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A REVIEW OF FLUORINE CELLS AND FLUORINE PRODUCTION FACILITIES

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ABSTRACT

The development of laboratory and industrial scale electrolytic cells used for the generation of fluorine is reviewed and the construction and operating characteristics of these cells are examined in detail.

In addition, the associated facilities required for the supply and treatment of raw materials, treatment of product gases and disposal of waste materials are described. Safety practices adopted in the design and operation of equipment including personnel protection and first aid procedures are also outlined.

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1. INTRODUCTION

Fluorine was named by Ampère in 1812 and isolated by Moissan in 1886 by the electrolysis of anhydrous hydrofluoric acid containing a small concentration of potassium fluoride, fluorine being liberated at the anode.

$$2HF \longrightarrow H_2 + F_2$$

The potassium fluoride rendered the covalent hydrogen fluoride conducting and it was this discovery that allowed the isolation of fluorine after many years of effort. Fluorine has been produced industrially for the last 30 years, mainly for the production of uranium hexafluoride in the nuclear industry and for propellants in space rockets. Smaller quantities are used for organic fluorochemicals, sulphur hexafluoride and other inorganic fluorides.

This report surveys the development of fluorine cells on both a laboratory and industrial scale, in particular the design, construction and operating features of modern production cells are described in detail. In addition to the electrolytic cell, the production of fluorine requires equipment (see Figure 1) for the storage and vaporisation of hydrogen fluoride, preparation of electrolyte, treatment and compression of the off-gases, and the disposal, in emergencies, of fluorine and hydrofluoric acid. The design and operation of this equipment are also described as well as aspects of protective clothing, safety equipment and first aid procedures for use with fluorine and hydrogen fluoride.

2. DEVELOPMENT OF LABORATORY FLUORINE CELLS

Electrolytic cells and associated techniques for the generation of fluorine were developed on a laboratory scale for many years before increased usage demanded industrial production. A substantial amount of data was gathered in this period and this assisted in the rapid development of industrial scale facilities during the Second World War.

Cells of three general types characterised by their operating temperatures were developed. Significant examples are listed in Table 1. The low temperature cell was used by Moissan (1886) to isolate fluorine. Historically this cell was followed by the high temperature cell of Argo et al. (1919) and the medium temperature cell of Lebeau and Damiens (1925). The medium temperature cell was developed industrially during and after the Second World War and cells of this type are now used universally for the industrial scale production of fluorine.

The low, medium and high temperature cells used potassium-hydrogen polyfluoride electrolytes of different compositions. The complete vapour pressure characteristics of the potassium-hydrogen fluoride system were first demonstrated by Cady (1934) and later by Neumark (1947). These results are presented in Figure 2 and show that only stable phases of KF.HF and KF.2HF exhibit a very low vapour pressure of HF at their melting point. These two phases correspond to those used in the high and medium temperature cells respectively. In low temperature cells, the vapour pressure of HF was maintained at an acceptable level by cooling to $-80^{o}C$.

2.1 Low Temperature Cells

The low temperature cell was developed by Moissan following his discovery that HF containing a small amount of dissolved KF conducted electricity and offered the possibility of producing fluorine by electrolysis. The initial cell shown in Figure 3 was a platinum/iridium 'U' tube (later replaced by copper) and used an electrolyte of KF.12HF. The cell was cooled to $-80^{o}C$ by immersing the cell in a bath of methyl chloride to keep the vapour pressure of HF to acceptable levels. The fluorine product was also cooled to $-50^{o}C$ to remove HF vapour. The rate of corrosion of the cell was high, particularly of the platinum anode, and 5 to 6 grams of platinum were consumed for every gram of fluorine produced. This loss was slightly reduced by using copper cells and such cells produced 2 to 3 $\ell\ h^{-1}$ of fluorine (Leech 1956). Another design for a low temperature cell was described by Poulenc and Meslans (1900). This cell featured a cylindrical body incorporating a perforated diaphragm to separate the gases and an internally cooled anode, but successful

operation was not reported. In the period 1936-1942, a number of attempts were made by ICI (Rudge 1941, 1949a, 1956, 1971) to develop a low temperature cell which operated at room temperature with an electrolyte of KF.8HF. Cells of 100-120 A capacity were developed but the process was abandoned because of corrosion problems (Ferguson 1942, Rudge 1956).

2.2 High Temperature Cells

The high temperature cell (Figure 4) was developed by Argo et al. (1919) to overcome the high level of corrosion and high vapour pressure of HF in the low temperature cell. It used potassium bifluoride (Fremy salt), KF.HF, as electrolyte which produced a very low vapour pressure of HF over the molten electrolyte at the operating temperature of the cell (250°C). The cell body, which also acted as the cathode, was of copper and the anode was of Acheson graphite. The graphite was attacked slighly; by contrast a graphite anode used in a Moissan low temperature cell disintegrated completely (Argo et al. 1919).

Many high temperature cells were developed subsequently and are listed in Table 1. Most cells were of the diaphragm type, however some 'V' or 'U' shaped cells were also used (Dennis et al. 1931, Miller and Bigelow 1936, Aoyama and Kanda 1937). In diaphragm cells, the corrosion of the diaphragm was high and numerous attempts to reduce this by insulating the diaphragm from the anode connection were tried. To limit corrosion, efforts were made to construct cell bodies entirely from graphite (Argo et al. 1919, Meyer and Sandow 1921, Mathers 1924), however these cells proved to be fragile. Bodenstein et al. (1935) developed a cell with air cooled electrodes entering the bottom of the cell and sealed in place using frozen electrolyte following a patent for this technique by Krekeler (1932). The cell of Bodenstein et al. used an 'Elektron' alloy (98% Mg, 2% Mn) tank and a louvred Elektron alloy diaphragm with a perforated silver cathode and graphite anode. Some of the aspects of this design were incorporated in industrial size cells developed in Germany (Carter et al. 1946).

Another high temperature cell design by Simons (1939) was used extensively and proved to be a very practical laboratory scale source of fluorine (Emeléus 1942, Burford et al. 1951). A cell of 30 A capacity was developed from the Simons design by increasing the size of the tank and using three graphite rods for the anode (Emeléus 1942).

The development of high temperature cells showed that copper, magnesium and silver were suitable materials of construction for such cells and that graphite was a successful anode material. For electrical insulation, Portland cement or calcium fluoride mixed with sodium silicate (see Table 1) proved

effective on the laboratory scale, though these were less effective in larger cells. In addition, high temperature cells had the following operating characteristics:

(a) The product fluorine contained approximately 5-15 vol.% of hydrogen fluoride which could be removed by contact with sodium fluoride (Mathers 1924, Dennis et al. 1931, Bigelow et al. 1933, Denbigh and Whytlaw-Gray 1934).

(b) The water content of the electrolyte had to be low for successful operation (Argo et al. 1919, Mathers 1924, Bancroft and Jones 1929, Schumb and Gamble 1930, Dennis et al. 1931, Miller and Bigelow 1936, Simons 1939). With 'moisture-free' electrolyte, fluorine was evolved immediately electrolysis commenced (Denbigh and Whytlaw-Gray 1934) and the risk of polarisation was reduced (Simons 1939). Water was removed by either drying for 24 to 48 hours at 140°C (Dennis et al. 1931, Denbigh and Whytlaw-Gray 1934, Miller and Bigelow 1936) or by electrolysis at a low current density (Argo et al. 1919, Mathers 1924, Bancroft and Jones 1929).

(c) A hard glass-like layer often formed on the anode resulting in a poor yield of fluorine and erratic operation of the cell (Fredenhagen and Krefft 1929, Dennis et al. 1931, Denbigh and Whytlaw-Gray 1934). This phenomenon was initially attributed to a deposition of silicon from the electrolyte on the anode (Fredenhagen and Krefft 1929, Dennis et al. 1931, Denbigh and Whytlaw-Gray 1934), however, later work indicated the coating was a layer of carbon monofluoride (Neumark 1947, Rüdorff and Rüdorff 1947).

(d) Regeneration of the electrolyte (i.e. addition of HF) had to be carried out in a container separate from the cell and was a difficult procedure (Argo et al. 1919, Mathers 1924, Dennis et al. 1931, Simons 1939).

(e) The graphite anodes gradually corroded to produce carbon tetrafluoride. Lebeau and Damiens (1925) stated that the proportion of carbon tetrafluoride contaminant in the fluorine increased with cell operating temperature, anodic current density and voltage.

2.3 Medium Temperature Cells

Lebeau and Damiens (1925) developed a medium temperature cell (Figure 5) which operated at 65 to 75°C using KF.3HF as electrolyte in order to overcome the carbon tetrafluoride contamination of fluorine experienced with the high temperature cell. The cell tank was a copper cylinder which acted as the cathode. A slotted copper diaphragm and a nickel or nickel-iron alloy anode were used. The anode materials corroded and produced a low current efficiency (problems similar to those in the low temperature cell) but the problems of formation of an anode surface film and carbon tetrafluoride contamination in high temperature cells were overcome. Nickel anodes were not successful in

high temperature cells because nickel fluoride was produced rather than fluorine (Fredenhagen and Krefft 1929). With the medium temperature cell, the electrolyte could be regenerated in situ by the addition of anhydrous HF vapour; however, the high vapour pressure of HF over molten KF.3HF resulted in the fluorine product being contaminated by a large proportion of HF.

A similar cell was described by Henne (1938) and followed a design by Dennis et al. (1931). This cell used graphite electrodes giving a greater current efficiency. Henne reported that water and silicates in the electrolyte had an adverse effect on the performance of the cell and that these impurities were removed by preliminary electrolysis. The glassy coating on the anode (the anode surface film) was removed by rubbing with sandpaper and the electrode returned to service.

Following the publication of the phase diagram for the KF-HF system, Cady (1939) developed a cell operating at 75°C which used KF.2·2HF as the electrolyte. Figure 2 shows that the vapour pressure of HF above molten KF.2·2HF is much less than that for KF.3HF used in the cell of Lebeau and Damiens. Cady claimed his cell had the following advantages:

(a) Commercial anhydrous HF vapour could be used to regenerate the electrolyte in situ.

(b) The vapour pressure of the HF over the electrolyte was very low.

(c) The composition of electrolyte could vary over a relatively wide range for only a small variation in the operating temperature of the cell.

(d) Corrosion of the anode and other cell components was reduced and steel could be substituted for monel as the material of the cell body.

Water and other undesirable materials were eliminated during preparation of the electrolyte by electrolysis of molten KF.HF using graphite electrodes before the addition of anhydrous HF to produce KF.2·2HF.

This initial cell was improved in a later design (Figure 6) reported by Cady et al. (1942). This cell used an electrolyte of KF.2HF and a perforated diaphragm to allow the electrolyte to circulate more readily. In addition the body of the cell was surrounded by a water jacket to allow closer control of the operating temperature. Both nickel and graphite were used as anode materials. An anode surface film did not form if the electrolyte was prepared by pre-electrolysis of the KF.HF as described earlier. Cady et al. (1942) preferred to use nickel anodes as they reduced arcing to the electrolyte, did not disintegrate or develop a high resistance surface film or produce volatile carbon compounds as did carbon anodes.

2.4 Other Electrolytes Used in Fluorine Cells

An ideal electrolyte for the preparation of fluorine should possess a low melting point, a low vapour pressure of HF, high conductivity and allow electrolysis to proceed with some tolerance of impurities. All metal fluorides have high melting points and are unsuitable (Table 2). Several acid fluorides have been investigated and the KF-HF system has been adopted universally (Table 3). The properties of this system were investigated by Cady (1934) and Neumark (1947) and have been described earlier. Caesium polyfluorides show the most promise of all the other polyfluorides, however the cost of this material is prohibitive.

Mathers and Stroup (1934) investigated several possible electrolytes other than the KF-HF system with the following results:

(a) The mixed salts K_2SnF_6, K_2TeF_6, K_2TiF_6, K_2MnF_6, K_2PbF_6, K_2SeF_6 and K_2SbF_6 had melting points higher than the KF-HF system alone.

(b) NaF.HF and LiF.HF both decomposed before melting.

(c) $NH_4F.HF$ melted at 112°C but fumed vigorously and decomposed to nitrogen and HF readily.

(d) The melting point of the KF-HF salt could be reduced slightly by adding NaF, $NaHF_2$, PbF_2 or SrF_2 (Meyer and Sandow 1921) however the overall effect was not advantageous.

(e) The fluoride salts of rubidium and caesium showed most promise.

Mathers and Stroup (1934) prepared and used CsF.1·5HF as an electrolyte in a cell made of magnesium with a graphite anode. Fluorine was evolved readily with little HF contamination. The cell operated over the temperature range 19 to 100°C and the electrolyte proved easy to regenerate. The very high cost of the caesium salt prohibited further use of this promising material.

Neumark (1947) stated that the melting points of the caesium and rubidium salts showed only a slight reduction over their potassium counterparts and concluded that the potassium polyfluorides were the most suitable electrolytes.

3. DEVELOPMENT OF INDUSTRIAL FLUORINE CELLS

The wartime requirements for fluorine in Germany (for the manufacture of chlorine trifluoride), England and the U.S.A. (for the manufacture of uranium hexafluoride) initiated research and development into the industrial scale production of fluorine. From 30 A laboratory scale cells, industrial scale cells of 1000-2000 A capacity were developed to which present day production cells operating at 5000-6000 A are directly related. These developments are listed in Tables 4 and 5.

All three techniques, low, medium and high temperature, were examined for possible development. The low temperature process was examined by Du Pont (Calcott and Benning 1936) using an electrolyte of KF.8-10HF at room temperature. A 1000 A cell of this type reached a practical stage of development, but excessive corrosion and low current efficiency caused this process to be abandoned (Downing 1946). Similar experiments on a smaller scale (100 A) by the Harshaw Chemical Company (Downing 1951a) and ICI (Rudge 1941, Ferguson 1942, Rudge 1949a, Rudge 1956) were also unsuccessful.

The high temperature process was examined by Johns Hopkins University in the U.S.A. (Fowler et al. 1947, Burford et al. 1951) and in Germany (Carter et al. 1946, Karr 1946, Neumark 1947). A 600 A cell was developed by Johns Hopkins using KF.HF electrolyte operating at 260°C. This cell operated satisfactorily however excessive corrosion of the anode assembly and difficulties experienced in the addition of HF resulted in the termination of the project. The Germans had more success and developed a 2000 A cell. A number of these were installed and operated on an industrial scale at Falkenhagen from 1942-1945 (Carter et al. 1946, Karr 1946, Neumark 1947).

The medium temperature process was examined in England, France, Germany and the U.S.A. A single 2000 A cell was developed and operated efficiently in Germany (Carter et al. 1946, Karr 1946, Neumark 1947). In the U.S.A. a large effort was focussed in the period 1943-1946 on medium temperature cells operating at 100°C with KF.2HF electrolyte. Several cells of 1000-2000 A capacity were developed (Downing 1944, 1946, 1951a, Williams et al. 1944, Stevenson 1945, Trepper 1945, Schumb 1946, 1951, Downing et al. 1947, Pinkston 1947, Schumb et al. 1947, Long et al. 1951). The design by the Hooker Corporation (Murray et al. 1946, 1947, 1951) was chosen for further development by the USAEC, resulting in the "C" and modern "E" Cells of 6000 A capacity (Dykstra et al. 1955) which were installed at the Oak Ridge and Portsmouth Gaseous Diffusion Plants (Smiley and Brater 1956, Goodyear Atomic Corporation 1967a, 1967b). In addition to the USAEC, the Pennsylvania Salt Manufacturing Co. and the Allied Chemical Corporation independently started

commercial fluorine production in 1946 (Neumark and Siegmund 1966). The former company operated a number of 2000 A cells (Porter 1948) but additional information is not available. The Allied Chemical Corporation developed cells of 4000-5000 A capacity and commenced operation in 1959 of the only commercial fluorine production plant at that time in the U.S.A. at Metropolis, Illinois (Allied Chemical Corporation 1961, Neumark and Siegmund 1966, Siegmund 1967).

In England, Imperial Chemical Industries Limited also developed medium temperature cells, commencing in 1948 with cells of 1000 A capacity and progressing to capacities of 1400, 2000 and finally 5000 A in 1959 (Rudge 1956, 1962, 1966, 1971). Cells of basic ICI design of 5000 A capacity have been operated since 1968 by the UKAEA (Rudge 1971, Rogan 1972a, 1972b). The French developments are more recent, a cell of 1500 A capacity was developed and operated from 1950-1955 (Level 1969) and more recently 6000 A cells similar to the USAEC "E" cells have been used in the Pierrelatte Chemical Works (Bergeret 1965, Level 1969).

3.1 High Temperature Cells

3.1.1 General features

High temperature cells are attractive because by using graphite anodes they offer operation at a high current density which results in a more compact cell, a low operating voltage and freedom from severe polarisation problems. These advantages have to be balanced against the increased corrosion rates experienced at the higher operating temperature and the accurate control of electrolyte composition and temperature which is necessary to ensure trouble-free operation.

The German cell used Elektron alloy (98% Mg, 2% Mn) as the major material of construction with graphite and silver being used for the anode and cathode respectively (Carter et al. 1946, Karr 1946, Neumark 1947). The cell (Figure 7) developed by Burford et al. (1951) at Johns Hopkins University used Monel metal (a nickel-copper alloy) for the cathode and most other major components. Graphite rods mounted in copper bus-bars were used as the anode.

The development of the American cell was terminated because of excessive corrosion problems. Similar problems were overcome successfully (Neumark 1947) in the German cell by continuous addition of HF to the electrolyte to ensure a constant electrolyte composition and cell operating temperature. In the American cell the HF was added intermittently (Burford et al. 1951) and this, coupled with a low electrolyte inventory, caused wide fluctuations in electrolyte composition and temperature.

3.1.2 Anode construction

Graphite was used without any special treatment for the anodes in both the American and German high temperature cells. The life of the Siemens graphite anodes used in the German cell was one year (Neumark 1947), those in the American cell were replaced more frequently due to deterioration of the electrical contacts.

The anode of the American cell consisted of a series of graphite rods inserted as a press-fit into holes bored into, but not through, a copper bus-bar. This electrical connection was augmented by a pin which was inserted axially into the centre of the top of each rod through a hole counter-bored in the bus-bar. The pin was silver-soldered to the bus-bar. Despite these precautions the contact resistance increased as corrosion products accumulated and this problem caused the development of the cell to be terminated.

In the German cell, the anodes were made from specially shaped pieces of graphite which passed through insulated packings in the cell cover plate (Figure 8). The packing material was a cement of calcium fluoride, lead oxide (Pb_3O_4) and glycerine with gas-tight seals of mitred graphite (Carter et al. 1946). To keep this assembly cool and to minimise corrosion problems it was mounted in extension tubes above the cover plate.

3.1.3 Cathode construction

A thorough series of corrosion tests were carried out (Neumark 1947) prior to the selection of a cathode material for the German cells at Falkenhagen. The results of these tests are reported in Table 6. Silver was chosen for the cathodes because of its resistance to corrosion by oxygen and anhydrous hydrofluoric acid and its very low corrosion rate during periods when the cell was shut down. The slight corrosion which occurred during electrolysis was tolerated because the recovery of silver from the electrolyte every 8 to 12 months was a simple operation with a good yield (Neumark 1947). Each cathode consisted of two 1.5 mm thick perforated silver plates welded to a frame of 12 mm silver tube. The vertical sides of the frame extended through the cover plate of the cell and were insulated and sealed in a manner similar to that used for the anode assembly.

The American cell used the Monel cell tank as the cathode and this had a life of 18 months. Sludge accumulated on the bottom of the cathode box and was removed every 14 days when the anodes were replaced.

3.1.4 Tank and skirt construction

Both the Falkenhagen and Johns Hopkins cells used a solid skirt which was mounted on the cover plate and dipped into the electrolyte to separate the

gases as they were liberated. The Monel skirt of the Johns Hopkins cell extended into the electrolyte as a grid diaphragm which was provided to prevent broken anodes from shorting with the cathode. In the Falkenhagen cell, the 6 mm thick Elektron skirt extended into the electrolyte and was cut with louvres to act as a diaphragm. The louvred area matched the area of the cathode to avoid bipolar corrosion of the diaphragm.

Vastly different methods were provided to control temperatures in the cells. The electrolyte tank of the Falkenhagen cell was encased in a light gauge Duralumin box with 150 mm clearance between the box and the cell tank. Thermostatically controlled electrical resistance heaters were mounted in this space in which air was circulated. The air temperature was controlled at 230 to 250°C. In the Johns Hopkins cell, the electrolyte tank was surrounded by a mild steel jacket in which diphenyl oxide was circulated to regulate the temperature. During shutdown periods the base of the jacket was heated by gas burners and during operation the diphenyl oxide distilled and was condensed in water-cooled condensers and returned to the cell.

3.2 Medium Temperature Cells

3.2.1 General features

The American studies on low, medium and high temperature cells resulted in the selection of the medium temperature cell as the most practical source of fluorine (Downing 1946, 1951a, Pinkston 1947, Katz 1951). This cell has relatively low rates of corrosion because of the temperature of operation (90°C) and the low vapour pressure of hydrogen fluoride over the molten KF.2HF electrolyte. In addition wide variations in electrolyte composition could be tolerated with little change in operating temperature. Initially the corrosion of anodes made from nickel was a major problem, however this was overcome by using ungraphitised carbon and this material is used for the anodes in all modern medium temperature fluorine cells.

Mild steel and Monel are the most common materials of construction, mild steel for the cathode and Monel for internal parts such as the skirt, diaphragm and cooling tubes. USAEC "C" and "E" cells (Figures 9 and 10) used Monel tanks with mild steel cover plates (Dykstra et al. 1955, Vavalides et al. 1958, Clark 1960) whereas the British cells used mild steel for both items (Rudge 1956, 1966, 1971, Rogan 1972b).

3.2.2 Anode construction

(a) Metal anodes

Large scale (1000 A) medium temperature cells initially used nickel anodes (Downing 1951a, Rudge 1956). The nickel anodes produced fluorine without any

polarisation problems and could operate with electrolyte containing moisture. However corrosion was severe and the anode current efficiency was 70 per cent (Downing 1944, 1946, 1951a, Carter et al. 1946, Long et al. 1951, Leech 1952, Rudge 1949a, 1956, 1971, Neumark and Siegmund 1966). As a result of corrosion the electrolyte became contaminated with dissolved or suspended nickel salts which interfered with electrolysis and prevented the recovery of large quantities of electrolyte (Neumark 1947, Downing 1951a, Rudge 1956). Consequently the cells required frequent overhaul and replacement.

A typical cell using nickel anodes of 1500 A capacity was developed by Du Pont (Downing 1944). The cell used an anode current density of 2050 A m^{-2} and the operating life of the anodes was 750,000 A h after which a sludge layer of nickel corrosion products had accumulated to 0.2 m depth.

A particular advantage of the nickel anode cell was the use of a welded anode assembly (the anode was welded to a steel support bar) which allowed the anode to be submerged wholly in the electrolyte and so promoted circulation of the electrolyte on a thermo-siphon principle (Downing 1944, 1951a, Benning et al. 1951). Nickel anode cells operated generally with an electrolyte of the composition KF.2·3HF to reduce the nickel consumption (Downing 1944, 1951a).

A number of materials have been tested unsuccessfully as anode materials by Calcott (1943). Mild steel, copper, Inconel, 18-8 stainless steel, brass, bronze, nichrome and magnesium passified when used as anodes; aluminium did not passify but was rapidly consumed. Monel operated erratically at current densities up to to 2370 A m^{-2} for short periods of time. Palladium produced fluorine initially but eventually disintegrated. A nickel anode containing 0.13% of graphitic carbon operated smoothly with a rate of corrosion of 2.1 kg F_2/kg nickel compared with a rate of corrosion of 3.5 kg F_2/kg nickel for an ordinary nickel anode.

At the time nickel anode cells were constructed, research programs to find a suitable form of carbon anode were already in progress (Neumark 1947, Downing 1951a, Rudge 1956). Graphite was tried initially but was found to disintigrate rapidly in KF.2HF electrolyte (Downing 1944, Neumark 1947, Long et al. 1951, Murray et al. 1951). A large number of non-graphite carbons were examined (Calcott 1943, Downing 1944, McLaren 1951, Rudge 1956) before the development of types which operated at high current efficiencies and replaced nickel as the anode material in fluorine cells.

(b) Carbon anodes

The value of a type of carbon as an anode material may be described in terms of its electrical resistance, physical strength, resistance to corrosive

attack or other ageing phenomena, the stability of an electrical contact with the material and the maximum current density which can be used before polarisation occurs (McLaren 1951). Unfortunately a thorough specification based on these properties has not been developed. The selection of a suitable carbon was based on trial and error methods which were complicated by the lack of consistent properties in some types of carbon. Impurities in carbons were claimed to be potential catalysts for either the generation of fluorine or polarisation but, in general, correlations with anode performance were not determined (Katz 1951, Ebel and Montillon 1952). For example the properties may vary from batch to batch in a carbon of nominally the same type (Dykstra et al. 1955).

The USAEC E-type cells used Union Carbide YBD grade carbon (Dykstra and Paris 1959, Powell et al. 1961) which is a hard ungraphitised material made from petroleum coke. Earlier versions of this cell (the Hooker, modified Hooker and C-type cells) used GA, GAA and YAA carbons which are similar materials from the same company (Ebel and Montillon 1952, Dykstra et al. 1955, Kelly and Clark 1967a, 1968a). Some of the properties of these materials are listed in Table 7.

To avoid the possibility of variations in the current-carrying capacity of GAA and YAA carbon anodes in the same cell (modified Hooker), attempts were made to correlate resonant frequency, electrical resistivity, hardness, porosity and spectrographic analysis. It was found that only resonant frequency (which roughly correlates the rigidity of an anode with its electrical properties, thermal properties and hardness) could be measured swiftly on a production basis and this property was used as a selection criterion. More than 300 cells were operated without start-up difficulty under this program (Dykstra et al. 1955). The selection of individual blades of YBD grade carbon to be parallelled electrically in the C and E-type cells was consequently based on a test of their resonant frequency. All blades used in a particular anode assembly were selected to be within 10 vibrations per second of each other (Huber et al. 1958, Powell et al. 1961, Union Carbide Corporation 1968). Higher frequencies were noted to give slightly longer-lived cells but it was not possible to identify unsuitable anodes as the anode frequency test was affected by carbon dimensions and density and other electrical properties (Powell et al. 1961). It was suggested that adopting a resonant frequency test is valid because this property is related essentially to the degree of graphitisation of carbon (Wada 1961).

Many attempts were made to improve the characteristics of the carbon used

in anodes. In one experiment with type GA carbon of the National Carbon Company, three anode blocks were pretreated before use. Pieces were subjected to a reducing atmosphere, an oxidising atmosphere, a special increase in density by impregnation and rebaking and, for comparison, one anode was left untreated. It was found that the untreated and reduced materials gave a similar performance whereas the performances of the oxidised and densified carbons were poorer (Downing 1946, Ebel and Montillon 1952). Coated and impregnated carbons were tried with varied success. Nickel plated carbon anodes were found to perform poorly (Calcott 1943) and a copper-sprayed carbon anode was completely consumed beneath the surface of the electrolyte (Downing 1946). Copper plating the carbon anode over the contact area appeared to offer improvement but the evidence was not conclusive (McLaren 1951). However, copper impregnated carbon anodes exhibited a number of advantages (Williams et al. 1944, Downing 1946, Pinkston 1947, Whitaker 1950, Long et al. 1951, Katz 1951, McLaren 1951).

The latter anode was made by vacuum-impregnating a solid block of type GA carbon with molten copper. With the impregnated carbon, there was a reduction in the carbon/bus-bar contact resistance by a factor of up to 30 (Downing 1946). In terms of current carrying capacity, the impregnated carbons were only slightly better than pure GA carbons initially, but after four months operation the impregnated blades carried 44% more current (Katz 1951). The copper impregnated anodes were somewhat stronger than plain carbon and were heavy enough to sink in the electrolyte if broken (Williams et al. 1944, Pinkston 1947, Long et al. 1951). These advantages were verified by the continuous operation of a number of 1000 A cells for over a year without polarisation or loss of anode/bus-bar contact (Long et al. 1951). Despite these apparent advantages this material was not investigated further probably because the Harshaw Cell in which it was used was not developed beyond the pilot plant scale.

The service life of thin (32 mm) YBD carbon anodes used in early production cells (Dykstra et al. 1958) was improved by impregnating the carbon with a phenolic resin ('Karbate'). The service life was increased by 32.7% when tested over an extended period. However, with the Karbate anode, the initial depolarisation process was more difficult and the initial operating voltage of cell was 0.4 to 0.8 volts higher (at 4000 A). This relative over-voltage was reduced over a long operating life having little significance after about 1000 hours service and it was suggested that Karbate anodes had advantages where thin anodes were necessary (Dykstra and Paris 1959). It is of interest to

note that in the USAEC E-type cell untreated YBD grade carbon 50 mm thick was used and had sufficient strength (Dykstra and Paris 1959).

A more recent development has been the use of carbon anodes impregnated with lithium fluoride. Tests on a laboratory scale showed that these electrodes were considerably more effective in lowering the anode potential (Watanabe et al. 1963a), see Section 4.1.6.

The carbon used in the German medium temperature cell at Leverkusen was very hard and graphite free. The carbon when properly prepared possessed a hardness rating similar to carborundum. A special pitch was used to impregnate the carbon and produce a high breaking strength (see Table 7). Care was taken in the selection of materials to choose those which were very resistant to graphitisation. Anodes of good quality lasted 18 months (Karr 1946).

Rudge (1966, 1971) stated that British fluorine cells were equipped with carbon anodes which were more highly permeable than those used in America and were completely immune to polarisation under all practical conditions of operation. The advantages of carbon of high permeability were first described by Howell and Hill (1950), Rudge et al. (1952) and Wilson and Hill (1955) and anodes of this material were used in industrial cells in the early 1950's (Rudge 1956, 1962, 1966, 1971). The permeability* of a suitable porous carbon can range from 1 to 30 whereas a carbon of the YBD type has a value of approximately 0.05 (Davies and Rudge 1960, 1961, 1964a, 1964b, Rudge 1966, 1971). The Carbide and Carbon Chemicals Co. (Katz 1951, McLaren 1951) also reported good success with porous carbons and concluded that, apart from structural difficulties, this type of carbon was a superior anode material. Tests revealed that porous carbon could carry a current density of 1080 A m^{-2} without polarisation whereas the type GA carbon was limited to a maximum of 270 A m^{-2} (McLaren 1951).

Advantages were claimed for a specially constructed anode using porous material in the lower part with denser material near the top, the junction being made below the electrolyte. This modification was claimed to reduce (from 7.1 to 4.6%) the high proportion of hydrogen fluoride obtained in fluorine generated with carbons of high permeability (Davies 1963).

(c) Carbon anode assemblies

Goode et al. (1964) stated that the deterioration of the anode contact,

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*expressed as the number of cubic feet of air per minute passing through one square foot of carbon, one inch thick, under a pressure equivalent to two inches of water (see Table 11)

that is the mechanical and electrical contact between the carbon anode block and the metal hanger or bus-bar, was the greatest single cause of cell failure. The anode contact was usually made within the cell and was subject to attack by fluorine, electrolyte and hydrogen fluoride vapour. This form of construction and associated problems were avoided in laboratory cells by passing the carbon anode through the cell cover plate and making the anode contact in a non-corrosive atmosphere. This technique was not employed in large medium-temperature cells.

The simplest form of anode connection consisted of a metal rod screwed into the top of a block of carbon. The rod then passed through the cover plate. This type of joint (Figure 11) was used successfully in the German cell at Leverkusen because extremely hard carbon was used (Carter et al. 1946, Karr 1946, Neumark 1947). A similar system with the addition of a clamping ring around the top of the block of carbon proved to be successful in the American Harshaw cell (Williams et al. 1944, Pinkston 1947, Long et al. 1951).

In other American cells, a series of carbon blocks were bolted with a clamping plate to a common metal hanger bar as shown in Figure 12 (Downing 1946, 1951a, Murray et al 1946, Osborne 1951, Stuart and Osborne 1951, Dykstra et al. 1955, Smiley and Brater 1956, Vavalides et al. 1958, Huber et al. 1958, Powell et al. 1960). Copper and chrome-molybdenum steel were used for the hanger bar. Copper was the more corrosion resistant material (Smith 1943, Murray et al. 1946, Downing 1946) but steel had a comparable life at one third the cost (Dykstra et al. 1955) and was sometimes preferred (Dykstra et al. 1955, Vavalides et al. 1958). The above method of construction was used initially by E.I. Du Pont de Nemours (Downing 1946) and the Hooker Chemical Company (Murray et al. 1946, Osborne 1951, Stuart and Osborne 1951) in assemblies in which the hanger bar was an inverted U-form as shown in Figure 13.

Du Pont reported (for a submerged contact) that the contact failed due to corrosion of the inner face of the copper holder by electrolyte which seeped through the carbon and to corrosion of the steel clamping bolts (the bolt heads and nuts in particular) which led to a gradual depreciation of contact. Copper bolts were later used to prevent this corrosion (Downing et. al. 1947). The deposition of corrosion products at the carbon-metal surface and the relaxation of clamping pressure gave a high resistance contact resulting in an uneven distribution of current, local overheating and cracking (Downing 1946). Attempts to alleviate the seepage of electrolyte by locating the contact in the gas phase were unsuccessful due to swelling of the carbon

above the electrolyte level (Downing 1946).

After experiencing similar problems, Hooker improved this method of clamping by mounting the contact surface in the gas phase and by using a carbon-water jointing compound. A thin layer of this compound was spread on the carbon surfaces before clamping and caused to set by baking after the bolts had been tightened. The joint was also improved by machining the carbon clamping surface to give a flat even contact (Murray et al. 1946, Osborne 1951). This system gave a cell life of 2.5×10^6 A h in a 2000 A cell. The success of this method was due entirely to the use of the anode compound which prevented the penetration of electrolyte into the joint. If the compound was not used, failure occurred due to the accumulation of a layer of potassium bifluoride which swelled and broke the carbon directly under the clamping plate (Murray et al. 1946).

The Hooker anode assembly was adopted by the USAEC and developed subsequently in 4000 and 6000 A versions. The first development was the use of a solid chrome-molybdenum hanger bar (which cost less than the channel type of support), machined to a scratch-free finish, and the machining of the upper 53 mm of the carbon block to a smooth finish. The carbon blocks were clamped in place between the solid bar and a separate copper contact plate using 115 N m of torque on 19 mm dia. chrome-molybdenum cap screws. The chrome-molybdenum cap screws were selected after operating experience with Monel, Everdur, copper and several types of steel cap screws. Most steels and Monel were unsatisfactory because of high dissolution rates. Everdur and copper were unsatisfactory because of torque limitations. The cap screw threads were lubricated with a powdered graphite-chlorotrifluoroethylene polymer (Dykstra et al. 1955). The use of the high torque assembly prevented electrolyte from seeping between the carbon and the support and under normal operating conditions the assembly had a service life of 5×10^6 A h in a cell of 4,000 A capacity (Dykstra et al. 1955, Smiley and Brater 1956).

A larger (4000 A - 6000 A) cell of a similar design (Vavalides et al. 1958) obtained an improved life of 16×10^6 A h by increasing anode thickness from 32 to 50 mm and by the use of construction materials of superior corrosion resistance (Simmons et al. 1956). Pressure plates of AISI 4140 steel were tried in this cell but were a total failure, giving a cell life of only 5.2×10^6 A h (Vavalides et al. 1958). Cell life was then doubled to 32×10^6 A h by increasing the size of the heads of the clamping bolts (89 x 19 mm dia.) from 29 to 38 mm. This modification increased the life of the bolt but also demanded the use of bolts manufactured to close tolerances. Such bolts were

necessary to ensure even bolt pressure at the torque of 170 N m required to produce the same bolt tension (Huber et al. 1958, Powell et al. 1960). In addition the contact resistance of each bolt in the anode assembly was measured and was required to be within the range 85-100 μΩ (Huber et al. 1958, Union Carbide Corporation 1968).

The final improvement in this type of anode assembly was the use of countersunk slot head bolts (of AISI 4140 steel) torqued to 163 N m (joint resistance of 49-65 μΩ) with the bolt head protected by a carbon plug, see Figures 14 and 15 (Powell et al. 1960, Cable et al. 1962). This system has given cell lifetimes of 85 x 10^6 A h in the 6000 A USAEC E-type cell, failure being due to excessive corrosion of the anode bars. In this cell, copper hanger bars were reintroduced because of their greater corrosion resistance (Kelly and Clark 1968a). The latest French 6000 A cell uses a similar type of anode assembly with a copper hanger bar (Bergeret 1965, Level 1969).

In addition to the above methods of construction several alternative schemes were investigated. In one case, an external anode contact and support (from the cell cover) was developed (Finley 1953) which increased the anode flexibility and cooling and reduced the cost of the anode assembly in comparison to the cost of that used in the modified Hooker cell (Dykstra et al. 1955). This method was not developed further, probably because of the later improvements to the original clamping method.

Bottom-entering anodes sealed with frozen electrolyte were unsuccessful due to corrosion of cooling water connections (Rudge 1956, Hertz and Nugent 1961) though this idea has been used in laboratory cells.

Anode structures made entirely of carbon were tried to overcome the corrosion of metal/carbon contacts and a maximum life of 6.1 x 10^6 A h was obtained in a 6000 A cell. Failures occurred through two major causes. Firstly the low tensile strength of the carbon allowed the structures to crack and secondly the carbon-carbon contact points overheated and deteriorated rapidly in the fluorine atmosphere (Goode et al. 1964).

Little information is available on the anode assemblies developed for other medium temperature cells. The Allied Chemical Corporation cell (Figure 16) used a system similar to the USAEC cells in which the carbon anodes were suspended from copper clamps and were held in place by bolts and backup plates (Neumark and Siegmund 1966). Rudge (1971) reported that the anode assemblies used in ICI cells fitted into twelve rectangular openings in the cell cover. Each anode assembly consisted of a flat plate of mild steel, to the underside of which was attached the rectangular skirt and inside which was located a

pair of anode blocks. The life of the anode was reported to be 19 x 10^6 A h in 1400 A cells (Rudge 1956) and 66 x 10^6 A h in 5,000 A cells (Rudge 1971).

Only the patent literature gives some indication of methods that were used in ICI cells to attach the anode blades to their supports. Rudge and Howell (1951) described a method of forming the electrical connection to carbon anodes which involved electro-depositing a layer of copper or nickel on the upper part of the anode and, after cleaning, welding the electrical conductor to the electroplated region. The thickness of the electro-deposited layer was 3.2 to 4.2 mm and the deposition current had a density of 21.5 to 86 A m^{-2} at the carbon surface. It was found later (Rudge and Howell 1953) that the deposited layer did not have a uniform thickness, was very hard and in a state of strain. In addition, the process of electro-deposition was time consuming and involved saturation of the carbon anode with an aqueous electrolyte which had to be removed before the anode could be used. An improved electrical connection was developed by spraying a 4.2 mm thick layer of copper or nickel on the upper part of the anode. The non-ferrous electrical conductor was welded to the sprayed metal layer or alternatively the electrically continuous junction was made by placing the conductor in contact with the pre-sprayed carbon and spraying metal over both carbon and conductor while the two were held firmly in their final relative position (Rudge and Howell 1953).

No details are available concerning the UKAEA cells except that they are of the basic ICI design (Rudge 1971).

3.2.3 Cathode construction

Steel cathodes were used in American, British and French industrial cells, whereas the German cells at Leverkusen used Elektron alloy. The latter was probably chosen following experience with its use in high temperature cells at Falkenhagen (Carter et al. 1946, Karr 1946, Neumark 1947). Tests showed that both steel and copper performed successfully as cathode materials, steel having a slightly higher rate of corrosion at 0.18 mm per month. However steel was preferred because of its greater availability (Downing 1944, Downing 1951a).

The design of the cathode assembly in the USAEC cells remained very similar to that used in the original Hooker cell (Murray et al. 1946, Dykstra et al. 1955, Dykstra et al. 1958, Henderson et al. 1962). The assembly used in the E-type cell is shown in Figure 17. The cathode is in the form of a box of 9.5 mm thick mild steel which surrounds the anode assembly. The electrical connection to the cathode is made through three electrode posts of

copper or steel which are brazed or welded to the steel box. In the Allied Chemical Corporation cell, Figure 16, (Neumark and Siegmund 1966) and the Pennsylvania Salt Manufacturing Co. cell (Porter 1948), the rectangular steel cell body was used as the cathode.

