

Production of fluorine gas for laboratory use: Process design and implementation

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A process for the laboratory-scale production of fluorine gas using CaF_2 as precursor was designed and commissioned. The first step uses a batch reactor in which anhydrous hydrogen fluoride (AHF) is produced by the reaction of CaF_2 with sulphuric acid. The AHF is stored, then transferred to a Pauling-type cell, preloaded with $\text{KF}\cdot\text{HF}$. The electrolyte, $\text{KF}\cdot 2\text{HF}$, which is a liquid at the working temperature, is formed *in situ*. AHF by itself is a weak acid and is not sufficiently electrically conductive for direct electrolysis. This problem is bypassed by using $\text{KF}\cdot 2\text{HF}$. Above its melting point, $\text{KF}\cdot 2\text{HF}$ dissociates to form K^+ en F_2H^- in HF, and is sufficiently conductive for electrolysis. The HF batch reactor showed provided a yield of 70%. The fluorine cell afforded an observable overpotential of 2.7 V, and its voltametric curve displayed the expected behaviour.

Keywords: Anhydrous hydrogen fluoride; fluorine gas; electrolysis; Pauling cell

Vervaardiging van fluoorgas vir laboratoriumgebruik: Proses-ontwerp en -bedryf: 'n Proses vir die kleinskaalse laboratoriumvervaardiging van fluoorgas met CaF_2 as die invoer-reagens is ontwerp en in bedryf gestel. Die eerste stap maak gebruik van 'n lotreaktor wat CaF_2 na anhidriese HF omskakel deur reaksie met anhidriese swawelsuur. Die vervaardigde HF word gestoor in 'n oordragsvat en dan na 'n Pauling-tipe fluoorsel, wat vooraf met $\text{KF}\cdot\text{HF}$ gelaai is, oorgedra. Die elektroliet, $\text{KF}\cdot 2\text{HF}$, wat by die bedryfstemperatuur van die sel in die vloeistoffase is, word *in-situ* gevorm. Waterstoffluoried (HF), op sigself, is 'n swak suur en is nie elektries geleidend genoeg vir elektroliese nie. Die gebrekkige elektriese geleidingsvermoë van HF word omseil deur gebruik te maak van $\text{KF}\cdot 2\text{HF}$ as elektroliet. $\text{KF}\cdot 2\text{HF}$ disosieer na die ione K^+ en F_2H^- in HF, in die vloeistoffase en gelei eletrisiteit genoegsaam om as elektroliet op te tree. Die HF lotreaktor toon 'n omskakelings-rendement van 70%. Die fluoorsel het 'n waarneembare bo-potensiaal van 2.7 V en die voltammetriese kromme toon die verwagte elektriese gedrag.

Sleutelwoorde: Anhidriese waterstoffluoried; fluoorgas; elektroliese; Pauling-sel

Introduction

The production of fluorine is a known process in South Africa. Historically it has been used for uranium enrichment, for power generation as well as for military use. Fluorine gas is generated via the electrolysis of hydrogen fluoride (HF) to form $\text{F}_2(\text{g})$ and $\text{H}_2(\text{g})$. In its turn, HF is produced from calcium difluoride (CaF_2), also known as fluorspar. The process is still of economic interest as South Africa has some of the largest fluorspar reserves in the world. The mineral ore is predominantly exported and enriched overseas – a loss to the South African economy. The commercial plant at the South African Nuclear Energy Corporation SOC Ltd (Necsa) is the only source of fluorine gas in South Africa. An increase in the use of elemental fluorine for various processes and products, such as surface fluorination and fluorination of organic compounds, is expected, as there is renewed interest in the expansion of the South African fluorochemical industry by various government and private players. Realistic predictions indicate that industry may well require small-scale production of fluorine at the various points of use as a result of the dangers inherent in the industrial-scale production, storage, and transport of the gas. The long-term aim of the work reported here is thus to demonstrate the design of small batch reactors for laboratory and industrial use. This is a first for fluorine technology in South Africa. The apparatus which is demonstrated was designed and commissioned at the University of Pretoria. Since the electrolyte, $\text{KF}\cdot 2\text{HF}$, is not readily available, the production of anhydrous hydrogen fluoride (AHF) had, of necessity, to be included in the research. Both batch reactors, for AHF and F_2 , as well as the transfer vessel

