	2,080	2,080	2,080	2,080	2,080	2,080	1,280	1,280
Operators/day	5	5	5	5	4	4	4	4

Table IV

Investments for Various OF₂ Production Processes
10,000 lb OF₂/12 month Contract

<u>Plant Sections</u>	<u>F₂-Caustic</u>	<u>F₂-Water (KF Cat.)</u>	<u>Electrolysis (Water + HF)</u>	<u>Electrolysis (O₂ + HF)</u>
Electrolyzer, \$	53,000	53,000	} 60,000	} 75,000
OF ₂ Reactor, \$	18,300	48,000		
OF ₂ Purification, \$	12,900	12,900	17,300	23,600
OF ₂ Compression, \$	19,200	19,200	19,200	25,000
Plant Site, \$	<u>11,000</u>	<u>11,000</u>	<u>11,000</u>	<u>11,000</u>
Total Plant Inv., \$	114,400	144,100	101,500	134,600
Process Development, \$	10,000	50,000	65,000	80,000
Cylinder Investment, \$	41,500	41,500	41,500	41,500
Shipping & Storage Inventory (Working Capital), \$	42,500	51,900	45,800	45,500

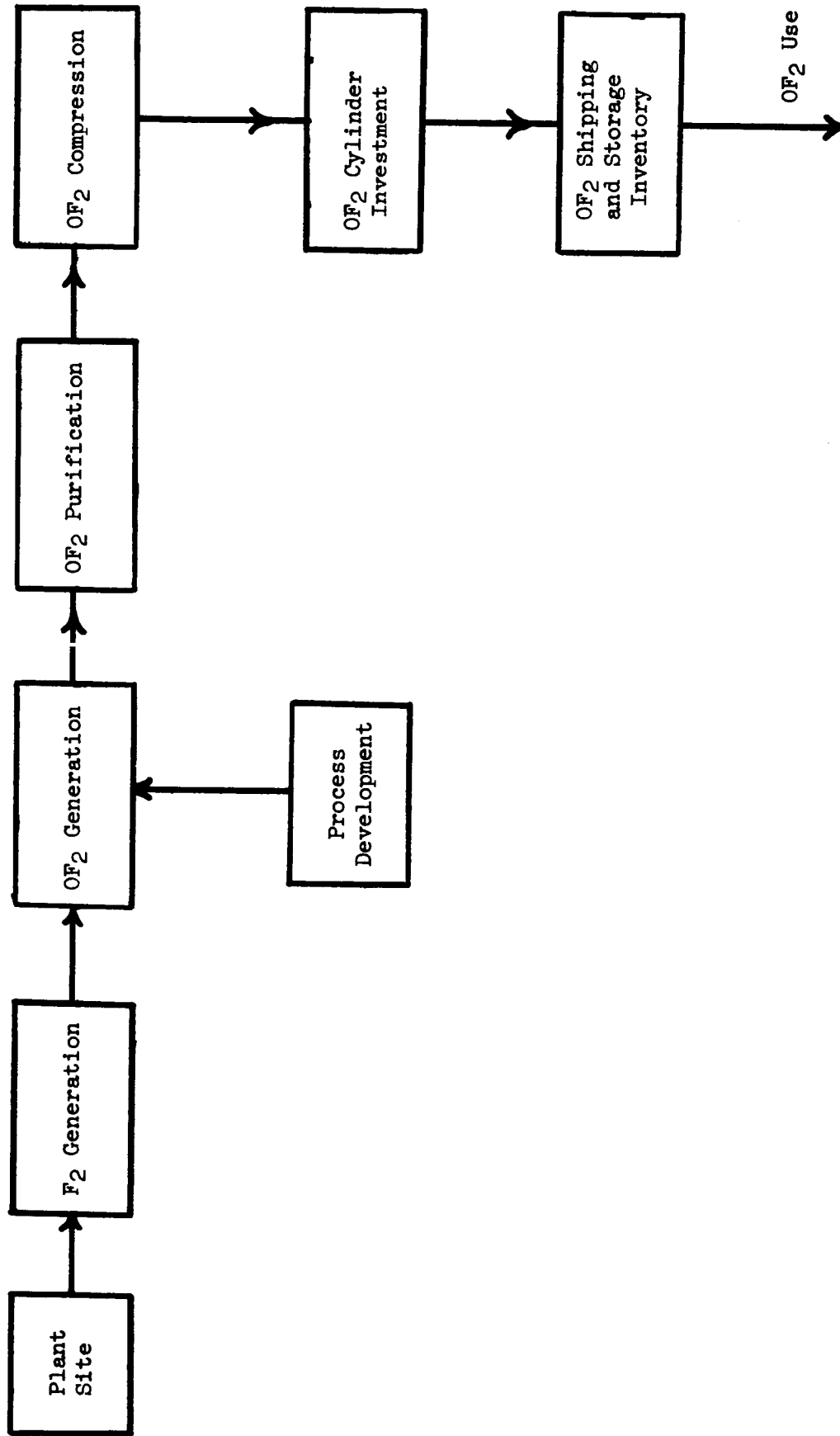
Table V

Investments for Various OF₂ Production Processes
20,000 lb OF₂/12 month Contract

Plant Section	F ₂ -Caustic		F ₂ -Water (KF Cat.)		Electrolysis of Water	
				in HF.....in O ₂
Electrolyzer, \$	100,000		100,000		} 110,000	} 75,000
OF ₂ Reactor, \$	36,600		86,000			
OF ₂ Purification, \$	25,800		25,800	31,000		23,600
OF ₂ Compression, \$	20,000		20,000	20,000		25,000
Plant Site, \$	<u>20,000</u>		<u>20,000</u>	<u>20,000</u>		<u>11,000</u>
Total Plant Inv., \$	202,400		251,800	181,000		134,600
Process Development, \$	10,000		50,000	65,000		80,000
Cylinder Investment, \$	83,000		83,000	83,000		83,000
Shipping and Storage Inventory (Working Capital), \$	61,200		72,400	60,500		57,000

Figure III:

Schematic Breakdown of the OF₂ Processes



purification, OF_2 compression, OF_2 cylinder investment OF_2 storage and shipping inventory and process development. The storage and shipping inventory investment includes the working capital investment for OF_2 product in storage and shipment. Tables IV and V give the estimated investment necessary in each area for the four processes considered.

Both fluorine processes assume that the OF_2 is produced by fluorine generated from one commercial 5,000 amp fluorine cell. Since the cost of the fluorine cell is about half of the total investment, the most economical way to produce 10,000 lb OF_2 or less would be to run the cell at full capacity for as long as necessary. Using a smaller cell if only 4,000 lb/yr or less are desired would be unwise since the saving in using the labor only part of a year would be a much greater saving than the few dollars of investment that could be saved using a smaller cell.

Investment costs for the fluorine-caustic system should be realistic if no additional equipment is needed for a 7 lb F_2 /hr plant over that required for the 2 lb F_2 /hr plant. Since the purification and compression equipment for all the plants are similar, these values should all be quite good. The electrolyzer investments especially for the porous anode process contain more uncertainty with the reactor investment for the fluorine-water process being the most uncertain. However, the initial reactor and associated equipment costs for the fluorine-water system will be greater than for the fluorine-caustic system.

The major pieces of equipment (eg. cells and compressors) instrumentation and piping should have a 10 year depreciable lifetime. Since the materials are corrosive and various pieces of equipment will have to be replaced, maintenance costs will probably be high. In calculating the operating costs maintenance costs have been estimated at 10 and 8% of the fixed investments for the fluorine and electrolytic processes respectively.

