The History of Fluorine—From discovery to commodity

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Fluorine was the last of the halogens to be isolated. The extreme difficulties and dangers of handling it retarded substantial commercial applications until World War II when it became essential for the development of nuclear devices. Development of industrial processes for the manufacture of hydrogen fluoride and chlorofluorinated hydrocarbons turned fluorine and its derivatives into a major chemical commodity. The end use pattern of fluorine has reflected the changes in social appreciation of environmental protection and safety.

Discovery of fluorine

The first historical reference regarding the use of fluorine compounds seems to be in the books of George Agricola (1494-1555), particularly in De Re Metallica. When describing the manufacturing of metals, particularly iron, he wrote: "Finally there now remains those stones which I call stones which easily melt in the fire, because when thrown into hot furnaces they flow. According to Hoover and Hoover there is little doubt that some of these stones included fluor spar. Agricola derived the names fluorine and fluor spar from the Latin fluere meaning flow or flux.

The systematic study of fluorine chemistry began in 1764 when Andreas Sigmund Marggraf (1709-1782) attempted to determine the composition of fluor spar by heating a mixture of it with sulphuric acid in a glass retort. He found a white saline sublimate suspended in the water of the receiver and concluded that sulphuric acid separates a volatile earth from fluor spar. In addition, he remarked that the retort was corroded into holes in several places. In 1771, Carl Wilhelm Scheele (1742-1786) repeated Marggraf's experiment and concluded that sulphuric acid separates a volatile earth from fluor spar. He also noted that the distillation flask was heavily corroded. The acid was called flussaëre and fluor spar was designated flussaërer kalk. Scheele also observed that heating caused fluor spar to lose its property of fluorescence, without change in weight. Scheele was perplexed by the deposit of silica obtained in the receiver and thought that flussaëre had the property of forming silica when in contact with water.

An interesting aspect of the history of fluorine is that André-Marie Ampère (1775-1831) coined its name before it was isolated. Ampère’s interest in chemistry led him to deduce that hydrogen fluoride was analogous to hydrogen chloride. He believed that "silicated fluoric acid" (hydrofluoric acid) contained a peculiar principle, analogous to chlorine and oxygen, united to the basis or silica, or silicum; the fluoric acid of the same principle united to boron; and the pure liquid fluoric acid as this principle united to hydrogen. During the Napoleonic wars with England Ampère succeeded in sending two letters to Humphry Davy (1778-1819) in which he exposed his ideas regarding fluorine. The first letter contained a suggestion that the unknown substance combined with hydrogen in hydrogen fluoride might be separated by electrolysis of the anhydrous acid using a carbon anode: it rests to know if electricity will decompose hydrogen fluoride in the liquid state, after most the water has been eliminated, delivering hydrogen on one side and hydrofluoric acid on the other.

In his second letter Ampère changed the name of the element from term oxy-fluorique to fluorine, to harmonize it with the then recently adopted name chlorine. Shortly thereafter, Ampère abandoned the term le fluore in favour of le phore (from the Greek phoros, destructive): I have selected the name phore from the Greek adjective φθορος, that is simultaneously a noun and an adjective, meaning to delete, that has the force to ruin, to destroy, to corrupt.

After Scheele’s preparation of impure hydrogen fluoride in 1771, it fell on Davy to recognize the presence of a new element in the compound. In a

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paper presented to the Royal Society of London he wrote: *It appears reasonable to conclude that there exists in the fluorine compounds a peculiar substance, possessed of strong interaction for metallic bodies and hydrogen and which combined with certain inflammable bodies forms a peculiar acid, which, in consequence of its strong affinities and high decomposition agencies, it will be very difficult to examine in a pure form, and for the sake of avoiding circumlocution it may be denominated fluorine, a name suggested to me by A. Ampère*.

Davy tried to electrolyse hydrogen fluoride (which he called fluoric acid and its salts fluates) without success, because his material contained an appreciable amount of water and thus no fluorine was formed. He did, however, observe that the electrical resistivity of the electrolyte increased considerably as the water content decreased. He attempted to overcome this difficulty by trying to decompose the acid by passing electrical sparks produced by the “great Voltaic batteries. of the Royal Institution”, but could not examine the results properly because the “surrounding atmosphere became filled with the fumes of fluoric acid.” He remarked that as a result of the fumes his fingers became sore under the nails, producing a most painful sensation in his eyes that lasted for hours.