used for the storage of the AHF and feeding the fluorine cell, were designed, commissioned and tested. Detailed computational fluid dynamic (CFD) modelling of the cell also formed part of the project. The CFD is not included in this paper; it can be found in the first author's master's dissertation (Oosthuizen, 2019).

Process overview and safety

Figure 1 shows a simplified process flow diagram for the fluorine production process. AHF is not readily available in small quantities and has, therefore, to be produced on site. CaF_2 is used to generate AHF in a batch reactor by its reaction with concentrated sulphuric acid. The gas-phase HF is frozen into a storage vessel, and from there is transferred to the fluorine cell, preloaded with $\text{KF}\cdot\text{HF}$ for the electrochemical production of $\text{F}_2(\text{g})$. AHF is a weak acid and is electrically non-conductive. $\text{KF}\cdot 2\text{HF}$ by contrast is conductive above its melting point and is used as the electrolyte. The byproducts, calcium sulphate and hydrogen, are discarded as waste.

Laboratory safety is of utmost importance. Both HF and F_2 can be lethal. Essential safety aspects are briefly discussed in the appendix.

Apparatus design and operation

HF batch reactor design

Stainless steel, aluminium and lead are sufficiently chemically resistant towards $\text{H}_2\text{SO}_4(\text{aq})$ and HF for laboratory use (Craig and Anderson, 1995, Francis, 2009). As a first attempt, two versions of the reactor were machined out of aluminium billets. Aluminium affords better chemical resistance in the presence of aqueous HF (Macur, 2016). These cylindrical reactors were machined with screw-on lids. For both versions the o-ring between the reactor body and lid failed and the designs were abandoned.

Figure 2 shows a P&ID (pipe and instrumentation diagram) of the reactor, along with a photograph of the final reactor as finally used.

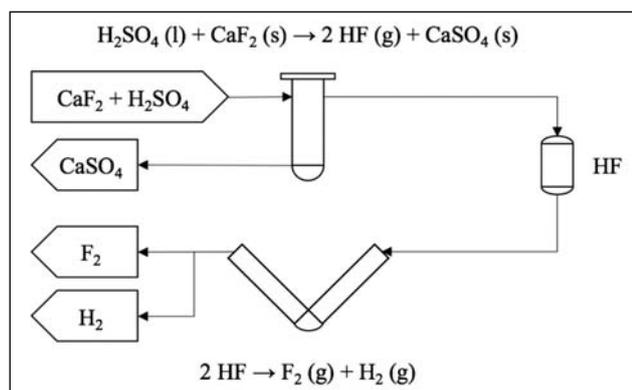


FIGURE 1: Process flow diagram of the laboratory system

A simpler design was arrived at, using a 248 mm DN 65 2½" schedule 40 316 stainless steel pipe. The bottom of the pipe was sealed with a welded lid. The top of the reactor was fitted with a DN 65 SANS 1123 table 1600/3 back flange, and was sealed off with a twin DN 65 SANS 1123 table 1600 blind flange. This flange served as access point for loading reactants and is supplied with a valve with a ¼" NPT thread. The flanges both had raised contact surfaces. A flat 1 mm Viton seal was used as packing. All additional equipment pieces were 316 stainless steel Swagelok components.

HF batch reactor operation

The batch reactor was mounted in the experimental set-up as illustrated in Figure 3. The reactor wall was placed in contact with a 400 W heating mantle and a type J thermocouple. Temperature was controlled with a Shinko PID-controller using the as-received factory settings. The metal frame for the set-up was designed to support both the transfer vessel and the batch reactor and to fit into a standard fume hood. A transparent PFA fitted with a T piece connected the reactor and the transfer vessels. The side stream from the T piece was connected to the vacuum pump via a shutout valve.