The other investment factor that weighs heavily on a process selection is the process development costs. Since the fluorine-caustic process is closest to reduction to practice \$10,000 was estimated for future work. For the other processes no scale up has been done past

small scale laboratory experiments. It would probably take a minimum from \$50,000 to \$100,000 of development funds to bring these processes to the necessary state to produce 10,000 lb OF₂/yr. The values given in Tables IV and V are our best estimates of the funds required to develop these processes. The comparative magnitude of the numbers reflect present thinking on the ease of developing the process and could vary as more experience is gained in developing the process. The \$80,000 value for process development of the porous anode electrolytic process is the most uncertain of the development numbers given and is probably somewhat optimistic. The fact that the development costs for this process will most likely be greater than any of the other processes considered is reflected in the values given in Tables IV and V. Whatever the development costs are they would be included in the OF₂ costs for an initial OF₂ production contract.

C-3. Raw Materials

The pounds of various raw materials necessary per pound of OF₂ are estimated for the various processes in Table VI. The fluorine-caustic is the most expensive process as far as raw material costs are concerned; however, the raw material costs are only a minor part of the operating cost for all the processes.

C-4. Purification

A 90% purification efficiency was assumed in Table III as a result of purification experiments reported in the experimental section of this report. This purification efficiency includes collection as well as purification losses. If no purification or collection losses occur the selling price could be reduced by a maximum of 10%.

D. Delivered Price

In addition to the selling price of OF₂ three factors contribute to the total delivered price which must be paid for OF₂. These three factors described briefly below are cylinder investment (liquid trailer cost if capacity warrants); shipping and storage inventory, which is a measure of the working capital needed; and transportation charges. These charges have been omitted from the selling price because they are independent of the method used and depend on the details of a procurement.

Table VI

Comparison of Required Raw Materials
for Various CF₂ Processes

<u>Process</u> <u>Raw Materials</u>	<u>F₂-Caustic</u>		<u>F₂-Water</u>		<u>Electrolysis of Water</u>		<u>Electrolysis Using O₂</u>	
	lb/lb OF ₂	lb/lb OF ₂	lb/lb OF ₂	lb/lb OF ₂	lb/lb OF ₂	lb/lb OF ₂	lb/lb OF ₂	lb/lb OF ₂
Hydrogen Fluoride	2.96	2.96	2.96	0.93	0.93	0.93	0.93	0.93
Potassium Bifluoride	0.25	0.25	0.50	-	-	0.25	0.25	0.25
Potassium Hydroxide	7.10	7.10	2.07	0.52	0.52	0.52	0.52	0.52
Liquid Nitrogen	17.30	17.30	7.8	22.8	22.8	32.2	32.2	32.2
Liquid Oxygen	-	-	16.0	-	-	-	-	-
Carbon Dioxide	1.0	1.0	-	-	-	6	6	6
Hydrochloric Acid	3.8	3.8	0.62	0.12	0.12	0.12	0.12	0.12
Calcium Chloride	5.0	5.0	2.05	0.51	0.51	0.51	0.51	0.51
Helium	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

The effect of these factors on the delivered price is shown for the four processes for a 12 month contract in Table VII. The delivered price for a depreciated plant with no development cost for the fluorine-caustic and electrolytic porous anode process is shown in Table VIII. One possible cost estimate for each of these three factors is described below.

D-1. Cylinder Investment

The OF_2 could be stored and shipped as a gas in cylinder at 400 psig. The standard OF_2 cylinder (10-5/8" O.D. x 55-1/2" height) would contain 9 lb OF_2 . The slightly smaller cylinder also used would hold 6-3/4 lb OF_2 .

New 9 lb and 6-3/4 lb cylinders with valves cost around \$75/cylinder. In addition if the cylinders to be used are new or have not been used previously for OF_2 or fluorine, the cylinder must be cleaned, passivated, and evacuated before use. Procedures for cylinder preparation have been published (D-1). The cost for this cylinder preparation would be minimal and would depend upon the condition of the cylinders.

As an example the capital investment in OF_2 cylinders would be \$83,000 for the 10,000 lbs of OF_2 production case (10,000 lb OF_2 /9 lb OF_2 per cylinder x \$75/cylinder = \$83,000). If the cylinders are depreciated to half value the investment write-off would be \$41,500.

D-2. Shipping and Storage Inventory

The shipping and storage inventory is a measure of the funds spent for which no payment has been received usually called the working capital. These values have been calculated and are presented in Tables IV and V for the 10,000 and 20,000 lb OF_2 /hr assuming a 12 month period between allocation and payment. The affect of these costs on the delivered prices are given in Tables VII and VIII for a single 12 month contract and for a second contract.

D-3. Transportation Costs

Freight charges for shipping OF_2 from U.S. east coast to west coast and returning the cylinder are \$5/lb OF_2 in either the 9 or 6-3/4 lb cylinder. Shipment one way with no return is \$3/lb. These costs are shown for a single 12 month contract and a second contract in Tables VII and VIII.

Table VII

Estimated Delivered Price for OF₂ - Single 12 Month Contract

<u>Production Rate, lb/yr</u>	<u>4,000</u>		<u>10,000</u>		<u>20,000</u>		<u>50,000</u>	
	\$	\$/lb	\$	\$/lb	\$	\$/lb	\$	\$/lb
<u>Fluorine-Caustic Process</u>								
Selling Price at Plant	250,900	62.73	386,100	38.61	562,800	28.14	978,000	19.56
Working Capital	28,000	7.00	42,500	4.25	61,200	3.06	108,500	2.17
Cylinder Costs	16,600	4.15	41,500	4.15	83,000	4.15	240,000	4.80
Transportation Cost	<u>20,500</u>	<u>5.05</u>	<u>50,500</u>	<u>5.05</u>	<u>110,000</u>	<u>5.05</u>	<u>50,000</u>	<u>1.00</u>
Delivered Price	316,000	78.93	520,600	52.06	793,000	39.65	1,376,500	27.53
<u>Electrolytic Oxygen Porous Anode Process</u>								
Selling Price at Plant	341,600	85.40	412,900	41.29	527,200	26.36	880,700	17.60
Working Capital	38,200	9.55	45,500	4.55	57,000	2.85	97,000	1.94
Cylinder Costs	16,600	4.15	41,500	4.15	83,000	4.15	240,000	4.80
Transportation Costs	<u>20,500</u>	<u>5.05</u>	<u>50,500</u>	<u>5.05</u>	<u>111,000</u>	<u>5.05</u>	<u>50,000</u>	<u>1.00</u>
Delivered Price	416,900	104.10	550,400	55.04	753,200	37.66	1,267,700	25.34

Table VII (Continued)

Estimated Delivered Price of OF₂ - Single 12 Month Contract

<u>Production Rate, lb/yr</u>	<u>4,000</u>	<u>10,000</u>	<u>20,000</u>
	<u>\$</u>	<u>\$/lb</u>	<u>\$</u>
		<u>\$/lb</u>	<u>\$</u>
<u>Fluorine-Water Process</u>			
Selling Price at Plant	341,300	85.34	468,800
Working Capital	38,300	9.55	51,900
Cylinder Costs	16,600	4.15	41,500
Transportation Costs	<u>20,500</u>	<u>5.05</u>	<u>50,500</u>
Delivered Price	416,700	104.09	612,700
		46.88	672,200
		5.19	72,400
		4.15	83,000
		<u>5.05</u>	<u>101,000</u>
		61.27	902,600
			33.06
			3.62
			4.15
			<u>5.05</u>
			45.13
<u>Electrolysis of Water in Hydrogen Fluoride Process</u>			
Selling Price at Plant	302,500	75.65	416,300
Working Capital	33,800	8.45	45,800
Cylinder Costs	16,600	4.15	41,500
Transportation Cost	<u>20,500</u>	<u>5.05</u>	<u>50,500</u>
Delivered Price	373,400	93.30	554,100
		41.63	556,900
		4.58	60,500
		4.15	83,000
		<u>5.05</u>	<u>101,000</u>
		55.41	786,400
			27.84
			3.02
			4.15
			<u>5.05</u>
			39.31