Davy also noticed that liquid fluoric acid immediately destroyed glass and all animal and vegetable substances and acted on all bodies containing metallic oxides. He remarked that he did not know of any other substances that are not rapidly dissolved or decomposed by fluoric acid, except metals, charcoal, phosphorus, sulphur, and certain combinations of chlorine. He found that the specific gravity of the acid was 1.0069 when distilled in a pure silver alembic and that it increased to 1.25 when dissolved in water. He also estimated that the atomic weight of fluorine was less than one-half that of chlorine (the actual ratio is 0.535).

Joseph-Louis Gay-Lussac (1778-1850) and Louis-Jacques Thénard (1777-1857) reported that they had prepared concentrated hydrogen fluoride by heating a mixture of virtually silica-free white fluorspar with concentrated sulphuric acid in a lead apparatus and condensing the vapours at 0°C. Their product fumed strongly in air, dissolved glass easily and fast, possessed a great affinity for water, and caused painful burns on contact with the skin. Gay-Lussac and Thénard elucidated the action of hydrogen fluoride on silica and also discovered boron trifluoride through heating fluorspar with boric oxide in an iron tube.

Louyet experimented on the possibility of isolating and putting in evidence *le radical de l'acide fluorhydrique* by heating sheets of transparent fluorspar in a vase made of fluorspar. He found that fluorine was a colourless gas that did not bleach vegetable colours, decomposed water without the assistance of light, attacked glass, and acted on all metals except gold and platinum (except when in the nascent state). In addition, while other silver halides were insoluble when anhydrous and did not decompose on heating, silver fluoride was deliquescent, decomposed on heating, and was impossible to dehydrate it completely. Similarly, calcium halides were deliquescent, while calcium fluoride was insoluble in water.

Louyet also determined the equivalent (atomic) weight of fluorine as 239.81 (based on oxygen as 1.0) in comparison with the value of 233.801 that had been determined by Berzelius. He was unable to explain the difference.

He ended his memoir with a warning regarding the problems of experimenting with fluorine and hydrogen fluoride and emphasizing the need to take extreme safety precautions: *In relation to the nature of fluorine, I must remark that if there are still doubts about it, these are due to the imperfections of the equipment we have been forced to use. It is necessary to take extreme precautions to avoid the action of hydrogen fluoride vapours because they seriously affect the human body. All the chemists that have dealt with fluorine have suffered its dangerous effects. Gay Lussac and Thénard have strongly insisted about its dangerous effects; among them, acute pain under the nails, temporary eye inflammation, eye fatigue, chest pain, prolonged pharynx irritation, heavy spitting, many times bloody, all of these symptoms requiring a long time for their recovery. Very seldom these effects are of short duration. Th. Knox felt that he was about to die, the effects disappeared only after using hydrogen cyanide for six months. His brother George J. Knox felt the effects of fluorine for more than three years and had to move to Naples to recover. Regarding myself, my health has been affected seriously and I have spit blood in several opportunities*. Louyet passed away a short time after writing these words.

Domange described the difficulties related to the isolation of fluorine as follows: *It is very clear that the isolation of fluorine could not be the result of a
well-reasoned experiment. At that time the properties of fluorine were unknown. Hydrogen fluoride is very dangerous and hard to manipulate in the anhydrous state, barring any possibility of obtaining fluorine as the result of a chance experiment. This same chance had, in the past, allowed the discovery of other elements.

The obstacle was finally removed by Edmond Frémy’s (1814-1894) discoveries that metallic fluorides were binary compounds (formed by two elements) and not “fluates”, that is, oxygen containing compounds, and that the hydrogen fluoride prepared by Gay-Lussac-Thenard’s method always contained water, sulphuric acid, sulphurous acid, hexafluosilicic acids, and other impurities. Louyet had tried to dehydrate it with phosphorus pentoxide, but Frémy believed he had not succeeded. After failing to purify and dehydrate the acid obtained by the action of sulphuric acid on fluorspar, Frémy decided on an alternative route based on potassium hydrogen fluoride (fluorhydrate de fluorure de potassium, KF.HF). This salt was prepared by treating potassium fluoride with hydrogen fluoride; KF.HF precipitated immediately because of its low solubility. Frémy recrystallized the salt several times to eliminate the impurity potassium hydrofluosilicate, and then heated it strongly in a platinum crucible to produce the first sample of anhydrous hydrogen fluoride. According to Frémy: Hydrogen fluoride obtained by this method is a gas at room temperature, but it can be condensed, by a mixture of ice and salt into a very fluid liquid that reacts vigorously with water and in contact with air gives white fumes less intense than those of boron fluoride.

