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23 Fluid Flow, Two-Phase Design to Froth Flotation

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imports amount to over 600.000 tons.* and are likely to increase to 1.2 million tons by the year 2000 to meet a projected domestic demand of 1.8 million tons. Most of the United States supply will probably evolve from production in Africa, Asia, and Mexico.

Fluorine demand in the rest of the world is expected to increase also, reaching 4.6 million tons in 2000. To keep abreast of accelerating demand, production will necessarily have to expand, particularly in Africa, Asia, Mexico, and the USSR.

At projected rates of consumption, all currently known fluorine resources in the fluorspar deposits of the world are expected to be depleted before the end of the century. In that event, the world's fluorine supply will have to be derived from new fluorspar deposits, or from phosphate rock. It is estimated that fluorine resources in phosphate rock are adequate to satisfy world demand well into the next century.

Industry Structure

Background

Fluorine was first isolated in 1886 by the French chemist Henri Moissan after nearly 75 years of unsuccessful attempts by several others. He applied a method originally suggested by both Davy and Ampere in 1810–1812. Moissan's success was attributed to his use of a dilute solution of potassium fluoride, KF, in completely anhydrous hydrogen fluoride, HF; the mixture corresponded approximately to $KF \cdot 12HF$. In the electrolytic process employed, hydrogen was liberated at the cathode and fluorine at the anode. For many years after its isolation, fluorine remained little more than a scientific curiosity, to be handled with extreme caution because of its toxicity. Commercial production of fluorine began during World War II when large quantities were required in the enrichment of the fissile ^{235}U isotope for the development of the atom bomb. Today, commercial production methods are essentially variations of the Moissan process, and safe techniques have been developed for the bulk handling of liquid fluorine.

Although trace amounts of free fluorine have been detected in radioactive fluorine minerals, the element is more generally found in combined form in nature. Combined fluorine has been estimated to comprise 0.065% by weight of the earth's crust. It is more abundant than chlorine, 5 to 10 times more abundant than zinc and copper, and probably 30 times more so than lead. Among the elements, it ranks 13th in order of abundance.

Traditionally, the most important commercial source of fluorine is the mineral fluorite, CaF_2 (calcium fluoride), more commonly known as fluorspar in the industry. Increasing amounts of fluorine are also being recovered as a byproduct, fluosilicic acid, H_2SiF_6, in the acidulation of fluorapatite, $Ca_5(PO_4)_3F$. Until about 1963, cryolite, Na_3AlF_6, had been mined from the world's only commercial cryolite deposit in Ivigtut, Greenland, to provide a

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*All quantities are in short tons of fluorine unless otherwise noted.

fluorine atom also explains the fundamental differences in physical and chemical properties between inorganic fluorides and the corresponding chlorides, bromides, and iodides. Many fluorine compounds, such as sulfur hexafluoride, nitrogen trifluoride, and the fluorocarbons, are inert; others, such as hydrogen fluoride and the halogen fluorides, are extremely reactive.

Chemical

By far the largest use of acid-spar is in the manufacture of hydrogen fluoride, HF, more commonly called hydrofluoric acid. Obtained by reacting fluorspar with sulfuric acid in a retort, hydrofluoric acid is an important chemical for the following reasons: (1) It is used in nonfluorinating processes as a catalyst, reaction medium, metal-pickling agent, and in many other applications; and (2) it is a key chemical in almost all fluorochemical-manufacturing processes. About 2.2 lb of fluorspar is consumed in the production of 1 lb of hydrofluoric acid. After purification by appropriate scrubbing, condensing, and distillation, the hydrofluoric acid of commerce can be either anhydrous (HF, a colorless, fuming liquid shipped in pressurized tank cars or trucks, or it may be absorbed by water to form the aqueous acid in various concentrations (usually at 70% HF). Hydrofluoric acid is often used within a closed system for the downstream production of many fluorine chemicals.