Table VIII

Estimated Delivered Price for OF₂ on a Second Contract

<u>Production Rate, lb/yr</u>	<u>4,000</u>	<u>10,000</u>	<u>20,000</u>	<u>50,000</u>
	<u>\$</u>	<u>\$/lb</u>	<u>\$</u>	<u>\$/lb</u>
<u>Fluorine-Caustic Process</u>				
Selling Price at Plant	160,200	40.06	287,100	28.71
Working Capital	17,600	4.40	31,200	3.12
Cylinder Costs	16,600	4.15	41,500	4.15
Transportation Charge	20,500	5.05	50,500	5.05
Delivered Price	214,900	53.66	410,300	41.03
			413,300	20.66
			634,800	12.70
			69,400	1.39
			240,000	4.80
			50,000	1.00
			994,200	19.89
<u>Electrolytic Oxygen Porous Anode Process</u>				
Selling Price at Plant	107,300	26.95	167,300	16.73
Working Capital	10,600	2.65	17,600	1.76
Cylinder Costs	16,600	4.15	41,500	4.15
Transportation Charges	20,500	5.05	50,500	5.05
Delivered Price	155,000	38.80	276,900	27.69
			245,000	12.25
			378,500	7.56
			40,200	.80
			240,000	4.80
			50,000	1.00
			708,700	14.16

E. Production Lead Time

The time needed to construct and prove operational the 7 lb F₂/hr facility for producing OF₂ as described in this report would be between 9 and 12 months, depending on the problems encountered in start-up. At the end of this period production of OF₂ could begin using 7 lb of F₂/hr.

F. Inflation Factors

The selling prices given in Figures I and II would hold for contracts committed in the fiscal year 1971. Prices beyond 1971 could possibly increase at a rate of 6 to 8%/yr.

G. Multiple Year Contracts

This report has been primarily concerned with the selling price of OF₂ produced by four different processes for a single 12 month contract. The change in the selling price for OF₂ produced by the fluorine-caustic and electrolysis of oxygen in HF using a porous anode with no process development costs and depreciated equipment was shown in Figure II. These reduced prices would apply to a second contract after plant and development costs have been met in the first contract.

Figures IV and V give the cumulative selling price for 10,000 to 50,000 lb OF₂ produced in a one to five year period for the fluorine-caustic and electrolytic porous anode processes. The cumulative selling prices were obtained using the costs given in Figures I and II. The one year costs were obtained from Figure I. For multiple year requirements it was assumed that equal amounts would be produced each year with second contract prices used for each year after the first. A minimum of 5,000 lbs was assumed produced each year. The figures show that the total cost increases as the number of producing years increases. The main reason for this increase is that the significant labor costs per lb increase as the number of producing years increases. The figures assume continuous production and that all the OF₂ produced in a year is shipped and paid for within the year. If payment is deferred over several years even though production is made in one year the shipping and storage costs would bring the one year cost closer to multiple year costs.

FIGURE IV

Cumulative Selling Price for OF₂ at Various Total Production Quantities by the F₂ - Caustic Process for Various Contract Periods. Selling Price Does Not Include Working Capital Charges, Transportation or Storage Costs. Multi-Year Production Assume Equal Production Each Year

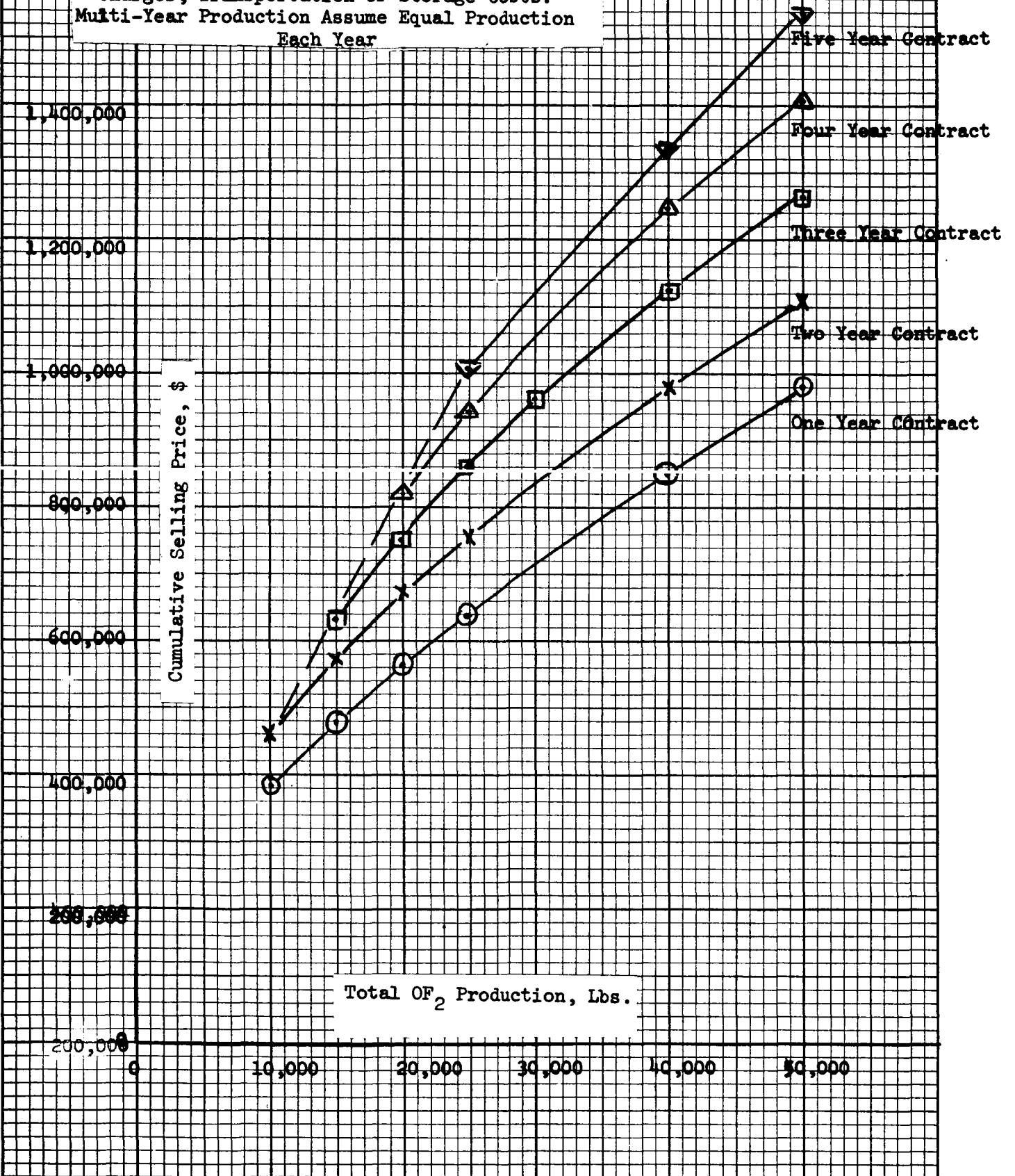
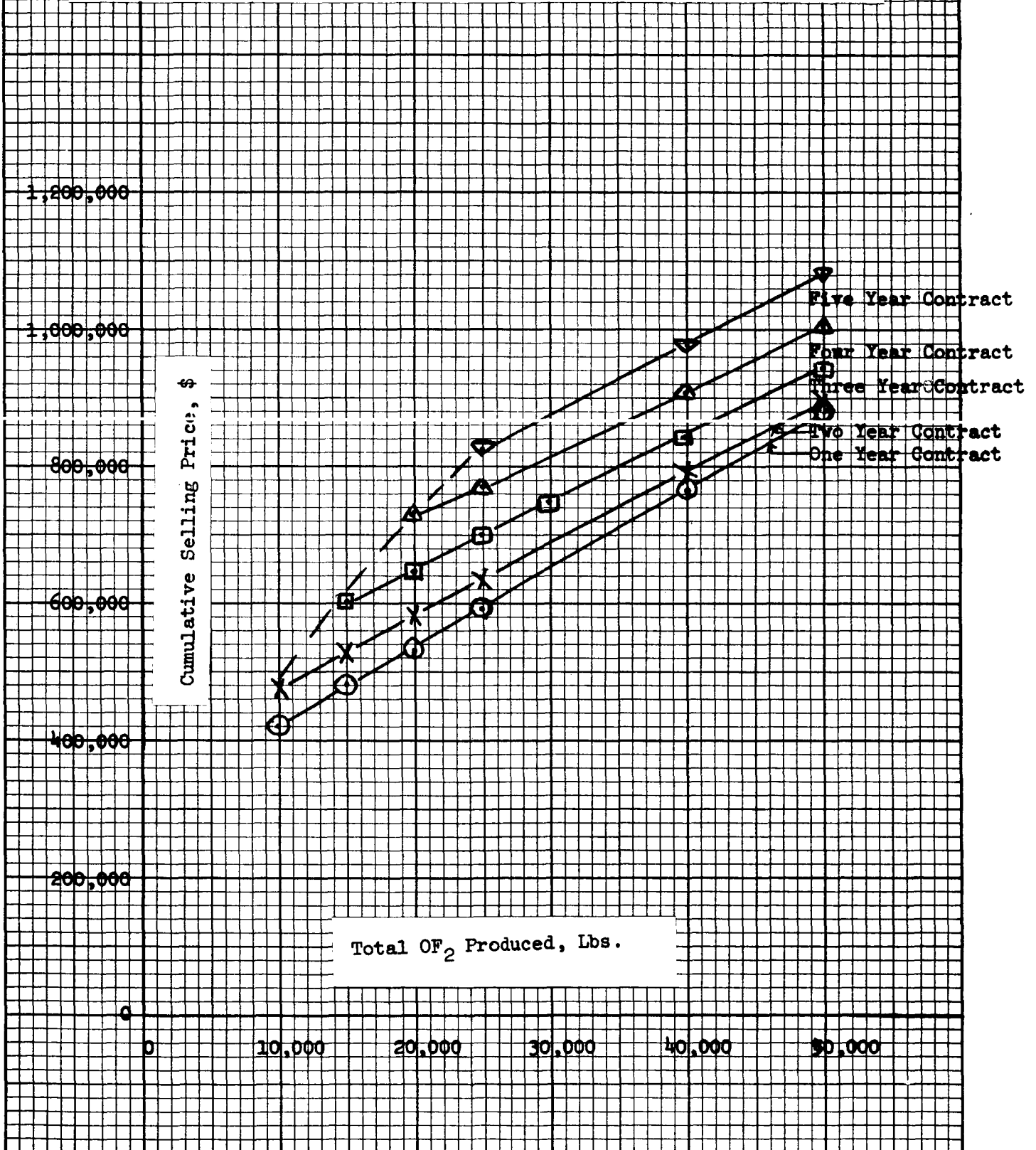