Frémy noted that electrolysis of an aqueous solution of hydrogen fluoride yielded hydrogen and oxygen at the electrodes as long as water was present; afterwards, the liquid ceased to conduct electricity. Electrolysis of molten calcium fluoride using a platinum crucible as cathode and a platinum wire as anode showed vigorous effervescence of a pungent gas that attacked glass, strongly corroded the electrolytic cell, and displaced iodine from iodides. In his own words: “Ce gaz me parait être le fluor” (It seems to me that this gas is fluorine). According to Frémy, the process occurring at the anode consisted of initial fluorination of the platinum to give platinum tetrafluoride, which decomposed at the high temperature used to give free fluorine and spongy platinum. Corrosion of the anode prevented the process being continued for any length of time.

Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) is usually considered the first to isolate fluorine and the first to develop a method capable of preparing the gas in appreciable quantity. However, as pointed out by Domange, it appears certain that Frémy was successful in producing a small amount of fluorine some 30 years before Moissan. Domange points out the curious fact that Frémy made no reference to the electrolysis of KF.HF, which has a melting of about 240°C, as compared to 88°C for potassium fluoride, so that attack of the anode might have been expected to be greatly reduced.

Moissan was well familiar with Frémy’s experiences and was convinced that he should not use the same procedure. In his own words: “I have started my researches from a preconceived idea. If we suppose, for a moment, that chlorine has not been isolated but we are well familiar with the preparation of metal chlorides, hydrogen chloride, the chlorides of phosphorus and similar compounds, it should be clear that we can increase the probability of isolating the element by addressing ourselves to the compounds that chlorine forms with metalloids. It seemed to me that it should be highly possible to obtain chlorine by trying to decompose phosphorus pentachloride or hydrogen chloride, than trying to hydrolyze calcium chloride or an alkaline chloride. Should it not be the same for fluorine?”

Moissan began his research on fluorine in 1884 but it was not until June 26, 1886, that he succeeded in preparing elementary fluorine for the first time on a scale sufficient to enable him to study its physical and chemical properties. For this purpose, he used as electrolytic cell a U-tube of platinum containing a dilute solution of potassium fluoride in anhydrous hydrogen fluoride prepared by Frémy’s method. The electrodes were of platinum or platinum-iridium alloy and were insulated as they entered the limbs of the U-tube by passing through fluorspar stoppers. The anode and cathode gases were led off through side arms on the limbs of the U-tube. Rapid loss of hydrogen fluoride from the electrolyte was diminished by cooling the cell with boiling methyl chloride, so as to maintain the temperature at about -25°C.

The discovery of the new element was reported to the Académie des Sciences by Henri Debray (1827-1888) during the session held on June 28, 1886. The Académie appointed a committee formed by Marcelin Berthelot (1827-1907), Debray and Frémy to verify this sensational result. When Moissan tried to repeat the experience it failed miserably, no current
passed through the bath and no gas was released. The committee abandoned his laboratory greatly disappointed. When Moissan examined the test he realized that the bath of his original experiments had contained accidentally small amounts of potassium fluoride that made it conducting. He was now able to repeat his experiment successfully in front of the committee who witnessed the brisk combustion of different elements (silicon, manganese, iron, arsenic, and antimony) with fluorine.

It is interesting to note that in his paper about the life and works of Moissan, Alfred Stock, a former student of Moissan, wrote that his teacher had told him that work on fluorine had shortened his life by ten years13.

The experimental difficulties in preparing fluorine and the physiological dangers in handling hydrogen fluoride reflect on the scarce amount of research done on the chemistry of the element until World War II (WWII). Between 1886 and 1919 only six papers dealing with elementary fluorine were published, while over the next 20 years less than twenty-five papers and nine patents dealt with fluorine cells14.

Fluorine was the last of the halogen family to be discovered and separated, after chlorine in 1774, iodine in 1811, and bromine in 1826.

**Fluorine sources**

Fluorine is an extremely reactive element and does not appear free in nature, except for trace amounts in radioactive materials; it is always combined with other elements. The “stinking fluor spar” — stinkfluors, also called antozonite, is a variety of fluorite CaF₂, which contains inclusions of uranium minerals. The fluorine is occluded in the spar and is liberated on fracture. It reacts then with the moisture in the air and gives the characteristic odour of ozone.

\[
\begin{align*}
F_2 + H_2O &\rightarrow 2HF + O \\
O + O_2 &\rightarrow O_3
\end{align*}
\]

(1)

It is very probably that fluorine is the result of the radiation reactions on calcium fluoride.