A maximum of 60 g HF may be produced per run. The reaction was executed with a five times molar excess of sulphuric acid. The limiting behaviour of the process is the various physical phases that form during the course of the reaction (Aigueperse *et al.*, 2000). The reaction mixture changes from a viscous liquid to a final powdery mass as Reaction (1) (see below) proceeds, with a concomitant change

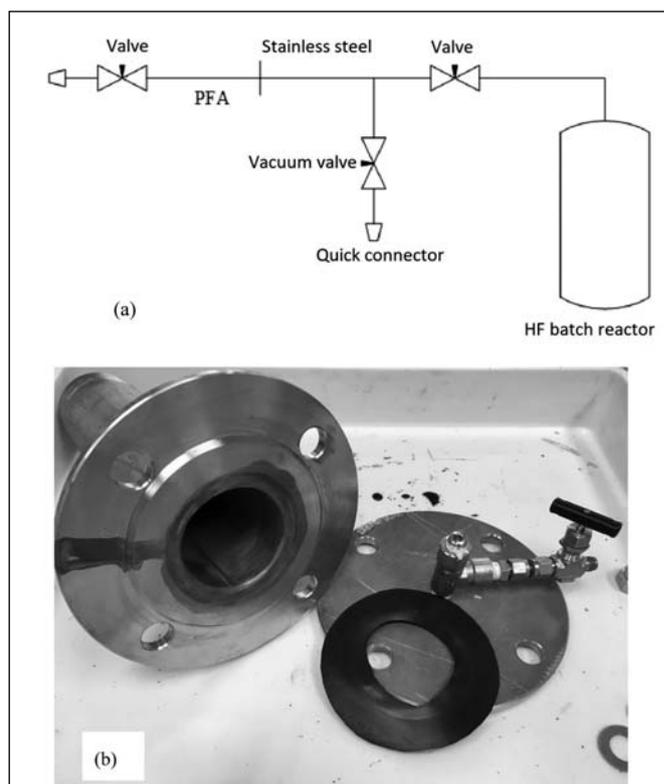


FIGURE 2: HF batch reactor: (a) P&ID of the setup; (b) a photograph of the reactor

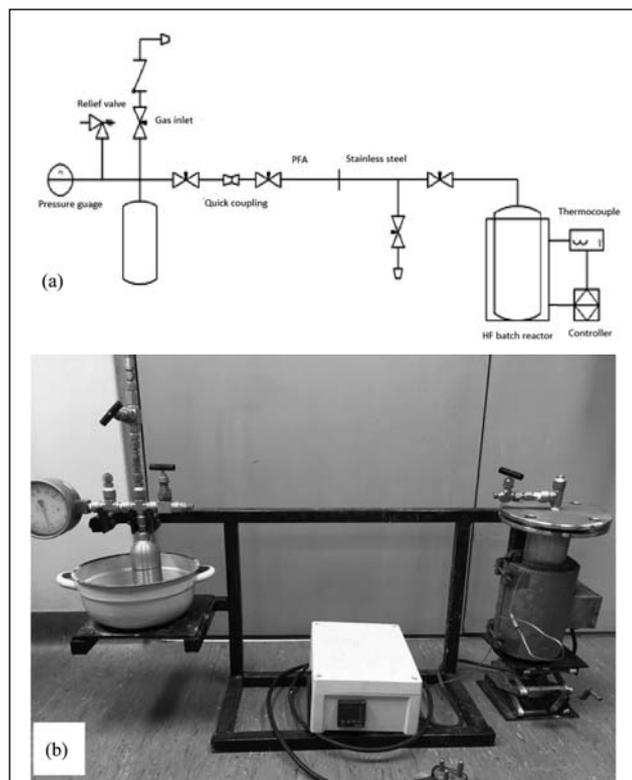


FIGURE 3: HF batch reactor experimental setup: (a) P&ID; (b) photograph

in total volume. This behaviour results in solids being dragged along with the product. Consequently the reaction volume had to be enlarged to prevent this.