A major use of hydrofluoric acid is in the manufacture of fluorocarbons, which are organic compounds containing fluorine. Almost all fluorocarbons are produced by the same general reaction involving anhydrous HF and chloroform or carbon tetrachloride. Expressed in simplest terms, the basic reaction involves the replacement of chlorine in a suitable organic chloride with fluorine by means of anhydrous HF in the presence of a catalyst. For example, in the preparation of dichlorodifluoromethane, CCl_2F_2 (or F-12), carbon tetrachloride and anhydrous HF in definite proportions are fed continuously to a heated reactor containing antimony trifluoride and a catalyst. The volatile reaction products pass into a distillation column where the fluorocarbon is isolated. By varying reactor conditions and by using other chlorinated methanes and ethanes, a large family of fluorocarbons can be produced. Five principal fluorocarbons account for most of United States production: CCl_3F (F-11), CCl_2F_2 (F-12), $CHClF_2$ (F-22), CCl_2FCClF_2 (F-113), and $CCl_2F_2CClF_2$ (F-114) (See the article *Fluorocarbons* in this volume.) Although consumption of hydrofluoric acid depends on the type of fluorocarbon produced, on the average, 1 ton of HF yields about 3 tons of fluorocarbon. Until recently, the main uses of fluorocarbons in the United States have been in aerosol sprays and in refrigerants, together accounting for well over 70% of total consumption. Currently, however, these major end uses have been sharply curtailed owing to environmental concerns. Other applications, which are gaining prominence, are in resins and elastomers, solvents and degreasing agents, stain repellants, surfactants and fire-extinguishing agents, pharmaceuticals, foaming and blowing agents, and a host of miscellaneous uses.

Next in importance as a consumer of hydrofluoric acid is the aluminum

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industry. Hydrofluoric acid is not consumed directly in aluminum smelting, but is used in the production of aluminum fluoride, AlF_3, and synthetic cryolite, Na_3AlF_6, by reaction with alumina or a mixture of alumina and caustic soda. Cryolite and aluminum fluoride are used with alumina in the molten bath from which aluminum is obtained by electrolysis. Aluminum fluoride is added to the electrolyte to lower its melting point, but only a limited amount can be added because it also reduces the electrical conductivity. To further reduce the melting point without lowering the electrical conductivity at the same time, small amounts of fluorspar are often added to the bath. Previously, some natural cryolite, primarily from Greenland and now rare, was used in the potlines, but today nearly all the fluorides are produced from hydrofluoric acid. The fluorides do not enter the final product but are absorbed by potlinings or escape into the air and are collected as particulates or gases. Fluoride consumption varies according to individual smelter practice, but averages 60 lb of aluminum fluoride and 50 lb of synthetic cryolite per ton of aluminum ingot produced. This is equivalent to about 70 lb of hydrofluoric acid per ton of aluminum. In the United States, however, the actual amount of hydrofluoric acid required is probably 20% less, or 56 lb ton, due to recycling of fluoride values from spent potlinings and flue gases, as well as the manufacture of aluminum fluoride and synthetic cryolite from fluosilicic acid.

The enrichment of uranium in the fissile isotope ^{235}U is effected either by the conventional gaseous-diffusion process or by the more recent gas-centrifuge process. Both processes involve the use of uranium hexafluoride, UF_6, the form in which the isotope separation takes place. Uranium hexafluoride is convenient for this purpose because it is gaseous at moderate temperatures. Yellowcake, containing 80 to 85% U_3O_8, is first refined to purified UO_3. This is followed by reaction with anhydrous hydrofluoric acid to produce greensalt, UF_4. The final stage involves the conversion of greensalt to uranium hexafluoride by means of elemental fluorine. Total hydrofluoric acid required by the process is estimated at 1.1 tons for each ton of uranium hexafluoride produced.

The hydrofluoric acid alkylation process is one of several processes available for the conversion of olefins and isoparaffins into an alkylate that consists of a mixture of heptane, octane, etc. In this process, anhydrous hydrofluoric acid acts as a catalyst, and approximately 0.33 lb of HF is used to manufacture 1 barrel of alkylate.