Fluorine is widely disseminated in nature and more abundant in the mineral kingdom than chlorine, if the hydrosphere is discounted. It ranks thirteenth in most tables of abundance of the elements in the Earth’s crystal rocks. The fluorine content of igneous rocks, which constitute 90% of the first ten miles of the earth’s crust, has been estimated as 600 ppm. The majority of fluorine in the earth’s crust is in phosphate rock in the form of fluorapatite. Recovery of these fluorine values as by-product fluorosilicic acid from phosphate production has grown steadily, partially because of environmental requirements. According to Smith15, chlorine and fluor are present in the mantle of the earth only in mica, amphibole, and apatite. Apatite with about 3 wt% fluor, 1 wt % chlorine, and 0.003 wt% bromine is the principal reservoir for halogens and mica is a secondary reservoir.

Table 1 gives the estimated contents, in kilograms, of the different halogens in the various zones13.

Fluorine is more abundant than combined chlorine by a factor of about seven. The reverse is overwhelmingly true for seawater, in which the F/Cl ratio is 6.75\times10⁻⁵. Considering all accessible halogen reservoirs (continental crust, oceanic crust, hydrosphere, sediments), chlorine is about 2.7 times more abundant than fluorine, whereas speculations concerning whole-Earth contents indicate that fluorine is the dominant halogen15.

In low concentrations, fluorine is distributed very widely in nature and it is also present in most fresh groundwaters to the extent of 0.1 to 7 ppm. Seawater contains very little fluoride, approximately 1.4 mg/L.

The fluorine content of soils is connected with the apatite content, suggesting that the actual component is fluorapatite to a large extent. The actual fluorine content of soils is about 200 ppm.

It is well known that plants absorb fluorine from the soil. Virtually all foods contain traces of fluoride and a noteworthy case is the tea plant that may contain 400 ppm, so that a cup of tea contains about 1 ppm. Fluoride ions are detrimental to biological processes and they inhibit the enzyme adenosine triphosphatase.

Although fluorine is widely distributed and is quite abundant, sources of fluorine suitable for industrial exploitation are relatively restricted. Only three minerals are of commercial importance:

| Table 1—Estimated contents of different halogens (KG) |
|----------|----------|----------|
|          | F        | Cl       | Br       |
| Hydrosphere | 19.10⁴⁴ | 13.10⁴⁵ | 27.10⁸  |
| Sediments  | 18.10⁴⁵ | 29.10⁴⁸ | 23.10⁹  |
| Continental crust | 18.10⁴⁸ | 29.10⁴⁸ | 48.10⁶  |
| Total      | 18.10⁴⁸ | 29.10⁴⁸ | 48.10⁶  |
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<table>
<thead>
<tr>
<th>Formula</th>
<th>Fluor content, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryolite 3NaF·AlF₃</td>
<td>54.5</td>
</tr>
<tr>
<td>Fluorspar CaF₂</td>
<td>48.5</td>
</tr>
<tr>
<td>Fluoroapatite CaF₂·3Ca₃(PO₄)₂</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The usual content of these minerals is less than the theoretical because of the presence of impurities.

Cryolite (Greenland spar) is a relatively rare mineral and all the deposits of commercial importance are located in Greenland. Although it is an essential raw material in the aluminum industry it is not very accessible, for this reason a considerable amount is made synthetically.

Fluorspar (fluorite) is by far the most important industrial source of fluorine. Exploitable deposits are found all over the world: America, Canada, Argentina, England, France, Germany, Italy, Spain, Tunisia, Morocco, South Africa, Russia, Korea, China, and Australia. In England the most important deposits are in Durham and Derbyshire, while in the U.S.A., Illinois accounts for over 50% of the country’s output. Twenty-six per cent of the world’s high quality deposits of fluorspar are in North America, most of them in Mexico. Fluorspar is invariably associated with other minerals, notably calcite, CaCO₃; quartz, SiO₂; galena, PbS; and barites, BaSO₄. It shows a wide variety of colour and is frequently fluorescent. Crystalline fluorspar has a very low index of refraction (1.433 to 1.435) and low dispersion; it has the unusual ability to transmit UV light, which makes it useful for optical applications.

Fluorspar has always been the most important source of fluorine and its compounds. Total world demonstrated and identified reserves stand at 135 and 262 Mt respectively, and about 4.5 Mt are produced worldwide per annum. About 40% of the fluorspar being mined is utilized as metallurgical flux, mainly in the steel industry, and most of the remainder is treated with concentrated sulphuric acid to provide hydrogen fluoride by the reaction:

\[ \text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4 \quad \cdots (2) \]

Although fluoroapatite is not of major importance as a source of fluorine today, it has a tremendous potential as such, because it is present in the vast quantities of phosphate rock that are processed for the production of phosphate fertilizers. During the processing of phosphate ore fluorine is liberated as silicon tetrafluoride, a toxic hazard to the environment. Many processes have been suggested to recover the fluorine as hydrogen fluoride or its derivatives. So far, the only viable ones recover the element as sodium fluosilicate or fluosilicic acid but the industrial outlet for these materials is limited. Hence, the fluorine content of fluoroapatite must at present be considered to have a nuisance value only.