The cathode assembly of the Leverkusen cell (Carter et al. 1946, Karr 1946) consisted of a total of ten separate sheets of metal arranged in rows of five on each side of the centrally mounted anodes.

The British cells of the ICI design were initially constructed with the cell body functioning as the cathode (Rudge 1949a). In more recent developments (Davies and Rudge 1961, Rudge 1971) separate cathodes which were internally cooled by the circulation of water were employed. It is claimed that this technique promotes operation at a lower anode temperature and consequently at a higher power efficiency. In the latest UKAEA cells, cooling coils act as the cathodes and the cathode connections are made to the case under the cell (Rogan 1972b).

3.2.4 Cell tank construction

(a) Tank materials

Early American experience with industrial cells indicated that Monel was the preferred material for construction of the tank, however steel was satisfactory if operating conditions were controlled carefully (Downing 1946). All cells constructed prior to 1950 had mild steel tanks which usually operated at cathode potential to minimise corrosion (Downing 1944, 1946, 1951a, 1951b, Williams et al. 1944, Stevenson 1945, Trepper 1945, Murray et al. 1946, Whitaker 1950, Benning et al. 1951, Osborne 1951, Stuart and Osborne 1951). In developing larger cells, several materials were examined for tank construction including low carbon-low silicon steel, nickel-electroplated steel, magnesium alloy and Monel (Dykstra et al. 1955). The service lives of these materials are listed in Table 8. As a result of this survey, the tanks of the USAEC C and E-type cells (Figure 18) have been constructed of Monel (operating at zero potential) and have given service lives in excess of 80 MA h in a 6000 A cell (Huber et al. 1958, Powell et al. 1960). Monel has also been used in the French cells (Bergeret 1965, Level 1969).

Other American cells developed by the Allied Chemical Corporation (Neumark and Siegmund 1966) and the Pennsylvania Salt Manufacturing Co. (Porter 1948) used mild steel tanks operating at cathode potential.

The German cell operated at Leverkusen had a tank (Figure 19) of Elektron (magnesium) alloy following the practice established with the high temperature cells used at Falkenhagen (Neumark 1947).

British cells, of both ICI and UKAEA (now BNFL) design, used mild steel tanks exclusively (Rudge et al. 1952, Wilson and Hill 1955, Rudge 1956, 1966, 1971, Davies and Rudge 1960, 1961, 1964a, 1964b, Rogan 1972b).

(b) Cell cover materials

The cell cover (Figure 20) was constructed of mild steel in most production cells (Downing 1944, 1946, 1951a, Porter 1948, Long et al. 1951, Dykstra et al. 1955, Rudge 1956, 1971, Vavalides et al. 1958, Neumark and Siegmund 1966, Kelly and Clarke 1967a, 1968a). The use of metals of higher corrosion resistance was generally unnecessary as corrosion of metal exposed only to the gases above the electrolyte was less severe than if the metal was immersed in the electrolyte. Downing (1946, 1951a) explained that this difference was due to the electrolyte dissolving away the protective coating which formed on metals exposed to gases.

Other materials that were used for the cell cover were Elektron alloy in the Leverkusen cell (Carter et al. 1946, Karr 1946) and Monel-clad mild steel in the French (Bergeret 1965, Level 1969) and one of the USAEC series of cells (Huber et al. 1958). There is no evidence to suggest that these materials were significantly better than mild steel. Lifetimes of steel covers in excess of 75 and 485 MA h were reported for 1400 A and 5000 A ICI cells, respectively (Rudge 1956, 1971).

(c) Cooling and heating systems

The voltage for decomposition of hydrogen fluoride to fluorine and hydrogen is 2.85 volts. Cells operate at between 8 and 12 volts, the excess voltage being required to overcome the resistance of the electrolyte, electrode connections in the cell and the over-voltages at the electrodes. For a 6000 A cell, it follows that from 30.9 kW to 54.9 kW of heat must be removed for the cell to operate at a constant temperature. Also, when the cell is shutdown it is necessary to supply heat to keep the electrolyte molten. Consequently, facilities have to be provided for both cooling and heating the cell.

Early American cells used water cooling with steel coils fitted inside the tank. These coils corroded rapidly and sometimes failed and diluted the electrolyte with water (Downing 1951a, 1951b). Subsequent cells were constructed with mild steel cooling jackets (Williams et al. 1944, Pinkston 1947, Downing et al. 1947, Whitaker 1950, Long et al. 1951, Downing 1951a, 1951b, Benning et al. 1951, Osborne 1951, Stuart and Osborne 1951) with the addition of either internal vertical fins (Downing 1944, 1951a, Trepper 1945, Stevenson 1945, Downing et al. 1947) or steel cooling pipes running through the cell as in the Hooker cell (Murray et al. 1946, 1947, Long et al. 1951, Downing 1951b)

to increase the rate of heat transfer.

The construction of the larger modified Hooker, USAEC C and E-type cells demanded increased heat transfer capacity which was attained by increasing the number of internal cooling tubes (using Monel in place of steel) (Dykstra et al. 1955, Smiley and Brater 1956, Huber et al. 1958, Vavalides et al. 1958, Clark 1960), by decreasing the width of the water space in the jacket to increase the water velocity (Smiley and Brater 1956, Dykstra et al. 1958), and by placing baffles in the water jacket (Dykstra et al. 1955, Vavalides et al. 1958). The use of a mild steel jacket with baffles and internal Monel tubes in the C-type cell (Huber et al. 1958, Dykstra et al. 1958) provided an adequate heat transfer area but corrosion of the jacket was a serious problem (Clark 1960). The accumulation of corrosion products caused flow restrictions, a decrease in heat transfer capacity and frequent plugging of the cooling jacket outlet requiring the premature removal of the cell for maintenance (Clark 1960). This problem was overcome in the E-type cell by using a water jacket constructed of thin gauge Monel with vertical corrugations to provide strength and to promote turbulence and heat transfer (Clark 1960). In addition, a multiple-pass cooling system within the jacket and an increased number of smaller diameter cooling tubes allowed more efficient heat transfer (Clark 1960). The other American cells of Allied Chemical Corp. (Neumark and Siegmund 1966) and Pennsylvania Salt Manufacturing Co. (Gall and Miller 1947, Porter 1948) relied only on the use of a mild steel water jacket.

The French cells at Pierrelatte use mild steel cooling jackets with additional cooling from Monel U-tubes suspended through the cover of the cell between the two anodic compartments (Level 1969).

The first industrial cell constructed by ICI relied on water cooled coils in the cell and natural convection from the cell walls to dissipate heat (Rudge 1956). In the latest ICI and UKAEA (BNFL) designs, improved temperature control is achieved by the use of a water jacket constructed of mild steel and internally cooled cathodes (Davies and Rudge 1961, Rudge 1966, 1971, Rogan 1972b). The body of the ICI cell is jacketed on the sides and separately on the bottom. Twenty-four pancake coils connected to inlet and outlet headers divide the cell transversely and function as the water-cooled cathodes. Dykstra et al. (1955) also reported a better distribution of cooling in a test cell with water-cooled cathodes; in addition the heat transfer coefficient of this cell was found to be larger than that of a cell with cooling tubes by a factor of 2 to 3. A similar result was reported by

Hertz and Nugent (1961).

The German cell at Leverkusen used a different cooling system (Figure 21) which had the advantage of continuous electrolyte circulation (Carter et al. 1946, Karr 1946). At one end of the cell compartment a screw propeller was fitted which caused the electrolyte to circulate along a 125 mm Elektron pipe beneath the cell and up into a separate compartment in which a nickel cooling coil and the HF feed pipe were located. Additional cooling capacity was provided by a nickel cooling tube inserted in the transfer pipe under the cell. The disadvantage of this system was the need to heat the electrolyte circulation pipe during shut-down periods (Karr 1946).

3.2.5 Skirt and diaphragm construction

Skirts are used to separate the hydrogen and fluorine above the electrolyte. The solid metal skirt is welded to the cell cover plate and extends vertically downwards into the electrolyte. In some cells the skirt extends further into the electrolyte as wire mesh or a perforated plate, this extension is called the diaphragm and acts to direct the flow of the gases as they are liberated.

Early American industrial cells used both mild steel and Monel skirts (Downing 1944, 1946, Williams et al. 1944, Stevenson 1945, Trepper 1945, Murray et al. 1946) which were maintained at cathode potential to reduce corrosion. Plant experience showed that Monel was more resistant to corrosion than steel (up to four times greater life), however, the rate of corrosion of steel skirts was decreased considerably if the hydrogen fluoride content of the electrolyte was less than 42% (Downing 1944, 1951a, Katz 1951). The most frequent source of failure of the skirt was corrosion of the weld connecting it to the cover plate. Improved techniques of welding were developed to overcome this problem (Downing 1944, 1951a, Katz 1951).

The USAEC C and E-type cells used Monel skirts (6.3 mm thick) welded to steel cover plates which were insulated from both electrodes (Dykstra et al. 1955, Huber et al. 1958, Vavalides et al. 1958, Henderson et al. 1962, Kelly and Clark 1967a, 1968a). The French cells used a similar system (Bergeret 1965, Level 1969).

Magnesium alloy skirts were tried experimentally in USAEC cells; they proved superior to steel but replacement of a Monel skirt was simpler and less expensive (Dykstra et al. 1955). The German cell at Leverkusen used thick (60 mm) magnesium alloy skirts bolted to the cell cover plate which was insulated from the electrodes (Karr 1946, Neumark 1947).

The Allied Chemical Corporation cell used a magnesium alloy skirt which

was part of the cell cover casting and was insulated from both electrodes (Neumark and Siegmund 1966). The cell developed by the Pennsylvania Salt Manufacturing Co. used a steel skirt welded to the cover plate which was bolted to the cell tank-cathode (Gall and Miller 1947, Porter 1948).

Initially ICI cells had skirts of mild steel which operated at anode potential and suffered from corrosion (Rudge 1956). In subsequent ICI and UKAEA cells, which were developed from the ICI design, Monel skirts have been used (Rudge 1956, 1966, 1971, Davies and Rudge 1960, 1961, 1964a, 1964b, Davies 1963, Rogan 1972b).

Diaphragms were not used universally. They were not used in the ICI, UKAEA, Allied Chemical, Pennsalt and German cells (Karr 1946, Porter 1948, Rudge 1956, 1966, 1971, Davies and Rudge 1960, 1961, 1964a, 1964b, Neumark and Siegmund 1966). In the ICI and German cells, tests on a laboratory scale showed that the diaphragm was unnecessary (Carter et al. 1946, Rudge 1949b, 1956, Rudge and Hill 1952). However, diaphragms were used in the majority of American cells.

Monel diaphragms, as perforated plate or wire mesh, were used in the Du Pont and Harshaw cells (Stevenson 1945, Trepper 1945, Downing 1946, Williams et al. 1946). Monel was chosen after corrosion tests were carried out to find the most suitable material (Calcott 1943, Downing 1944). Magnesium and Dowmetal showed higher corrosion resistance but these materials tended to become brittle. Steel was not satisfactory as corrosion products plugged the mesh or perforations (Downing 1951a). These tests also showed no relationship between cell efficiency and the free area of the diaphragm, however the cell efficiency was lower with no diaphragm present. It was also necessary to place the diaphragm equidistant from the anode and cathode to prevent bipolar corrosion (Schumb 1946, 1951, Downing 1946, Murray et al. 1946).

The Hooker cell was developed originally with a solid metal diaphragm incorporating screen windows set opposite the anode. Bipolar corrosion was severe and a continuous steel screen was introduced to overcome this problem (Murray et al. 1946). The modified Hooker cell used perforated Monel plate diaphragms following the experience with the Harshaw and Du Pont cells (McLaren 1951, Dykstra et al. 1955). Subsequently the USAEC C and E-type cells used woven Monel wire mesh screens welded to a Monel frame with suitable strengthening pieces to provide rigidity (Figure 22). The diaphragm in these cells was attached to the skirt but insulated from it (to reduce bipolar currents) using Teflon gaskets, sleeves and washers (Huber et al. 1958, Vavalides et al. 1958, Kelly and Clark 1967a, 1968a). With this arrangement, corrosion was reported

as negligible (Dykstra et al. 1955). Powell et al. (1961) stated that the diaphragm was not necessary to separate gases in these cells (some cells were operated without them), but it did prevent broken anode blades from arcing and damaging the cell.

A similar arrangement was used in the French cells at Pierrelatte and a lifetime of 3 to 4 years was reported (Bergeret 1965, Level 1969).

3.2.6 Insulation and gasket materials

Insulation and gasket materials used commonly in industrial cells are listed in Table 5. Since the development of PTFE, this material, in the shape of concentric rings, has been widely used as an insulator in packing glands (Figure 23) which support the anode and cathode conductor posts. The pure polymer was generally loaded with from 25 to 50 per cent powdered calcium fluoride and placed in the bottom of the packing gland to reduce the likelihood of rapid attack (Downing 1946, 1951a, Dykstra et al. 1955, Huber et al. 1958, Kelly and Clark 1967a, 1968a). The diaphragm was insulated from the skirt by a PTFE gasket and the same material in the form of washers and sleeves was used to insulate bolts from surrounding materials (Huber et al. 1958, Vavalides et al. 1958, Kelly and Clark 1967a, 1968a). However in ICI cells, the anodes were insulated from the skirt assembly and from the cell top by means of Neoprene gaskets (Rudge 1971).

Rubber or Neoprene gaskets were used in most cells to form a seal between the cell body and the cell tank (Downing 1946, 1951a, Dykstra et al. 1955, Rudge 1956, 1971, Huber et al. 1958, Vavalides et al. 1958, Neumark and Siegmund 1966, Kelly and Clark 1967a, 1968a, Level 1969). This type of gasket, when compressed, was satisfactory for fluorine service as the rubber exposed to fluorine formed an organic fluorocarbon which expanded and resisted further penetration of fluorine (Dykstra et al. 1955). However, thin sheets of material were used to minimise the surface area exposed to the gas (Rudge 1971).

4. POLARISATION

In fluorine cells, this term has been used to describe the phenomenon which occurs when the potential required to operate the cell rises markedly from its normal value, the current drops sharply and little or no fluorine is produced. Anode polarisation has been the single greatest cause of cell failure throughout the development of fluorine cells (Downing 1946, McLaren 1951, Ebel and Montillon 1952, Rudge 1956, 1962, 1966, 1971, Powell et al. 1961).

Ebel and Montillon (1952) stated that a normal fluorine generator always exhibits polarisation and excessive polarisation (or anode effect) is a troublesome problem usually encountered during start-up of a cell, occasionally during the life of the cell and at cell failure.

In addition to the polarisation of the anode, a similar phenomenon has occurred at the cathode in cells of poor design.

4.1 Anode Polarisation

Anode polarisation was a feature of all cells developed in America prior to 1950 and a number of theories and means of preventing or curing this phenomena were advanced (Katz 1951, McLaren 1951). The occurrence of polarisation was reduced (but not eliminated) in later American cells by implementing refined versions of the more successful techniques developed previously (Dykstra et al. 1955, Jacobson et al. 1955, Penland 1955, Smiley and Brater 1956, Vavalides et al. 1958, Huber et al. 1958, Powell et al. 1961, Goodyear Atomic Corporation 1967a).

The cells developed by ICI used a type of anode carbon which was free from polarisation difficulties (Rudge et al. 1952, Wilson and Hill 1955, Rudge 1956, 1962, 1966, 1971, Davies and Rudge 1960, 1961, 1964a, 1964b). The superior performance of this carbon was attributed to its high permeability which was approximately 20-50 times greater than that of the carbon of the American cells.

Despite the significant effects of anode polarisation, only the works of Rudge (1947, 1949a, 1949b, 1956, 1962, 1966, 1971) and Watanabe et al. (1961a, 1961b, 1963a, 1963b, 1964) present a systematic attempt to explain the mechanism of fluorine generation and hence anode polarisation in electrolytic cells.

4.1.1 Mechanism of fluorine generation

Rudge (1949a) and Watanabe et al. (1961a) stated that the mechanism of fluorine evolution from an electrode is determined by the contact angle at the electrode/electrolyte/gas interface (see Figure 25). The smaller the contact angle (θ), the more the electrolyte wets the anode. A contact angle as high

as 140^{o}-150^{o} has been reported by Rudge (1949a, 1962, 1966) and Watanabe et al. (1961a), verifying the earlier observations of the non-wetting characteristics of carbon anodes in high temperature cells by Fredenhagen and Krefft (1929) and Fredenhagen (1930, 1932), and in medium temperature cells by Cady et al. (1942). However if the carbon is not at an anodic potential, the carbon is wetted by the electrolyte (Cady et al. 1942, Rudge 1962, 1966, 1971). Rudge (1962, 1966, 1971) and Watanabe et al. (1961a) proposed that this change in the anode surface is the result of the formation of a thin film of the intercalation compound carbon monofluoride $(CF)_x$. The presence of this compound was demonstrated by a number of investigators (Rüdorff and Rüdorff 1947, Watanabe et al. 1964, 1971, Rudge 1971).

The existence of a large contact angle (non-wetting condition) has a number of significant effects; the shape of the gas bubbles produced at the anode surface is lenticular, or flattened, and the tendency for them to break away from a vertical electrode with low permeability and rise through the electrolyte is very much reduced. As a consequence, the transfer of gas to the electrolyte surface usually takes place by a process of coalescence and transfer of gas from bubble to bubble or by the bubbles sliding up the face of the electrode under the influence of buoyancy forces (Rudge 1947, 1949a, 1956, 1962, 1966, 1971, Watanabe et al. 1961a, 1963a).

4.1.2 Mechanism of anode polarisation

Anode polarisation has been attributed to the mechanism of fluorine evolution at the surface of the anode (Rudge 1947, 1949a, 1956, 1962, 1966, 1971, Katz 1951, Watanabe et al. 1961a, 1963a). Watanabe et al. (1961a) and Wilson and Hill (1955) have proposed that the condition of electrolysis is determined by the rates of adsorption of fluorine gas on the electrode surface (i.e. local formation rate at the electrode) and desorption of fluorine from the surface. The rate of adsorption of fluorine depends directly on the current per unit area of anode (current density) and the current efficiency. The desorption rate is influenced by the contact angle (wettability) at the anode surface, the ease of desorption decreasing as the contact angle increases. Watanabe et al. (1961a) demonstrated that the contact angle is also a function of the current density, the angle increasing as the current density increases. Polarisation occurs at a limiting current density when the rate of adsorption is greater than the rate of desorption of fluorine. Watanabe et al. (1961a) stated that at low current densities, fluorine leaves the anode surface in the ways described above. However, as the current density, and consequently the contact angle and rate of fluorine generation, is increased, a constant value

of the contact angle is reached. Further growth of bubbles can only occur by an increase in the length of bubble perimeter with a resultant reduction in the area of the anode in contact with the electrolyte, this causes a further increase in current density at the areas not covered by gas (Rudge 1966, 1971). At this increased current density, fluorine accumulates on the available anode area and produces anode polarisation (Ebel and Montillon 1952, Watanabe et al. 1961a, 1963a, Rudge 1956, 1962, 1966, 1971).

Rudge (1966, 1971) proposed that the sheathing of the anode surface by bubbles of fluorine at the onset of polarisation was a transient unstable state. Under these conditions, the effective anode area is so low that the current and consequently the rate of fluorine production fall spontaneously and the gas contained in the bubbles is discharged into the pores of the carbon. Rudge stated that as this occurs, the electrolyte approaches the surface of the electrode until only surface asperities are in physical contact with the electrolyte and the small residual current which flows, even in the polarised state, corresponds to this small part of the surface which remains in contact with the electrolyte. Any increase in the current further reduces the effective anode surface unless the fluorine generated can travel through the pores of the carbon anode.

4.1.3 Anode effect

An increase in the internal resistance of a fluorine cell at the anode can produce two effects. If the voltage cannot rise appreciably above the normal operating voltage the cell polarises (the current decreases). Alternatively, if a sufficient increase in voltage takes place, polarisation leads to the 'anode effect' (Leech 1949, Katz 1951, Watanabe et al. 1961a, Rudge 1966, 1971). Rudge (1966, 1971) offered the following explanation of the anode effect. If the voltage is increased sufficiently across a cell which is in the polarised state, the current increases in spite of the high electrical resistance. The current flowing is now restricted to such parts of the anode that are not masked by gas. These electrical 'bridges' become overheated because of the very high local current density and eventually break down. In the act of breaking the contact at these points, minute arcs or sparks are produced. This disturbance produces an unstable condition and equilibrium is re-established by the electrolyte coming into contact with the anode in other spots, possibly where the local temperature is somewhat lower. These events are repeated with high frequency over the anode surface and explain the shifting arcs and sparks which are a feature of the phenomenon, while the local liberation of energy may be so high that the gas becomes

incandescent. If the carbon of the anode is capable of reacting readily with the anode gas at high temperature, a 'clean' easily wetted surface is produced and electrolysis resumes its normal course.

Ebel and Montillon (1952) stated that if the anode is burned and a new surface developed, the limiting current density of the anode may increase, but there is a maximum to which a limiting current density can be increased by this means. If the current density of an anode whose surface is fully developed is exceeded, the electrical discharge across the gas film overheats the gas and perpetuates the anode effect by expanding the gas. However if the current is lowered, electrolysis will continue until the limiting current density is exceeded.

4.1.4 Causes of anode polarisation

Since the development of carbons capable of carrying high currents, polarisation is generally produced by other factors which cause the actual current to exceed the limiting current density. Anode polarisation can be provoked by the rapid addition of HF. Controlled regular addition overcomes this problem as discussed in Section 5.2.3. Ebel and Montillon (1952), Hertz and Nugent (1961) and Goode et al. (1964) stated that the most serious cause of polarisation is the loss of anode surface by anode breakage or by failure of the electrical contact of the anode. However, anode surface may be lost in the following ways (Downing 1946, Katz 1951, McLaren 1951, Ebel and Montillon 1952);

(1) Sludge may build up on the bottom of the cell and partially cover the blades.

(2) Dispersed solids or impurities in the electrolyte may coat out on the anode and render such areas ineffective.

(3) The electrolyte may freeze out on the anode.

(4) Local overheating could be responsible for a change in the process by which the fluorine gas escapes.

(5) The presence or absence of critical impurities (water in particular) could affect the wetting characteristics of the electrolyte and lower the limiting current density by altering the pattern by which fluorine gas escapes. Low concentrations of HF have been shown to produce conditions where the anode was less wetted (Watanabe et al. 1961a).

(6) Local polarisation of the cathode could occur and render facing anodes inoperative.

4.1.5 Methods of overcoming anode polarisation in British cells

Rudge (1956, 1962, 1966, 1971) claimed that the use of carbon anodes with a high permeability eliminated the problem of anode polarisation from ICI and UKAEA cells. This type of carbon allows fluorine to escape to the surface of the electrolyte via interconnected pores in the carbon anode and eliminates the formation of bubbles on the face of the anode. This system is only possible if the pores of the electrode are not flooded by the electrolyte. Flooding occurs if the contact angle is greater than 90^{o} and the surface tension forces of the electrolyte within the pores exceed the hydrostatic head of electrolyte over the carbon anode. The surface tension force is directly proportional to the surface tension of the liquid and the cosine of electrode/electrolyte contact angle and is indirectly proportional to the radius of the pores in the anode. If the contact angle is greater than 90^{o}, the use of a carbon with a suitable pore size, depending on the depth of immersion, allows flooding to be avoided (Rudge 1966, 1971).

Rudge (1966, 1971) demonstrated by the simultaneous operation of a number of anodes of different materials that the performance of an anode is related directly to its permeability (Table 11). However, some care must be exercised in interpreting these results as a total permeability to air was used to characterise the carbon, whereas it is the effective permeability (the contribution of suitable pore sizes) which determines the number of pores which are not so large as to be flooded. In addition, changes in the surface to volume ratio of electrodes of different shapes and sizes must be considered.

Precise specifications of the carbon used in the ICI and UKAEA cells are not available. Rudge (1966) reported that the electrical resistance and fragility of a carbon increase with its permeability and consequently a carbon with a very high permeability may not be the best choice. Carbon anodes having a permeability of about 1.0 (see Table 11 for units) have been operated at ICI in a long term works-scale trial for periods in excess of 19 months without polarisation difficulties at current densities up to 2310 A m^{-2}. The carbon was more robust than most grades of 'Carbocell' and had about one-third the electrical resistivity. Anodes having a permeability of 2 were also operated under the same conditions without any replacements for over 30 months (Rudge 1966). An additional feature of operation with highly permeable carbon anodes is that rigid controls of the electrolyte composition and the impurity level in the HF feed are not required to maintain the resistance of the anodes to polarisation (Rudge 1956, 1962, 1966, 1971). In addition, ICI cells do not require conditioning except that cells with fresh electrolyte, which may

contain up to 0.5% water, must be started up at a low load because the resistance is abnormally low until water is removed by electrolysis (Rudge 1971).

The disadvantage of using carbons having a high permeability is that the fluorine discharged through the interconnected pores can have an abnormally high hydrogen fluoride content, 20 to 30 vol. %, corresponding to the partial pressure of hydrogen fluoride over the electrolyte at the temperature of the anode surface. A high surface temperature is caused by poor heat transfer from the face of the anode (Rudge 1971). In practice, the temperature of the anode surface (and the concentration of hydrogen fluoride in fluorine) was reduced by using water-cooled cathodes and a smaller anode/cathode separation to reduce the energy consumed by the resistance of the electrolyte (Davies and Rudge 1960, 1961, Rudge 1971). If desired, a further reduction in the anode surface temperature can be achieved by controlling the level of certain impurities in the electrolyte (see Section 4.1.7) such that a proportion of fluorine is liberated as free bubbles and provides sufficient turbulence (and heat transfer) to reduce the surface temperature of the anode (Davies and Rudge 1961, 1964a, 1964b, Rudge 1966, 1971).

In the absence of additives to induce the evolution of free bubbles of fluorine, a number of methods were proposed to reduce the hydrogen fluoride content of fluorine liberated at anodes of high permeability. In one method, fluorine is bubbled through electrolyte in a separate compartment of the cell where the partial pressure of hydrogen fluoride is lower (Hill and Rudge 1957) or alternatively, a composite anode (described in Section 3.2.2 (b)) using porous material in the lower part with denser material near the top may be used (Davies 1963).

4.1.6 Methods of overcoming polarisation in American cells

Polarisation was overcome in American cells by the addition of lithium fluoride to the electrolyte or by operation with nickel or carbon anodes at a low current density. Alternatively the application of a high voltage was used to condition both the surface of the anode and the electrolyte. The basic function of these practices was to remove water from the electrolyte as this impurity was suspected of causing polarisation (Williams et al. 1944, Downing 1946, 1951a, Murray et al. 1946, 1951, Long et al. 1951, McLaren 1951, Katz 1951, Dykstra et al. 1955, Jacobson et al. 1955, Penland 1955, Huber et al. 1958).

Rudge (1949a, 1962, 1966) demonstrated that a large contact angle between the electrolyte and anodes of any permeability leads to polarisation problems. Unlike the British cells, American cells used carbon anodes having a low

permeability and Rudge (1971) claimed that the reason for the successful operation of the latter cells was almost certainly the presence of deliberately added, or adventitious, impurities in the electrolyte which have the effect of bringing about a reduction in the anode/electrolyte contact angle.

The methods adopted to achieve satisfactory operation of American cells are described below.

(a) Conditioning the electrolyte with nickel anodes

Preliminary operation of cells with nickel anodes was found by the Du Pont, Harshaw, Pennsylvania Salt Manufacturing and Hooker companies to reduce the occurrence of anode polarisation (Williams et al. 1944, Trepper 1945, Murray et al. 1946, 1951, Gall and Miller 1947, Katz 1951, Long et al. 1951). The practice of the Hooker and Du Pont companies was to use nickel anodes for 3 to 5×10^4 A h (1000-1500 A cell) before operations with carbon electrodes (Trepper 1945, McLaren 1951) or more specifically Katz (1951) reported Du Pont practice was to condition a cell for 66 A h per kg of electrolyte capacity. In addition, cells which had polarised functioned normally after operating for a short time with nickel anodes (Downing 1951b). The success of this conditioning technique was attributed initially to the removal of water from the electrolyte although it was later found that even practically anhydrous electrolyte required conditioning (Downing 1946). Katz (1951) stated that the opinion at the Harshaw Chemical Company was that the presence of nickel also aided in wetting the carbon anode. Conditioning of the electrolyte could also be accomplished with carbon electrodes by running at low current densities (Downing 1946). However nickel anodes removed water more effectively as fluorine bubbled through the electrolyte with no tendency to adhere to the electrode surface (Rudge 1949a). Experiments at ICI also confirmed that the use of an auxiliary nickel anode decreased anode polarisation (Rudge 1949b).

The practice of conditioning the electrolyte with nickel anodes was not employed in cells constructed after 1950 because the practice of bubbling fluorine through the electrolyte during preparation to remove moisture was adopted. This technique reduced the moisture content of the electrolyte to 0.001 - 0.003% (Dykstra et al. 1955, 1958, Huber et al. 1958, Goodyear Atomic Corporation 1967a, 1967b), whereas electrolytes used prior to 1950 contained from 0.05 to 0.2% water (Du Pont de Nemours and Co. 1944, Trepper 1945, Stevenson 1945). In addition the amount of water introduced into the electrolyte by the continuous feeding of hydrogen fluoride was reduced considerably by the use of acid of 99.95% purity (Dykstra et al. 1955, Jacobson et al. 1955, Smiley and Brater 1956, Vavalides et al. 1958, Huber et al. 1958) whereas

alkylation grade hydrogen fluoride of 99.2% purity containing 0.35% water was used previously (Trepper 1945, Stevenson 1945).

(b) The addition of lithium fluoride to the electrolyte

Lithium fluoride was often added to prevent polarisation of cells using carbon anodes of low permeability (Williams et al. 1944, Trepper 1945, Downing 1946, 1951a, Schumb 1946, 1951, Pinkston 1947, Schumb and Stevens 1947, Whitaker 1950, Long et al. 1951, Katz 1951, Ebel and Montillon 1952, Dykstra et al. 1955, Penland 1955, Jacobson et al. 1955, Huber et al. 1958). Initially quantities of lithium fluoride equivalent to approximately 2 to 4% of the weight of the electrolyte were added to the electrolyte during preparation, but later practice was to add 2.3 kg (0.17%) of lithium fluoride (in 6000 A cells) if the presence of excess moisture was suspected (Dykstra et al. 1955, Penland 1955, Jacobson et al. 1955, Huber et al. 1958).

Lithium fluoride was first added to the electrolyte with the intention of reducing its melting point and consequently its losses of hydrogen fluoride by vaporisation (Schumb 1946, 1951, Schumb et al. 1947, Downing 1946). Its apparent ability to reduce polarisation was discovered by chance (Katz 1951). However, the addition of lithium fluoride had the definite disadvantage of causing sludging in cells (Schumb 1946, 1951, Schumb et al. 1947). The effectiveness of lithium fluoride as a depolarising agent was attributed to a number of factors including a supply of colloidal particles (Schumb 1946, 1951, Schumb et al. 1947), improvement of the wetting characteristics of the electrolyte (Downing 1946, Schumb et al. 1947, Pinkston 1947) and its ability to act as a carrier ion to remove impurities from the electrolyte (Katz 1951). Rudge (1949a, 1949b) stated that the addition of lithium fluoride had a very transient effect because such materials rapidly settle out. Rudge (1949a) proposed that this effect was possibly due to increased wetting of the anode, although the contact angle was never reduced below 90^{o}. Ebel and Montillon (1952) stated that, in the final analysis, the use of lithium fluoride reflected on the experience of operating personnel who found it helpful in conditioning cells, although low current treatment (500 A for one hour) was still required (Penland 1955, Dykstra et al. 1955).

The use of lithium fluoride was less common in later cells owing to the exacting raw material specifications (moisture and impurities) and careful preparation of the electrolyte which were considered essential for polarisation-free operation (Dykstra et al. 1955, Smiley and Brater 1956, Huber et al. 1958, Vavalides et al. 1958, Powell et al. 1961). However, the continuing practice of adding lithium fluoride possibly promoted a more rapid removal of water in

conjunction with the normal conditioning procedure at a low current.

The beneficial effects of lithium fluoride, often demonstrated by operating experience, were eventually confirmed by Watanabe et al. (1961a) who found that the addition of lithium fluoride to the electrolyte in sufficient quantities (> 1%) to form a colloidal dispersion was effective in preventing anodic polarisation. However if a colloidal solution was not formed, the incidence of polarisation was not affected. This was attributed to the adsorption of colloidal particles onto the surface of bubbles at the anode/electrolyte interface which facilitated the separation of the gas bubble from the anode surface by increasing the wettability of the electrolyte on the anode surface and decreasing the difficulty of the liberation of the fluorine gas (Watanabe et al. 1963a). These effects were reduced as colloidal lithium fluoride particles coagulated. Additional experiments revealed that the use of an anode impregnated with lithium fluoride was more effective than the direct addition of lithium fluoride to the bath (Watanabe et al. 1963a).

(c) The adjustment of the operating voltage

Special techniques for the elimination of polarisation were developed which relied on the manipulation of the operating voltage of the cell. With one technique, newly-assembled 6000 A cells were started up at 1000 A and operated at that level for 2 hours. The current was then increased by increments of 500 A every 2 hours until an equilibrium condition at 6000 A was established. The cell would then operate under production conditions without polarisation (Huber et al. 1958). A similar system was also used in the French cells (Level 1969). Low current conditioning of this type was also used in conjunction with the addition of lithium fluoride (Dykstra et al. 1955, Penland 1955).

An alternate procedure involved the startup of one half of the cell at 500 A with an increase to 3000 A within 15 minutes. A typical cell polarised almost immediately and operated at 15 to 45 volts. The polarised condition usually terminated within 15 minutes with an immediate reduction to 7 to 9 volts. If the voltage did not decrease within the 15 minute period, the cell was shut down. It could then be restarted and operated at the normal voltage without further difficulty. Following this step the other half of the cell was subjected to the same treatment. Only half the cell was conditioned at one time to avoid half-cell polarisation after installation (Dykstra et al. 1955, Penland 1955, Vavalides et al. 1958, Huber et al. 1958, Goodyear Atomic Corporation 1967a). Similarly polarisation or anode effect, when encountered during cell operation, was removed by a 15 to 20 minute treatment at 38 to 40

volts, using a current density of 321 to 375 A m^{-2} (Dykstra et al. 1955, Powell et al. 1961).

Operation at low voltage removed water from the electrolyte without the sludge produced by the use of nickel anodes, whereas the high voltage technique burned and developed a new anode surface (Ebel and Montillon 1952).

4.1.7 The influence of electrolyte purity on anode behaviour

Rudge (1966) conducted a series of experiments to determine the influence of electrolyte purity on anode behaviour and found that the concentrations of water and nickel were by far the most important and were interdependent. The results of this investigation were summarised as follows:

Water

The addition of 2% of water to the electrolyte prevented polarisation of carbon anodes with a low permeability until the water was consumed by electrolysis. The presence of water was presumed to cause, probably by oxidising the carbon, the partial or complete removal of the carbon monofluoride film which resulted in the large anode/electrolyte contact angle. Similar beneficial effects of large amounts of water had previously been noted by the Du Pont company (Katz 1951) and Davies and Rudge (1961).

Nickel

The addition of nickel salts had no effect provided the water concentration was between 2 and 0.1%. When the water content of the electrolyte was below 0.1%, the presence of nickel in the electrolyte caused wetting of the anode and breakaway of fluorine bubbles from the surface. This effect resulted from the migration of nickel salts to the anode surface.
An anode operating in an electrolyte containing only 7 ppm of nickel eventually acquired a coating of electrolyte containing 105 ppm of nickel. It appeared that in order to produce this effect the nickel had to be in a high state of oxidation, possibly as K_2NiF_6, which was red in colour and unstable in the presence of water. Exposure of the electrolyte to the atmosphere resulted in the rapid pickup of water and disappearance of the red colour as the nickel returned to a lower valency state. In this condition, the nickel was no longer effective in causing the wetting of the anode. Only nickel salts in suspension were capable of bringing about wetting of the anode. If the addition of nickel fluoride was not continuous, the salt eventually settled out and its effect disappeared.

Other Impurities

The fluorides of copper, iron, sodium, lead and calcium and potassium silicofluoride were found to produce virtually no improvement in the wetting of

carbon anodes by KF. 2 HF electrolyte. However, a concentration of 2% potassium sulphate produced some attack of the carbon anode while 5% resulted in complete disintegration.

Rudge (1966, 1971) provided the following explanations for the effect of nickel on the successful operation of the carbon anodes in the American cells. Low concentrations of nickel were introduced continuously into the electrolyte by corrosion of the Monel skirt or diaphragm and the very low water content of the electrolyte ensured that suspended nickel salts were converted to, and remained in, a high valency state. Similarly the practice of conditioning a cell by the use of nickel anodes not only served to reduce the water content, but also added nickel in the appropriate form. Watanabe et al. (1961a) have also attributed the effects of conditioning with nickel anodes to the formation of colloidal nickel fluoride. The high voltage technique of depolarisation, as well as preparing a new anode surface by combustion, also accelerated the corrosion of the Monel cell components and added nickel salts to the electrolyte. The technique of operating at a low current removed water and transferred sufficient nickel into solution to promote wetting by the electrolyte and operation at higher current densities.

The concentrations of water and nickel salts that cause electrolyte to wet any type of carbon anode, and hence permit the use of carbons of a low permeability, detract from the performance of carbons of higher permeability (Davies and Rudge 1961, 1964a, 1964b, Rudge 1966). If the latter type of carbon is wetted by the electrolyte, fluorine cannot pass through the pores of the carbon but leaves the anode surface as bubbles in the usual manner. The possibility of this occurrence has prevented the use of small anode to skirt gaps in industrial sized cells operating with carbons of high permeability (Davies and Rudge 1964a, Rudge 1966). However the evolution of a proportion of fluorine as bubbles is sometimes encouraged in ICI cells to reduce the hydrogen fluoride content of the fluorine (see Section 4.1.5). The compositions of electrolyte required for either mode of cell operation have been patented by ICI. To ensure a proportion of fluorine is liberated as bubbles the electrolyte must be 'substantially' dry (less than 0.1% water) and contain from 30 to 200 ppm of nickel (Davies and Rudge 1964a). Alternatively, to ensure substantially no evolution of fluorine as free bubbles, the electrolyte must contain greater than 0.1% by weight of water or 0.1 to 1.0% of water if the concentration of nickel salts is from 30 to 300 ppm (Davies and Rudge 1964b). As wetting of the anodes is not necessary, the use of electrolyte of high purity and hydrogen fluoride with a low water content is not usually

critical in ICI cells (Rudge 1956, 1962, 1966, 1971, Davies and Rudge 1964b). Although the UKAEA (BNFL) cells are of basic ICI design (Rudge 1971), the hydrofluoric acid used in the former cells has to satisfy a demanding specification with regard to water and combined sulphur content (Rogan 1972b).

4.2 Cathode Polarisation

The most serious form of cathode polarisation is induced by bipolarity of the skirt, but at a low current density the bipolarity has little effect on the performance of the cell. As the current density is increased, the anodic area of the skirt becomes passive and reaction ceases, this causes a sudden rise in the skirt to cathode voltage. The cathodic face of the skirt remains active and the anode to skirt voltage does not change greatly. If the rate of evolution of hydrogen in the anode compartment reaches a sufficient rate, explosive interaction with fluorine results (Schumb 1946, 1951, Schumb et al. 1947). Typical voltages produced by this condition are shown in Table 10 and for comparison voltages obtained during normal operation are given in Figure 24.

Other causes of cathode polarisation are low electrolyte temperatures and low concentrations of hydrogen fluoride. Under these conditions, the electrolyte may freeze out on the cathode creating an additional resistance to the flow of current (Downing 1946, 1951a, Murray et al. 1946, 1951).

Bipolarity of the diaphragm may also result in cathode polarisation. The former condition can be caused directly by incorrect positioning of the diaphragm or indirectly as the result of interference to electrolyte circulation. Poor electrolyte circulation promotes local overheating and corrosion resulting in the formation of sludge which blocks the diaphragm and induces bipolarity (Murray et al. 1946, McLaren 1951, Finley 1953). Poor circulation over the cathode surface is also sufficient to create polarisation (Schumb 1946, McLaren 1951) and in extreme cases the deposition of impurities (corrosion products) on the cathode may result and accentuate the effect (McLaren 1951).

The causes of cathode polarisation were identified and overcome in the initial period of the development of fluorine cells. Modern cells, by following good design practice, do not suffer from this problem.