Figure 4 shows a photograph and the P&ID of the transfer vessel in which the AHF is stored. Explicit reference is made to the transfer vessel in the description of the heating/cooling cycle of the HF content. The material of construction of the transfer vessel and all its attachments was 316 stainless steel. Swagelok compression seals and $\frac{1}{4}$ " tubing were used throughout. Only standard off-the-shelf components were used. The horizontal flow line is used for loading and emptying the vessels. HF is extracted by bubbling $\text{N}_2(\text{g})$ through the AHF reserve. This may be done controllably, e.g. for thermogravimetric analyses where the reaction of AHF with solid samples is studied.

The transfer vessel is placed in liquid nitrogen using a Dewar flask before operation. The reactor is at room temperature upon loading with reagents and sealing. After this the full system is evacuated. The necessary pressure drop is thus maintained for transfer of the AHF to the transfer vessel as it is produced. When the AHF is again moved from the transfer vessel, it is placed in warm water to produce a positive pressure to effect the movement of the mass.

The batch reactor is washed with water before and after each run and placed in a drying oven at 50°C to ensure that no water is present. The dry reactor is charged with a

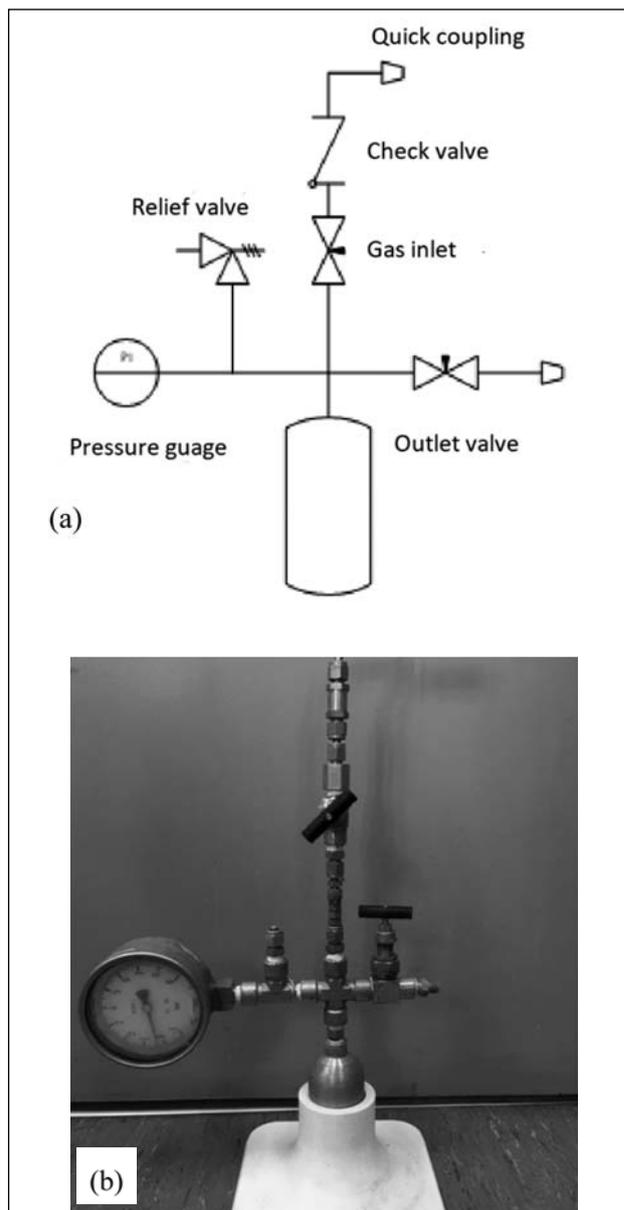


FIGURE 4: Anhydrous HF transfer vessel: (a) P&ID; (b) photograph of the vessel in a 3D-printed stand

