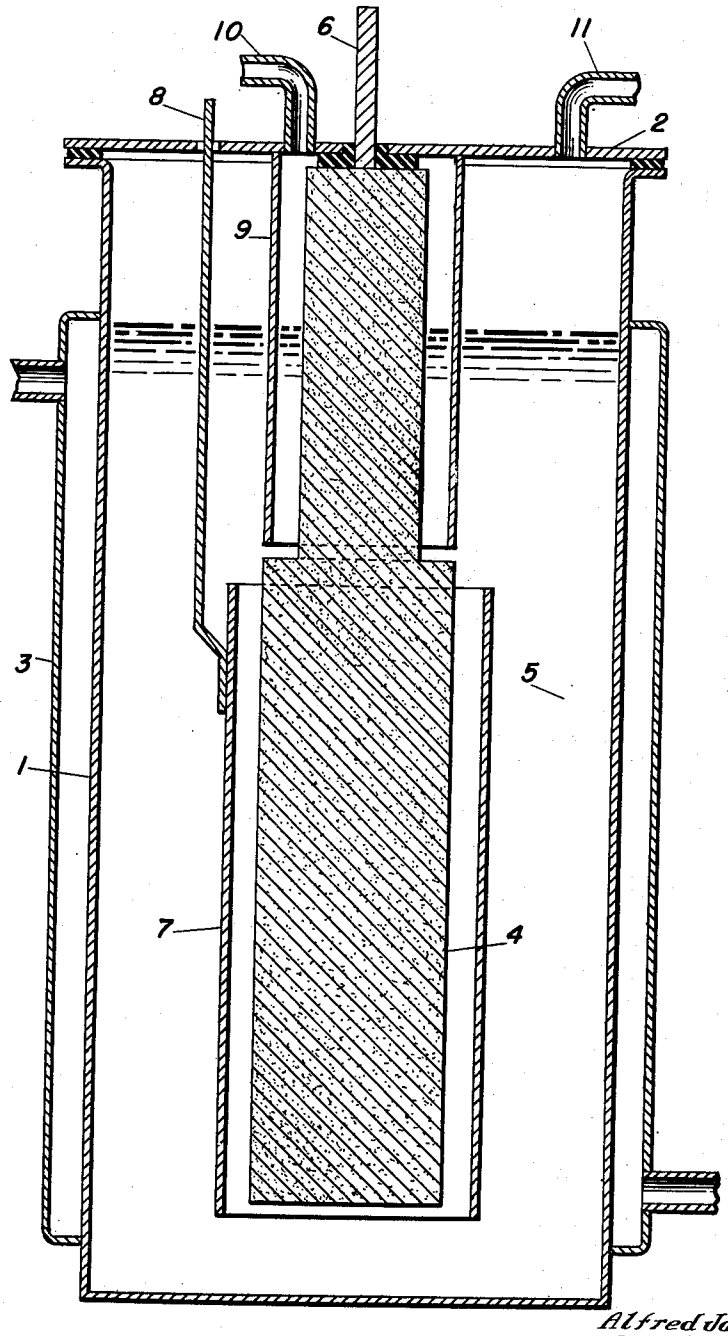
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APPARATUS FOR THE ELECTROLYTIC PRODUCTION OF FLUORINE

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APPARATUS FOR THE ELECTROLYTIC PRODUCTION OF FLUORINE

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This invention relates to improvements in electrolytic apparatus and processes in particular to apparatus and processes for the electrolytic production of fluorine.

It is well-known to manufacture fluorine by electrolysis of substantially dry fused mixtures of fluorides, in particular mixtures of an alkali metal fluoride and hydrogen fluoride. Further, in such a process, it is well-known to use anodes of carbon or graphite, the cathode being of mild steel or other metal resistant to the action of the electrolyte. Hydrogen is evolved at the cathode and fluorine, with varying amounts of oxygen and other impurities, at the anode. Mixtures of hydrogen and fluorine give rise to violent explosions, therefore, an essential feature of all such fluorine cells is a diaphragm or partition having as its function the prevention of mixing of the gases evolved at the two electrodes. In some cells this diaphragm or partition extends downward in the interelectrode space for a distance equal to or even greater than that of the downward extension of the electrodes. In other fluorine cells, for example in that described in British patent specification No. 668,465, the separating diaphragm or partition extends downward for a short distance only into the interelectrode space. It will be apparent, therefore, that a disadvantage of all fluorine cells of the type above described is that the interelectrode distance must be sufficiently great to accommodate the gas-separating diaphragm between the electrodes and to prevent the hydrogen entering the anode compartment; this results in a longer interelectrode path for the electric current, and consequently greater power consumption, than would be necessary if the diaphragm were absent from the interelectrode space and the cathode located much nearer to the anode. In practice the interelectrode gap must not be less than a certain critical minimum which is determined by a number of factors including the depth of the cathode and the state of its surface as well as the current density.