FIGURE V

Cumulative Selling Price of OF_2 at Various Production Levels
by the Electrolysis of Oxygen in HF for Various Contract Periods

Selling Price Does Not Include Transportation
Working Capital and Storage Charges. Multi-Year
Productions Assume Equal Production Each Year



V. Experimental

A. Fluorine-Caustic System

A-1. Experiments at 0.1 and 0.2 lb F₂/hr.

a. Experimental Procedures

A schematic representation of the experimental apparatus is shown in Figure VI. The apparatus is pictured in Figures VII and VIII. The major components are the reactor, freezeout drier, CO₂ trap, and liquifier.

The fluorine is fed from a cylinder to a surge volume maintained at a constant pressure to help maintain a constant flow rate to the reactor. From the surge vessel it goes through a glass flowmeter into the reactor. Dilute 2% caustic solution is pumped from a make up tank through a flowmeter to the reactor. The liquid level in the reactor is maintained by a liquid leg in the caustic exit line which is vented to prevent siphoning. The exit line also contains a thermocouple to measure the temperature of the caustic. The fluorine enters through orifices which are usually four inches below the caustic surface. The oxygen and oxygen difluoride formed exit through the top of the reactor.

Two reactors have been used. The first was a modified 500 cc gas washing bottle. The fritted disc was replaced by a glass bulb containing one, two or four 0.1" orifices through which the fluorine entered the system. These bulbs were severely attacked and had to be replaced frequently as the openings expand with use. A majority of the runs except those with sparger depth variation have been done with the 2" diameter glass reactor. The second reactor was a 2 ft. long 2" diameter piece of teflon pipe with machined caps on both ends. The inlets and outlets were the same as the glass reactor except for the fluorine inlet which was a 1/4" piece of teflon pipe plugged at the bottom which can be raised or lowered to any depth. The bottom inch of the pipe was drilled with 70-0.020" holes. These reactors were used for the 0.1 (500 cc F₂/min) and 0.2 (1,000 cc F₂/min) lb F₂/hr runs.