**Thermodynamic properties of fluorine and its solutions**

Cady and coworkers measured several fundamental properties of elementary fluorine and some of its solutions. For example, Cady and Hildebrand measured the vapour pressure of liquid fluorine between 72 and 86 K and correlated their results with the equation:

\[
\log P = 7.3317 - \frac{406.8}{T} - 0.007785T
\]

with \( P \) in cm Hg and \( T \) in kelvins. The equation yields a normal boiling point of 84.93 K. Cady and Hildebrand also reported the critical temperature and pressure of fluorine as 144 K and 55 atmospheres respectively.

In another publication, Cady reported the freezing points of the system hydrogen fluoride-water at atmospheric pressure and the presence of three distinct hydrates, \( \text{H}_2\text{O}.\text{HF}, \text{H}_2\text{O}.2\text{HF}, \) and \( \text{H}_2\text{O}.4\text{HF}. \) The second hydrate did not melt congruently.

Probably Cady’s most important publication is the one describing the freezing point and vapour pressure of the system \( \text{KF} + \text{HF} \), the basic electrolyte used for manufacturing anhydrous hydrogen fluoride. The pertinent results appear in Figs 1 and 2. Cady and Hildebrand found that in addition to the solvates which were known before (KF.HF, KF.2HF, and KF.3HF), there were two new ones, KF.4HF and 2KF.5HF, and also that KF.HF could exist in two different solid forms.

As will be shown later, knowledge of the phase diagram of the system \( \text{KF} + \text{HF} \) led to substantial improvements in the electrolytic process for the production of hydrogen fluoride.
Development of the manufacturing process

The chemical synthesis of elemental fluorine has been pursued for at least 175 years by many chemists, including Davy, Frémy, Moissan and Otto Ruff. All their attempts failed and the only practical synthesis of fluor is Moissan’s electrochemical process, which was discovered in 1886. After Moissan’s work, the preparation of even small quantities of fluorine continued to be an undertaking of some difficulty. Before 1940 only a handful of investigators, of whom Ruff was a notable example, had first-hand knowledge of the element.

Although in principle the thermal decomposition of any fluoride is bound to yield fluorine, the required reaction temperatures and conditions are so extreme that rapid reaction of the evolved fluorine with the hot reactor walls preempts the isolation of significant amounts of fluorine. Ruff repeated with no success the experiments of Brauner, which claimed that when heating PbF$_4$.3KF.HF a gas was released containing some fluorine, as evidenced by the odor, the setting of free iodine from potassium iodide, and its explosive combination with silicon.

The next important stage after Moissan’s work occurred in 1919 when Argo et al. showed that fluorine could be produced in quantity by electrolysis of fused KF.HF contained in a copper cell, which served as cathode. Argo’s cell consisted of a graphite anode hung centrally in the cell and surrounded by a diaphragm closed at the bottom, which kept the hydrogen and hydrogen fluoride from mixing. The KF.HF bath was heated to 225° to 250°C by a nichrome coil wrapped around the copper cell. Operation of this cell was not without problems because of erratic current fluctuations and a rapid increase in the melting point of the electrolyte as it became depleted in hydrogen fluoride. Argo also tested the process suggested by Moissan and found it impractical for quantity production because of the rapid solution of the platinum anodes and because the apparatus had to be kept surrounded by a freezing mixture.

Lebeau and Damiens were the first to experiment with an electrolyte of composition KF.3HF, intermediate between that used by Moissan’s low temperature cell and that employed by Argo in his high temperature unit. They demonstrated that with such an electrolyte it was possible to use a nickel anode, though it suffered appreciable corrosion.

In 1942, Cady and co-workers used an electrolyte with the approximate composition KF.2HF and similarly to Lebeau and Damiens, they proved that with such an electrolyte it was possible to use a carbon anode provided that the temperature and composition of the electrolyte were controlled. They also reported, for the first time, the existence of high hydrogen overvoltage, which nearly doubled the potential that had to be applied to the cell to cause the flow of current. In practice, they preferred a nickel anode because of the absence of current fluctuations, which occurred with carbon, as in the case of graphite in the high temperature cell. Cady’s cell may be regarded as the forerunner of the fluorine cells in use today.

Development of nuclear devices during WWII accelerated the development of fluorine chemistry as a result of the need for elementary fluorine on an industrial scale; mostly for the manufacture of uranium hexafluoride for isotopic enrichment of the uranium in the U.S. and Great Britain, and chloride trifluoride in Germany.