5. OPERATING CHARACTERISTICS OF FLUORINE CELLS

In addition to the major problem of anode polarisation numerous other minor problems affect the performance of fluorine cells. These problems and their inter-related nature are presented in Table 9 which is based on a study by Finley (1953) describing the relationship between malfunctions and the design and operating features of a modified Hooker cell (McLaren 1951, Ebel and Montillon 1952, Dykstra et al. 1955, Smiley and Brater 1956).

5.1 Bipolar Corrosion

This type of corrosion occurs in a solid metal skirt which is placed between the anode and cathode. The surface of the metal exposed to the anode becomes cathodic and the opposite side anodic. This results in severe corrosion of the cathodic side (Schumb 1946, Downing 1946, Murray et al. 1946, Rudge 1956). This condition arises if any material shadows the cathode from the anode and becomes more serious as the rate of corrosion increases. The problem was overcome by positioning the cathode below the level of the skirt (Downing 1946, Pinkston 1947).

5.2 Composition and Temperature of Electrolyte

A high hydrogen fluoride content in the electrolyte promotes corrosion, misting and anode polarisation (Downing 1946, 1951a, Murray et al. 1951, Ebel and Montillon 1952). Operation at an excessive temperature results in increased corrosion and a high vapour pressure of HF, particularly with anodes of high permeability (Murray et al. 1946, 1951, Smiley and Brater 1956, Rudge 1956, 1966, 1971, Davies and Rudge 1961, Goode et al. 1964, Goodyear Atomic Corporation 1967a). With comparatively low HF concentrations, the major operating problem is that solids may separate from the electrolyte if the temperature becomes too low. If this occurs, the solid crystals are very difficult to redissolve after normal conditions have been restored (Pinkston 1947, Downing 1951a, Murray et al. 1951). In addition, low temperature and HF content decrease the conductance of the electrolyte and hence increase the cell operating voltage leading to cathode polarisation (Downing 1951a), as discussed in Section 4.2.

5.2.1 Corrosion

Plant data obtained during operation of cells with mild steel bodies, using electrolyte containing 40% HF, indicated a corrosion rate only 1/10 to 1/5 as great as was found at concentrations of about 44%. Experimental runs on a smaller cell showed acid concentration influenced corrosion rate but not to the same extent (Downing 1946, 1951a). As a result of these findings, most cells operated prior to 1950 (see Table 4) used electrolyte containing 39.0 -

40.5% HF at a temperature of 95 - 110°C. The German cell at Leverkusen was an exception (Carter et al. 1946, Karr 1946); the low operating temperature of this cell (72 - 90°C) and the use of magnesium to limit corrosion was probably a result of the high HF content (46.3%) of the electrolyte.

In later American, USAEC, ICI, UKAEA and French cells, the optimum electrolyte concentration was regarded as 40 - 41.5% HF (Dykstra et al. 1955, Rudge 1956, 1971, Vavalides et al. 1958, Huber et al. 1958, Davies and Rudge 1960, 1961, 1964a, 1964b, Bergeret 1965, Goodyear Atomic Corporation 1967a, Level 1969, Rogan 1972b). Further plant scale tests showed that "concentrations below 40% HF can be responsible for permanently higher voltages; concentrations above 43% grossly accelerate corrosion with a consequent deterioration of anodic contacts and increase of sludge formation" (Huber et al. 1958). The optimum temperature range for a cell operating with 40 - 41.5% HF in the electrolyte was reported as 88 - 99°C, although it was stated that a cell could operate satisfactorily in the range 82 - 115°C (Goodyear Atomic Corporation 1967a). However, a low range of operating temperatures (80 - 85°C) was used in the ICI cells (Rudge 1966, 1971). This action was probably necessary to reduce the high carry over of HF encountered with porous carbon anodes (Hill and Rudge 1957, Davies and Rudge 1960, 1961, 1964a, 1964b, Davies 1963, Rudge 1966, 1971).

5.2.2 Misting

The contamination of the product gases with a mist of fine solid particles is a common problem which was more pronounced in the first industrial cells. Analyses showed that the mist was entrained particles of electrolyte (Downing 1946, 1951a, Level 1969) and excessive misting was promoted by high hydrogen fluoride and iron concentrations in the electrolyte (Downing 1946, 1951a, Katz 1951). These causes of misting were eliminated partially by the use of electrolytes having a lower HF content and of materials of construction of greater corrosion resistance. However, the entrainment of electrolyte still occurred and was overcome by using large off-take lines for the product gases (Bergeret 1965, Kelly and Clark 1967a, 1968a) and providing mist eliminators in the lines after the cell (see Section 6.3).

5.2.3 Effect on anode polarisation

Although a fluorine cell will operate satisfactorily over a reasonable range of electrolyte compositions and temperature (Katz et al. 1955), it was found that rapid additions of large amounts of HF can often result in polarisation of anodes of low permeability (Williams et al. 1944, Murray et al. 1946, Downing 1946, 1951a, Downing et al. 1947). Volatilisation of hydrogen fluoride was proposed

as the direct cause of this effect (Ebel and Montillon 1952) although the results of Rudge (1966) suggest that sudden increases in the local water content of the electrolyte could be responsible. This form of anode polarisation was eliminated and improved cell performance was gained by the use of a metered continuous feed of HF to the cell (Ebel and Montillon 1952, Penland 1955, Dykstra et al. 1955, Jacobson et al. 1955, Smiley and Brater 1956, Huber et al. 1958, Dykstra et al. 1958, Neumark and Siegmund 1966, Kelly and Clark 1967b, Goodyear Atomic Corporation 1967a, 1967b, Level 1969, Rogan 1972b).

5.3 Circulation of Electrolyte and the Accumulation of Sludge

In the early development of fluorine cells, good circulation of electrolyte was thought to be desirable to maintain a uniform composition (Downing 1946). Later developments showed that the rate of dispersion of HF is high by comparison with the rate of evolution of fluorine and good circulation is not essential to maintain a uniform electrolyte composition (Downing 1946, Ebel and Montillon 1952). However, good circulation is necessary to promote the rapid dissipation of heat from the cell (Downing 1946, 1951b, Schumb 1946, 1951, Benning et al. 1951, Ebel and Montillon 1952, Dykstra et al. 1955, Davies and Rudge 1961, 1964a, Rudge 1966, 1971). A temperature difference of up to 15 K was observed between the centre and edge of a 2000 A cell. With another type of cell using a central cathode, a temperature difference of 10 K was observed with a solid cathode, however with a perforated cathode (allowing a greater circulation of electrolyte) the temperature was more uniform (Downing 1946). Temperature variations in a cell can result in the adverse effects described in Section 5.2.

Downing (1946) and McLaren (1951) stated that the circulation of electrolyte was seriously hindered by sludge which accumulated on the base of the cell and blocked the openings in the diaphragm. Sludge is produced by the build-up of corrosion products in the cell. By choosing materials of construction which are more resistant to corrosion, most of the problems of sludging were reduced considerably in the French and USAEC C and E-type cells (McLaren 1951, Dykstra et al. 1955, Vavalides et al. 1958, Powell et al. 1961, Level 1969). Tests demonstrated that sludge produced in these cells tends to pack in the space between the cathode and the diaphragm hindering the movement of electrolyte and causing the diaphragm to become cathodic (Powell et al. 1960). The E-type cell has a diaphragm which is offset towards the anode (Kelly and Clark 1967a, 1968a); this arrangement was probably used to reduce the frequency at which the cell required desludging.

Provisions are made in the designs of cells to incorporate clear paths for electrolyte circulation which is promoted by the gas bubbles evolved at the electrodes and by the convection currents set up due to heat generated in the cell (Schumb 1946, Benning et al. 1951, Osborne 1951, Stuart and Osborne 1951, Dykstra et al. 1955, Smiley and Brater 1956). In cells with porous carbon anodes, circulation currents are reduced in strength as fluorine percolates through the anodes instead of rising through the electrolyte. Cooled cathodes were introduced to improve heat dissipation in this type of cell (Davies and Rudge 1961, Davies 1963, Rudge 1966, 1971).

A number of systems have been proposed to improve electrolyte circulation. Forced circulation of electrolyte was used in the German cells at Leverkusen (Carter et al. 1946, Karr 1946) and this system was claimed to provide a uniform temperature and concentration in the electrolyte and to sweep the anode to remove bubbles of fluorine (Ebel and Montillon 1952). Ebel and Montillon (1952) also suggested improvements to the standard cell to promote increased circulation (Figures 26 and 27).

5.4 Anode to Cathode Separation and the Position of the Skirt

Ebel and Montillon (1952) stated that the optimum anode to cathode spacing is a function of fluid flow, electrical resistance, and the possibility of fluorine-hydrogen gas mixing. Large cathode to anode spacings allow the electrolyte to circulate more easily and decrease the chance of the gases mixing, but the resistance of the electrolyte is directly proportional to and increases with the distance between the electrodes (Schumb 1946, 1951, Downing 1946, 1951a, Ebel and Montillon 1952, Smiley and Brater 1956, Davies and Rudge 1960, 1961, 1964a, 1964b, Rudge 1966, 1971).

In production cells, it is desirable to achieve as high an energy efficiency as possible and to accomplish this the anode to cathode spacing, and in consequence the resistance of the electrolyte, is kept to a minimum. A number of authors presented data demonstrating the advantages gained by decreasing electrode separation (Ebel and Montillon 1952, Davies and Rudge 1960, 1961, Rudge 1971) but only the experiments of Davies and Rudge (1960) and Rudge (1971) fully investigated the situation. Rudge (1971) found that the voltage saving in a 200 A cell for a decrease in electrode separation from 55.9 to 34.9 mm varied between 1.2 and 2.3 V, depending on composition and temperature of the electrolyte. For electrolytes in a similar condition, the voltage across the cell decreased from 12.1 to 10.3 volts. It was also found that for a given separation of the electrodes, the working voltage was not always directly proportional to the separation; variations in the

circulation of electrolyte, overvoltages at the electrodes and non-uniform temperatures in the electrolyte were believed to be the cause of this effect.

If adequate cooling and circulation of the electrolyte can be maintained, the minimum spacing of the electrodes and the optimum position of the skirt (and hence the diaphragm) is determined by the migration of hydrogen and fluorine from their respective electrodes. The Hooker, modified Hooker and the USAEC C and E-type cells (carbon anodes of low permeability) used an electrode separation of 38 mm (see Table 5). The diaphragm was placed at the same distance from both electrodes in all cells except in the E-type where the diaphragm and skirt were 12.5 mm from the anode, and 20.5 mm and 18.8 mm respectively from the cathode. These figures correspond closely to minimum electrode separations of 30.5 to 38 mm recommended by Davies and Rudge (1961, 1964a) for cells with carbon anodes of low permeability.

The first large cells (1400 - 2130 A) constructed by ICI had a large distance (64 mm) between the electrodes (carbon anode of high permeability), no diaphragm and the skirt placed 11 mm from the anode (Rudge 1956, Davies and Rudge 1961, Rudge 1966). In later cells of 2500 - 5000 A capacity (carbon anodes of high permeability), the separation of the electrodes was decreased to 31.6 mm but the anode/skirt gap was maintained at 11 mm although operation was possible at gaps as low as 6.4 mm under certain conditions of electrolyte composition (Davies and Rudge 1964a, 1964b, Rudge 1966). Carbon anodes of high permeability permitted operation of 2500 A cells where the electrolyte composition was carefully controlled at anode/skirt gaps as low as 1.52 to 3.05 mm (Davies and Rudge 1961, 1964b).

Small gaps between anode and skirt can be tolerated with carbon anodes of high permeability because of the discharge mechanism of fluorine at the anode and these anodes can have advantages over those of lower permeability (see Section 4.1.5). However, from the latest information on the American and British cell designs, the minimum anode/skirt gap for completely safe operation with both types of carbon is approximately 11 to 12.5 mm (Rudge 1966, 1971, Kelly and Clark 1967a, 1968a).

The mechanism of hydrogen discharge at the cathode requires a larger clearance between the cathode and the skirt than is necessary between the anode and the skirt. Hydrogen is evolved at the surface of the cathode as free bubbles which do not migrate through the electrolyte very far in the horizontal direction (Katz 1951, Rudge 1971). It was found that this migration increased greatly if the hydrogen fluoride content of the electrolyte was low (Katz 1951). The mechanism of the evolution of hydrogen from the cathode is

not affected markedly by the condition of the cathode or electrolyte and experiments have shown (current densities were not quoted) that 95% of the bubbles liberated at a cathode (305 mm deep) do not move more than 19 mm from the face of the cathode (Rudge 1971). The cathode/skirt gap used in USAEC E-type and latest ICI cells is close to this figure and improvements in cell performance by reducing this separation would seem unlikely.

Further significant decreases in the separation of the electrodes will have to be accompanied by improvements in methods of heat removal from the inter-electrode space (Ebel and Montillon 1952).

5.5 Current Density

The current per unit area of an electrode is expressed as the current density at the electrode. Operation at a high current density provides the maximum amount of fluorine for a fixed cell volume and, therefore, reduces the capital cost of a fluorine cell. McLaren (1951) and Ebel and Montillon (1952) used the term limiting current density specifically to describe the current at which an anode polarises, but in fact a variety of limiting current densities exist under different circumstances which, if exceeded, can produce a number of unfavourable operating conditions.

The area of the cathode is generally sufficient to avoid problems caused by high currents, however problems still occur and these are more prevalent in cells without a diaphragm. At a high current density, sufficient hydrogen bubbles may be produced to enter the fluorine compartment (Rudge 1962, 1966). More commonly a brisk evolution of hydrogen combined with a small vertical separation between the top of the cathode and the bottom edge of the skirt may lead to hydrogen bubbles crowding within this space and so increase the chance of hydrogen flowing past the skirt (Davies and Rudge 1960, 1961, 1964a, 1964b). Typical cathode current densities are not often reported in the literature, however the USAEC E-type cell operated at a density of approximately 1250 A m^{-2} (Kelly and Clark 1967a, 1968a) whereas an earlier Du Pont cell (Downing 1944) functioned satisfactorily at 2070 A m^{-2} (note that the cathode densities of 460 to 770 A m^{-2} for American cells given by Rudge (1971) appear to be incorrect). ICI cells were operated at considerably lower cathode current densities than the American cells, densities of 540 and 360 A m^{-2} were reported for 1400 A and 5000 A cells respectively (Rudge 1956, 1971). Operation at low densities may have been necessary to minimise the chance of hydrogen mixing with fluorine as diaphragms were not used in these cells.

The anode current density is an important factor which affects the operation of a fluorine cell in a number of ways. For any cell or type of carbon

anode, limiting current densities exist which, if exceeded, produce the following effects (Schumb 1946, Downing 1946, McLaren 1951, Osborne 1951, Katz 1951, Ebel and Montillon 1952, Finley 1953, Powell et al. 1960, Hertz and Nugent 1961, Cable et al. 1962, Goode et al. 1964, Rudge 1962, 1966, 1971):

(a) Polarisation of the anode.

(b) The entry of fluorine into the hydrogen compartment.

(c) An excessive anode temperature leading to a high electrolyte temperature and high hydrofluoric acid losses.

(d) Failure of the anode connections to carry current and deterioration of the carbon-metal contacts at the anode hanger bar.

The American C and E-type cells (with carbon anodes having a low permeability) operated at an anode current density of approximately 1500 to 1600 A m^{-2} without polarisation difficulties (Vavalides et al. 1958, Huber et al. 1958, Kelly and Clark 1967a, 1968a) and it was reported that this type of carbon was used at current densities of 3750 A m^{-2} in laboratory and experimental generators (Ebel and Montillon 1952). Failure to find a suitable method of supporting the carbon anode and providing an electrical contact has probably prevented higher anode current densities being obtained in production cells. Anodes of permeable carbon were found to operate without polarisation at higher current densities than the non-permeable types (McLaren 1951, Katz 1951, Davies and Rudge 1961, Rudge 1966, 1971). However, this advantage was not obtained in industrial scale cells until the cooling of the cells was improved (Rudge 1956, Davies and Rudge 1960, 1961). The highest current densities that were reported for ICI cells are 2300 A m^{-2} for a long-term works-scale trial (Rudge 1966) and 1800 A m^{-2} for a production cell (Rudge 1971). The relatively short lifetime of the anodes in the ICI cells (Rudge 1971) suggests that the current carrying capacity of permeable carbons is also limited by the method of supporting the anode.

6. INDUSTRIAL PRODUCTION OF FLUORINE

Plants for the production of fluorine have been described by Carter et al. (1946), Karr (1946), Neumark (1947), Jacobson et al. (1955), Penland (1955), Smiley and Brater (1956), Giffels and Vallet (1956a, 1956b), Rudge (1956, 1962, 1966, 1971), Dykstra et al. (1958), Huber et al. (1958), Bergeret (1965), Goodyear Atomic Corporation (1967a, 1967b) and Level (1969). A flow diagram of a typical modern plant is given in Figure 1. The plant has a bank of medium temperature fluorine cells which are supplied with hydrogen fluoride, direct current electricity and, initially, a charge of electrolyte. The product gases are filtered to remove any entrained mist of electrolyte and refrigerated to reduce the HF vapour to 2 - 3 vol. % and passed through sodium fluoride traps for further HF removal. The recovered HF is recycled. Following this treatment, the hydrogen is vented or burned and the fluorine perhaps compressed before distribution and further processing. Facilities are also provided for the disposal of large quantities of fluorine and hydrogen fluoride in emergencies.

6.1 Hydrogen Fluoride Feed Systems

Table 12 lists the various techniques which were developed for feeding hydrogen fluoride into a fluorine cell. A typical arrangement is shown in Figure 28 in which hydrogen fluoride was supplied in bulk to a tank farm which was remote from the production area (Jacobson et al. 1955, Penland 1955, Smiley and Brater 1956, Huber et al. 1958, Goodyear Atomic Corporation 1967a, 1967b). For a plant containing forty 6000 A cells, three steel storage tanks of 50 m^3 capacity each were used, the tanks were approximately 7.95 m long and 2.75 m in diameter and were designed for an internal gauge pressure of 689 kPa. Each tank was provided with connections to pipework for the supply, discharge and draining of hydrogen fluoride. In general mild steel piping was used (Goodyear Atomic Corporation 1967b). Liquid hydrogen fluoride was transferred to and from the storage tanks by a regulated surface pressure of dry nitrogen or air with a dew point less than -51^{o}C (Smiley and Brater 1956). The tanks were mounted on strain gauge load cells, the weight being recorded in the control room, and located in a concrete catch basin which drained to a dilution pond. The capacity of the basin was sufficient to retain the contents of the three storage tanks in the event of leakage or breakage. A simple shelter was usually built over the tanks to prevent the heat of the sun from increasing the vapour pressure of hydrogen fluoride unduly. Hydrogen fluoride was transferred from the storage tanks to a day tank from which liquid hydrogen fluoride was supplied continuously to a vaporiser, usually a steel pressure vessel with

a steam or hot water jacket (Jacobson et al. 1955). The day tank was mounted on platform scales with a continuous weight recording system to measure the feed rate of hydrogen fluoride. The day tank was maintained at a gauge pressure of 90 - 103 kPa for feeding liquid HF by pressurisation with dry nitrogen.

In another system (Penland 1955, Huber et al. 1958, Goodyear Atomic Corporation 1967a, 1967b), a day tank was not used and hydrogen fluoride was transferred continuously from the storage tanks to the vaporiser system. The rate of flow was automatically controlled to maintain a constant liquid level in the vaporisers and the rate of use was determined by the loss in weight of the storage tanks. The rate of steam flow to the vaporiser jacket was controlled to maintain a vapour pressure of HF of 70 kPa (gauge). For a plant with forty 6000 A cells, the vaporiser station consisted of two mild steel vaporisers, each capable of supplying 364 kg h^{-1} of hydrogen fluoride. Additional tank connections and piping systems were provided to each vaporiser for venting, draining and purging. Although only high purity hydrogen fluoride was used, impurities such as water accumulated in the vaporisers and consequently the vaporisers were shut down periodically and the residue discarded (Jacobson et al. 1955, Goodyear Atomic Corporation 1967a, 1967b). Wastes drained from the vaporisers were passed through a water-spray scrubber, volatile gases were vented to the atmosphere and the acidic liquid and suspended solid wastes were diluted to about 10 per cent hydrogen fluoride solution and discharged to a neutralisation pit. Waste products from the storage area were treated by the same equipment (Goodyear Atomic Corporation 1967b).

The hydrogen fluoride vapour leaving the vaporiser was fed into the cathode compartment of the cell through a dip tube below the electrolyte level. In general hydrogen fluoride was added continuously to the cell, the rate of addition was regulated by monitoring the level of electrolyte in the cell which was maintained within fixed limits. The level is related directly to the composition of the electrolyte which was checked periodically by sampling. In one method, the rate of hydrogen fluoride addition was metered and manually adjusted by a needle valve to maintain a constant electrolyte level which was checked manually (Jacobson et al. 1955, Penland 1955, Smiley and Brater 1956, Goodyear Atomic Corporation 1967a, 1967b). Before metering, the hydrogen fluoride vapour had to be heated to 93°C to breakdown the association compounds of high molecular weight (Giffels and Vallet 1956a).

A second method involved the use of a level control device (Huber et al.

1958, Henderson et al. 1962) which was described by Kelly and Clark (1968b). This device consisted of a probe which passed into the cell and terminated at the desired operating level of electrolyte. The base of the probe was heated and its temperature detected by a thermocouple. The extent to which the end of the probe was covered by electrolyte affected the transfer of heat from the probe and in consequence its temperature. The output of the thermocouple was used through a controller and relay to operate a solenoid-actuated valve on the hydrogen fluoride supply line. By such a method, the electrolyte level could be controlled in the range $\pm$ 6.4 mm and hydrogen fluoride concentrations within $\pm$ 0.5% (Huber et al. 1958).

Irrespective of the type of feed system used, nitrogen was introduced automatically to the feed line if the hydrogen fluoride pressure dropped below a predetermined value (34.4 kPa gauge) or if the flow was shut off. This prevented suck-back of electrolyte into the hydrogen fluoride feed system (Jacobson et al. 1955, Dykstra et al. 1958, Goodyear Atomic Corporation 1967a).

Only the ICI, UKAEA and Leverkusen cells used a feed of liquid hydrogen fluoride to the cell (Carter et al. 1946, Karr 1946, Rudge 1956, 1966, 1971, Rogan 1972b). In the ICI and Leverkusen cells, the level of electrolyte was maintained by the intermittent addition of hydrogen fluoride. However in the BNFL cells (Rogan 1972b), the hydrogen fluoride content of the electrolyte was controlled by automatic addition to maintain a preselected level. The necessary control was achieved by using a transducer to monitor the change in pressure on a dip pipe caused by variations in level (maximum variation allowed was 4.8 mm) and to transmit a signal which actuated the hydrogen fluoride feed valve.

6.1.1 Alarm systems

The following alarm circuits were considered necessary for the hydrogen fluoride feed system of a plant containing forty 6000 A cells (Goodyear Atomic Corporation 1967a).

(a) There was a low level alarm for the contents of the hydrogen fluoride storage tanks. When the alarm registered the area operator switched storage tanks to assure an ample supply of liquid feed to the vaporiser.

(b) Each vaporiser had a high level alarm. If the alarm was activated, the control valve in the feed line was closed manually. If the level did not drop in a reasonable time, isolating valves were closed and, if necessary, the other vaporiser was used.

(c) A high pressure alarm was installed for each vaporiser which automatically shut off the steam supply to the jacket and vented the vaporiser heating shell.

(d) A low pressure alarm was installed in the feed line to the cells. If this alarm was activated, the level of HF and the pressure in the vaporiser were checked.

6.2 Electrolyte Preparation

Table 13 describes the processes which have been used to prepare electrolyte. In American plants, electrolyte was prepared by adding hydrogen fluoride gas to high purity potassium bifluoride powder in an agitated reaction vessel which was jacketed to allow removal of the heat of reaction. The electrolyte was treated with fluorine to remove impurities, particularly water which was reduced from 1000 to 400 ppm before the electrolyte was used in the cell (Huber et al. 1958, Dykstra et al. 1958, Goodyear Atomic Corporation 1967a, 1967b). In addition to the electrolyte preparation vessel, blow case receivers were provided to handle either 'good' or contaminated electrolyte from the cell. The contaminated electrolyte was discharged from the blow case to waste disposal drums and the hydrogen fluoride salvaged. The electrolyte to be re-used was discharged from the other blow case to an electrolyte settling tank. After settling, the electrolyte was piped to the electrolyte preparation system for re-use. The sludge and sediment from the tanks were discharged to disposal drums (Goodyear Atomic Corporation 1967b).

The French used a different process in which the Fremy salt was placed in a basket suspended in the reaction vessel. The salt was irrigated by addition of liquid hydrogen fluoride and the refluxing effect of hydrogen fluoride vapour to produce electrolyte of the required composition (Level 1969).

6.3 Treatment of Cell Off-Gases

Fluorine and hydrogen pass from the cells through separate systems which must be maintained at a similar pressure to eliminate the possibility of these gases mixing and exploding within the cell. In addition both gases leave the cell carrying approximately 10 vol. % of hydrogen fluoride and a mist of electrolyte which becomes a dust if cooled. The entrained electrolyte must be removed to protect valves, pumps and other equipment downstream of the cells and hydrogen fluoride must be recovered and recycled to provide essentially pure fluorine for further processing and to reduce production costs. Table 14 lists the various methods that have been used to remove hydrogen fluoride from fluorine and hydrogen.

The off-gas systems used in American production plants at Oak Ridge (Tennessee), Paducah (Kentucky) and Portsmouth (Ohio) were described by Jacobson et al. (1955), Penland (1955), Smiley and Brater (1956), Dykstra et al. (1958), Huber et al. (1958) and Goodyear Atomic Corporation (1967a, 1967b).

The systems were very similar and this general arrangement was later used at the Pierrelatte Chemical Factory (Bergeret 1956, Level 1969). Such a system for a plant containing forty 6000 A cells is described below.

The gas headers from the cell were used as the first electrolyte separators. These headers were grossly oversized for the flow of gas to allow entrained electrolyte to settle out without blocking the pipe. Because a relatively high voltage is applied to the terminal cells in a series arrangement, electrically insulated flanged joints were used between the cell and the headers (McGuffey et al. 1962). At the end of the headers, entrainment separators were used to remove electrolyte still present. In the American plants the separators were cylindrical mild steel vessels consisting of a cyclone section and a filter section, the filtering medium being a Monel-wool pad or porous Monel tubes (McGuffey et al. 1962). In the French plant (Level 1969), electrolyte was removed by incorporating an electrostatic precipitator using nickel wire at a potential of 15,000 volts. Initially, no provisions were made for the removal of electrolyte in ICI plants (Rudge 1956), however, a small catch pot and a cyclone to protect the automatic control valve were later considered necessary (Rudge 1971). From the entrainment separators, both the fluorine and hydrogen passed through surge tanks of 14 m^3 volume which were provided to dampen pressure fluctuations resulting from either blower operations or explosions within the cell.

At this point the fluorine and hydrogen systems differed slightly. The fluorine flowed through a bank of three special sintered metal filters with a piping arrangement that allowed the filters to be purged and replaced one at a time. These filters were placed ahead of the five stage centrifugal compressor (positive displacement lobe-type blowers were used previously (Jacobson et al. 1955) and a Corblin double membrane compressor was later preferred in the French installation (Level 1969)) to protect it from electrolyte particles. A build-up of electrolyte caused an unbalanced condition which resulted in vibrational failure of either the compressor or the seal. For the hydrogen system, filters were placed either before or after a standard rotary lobe blower. This type of compressor was not as prone to vibrational failure and consequently was located ahead of the filters to make sure that the pressure in the hydrogen system did not fall below atmospheric (Penland 1955). This precaution was not considered necessary in other plants (Huber et al. 1958). Sealing was anticipated to be a major problem with the rotary lobe compressor but blended copper and PTFE rings were found to require very little maintenance.

Pressure inbalances between the two gas systems were avoided by using a pressure control system. The equalising of the pressures was accomplished by regulating control valves in the suction header of the fluorine compressor and in a recycle line about the hydrogen blower. The datum for the system was the pressure in the hydrogen surge drum which was carefully controlled to $\pm$ 0.5 kPa relative to atmospheric pressure; the pressure in the fluorine surge drum was maintained at $\pm$ 0.5 kPa relative to the hydrogen pressure.

A different system of pressure control was used in the ICI and UKAEA plants. Practice at ICI was to control automatically the pressure on the fluorine side of the cell at 62 Pa relative to atmospheric pressure by a control valve in a bypass on the booster fan. The pressure on the hydrogen side of the cell was controlled at the same figure by a lute into 10 per cent caustic potash liquor. Surge tanks were not considered necessary (Rudge 1971). In the BNFL plant, the pressure of the fluorine and hydrogen in the cells was controlled at 0.49 kPa relative to atmospheric pressure. Fluorine leaving the cells passed through a surge vessel which minimised pressure fluctuations and allowed smoother operation of the electrolyte level and pressure control systems (Rogan 1972b).

In the American plant fluorine and hydrogen containing hydrogen fluorine at gauge pressures of 17.2 and 6.9 kPa respectively then passed from the compressors to identical systems for the recovery of hydrogen fluoride. Each system consisted of three Monel condensers maintained at -85^{o}C to condense the hydrogen fluoride. In the case of fluorine, the hydrogen fluoride content was reduced from 11 to 4 vol. %; for hydrogen from 9 to 3 vol. %. Removal of the hydrogen fluoride was limited by its polymerisation properties to a level of 2 vol. %. As an alternative, if a low level of contamination was required (as low as 0.05 vol. %, Level 1969), sodium fluoride tray absorbers were used instead of condensers or as a secondary absorption system (see Table 14). Condensed hydrogen fluoride was accumulated in run down tanks of 0.586 m^{3} capacity (American plant) and transferred at regular intervals with nitrogen pressure to the vaporising system. From the condensers, the fluorine was passed for further processing or to a fluorine storage facility. Hydrogen from the condenser system was scrubbed with water to remove the final traces of hydrogen fluoride and then passed through an entrainment separator to remove water, a meter and a dual installation of flame arrestors from which the hydrogen was discharged to atmosphere. The meter consisted of a special hydrogen analyser and wet test gas meter to check the total plant efficiency (Katz et al. 1955).

6.3.1 Alarm and control systems

The following instrumentation and alarm systems were provided for the off-gas treatment systems in a plant containing forty 6000 A cells (Goodyear Atomic Corporation 1967a, 1967b).

(a) Pressure switches were attached to the fluorine and hydrogen surge drums and activated high pressure indicating lights if the pressure settings were exceeded.

(b) Adjustable high and low audible alarms were incorporated with the cell voltage recorder to detect large changes in voltage.

(c) The two fluorine pumps were equipped with an audible alarm to indicate when both pumps were off, an interlock which prevented the operation of either pump unless an emergency shutdown circuit was energised and a second interlock with the fluorine header control valve.

(d) The hydrogen pumps were similarly equipped.

(e) An emergency shutdown circuit activated by any of the following conditions:

(i) High or low fluorine pressure in the gas header.

(ii) High positive or high negative differential pressure in the fluorine header.

(iii) Operation of five emergency shutdown controls.

The relays for the pressure conditions were provided with time delays which were adjustable between 0 and 60 seconds. Activation of the emergency shutdown circuit switched off both fluorine pumps, both hydrogen pumps and the main and conditioning rectifiers.

6.4 Cell Handling and Cleaning Facilities

Fluorine cells have a short operating life and must be removed from service and overhauled (Goodyear Atomic Corporation 1967a, 1967b). Goodyear Atomic Corporation (1967a, 1967b) reported that the following steps were necessary in the reconditioning process (production plant containing forty 6000 A cells, with up to 50 cells per month requiring rebuilding):

(a) The cell was removed from its operating station and transported to the cell neutralisation area. Cell handling equipment consisted of an overhead monorail system with two electrically operated five-ton capacity hoists for cell disassembly and assembly, and two special fork-lift trucks capable of accurately positioning the cells in the cell room.

(b) The electrolyte was removed from the cell via a blow case transfer system using pressurised air from the plant air system.

(c) The cell cover was removed and all parts neutralised.

(d) The cell was dismantled into its various components.

(e) The shell and/or cover were transferred to a separate building for cleaning.

(f) The cell was reassembled with new or reconditioned parts.

(g) The cell was steamed and air dried to remove moisture and electrolyte was added.

(h) The cell was transported to the cell conditioning area and placed on-stream in the cell room.

The cell neutralisation facility consisted of a shell-dumping device, a dip tank, spray piping and a neutralising pit, and a tank and pump for caustic solutions. The installation was primarily a system for washing the cell or cell parts with a caustic solution; the cell head was neutralised in a dip tank and the shell was washed on a rotating fixture in a spray system. Both drain pits discharged in a sludge pit from which the effluent passed to a neutralisation pit. The air exhaust system from the cell neutralisation area was equipped with a scrubber system to remove the relatively high (2 vol. %) concentration of hydrogen fluoride fumes anticipated in this area.

The cleaning processes were carried out in a separate building which contained eight large tanks and an overhead crane. The contents of the tanks were (in the following order) alkali and warm water ($64^{o}C$), 'troxide' (for copper), 'troxide' (for steel), chromic acid and cold water, ammonia and hot water ($88^{o}C$). The cell cathodes, head and shell were cleaned by immersion in baths of alkali and acid in the following order (Union Carbide Corporation 1968):

(1) Alkali - All items were stored overnight. The cathode was then scraped free of sludge and soaked for a second similar period. All items were rinsed in warm water after this treatment.

(2) 'Troxide' - All items were soaked in 'troxide' solution for 30 minutes. One bath was used for steel items another for copper alloys. All items were then rinsed in cold water. At this point the cathode was dipped in a bath of ammonia to neutralise the 'troxide'. All items were then rinsed in hot water to promote drying. After this treatment the cathode was considered to be clean.

(3) Chromic Acid - The Monel skirt on the head was dipped into a chromic acid bath and the Monel shell was splashed with chromic acid in the final etching treatment. Both items were then washed in cold water; the head was stored at this point and the shell was washed finally with hot water to promote drying before storage.

A cell-purging station was also provided for the cleaning of cells prior to refilling with electrolyte. The station consisted of a system for introducing steam for cleaning purposes and air for drying after cleaning was accomplished. Liquids from the station were piped to an outside drainage system and vapours were vented to the atmosphere.

6.5 Storage and Transportation of Fluorine

McGuffey et al. (1962) described the procedures used in the compression and storage of fluorine at the Oak Ridge Plant of the Union Carbide Corporation. Modified piston-type compressors, or diaphragm compressors either in series or parallel with the piston-type compressors, were used to compress the fluorine to a gauge pressure of 516 kPa. The compressors were located in a special enclosure and were designed to ensure safe operation and freedom from fires. The discharge from the compressors was connected to piping using a flanged joint and an aluminium gasket. Further downstream piping was of all welded construction. Valves were operated by extension hand wheels through the enclosure.

Fluorine gas was stored in three tanks, each having a capacity of 16.8 m^3, which were housed in individual cubicles. All tanks had double valving operated by extension handwheels on both the inlet and discharge piping. The individual cubicles protected the tanks and valves against weather, restricted unauthorised entry, and simplified the ventilation system. Two exhaust blowers with a capacity of 23 $m^3\ s^{-1}$ removed air from the cubicle and provided a forced draft to a 24.4 m disposal stack. Vent lines from the tanks were also connected to the stack to dilute any release of fluorine. Each vent line was equipped with two valves, normally locked open, followed by three Monel safety heads and rupture disks in series to protect each storage tank from damage due to excessive pressure. The first disk protected the middle disk from corrosion by fluorine, and the third disk protected the middle disk from atmospheric corrosion.

Fluorine was transported long distances in steel tanks mounted on trailers. The tanks had a capacity of 4.14 m^3 and a maximum working gauge pressure of 516 kPa, the tanks had double valving but bursting disks were not used (McGuffey et al. 1962). At Allied Chemical Corporation, fluorine gas was shipped in steel cylinders at a pressure of 2.75 MPa, the maximum capacity of a cylinder was 2.72 kg (Neumark and Siegmund 1966, Siegmund 1967). Bulk quantities of liquid fluorine were shipped in loss-free Dewar-type tanks (2,260 kg net payload), consisting of three concentric shells and heads (Neumark and Siegmund 1960). The inner stainless steel shell contained the

product, the intermediate stainless steel shell was filled with liquid nitrogen and the outer shell of carbon steel was evacuated and filled with an insulating powder. Siegmund (1967) stated that the design of the tank was based on the difference in boiling points of liquid nitrogen and liquid fluorine, -195.5 and -187.5°C respectively, and fluorine was kept loss-free at the expense of boiling liquid nitrogen. A cabinet at the rear of the trailer contained instrumentation, valves and auxiliary equipment. Sound and visual alarms were provided to warn of a low level of liquid nitrogen and additional safety was provided by alarms to indicate a high pressure of fluorine. This system carried over 363 Tg m without incident (Neumark and Siegmund 1966, Siegmund 1967).

6.6 Disposal of Fluorine and Hydrogen Fluoride

Methods used in fluorine production plants for the disposal of waste fluorine and hydrogen fluoride are listed in Table 14.

6.6.1 Fluorine disposal

Navratil (1968) presented a literature survey which described many methods for the disposal of fluorine, however the following systems were used most commonly on a large scale (Schmidt 1967, Navratil 1968).

(a) Scrubbing with water or caustic solution (Landau and Rosen 1948, Burford and Hamilton 1951, Liimatainen and Levenson 1953, Liimatainen and Mechan 1955, Rudge 1956, 1962, 1971, Smith 1957, Milford 1958, Camozzo and Pizzini 1960, Ruch 1960, Henderson et al. 1962, Neumark and Siegmund 1966).

(b) Direct burning with fuels such as methane or propane (Compton 1946, Landau and Rosen 1951, Long 1955).

(c) Reaction with solid disposal agents such as charcoal, alumina, limestone, lime and soda lime. (Landau and Rosen 1951, Liimatainen and Levenson 1953, Schmidt 1959, Houston 1960, Schmidt 1967, Davratil 1968, Pulley and Harris 1972).

(d) Reaction with superheated steam (Schmitt 1952, Smiley and Schmitt 1954).

The merits of various liquid scrubbing systems were compared by Ruch (1960). Water, although an excellent absorbent for HF, was unsatisfactory for fluorine as an intermediate compound (OF_2) was sometimes formed which reacted more slowly than fluorine. The fluorine reaction with water was also reported to be unpredictable and occasionally produced violent explosions. In addition, the accelerated corrosion rate of Monel equipment when exposed to aerated dilute hydrofluoric acid and the need to neutralise the resulting acid made the use of water undesirable. Both sodium and potassium hydroxide solutions

destroyed fluorine satisfactorily but a potassium solution was better for two reasons.

(1) Potassium fluoride formed by the adsorption of fluorine was more soluble than the equivalent sodium salt.

(2) The oxide of fluorine (OF_2) reacted slowly in the presence of sodium but this compound and fluorine both react quickly with potassium hydroxide solution. (This disadvantage of sodium hydroxide can be overcome by having a sufficient residence time in the system.)

A concentration range of 5 to 10% potassium hydroxide was usually selected because experiments showed that, in this range, the potassium hydroxide concentration did not have an appreciable effect on the overall mass transfer coefficient. The cost of disposal by caustic soda or potash solutions can be reduced by using lime to regenerate the caustic and precipitate a solid fluoride waste, calcium fluoride. The feasibility of this regeneration process was demonstrated commercially by Landau and Rosen (1948). Ruch (1960) concluded that although several types of equipment for contacting liquid and gas were available, a spray column was the most suitable for use with the potassium hydroxide-fluoride system and standard equipment could be used as the corrosion effect of the fluoride ion is negligible under normal operating conditions (Smith 1957). With a spray system, the concentration of fluorine in the outlet gas was reduced to a few parts per million for any inlet concentration of fluorine if sufficient contact time (60 seconds) was provided (Burford and Hamilton 1951, Liimatainen and Levenson 1953, Liimatainen and Mechan 1955, Smith 1957).

The reaction of fluorine with hydrocarbons produced a mixture of carbon and hydrogen fluorides as products. The carbon compound was inert and was vented after hydrogen fluoride had been scrubbed from the gas stream with water or alkaline solutions. This system had the disadvantage of requiring the combustion of some fuel at all times and was particularly unsuitable for widely varying loads (Landau and Rosen 1951).

Alumina, limestone and soda lime beds were used to dispose of fluorine on a small scale by an adsorption process but ultimately the beds must be regenerated and the fluorine disposed of chemically (Liimatainen and Levenson 1953, Davratil 1968). Ruch (1960) investigated several solid disposal methods and concluded that they were inferior to other methods and unsatisfactory for fluorine service as their efficiency rapidly decreased due to the formation of a surface coating of reaction products. In addition the solid beds become plugged with the reaction products, with a resulting increase in the pressure

drop.