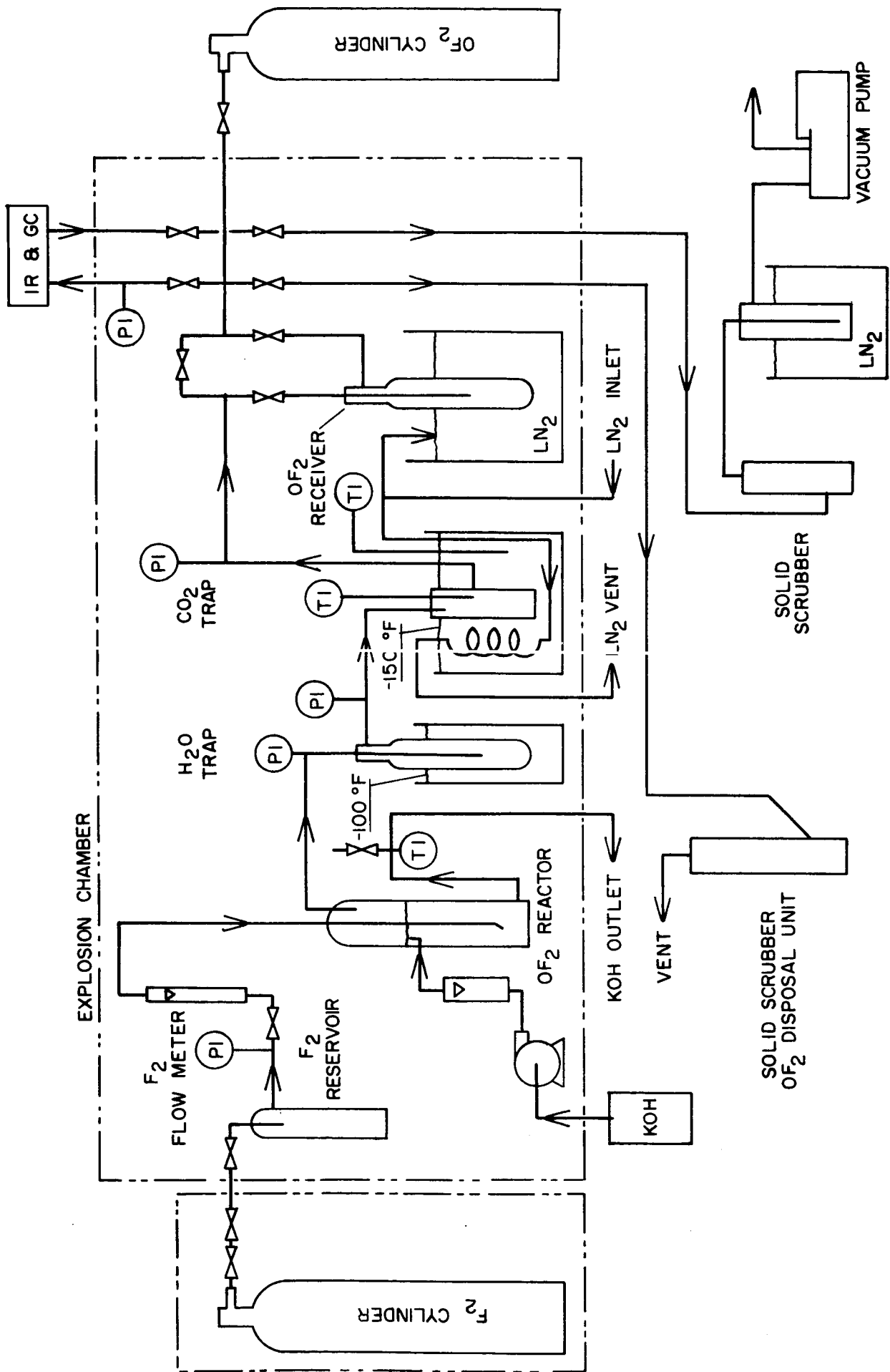


FIGURE VI. FLUORINE-CAUSTIC EXPERIMENTAL SYSTEM FOR PRODUCING OF₂

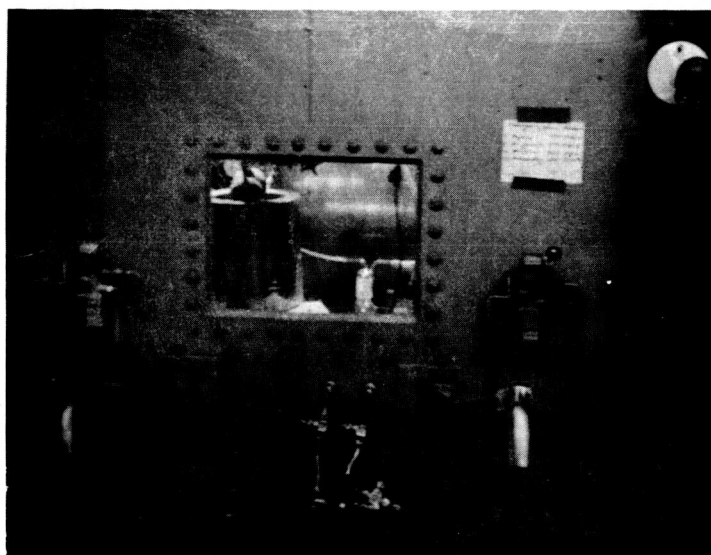


Figure VII. OF_2 Explosion Chamber

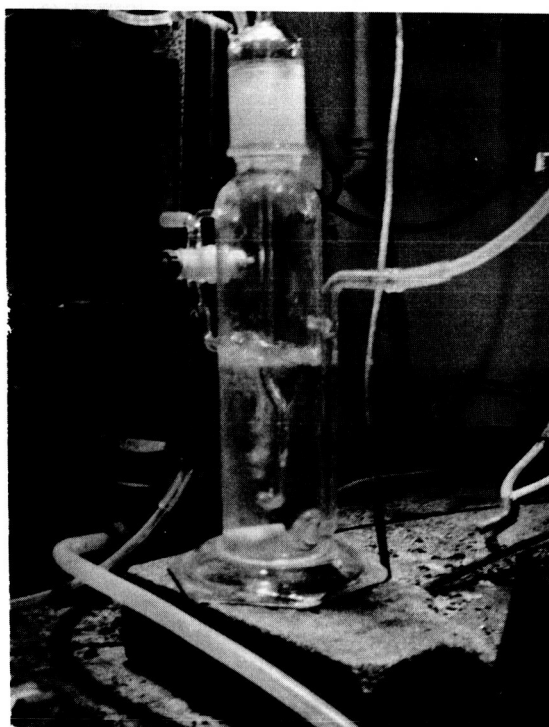


Figure VIII. OF_2 0.1 lb F_2 /hr Reactor

The OF_2 and oxygen exiting from the top of the reactor pass into a 300 cc cylinder equipped with a dip tube. The cylinder is placed in a CO_2 cooled trichlor bath at -100°F . The purpose of the trap is to freeze out any water entering with the product gases.

The second trap operated at about -150°F , removes CO_2 from the gas stream. The trap is cooled by adding liquid nitrogen to R-11 or methylene chloride until the liquid slushes. This trap was installed after persistent plugging of liquifier inlet shortened or wiped out several runs. From this trap the product gases are liquified in a 300 cc cylinder immersed in liquid nitrogen.

The cold traps are evacuated at the beginning of the run and kept under vacuum during the run. The inlet line to the vacuum pump is equipped with a combination charcoal-soda lime trap plus a LN_2 trap to protect the pump. OF_2 is vented from the receiver through a scrubber packed with charcoal, soda lime, KI crystals and rubber. Both scrubbers have worked well when used.

After collection of OF_2 in the receiver for about 2 hours the receiver is warmed up and the pressure is equalized with a 2150 cc evacuated cylinder. The yield is calculated from the OF_2 analysis in the cylinder and receiver, the system pressure and the fluorine reacted. Occasionally when the fluorine flow deviates from the set point, the yield is corrected by using the system pressure which is a check on the fluorine flow. The OF_2 in the cylinder or receiver was analyzed by IR or GC.

b. Experimental Difficulties

Corrosion - As in all fluorine systems corrosion has been a problem in the flowmeter, reactor and water freeze out trap. Constituents containing dry OF_2 have been generally free of corrosion. All fluorine and OF_2 lines are copper, traps are 304 s.s. or copper, and the valves are Hoke Monel valves, model number 343.

Corrosion of the glass reactor inlet and flowmeter due to HF were expected and have occurred. The inlet dip tube on the freeze out trap plugged several times with green metal fluorides. Plugging was most noticeable when metal demister was placed in the top of the reactor at high fluorine flow rates to prevent liquid carry over. The demister was removed as was metal packing in the freezeout trap which became corroded.

The fluorides also attacked the vanes in the vacuum pump but left the Kel-F oil untouched. The problem was improved when the pump trapping system was installed.

CO₂ - Initial runs at 500 cc/min fluorine gave little or no evidence of CO₂ generation. Problems with CO₂ plugs in the receiver started when a new cylinder of fluorine was used. Although carbonates in the water and caustic can form CO₂ in the presence of fluorine, CO₂ in the fluorine was believed to be the main source of the CO₂ problem. For the two runs done with distilled water the CO₂ problem halted the run before completion when a higher fluorine to caustic ratio was employed. Since distilled water alone could not be counted on to insure a CO₂ free system a CO₂ freeze-out trap was installed. With this trap CO₂ plugs have been observed using regular tap water and caustic.

Operation - Although in general operation of the experimental system was good once operational, the problem was getting a run started. Problems with frozen lines, plugs, leaks, and corrosion were prevalent on start up. This condition is common with fluorine systems and continuous operation is desired if possible.