In a communication to Nature (vol. 160, p. 504, October 11, 1947) the applicants reported their discovery that, in the electrolysis of potassium fluoride-hydrogen fluoride mixtures using amorphous carbon anodes, the gaseous fluorine appears almost wholly at the junction of the anode with the electrolyte surface, if the current density

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is maintained below a critical maximum which is determined by a number of factors. The applicants have further discovered that, even when such an anode has a horizontal part below the electrolyte, the fluorine is not liberated from this horizontal portion, but passes along it towards the vertical part of the anode.

In U. S. Patent No. 2,592,144 is described a diaphragmless fluorine cell in which the porous carbon anode is wholly immersed in the electrolyte which does not enter the pores of the carbon. The fluorine liberated as a result of the electrolytic process passes inwards through the pores of the carbon and is conducted therefrom through a suitable conduit infixed in the upper end of the immersed anode.

According to the present invention, a cell for the production of fluorine by electrolysis of a liquid mixture of flourides includes the following features.

The cell comprises a container for the electrolyte provided with a cathode and a carbon anode. A heating jacket surrounds the container to a height of at least one half of the longitudinal length of said container. The top of the jacket defines the normal operational level of electrolyte. The upper portion of said carbon anode is of smaller cross sectional area and longitudinal length than the lower portion thereof and the said lesser upper portion is positioned above the level of the top of the cathode and below the normal operational level of the electrolyte.

A gas collecting hood of metal resistant to attack by the electrolyte and electrolytic products is positioned to surround only the said lesser upper portion of the anode without contacting the same. The downward geometrical projection of the edge of the gas collecting hood lies substantially within the periphery of the major lower portion of the anode. In addition, the upper portion of the said hood is provided with an outlet for gas collected therein.

In the process according to the invention the fluorine liberated as a result of the electrolysis passes mainly up the vertical surface of the anode and travels round the shoulder thereof and is discharged into the space under the hood or bell. No appreciable amount of fluorine is liberated in the form of detached bubbles into the interelectrode space. A portion of the fluorine may find

its way into the bell through the pores in the mass of the carbon anode, the relative proportion of the gas following this route is, of course, dependent on the porosity of the carbon, the surface roughness thereof, and probably on other factors.

Although electrolytes containing varying proportions of the metal fluoride and hydrogen fluoride may be employed in the present invention we prefer to employ electrolyte having compositions lying within the range 1 KF/1.8 HF to 1 KF/2.2 HF and to carry out the electrolysis at temperatures within the range 80° C. to 110° C. If temperatures of the order of 250° C. are employed the electrolyte should approximate in composition to 1 KF/1 HF.

Suitable cells according to the invention comprise a mild steel container for the electrolyte which container may be cylindrical or rectangular as desired, provided with a jacket which is adapted for hot water or steam heating, alternatively it may be heated by suitable electrical means. The shape of cross-section of the anode is in no way critical although it is generally convenient that it should be circular. At the region where the cross-section of the anode changes from that of the main portion to that of the upper part the transition from the greater to the lesser anode dimensions may be effected by means of a step or shoulder, which step or shoulder may be horizontal or inclined inwardly toward the vertical. On the other hand, the anode top may be tapered so that it can be conveniently housed under the bell or hood.

In one preferred form of our invention we use anodes formed of porous carbon or graphite having a permeability of more than 10, permeability being defined in terms of cubic feet of air per square foot of surface capable of passing through one inch thickness of the carbon per minute under an imposed pressure equivalent to two inches of water. However, the employment of anodes of high permeability is not essential for the production of fluorine according to the present invention, since quite satisfactory results may be obtained with a relatively dense and impervious carbon anode.