known mass of reagents and the flange is sealed. Valves are shut and the system is evacuated. The valve to the vacuum pump is shut and the pump decoupled. The heating mantle is activated with a setpoint of 80°C . After one hour the setpoint is changed to 150°C and after another hour to 170°C . The Viton seal remains well below its service temperature of 205°C . Each run takes roughly three hours from the moment the mantle is turned on. The translucent PFA transfer tube allows inspection of the product flow, the AHF being partially condensed. The pressure gauge is used to ensure that the AHF is frozen in the vessel.

On completion of the reaction, the transfer vessel is shut down and the transfer tube decoupled. The heating mantle is turned off and excess AHF is allowed to escape through the scrubbing system. To quantify the mass AHF produced, the vessel is weighed before and after each run.

Fluorine cell design

The fluorine cell is operated at a temperature of roughly 80 °C and at atmospheric pressure. The cell is designed as a so-called medium-temperature reactor with an electrolyte composition of KF·2.2HF (Rudge, 1971). Every AHF charge can deliver up to 10 g F₂(g). The cell design is based on the Pauling geometry (Pauling, 1957), similar to that of the original concept used by Moissan (Cady *et al.*, 1942). A low energy efficiency may be expected from this design because of the high degree of electrode shielding. A high potential drop is expected because of the internal circuit of the cell (Walsh, 1993). Given that the safe operation of the cell, and its ability to produce fluorine for laboratory use, were the primary objectives, low energy efficiency was not considered to be a major problem. Importantly, the chosen shape of the cell hull prevents the explosive recombination of the product gases (Shia, 2003). Such losses are common and in general are prevented by shielding by Monel gauze (Roustan *et al.*, 1998).

The mechanical design drawing of the cell is illustrated in Figure 5. The most important dimensions are provided. The length of the tubing to connect the various ancillary components is arbitrary.

For the cell hull and all ancillary components 304 and 316 stainless steel were used, in spite of their lower resistance to corrosion by HF (Craig and Anderson, 1995). Attack by F₂(g) should, on the other hand, not result in excessive corrosion of the construction material (Rudge, 1971). Mild

steel and nickel were employed for the cathode and anode. It is possible to substitute non-graphitic carbon for nickel (Groult *et al.*, 2005; Ring and Royston, 1973). This substitution is recommended for further research since most commercial cells use hard carbon as anode material (Rudge, 1971). This substitution would make the study of the interaction of F₂(g) with the carbon surface possible, where lenticular bubbles form, very adhesive to the surface (Groult, 2003). In addition to these interesting bubble formation phenomena, the chemical reactions between the gas and the solid surface is also of great importance (Shia, 2003).

The cell was designed for a current density of roughly 100 mA·cm⁻² (Leech, 1949) when a current of 3.6 A is sustained. The resultant active length of both cathode and anode is thus 200 mm if ¼ " rods are used. The final length of the electrodes for electrical contact outside the cell is determined by the geometry of the cell hull, and the ancillary components that require mounting. All components were standard, off-the-shelf items, comprising tubes, reducing pieces, and elbow, and T pieces. The only special modification was the use of PFA shrink tubing, to insulate the electrodes from the electrically earthed outer shell.

The reducing pieces were machined out to an ID of 6.5 mm to 6.7 mm to allow free passage of electrode rods shrink-wrapped in their PFA sleeves.

The cell was pressure tested for 2 bar gauge. The diameter of the reaction tubes was chosen such that the change in electrolyte level would not result in a substantive change of the power density from the range 80 mA·cm⁻² to 100 mA·cm⁻² (Leech, 1949). Along with this, the cell had to be capable of producing the required mass of F₂(g) before AHF replenishment. During operation, the current density and the electrolyte composition vary from 112 mA·cm⁻² and KF·2.2HF with a full load, to 118 mA·cm⁻² and KF·2.02HF after production of 10 g of product. The reaction tubes are 250 mm long to provide a disengagement height of 50 mm above the electrolyte upper surface. This serves to prevent transfer of condensed material to the pressure gauges and the ¼ " outlet tubes.