Fluorine - Fluorine break through did occur at high fluorine to caustic ratios. This resulted in corrosion in the water trap and created problems with the analytical equipment especially the AgCl windows on the infra red analyzer. Fluorine in the gas chromatograph was less of a problem; however, some sensitivity was lost in the instrument.

Fires - One batch of caustic was made up with caustic from a large storage tank of 45% KOH. This caustic contained corrosion products or sediments from the tank and was dirty in appearance. When used numerous fires occurred at the fluorine inlet of both the glass and teflon reactor. The fires were quickly extinguished by shutting off the fluorine. In the teflon system black spots appeared on the walls of the reactor and two holes were burned in the sparger tube. After that fresh 45% caustic was purchased and no further fires occurred in either system.

c. Operating Variables

The operating variables studied included fluorine to caustic flow ratio, sparger depth, caustic type, fluorine orifice velocity (bubble size) and agitation. Sample data illustrating the effect of these variations are given in Table IX.

Most of the experiments were performed at a fluorine flow rate of 500 cc/min with caustic flow variations from 0.4 to 1.3 based on the fluorine volumetric inlet flow. The molar ratio of caustic to fluorine for these flow rates are 3.4 to 10.7. At no time was molar ratio of caustic to fluorine less than 1 to 1. Initial experiments were performed using sodium hydroxide; however, potassium hydroxide was used for most of the runs because of the increased solubility of potassium fluoride over sodium fluoride in an aqueous system.

Sparger position and construction were also studied. Experiments were performed with the sparger immersed in four, eight and twelve inches of 2% caustic (Runs 34-36). The orifice diameter varied from 0.02" to 0.25". The flow velocity through each orifice was maintained over a 10 to 1 range by varying the number of orifices.

Two runs were made with a magnetic stirrer in the bottom of the glass reactor (Run 37). Other runs were made with 5% potassium fluoride to simulate the effect of recycling caustic. The effect of temperature was not studied. Since the caustic was outside additional cooling was not required. The temperature of the exiting caustic was a few degrees higher than the inlet and averaged about 50°F.

TABLE IX

Experimental OF₂ Yield Data Using the Fluorine-Caustic System

Run	<u>11</u>	<u>12</u>	<u>13</u>	<u>18</u>	<u>19</u>	<u>22</u>	<u>37*</u>	<u>34</u>	<u>35</u>	<u>36</u>
<u>Rates</u>										
F ₂ Rate cc/min	493	493	493	354	490	1000	500	500	500	500
Caustic Type	2% NaOH	← 2%	KOH							
Caustic Rate cc/min	200	200	340	450	450	1200	490	490	490	490
Moles Caustic/Mole F ₂	4.7	3.4	5.7	10.7	7.7	9.9	8.1	8.1	8.1	8.1
<u>Reactor</u>										
Sparger Depth, inches	4	4	4	4	4	4	4	8	12	4
Sparger Orifice, Number										
Diameter, inches	1/0.25	1/0.25	1/0.25	1/0.1	1/0.1	4/0.1	2/0.1	70/0.02	70/0.02	70/0.02
Orifice Area, in ²	0.196	0.196	0.196	0.931	0.031	0.126	0.062	0.088	0.088	0.088
Construction	← 2"	Diameter	Glass					← 2"	Dia. Teflon	→
<u>Run</u>										
Duration, Min.	120	120	120	120	120	75	100	110	90	120
On Stream Analysis, % OF ₂ by IR	60-67	45-49	49-52	68-77	64-76	67-71	73-77	72-74	68-74	75-76
On Stream Analysis, % OF ₂ by G. C.	60	53	47-54	68-76	-	-	72-80	64-80	67-79	64-79
<u>Crude Product</u>										
Pressure, psi	87	110	196	128	155	150**	70	145	110	145
Analysis, % OF ₂ Receiver	-/98	-/93	46/-	69/99	67.5/99	60/99	75/100	60/99	68/99	68/99
Yield, % (Based on F ₂ + Press)	54	57	53	62	68	69	42	66	66	64
Yield, % (Based on O ₂ /OF ₂ Ratio)	-	-	-	73	72	72	78	65	72	72
Act. Receiver Press.										
Theor. " Press. from F ₂ Feed Rate	-	-	-	74	96	94	57	97	93	89

* Magnetic Agitator Used

** 1000 ml receiver used

d. Discussion of Results

Several of the main runs illustrating the effect of operating variables are given in Table IX. Other experimental data are given in Tables X, XI and XII. The effect of various operating conditions are given below.

Type of Caustic

Most runs were done with KOH because of the increased solubility of KF over that of NaF. No yield difference was noted but KOH experiments were easier to run because the NaF tended to plug the fluorine sparger and caustic lines.

Flow Ratio

Yields around 65% were attainable using a volumetric ratio of caustic solution to fluorine of at least 1:1. At a lower ratio the yield decreased into the 50's (Runs 12, 13, 18, 19). At a 0.5:1 caustic to fluorine ratio at 1000 cc/min fluorine some breakthrough of fluorine occurred at a 4 inch sparger depth.

Sparger Depth

Sparger depths of four, eight, and twelve inches were studied at 1:1 volumetric flow ratios. The yields of all experiments were about 65%.

Sparger Construction

Orifice diameter (bubble size) had no noticeable affect on the yields. The main purpose in running with various sizes was to study the corrosion on the glass and teflon sparger.

Severe corrosion was noted with the glass sparger where a liquid pool of HF collected in the bottom on the glass bulb and dissolved the bottom of the bulb. The glass orifices were continually being enlarged by the action of HF. The glass spargers lasted two to three runs and then had to be replaced.

Summary of Experimental OF₂
Results by Caustic - Fluorine Method
October, 1964

Run	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>
Date	10/14	10/17	10/20	10/21	10/27	10/29	10/30	10/31
Fluorine Rate, cc/min.	493	493	493	493	490	490	490	490
<u>Caustic</u>								
Type	NaOH	NaOH	KOH	KOH	KOH	KOH	KOH	KOH
Rate cc/min.	180	200	200	340	450	450	450	450
Conc. wt %	2	2	2	2	2	2 → 1	2	2
<u>Alkali Fluoride Conc., wt %</u>	-	-	-	-	-	5 → 6	5	5
<u>Reactor</u>								
Dia, inches	2	2	2	2	2	2	2	2
Material	glass	glass	glass	glass	Teflon	Teflon	Teflon	Teflon
Sparger Depth, inches	4	4	4	4	4	4	4	4
Orifice number	1/0.1	1/0.25	1/0.25	1/0.25	70/0.02	70/0.02	70/0.02	70/0.02
<u>diameter</u>								
<u>Run</u>								
Time, hrs.	1.0	2.0	2.0	2.0	2.0	2.0	1.0	2.0
Analysis, % OF ₂ by IR		60-67	45-49	49-52	59-63	57-68	57-76	41-72
Analysis, % OF ₂ by GC		60	53	47-54	-	-	-	-
<u>Crude Product</u>								
Pressure, psig				196		180		235
Analysis, % OF ₂				46		57		57
Yield, %				53		66		78
<u>Purified Product</u>							Receiver Plugged	
Pressure, psig		87	110		130	90		160
Analysis, % OF ₂		98	93		72	94		94
Yield, %		54	57		57	48		82

1.0 Used Material for Analytical Calibrations

TABLE XI

SUMMARY OF EXPERIMENTAL OF F_2 RESULTS BY CAUSTIC-FLUORINE METHOD

NOVEMBER 1969

Run	18	19	20	21	22	23
Date	11/6	11/7	11/11	11/13	11/14	11/17
F_2 Rate cc/min.	354	490	1,000	1,000	1,000	1,050