The use of charcoal beds for the disposal of fluorine was initially avoided because the large amount of heat evolved made the design of equipment difficult and the existence of an explosive reaction product was suspected (Landau and Rosen 1951). More recently, tests have shown that fluorine can be readily and efficiently reacted with charcoal to form an inert carbon tetrafluoride product (Schmidt 1959, 1967, Houston 1960, Pulley and Harris 1972). It was found that explosive reactions could be eliminated by the use of low surface area amorphous (non-activated) charcoal, such as wood charcoal (Pulley and Harris 1972). Operation of carbon-fluorine disposal systems for a number of years at the Lewis Research Centre, Ohio, was summarised by Schmidt (1967) as follows:

(i) Fluorine or fluorine diluted with nitrogen may be disposed of efficiently.

(ii) The maximum flow rate increased with a decrease in the charcoal particle size.

(iii) A charcoal moisture content as high as 30% had no appreciable effect on efficiency after the moisture was driven off by the heat of reaction.

(iv) No evidence of charcoal-bed poisoning was indicated.

(v) For pure fluorine, the concentration of fluorine in the effluent gas was generally in the range 10 to 150 ppm.

As a result of more recent work, Pulley and Harris (1972) concluded that, to obtain the best results, purified dry charcoal should be used and the bed should be maintained at a temperature exceeding 121°C, preferably near 315°C. Under these conditions fluorine concentrations from 0.1 to 10 per cent were readily reduced to less than 50 ppm fluorine.

Fluorine was successfully reacted with superheated steam on a pilot plant scale but the need to provide a spray tower for the disposal of the resulting steam-hydrogen fluoride gaseous mixture made this method unattractive (Schmitt 1952, Smiley and Schmitt 1954, Smith 1957).

6.6.2 Hydrogen fluoride disposal

The following systems were used for the disposal of hydrogen fluoride:

(a) Scrubbing with caustic solution (Landau and Rosen 1948, 1951, Liimatainen and Levenson 1953, Liimatainen and Mechan 1955, Rudge 1956, 1971, Smith 1957, Ruch 1960, Camozzo and Pizzini 1960, Molyneux 1970).

(b) Scrubbing with water (Compton 1946, Landau and Rosen 1951, Schmitt 1952, Smiley and Schmitt 1954, Penland 1955, Smiley and Brater 1956, Giffels and Vallet 1956b, Ruch 1960 Goodyear Atomic Corporation 1967b).

(c) Absorption by a limestone bed. (Reilley 1951, Liimatainen and Levenson 1953, Gilbert et al. 1953, Ruch 1960).

(d) Absorption by sodium fluoride (Compton 1946, Froning et al. 1947, Porter 1948, Smiley and Brater 1956, Jacobson et al. 1956, Rudge 1956, 1971, Watson 1957, Tyner 1958, Dykstra et al. 1958, Ravenscroft and Rudge 1959, Camozzo and Pizzini 1960, Level 1969, Rogan 1972b).

(e) Bubbling through a lime slurry was reported by Reilley (1951), but this method has not received any further attention.

Hydrogen fluoride can be effectively destroyed by scrubbing with caustic solutions using the same process as for fluorine (Smith 1957). Alternatively, water can be used as the scrubbing fluid but the additional corrosion and disposal problems mentioned previously are encountered (Reilley 1951, Ruch 1960).

Giffels and Vallet (1956b) described a scrubber designed to destroy any hydrogen fluoride present in gases vented from the hydrogen fluoride feed system of a fluorine plant. The scrubber was a wet cell air washer with a single bank of spray nozzles, one bank of 101 mm deep wet cells and one bank of 51 mm deep dry cell moisture eliminators. The medium for both cells was Saran fibre and the spray nozzles were fabricated of hard rubber. The casing of the scrubber was constructed of PVC coated steel and all pipes and flanges were unplasticised PVC.

A packed limestone bed absorbed hydrogen fluoride more readily than fluorine, owing to formation of a slow-reacting intermediate compound in the latter case. Hydrogen fluoride was absorbed with both high efficiencies and capacities initially but a rapid decrease in efficiency occurred as a calcium fluoride layer formed on the surface of the limestone particles (Liimatainen and Levenson 1953). As a result, the utilisation of limestone was of the order of 50 to 75 per cent (Reilley 1951, Liimatainen and Levenson 1953).

Sodium fluoride traps (see Table 14) are very efficient and are generally used to remove hydrogen fluoride from fluorine (Rudge 1971). Froning et al. (1947) showed that the efficiency of absorption does not decrease until about 80 per cent of the sodium fluoride is converted to the bifluoride. The spent absorbent is then regenerated by heating to 300^{o}C and driving off the absorbed hydrogen fluoride (see Table 14). Rudge (1971) stated that absorption on potassium fluoride is an obvious alternative but was not used because of a tendency to produce liquid products.

6.7 Equipment Design

6.7.1 Materials of construction

The resistance of various materials to corrosion by fluorine and hydrofluoric acid under a wide range of controlled conditions were reported by Lafferty et al. (1947), Myers and Delong (1948), Doescher (1949), Landau and Rosen (1951), Zima and Doescher (1951), Landau (1952), Brown et al. (1953), Pray et al. (1953), Gundzik and Feiler (1954), Schussler (1955), Braun et al. (1957), Price and Douglass (1956, 1957), Steindler and Vogel (1957), Ericson et al. (1958), Worthington (1958), Bennet (1959), Shuler (1959), Boyd and White (1960), Jackson (1960), White and Fink (1960), Miller et al. (1962), Cabaniss and Williamson (1963), Miller et al. (1963), Singleton et al. (1965), Vincent et al. (1969a, 1969b) and Meile et al. (1971).

McGuffey et al. (1962) described materials (Table 15) used for the handling of fluorine at the Oak Ridge Gaseous Diffusion Plant constructed by Union Carbide. Carbon steel was used up to 205°C for all pipes and fittings in the system and no replacement because of corrosion was necessary in 12 years. Monel piping used in an earlier system showed no significant corrosion after 17 years of continuous service. For service above 205°C, Monel was the most corrosion-resistant material. Monel was also used for orifice plates, impellers, instrument parts and bellows where corrosion deposits could cause operational difficulties. At low temperatures (-85°C), copper and Everdur tube sheets were used in contact with fluorine-hydrogen fluoride mixtures and no leaks had developed after 12 years of service. The fluorine plant constructed by the Goodyear Atomic Corporation at Portsmouth, Ohio was based on the Union Carbide design (Penland 1955, Goodyear Atomic Corporation 1967b) and detailed specifications of all pipes, flanges, gaskets, instruments and valves can be obtained from detailed bills of material published by Giffels and Vallet (1956a, 1956b) which are summarised in Table 16.

Plant practice at Allied Chemical Corporation was described by Neumark and Siegmund (1966) and Siegmund (1967), see Table 17. Carbon steel was used for pipes and fittings in gaseous service and, in sizes up to 2.5 cm, flare-tube or compression-type fittings were also satisfactory. It was recommended that valves should have plugs and seats of dissimilar metals.

Information on materials suitable for the industrial handling of hydrogen fluoride has been published by Hill and Knott (1960), Stauffer Chemical Company (1964), Forry and Schrage (1966), Thornton (1970) and Imperial Chemical Industries Limited (1971). Some of the available data are summarised in Tables 18, 19 and 20. A significant amount of this data was taken from a

publication by the Manufacturing Chemists' Association (1970) and this article should be consulted for recommended practices on all phases of the handling of hydrogen fluoride. For general piping, Imperial Chemical Industries recommend steam quality seamless pipe constructed of mild steel with flanged joints. Copper is recommended for small scale work and joints made by compression fittings are allowed. Mild steel is also a satisfactory material of construction for pressure vessels containing anhydrous hydrogen fluoride, provided that high standards of construction are observed (Hill and Knott 1960, Forry and Schrage 1966, Thornton 1970). However, despite the data on corrosion which are available, the Stauffer Chemical Company (1964) advised that prior to the final selection of materials, any situation should be investigated by corrosion tests under conditions similar to those to be encountered. Those variables which have the greatest effect on corrosion were stated to be:

Degree of agitation
Flow and/or turbulence
Aeration
Temperature and pressure
Erosion which removes protective film
Fluctuations in any of the above
Organic and inorganic impurities (may inhibit or accelerate action)

6.7.2 Fabrication techniques

Rapid corrosion is promoted by the presence of slag or porosity in welds for fluorine and hydrogen fluoride service. A high quality of welding was obtained by strict adherence to good welding practice and the development of special welding techniques (Dykstra et al. 1955, Barnett 1959, Clark 1960, Phillips 1961, Edwards 1961, Chilenskas and Gunderson 1965, Smiley 1965, Smiley et al. 1966, McGraw 1967, Schmidt 1967, Henry Wiggin and Co. 1971). Schmidt (1967) described in detail a welding procedure adopted at Lewis Research Centre for fluorine or fluorine-oxygen service. Welding was performed by a qualified welder using a shielded arc process with an inert gas backup to prevent the pipe from being contaminated with slag which could not be removed by normal cleaning procedures. The weld was protected by a purge with argon or helium gas before welding was started, but during welding the purge was reduced to prevent blowout of the weld. An appropriate filler rod was added on the first pass and the remaining passes were metal-arced to minimise distortion and carbon precipitation in susceptible alloys and to increase welding speed. After the first pass, the weld was inspected carefully for cracks, craters, pinholes or slag. Craters, cracks and rough spots were

ground out before the weld was continued. Welded joints were stress relieved, if necessary, by heat treating and then radiographed. Welds with poor penetration, flux or slag inclusions, pockets, bubbles or surface flaking were not permitted.

Similar welding practices were adopted for equipment in HF service. Thornton (1970) stated that all vessels routinely in contact with HF or trace acid service were specified to be postweld heat treated whether or not applicable codes required this. Such vessels were also 100 % radiographed for further assurance of quality, particularly for freedom from slag inclusions in welds and plates as the silicon content of the metal and the slag from welding were major sources of corrosion. No major repair welding was permitted without re-radiographing and re-heat treating the repair.

6.7.3 Procedures prior to plant operation

All equipment, lines and fittings for fluorine service must be cleaned thoroughly to minimise uncontrollable fluorine reactions with grease, oil or any foreign matter. McGuffey et al. (1962) stated that pipe and fittings were vapour degreased and acid cleaned. Subassemblies were shop-fabricated and acid cleaned so that only field closure joints were in the as-welded condition. Each valve was disassembled, degreased, and inspected for acceptable materials. Gaskets and thin-wall assemblies such as rupture discs were degreased and installed with clean cotton gloves. The practice at Allied Chemical Corporation (Siegmund 1967) was to flush the assembled system with a non-aqueous degreasing solvent such as trichlorotrifluoroethane.

After cleaning, piping 3 inches (approx. 78 mm i.d.) and smaller was soap tested at gauge pressures up to 345 kPa using dry air or nitrogen. A hydrostatic test was applied to larger pipe and also for those parts of the system which operated at higher pressure. After testing the components were dried with air until a dew point of -40^{o}C in the exhausted air was reached. At this point the system was purged and filled with nitrogen to ensure that no volatiles were present (McGuffey et al. 1962). By contrast, Siegmund (1967) reported that Allied Chemical Corporation practice was to pressure test fluorine systems before cleaning. The final step before operation consisted of slowly displacing the dry nitrogen in the system with gaseous fluorine at essentially atmospheric pressure. This procedure was intended to remove the last traces of foreign material (and prevent an uncontrollable fluorine reaction) and to form a passive fluoride film on metal surfaces. The displacement of nitrogen was continued until there was evidence of strong fluorine gas at the exit end of the system. The system pressure was gradually

brought up to the working level over a period of 2 hours, and held at that level for 2 hours to complete the passivation process (McGuffey et al. 1962, Neumark and Siegmund 1966, Siegmund 1967). The duration for which the system was held at working pressure was apparently important as earlier practice was to hold working pressure for only 5 to 10 minutes (Allied Chemical Corporation 1961).

6.8 Safety Practices and Equipment

The experience of Allied Chemical Corporation and Union Carbide Corporation at the Oak Ridge Gaseous Diffusion Plant showed that the industrial handling of fluorine does not present any problems greater than those associated with other reactive or toxic chemicals. McGuffey et al. (1962) reported that not a single lost-time injury occurred during a 17 year period of fluorine handling at Oak Ridge. Allied Chemical Corporation reported a similar record (Neumark and Siegmund 1966, Siegmund 1967). These records were mainly as a result of considerations of safety in both plant design and operational procedures leading to the observance of rigid material and welding specifications and strict cleaning and purging practices (Huber et al. 1958, McGuffey et al. 1962, Neumark and Siegmund 1966, Siegmund 1967). Huber et al. (1958) stated that the most serious potential hazards were associated with liquid hydrogen fluoride and molten electrolyte and emphasised the importance of an extended period of showering and surgical scrubbing in the event of possible exposure to liquid hydrogen fluoride of any concentration. The Manufacturing Chemists' Association (1970) also stressed the importance of showering and prompt removal of contaminated clothing following contact with liquid acid of concentrated vapours. The Association stipulated that readily accessible, well marked and frequently inspected rapid-action safety showers must be available. They should be capable of supplying large quantities of water under moderately high pressure. Blankets should be located near the safety showers. Special eye washing fountains, bubbler drinking fountains or hoses with a gentle flow of tap water of drinking quality should also be available for eye irrigation. They should be readily accessible in the work area and should be inspected frequently.

Other accessories considered necessary for hydrofluoric acid handling are:

(a) Clean water in ample quantities

(b) Hose connections for flushing spilled acids

(c) Soda ash or lime for neutralising spilled acids

(d) Adequate facilities for washing protective clothing before removal.

The Manufacturing Chemists' Association (1970) summarised the most important factors in the prevention of injury by hydrofluoric acid and these factors are equally applicable to the handling of fluorine.

(a) All contact of gas, vapour or liquid with eyes, skin, gastro-intestinal tract or the respiratory system must be prevented.

(b) All employees must be fully aware of the hazardous nature of the products and properly trained in routine operations and emergencies.

(c) Adequate ventilation must be provided in operational areas at all times. Under normal conditions, good natural ventilation may be sufficient, otherwise mechanical ventilation should be provided.

The maximum allowable concentration values for continuous 8 hour exposure for fluorine and hydrogen fluoride set by the American Conference of Government Industrial Hygienists (1970) are 0.1 ppm and 3 ppm respectively. Emergency exposure limits for these materials were established by the Committee on Toxicology of the National Research Council (U.S.A.), these were reported by Siegmund (1967) and are listed in Table 24. Siegmund (1967) suggested that extrapolation of these figures shows that exposure to 12 ppm of fluorine for five minutes would cause no irreparable damage.

(d) An adequate supply of approved personal protective clothing must be acquired and maintained in perfect condition while it is being used in operations or while it is in a convenient storage location for use in emergencies. Locations of such equipment should be marked clearly. However, it is warned that personal protective equipment is not an adequate substitute for good, safe working conditions, adequate ventilation and intelligent conduct on the part of employees.

6.8.1 Ventilation

The fluorine plants operated by the Union Carbide Corporation, Goodyear Atomic Corporation, Allied Chemical Corporation, La Societe des Usines Chimiques de Pierrelatte have forced ventilation systems designed to provide fresh air for personal comfort and safety (Smiley and Brater 1956, McGuffey et al. 1962, Bergeret 1965, Goodyear Atomic Corporation 1967a, 1967b, Siegmund 1967). The fluorine production facilities at Oak Ridge (Tennessee) and Portsmouth (Ohio) were each housed in single buildings in which the ventilation systems were designed to provide both normal and emergency rates of air change (see Table 22) in several areas of the process which were considered to be

critical in the event of chemical leakage. These areas were maintained at negative pressure with respect to their surroundings to ensure any releases were localised and withdrawn with the exhaust air and discharged through a 20.8 m stack which vented above adjacent buildings. At the top of the stack, a venturi section introduced sufficient air to provide a 50 per cent dilution of the exhaust gas (Smiley and Brater 1956, McGuffey et al. 1962, Goodyear Atomic Corporation 1967b). The ventilation system was designed to provide a noise level below 70 decibels to ensure satisfactory working conditions (Goodyear Atomic Corporation 1967b). In addition to the main ventilation system, spot ventilation and hoods were provided as required. Despite these precautions routine air-monitoring was considered to be a necessary adjunct to the overall safety program (Smiley and Brater 1956). Details of two commercial detection devices suitable for monitoring small concentrations of fluorine and hydrogen fluoride in air have been described by Neumark and Siegmund (1966) and Siegmund (1967).

Virtually no information is available on the ventilation systems at the Allied Chemical Corporation's plant and the Pierrelatte Chemical Factory. Bergeret (1965) stated that as a result of cell arrangement in the latter installation, the flues ventilating the electrolysis hall were kept close to each line of cells. This arrangement enabled continued cleaning of the working areas occupied by operators. The clean air entered by ventilators in the walls, crossed pipework and was discharged, after purging the equipment, by orifices which led into ventilation pipes below the floor. The normal rate of air change was three changes per hour but in the case of a large leak, this rate was doubled.

6.8.2 Protective clothing - handling of hydrogen fluoride

Hill and Knott (1960), Stauffer Chemical Company (1964), Forry and Schrage (1966), Thornton (1970) and Imperial Chemical Industries (1971) described protective clothing suitable for various operations involving the handling of hydrogen fluoride. The practices adopted followed closely the recommendations published by the Manufacturing Chemists' Association (1970) which are summarised below:

Employees should wear full coverage of clothing at all times. Working bareheaded, with shirt sleeves rolled up, or in an undershirt is exceedingly hazardous. Rubber shoes soled with Neoprene or an equally resistant material or rubbers made of same materials, a hat or protective head covering, a full face mask or chemical goggles with plastic lenses and gauntlet-type gloves made of Neoprene, plasticised polyvinyl chloride (0.71 ± 0.025 mm thick) or an

equally resistant material, should be used at all times in operating areas.

Full protective equipment recommended when making repairs, connecting and disconnecting tank cars, discharging containers, etc., consists of an acid hood with plastic window, an acid coat, rubber, Neoprene or plasticised polyvinyl chloride overalls and gauntlet-type gloves made of Neoprene, plasticised polyvinyl chloride or an equally resistant material. When leakage is abnormally large and the hydrofluoric acid vapor concentration is high or unknown, positive pressure hose masks, air line masks or self-contained breathing apparatus should be used. The highest degree of protection is afforded by the use of an acid-proof air inflated suit with a mask and safety belt included.

Recommended Types of Protective Clothing

Chemical safety goggles

Positive eye protective equipment such as cup-type rubber or soft plastic framed goggles equipped with plastic or impact-resistant glass lenses should be worn whenever there is danger of hydrofluoric acid coming in contact with the eyes. Goggles should be carefully fitted by adjusting the nose piece and head band to ensure maximum protection and comfort.

Spectacle-type safety goggles

Metal or plastic rim safety spectacles with side shields which can be obtained with prescription safety lenses or suitable all-plastic safety goggles may be used where continuous eye protection is desirable, as in laboratories. These types, however, should not be used where complete eye protection against hydrofluoric acid is needed.

Face shields

Plastic shields (full length 204 mm minimum) with forehead protection may be worn in addition to chemical safety goggles, where complete face protection is desirable. Chemical safety goggles should always be worn as an added protection where there is danger of material striking the eyes from underneath or from around the sides of the face shield.

Respiratory protection

Severe exposure to hydrofluoric acid may occur during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposures should be provided with proper respiratory protection and trained in its use and care. Available types are described below.

(a) Self-contained Breathing Apparatus which permits the wearer to carry a supply of oxygen of air compressed in the cylinder, and the self-

generating type which produces oxygen chemically. These allow considerable mobility. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air, oxygen or regenerating material carried. Compressed oxygen should not be used where there is danger of contact with flammable liquids, vapors, or sources of ignition, especially in confined spaces such as tanks or pits.

(b) Positive Pressure Hose Masks supplied by blowers requiring no internal lubrication. The wearer must be able to use the same route for exit as for entrance and must take precautions to keep the hose line free of entanglement. The air blower must be placed in an area free of contaminants.

(c) Air-line Masks supplied with clean compressed air. Unless equipped with 'demand' valve and a small reserve cylinder of compressed air, these are suitable only where conditions will permit safe escape in case of failure of the compressed air supply. These masks are usually supplied with air from a plant air system or from a compressor. The safer method is a plant air system which is specified and carefully maintained to furnish 'breathing air'. Local oil separators may be needed even with such a system. Local compressors may be used but care is needed to make sure that the air intake is safely located. Compressors not requiring internal lubrication are preferred for this service.

(d) Industrial Canister Type Gas Masks, equipped with full face pieces and approved by the U.S. Bureau of Mines, fitted with the proper canister for absorbing hydrofluoric acid. These will afford protection against concentrations not exceeding 2 per cent by volume when used in accordance with the manufacturer's instructions. The oxygen content of the air must not be less than 16 per cent by volume. The masks should be used for relatively short exposure periods only. They may not be suitable for use in an emergency, since, at that time, the actual vapor concentration is unknown and an oxygen deficiency may exist. The wearer must be warned to leave the contaminated area immediately on detecting the odor of a harmful vapor. This may indicate that the mask is not functioning properly, the vapor concentration is too high, the canister is exhausted or the mask is not properly fitted.

NOTE: Where carbon monoxide or other gas having little or no odor may be encountered in addition to hydrofluoric acid, the mask should be equipped with an 'all purpose canister' and a 'timing device' or a colorimetric window indicator as approved by the U.S. Bureau of Mines. Whenever the concentration of contaminants might exceed the filtering capacity of the canister, a self-contained or supplied-air unit must be used.

(e) Hats. Safety or 'hard' hats will provide protection against

accidental liquid leaks, falling tools or other objects. Brimmed felt hats may be substituted for safety hats where the danger of falling objects is remote.

6.8.3 Protective clothing - handling of fluorine

Clothing and protective equipment suitable for use in fluorine plants are generally similar to the types recommended for use with hydrogen fluoride. The specific practices adopted at most fluorine plants have been consistent although a relaxation of requirements was evident after a number of years of operation.

Oak Ridge Gaseous Diffusion Plant

Safety clothing (coveralls, safety shoes, and safety glasses) were worn in the cell room. In addition acidproof goggles or safety glasses and a face shield were worn when cells were being filled, electrolyte levels or samples were being taken or electrical switching was being done. Only minor work was done on a fluorine cell while it was in operation, and personnel were required to work from an insulated stand and to wear insulated rubber gloves in addition to other protective clothing (Jacobson et al. 1955). In most releases of fluorine or HF, Army assault masks provided sufficient protection. For extreme cases oxygen-generating masks were required. Filter-type respirators were used during the handling of potassium bifluoride powder (Huber et al. 1958).

Protective clothing such as Neoprene gloves, suits, gas masks and oxygen masks, protective goggles or face shields, and footwear were available where needed for both routine and emergency operation. Purging and testing of equipment contents before opening was standard procedure (Smiley and Brater 1956).

For normal operation with low pressure fluorine, the operator wore safety glasses and polyvinyl chloride gloves, but if the pressure was above 17.2 kPa gauge, a Fluorethene face shield was worn also. Respirators equipped with an M-11 canister were provided, and for emergencies additional protective gear, such as combat masks and impermeable suits, were used.

An impermeable suit of PVC, calendered to both sides of a nylon base, was developed. The suit completely covered the wearer, and fresh air was supplied through a hose connection for both respiratory and cooling purposes. A sound powered telephone was built into the mask. Replaceable fabric gloves dip-coated with PVC were attached to the sleeves by a simple but foolproof method of sealing. A tapered hollow cone inside the cuff of the glove was seated downward to match another tapered cone attached to the sleeve. The

suits, procured from the Mine Safety Appliance Co., were used during vessel inspection, and experience showed that clean PVC could withstand a jet of pure fluorine. These suits were therefore available for extreme emergencies, rescue work, and vessel inspection.

The Mine Safety Appliance Co.'s Gasfoe respirator with GMA chemical cartridge was satisfactory for nuisance concentrations, and was tested up to 500 ppm of fluorine. The M-9 combat mask with the M-11 canister was safe for concentrations up to 5000 ppm provided there was sufficient oxygen in the atmosphere and the body was protected by an impermeable suit (McGuffey et al. 1962).

Portsmouth Gaseous Diffusion Plant

During the entire transfer operation of hydrogen fluoride, 'Neoprene Supreme' type rubber gloves were worn and an assault mask was kept at stand-by. A 'Gra-Lite' suit and hood were worn when making and breaking all connections. Gloves and a face shield were worn in the cell room at all times (Goodyear Atomic Corporation 1967a).

Allied Chemical Corporation's Plant at Metropolis

Neoprene gloves, coats and boots were recommended for over-all body protection for short intervals of contact with low-pressure fluorine and hydrofluoric acid. All protective clothing was designed and used in such a manner that it could be shed easily and quickly. Safety glasses were worn at all times and face shields made of conventional materials, or preferably transparent, highly fluorinated polymers, such as Aclar or Kel-F were worn whenever operators approached equipment containing fluorine under pressure. For respiratory protection, a face mask with a self-contained air supply, such as a Scott Pak, was available (Neumark and Siegmund 1966, Siegmund 1967).

6.8.4 First aid procedures

Toxicity

Fluorine is a highly toxic gas, it has a sharp penetrating and characteristic odor detectable in low concentrations. Because of this, the inhalation of seriously toxic quantities is unlikely. In contrast with thermal-type burns produced by contact with high fluorine concentrations on the skin, experience has shown that lower fluorine concentrations on the skin produce a chemical type burn resembling those produced by hydrofluoric acid (Matheson Co. 1966). Braker and Mossman (1970) recommend that the first aid treatment to be followed for fluorine is that for hydrofluoric acid and fluorine-containing compounds which form hydrofluoric acid on hydrolysis by moisture.

Hydrofluoric acid is strongly corrosive. Both the liquid and vapour are

dangerous when in contact with the eyes, skin, or mucous membranes and, if taken by mouth, the liquid will have a corrosive effect on the gastro-intestinal tract. Either the liquid or vapor of anhydrous hydrogen fluoride in contact with any part of the body immediately causes serious and extremely painful burns if not properly treated. Concentrated aqueous solutions may also cause early sensations of pain; however, dilute solutions may not give any indication of pain or visible effect until hours after skin exposure, during which time the fluoride ion has already penetrated the skin causing possible destruction of tissues and, if severe enough, possible later development of skin ulcers. One does not become accustomed to low vapor concentrations. The vapor has such a sharp and penetrating odor that the inhalation of seriously toxic quantities is not likely unless the victim is trapped in such a location that escape from the vapor is impossible. In such an emergency and for escape purposes only, breathing through cloth or dry clothing may reduce the concentrations of vapors sufficiently to save one's life.

First Aid

The Manufacturing Chemists' Association (1970) recommended the following first aid actions for exposure to hydrofluoric acid.

General Principles

Speed in removing the patient from the contaminated atmosphere and in removing hydrofluoric acid from the skin or eyes is of primary importance. First aid must be started immediately in all cases of contact with hydrofluoric acid in any form. All affected persons should be referred to a physician, even when immediate injury seems slight, and the physician should be given a detailed account of the accident.

Specific Actions

(a) General First Aid after Skin Contact with Liquid or Vapor

Workers who have had contact with hydrofluoric acid should be subjected immediately to a drenching shower of water. The clothing should be removed as rapidly as possible, even while the victim is in the shower, and medical assistance obtained immediately. It is essential that the exposed area be washed with copious quantities of water for a sufficient period of time to remove all hydrofluoric acid from the skin. Following this, an iced aqueous or alcholic solution, 0.13 % (1:750), of benzalkonium chloride ('Zephiran' Chloride); an ice-cold saturated solution of magnesium sulfate (Epsom Salt); or iced 70 % alcohol should be applied for at least 30 minutes. If the burn is in such an area that it is impracticable to immerse the part, then the iced solution should be applied with saturated compresses, which should be

changed at least every two minutes. The physician should be available by then to administer further treatment before the completion of the iced solution treatment. If, however, a physician is not available by that time, the treatment with one of the iced solutions should be continued for two to four hours. It is then permissible to apply a generous quantity of paste made from powdered magnesium oxide and glycerine, freshly prepared. This is prepared by the addition of U.S.P. glycerine to U.S.P. magnesium oxide to form a thick paste. Oils and greases should not be applied except under instruction from a physician.

(b) Contact with Eyes

The magnesia paste recommended for hydrofluoric acid burns should be used only for skin burns, not for eye burns. If liquid hydrofluoric acid has entered the eyes or if the eyes have been exposed to strong concentrations of the vapour, they should be irrigated immediately and copiously with clean water for a minimum of 15 minutes. The eyelids should be held apart during the irrigation to insure contact of water with all the tissues of the surface of the eyes and lids. A physician, preferably an eye specialist, should be called in attendance at the first possible moment. If a physician is not immediately available, instill one or two drops of 0.5 % pontocaine solution, or an equally effective aqueous topical anaesthetic followed by a second irrigation for 15 minutes. No oils or oily ointments should be instilled unless ordered by a physician.

(c) If Taken Internally

Ingestion of hydrofluoric acid causes severe burns of the mucous membrane of the mouth, throat, esophagus and the stomach. Here copious irrigation is not feasible and no attempt should be made to pass a stomach tube except by the attending physician. The patient should be encouraged to drink a large quantity of water without delay. After the hydrofluoric acid has been diluted with water, milk or 2 ounces of milk of magnesia may be administered for their demulcent or soothing effect.

(d) Inhalation

A worker who has been suspected of a possible severe exposure to gaseous hydrofluoric acid should be carried at once into an uncontaminated atmosphere. Even in the absence of symptoms, a worker must not be permitted to return to work for at least 24 hours after a severe exposure because of the potential danger of developing severe edema of the lungs. A physician should be called immediately and first aid started at once.

If breathing has stopped, begin artificial respiration (mouth to mouth

resuscitation). Before starting, remove patient's dentures, if present, and clear the mouth and throat of any foreign material to allow free passage of air.

If inhalation-equipment and a trained attendant are available, oxygen administration should be started at once.

All individuals breathing hydrofluoric acid vapor should be examined by a physician and held under observation for at least 24 hours following exposure. It is possible for a delayed reaction of a serious nature to occur even in persons inhaling only mild to moderate concentrations of hydrofluoric acid vapor.

Patients should remain quiet - preferably lying down and kept warm and comfortable. Stimulants should not be given unless ordered by a physician.

Under no circumstances should a patient be permitted to return home or back to work until examined and discharged by a physician who is aware of the nature of his exposure.

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TABLE 1

EARLY LABORATORY CELLS

Investigators	Year	Electrolyte	Temp. (°C)	Cell Shape	Body	Cathode	Anode	Diaphragm	Insulation/Cement	Current (A)	Voltage (V)
Moissan	1886	KF.12HF	-23 to -80	U Tube	Pt/Ir or Copper	Body	Platinum		Ground fluorspar, lead washers and shellac		
Argo et al.	1919	KF.HF	225-250	Cylindrical	Copper, 89 mm diameter	Body	Graphite	Copper (slotted)	Finely powdered fluorspar	10	12 - 15
Meyer and Sandow	1921	KF.HF	240-250	Cylindrical	Graphite	Body	Acheson graphite	Copper	Compressed ring of calcium fluoride	9 - 11	14 - 16
Simons	1924	KF.HF	220-280	Cylindrical	Copper	Body	Graphite	Copper (slotted)	Portland Cement	10 - 15	10
Mathers	1924	KF.HF		Cylindrical	Graphite	Body	Graphite	Graphite	Ground fluorspar and melted KF.HF		12 - 15
Bancroft and Jones	1929	KF.HF	220-300	Cylindrical	Magnesium, 95 mm diameter	Body	Graphite	Magnesium	Portland Cement	5 - 6	
Fredenhagen and Krefft	1929	KF.HF → KF.1·8HF	160-250	Cylindrical	Copper	Body	Graphite			20	8.5 - 9
Schumb and Gamble	1930	KF.HF	220-300	Cylindrical	Monel, 105 mm diameter	Body	Graphite	Monel (slotted)	Portland Cement	12 - 15	3 - 4
Dennis et al.	1931	KF.HF	230-280	V-shape	51 mm copper pipe	Graphite	Acheson graphite		Bakelite Cement	10	18
Bigelow et al.	1933	KF.HF	250-300	Cylindrical	Copper	Body	Graphite	Copper (slotted)	Fluorite rings	5	8 - 10
Denbigh and Whytlaw-Gray	1934	KF.HF	230-280	Cylindrical	Copper, 127 mm diameter	Body	Acheson graphite	Copper	Paste of CaF_2 and water glass	12 - 15	13
Bodenstein et al.	1935	KF.HF	250	Cylindrical	Elektron alloy	Silver	Graphite	Elektron (slotted)	Frozen electrolyte		
Miller and Bigelow	1936	KF.HF	250	U-Tube shape	Nickel	Graphite	Graphite		Ground fluorspar and sodium silicate	5	18 - 20
Simons	1939	KF.HF	220-260	Cylindrical	Copper, 76 mm diameter	Body	Graphite	Copper (perforated)	Portland Cement	10	10 - 20
Aoyama and Kanda	1937	KF.HF	240-250	V-shape			Acheson graphite			5	15
Lebeau and Damiens	1925	KF.3HF	60 - 70	Cylindrical	Copper	Body	Nickel	Copper (Slotted)			
Von Wartenberg and Klinkott	1930	KF.3HF	70	Cylindrical	Copper, 89 mm diameter	Body	Coiled Nickel Wire	Copper	Calcium fluoride-starch mixture	6	
Henne	1938	KF.3HF	70 - 100	V-shape	Copper	Graphite	Graphite		Portland Cement or polymerised varnish		
Cady	1939	KF.2·2HF	73- 75	Cylindrical	Monel, 102 mm dia.	Body	Nickel	Copper	Portland Cement	12	
Cady et al.	1942	KF.2HF	73 - 80	Cylindrical	Steel	Body	Nickel (or graphite)	Copper	Portland Cement	2 - 18	6 - 20

TABLE 2

MELTING POINTS OF METAL FLUORIDES

(After Weast 1970)

Compound	Melting Point (^{o}C)
NaF	988
CuF	908
ZnF_2	872
MnF_2	856
PbF_2	855
KF	846
LiF	842
RbF	775
CsF	682
HgF	570
AgF	435

TABLE 3

MELTING POINTS OF ALKALI POLYFLUORIDES (^{o}C)

Compound \ Source of Data	Neumark (1947)	Winsor and Cady (1948)	Cady (1934)	Prideaux and Webb (1937)	Mathers and Stroup (1934)
KF.HF	239		239		
RbF.HF	210			204-205	
CsF.HF	169	176			142
CsF.1·5HF		60			30
KF.2HF	71.9		71.7		
RbF.2HF	62.5			51.6	
CsF.2HF	48.0°	50.2			
KF.2·5HF	64.0		64.3		
CsF.2·5HF		24.0			
KF.3HF	65.8		65.8		
RbF.3HF	52.0			0	
CsF.3HF	33.0	32.6			
KF.4HF	72		72		
RbF.4HF	32				
CsF.4HF	Below 0	0			

TABLE 4

INDUSTRIAL CELLS - OPERATING CHARACTERISTICS

CELL TYPE	Units	I.G.Farbenindustrie Falkenhagen 1940	I.G.Farbenindustrie Leverkusen 1942	Hooker 1943 - 1944	Hooker 1943 - 1944	Hooker 1944	Du Pont (Semi-Works Area) 1944	Du Pont (Blue Products Area) 1945	Du Pont (East Area) 1945
Normal Current Capacity	A	2,000	2,000	2,000	1,500	1,000	1,500	1,000	1,200
Maximum Current Capacity	A	2,500			2,000				1,500
Fluorine Output (Normal)	kg/h	1.41	1				>0.68	0.6	0.76
Current Efficiency	%	95	85			90 or better	66	85	90
Voltage at Normal Load	V	6-6.5 (increases with time)	11 - 13				Increased from 9 to 11.5	Not allowed to exceed 10.5	10-11.5
Anode Current Density at Normal Load	A/m^2	650-775	1,000	895	672	770	2,040		
Cathode Current Density at Normal Load	A/m^2		1,310			approx. 655	2,020		
Electrolyte Temperature	^oC	250	72-90			105	90-105	95-110	95-110
HF Content of Electrolyte	Wt%	25.6	46.3			39	44.5	38.5-40.5	38-40
Electrolyte Purity and Preliminary Treatment		Electrolyte is pre-electrolysed at 5-10 volts to remove water and other impurities	Electrolyte purity is not critical		Water removed by electrolysis with nickel electrodes	Water removed by electrolysis with nickel electrodes		Moisture <0.2%; water removed by electrolysis with nickel electrodes for 2 days	Moisture <0.2% conditioned with nickel anode at 400-500 A for 60 h
HF Feed Purity		HF was vaporised and reacted with fluorine to remove water and SO_2.	Technical grade (96.5% HF) was used					Impurities less than 0.8%	Impurities less than 0.8%
Life of Cell Body	A h					17×10^6			
Life of Diaphragm	A h					8.6×10^6			
Life of Anodes	A h	26×10^6	26×10^6			$18 - 21 \times 10^5$			
Cell Service Life	A h	$17 - 26 \times 10^6$					7.5×10^5	1.5×10^6	
Polarisation Frequency		Not frequent	Not frequent	10 days	Never	Periodic			
Methods of Overcoming/Preventing Polarisation		Cell is run at 500-800 A and 30-60 V initially to condition the anode surface	Cell is initally run at 500 A		Carbon powder-water paste used on anode	Maintain optimum electrolyte composition and temperature		2% LiF (13.6 kg) added to electrolyte	2% LiF added to electrolyte
HF in Fluorine	Vol.%		8.5			4 to 8	5 to 15	5 to 15	5 to 15
HF in Hydrogen	Vol.%								
Cooling Water Temperature Inlet/Outlet	^oC								
Problems/Features		Cell service life is determined by need for electrolyte regeneration		Swelling and breaking of anodes	Bipolar corrosion of the diaphragm	Anode paste not fully effective	Sludge accumulated from corrosion of skirt and anode support	Too rapid addition of HF caused explosions	
References		Carter et al.1946 Neumark 1947	Carter et al.1946 Karr 1946	Murray et al.1946 1947, 1951	Murray et al.1946 1947, 1951	Murray et al.1946 1947, 1951	Downing 1944	Trepper 1945	Stevenson 1945

TABLE 4 (Cont'd.)

INDUSTRIAL CELLS - OPERATING CHARACTERISTICS

CELL TYPE	Units	Du Pont 1946	Harshaw 1944	Harshaw 1944	Johns Hopkins University 1946	Pennsalt 1946	Pennsalt 1948	Union Carbide 1955	Union Carbide C-Type 1956
Normal Current Capacity	A	1,500	1,000	1,000	600	250	1,500	3,500	4,000
Maximum Current Capacity	A			1,500	650		2,000	4,000	6,000
Fluorine Ouput (Normal)	kg/h	0.91			0.34	0.15	1.14	2.84 (at 4,000 A)	4.1 (at 6,000 A)
Current Efficiency	%	88	Approx. 95	95 or better	90-95, falling to 55			90-95	97
Voltage at Normal Load	V	8.5-10	9.1	9	6-8	8.5-9.0		8-10	8-12
Anode Current Density at Normal Load	A/m^2	806	1,020	1,620	3,240	806		1,180	1,010
Cathode Current Density at Normal Load	A/m^2	1,020	1,080	1,080		560			
Electrolyte Temperature	°C	100-110	107	105	260-310	95-105	105-110	100-105	91-108
HF Content of Electrolyte	Wt%	39-40.5	38.7	38.7	25.5	38-40	40	41	40-42
Electrolyte Purity and Preliminary Treatment		Conditioned with nickel anode for 3×10^4 A h.	Water removed by electrolysis with nickel anodes for 24 h at 8 V	Water removed by electrolysis with nickel anodes, or carbon anodes, at low current density		Conditioned with nickel anode at 150 A for 8 h	$H_2O<0.05\%$; $K_2SiF_6<0.2\%$; $SO_4<0.1\%$; $Cl<0.05\%$	Moisture is 0.001 to 0.003%, fluorine is used to precondition electrolyte.	Fluorine is used to precondition the electrolyte
HF Feed Purity		Impurities less than 0.8%					$H_2O<0.2\%$, $SO_2<0.06\%$, $H_2SiF_6<0.1\%$	Impurities less than 0.1%	HF is 99.95% pure when fed to the cell
Life of Cell Body	A h							$>40 \times 10^6$	
Life of Diaphragm	A h				7.8×10^6			40×10^6	
Life of Anodes	A h		$2\text{-}20 \times 10^5$	$>8.6 \times 10^6$	1.87×10^5			5×10^6	16×10^6
Cell Service Life	A h	1.29×10^6						3.5×10^6	16×10^6
Polarisation Frequency			Irregular	Greater than 1 year	Periodic, increasing with age			Occasional	Infrequent
Methods of Overcoming/ Preventing Polarisation		2% LiF added to electrolyte	Use of nickel anode and initial addition of LiF	Addition of 1.0 to 1.5% LiF	Increase voltage until current returns to normal			Cell is run at 30-48 V for 2-10 minutes; LiF is added	Cell is run at high voltage initially
HF in Fluorine	Vol.%					10	10	Approx.	Approx. 15
HF in Hydrogen	Vol.%							Approx. 15	Approx. 15
Cooling Water Temperature Inlet/Outlet	°C		98/98	98/98				51/69	32-49/53-60
Problems/Features		Plugging of pipe lines and failure of cell jacket	Addition of large amounts of HF caused polarisation		Corrosion products accumulated on the anode bars	Explosion occured frequently	Composition and temperature of electrolyte need close control	Broken anodes caused by explosions.	Corrosion of metal parts of the anode assembly
References		Downing et al.1947 Downing 1951	Williams et al.1944 Long et al.1951	Williams et al. 1944, Long et al. 1951	Fowler et al.1947, Burford et al.1951	Gall and Miller 1947	Porter 1948	Dykstra et al.1955, Smiley and Brater 1956	Smiley and Brater 1956, Vavalides et al. 1958

TABLE 4 (Cont'd.)