Fluorine cell operation

Before startup the cell is charged with 215 g KF·HF (s) for preparing the KF·2.2HF electrolyte. The one inch compression seals at the top of the reaction tubes are first opened and, after loading, screwed on tightly. All valves are closed off and the cell is put under vacuum for five minutes to remove air and residual water vapour. The removal of water is important because of the corrosive nature of aqueous HF. Pressure tightness is tested by increasing the reactor pressure with nitrogen to 2 bar gauge. After this the cell is coupled to the transfer vessel, cooled in a methanol-ice slurry, and evacuated. The salt is crystalline and finely divided with a high bulk density. The reactor is thus easily evacuated with the valve to the

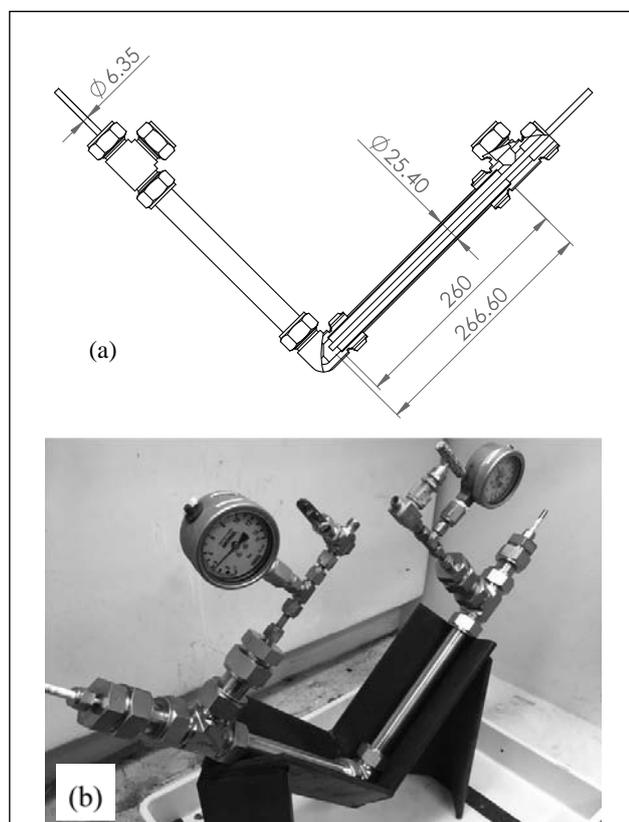


FIGURE 5: (a) Mechanical design sketch, and (b) a photograph of the fluorine cell

transfer tube open. The transfer line is thus also evacuated. The reaction tube at the vacuum-pump end is then closed and the vacuum pump shut down.

The transfer vessel is now placed in warm water and its valve opened and AHF is transferred to the fluorine cell under the pressure difference induced. During this process, HF evaporates and condenses in the fluorine cell in the form of the potassium acid fluoride. For the first charge, 66.2 g HF (g) is transferred to the fluorine cell to yield the correct electrolyte composition.

The cell is now removed from the methanol-ice bath and left to attain ambient temperature. After this it is heated in 10 °C steps to control possible pressure build-up due to local overheating. It is then left at 100 °C until a closed electric circuit is observed for the electrolyte. The temperature is lowered to the operating temperature of 80 °C and operation starts. The temperature is controlled using a Shinko PID controller and a J-type thermocouple placed between the reactor outer tube surface and the heating tape. Carbon wool is placed around the reactor tubes and heating tape to minimise heat losses.

The procedure described above is repeated to replenish the HF reserve after the cell has been run. An electron balance is used to estimate the amount of HF that would be required, using an Coulomb efficiency of 70% (Rudge, 1971).

Construction costs

The costs incurred for the hardware acquired, excluding tubes, stands, sealing material and reagents, are listed in Table I to give an indication of the type of funding required; especially important for researchers without large capital budgets.