<u>Caustic</u>	KOH					
Type	←-----→					
Rate cc/min.	450	450	450	1,200	1,200	500
Conc., Wt. %	2	2	2	2	2	2

<u>Reactor</u>						
Dia. inch	2	2	2	2	2	2
Material	glass	glass	glass	glass	glass	glass
Sparger Depth, inch	4	4	4	4	4	4
Orifice number diameter, inch	1/0.1	1/0.1	2/0.1	2/0.1	4/0.1	4/0.1

<u>Run</u>						
Time, min.	120	120	10	50	75	85
Analysis % OF_2 by I. R.	68 - 77	64 - 76	----	63 - 73	67 - 71	----
Analysis % OF_2 by G. C.	68 - 76	----	----	----	----	----

<u>Crude Product</u>						
Pressure	128	155	No N_2 Yields			200*
Analysis % OF_2 cylinder receiver	69/99	67.5/99	Break Through			56/99
Yield, %	62	68	Back Pressure			77

* 1000 ml. receiver

Summary of Experimental OF₂ Results by Caustic-Fluorine Method
December 1965

Run	25A	26	27	28	30	31	32	33	34	35	36	37
Date	11/24	11/25	11/26	12/5	12/9	12/10	12/11	12/12	12/29	12/30	1/2	1/6
F ₂ Rate cc/min.	1000	500	500	500	500	1000	400*	500*	500	500	500	500
<u>Caustic</u>												
Type	KOH											
Rate, cc/min.	490											
Conc., wt %	2											
Others	←5% KF →											
<u>Reactor</u>												
Dia, inches	4											
Material	Glass											
Sparger Depth, Inches	4											
Orifice number	4											
diameter, inches	4/0.1											
	4/0.1	4/0.1	4/0.1	4/0.1	2/0.1	2/0.1	2/0.1	2/0.1	2/0.1	70/.02	70/.02	2/0.1
	←Distilled Water →											
	Magnetic Stirrer											
	←Teflon →											
	Glass											
	Magnetic Stirrer											
Run	30	75	40	60	120	90	90	46	110	90	120	100
Time, min.	-	-	-	-	-	-	76-79	-	72-74	68-74	75-76	73-77
Analysis, % OF ₂ by IR	67	60-63	60-67	74-76	70-80	74-78	75-80	85	64-80	67-79	64-79	72-80
Analysis, % OF ₂ by GC												
<u>Crude Product</u>												
Pressure, psig	-	-	-	-	100	-	70	80/90	145	110	145	70
Analysis, % OF ₂ cylinder receiver	-	-	-	-	NO CO ₂ Plug	-	66/97.5 70* CO ₂ Plug	66/98.5 70*	60/99 66	68/99 66	68/99 64	75/100 42
Yield, %												

*F₂ flows in error, yield based on volume of OF₂ and O₂ collected plus pressure

Agitation

The yield for the agitation run was only 42%. A second run gave a 98% yield based on fluorine added. The problem is probably with the placement of the magnetic agitator in the bottom of the reactor. The agitator draws fluorine or OF_2 down into the reactor and out the caustic drain line. Bubbles observed in the line confirm this, but from the divergence of yields it would seem as if fluorine was removed in one case and OF_2 in the other. From the on-stream analysis and product analysis both runs should have a 70% yield. The yields are diverted because of the cylinder pressure. Product analysis for the runs was typical. Yields based on the O_2/OF_2 analysis ratio gave a 70% yield for both runs.

KF Addition

Runs with 5% added KF were similar to other runs and gave about a 66% yield. If the caustic is kept in a closed system with no fresh caustic added, the yield dropped off as the KOH concentration dropped to one per cent.

General

Infra red spectra and gas chromatograms were obtained on the final product and periodically on the gas stream entering the receiver.

On-stream yields for runs using a 1:1 flow ratio ranged from 70 to 80% yet the final product yields calculated from the fluorine flow rate, cylinder pressure and OF_2 analysis were always about 65%. If only the oxygen to OF_2 ratio is used, the yields average about 72%. This yield assumes that all the fluorine is converted to OF_2 or O_2 and none is left unreacted. If only O_2 and OF_2 are made and no fluorine goes unreacted the pressure in the receiver can be easily calculated. The ratio of the actual and theoretical pressures are given in Table IX. A low value would indicate that the fluorine rate is off, leaks are present or as in the agitated run the gas is being sucked out with the caustic. A value over 100% would indicate unreacted fluorine or vacuum side leaks.

A-2. Experiments at 2.0 lb F₂/hr

a. Procedures

A larger glass reactor made from the glass resin reactor was operated at fluorine rates up to 3 lb F₂/hr. The system was designed to operate at 2 lb F₂/hr. Two homemade copper traps operated at -100 and -150°F were used for water and CO₂ removal. The OF₂ was liquefied in two 1000 ml high pressure s.s. cylinders. The rest of the system was essentially the same as before. The system was operated as the 0.1 lb F₂/hr apparatus.

The major problem with the system revolved around the fluorine sparger. Teflon spargers were found unsatisfactory. The fluorine appeared to burn the teflon which led to explosions in the reactor. These explosions were sometimes preceded by a clouding of the caustic and followed by a black discharge from the sparger. The explosions were prevalent when the sparger was teflon but also occurred at other times when no teflon was present.

b. Results

The results from these runs are summarized in Table XIII. On-stream analysis have generally been over 70% OF₂ and yields 65% or greater.

c. Purification

Some crude OF₂ (76 mole % OF₂, 23 mole % O₂, 1 mole % CO₂) was purified by purging with 0.5 to 1.0 SCFH of helium at 10 to 20 mm Hg. The product was checked every half hour for purity. After about 2 hours, the OF₂ was 98.6 mole %. The remainder was equally divided between CO₂ and O₂. The recovery with all the sampling and handling losses was over 80%. It should be noted that the CO₂ content did not decrease significantly. The experiment proves that OF₂ and O₂ can be separated without distillation by purging with helium.

Table XIII

Experimental OF₂ Data Using the 2 lb/hr
Fluorine-Caustic System

Run	38	42	44	45
Date	1/28	3/18	4/8	4/9
<u>Rates</u>				
Fluorine, lb/hr	0.18-0.36	1.0	1.0	3.0
KOH, gpm	0.6	1.2	2.0	2.0
<u>Reactor</u>				
Sparger Material	Teflon	Teflon	S.S.	S.S.
Fluorine Inlet Line	Monel	Teflon	Monel	Monel
<u>Run</u>				
Duration, Minutes	110	60	120	25
On-stream Analysis, % OF ₂ by G.C.	72-73	65-75	79-81	75-77
<u>Crude Product</u>				
Pressure, psig <u>receiver</u> cylinder	175/175	90/90	215/195	155/135
Analysis, % OF ₂ <u>receiver</u> cylinder	94/78	90.6/71	97.5/79	90.5/75
Yield, % (Based on F ₂ and pressure)	65	65	73	91
Yield, % (Based on O ₂ /OF ₂ Ratio)	*	73	87	82

*Vented Pressure During Run

B. The Electrolytic Oxygen Porous Anode System

B-1. Procedure

An experimental electrolytic cell was set up as shown in Figure IX. The cell was constructed from 4" monel pipe. The cell contained a central porous anode surrounded by a nickel diaphragm and a steel cathode. The volume of the cell was about 2 liters. Several designs for the porous anode have been tried. The first anode was a 1-1/2" O.D. porous carbon cylinder plugged at both ends. This design was discarded for several reasons. None of the sealants tried could withstand the corrosion and electrolyte leaked into the annulus and plugged the bottom of the gas inlet line. The oxygen for OF_2 is added as a 25% mix with helium. The result was that the oxygen either leaked out the top or came through the pores at the top of the anode. A second anode with a hole 3/4 of the way down the center was scrapped for similar reasons. The final anode tested introduced the oxygen into the bottom of a 1" x 1" x 4" rectangular anode. The oxygen distribution was better than the first two but still not what is desired.