INDUSTRIAL CELLS - OPERATING CHARACTERISTICS

CELL TYPE	Units	Goodyear Atomic(Modified C-Type)1956	ICI 1956	Union Carbide 1958	Union Carbide (E-Type)1959	Allied Chemical 1959 - 1960	Union Carbide 1962	Pierrelatte Chemical Plant 1965	ICI 1960 - 1970
Normal Current Capacity	A	4,000 - 6,000	1,400	6,000	6,000	4,000	1,000	6,000	5,000
Maximum Current Capacity	A					5,000			6,500
Fluorine Output (Normal)	kg/h	3.8 (at 4,000 A)	0.91	3.8			0.75		3.3
Current Efficiency	%	90	93					95-96	93
Voltage at Normal Load	V		10	8-12				8.5-10	10 (at 5,000 A)
Anode Current Density at Normal Load	A/m^2		1010	1,540	1,500-1,600			1,300	1,800
Cathode Current Density at Normal Load	A/m^2		540	1,250	1,250				360
Electrolyte Temperature	^oC	88-99	80-85	91-108		95	82-104	85-95	80-85
HF Content of Electrolyte	Wt%	40-41.5	40-41.5	40-42		40-42		40.8	40-41.5
Electrolyte Purity and Preliminary Treatment		Fluorine is used to precondition the electrolyte	Purity is not critical	Electrolyte is prepared from high purity KF.HF and HF. Fluorine is used to precondition electrolyte		Electrolyte is prepared from high purity KF.HF and HF		Fluorine is used to precondition the electrolyte	Purity not critical, cell is started at low load to remove water
HF Feed Purity			Water content is not critical	HF is 99.95% pure when fed to the cell		Rigid specifications of purity are maintained	HF purity is 99.9%		Purity not critical
Life of Cell Body	A h		$>75 \times 10^6$	80×10^6					$>48.5 \times 10^7$
Life of Diaphragm	A h		25×10^6					$15-20 \times 10^7$	17.6×10^7
Life of Anodes	A h		19×10^6	32×10^6	85×10^6				66×10^6
Cell Service Life	A h		13×10^6	$15-30 \times 10^6$	85×10^6			20×10^6	44×10^6
Polarisation Frequency			No polarisation in 5 years.	Several months before trouble is likely					No polarisation has ever occurred
Methods of Overcoming/ Preventing Polarisation		LiF is added to the electrolyte		Cell is run at high voltage or low current at start-up				Cell is conditioned at 1,500 A	
HF in Fluorine	Vol.%		10	11				6-8	6
HF in Hydrogen	Vol.%		4	9					4
Cooling Water Temperature Inlet/Outlet	^oC		Approx.65/67	74-80/77-83		Approx.75/75			65/67
Problems/Features				Corrosion products increased 50% over earlier cells	Cell has to be desludged at half life			Electrolyte mist is removed by an electrostatic precipitator	
References		Penland 1955, Goodyear Atomic Corporation 1967a, 1967b	Rudge 1956	Huber et al.1958, Powell et al. 1960	Clark 1960, Kelly and Clark 1967a	Neumark and Siegmund 1966	Henderson et al. 1962	Bergeret 1965, Level 1969	Rudge 1971

TABLE 5

INDUSTRIAL CELLS - CONSTRUCTION DETAILS

Cell Type	Units	I.G. Farbenindustrie Falkenhagen, 1940	I.G. Farbenindustrie Leverkusen, 1942	Hooker 1943-1944	Hooker 1943-1944	Hooker 1944	Du Pont (Semi-Works Area) 1944	Du Pont (Blue Products Area) 1945	Du Pont (East Area) 1945
Materials of Construction									
Cell Body		Elektron	Elektron	Steel	Steel	Steel	Steel	Steel	Steel
Cell Cover		Elektron	Elektron	Steel	Steel	Steel	Steel	Steel	Steel
Diaphragm		Slotted Elektron	Not used		Partly solid plate	6 Mesh steel screen	Perforated Monel Plate	Monel screen	Perforated Monel
Skirt		Elektron	Elektron			Steel	Steel Plate	Monel	Monel
Anode		Graphite	Carbon	Carbon	Carbon	Carbon	Nickal plate	Carbon	Carbon
Anode Support		-	Copper	Copper	Copper	Copper	Steel bar	Copper	Copper
Cathode		Silver (perforated)	Elektron			Steel plate	Steel plate	Steel	Steel
Dimensions of Cell Body									
Length (internal dim. of tank)	mm	1200	3020			1520	1220	1220	1220
Width (internal dim. of tank)	mm	685	310			305	508	508	508
Height (internal dim. of tank)	mm	890	450			635	910	910	910
Electrolyte Capacity	kg	1000	600				685	685	685
Total No. of Anode Blocks		6	15	24	24	14	6		
Number of Anode Assemblies		6	15		2 (Two parallel rows of 6)	1 (Two rows of 7)	2		
Method of Anode Attachment to Support		Neck of anode passes through the cell.		Bolted with aid of copper backing plate.	Bolted with aid of copper backing plate.	Bolted (4 bolts/ blade) with aid of copper backing plate.	Nickal plate is welded to the steel hanger bar.		
Anode Bolts — Diameter	mm					12.7	-		
Torque	Nm								
Head Size	mm					24			
Size of Anode Blocks (a) length (b) width (c) thickness	mm	(a) 460 (b) 460 (c) 46	(a) 350 (b) 130 (c) 50	(a) 457 (b) 159 (c) 31.8	(a) 457 (b) 159 (c) 31.8	(a) 457 (b) 159 (c) 31.8	(a) 406 (b) 295 (c) 6.4		
Type of Carbon		Siemens Plania Works	Griesham Plant	National Carbon Co. Type GA	National Carbon Co. Type GA	National Carbon Co. Type GA	-		
Anode/Cathode Separation	mm	30	95			38			
Anode/Diaphragm Gap	mm	10	47.5			Approx. 16			
Cathode/Diaphragm Gap	mm	10	47.5			Approx. 16			
Cooling Arrangements		Cold air in an insulating box.	Cooling coils and external cooling tube in electrolyte circulation pipe.	Water jacket	Water jacket	Water jacket	Water jacket with fins.	Water jacket with fins.	Water jacket with fins.
Method of HF Addition		Continuous	Intermittent liquid feed.		Continuous	Intermittent every 16 hours	Intermittent	Periodic, vapour added at ratio of 0.4 to 0.9 kg/h	Intermittent, every 16 hours
Insulation		See Figure 8	Buna rubber, sintered corundum			Teflon and Teflon impregnated with CaF_2	Teflon rings	Teflon	Teflon
References		Carter et al. 1946, Neumark 1947.	Karr 1946 Carter et al. 1946, Neumark 1947.	Murray et al. 1946, 1947, 1951.	Murray et al. 1946, 1947, 1951.	Murray et al. 1946, 1947, 1951.	Downing 1944	Trepper 1945	Stevenson 1945

TABLE 5 (Cont'd.)

INDUSTRIAL CELLS - CONSTRUCTION DETAILS

Cell Type	Units	Du Pont 1946	Harshaw 1944	Hawshaw 1944	Johns Hopkins University 1946	Pennsalt 1946	Pennsalt 1948	Union Carbide 1955	Union Carbide 1956
Materials of Construction									
Cell Body		Steel	Steel	Steel	Monel	Steel	Steel	Monel	Monel
Cell Cover		Steel	Steel	Steel	Copper	Steel	Steel	Steel	Steel
Diaphragm		Perforated Monel Sheet	Monel screen	Monel screen (8 mesh)	Monel strips	Not needed	Not needed	Monel screen (6 mesh)	Monel screen (6 mesh)
Skirt		Monel	Steel	Steel	Monel		Steel	Monel	Monel
Anode		Carbon	Carbon	Carbon (copper impregnated)	Carbon rod	Carbon	Carbon	Carbon	Carbon
Anode Support		Copper	Copper	Copper	Copper	Copper	Special alloy	Steel (AISI-4140)	Steel (AISI-4140)
Cathode		Steel plate	Steel (perforated)	Steel (perforated)	Monel cell body		Steel	Steel	Steel
Dimensions of Cell Body									
Length (internal dim. of tank)	mm	1220	1810	1810	865	764		1725	2080
Width (internal dim. of tank)	mm	508	464	464	102	330		811	811
Height (internal dim. of tank)	mm	910	609	609	406	685		762	762
Electrolyte Capacity	kg	685	745	745	45.5	228		910	1360
Total No. of Anode Blocks		12	96	96	16	2		24	32
Number of Anode Assemblies		2	96	96	1	2		2	2
Method of Anode Attachment to Support		Bolted with the aid of a copper facing plate.	6 mm Copper rod pressed into top of carbon.	6 mm Copper rod pressed into top of carbon	6 mm Copper dowel screwed into top of anode dowel silver soldered to anode bar.	Bolted by 4 vertical copper bolts.		Bolted (4 bolts/ blade) to support via copper contact plate.	Bolted (4 bolts/ blade) to support via copper contact plate.
Anode Bolts — Diameter	mm	-	-	-	-	12		19	19
Torque	Nm					-		115	115
Head Size	mm					-		29	29
Size of Anode Blocks (a) length (b) width (c) thickness	mm	(a) 610 (b) 159 (c) 25	(a) 452 31.7 dia.	(a) 305 31.7 dia.	(a) 228 25 dia.	(a) 457 (b) 203 (c) 51		(a) 457 (b) 204 (c) 31.7	(a) 525 (b) 204 (c) 51
Type of Carbon		National Carbon Co. Type GA.	National Carbon Co. Type GA.	National Carbon Co. Type GA.	Stackpole Carbon Co., Grade K1.	National Carbon Co. Type GA.		National Carbon Co. Type GAA or YAA	National Carbon Co Type YBD.
Anode/Cathode Separation	mm		38	38	35	Approx. 85		38	38
Anode/Diaphragm Gap	mm		19	19	16			16.5	16.5
Cathode/Diaphragm Gap	mm		19	19	14.2			16.5	16.5
Cooling Arrangements		Water jacket with fins.	Water jacket	Water jacket	Jacket containing diphenyl oxide	Jacket, air cooling.	Jacket	Jacket and three 76 mm internal cooling tubes.	Jacket and twelve 31.7 mm internal cooling tubes.
Method of HF Addition		Intermittent, every 4-8 hours.	3.2 kg of vapour every 4 hours.	3.2 kg of vapour every 4 hours.	Periodic, 1-1.5 kg every 3.5 hours.	Approx. once per day for 3-4 hours.	Continuous	Continuous	Continuous
Insulation		Teflon, neoprene, rubber.	Teflon and Teflon impregnated with CaF_2.	Teflon and Teflon impregnated with CaF_2.	Teflon	Teflon and iron phosphate cement.		Rubber and Teflon	Rubber and Teflon
References		Downing et al. 1947, Downing 1951 a.	Williams et al. 1944, Pinkston 1947, Long et al. 1951.	Williams et al. 1944, Pinkston 1947, Long et al. 1951.	Fowler et al. 1947, Burford et al. 1951	Galland Miller 1947	Porter 1948	Dykstra et al. 1955, Smiley and Brater 1956.	Smiley and Brater 1956, Vavalides et al. 1958.

TABLE 5 (Cont'd.)

INDUSTRIAL CELLS - CONSTRUCTION DETAILS

Cell Type	Units	Goodyear Atomic (Modified C-Type) 1956	ICI 1956	Union Carbide 1958	Union Carbide (E-Type) 1959	Allied Chemical 1959-1960	Union Carbide 1962	Pierrelatte Chemical Plant 1965	ICI 1960-1970
Materials of Construction									
Cell Body		Monel	Steel	Monel	Monel	Steel	Monel	Monel	Steel
Cell Cover		Steel	Steel	Steel, monel-clad	Steel	Magnesium alloy	Steel	Monel plated steel	Steel
Diaphragm		Monel screen (6 mesh).	Not needed	Monel screen (6 mesh).	Monel screen (6 mesh).	Not needed	Monel screen		Not needed
Skirt		Monel	Monel	Monel	Monel	Magnesium alloy	Monel	Monel	Monel
Anode		Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon	Carbon
Anode Support		Copper (A.S.T.M. B-13349T)		Steel AISI-4140	Copper	Copper		Copper	Mild steel
Cathode		Steel	Steel	Steel	Steel	Steel	Steel	Steel	Steel coils
Dimensions of Cell Body									
Length (internal dim. of tank)	mm	2080	1700	2080	2080		737		3020
Width (internal dim. of tank)	mm	786	674	814	787		356		710
Height (internal dim. of tank)	mm	786	47	761	761		761		560
Electrolyte Capacity	kg	1400	725	1360	1360				1730
Total No. of Anode Blocks		32	12	32	32		4	32	24
Number of Anode Assemblies		2	1	2	2		4	2	12
Method of Anode Attachment to Support		Bolted (4 bolts/ blade) to support via a copper contact plate.	-	Bolted (4 bolts/ blade) to support via a copper contact plate.	Bolted (4 bolts/ blade) with slot-head bolts protected by carbon plugs.	Held in place by bolts and back up plate.	Bolted to support (4 bolts/blade) via a copper contact plate.	Bolted to support (4 bolts/blade) with slot head bolts protected by carbon plugs.	-
Anode Bolts Diameter	mm	19	-	19	19		19		-
Torque	Nm	-		170	163		170		
Head Size	mm	29		38	38		38		
Size of Anode Blocks (a) length (b) width (c) thickness	mm	(a) 525 (b) 204 (c) 51	(a) 343 (b) 280 (c) 70	(a) 525 (b) 204 (c) 51	(a) 525 (b) 204 (c) 51		(a) 525 (b) 204 (c) 51		(a) 343 (b) 279 (c) 69.9
Type of Carbon		National Carbon Co. Type GA		National Carbon Co. Type YBD	National Carbon Co. Type YBD		National Carbon Co. Type YBD	Union Carbide CISA, SERS	Carbon having a high permeability
Anode/Cathode Separation	mm	38	58.5 - 64	38	38		38		Probably 31.7
Anode/Diaphragm Gap	mm	16.5	11.1	16.5	12.5		1		Probably 11.2
Cathode/Diaphragm Gap	mm	16.5		16.5	20.5				Probably 19
Cooling Arrangements		Water jacket and twelve 38 mm internal cooling tubes.	Water cooled coils and natural convection from walls.	Water jacket and twelve 51mm internal cooling tubes.	Water jacket (Monel) and twenty-seven 25 mm internal cooling tubes.	Water jacket.	Water jacket.	Jacket and internal coils.	Water cooled cathodes and jacket.
Method of HF Addition		Continuous	Intermittent liquid feed every 12 hours.	Continuous	Continuous	Continuous	Intermittent	Continuous	Intermittent, liquid feed every 12 hours.
Insulation		Rubber and Teflon	Neoprene and Tufnol	Teflon and rubber	Teflon and rubber	Rubber	Teflon and rubber	Teflon and Neoprene	Neoprene, Tufnol and Fluon.
References		Penland 1955, Goodyear Atomic Corporation 1967a, 1967b.	Rudge 1956.	Huber et al. 1958, Powell et al. 1960, Kelly and Clark 1968a.	Clark 1960, Kelly and Clark 1967a.	Neumark and Siegmund 1966.	Henderson et al. 1962.	Bergeret 1965, Level 1969.	Rudge 1971.

TABLE 6

CORROSION OF CATHODE MATERIALS IN KF.HF ELECTROLYTE AT 250°C

(After Neumark 1947)

Corrosion rates in $g/m^2/day$ are reported as follows:

WOC Without Current Flow

WC With Current Flow

Material	WOC	WC		Comments
Silver	-	-		Slightly soluble in the electrolyte and is redeposited on the cathode in form of fine needles. When silver concentration in melt reaches a certain point, corrosion velocity is extremely slow. During electrolysis, continuous corrosion and redeposition takes place and a metallic silver sludge accumulates on the bottom of the cell.
Lead	38	-		Redeposited lead is more spongy than silver needles and corrosion at the liquid level line is much more severe than in the case of silver.
		In the Melt	Liquid-Gas Level	
Copper	% HF 48.72	0.86	0.06	Corrosion is considerably increased if electrolyte contains some SO_2.
	50.00	0.7	0.18	
	51.16	2.0	1.39	
Iron	72	180		Corrosion product cannot be recovered (current density 500 A/m^2).
Nickel	28	5.5		Corrosion product is soluble in water (current density 500 A/m^2).
Brass	10	8		-
Magnesium	-	90		Corrosion is especially heavy on the liquid level line (current density 500 A/m^2). Without current flow a dense coating of magnesium fluoride is formed which prevents further attack.

TABLE 7

PHYSICAL PROPERTIES OF CARBON ANODES

(After Karr 1946, Dykstra et al 1955, Huber et al. 1958)

Property \ Type of Carbon	GAA	YAA	YBD	GRIESHEIM (Leverkusen)
Bulk Density ($g\ cm^{-3}$)	1.55	1.70	1.55	1.5-1.55
Resistivity (Ω/m for a mm^2 cross section)	43	33		50-65
Flexural Strength ($kg\ mm^{-2}$)	2.1	2.18		-
Hardness	-	-		Equivalent to Carborundum
Breaking Strength ($kg\ mm^{-2}$)	Typically 4 to 4.5			6

TABLE 8

SERVICE LIVES OF CELL TANKS

(After Dykstra et al. 1955)

Material of Cell Tank	Service Life Ampere Hours (A h)
Steel	12×10^6
Nickel-Plated Steel	20×10^6
Magnesium Alloy	20×10^6
Monel	$> 40 \times 10^6$

TABLE 9

THE INTER-RELATIONSHIP BETWEEN DESIGN FEATURES AND RESULTING MALFUNCTIONS IN FLUORINE GENERATORS

(After Finley 1953)

1. Conditions for which Generators are Removed from Service	Reason for Condition	Possible Effects
Complete Failure of Anodes	Polarized anodes Broken anodes	
Excessive voltage	Polarized anodes Broken anodes Corrosion product films at anode-bus bar junctions Cathode polarization	Excessive electrolyte temperature
Excessive electrolyte temperature	Localised over heating Hydrogen-fluorine recombination Cooling surface inadequate in area and location Sludge Excessive voltage	Corrosion Variations of HF concentration in electrolyte Variations of electrolyte level
Sludge	Corrosion	Excessive electrolyte temperature Cathode polarization
Corrosive Penetration of Separating Walls	Broken anodes Corrosion Hydrogen-fluorine recombination	Hydrogen-fluorine recombination Increase in electrolyte moisture content.
2. Intermediate Causes and Evidence of Generator Malfunctions	**Reason for Condition**	**Possible Effects**
Polarized anodes	Broken anodes High electrolyte moisture content Localised over heating Corrosion product films at anode - bus bar junction	Complete failure of anodes Excessive voltage Induced bi-polar potentials Localised over-heating

TABLE 9 (Cont'd.)

Broken anodes	Corrosion product films at anode - bus bar junction Hydrogen fluorine recombination Poor design of anode assembly.	Complete failure of anodes Polarized anodes Excessive voltage Induced bi-polar potentials Localised over heating.
Cathode Polarization	Sludge	Excessive voltage
Corrosion product films at anode - bus bar junction	Poor design of anode assembly	Excessive voltage Broken anodes Polarized anodes Complete failure of anodes Induced bi-polar potentials.
Hydrogen fluorine recombination	Corrosive penetration of separating walls Plugs in product and purge gas lines Poor design of gas separators Variation of electrolyte level	Excessive electrolyte temperature Broken anodes Plugs in product and purge gas lines
Induced bi-polar Potentials	Polarized anodes Corrosion product films at anode - bus bar junction Poor design of cathode Poor design of anode assembly Insufficient cooling	Corrosion
Localised over heating	Insufficient cooling Polarized anodes Corrosion product films at anode - bus bar junction	Corrosion Excessive electrolyte temperature Polarized anodes
Corrosion	Localised over heating Excessive electrolyte temperature Induced bi-polar potentials Poor design of anode assembly Poor design of gas separators	Corrosive penetration of separating walls Electrolyte misting Electrolyte salts and impurities

TABLE 9 (Cont'd.)

Corrosion (Cont'd.)	Variations of HF concentration in electrolyte High moisture content of electrolyte Electrolyte misting Electrolyte salts and impurities	
Plugs in Product and Purge Gas Lines	Hydrogen-fluorine recombination Electrolyte misting	Hydrogen-fluorine recombination
Electrolyte misting	Corrosion Electrolyte salts and impurities	Plugs in product and purge gas lines Variations of HF concentration in electrolyte Variations of electrolyte level

TABLE 10

VOLTAGES PRODUCED BY CATHODE POLARISATION

(After Schumb 1946)

Skirt to Cathode Voltage	Anode to Skirt Voltage	Current (A)
1.8	6.0	33.0
14.0	7.5	27.5
15.0	7.6	
16.5	8.0	15.1
17.0	8.2*	

* Wavers followed by explosion

TABLE 11

RELATIONSHIP BETWEEN AIR PERMEABILITY OF CARBONS AND THEIR TENDENCY TO POLARISE

(After Rudge, 1966, 1971)

Grade of Carbon	Air Permeability*	Period of Operation Before Polarisation (h)		
		Current Density (A/m^2)		
		770	1540	3080
"Carbocell" 20+	18.0	>242	>99	24
"Carbocell" 30+	16.0	>242	>99	24
"Carbocell" 40+	19.0	>242	>99	
"Carbocell" 50+	3.2	>242	>99	
"Carbocell" 60+	2.3	181		
"Carbocell" C+	0.08	3.4		
GA1260 +	0.06	1.2		
British Acheson (Ungraphitised)	0.5	1.3		

Test Conditions:

Anode size 19 mm diameter and 48.4 mm long

Electrolyte composition KF 60%, HF 40% (± 0.3%)

Initial water content of electrolyte 0.24% (± 0.05%)

Electrolyte temperature 85.5°C (± 2.5K)

+ Products of the National Carbon Co. of America

* Permeability is expressed as the number of cubic feet of air per minute passing through 1 square foot of carbon 1 in. thick under a pressure equivalent to 2 in. of water. Measurements were made on specimens 1 in. diameter and 1 in. long.

To convert to l/s per m^2 per m under a pressure equivalent to 500 Pa multiply above figures by 0.129.

TABLE 12

SUPPLY AND HANDLING OF HF

Cell Type	I.G.Farbenindustrie Leverkusen	Hooker Electrochemical Co.	Harshaw Chemical Co.	E.I. Du Pont de Nemours and Co.	Pennsylvania Salt Manufacturing Co.	Union Carbide Nuclear Co.	Goodyear Atomic Corporation	Imperial Chemical Industries Ltd.
Basic Method of Cell Supply	Liquid HF is fed from container	HF vapour is fed from cylinders	HF is fed from reboiler tank	HF is fed from a vaporizer		HF is fed from a vaporizer	HF is fed from a vaporizer	Liquid HF feed
Description of Vaporizer				Vertical cylindrical vessel		Vertical cylindrical vessel	Vertical cylindrical vessel	
Capacity				1780 kg			Approx. 560 kg	
Dimensions				1.2m dia.and 1.2m high			0.76m dia. 1.68m high	
Operating Pressure						Approx.89-103 kPa gauge	450 kPa gauge	
Operating Temperature							57°C	
Material of Construction				Mild Steel			Steel	
Heating Method				Bottom 1/3 jacketed			Bottom 5/6 jacketed	
Heating Medium				Steam		Steam	Steam	
Pressure Relief				310 kPa gauge platinum rupture disc and 275 kPa gauge pop valve			Rupture disc	
HF Feed Temp.into cell Feed Pressure	40°C		45°C				93°C 13.8 kPa gauge	
Feed Line into Cell (a) Material and size	1 in. N.B. magnesium pipe	Iron pipe	3/8 in. N.B. extra heavy steel pipe	1/4 in. N.B. extra heavy steel pipe steel pipe	1/4 in. N.B. steel pipe			
(b) Position	In a separate end compartment			Rear of anode compartment	In corner of cell tank		Rear of cathode compartment	Cathode compartment
(c) Depth of Outlet	Approx. 38 mm above the bottom of the cell	200mm below electrolyte level	50mm above bottom of the cell	50mm above the bottom of the diaphragm	200mm below the level of electrolyte			150mm below electrolyte level
Flow rate of HF		Cylinders on scales	Tank on scales	Tank on scales		Orifice plate	Kel-F rotameter with Monel float	
Prevention of Suck-Back of HF		Nitrogen is introduced to the feed line	Inlet line is swept with nitrogen before and after feeding of HF	HF is added with a slow continuous stream of nitrogen		If the pressure in the line falls below 34 kPa gauge, nitrogen is introduced automatically	Nitrogen is bled continuously into the feed line	
Method of Determining HF Requirement of Cell	Electrolyte composition determined by level reading	Electrolyte level determined by a bubbler pipe and manometer using dry nitrogen	Electrolyte level is determined by a bubbler pipe using nitrogen and a manometer	Electrolyte level is determined by a nitrogen bubbler	Charging is controlled manually with the aid of a visual level indicator consisting of a nickel float bearing a vertical copper wire	A level measuring device is used, the device features a heated thermo-couple probe		Electrolyte level is determined
References	Carter et al.1946, Karr 1946	Murray et al.1946, 1951	Williams et al. 1944, Long et al. 1951	Dupont de Nemours and Co.1944	Porter 1948	Smiley and Brater 1956, Huber et al.1958	Giffels and Vallet 1956b, Goodyear Atomic Corporation 1967a, Kelly and Clark 1967b	Rudge 1971

TABLE 13

PREPARATION OF ELECTROLYTE

Cell Type	I.G.Farbenindustrie Leverkusen	Hooker Electrochemical Co.	Harshaw Chemical Co.	E.I. Du Pont de Nemours and Co.	Union Carbide Nuclear Co.	Goodyear Atomic Corporation	Pierrelatte Chemical Factory
Basic Method	Gaseous HF is reacted with KF	Gaseous HF is reacted with powdered KF.HF	Gaseous HF is reacted with powdered KF.HF and LiF	Liquid HF is reacted with powdered KF.HF	Gaseous HF is reacted with powdered KF.HF	Gaseous HF is reacted with powdered KF.HF	Liquid HF is reacted with KF.HF
Reaction Vessel	Tank	Cell or special reaction vessel	Cell tank or special make-up tank	Vertical Cylindrical Tank	Vertical cylindrical Tank	Vertical cylindrical Tank	Vertical Cylindrical Tank
Capacity	25 kg			2400 kg	3600 kg	4550 kg	
Dimensions				1.27m dia. 1.76m high		1.45m dia. 3m high	
Material of Constr.	Elektron alloy			Steel	Steel	Steel	
Operating Pressure				82-103 kPa gauge		103 kPa gauge	
Operating Temperature			Maintained at 80 to 95°C	110-115°C	104°C	138°C	
Heating/Cooling Method		Vessel is jacketed		Vessel is jacketed	Vessel is jacketed	Vessel is jacketed	Vessel is jacketed
Heating/Cooling Fluid		Steam		Steam		Steam and water mixtures	Warm water
Safety Relief				310 kPa gauge, platinum rupture disc and relief valve			
Agitation and Process Description			After all HF has been added, the charge is mechanically agitated for 8 h to ensure all the LiF is dissolved	Propeller agitator, 1800 kg of KHF_2 is added to tank with agitator on. After HF addition is complete, agitate for 1 h	Agitator; powder is agitated during addition of HF	Paddle agitator rotates at 0.53 Hz as soon as mixture is liquefied, agitator is switched on	No agitation required. KF.HF is refluxed with HF to form electrolyte. (See Section 5.3)
HF Feed Line		Feed line is a pipe which projects under the surface of the KF.HF	HF is fed in under the surface of the solids	Stand pipe for HF addition	Feedline extends below the powder surface	1 in. N.B. monel pipe feeds HF to the bottom of the vessel under the agitator	
Special Features			After agitation the electrolyte is allowed to settle for one hour and the froth is then skimmed to remove foreign material	Bottom outlet valve is jacketed			The electrolyte is electrolysed elsewhere before passing to a cell
Reference	Carter et al.1946 Karr 1946	Murray et al.1946, 1951	Williams et al. 1944, Long et al. 1951	Du Pont de Nemours and Co.1944	Huber et al.1958	Kelly and Clark 1967b Goodyear Atomic Corporation 1967b	Bergeret 1965

TABLE 14

DISPOSAL OF FLUORINE AND HYDROGEN FLUORIDE

(1) Removal of Hydrogen Fluoride from Fluorine

Cell Type	I.G.Farbenindustrie Leverkusen	E.I. Du Pont de Nemours and Co.	Pennsylvania Salt Manufacturing Co.	Union Carbide Nuclear Co.	Union Carbide Nuclear Co.	Goodyear Atomic Corporation	Pierrelatte Chemical Factory	Imperial Chemical Industries Ltd.	U.K.A.E.A.
HF Content of Fluorine (Vol.%)		5-15	10	11	10-12	10-20	6-8	4-5	5-7
Final HF Content of Fluorine		<0.5		<0.01	2	<2	2	2	0.1
Processes Used	Two stage condensation	(a) Partial HF condenser (b) Two NaF towers connected in series	Tower packed with NaF	(a) Condenser (b) Tower packed with NaF	(a) Partial condenser (b) Tray absorber	Partial condenser	(1) Partial condenser (2) NaF traps	Tray absorber	(a) Primary absorber (b) Secondary absorber
Description of Equipment	Fluorine was passed through an iron coil surrounded by pulverized dry ice (-78°C). Fluorine was next passed through another coil which was immersed in liquid oxygen (-183°C). This treatment froze out remaining HF and CF_4.	(a) HF is condensed at -80°C in a 12 mm copper coil. The coil is installed in a lagged, closed dry ice chamber. (b) Towers are 3 in. N.B.flanged steel pipe, 1.52 m long. Towers have air jackets which are heated with 2.5 kW resistance heaters. A 12 mesh monel screen supports 4 mm pellets. Towers are operated at 100°C.		(a) Most HF is removed in Monel condensers maintained at -85°C by evaporating Freon 13. Condensers have monel shells and 19 mm copper tubes. The process gases are precooled in 3 heat exchangers. (b) Tower is 4 in. N.B. Monel pipe, 1.4 m long. 3.2 mm NaF pellets are supported on a porous nickel plate. First 0.61 m of bed is heated to 100°C, lower 0.61 m is cooled to 25°C by external water coils for more complete HF removal.	(a) Fluorine is passed through copper coils immersed in a slush of dry ice and trichloroethylene at -57°C. (b) The absorber is a mild steel chamber 0.6 m dia. x 1.2 m high fitted with 8 shallow trays. The absorber is baffled to direct the gas flow in series over the surface of the trays which are charged with a 50mm depth of NaF pellets.	Condenser operates at -80°C. Freon 13 is the refrigerating agent. Gas is precooled before entering the condenser	Condenser operates at -80°C. Freon 13 is the refrigerating agent. Condenser is standard heat exchanger with baffled tubes. (b) If required, an NaF trap at 100°C is used to reduce the HF content to 0.05%	NaF powder is used in a multiple pass tray arrangement. A scrubber containing 205 kg of NaF is capable of treating 1,820 kg of fluorine before regeneration is required. A tower packed with NaF pellets can be used to further reduce the hydrogen fluoride content	(a) Mild steel primary absorber contains NaF powder (b) Mild steel secondary absorber contains NaF pellets

TABLE 14 (Cont'd.)

DISPOSAL OF FLUORINE AND HYDROGEN FLUORIDE

(1) Removal of Hydrogen Fluoride from Fluorine

Regeneration of Materials		The NaF is regenerated after the passage of 45 kg of fluorine; a slow stream of nitrogen at 100°C is passed through the scrubbers for 8 h	The NaF is regenerated by taking the tower off stream and heating it to 300°C.	Regeneration of NaF is accomplished by heating the tower to 300-350°C and maintaining a small flow of nitrogen. Regeneration is necessary after the passage of 69 kg of fluorine.	The NaF is regenerated by the passage of air at 216°C, air is then vented. The NaF pellets must be replaced every 6 months.			Sheathed electrical elements beneath the trays permit regeneration.	The primary absorber is provided with electrical heaters to enable the NaF to be regenerated.
References	Karr 1946	Compton 1946	Porter 1948	Smiley and Brater 1956, Watson 1957, Milford et al. 1960.	Vavalides et al. 1958, Dykstra et al.1958	Goodyear Atomic Corporation 1967b	Bergeret 1965 Level 1969	Rudge 1971	Rogan 1972b

(2) Disposal of Hydrogen Fluoride and Fluorine

E.I. Du Pont de Nemours and Co.	Pennsylvania Salt Manufacturing Co.	Union Carbide Nuclear Co.	Union Carbide Nuclear Co.	Union Carbide Nuclear Co.	Goodyear Atomic Corporation	Imperial Chemical Industries Ltd.	Pierrelatte Chemical Factory
Fluorine was destroyed by burning a mixture of butane and air in a specially designed burner. Hydrogen fluoride (and fluorine) were destroyed by absorption in water via a wooden eductor with a brass spray nozzle. To destroy OF_2 a second scrubber using 5% Na_2SO_3 — 5% $NaHCO_3$ — 0.1% brucine was used. (Compton 1946)	Fluorine was destroyed by using a chemical disposal system. Vaporized HF (from NaF towers) was collected in a water cooled condenser and receiving system. (Porter 1948)	Condensed HF is returned to the process. Hydrogen (after HF removal by condensation) is scrubbed with water and vented. Excess fluorine is reacted with 5-10% solution of KOH in a Monel spray tower (304 mm o.d. 3.05 m high). A total of six nozzles are used. (Smiley and Brater 1956, Watson 1957, Milford et al.1960).	Hydrogen containing HF is vented to atmosphere. Excess fluorine is reacted with 5-10% solution of KOH in a Monel spray tower (304 mm o.d. 3.05 m high). A total of six nozzles are used. (Vavalides et al.1958, Dykstra et al.1958)	A burner is used for the disposal of hydrogen. Fluorine is scrubbed in a spray tower (203 mm dia. x 1.85 m high) with 5-10% solution of KOH. The tower is constructed of Monel, liquid is distributed by one spray head at the top of the tower. Tower is 203 mm dia. x 1.85 m high. (Henderson et al.1962)	The hydrogen fluoride in the hydrogen stream is partially condensed at -80°C. All condensed HF is transferred by nitrogen pressure back to the HF storage tanks. Hydrogen is then scrubbed with water and vented. (Goodyear Atomic Corporation 1967b)	Waste fluorine and the hydrogen fluoride in the hydrogen stream are scrubbed in spray towers by reaction with 10% KOH solution. (Rudge 1956, 1971)	The hydrogen fluoride in the hydrogen stream is partially condensed at -80°C. Hydrogen is then scrubbed with water and released to the stack. All condensed HF is recycled to the cell feed system. (Bergeret 1965, Level 1969)

TABLE 15

MATERIALS OF CONSTRUCTION FOR HANDLING FLUORINE - OAK RIDGE GASEOUS DIFFUSION PLANT

(After McGuffey et al. 1962)

Item	Size (in.)	Specification
Gauge Pressure, 0 to 5 psi (0 to 34 kPa); Temp., to -85°C		
Pipe (to -44°C)	All	Steel, seamless, ASTM A106 normalised.
Pipe (-44° to -84°C)	All	Copper, seamless, standard weight, ASTM B42.
Tube	1/8-1	Copper, seamless, ASTM B88, Type K.
Fittings	All	Copper, wrought, per ASA B-16.22.
Gauge Pressure, 0 to 5 psi (0 to 34 kPa); Temp., 205° to over 540°C		
Pipe	All	Monel, seamless, Schedule 40, ASTM B165.
Fittings	All	Monel, 2000-lb. forged, made from ASTM B127, B165 or B164, grade A material, butt weld ends.
Flanges	All	Monel, forged from ASTM B127 or B164 material, 150-lb. dimensions to MSS-SP-42.
Gaskets (177°C max.)	All	Teflon, ring-type, impregnated with 30% calcium fluoride.
Valves	All	To 315°C max; Globe, Monel body with integral seats, rising Monel stem with phosphor-bronze inner bellows, screwed, demountable bonnet with aluminium gasket.

TABLE 15 (Cont'd.)

Gauge Pressure, 0 to 75 psi (0 to 520 kPa); Temp., -18 to 205°C		
Item	Size (in.)	Specification
Pipe	1-1/2 and under	Steel, seamless, Schedule 80, ASTM A53 or A106 grade A.
Pipe	2 and over	Steel, seamless, Schedule 80, ASTM A53 grade A.
Fittings	1-1/2 and over	Steel, forged 3000-lb. ASTM A105, socket weld ends, per ASA B-16.11.
	2 and over	Steel, forged, seamless, ASTM A234 grade WBP, butt weld ends, per ASA B-169.
Flanges	All	Steel, forged 150-lb. ASTM A181, grade 1, slip-on, per ASA B-16.5
Gaskets	All	Teflon, ring-type, impregnated with 30% CaF_2.
Bolts, nuts	All	Steel, ASTM A307 grade B.
Valves	1/4-2	Globe, Monel body with integral seats, rising Monel stem with phosphor-bronze inner bellows, screwed, demountable bonnet with aluminium gasket.
	2-6	Gate, 150-lb. steel, Monel trim, flanged, Teflon packing.

TABLE 16

MATERIALS OF CONSTRUCTION FOR HANDLING HYDROFLUORIC ACID AND FLUORINE - PORTSMOUTH GASEOUS DIFFUSION PLANT

(After Giffels and Vallet 1956a)

Hydrofluoric Acid and Hydrogen Fluoride Vapour

(A) Steel Piping System

- Maximum Service Conditions : 120 psig (825 kPa gauge); - 18°C to 49°C.

Pipe:

1 - 1-1/2 in. and under - shall be seamless steel, Schedule 80 to applicable sections of ASTM A-83 Specification with tests certified to applicable sections of ASTM A-106 Gr. B Specifications.

2 in. and over - shall be seamless steel, Schedule 80, ASTM A-53 Gr. B.

Copper Tubing: - shall be as tabulated below.

Tube o.d. (in.)	Wall Thickness (in.)
1/4	.035
3/8	.035
1/2	.049
5/8	.049
3/4	.049
7/8	.065
1-1/8	.065

Up to 1-1/8 in. o.d. Incl. - shall be seamless copper tubing meeting all the requirements of ASTM B-68 Type DHP, and shall be coiled, light annealed after coiling, suitable for bending and flaring, embrittlement tested, and with ASTM tolerances for tube o.d. and thickness.

All coiled tubing shall be furnished in the longest available lengths (100 ft.minimum), shall be dehydrated, and shall be shipped with the ends sealed. All copper tubing supplied in coils shall be submitted to a 100 psig internal air pressure while submerged under water. Any portion showing leaks shall be cut out and rejected, and the remainder shall be retested until no leaks are apparent.