Essentially all further developments of the electrolytic processes are based on the findings of Cady and Lebeau and Damiens that the appropriate electrolyte is a solution of potassium fluoride in anhydrous hydrogen fluoride (as shown by Frémy). Potassium fluoride is indispensable because pure anhydrous hydrogen fluoride is very little ionized and is, therefore, a non-conductor of electricity. The phase diagram of the solution has played a critical role in finding the best operating conditions.

Presently, all fluorine made on an industrial scale is produced using an electrolyte of approximate composition KF.2HF and containing 39 to 41% of hydrogen fluoride. Selection of this composition may be explained making use of Figs 1 and 2: Both gaseous phases produced during electrolysis (hydrogen and fluorine) are saturated with hydrogen fluoride at a concentration corresponding to the partial pressure of the acid over the electrolyte. In addition to the hydrogen fluoride decomposed by electrolysis, acid is carried off in the gaseous products and, unless it is recovered, represents a loss of valuable raw material. It is obvious, therefore, that the concentration of hydrogen fluoride in the fluorine and hydrogen should be as low as possible. Figure 2 shows that there are two regions in which the partial pressure of hydrogen fluoride is low, these correspond to the compositions KF.HF and KF.2HF.
Figure 1 shows that fusion of an electrolyte of composition KF:HF not only occurs at relatively high temperatures (240°-280°C) but also that the melting point changes rapidly with small changes in composition. On the other hand, a composition in the range of KF:2HF melts at about 70°C and the melting temperature varies little over the range 38 to 42% hydrogen fluoride. In addition, at 80-100°C corrosion of the cell components is less severe than that at 240-250°C.

Modern fluorine generating cells are classified in three distinct types, based on their operating temperatures: low (-80 to 20°C) temperature cells, medium (60 to 100°C) temperature cells, and high (220 to 300°C) temperature cells. Cells operating at low and high temperatures were developed first, but discontinued because of corrosion and other problems.

All commercial fluorine installations employ medium temperature cells having operating currents of 5000 A or higher. The medium temperature cell takes advantage of all the features shown in Figs 1 and 2: (a) low vapour pressure of hydrogen fluoride over the electrolyte, (b) the composition of the electrolyte can vary over a relatively wide range for only a small variation in the operation of the cell; (c) decreased corrosion or deterioration of the anode; (d) tempered water can be used as cell coolant; and (e) the formation of a highly resistant film on the anode surface is considerably reduced compared to the high temperature cell.

Fluorine cell anodes are the most important cell component. As mentioned before, early electrodes were constructed of nickel and graphite and discontinued when it was found that hard non-graphitized carbon gave longer life. From the 1990s onwards, anodes are made from petroleum coke and a pitch binder, which is calcined at temperatures below that needed to convert the material to graphite. The anode carbon has low electrical resistance, high physical strength, and is resistant to reaction with fluorine.

In 1986 Christe reported the first purely chemical synthesis of elemental fluorine in significant yield and concentration. Christe’s process was based on the fact that thermodynamically unstable high-oxidation-stable transition-metal fluorides can be stabilized by anion formation, as illustrated by the following reactions:
Christe carried out the above reactions and showed that it was possible to obtain fluorine in yields above 40% of the expected conversion.

The main use of fluorine in the 1990s was in the production of UF₆ for the nuclear power industry. However, its use in the preparation of some specialty products and in the surface treatment of polymers is growing.

Anhydrous hydrofluoric acid

It has been mentioned that although Scheele probably prepared crude hydrogen fluoride in 1771, the difficulties in handling the acid with the knowledge and apparatus then available delayed the preparation of anhydrous acid of high purity until the middle of the nineteenth century, when Frémy showed that substantially anhydrous hydrogen fluoride could be made by heating potassium bifluoride, KF·HF (Frémy’s salt). Frémy’s salt is readily made by half neutralizing aqueous acid with caustic potash. It has a melting point of about 240°C and may be heated up to at least 150°C with little loss of hydrogen fluoride. Above the melting point the vapour pressure of hydrogen fluoride increases until it reaches one atmosphere at about 400°C. By further heating to 500°C it is possible to distil the bulk of the acid, which may be collected in a refrigerated condenser.

Anhydrous hydrogen fluoride is made on an industrial scale by heating a mixture of fluorspar and concentrated sulphuric acid

\[ \text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF} \quad (2) \]

The sulphuric acid should be at least 98% strength and fluorspar must be of high purity acid grade. Reaction 1 is accompanied by some side reactions involving the impurities present, for example,

\[ \text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \]

\[ \text{CaS} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{S} \quad (7) \]

The steel of the retort in which the reaction is carried out is slowly attacked by the sulphuric acid, and probably by the reaction

\[ \text{Fe} + 2\text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2 \quad (8) \]

since sulphur dioxide is found in the reaction gases.