TABLE I: Costs in 2018

Reactor	Costs (ZAR)
HF batch reactor	4 800
Fluorine cell	23 400

Experimental

Chemicals

97% pure CaF₂ powder from Merck was used, along with 98% sulphuric acid supplied by ACE. The electrolyte precursor was 99.99% pure KF·HF from Sigma Aldrich.

Typical experimental design

In order to raise the HF content of 215 g KF·HF(s) to KF·2.2HF(s), 66.2 g HF is required. To prevent any transfer difficulties, two runs thus had to be completed to supply a sufficient quantity of HF (Table). The HF produced is now transferred to the fluorine cell for the experiments to be completed.

TABLE II: HF batch reactor experiments

Experiment	Mass CaF ₂ (g)	Mass H ₂ SO ₄ (g)	Expected yield (g)
HF1	64.6	406	33.1
HF2	64.6	406	33.1

Table III contains a description of the voltametric-curve experiments. The two experiments were conducted directly after one another in order for the results to be compared.

TABLE III: Voltametric experiments

Experiment	Description
F1	The applied voltage is increased stepwise by 1 V and the current drawn is noted as soon as it has stabilised. The process is continued until the current curve flattens out, and the voltage adjustment is repeated, stepwise, in the reverse direction.
F2	The applied voltage is increased stepwise by 1 V up to the expected operating voltage of 12 V, and then further up to 18 V to determine the current drawn at each step. At each voltage setting the current is recorded for roughly five minutes.

Results and discussion

The mass HF produced along with the conversion efficiency is reported in Table IV. The white clouds released by the production of AHF confirm the anhydrous nature of the product. The reactor is easy to clean after completion of the reaction and cooling. If the reactor is left overnight to cool, the solid products become hard and adhesive and difficult to remove from the surface. For safety reasons it is better to avoid having to use too much force for cleaning.

Initially, during execution of HF1, the reactor flange was not tightened sufficiently. This led to ingress of air and negatively affected transfer of AHF. The reactor was then resealed and the transfer vessel evacuated again. The run was then completed with a sufficient pressure drop. Excess air present in the transfer vessel after the experiment, was again removed by evacuation.

TABLE IV: HF batch reactor experiment results

Experiment	Mass HF (g)	Yield (%)
HF1	25.4	77
HF2	23.5	70

Some AHF from a previous experiment was present in the transfer vessel from a previous version of the batch reactor. A total of 97.4 g was then introduced into the fluorine cell, yielding an electrolyte composition of KF·2.77HF.

The voltametric data for experiment F1 are given in Figure 6. The first indication of current flow was observed at 5.6 V. The reversible potential for the reaction is 2.9 V; the overpotential is thus a maximum of 2.7 V (Rudge, 1971). The production of F₂(g) was confirmed using filter paper wetted with KI (aq). This solution immediately turned black, indicating the product to be fluorine.

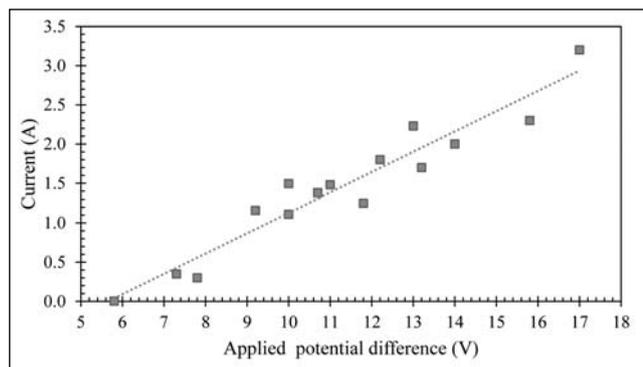


FIGURE 6: Fluorine cell voltametric curve, experiment F1

The data points for experiment F2 were collected at one second intervals and are plotted in Figure 7. From these data a linear regression line, similar to Figure 6, was obtained. The regression lines along with the correlation coefficients are reported in Table V. The random peaks observed in Figure 7 may be attributed to mass transfer effects.