TABLE 16 (Cont'd)

Pipe Fittings:	
1 - 1-1/2 in. and under	- shall be 3000 lb. forged steel, ASTM A-181 Gr. 1, socket weld, to ASA B16.11 (bored for Schedule 80 pipe).
2 in. and over	- shall be Schedule 80 steel, ASTM A-181 Gr. 1, seamless butt weld, to ASA B16.9.
Copper Tubing Fittings:	- shall be seamless wrought copper, solder-joint type, to ASA B16.22.
Weld-O-Lets:	
1 - 1-1/2 in. and under	- shall be steel, ASTM A-181 Gr. 1, socket weld Bonney Weld-O-Let (bored for Schedule 80 pipe),
2 in. and over	- shall be steel, ASTM A-181 Gr. 1, Schedule 80, butt weld, Bonney Weld-O-Let.
Couplings:	
2 in. and under	- shall be 3000 lb. forged steel, ASTM A-181 Gr. 1, socket weld, to ASA B16.11 (bored for Schedule 80 pipe).
Unions:	
2 in. and under (to be used on tank car station only)	- shall be standard weight forged steel, ASTM A-181 Gr. 1, socket weld, steel to monel seat, (bored for Schedule 80 pipe).
Flanges:	
1/2 in. and over	- shall be 150 lb. forged steel, ASTM A-181 Gr. 1 raised face, slip-on or welding neck type (bored for Schedule 80 pipe), to ASA B16.5 - or shall be 300 lb. forged steel, ASTM A-181 Gr. 1, ring joint, slip-on or welding neck type (bored for Schedule 80 pipe), to ASA B16.5. The flanges shall be used with positive shut-off valves only.
Bolting:	- shall be square head machine bolts and hex nuts, conforming to ASTM A-307.
Gaskets:	- shall be Teflon, impregnated with 30% calcium fluoride, ring type gaskets to be used with raised face flanges or full face type gaskets to be used with flat face flanges, - or shall be soft iron, oval shaped rings to be used with ring joint flanges.
Electrical Flange Insulation	- shall be phenol formaldehyde or Teflon plastic insulating sleeves and washers which shall be used where steel flanges are connected to monel flanges.

TABLE 16 (Cont'd)

Safety Bands and Shields:	- shall be polyethylene protective bands and shields for all flanges and valves in all lines (except vent lines).
Valve Stem Packing:	- shall be chevron type Teflon rings.
Solder:	- shall be silver solder, U.S. Navy Specification 47-S-13 Grade 4.
Valves:	
Gate Valves:	
3 in. and under	- shall be 150 lb. cast carbon steel body and monel trim, wedge type gate valve with raised face flanged ends,O.S. and Y.,bolted flanged body and stuffing box, Teflon bonnet gasket, and Teflon stem packing. The wedge, stem and seat shall be monel.
Globe Valves:	
3 in. and under	- shall be 150 lb. cast carbon steel body and monel trim, globe valve with raised face flanged ends, O.S. and Y., bolted flanged bonnet and stuffing box, Teflon bonnet gasket, and Teflon packing rings. The stem, disc and seat shall be monel.
Plug valves:	
1/2 in. to 3 in. inclusive	- shall be 150 lb. all monel, non-lubricated type plug valve with raised face flanged ends, Teflon sleeve, and Teflon diaphragm.
Positive Shut-off Valves:	
1 in. to 3 in. inclusive	- shall be 300 lb. steel body and monel trim "Y" type valve with ring joint flanged ends, bolted ring joint flanged bonnet,O.S. and Y.,Teflon packing, fully guided plug, multiple seating, and back seating bushing.
Pressure Relief Valves:	- shall be bellows-seal type, angle pressure relief valve with 150 lb. raised face inlet and outlet flanges, vapour tight bonnet for spring and stem assembly, and packed lifting gear. All parts in contact with the process flow shall be of monel construction, and gaskets for the monel parts shall be Teflon. No packing of the valve will be acceptable.
SMMD Valves	
1/2 in. to 2 in. inclusive, 3 in.	- shall be socket end, bellows-seal type globe valve with a forged monel body, monel seat with machined surface, double bellows sealed monel stem, and a screwed phosphor bronze bonnet.

TABLE 16 (Cont'd)

(B) Monel Piping System

- Maximum Service Conditions: 65 psig (446 kPa gauge); - 96°C to 48°C

Pipe:	
4 in. and under	- shall be seamless monel, Schedule 40, ASTM B-165.
Copper Tubing:	- as for mild steel piping system
Pipe Fittings:	
1-1/2 in. and under	- shall be 2000 lb. forged monel, ASTM B-164 Class A, socket weld (bored for Schedule 40 pipe), to ASA B16.11.
2 in. and over	- shall be Schedule 40 Monel, ASTM B-165, butt weld, to ASA B16.9.
Copper Tubing Fittings:	- as for mild steel piping system
Weld-O-Lets:	
1-1/2 in. and under	- shall be monel, ASTM B-164 Class A, socket weld, Bonney Weld-O-Let (bored for Schedule 40)
2 in. and over	- shall be Schedule 40 monel, ASTM B-164 Class A, butt weld, Bonney Weld-O-Let.
Couplings:	
2 in. and under	- shall be 2000 lb. forged monel, ASTM B-164 Class A, socket weld (bored for Schedule 40 pipe), to ASA B16.11.
Flanges:	
1-1/2 in. and under	- shall be 150 lb. forged monel, ASTM B-164 Class A, socket weld type, raised face, to ASA B16.5.
2 in. and over	- shall be 150 lb. forged monel, ASTM B-164 Class A, welding neck or slip-on type, raised face, to ASA B16.5.
	- or shall be standard weight seamless monel lap joint stub ends (ASTM B-165) with 150 lb. forged carbon steel lap joint flanges (ASTM A-181 Gr. 1).
Gaskets:	
For temperature to 150°C	- shall be Teflon envelope type with asbestos insert.
For temperature over 150°C	- shall be copper envelope type with asbestos insert.

TABLE 16 (Cont'd)

Bolting:

For temperatures above 150°C	- bolts shall be ASTM A-193 Gr. B7a; nuts shall be ASTM A-194 Gr.4.
For temperatures minus 29°C to 250°C	- bolts and nuts shall be ASTM A-307.
For temperatures minus 60°C to minus 29°C	- bolts shall be ASTM A-320 Gr. L7; nuts shall be ASTM A-194 Gr. 4.

Electrical Flange Insulation: - shall be phenol formaldehyde or Teflon plastic insulating sleeves and washers which shall be used where monel flanges are connected to steel flanges.

Safety Bands and Shields: - shall be polyethylene protective bands and shields for all flanges and valves in all lines (except vent lines).

Valve Stem Packing: - shall be chevron type Teflon rings.

Solder: - shall be silver solder, U.S. Navy Specification 47-S-13 Grade 4.

Valves:

Gate Valves

3 in. and under	- shall be 150 lb. all monel wedge type gate valve with raised face flanges, O.A. and Y., bolted flanged body and stuffing box, Teflon bonnet gasket, and Teflon stem packing.

Glove Valves

3 in. and under	- shall be 150 lb. all monel globe valve with raised face flanges, O.S.and Y., bolted flanged bonnet and stuffing box, Teflon bonnet gasket, and Teflon packing.

HGP Valves

1/4 in.	- shall be a stemless, bellows-seal type globe valve suitable for high vacuum service which shall be supplied with a monel body, monel spindle, phosphor bronze bellows, Kel-F seat, Kel-F gasket, and a knurled and chromium plated brass cap. The valve shall be furnished with copper tubing (ASTM B-68 Type DHP with 1/4 in. o.d. x 0.035 in. wall thickness) stubs for soldered corrections.

TABLE 16 (Cont'd)

Plug Valves

½in. to 3in. inclusive - shall be 150 lb. all monel, non-lubricated type plug valve with raised face flanged ends, Teflon sleeves, and Teflon diaphragm.

Pressure Relief Valves - As for Steel Piping System

SMMD Valves - As for Steel Piping System

Fluorine

Steel Piping System

- Maximum Service Conditions: 100 psig (690 kPa gauge); 370°C
Unless stated, pipes and pipe fittings are the same as those used in the Steel Piping System for hydrofluoric acid and hydrogen fluoride vapour.

Bolting: - shall be square head machine bolts and hex nuts, conforming to Paragraph 212 of Section 2 of ASA B31.1 Code for Pressure Piping .

Gaskets:

For temperatures to 360°C - shall be Teflon, impregnated with 30% calcium fluoride, ring type gaskets to be used with raised face flanges or full face type gaskets to be used with flat face flanges.

For temperatures over 360°C - shall be copper envelope type with asbestos insert.

Valves:

Gate Valves

1-1/2 in. and under - shall be 150 lb. cast carbon-steel body and monel trim, wedge type gate valve with socket weld ends,O.S.and Y., bolted flanged bonnet and packing gland, Teflon bonnet gasket, and Teflon ring packing. The wedge, stem and seat shall be monel.

2 in. and over - shall be 150 lb. cast carbon steel body and monel trim, wedge type gate valve with raised face flanged ends,O.S.and Y., bolted flanged body and stuffing box, Teflon bonnet gasket, and Teflon stem packing. The wedge, stem and seat shall be monel.

Needle Valves

1 in. and under - shall be suitable for 150 lb. service and shall be bar stock globe type needle valve of monel

TABLE 16 (Cont'd)

Needle Valves	
1 in. and under (Cont'd)	- construction with screwed ends, integral seat and plug, inside, screw, and rising stem and wheel. The valve shall be supplied with an indicator and indicator wheel.
Pressure Relief Valves and SMMD Valves	- same specification as used in the Steel Piping System for hydrogen fluoride.

TABLE 17

RECOMMENDED MATERIALS FOR HANDLING FLUORINE -

ALLIED CHEMICAL CORPORATION

(After Neumark and Siegmund 1966, Neumark 1967)

MATERIALS		
Component	Gaseous Service	Liquid Service
Lines, fittings and flanges	Nickel Monel Copper Brass Stainless steel, 300 series Aluminium 2017, 2024, 5052 6061 Mild Steel (low pressure)	Monel Stainless Steel, 300 series Copper Aluminium 2017, 2024, 5052
Storage tanks	Stainless steel, 300 series Aluminium 6061 Mild steel (low pressure)	Monel Stainless steel, 300 series Aluminium 6161
Valve bodies	Stainless steel, 300 series Bronze Brass	Monel Bronze Stainless steel, 300 series
Valve seats	Copper Aluminium 1100 Stainless steel, 300 series Brass	Copper Aluminium 1100 Monel
Valve plugs	Stainless steel, 300 series Monel	Stainless steel, 300 series Monel
Valve packing	Tetrafluoroethylene polymer	Tetrafluoroethylene polymer
Valve bellows	Stainless steel, 300 series Monel Bronze	Stainless steel, 300 series Monel Bronze
Gaskets	Aluminium 1100 Copper Tetrafluoroethylene polymer Lead Red Rubber (< 34 kPa gauge) Neoprene (< 34 kPa gauge)	Aluminium 1100 Copper Tetrafluoroethylene

TABLE 17 (Cont'd.)

EQUIPMENT	
Valves	Fluorine valves should have plugs and seats of dissimilar metals to prevent galling. For liquid fluorine service packless valves with stainless steel bodies of the bellows type with a secondary P.T.F.E. stem packing are preferred. For gaseous service (low pressure) P.T.F.E. - packed gate and globe valves with carbon steel or bronze bodies are commonly used. A dual packing gland is used for high pressure service.
Gauges	Pressure is measured with stainless steel Bourdon-type gauges, or alternatively pressure transducers are used in which the transducer-pickups are standard all-stainless-steel units.
Temperature	Standard thermocouples, such as the stainless-steel shield type, inserted through a threaded compression fitting welded into the line are used for all temperature measurement.
Flowmeters	Gas flow rates are measured with orifices or rotameters (Standard Pyrex rotameters with stainless steel or aluminium balls have been used). Orifices or venturi meters are used for liquid flow.

TABLE 18

RESISTANCE OF MATERIALS TO HYDROFLUORIC ACID AND HYDROGEN FLUORIDE VAPOUR - IMPERIAL CHEMICAL INDUSTRIES

(After Imperial Chemical Industries Limited 1971)

	Dry HF Gas	80-100% HF	65-80% HF	Below 65% HF
Mild Steel (1)	Excellent	Excellent	Satisfactory	Unsatisfactory
Chemical Lead	Unsatisfactory	Unsatisfactory	Unsatisfactory	Satisfactory
Copper (2)	Excellent	Excellent	Excellent	Satisfactory
Monel (3)	Excellent	Excellent	Excellent	Satisfactory
Magnesium	Excellent	Excellent	Excellent	Excellent
Cast Iron	Unsatisfactory	Unsatisfactory	Unsatisfactory	Unsatisfactory
Platinum	Excellent	Excellent	Excellent	Excellent
Silver (4)	Excellent	Excellent	Excellent	Excellent
Polythene ('Alkathene')	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Natural Rubber	-	Unsatisfactory	Unsatisfactory	Unsatisfactory
Neoprene (5)	-	Unsatisfactory	Unsatisfactory	Satisfactory
Glass or Ceramics	Unsatisfactory	Unsatisfactory	Unsatisfactory	Unsatisfactory

NOTES

1. Some steels are more resistant than others - a deoxidised steel with the non-metallic inclusions at a minimum is the best.

2. Copper is attacked in the presence of sulphur dioxide, oxygen or oxidising agents.

3. One of the most resistant alloys, but is attacked in the presence of sulphurous acid.

4. Silver is attacked in the presence of sulphides and appreciable quantities of sulphuric acid.

5. Neoprene is the most resistant of the synthetic rubbers.

Jointing Materials — Polythene (for pressures less than 138kPa gauge and temperatures less than 25°C); bonded stainless steel/polythene gasket (for higher pressures).

TABLE 18 (Cont'd.)

Gland Packings	Copper braided graphitised asbestos, Cereclor impregnated packing ring and P.T.F.E. (particularly for valves).
Valves	Forged steel, and for fine control work a needle-valve with a monel metal spindle.
Pressure Gauges	Diaphragm type should be employed. Monel metal diaphragm chamber with a silver protected steel diaphragm or alternatively a mild steel chamber with a monel diaphragm. If moisture is present P.T.F.E. coatings should be employed.

TABLE 19

RECOMMENDED MATERIALS FOR HANDLING HYDROFLUORIC ACID (HF CONTENT > 60%) -

STAUFFER CHEMICAL COMPANY

(After Stauffer Chemical Company 1964)

MATERIALS	
Piping	Extra heavy seamless steel.
Fittings	Extra heavy forged steel.
Unions	Forged steel screw type with steel to steel seats or forged steel flanges with gaskets.
Valves	Forged steel with outside screw and yoke.
Pressure Gauges	Provided with steel Bourdon tubes, or to be of the diaphragm type with steel diaphragms.
Pipe Joints	Screwed connections recommended. Threads to be cut true to form and taper. Screwed joints should be lubricated with a mixture of graphite and oil to prevent freezing.
Gaskets	If gaskets are necessary polyethylene is preferred; it is optional to use soft copper, soft iron, soft silver, neoprene or saran.
Pumps	For anhydrous hydrofluoric acid centrifugal, rotary, or positive pressure pumps, fabricated of steel or Monel are satisfactory.
EQUIPMENT	
Valves	Teflon-lined plug valves are used on tank trailer cars.

TABLE 20

CORROSION RESISTANCE OF MATERIALS TO HYDROFLUORIC ACID - STAUFFER CHEMICAL COMPANY

(After Stauffer Chemical Company 1964)

Degree of Corrosion	Anhydrous H F	70% H F
Fairly Resistant	Cast Iron (20°C) Polyethylene (25°C) Polystyrene (0-25°C)	Cast Iron (25°C) Steel (25°C) Copper (25°C) Nickel (50°C) Polyethylene (25°C) Polystyrene (25°C)
Resistant	Steel (0-25°C)	Monel (50°C)
Extremely Resistant	Copper (20°C) Monel (25-50°C) Nickel (50°C) Magnesium (25°C)	Magnesium (25°C)

CODE:	For Metals	For Plastic Materials
Fairly Resistant	0.127-0.763 mm penetration/year	Resistance of plastic materials was judged mainly visually by observing swelling and distortion.
Resistant	0.025-0.127 mm penetration/year	
Extremely Resistant	less than 0.025 mm penetration/year	

Notes

(a) Copper and copper alloys are subject to attack if sulfur compounds are present.

(b) Magnesium is severely attacked by weak HF mists which form when strong HF is exposed to moist air.

(c) Cast iron must be free from sand inclusions. Some castings are subject to severe pitting because of non-uniformity of composition.

(d) In handling weaker acid in the 0-30% range, rubber-lined or lead equipment is normally used. Butyl rubber and neoprene have better resistance to hydrofluoric acid attack than natural rubber. Silver gives excellent service whenever the cost is warranted and polystyrene or polyethylene are completely resistant but subject to their temperature limitations.

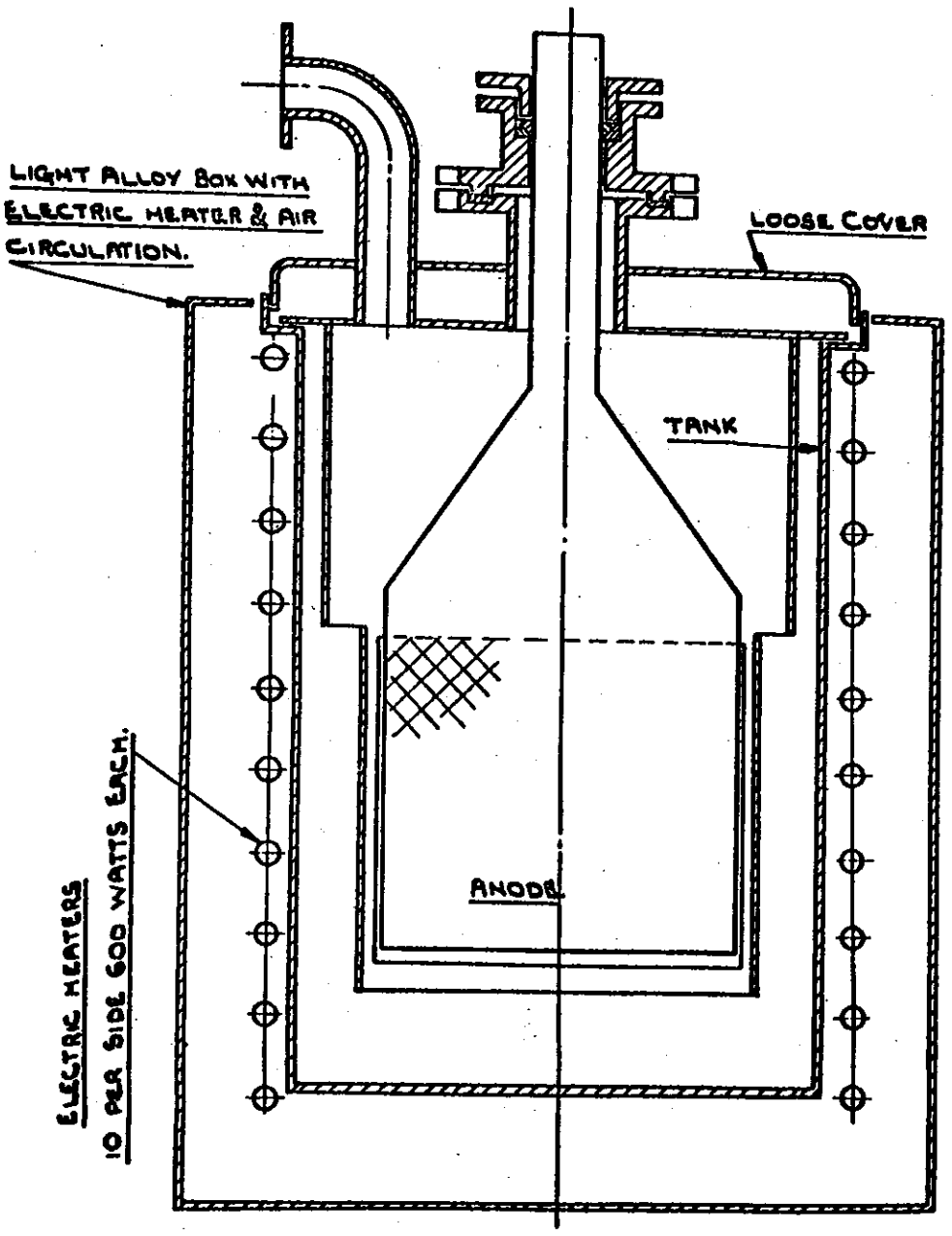
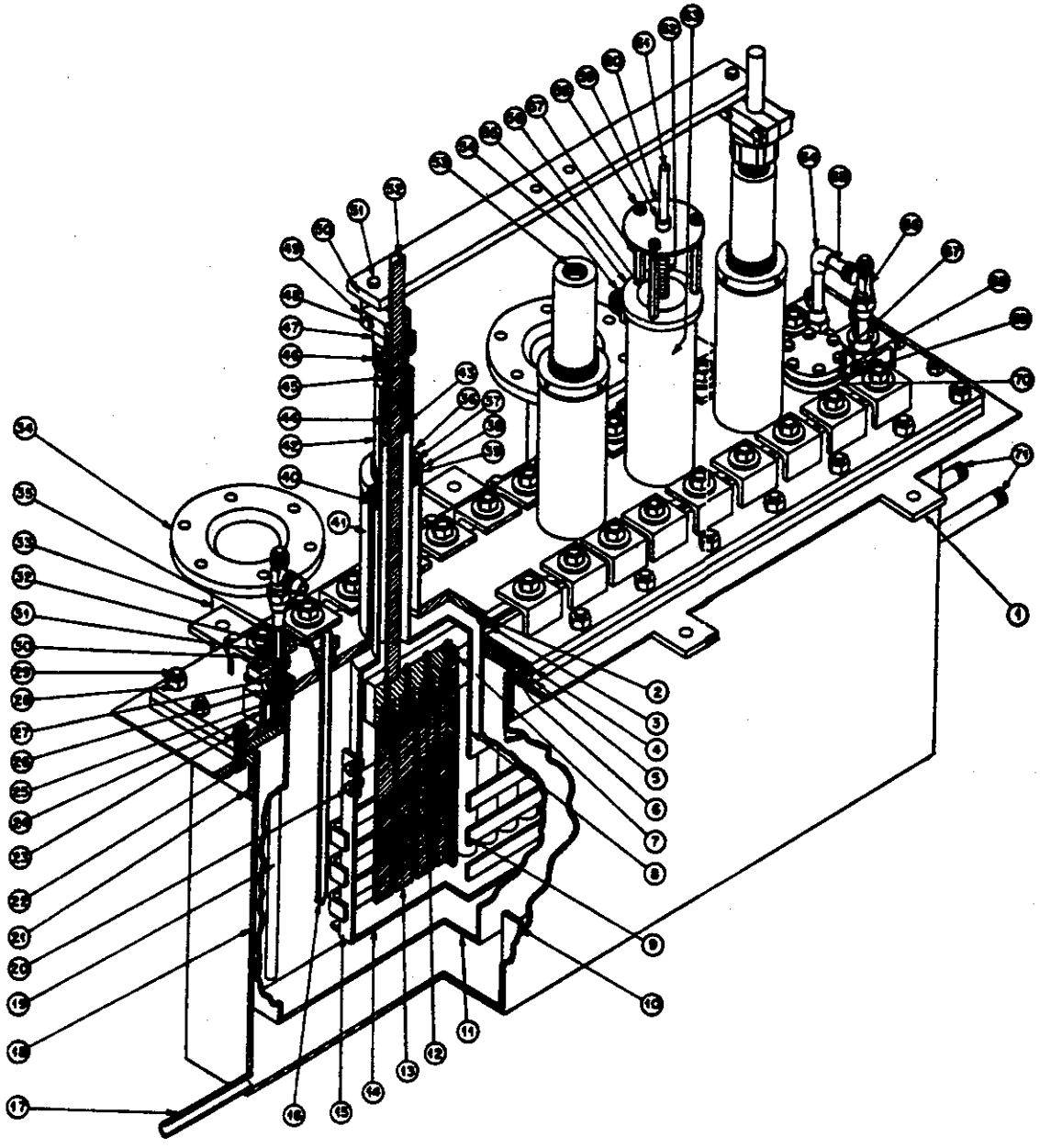


FIGURE 8. METHOD OF ANODE SUPPORT - FALKENHAGEN CELL
(After Carter et al. 1946)



Part No.	Nomenclature	No.* Required	Material
1	Lug	6	Steel
2	Head plate	1	Copper
3	Head plate gasket	1	Copper and asbestos
4	Clamp flange	1	Steel
5	Cathode-box flange	1	Monel
6	Coolant-box gasket	1	Lead
7	Anode bar	1	Copper
8	Skirt	1	Monel
9	Diaphragm-cage bar	6	Monel
10	Coolant-box rib	10	Steel
11	Cathode-box	1	Monel
12	Copper dowel pin	19	Copper
13	Carbon rods	19	Carbon
14	Diaphragm-cage bottom	1	Monel
15	Diaphragm-cage end	2	Monel
16	Thermocouple well	1	Monel
17	Coolant drain pipe	1	Iron
18	Coolant box	1	Steel
19	Regeneration tube	4	Monel
20	Monel bolt	4	Monel
21	Coolant-box flange	1	Steel
22	Flange bolt-end	6	Steel
23	Flange nut-end	6	Brass
24	Head-plate clamp	28	Steel
25	Clamp stud	28	Steel
26	Clamp washer	28	Steel
27	Clamp nut	28	Brass
28	Flange nut-side	22	Brass
29	Flange bolt-side	22	Steel
30	Packing gland	4	Copper
31	Packing nut	6	Brass
32	Packing	4	TFE
33	Condenser elbow	2	Steel
34	Condenser flange	2	Brass
35	Thermocouple nut	1	Steel
36	Diaphragm clamp ring	3	Bronze
37	Lock ring	3	Bronze
38	Packing	3	TFE
39	Cathode riser ring	3	Bronze
40	Packing	3	TFE
41	Cathode tube	3	Copper
42	Anode tube (diaphragm riser)	3	Monel
43	Anode packing gland	2	Bronze
44	Packing	4	TFE
45	Insulation sleeve	2	Mica
46	Anode packing nut	2	Brass
47	Spacer	2	Bakelite
48	Clamp—block bolt and nut	4	Steel
49	Clamp—block	2	Copper
50	Anode bus bar	1	Copper
51	Anode bus bar bolt and nut	2	Steel
52	Anode bar riser	2	Copper
53	Gas outlet fitting	1	Bronze
54	Hydrogen outlet	1	Brass
55	Valve-seat plate	1	Bronze
56	Valve plunger	1	Brass
57	Spacer	2	Brass
58	Spacer nut	6	Brass
59	Bushing	1	Brass
60	Guide plate	1	Brass
61	Valve stem	1	Brass
62	Valve spring	1	Steel
63	Gas outlet tube	1	Copper
64	Elbow	2	Brass
65	Nipple	2	Monel
66	T	2	Brass
67	Inspection-port bolt	6	Steel
68	Inspection-port cover	1	Brass
69	Inspection-port gasket	1	TFE
70	Inspection-port ring	1	Bronze
71	Coolant overflow	2	Iron

* For one fluorine cell

FIGURE 7. HIGH TEMPERATURE CELL OF JOHNS HOPKINS UNIVERSITY (After Burford et al. 1951)

TABLE 21

CONCENTRATIONS OF FLUORINE AND HYDROGEN FLUORIDE

ALLOWED IN A WORKING ENVIRONMENT

(After Siegmund 1967)

Basis of Exposure	Time of Exposure	Fluorine ppm	Hydrogen Fluorine ppm
Maximum allowable concentration, continuous 8 hour exposure (American Conference of Government Industrial Hygienists, 1970)	8 hours	0.1	3
Emergency exposure limits (Siegmund 1967)	60 mins 30 mins 10 mins	1 2 3	8 10 20

TABLE 22

VENTILATION RATES - OAK RIDGE AND PORTSMOUTH GASEOUS DIFFUSION PLANTS

(After Goodyear Atomic Corporation 1967b, Smiley and Brater 1956)

Area	Air Changes per Hour for Normal Use	Emergency Use	Air Pressure
HF Condenser Room	6	20	Negative
Cell Rooms	30	60	Negative
Cell Neutralisation Rooms	50	100	Negative
Cell Maintenance Room	6	30	
Electrolyte Makeup Room	25	50	Negative
Hydrogen and Fluorine Pump Rooms	25	50	Negative
HF Vaporizer Room	25	50	Negative

Other areas and rooms were provided with from six to twelve air changes per hour.

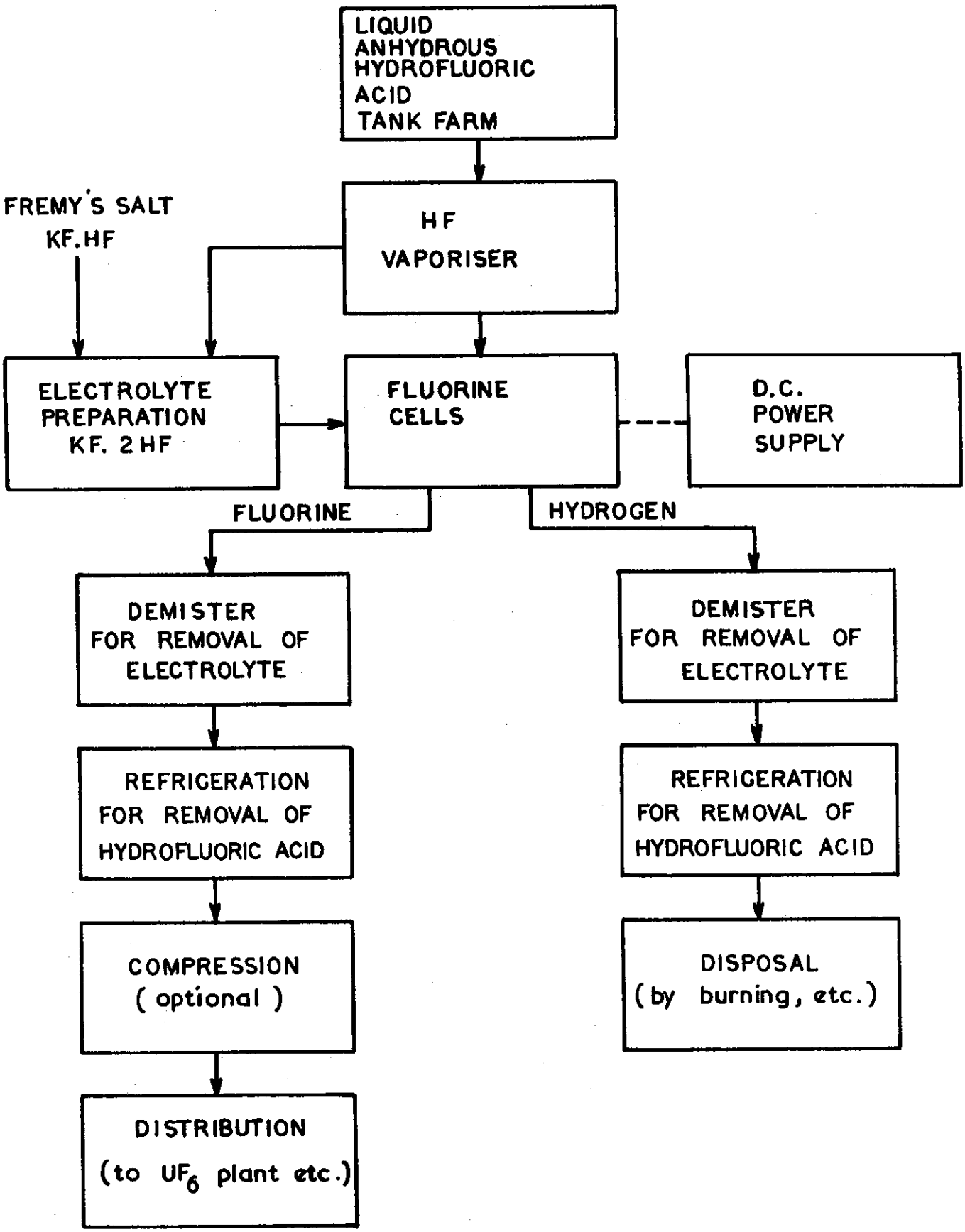
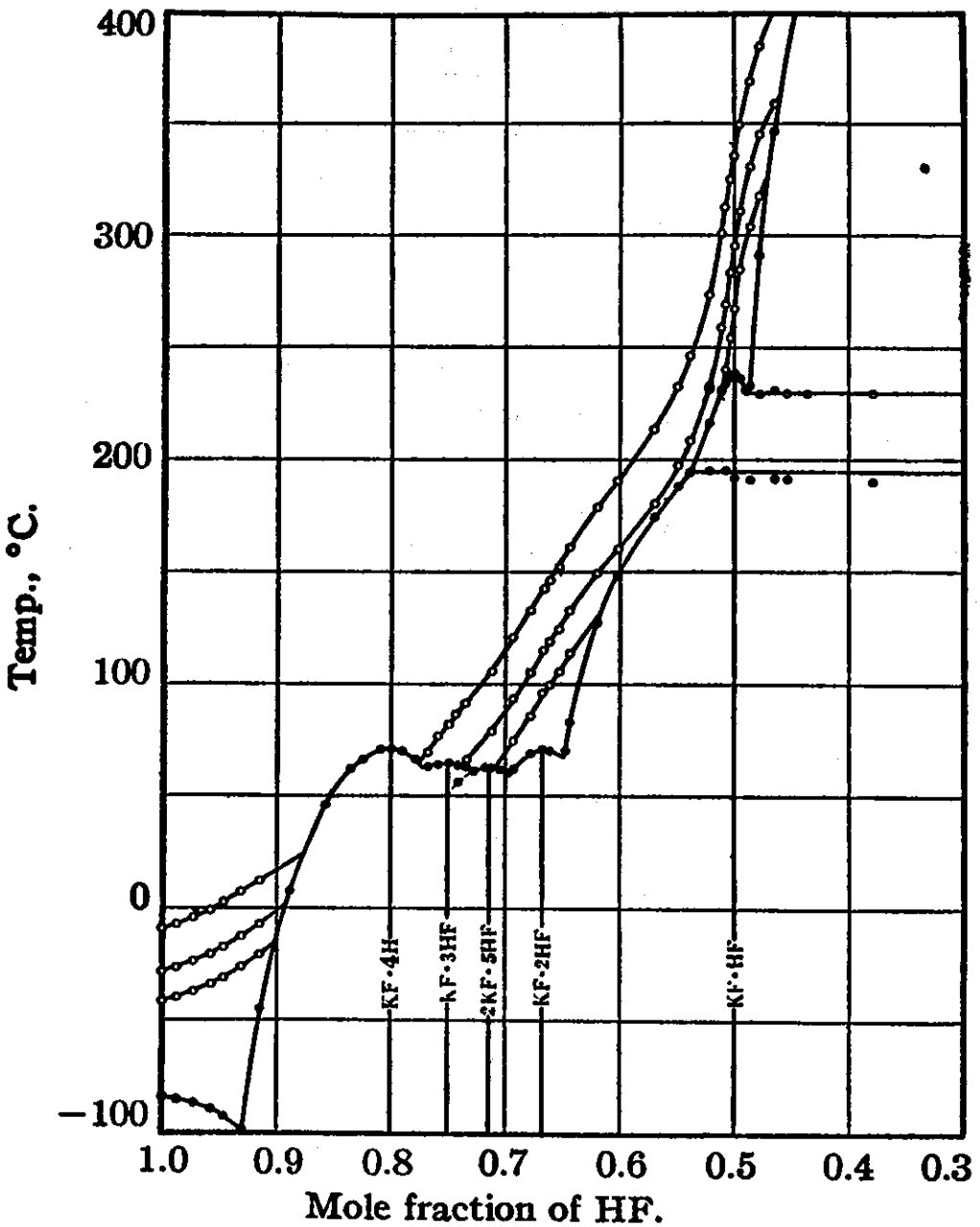


FIGURE 1. FLOW DIAGRAM OF A FLUORINE GENERATION PLANT



The system potassium fluoride–hydrogen fluoride: ●, freezing point; ◓, eutectic point; ◑, transition point; O, vapor pressure. The highest vapor pressure curve is for a pressure of 25 cm., the middle for 10 cm. and the lowest for 5 cm. of mercury.