Using anodes as above described and working under the above specified conditions it is possible to operate fluorine cells with interelectrode gaps of ½ inch or less without danger from intermingling of the electrolytic gases and with considerable saving in energy consumption.

A cell suitable for carrying out the invention is shown in the attached drawing not drawn to scale, which represents a vertical section through the said cell. Referring to the drawing, 1 is a container of mild steel or other suitably resistant metal, provided with a lid 2, and a jacket 3 adapted for water or steam heating surrounds the container 1. The carbon anode 4, the upper portion of which is of narrower cross-section than the lower portion is partially submerged in the electrolyte 5. An electrically conducting rod 6 insulated from the cell lid 2 is connected to the anode 4. At close proximity to the anode is a cathode 7 which may be of mild steel, copper or other material substantially resistant to the electrolyte and products of electrolysis. The cathode is supported by an electrically-conducting rod 8 which rod is insulated from the cell lid through which it passes. Surrounding the upper portion of the anode and which dips into the electrolyte 5 is a hood 9. The pipe 10 for fluorine take-off is connected through the cell lid to the space between the upper portion of the anode and the bell 9. The pipe 11 connected through the cell lid is for take-off of hydrogen.

The following example illustrates but does not limit the invention.

Example

The cell used in this example was of the shape described in the drawing. The container of the cell was a jacketed mild steel vessel which was heated by hot water. The anode was cut from a block of hard carbon having a very low permeability. The height and width of cross-section of the lower portion of the anode was 9⅝ inches and 3¼ inches respectively; the height and width of cross-section of the upper portion of the anode was 8 inches and 2 inches respectively. The anode/cathode separation was 0.48 inch. All the fluorine was evolved up the vertical surface of the upper portion of the anode and was withdrawn between this part of the anode and the bell or hood which enclosed it.

The following measurements were noted when the cell voltage was 7.6 volts and the temperature of the electrolyte was 80° C. to 85° C.

Current	60 amps.
Anode surface area (opposite cathode)	98 sq. ins.
Anode current density	0.60 amps./in^2
Current efficiency on fluorine	>90% of theory
Percent HF in electrolyte	42
Fluorine content of anode gas	96.2% (rest mainly oxygen)

By way of contrast when the run was repeated under similar conditions to the above but with an anode/cathode separation of 3 inches the voltage was 8.6 volts.

Having now particularly described and ascertained the nature of our invention and in what manner the same is to be performed, we declare that what we claim is:

1. A cell for the production of fluorine by electrolysis of a liquid mixture of fluorides which comprises a container for the electrolyte provided with a cathode and a carbon anode, the upper portion of said carbon anode being of smaller cross-sectional area and longitudinal length than the lower portion thereof and said lesser upper portion being positioned above the level of the top of said cathode, and a gas collecting hood of metal resistant to attack by the electrolyte and electrolytic products positioned to surround only the said lesser upper portion of said anode without contacting the same, the downward geometrical projection of the lowest edge of which hood lies substantially within the periphery of the major lower portion of the said anode, and the upper portion of the said hood being provided with an outlet for gas collected therein.

2. A cell as set forth in claim 1 wherein the anode is formed of carbon selected from the group consisting of amorphous carbon and graphitized carbon of a permeability greater than 10, said permeability being defined in terms of cubic feet of air per square foot of surface capable of passing through one inch thickness of the anode material per minute under an imposed pressure equivalent to two inches of water.

3. A cell as set forth in claim 1 wherein said container is provided with an external heating jacket.

4. A cell for the production of fluorine by electrolysis of a liquid mixture of fluorides which

comprises a container for the electrolyte provided with a cathode, a carbon anode and a heating jacket surrounding said container to a height of at least one-half of the longitudinal length of said container, the top of said jacket defining the normal operational level of electrolyte and the upper portion of said carbon anode being of smaller cross-sectional area and longitudinal length than the lower portion thereof, at least part of the said upper portion extending below the said normal operational level of electrolyte and being positioned above the level of the top of said cathode, and a gas collecting hood of metal resistant to attack by the electrolyte and electrolytic products positioned to surround only the said lesser upper portion of said anode without contacting the same, the downward geometrical projection of the lowest edge of which hood lies substantially within the periphery of the major lower portion of the said anode, and the upper portion of the said hood being provided with an outlet for gas collected therein.

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