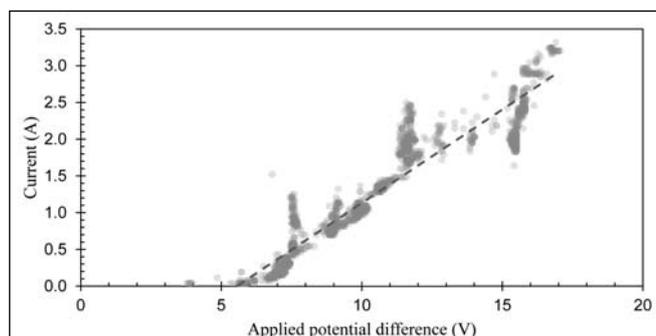


FIGURE 7: Fluorine voltametric data, experiment F2

TABLE V: Regression line and correlation coefficients for voltametric data

Experiment	Regressio line	Correlation coefficient
F1	$I = 0.259V - 1.46$	0.920
F2	$I = 0.255V - 1.41$	0.890

During both experiments the fluorine flow was observed to be non-continuous. This observation, along with audible recombination events, indicate that the electrodes should not be positioned too closely together. Some solid transfer to the $\frac{1}{4}$ " tubing was also noted, suggesting a suboptimal disengagement height, i.e. too short a distance between the electrolyte surface and the gas exit.

Conclusions

The process as described above was shown to be successful and safe for the laboratory production of fluorine gas. The AHF batch reactor afforded a 70% yield based on the limiting reagent. Anhydrous HF was successfully produced, stored, and transferred. The fluorine cell was operated successfully, demonstrating an overpotential of 2.7 V. Some recombination of product gases was observed, suggesting too low an inter-electrode distance. Blocking of the $\frac{1}{4}$ " outlet tubes indicates that the height of the free zone above the electrolyte surface should be revised in future designs

to ensure ease of operation. At this stage no attempt has been made to analyse the quality of the fluorine or to identify contaminants; the corrosive and lethal nature of fluorine makes this tedious, complicated, and expensive, requiring substantial further work.

Appendix

The processes discussed in this paper are inherently dangerous because of the reactive nature of the products. HF is a colourless liquid or gas, boiling point 19.9 °C, with a strong irritating smell (NECSA, 2017). Accidental exposure to HF is an extremely serious matter. It is a weak acid in aqueous solution, but penetrates human tissue very rapidly because of the small size of the molecule and causes serious chemical burn wounds. It is classified as toxic and corrosive for exposure through breathing and contact. To place the risk in perspective, death may result for an exposure area as small as the palm of one hand. In case of exposure the contact area should immediately be washed in cold running water, and after that treated with calcium gluconate gel. Additional medical attention is required subsequent to any first aid treatment. In the case of inhalation of HF fumes, the person exposed should be put in a semi-upright position in fresh air. Artificial respiration may be required and medical attention should be sought immediately after initial first aid (International Labour Organization, 2017b).

Exposure to F₂ is of similar gavity. For inhalation, identical steps to inhalation of HF should be taken (International Labour Organization, 2017a). For skin contact, the area should be treated with cold running water, clothes removed after that, the area treated with calcium gluconate gel, and formal medical care sought.

Any user of this process is strongly encouraged to obey safety rules diligently and acquire the recommended PPE (NECSA, 2017, Rudge, 1971). Direct training in the handling of the materials is also strongly advised. All experimental work needs to be done inside a fume hood. Chemically resistant laboratory coats and full face masks should be worn at all times. Hands should be rubbed with calcium gluconate gel before putting on a first layer of nitrile gloves. Since gloves may tear during operation, the outside of the gloves should also be covered with gluconate gel. An outer pair of gloves is then required, covering the inner glove layer. Covered shoes and a pair of chemically resistant trousers are also required.

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