FIGURE 2. PHASE DIAGRAM OF THE POTASSIUM FLUORIDE -HYDROGEN FLUORIDE SYSTEM (After Cady 1934)

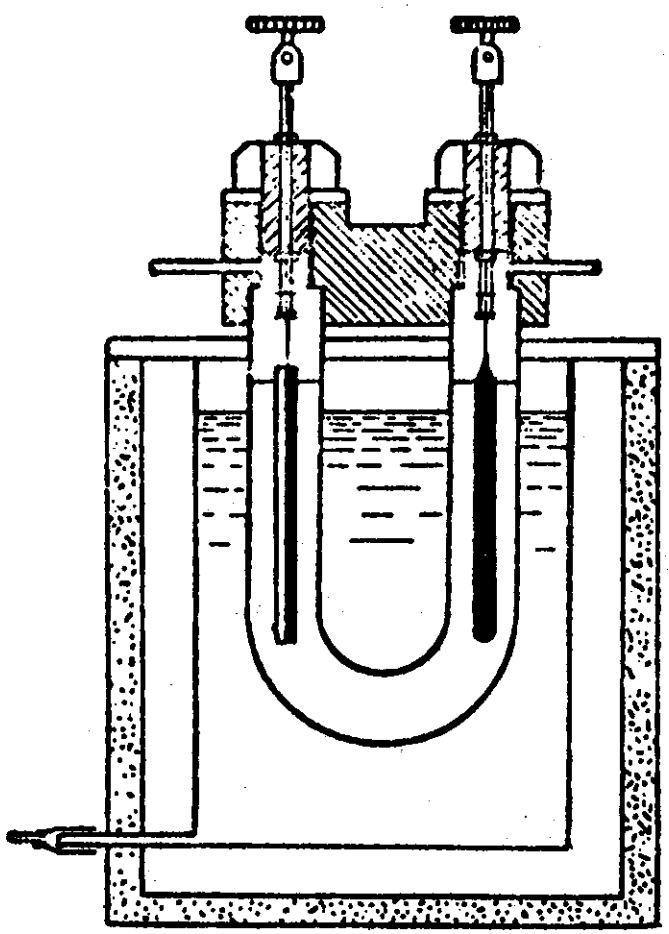


FIGURE 3. LOW TEMPERATURE CELL OF MOISSAN (1886)
(After Cady et al. 1942)

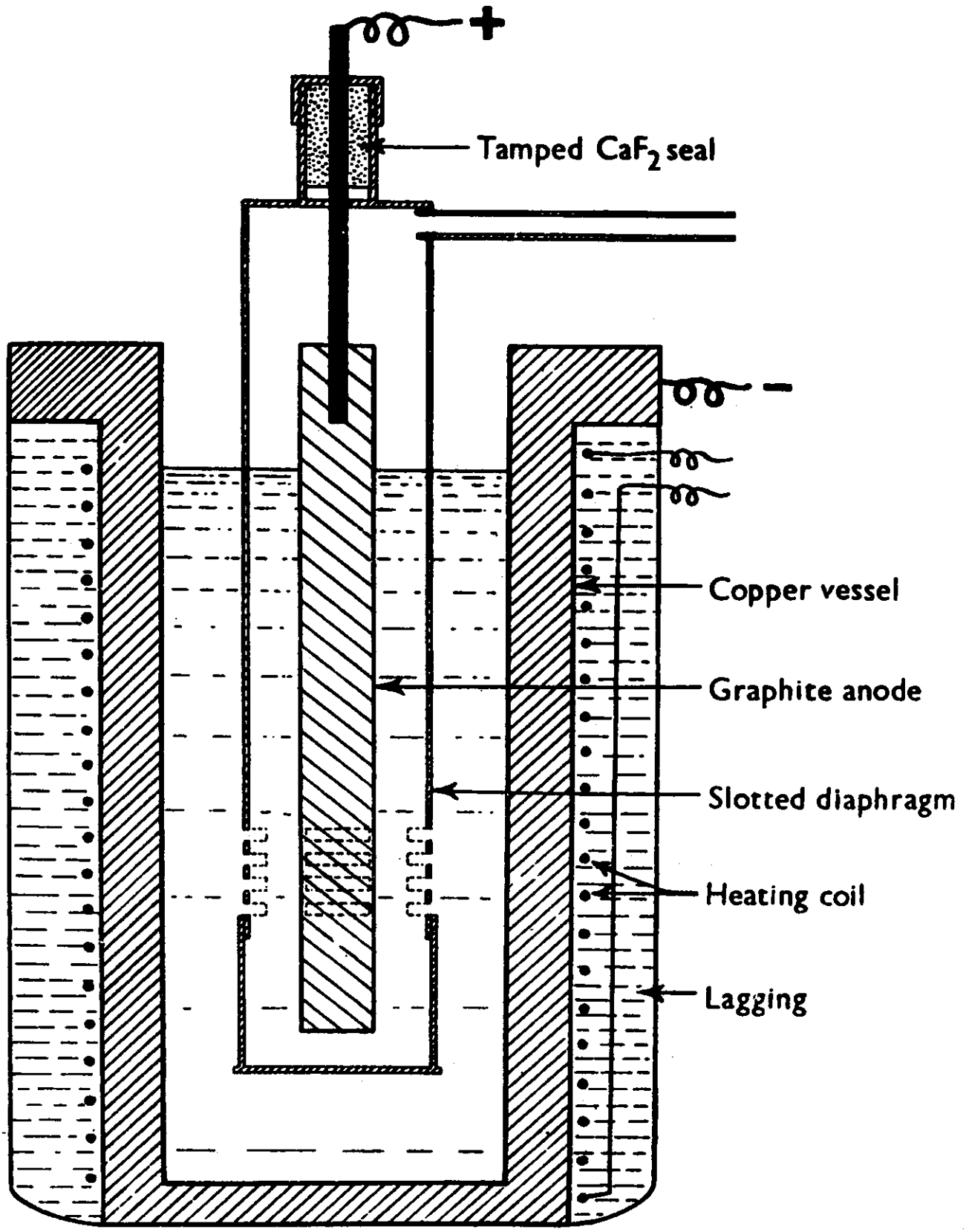


FIGURE 4. HIGH TEMPERATURE CELL OF ARGO et al. (1919)
(After Leech 1956)

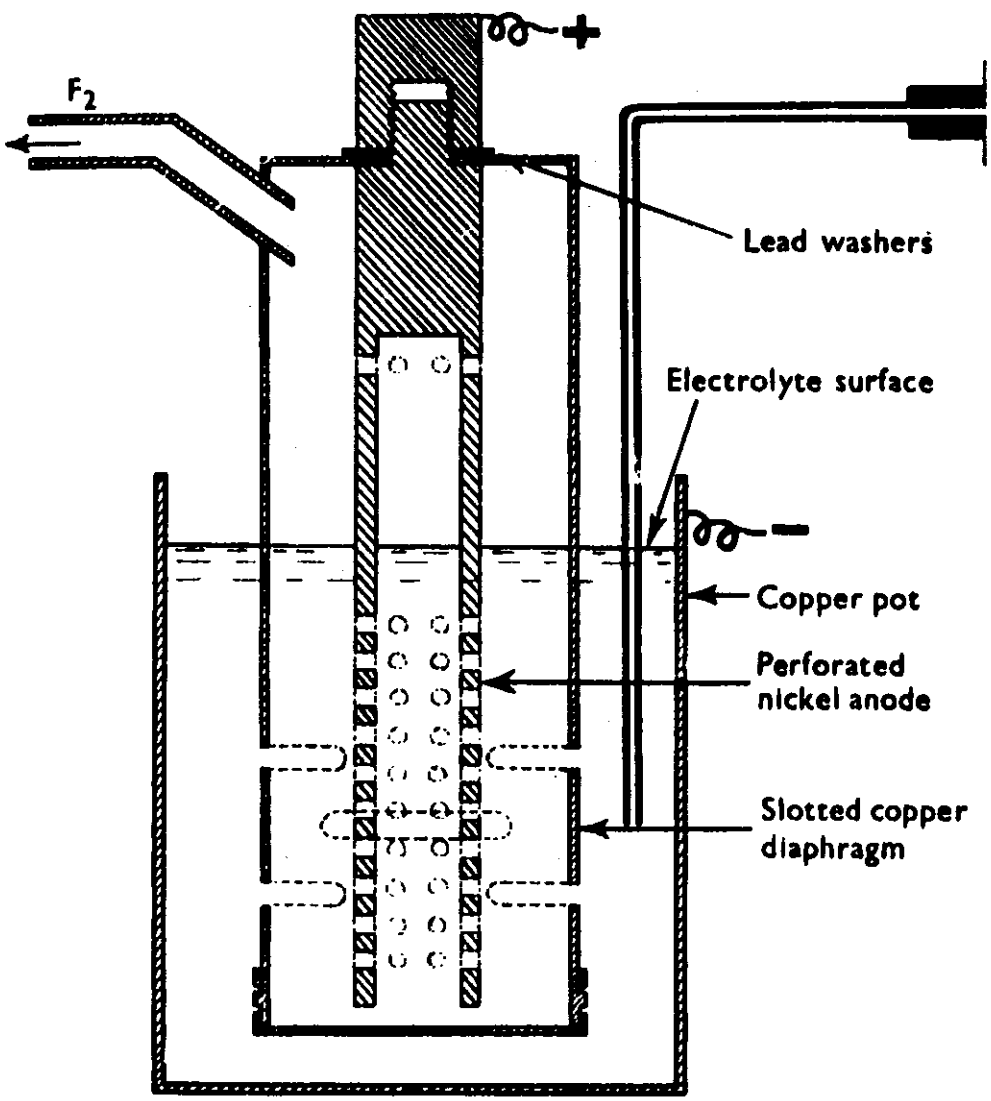


FIGURE 5. MEDIUM TEMPERATURE CELL OF LEBEAU AND DAMIENS (1925) (After Leech 1956)

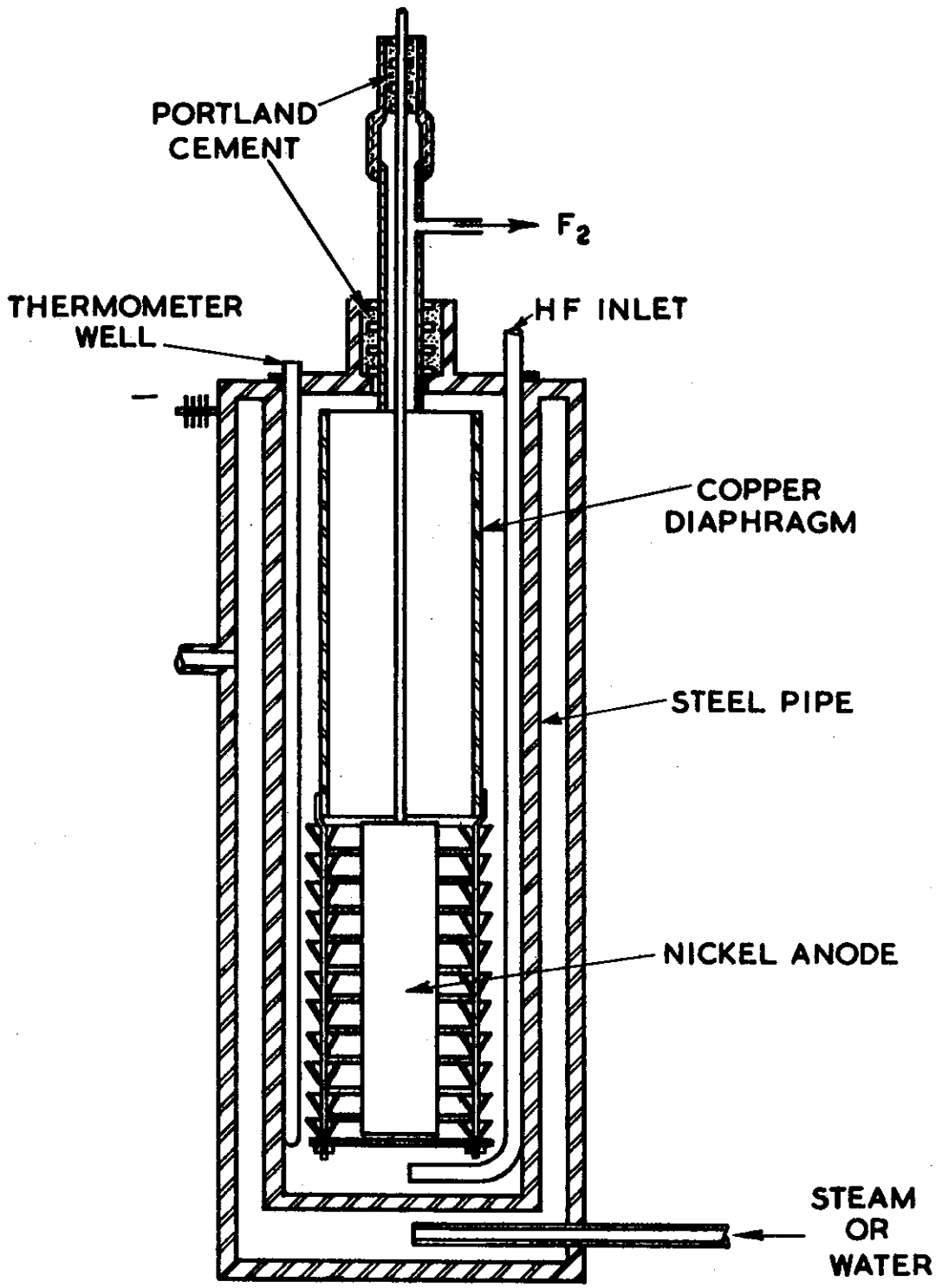


FIGURE 6. MEDIUM TEMPERATURE CELL OF CADY et al. (1942)
(After Cady et al. 1942)

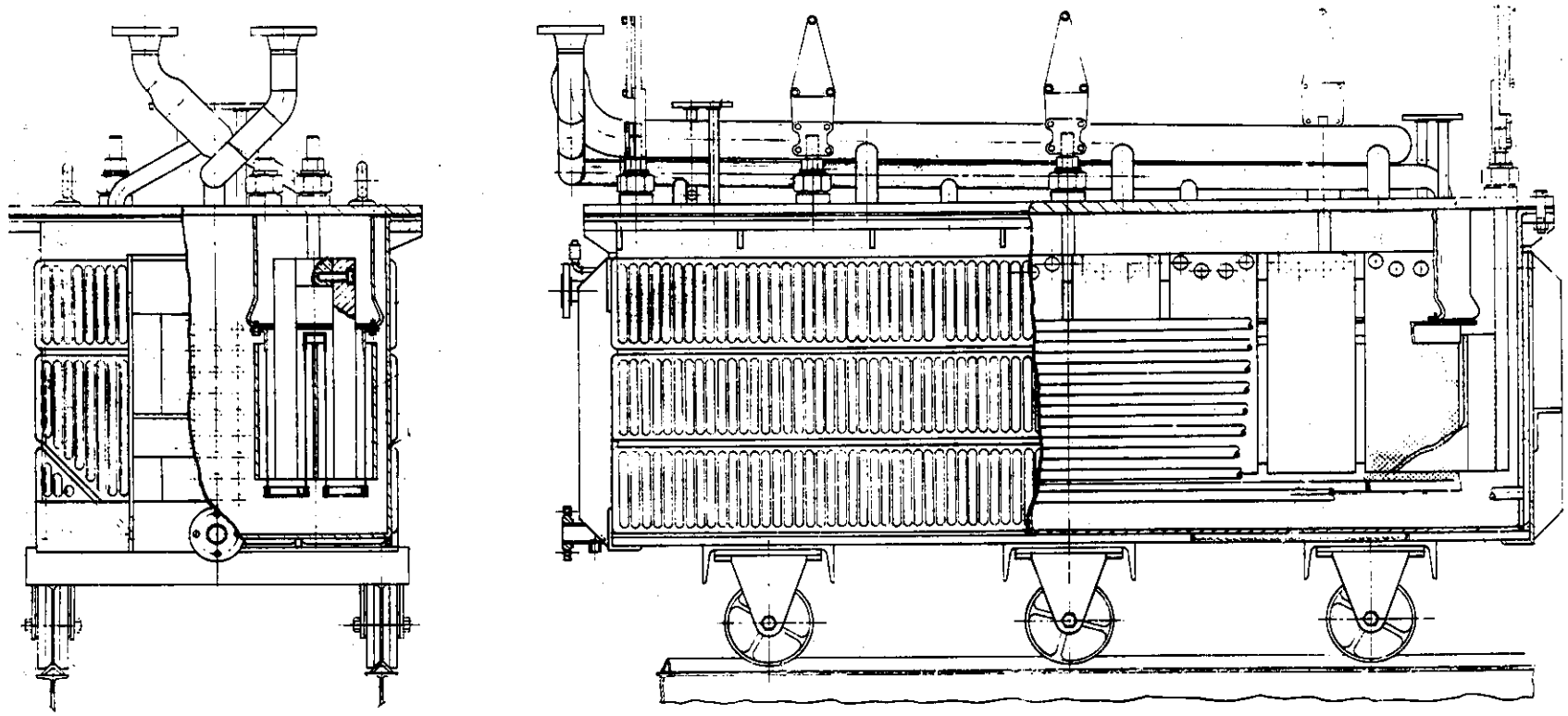


FIGURE 9. GENERAL ASSEMBLY OF USAEC E-TYPE CELL (After Kelly and Clark 1967a, 1968a)

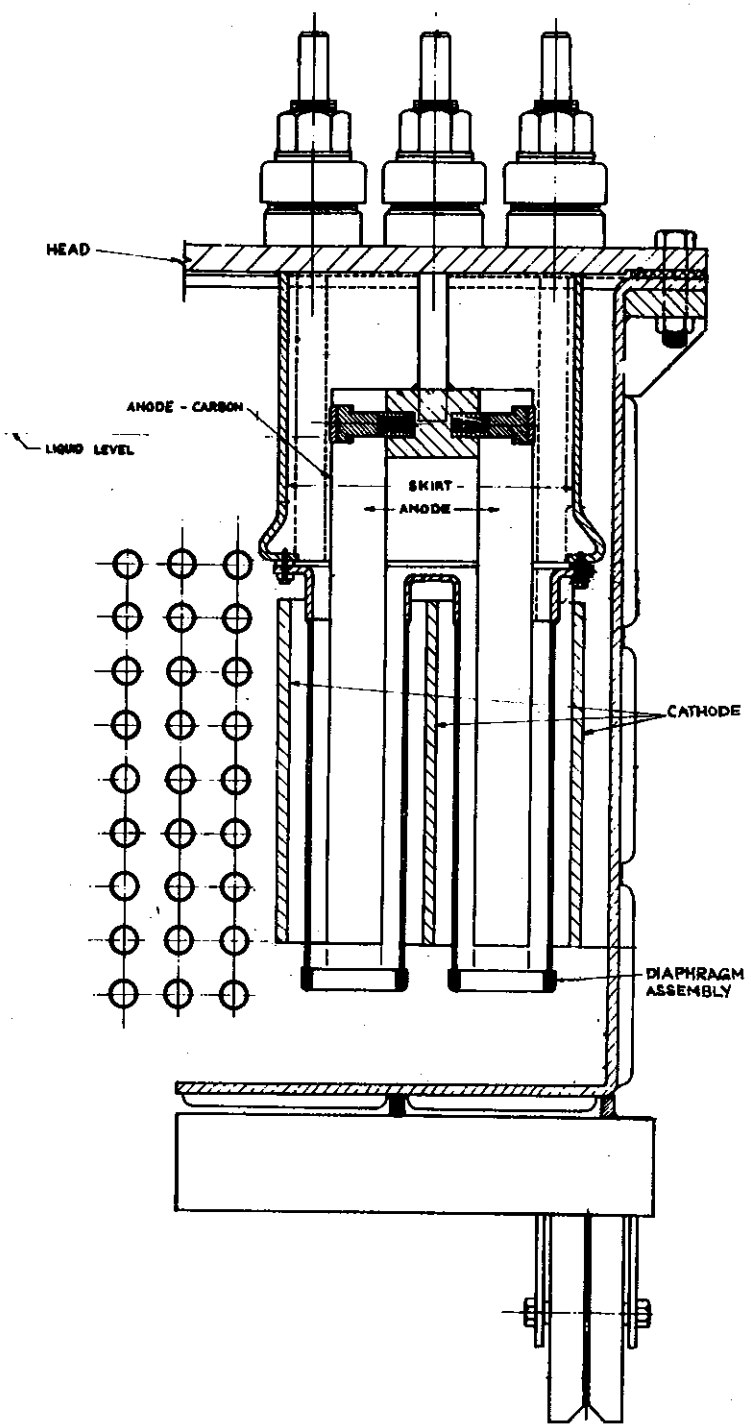


FIGURE 10. HALF SECTION OF USAEC E-TYPE CELL (After Kelly and Clark 1967a, 1968a)

ARRANGEMENT FOR TIGHTENING ANODE COMPARTMENT.

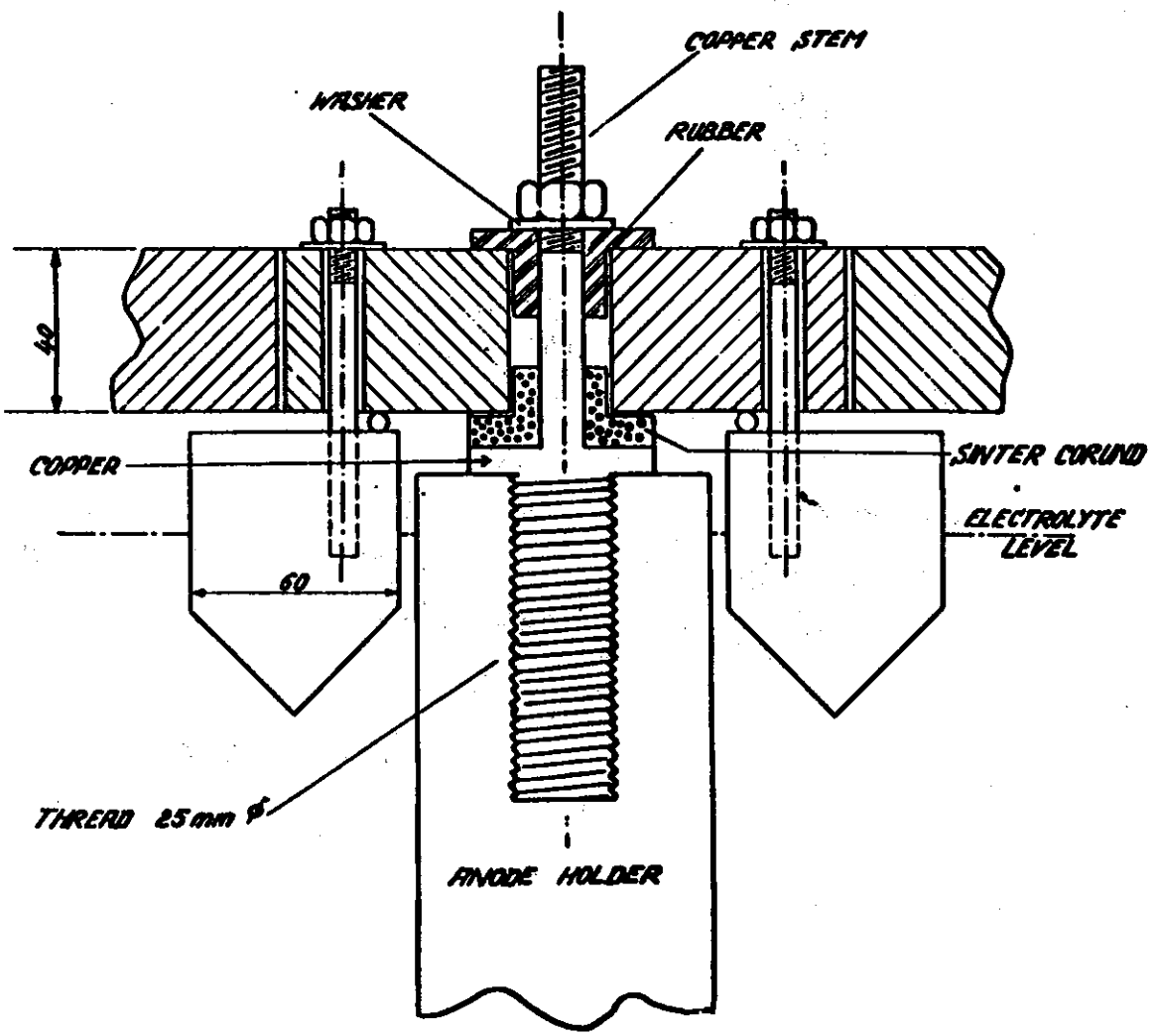


FIGURE 11. ANODE CONNECTION - LEVERKUSEN CELL
(After Karr 1946)

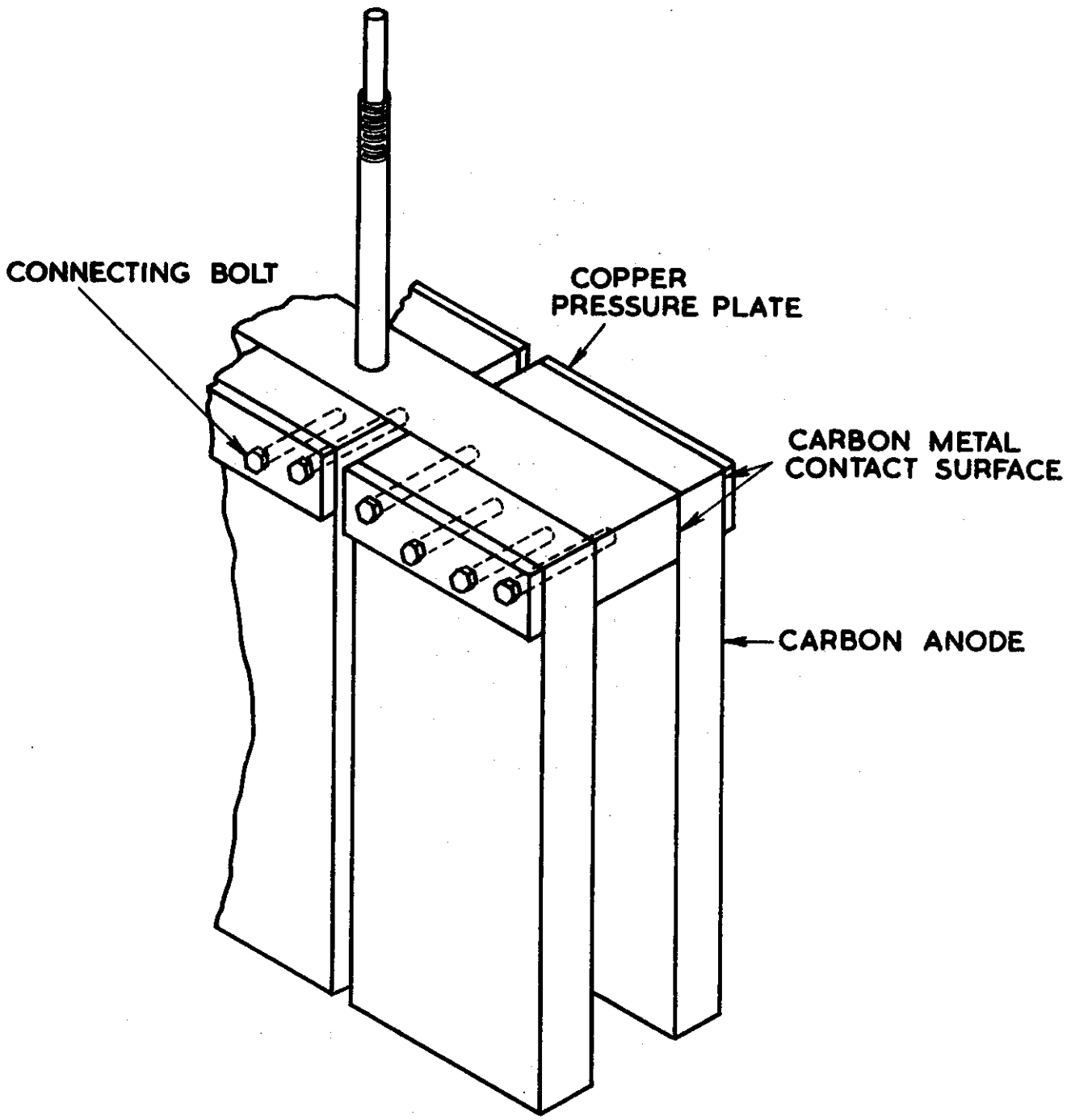


FIGURE 12. ANODE CONNECTION - USAEC C-TYPE CELL
(After Vavalides et al. 1958)

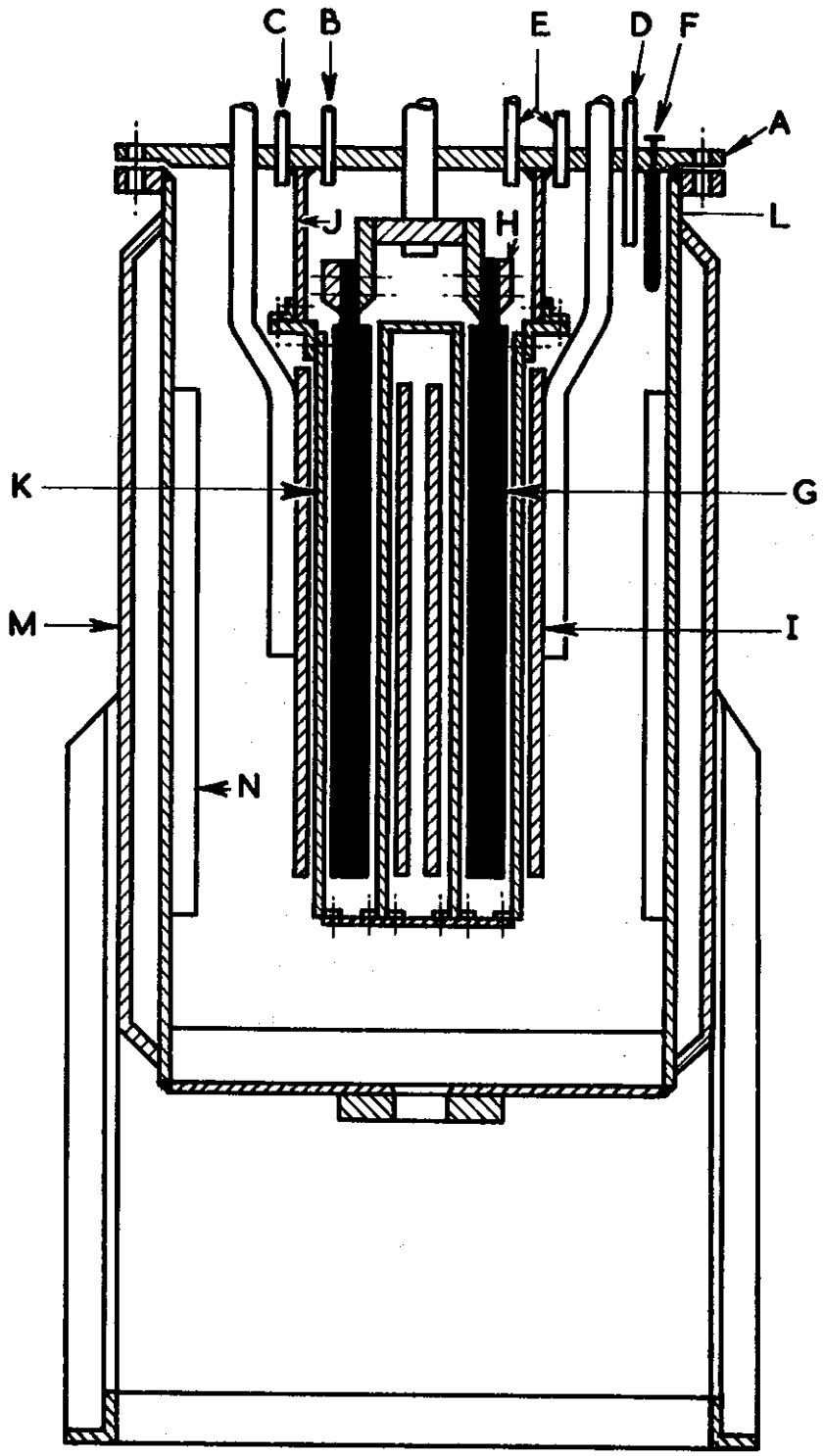


FIGURE 13. METHOD OF ANODE SUPPORT - HOOKER AND DUPONT CELLS (After Downing 1951a)

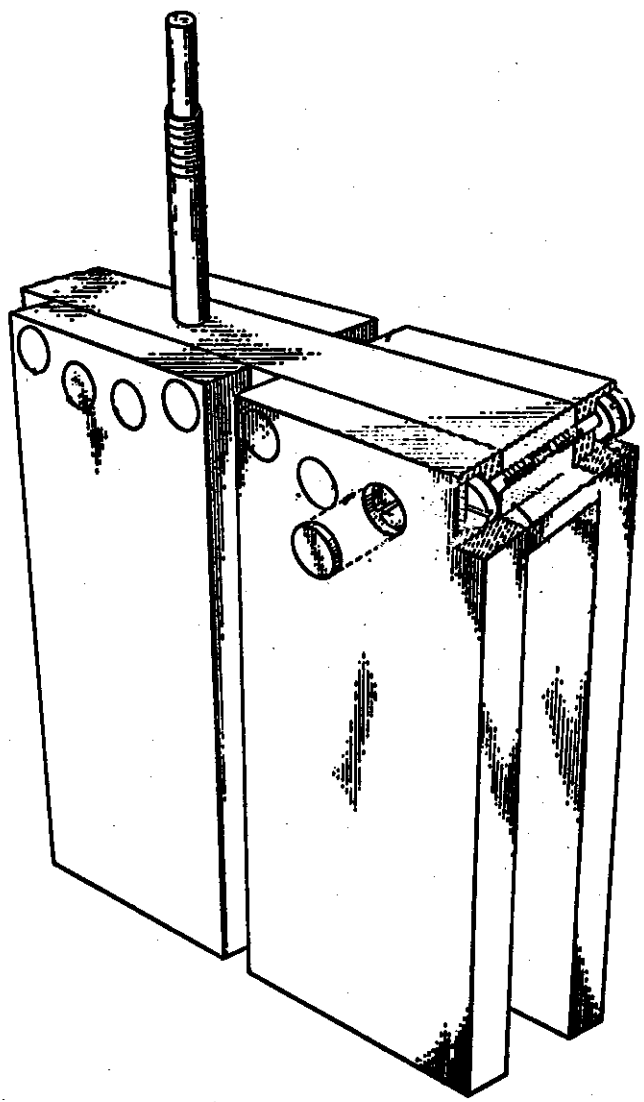


FIGURE 14. ANODE CONNECTION - USAEC E-TYPE CELL.
(After Cable et al. 1962)

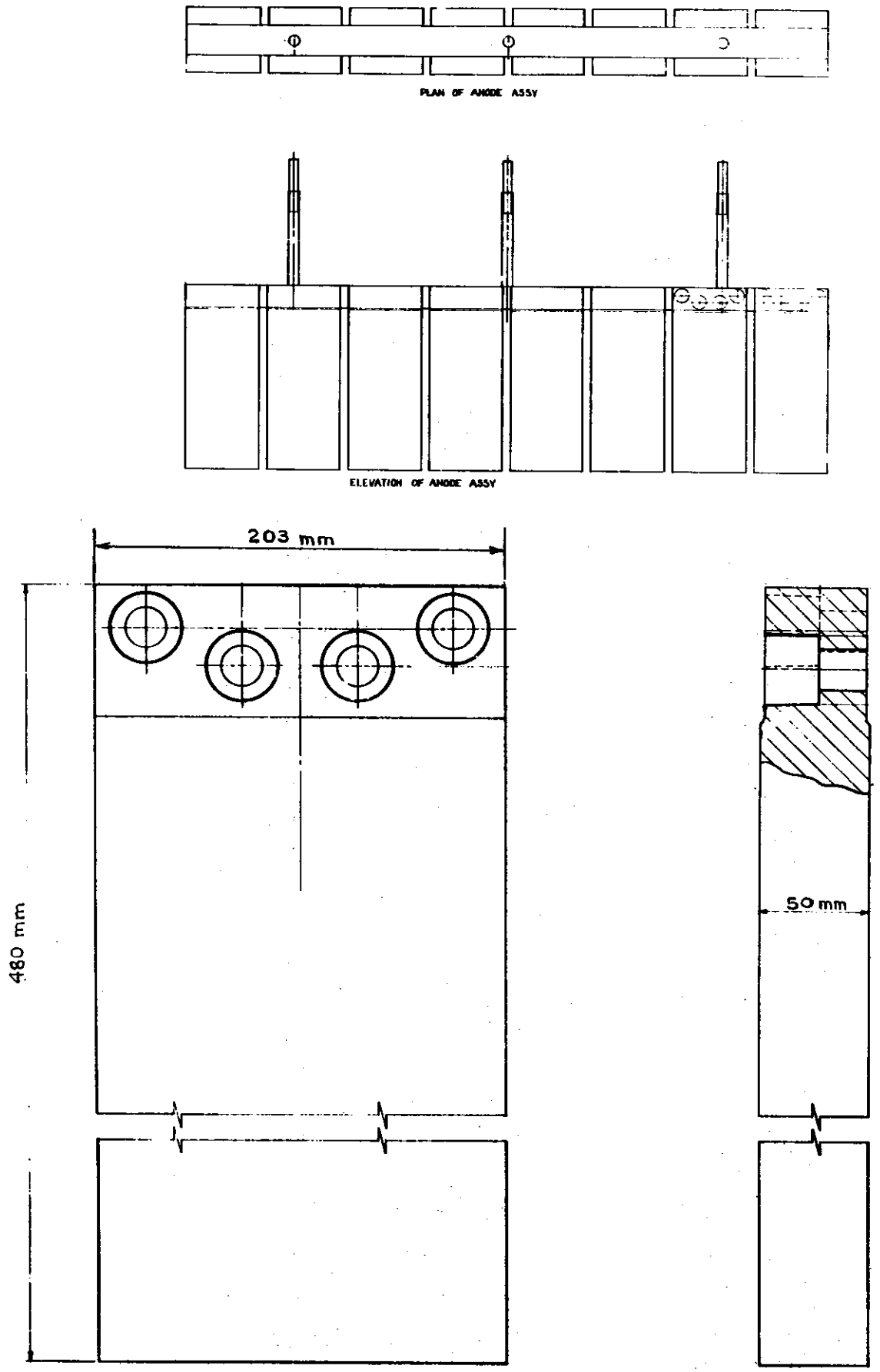


FIGURE 15. ANODE ASSEMBLY - USAEC E-TYPE CELL (After Kelly and Clark 1967a, 1968a)

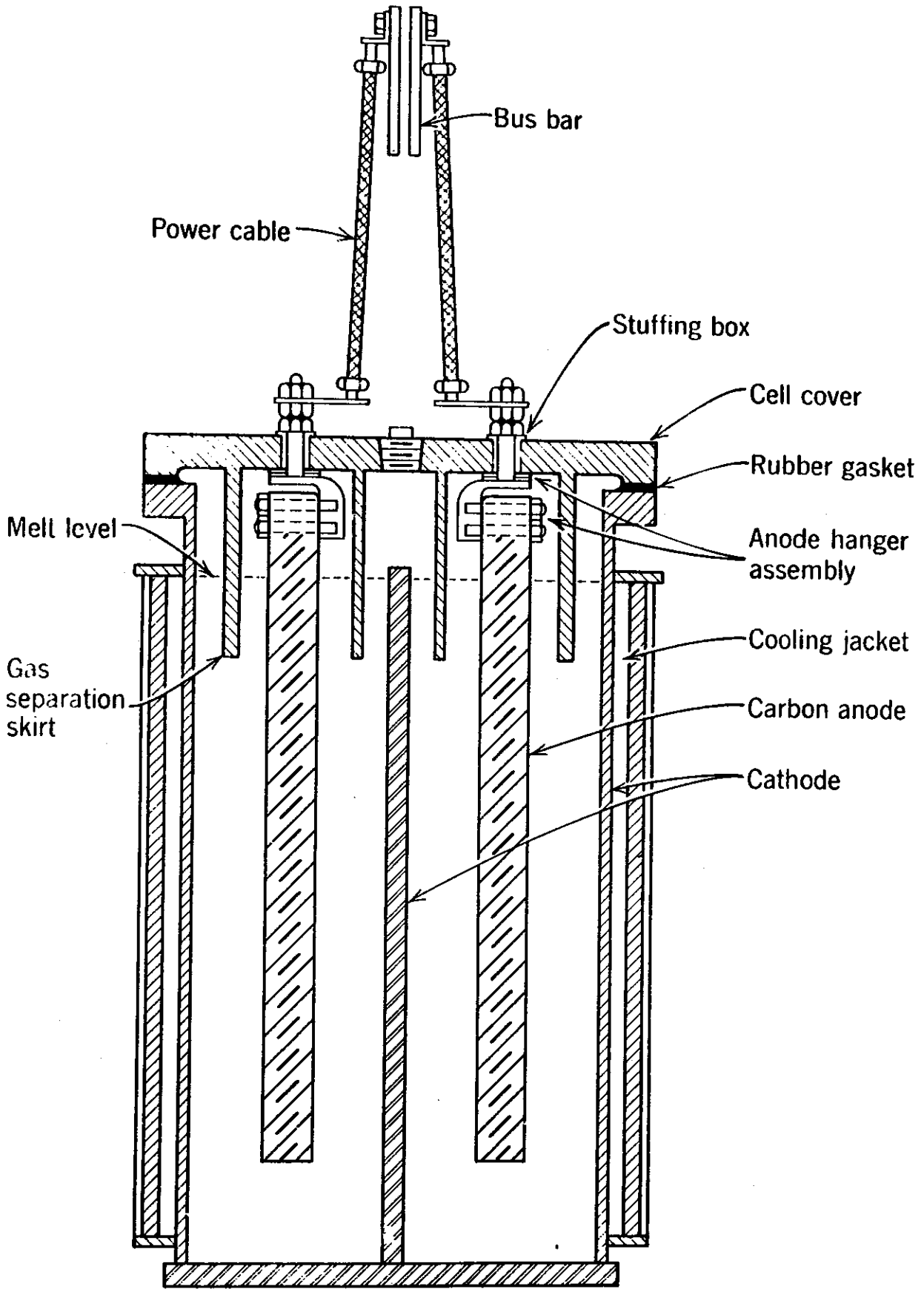
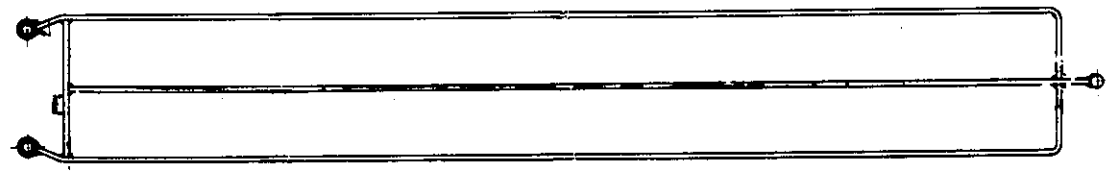
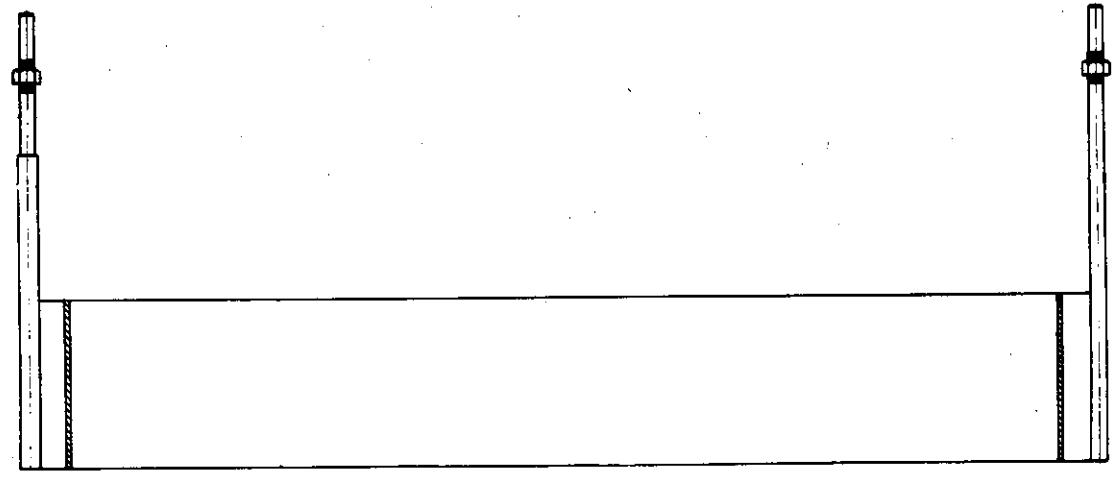