The reaction is carried out in an inclined cylindrical retort, heated externally and fed with a thin paste of sulphuric acid and fluorspar prepared beforehand. Upon heating the slurry thickens while hydrogen fluoride and the by-product gases (sulphur dioxide, hydrogen sulphide, silicon tetrafluoride, sulphuric acid, etc.) are released. Crude hydrogen fluoride is condensed with refrigerant and is further purified by distillation.

Patterns of use and historical development of the market

According to Rudge, the development of industrial fluorine chemistry may be conveniently be divided into two parts, namely that prior to the production of anhydrous hydrogen fluoride in commercial quantities (1931 in United States and 1941 in England), and the following period.

In the first period, the most important fluorine compounds were calcium fluoride, which was used as a flux in metallurgical processes, and aqueous hydrofluoric acid, which had a variety of applications. Fluorspar has been used as a flux in the steel industry since the introduction of the open-hearth process in 1888. In 1900 U.S. fluorspar production was 16,700 metric tons, with more than 80% mined in Kentucky. Processing of the product simply consisted of washing and screening, although in 1900, it began to be grounded prior to sale. In 1920, the flotation process was introduced, which allowed production of fluorspar of more than 97% purity (expressed as CaF₂), which became known as acid-grade fluorspar. At the beginning of the twentieth century small amounts of fluorspar were consumed for ceramics, enamels, foundry work, glass, hydrofluoric acid, and steel.

For most of the twentieth century, demand for fluorspar grew steadily, driven first by the steel market and, from the 1930s on, by the steel market and hydrogen fluoride. Demand peaked in 1974 when U.S. consumption reached 1.38 million metric tons. The following years showed a substantial decrease in fluorspar’s use in steel making and CFC production was discontinued for environmental reasons. By the
end of the twentieth century, domestic consumption of fluorspar had levelled off in the 500,000 to 600,000 ton range, with consumption for hydrogen fluoride accounting for more than 80% of apparent production. Domestic mining of fluorspar in the U.S has ceased entirely and the demand is met by imports and the national stockpile.

Traditionally there have been three grades of fluorspar: acid grade, containing more than 97% CaF₂; ceramic grade, containing 85% to 95% CaF₂; and metallurgical grade, containing 60% to 85% or more CaF₂. Acid-grade fluorspar was used primarily as a feedstock in the manufacture of hydrogen fluoride. The largest use of hydrogen fluoride was in the production of a wide range of fluorocarbon chemicals, including hydrochlorofluorocarbons (HCFCs), and fluoropolymers. Acid-grade fluorspar has been used in the production of aluminum fluoride, which is the main fluorine compound used in aluminum melting. On a worldwide average, the aluminum industry consumes about 23 kilograms of fluorides (measured as AlF₃ equivalent) for each metric ton of aluminum produced.

Metallurgical-grade fluorspar has been used primarily as a fluxing agent by the steel industry. Fluorspar is added to the slag to make it more reactive by increasing its fluidity (by reducing its melting point) and thus increasing the chemical reactivity of the slag. Reducing the melting point of the slag brings lime and other fluxes into solution to allow the absorption of impurities.

**Hydrogen fluoride**

Anhydrous hydrogen fluoride is the key element in the development of fluorine chemistry, which has taken place in the last 60 years. Today it is the most important manufactured fluorine compound. It is the largest in terms of volume, and serves as the raw material for most other fluorine-containing chemicals. It is available either in anhydrous form or as an aqueous solution (usually 70%).

During WWII hydrogen fluoride was used in alkylation catalysts to produce aviation gasoline and in the manufacture of fluorspar to produce volatile UF₆ from UF₄ for concentrating uranium isotope 235 essential for nuclear fuel and fission explosive. The use of the very corrosive UF₆ also stimulated development of fluorinated organic compounds for lubricants and seals that are resistant to UF₆. Today, anhydrous hydrogen fluoride is used both as a reactant and as a solvent in the manufacture of inorganic fluorides that include chlorine trifluoride, lithium fluoride, sodium fluoride, sulphur hexafluoride, tungsten hexafluoride, and others that are used in dielectrics, metallurgy, wood preservatives, herbicides, mouthwashes, decay-preventing dentifrices, and water fluoridation.