Another major use of anhydrous hydrofluoric acid is in stainless steel pickling, which utilizes the acid for descaling after rolling operations. However, not all grades of stainless steel are pickled with hydrofluoric acid; some require only nitric acid or a molten caustic bath. Consumption of hydrofluoric acid for this end use varies, but averages 25 lb/ton of steel pickled.

Other inorganic fluorides, apart from synthetic cryolite and aluminum fluoride, are derived from hydrofluoric acid, each with its individual properties and uses. Most of the common inorganic fluorides are prepared by reacting aqueous hydrofluoric acid with the corresponding carbonates, oxides, or hydroxides. The bifluorides or acid fluorides are formed with an excess of acid. Boron trifluoride, BF_3, prepared from anhydrous HF, is used in the manufacture of coumarone-indene resins, petroleum resins, lubricating-oil additives, and as a catalyst in organic syntheses; for example, in the manufacture of a nitroalkane propellant for long-range Polaris submarine missiles. Sodium fluoride, NaF, is used in water fluoridation and in the manufacture of rimmed steel ingots, opaque glass, toothpaste, wood preservatives, and insecticides. Synthetic optical crystals of barium, calcium, lithium, magnesium, potassium, rubidium, and sodium fluorides are available for scientific instruments in which high transmission of infrared and ultraviolet light is desired. Some of the crystals are coated or "doped" with special elements for laser applications. Bifluorides of ammonia, potassium, and sodium have been used in the frosting and etching of glass, also a common application of hydrofluoric acid. Ammonium and sodium bifluorides are also used in laundry sours and descaling agents, and potassium bifluoride is an electrolyte in the manufacture of fluorine gas. Fluoboric acid, HBF_4, prepared from boric acid or borax with hydrofluoric acid, is used in the cleaning and pickling of metals, electropolishing of aluminum, and in organic syntheses. Certain fluoborates are used in baths for specialty electroplating of cadmium, chromium, copper, indium, iron, lead, lead-tin, nickel, silver, tin, and zinc. Ammonium fluoborate is added to magnesium castings to prevent oxidation, sodium fluoborate is used in the heat treatment of aluminum alloys to prevent blistering and crack formation, and potassium fluoborate is an additive in brazing and soldering fluxes and in grinding wheels. Silicon tetrafluoride, SiF_4, has been useful in sealing permeable zones during oil and gas exploration. Upon injection into a water zone in the well, SiF_4 hydrolyzes to a fluosilicic-acid gel and plugs up the pore passages. Tungsten metal is being produced by the reduction of tungsten hexafluoride, WF_6, with hydrogen. Several fluorinated sulfur compounds are now commercially available. Sulfuryl fluoride, SO_2F_2, is used in organic syntheses and as a fumigant in pest control. Sulfuryl chlorofluoride, SO_2ClF, is used in syntheses of organic compounds; sulfur tetrafluoride, SF_4, in special fluorinating processes; and sulfur hexafluoride as a gaseous dielectric in transformers, X-ray tubes, and electronic equipment. In addition to sodium fluoride, stannous fluoride, SnF_2, sodium fluophosphate, Na_2PO_3F, and zirconium fluoride, ZrF_4, can also be used as decay preventives in toothpaste. Space-age technology has stimulated the development of many fluorine compounds, some of which were considered rarities decades ago, and the number seems to be steadily increasing. An interesting family of compounds is the fluorides of the rare gases; the first of these to be synthesized was xenon tetrafluoride, XeF_4. The discovery that the rare gases, originally thought to be inert, could be fluorinated is considered to be a milestone in modern chemistry.

Miscellaneous Uses of Fluorspar

In the manufacture of portland cement, the addition of 1 to 5% of low-grade fluorspar to the mix results in lower fuel costs, increased kiln capacity, longer liner life, and a better quality product. Fluorspar lowers the sintering temperature and acts as a mineralizer in promoting the formation of tricalcium