FIGURE 16. SECTION OF THE ALLIED CHEMICAL CORPORATION CELL
(After Neumark and Siegmund, 1966)



TOP VIEW



SECTIONAL ELEVATION

FIGURE 17. CATHODE ASSEMBLY - USAEC E-TYPE CELL
(After Kelly and Clark 1967a, 1968a)

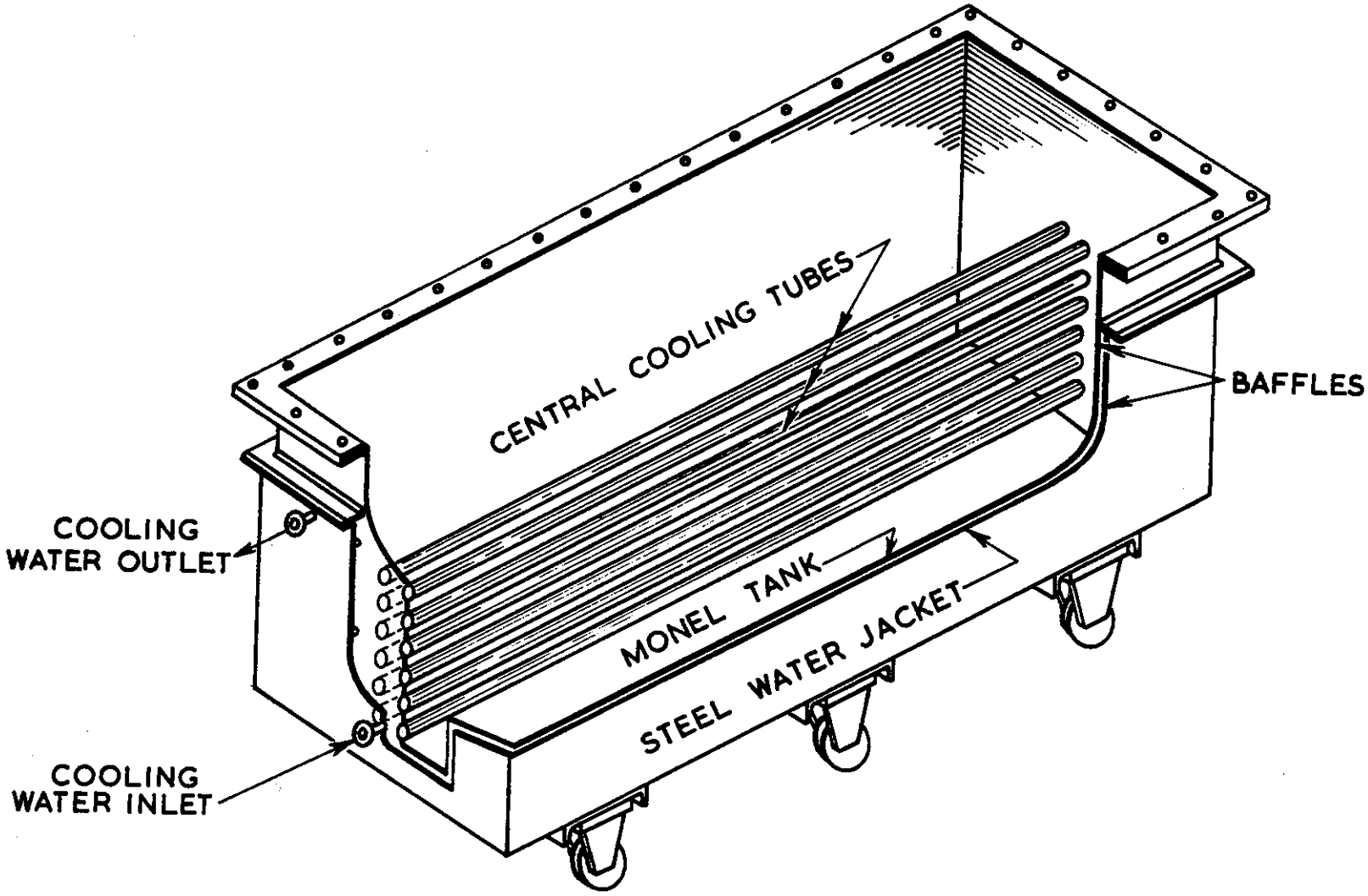


FIGURE 18. TANK CONSTRUCTION - TYPICAL USAEC CELL (After Dykstra et al. 1958)

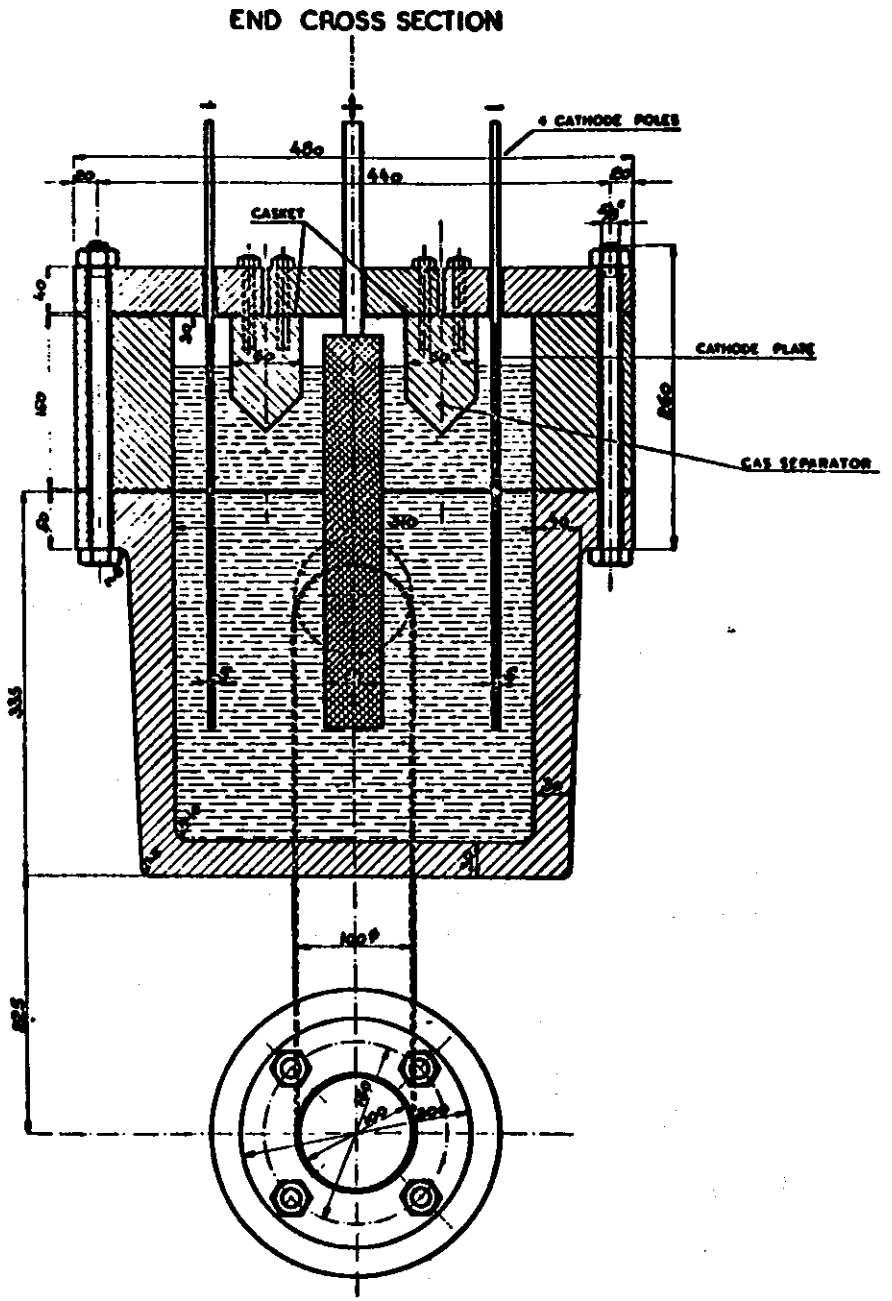


FIGURE 19. TANK CONSTRUCTION - LEVERKUSEN CELL
(After Karr 1946)

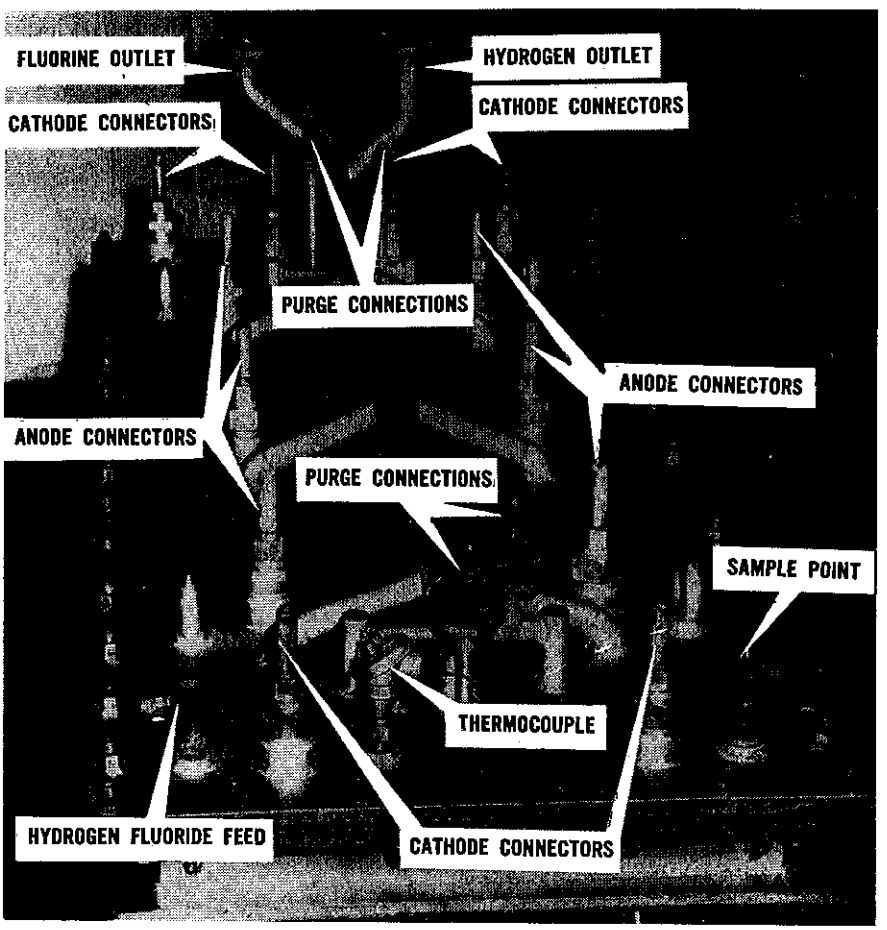


FIGURE 20. CELL COVER - TYPICAL USAEC CELL
(After Dykstra et al. 1958)

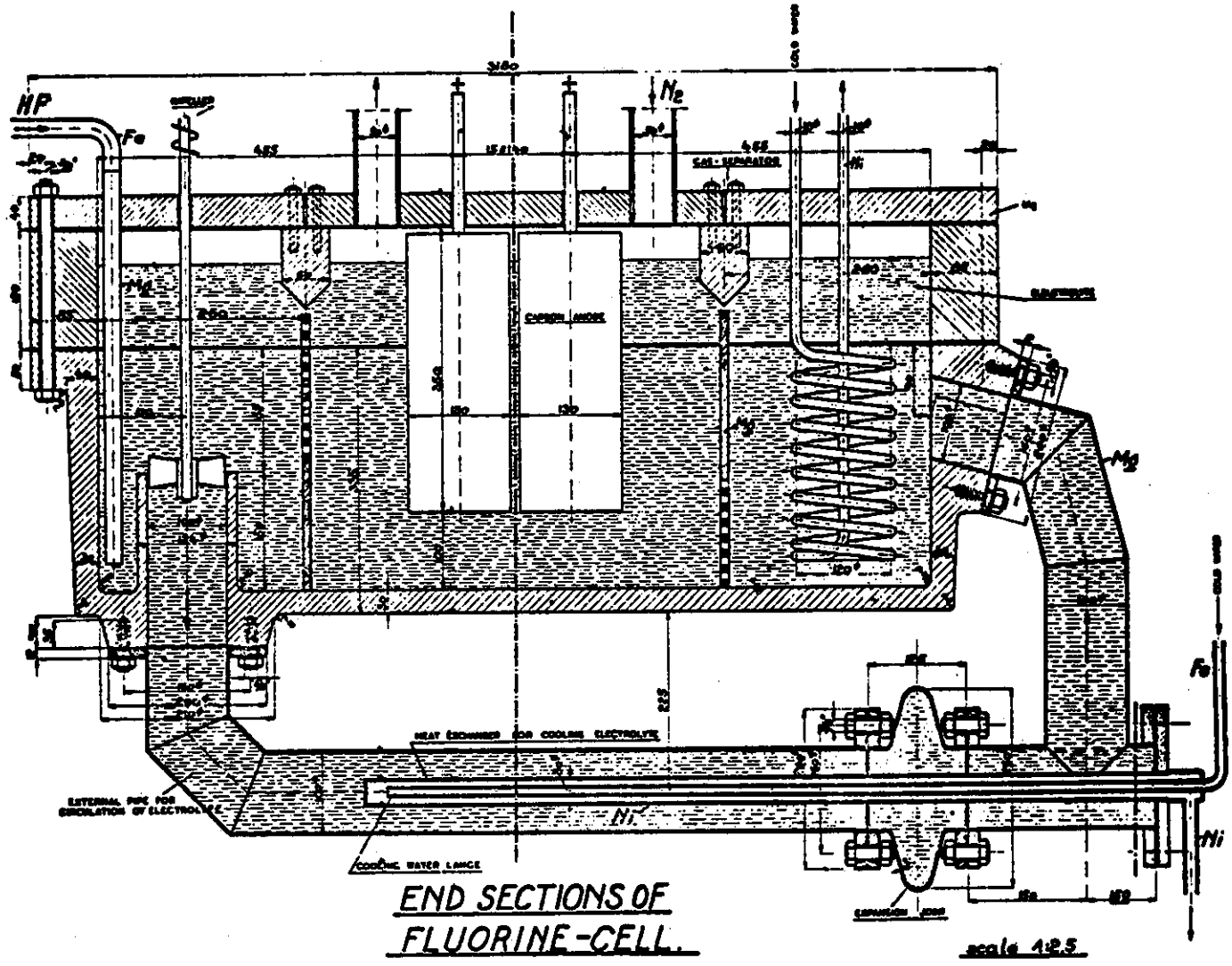


FIGURE 21. COOLING SYSTEM - LEVERKUSEN CELL (After Karr 1946)

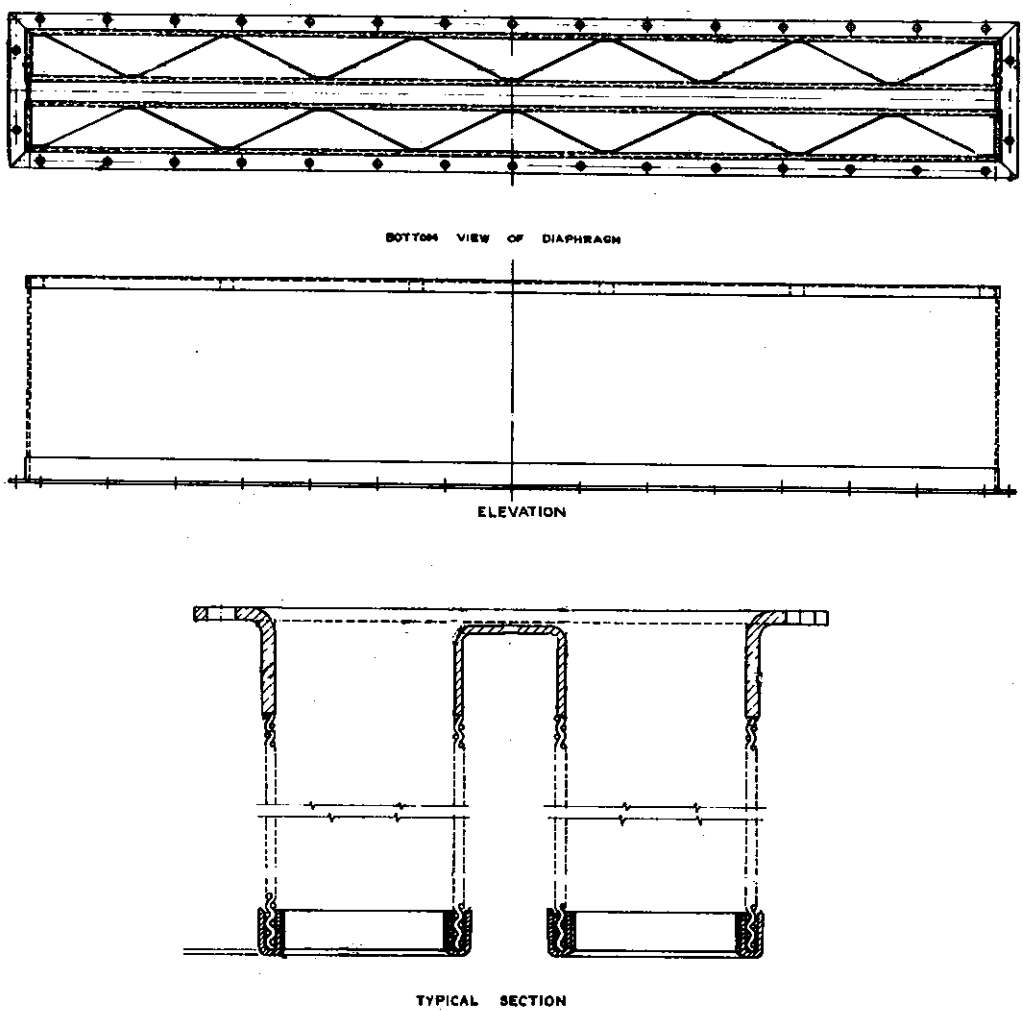


FIGURE 22. DIAPHRAGM ASSEMBLY - USAEC E-TYPE CELL (After Kelly and Clark 1967a, 1968a)

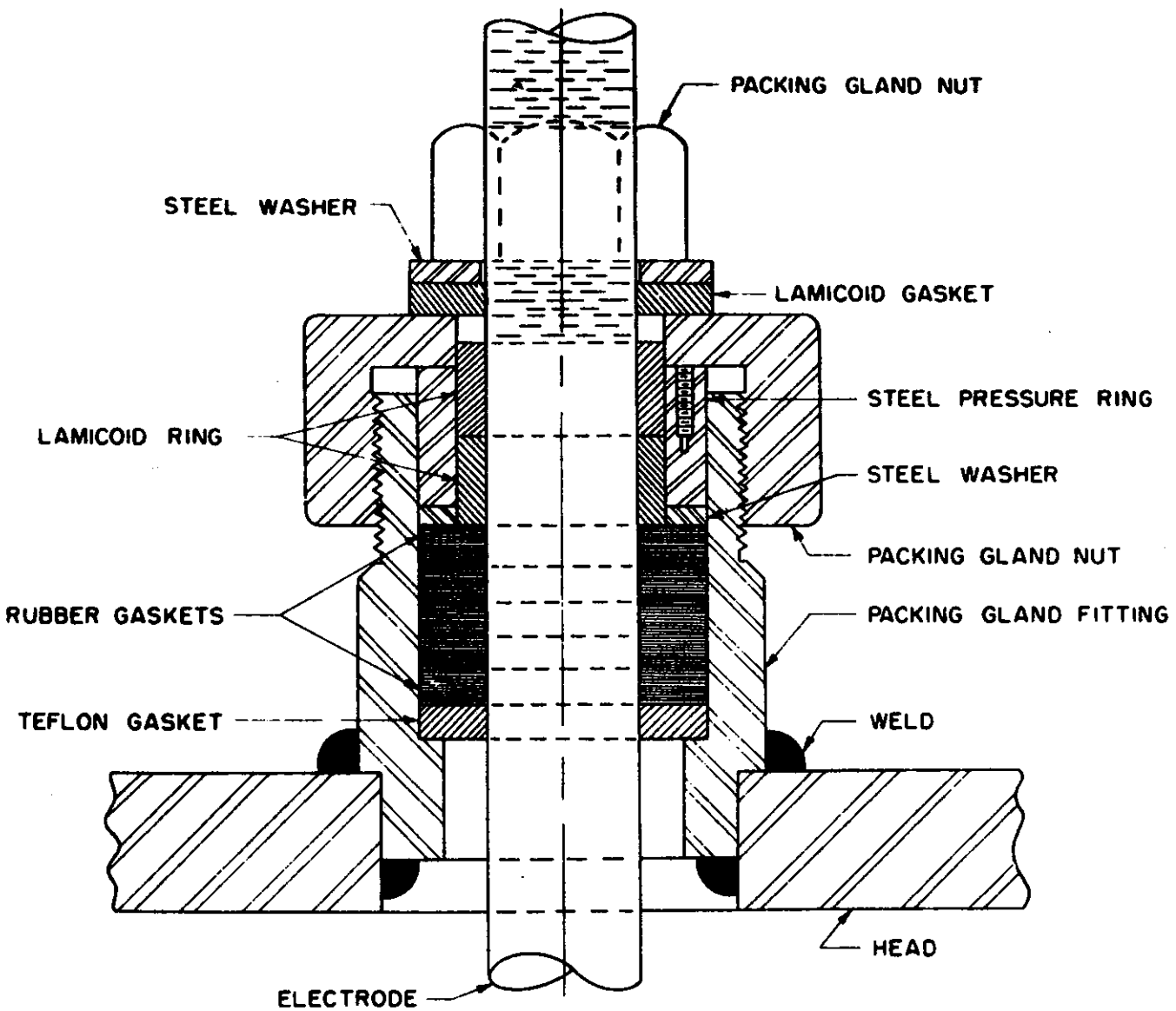


FIGURE 23. PACKING GLAND - TYPE USAEC CELL
(After Huber et al. 1958)

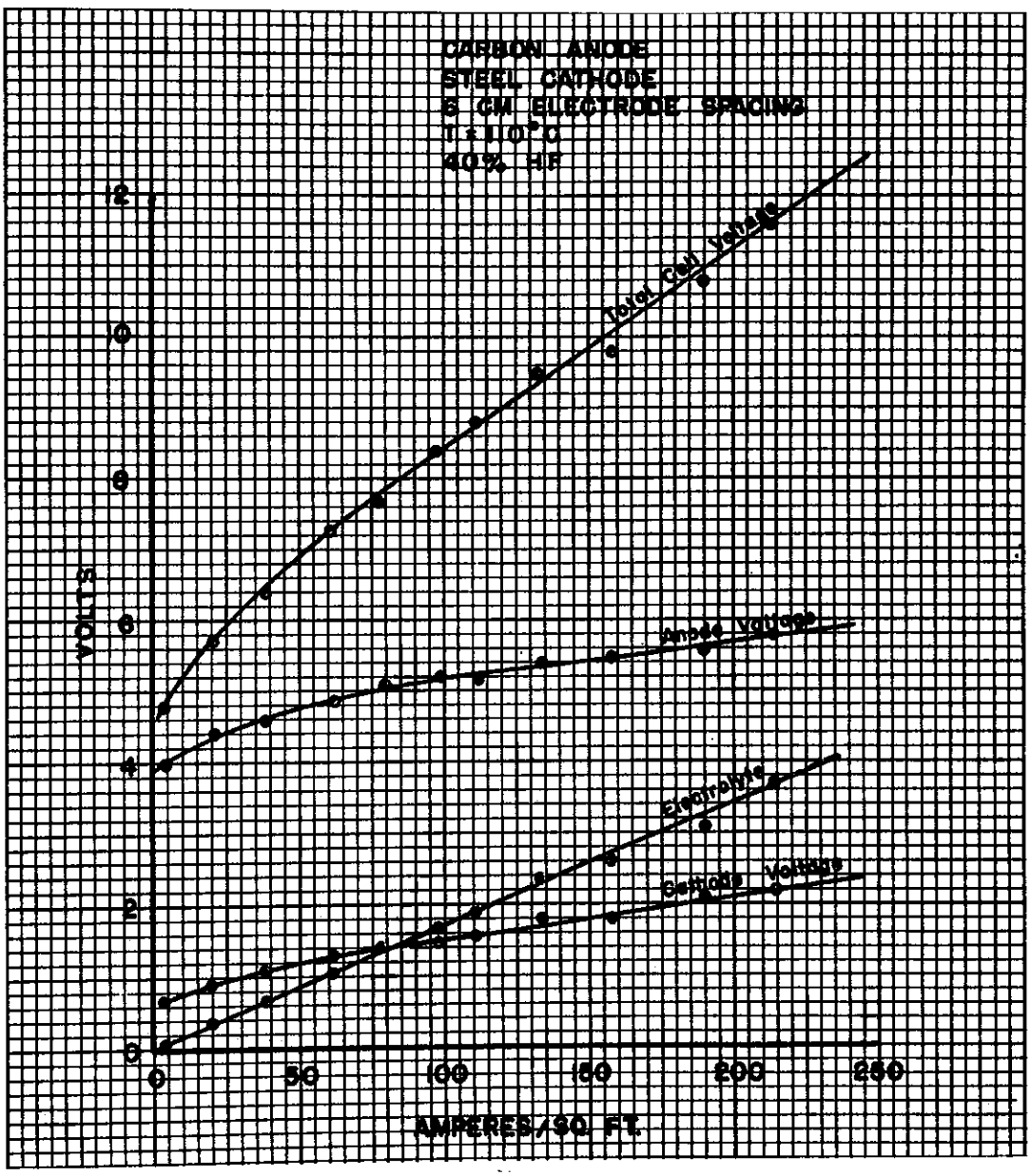


FIGURE 24. CHARACTERISTIC CELL VOLTAGE CURVES
(After Ebel and Montillon 1952)

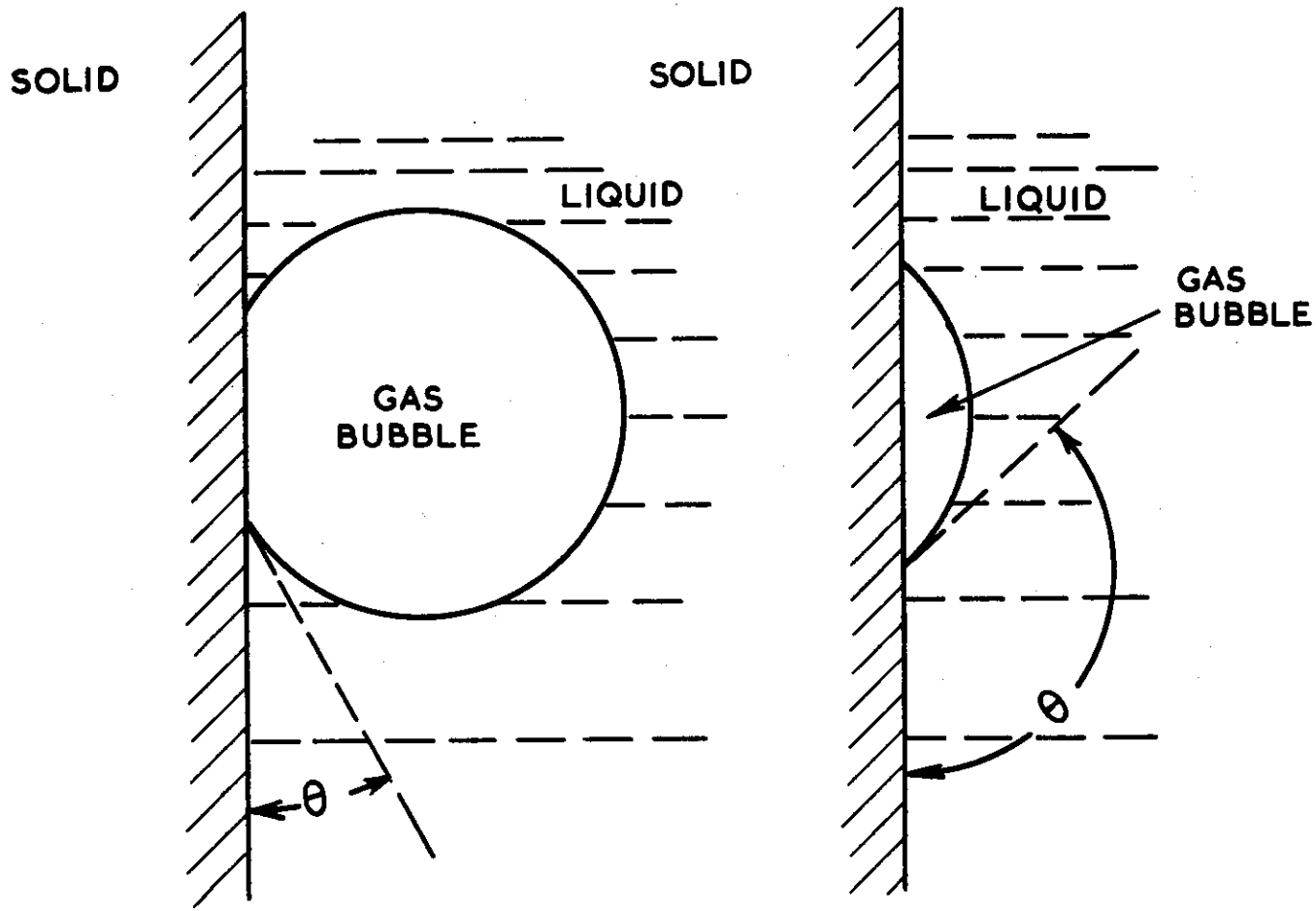


FIGURE 25. THE INFLUENCE OF CONTACT ANGLE (θ) ON BUBBLE SHAPE (After Rudge 1956)

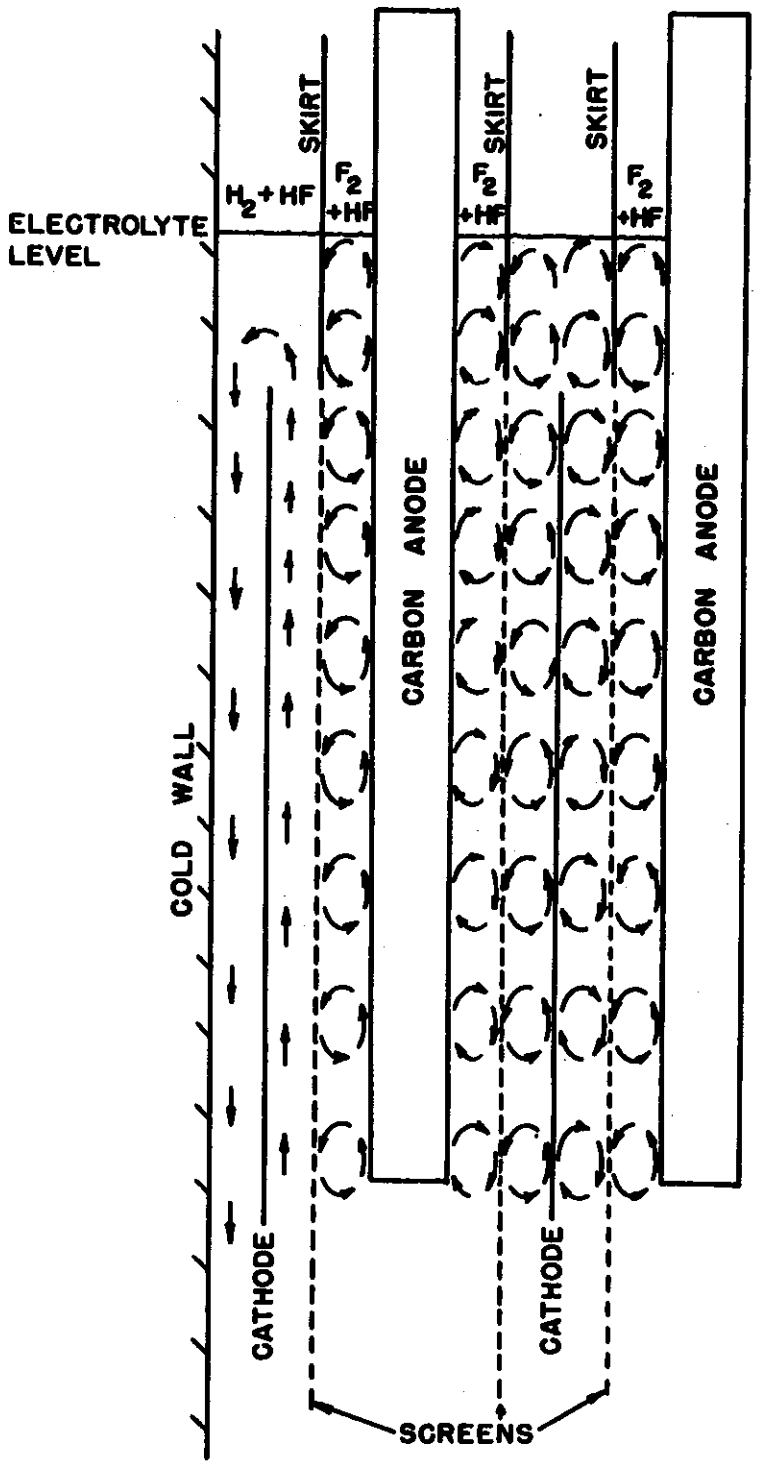


FIGURE 26. SCHEMATIC SKETCH OF ELECTROLYTE FLOW (STANDARD CELL)(After Ebel and Montillon, 1952)

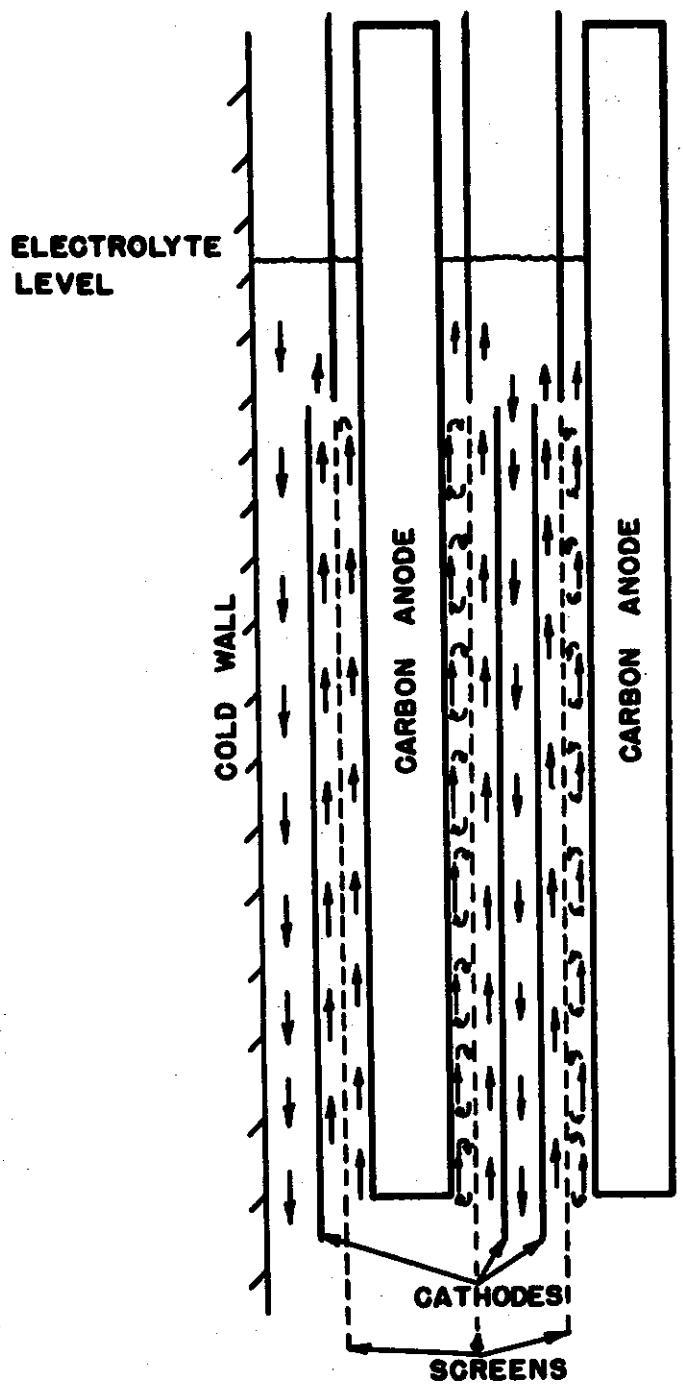


FIGURE 27. IMPROVED CIRCULATION AND REDUCED ELECTRODE SPACING (MODIFIED CELL) (After Ebel and Montillon 1952)

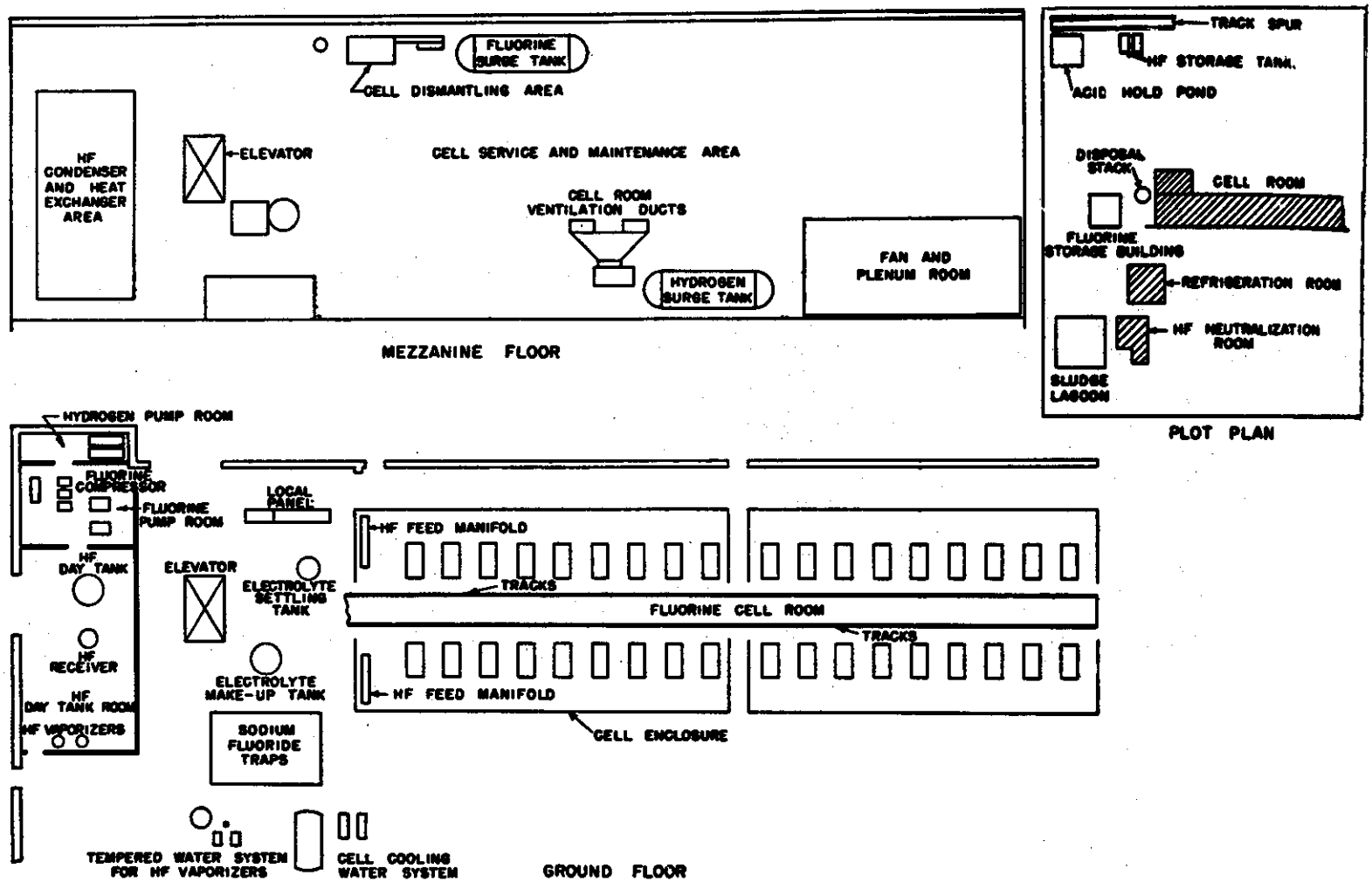


FIGURE 28. LAYOUT OF FLUORINE PLANT (After Jacobson et al. 1955)