In organic chemistry, anhydrous hydrogen fluoride is used extensively for the replacement of chlorine by fluorine, and this type of reaction is the basis of the rapidly expanding chlorofluorocarbon industry. Fluorinated steroids, other fluorinated drugs, and anaesthetics have medical applications. The stability, lack of reactivity, and therefore, lack of toxicity of some fluorine compounds are also demonstrated by studies reporting survival of animals in an atmosphere of 80% SF₆ and 20% oxygen, and use of perfluorochemicals as short-term blood substitutes because of the ability to efficiently transport oxygen and carbon dioxide. Many fluorides have applications in catalysis.

The key piece of equipment in hydrogen fluoride manufacturing is the reaction furnace where CaF₂ is treated with sulphuric acid. The reaction is endothermic (1400 kJ/kg of hydrogen fluoride) and for good yields the reaction must be carried out in the range of 200°C. Most industrial furnaces are horizontal rotating kilns, externally heated.

Because of the large quantity of phosphate rock reserves available worldwide, recovery of fluoride values from this raw material source has frequently been studied. Strategies involve recovering the fluoride from wet-process phosphoric acid plants as fluosilicic acid (H₂SiF₆) and then processing this acid to form hydrogen fluoride. Numerous processes have been proposed, but none has been commercialized on a large scale. The overall reaction in such a process is

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H₂SiF₆ + 2H₂O → 6HF + SiO₂ \]  (9)

A new technology proposes reacting the fluosilicic acid phosphate rock to make phosphoric acid and byproduct calcium silicon hexafluoride, CaSiF₆. Hydrolysis of the latter at 100°C produces silica and calcium fluoride, which are separated by centrifuging and settling. Calcium fluoride is then reacted with sulphuric acid to produce hydrogen fluoride.

The future of these technologies remains uncertain. Economic comparisons with fluorspar-based processes indicate that as long as fluorspar supplies remain abundant, there is little justification to proceed with such processes.
In the U.S. hydrogen fluoride market, approximately 70% goes into the production of fluorocarbons, 4% to the nuclear industry, 5% to alklylation processes, 5% to steel pickling, and 16% to other markets.

**Fluorocarbons**

Fluorocarbons are a family of products that have properties that render them valuable as refrigerants, blowing agents, solvents, and sources of raw material for production of fluoropolymer materials. Hydrogen fluoride is used as a source of fluorine for production of all the various fluorocarbon products.

The overwhelming evidence on the negative effects of CFCs and Halons on the ozone layer led the United Nations Environmental Program to begin negotiations in 1981 aimed at protecting this layer. On September of 1987, the Montreal Protocol (Montreal Protocol on Substances that Deplete the Ozone Layer) was signed by 24 nations and took force on January 1, 1989. This treaty called for (a) limiting production of specified CFCs, including CFC11, 12, 113, 114, and 115, to 50% of 1986 levels by 1998, and (b) freezing production of specified Halons 1211, 1301 and 2402 at 1986 levels starting in 1992. In June 1990 the protocol was amended to expand the list of chemicals to include carbon tetrachloride and 1,1,1-trichloroethane, and specify stepped-up timetables for total phase out of ozone depleting chemicals by the year 2000.

As a matter of information, in the United States HFCs and HCFCs used as refrigerants in large cooling chillers are in the demand as the conversion from CFC chillers to non-CFC chillers continues. Chillers cool water that is circulated through buildings to air conditioning factories, hospitals, malls, offices, etc. Some of the existing or potential fluorocarbon replacements for the banned CFCs are HCFCs 22, 123, 124, 141b, 142b, and 225, having ozone depletion potential that are much lower than those of CFCs 11, 12, and 113, which together have accounted for more than 90% of the CFC consumption. HCFC 22 has been used as a high-pressure refrigerant (i.e., in home air conditioning) for year s; HCFC 123 is being used as a replacement for CFC 11 in low-pressure centrifugal chillers; HCFC 124 is a potential replacement for CFC 114 in medium-pressure centrifugal chillers and for CFC 12 as a diluent in sterilizing gas; and HCFCs 141b and 142b have replaced most of the CFCs 11 and 12 used in foam blowing. However, because of the current phase-out schedule for the HCFCs, the market for HCFCs will exist only for a short time, and perfluorocarbons are in the list of gases that contribute to global warming. Of most immediate concern is the ban of production and importation of HCFC 141b, which is scheduled to go into effect from January 1, 2003.

The HFC replacements have no ozone depletion potential because they do not contain chlorine. The most successful HFC replacement compound is HFC 134a, which is currently being used as replacement for CFC 12 in automobile air conditioners, as a refrigerant in new commercial chillers and refrigerators, and as the propellant in aerosols and tire inflators.

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