B-2. Results

Several positive results have come from these initial experiments. There were no problems in getting the cell to conduct properly. The voltage has been 5 to 7 volts for current densities up to 75 amps/ft². OF_2 was produced with each anode design. The only other gases evolved have been F_2 and traces of CO_2 and COF_2 .

The major problem has been in obtaining desirable current efficiencies. The current efficiencies obtained are around 5% for these preliminary experiments. These values can be explained by poor oxygen distribution in the anode, oxygen leaks around the anode, and leaks in the experimental apparatus. If the oxygen distribution in the anode can be improved so that fluorine manufacture is prevented improved current efficiencies should result.

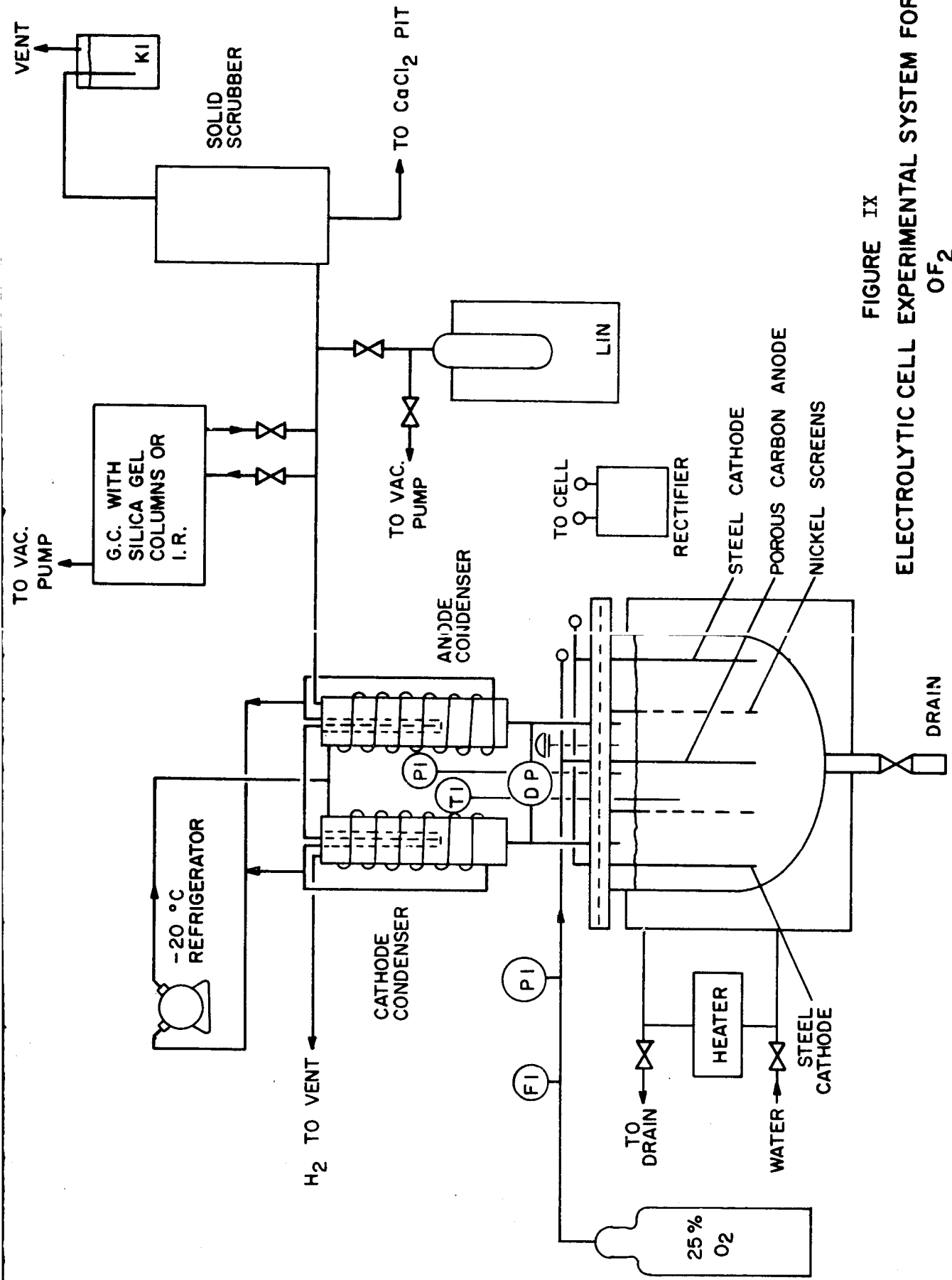


FIGURE IX
ELECTROLYTIC CELL EXPERIMENTAL SYSTEM FOR
OF₂

C. Analytical Procedure and Equipment

The OF_2 produced has been analyzed by infra red and gas chromatographic techniques. Using a 2 mm fixed path gas, silver chloride windowed cell, a calibration curve was obtained for the first spike of the strong triplet peak at 12 microns. The infra red compared well with chromatographic results. The two are usually within 2 to 3% of each other. The gas chromatograph results are used for calculations since they can be read more precisely especially at OF_2 values near 100%. Two different gas chromatograph systems have been used. The first consisted of a Beckman GC-1 chromatograph operated at room temperature with a 11 ml sample loop. The column was 4 ft. by 3/16" O.D. s.s. tubing packed with Davison Grade 08 silica gel. The instrument worked well but began to lose sensitivity after fluorine analysis. The present instrument is a Beckman GC-2A chromatograph operated at 40°C. The column is 10 ft. by 3/16" O.D. s.s. tubing packed with Fisher Scientific Grade 28 silica gel. The silica gel used for both separates oxygen and OF_2 with CO_2 trailing out after 13 minutes. Any fluorine or nitrogen will elude with the oxygen. A Beckman integrator-recorder is used to record the results.

VI. Conclusion

Of the processes studied, the fluorine-caustic process is recommended for immediate production of OF_2 on a commercial basis unless the quantity desired is large enough to write off the process development costs associated with other processes (e.g. the oxygen porous anode process). The fluorine-caustic process is suggested for the following reasons: 1) The process has been scaled up to 2 lb F_2 /hr. compared to the projected production rate of 7 lb F_2 /hr. Other processes have only been operated on a gram scale 2) The scale-up has allowed more accurate estimation of the investment costs. The largest investment factor in the investment for the fluorine-caustic process is the fluorine cell which has been designed and operated for many years. In all the other processes a major piece of equipment has yet to be designed and problems in its operation are not known. 3) Literature yields have been obtained on a laboratory and scaled up reactor for the fluorine-caustic system. The main disadvantages of the fluorine-caustic system are the low on-stream time and high maintenance allowances.

Although all the other possible OF_2 processes have an operating cost advantage over the fluorine-caustic system, the only one that could be worth the gamble of scale-up is the oxygen electrolytic porous anode process because of the potential based on the superior literature yield. If these yields can be obtained commercially the labor and investment costs would be substantially below the fluorine-caustic method. If the total amount of OF_2 to be produced for NASA programs is in excess of 20,000 lbs it is recommended that some additional development work should be done on the oxygen porous anode process in a scaled up version of Childs 3 amp cell. If the yields reported for the 3 amp cell can be realized in larger commercial sized units (4,000-6,000 amps), then the oxygen porous anode process could present the most economical method for producing OF_2 .

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