Recovery of fluoride values from carbonaceous waste cathode materials is achieved by reacting the waste materials with oxygen, water, and sulfur dioxide at temperatures between about 600°C and 1200°C.
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RECOVERY OF FLUORIDE VALUES FROM CARBONACEOUS MATERIALS

Background of the Invention

This invention relates to the recovery of fluoride values from waste cathodes and materials used for the lining of aluminum electrolytic cells. More specifically, this invention relates to an improved method for the recovery of valuable components from reduction cell linings and cathodes.

The cathodes of electrolytic furnaces used in the production of aluminum are lined with carbon block and carbon lining paste compositions which are electrically conductive. During electrolytic operations, the carbon linings and cathodes gradually absorb bath materials, such as cryolite (Na₃AlF₆), aluminum fluoride (AlF₃), calcium fluoride (CaF₂), alumina, and metallic aluminum. This absorption, principally of cryolite, frequently doubles the cathode weight of a cell during operation. When it becomes necessary to remove the spent cathodes and pot linings, a considerable amount of very expensive fluoride materials is involved. At the present time, due to the lack of feasible recovery systems, most of this spent or waste cell lining material is merely stockpiled, presenting environmental concerns relative to the possible leaching of fluoride salts into ground waters. In addition, the value of the fluoride materials involved, if suitably recoverable, is substantial.

Prior art methods for recovering cryolite from spent cathode materials have included extraction by sodium hydroxide, sodium carbonate, or water. U.S. Patents
1,871,723 and 2,732,283 teach the treatment of carbon cell lining material with aqueous caustic solutions to yield sodium fluoride and sodium aluminate, which solutions may be processed to precipitate cryolite. U.S. Patent 3,106,448 teaches reaction between fluoride values in spent liner and a water soluble carbonate to produce water soluble sodium fluoride, which may in turn be precipitated with sodium aluminate to form a cryolite. In addition, the extraction and recovery of alumina and fluoride values with dilute ammonia solutions is known.

One of the more recent methods for recovery of fluoride and aluminum values involves the pyrohydrolysis of the carbonaceous material, preferably in a fluidized bed reactor. Pyrohydrolysis involves contacting the spent cathode and/or cell lining with water or steam at high temperatures, whereby the water introduced reacts with the fluoride compounds to form HF. However, it has been found that while the pyrohydrolysis of aluminum fluoride is relatively easy, calcium fluoride and, particularly, sodium fluoride are more difficult to react. U.S. Patents 4,113,832, 4,158,701, 4,160,808, and 4,160,809 all relate to pyrohydrolysis techniques for the recovery of fluoride values from spent cell linings. However, these references fail to provide a feasible and economic method, due to exceptionally high temperature and excessive steam requirements. It has been found that temperatures in excess of 1100°C are required for the recovery of fluoride from cathode waste by pyrohydrolysis. Fluoride recovery is enhanced by increasing temperature, increasing exposure time, and by the use of considerable quantities of steam.

Thus, it may be observed that there is a well defined need for a suitable fluoride recovery technique, whereby more efficient and economical results may be obtained. It is a purpose of the present invention to provide such a method.
It is a further purpose of the present invention to provide a method for the treatment of cathode waste materials which efficiently decomposes the fluorine-containing components therein and provides for their efficient recovery in the form of aluminum trifluoride, and/or cryolite.

Summary of the Invention

A process is provided for the recovery of fluorine, sodium, and aluminum values from spent or waste materials generated in electrolytic aluminum production facilities. The reaction of the waste cathode material is conducted at a temperature between 800°C and 1,000°C, utilizing a gaseous mixture of air, steam, and sulfur dioxide. The sulfur dioxide is provided in sufficient quantity to convert essentially all of the metallic fluoride salts present to metallic sulfates. The reaction may be conducted in suitable reactors such as a multiple stage fluidized bed, a multi-level furnace reactor, or a closed, refractory lined, furnace. The HF enriched gas exiting the reactor may be fed to a second reactor to be reacted with various feed materials for the production of fluorine-containing materials. In a preferred embodiment, aluminum trifluoride is produced through reaction of the HF enriched gas with aluminum trihydrate in a fluidized bed reactor. Alternatively, a mixed cryolite/aluminum trifluoride reduction cell bath material is made by chemisorption of the HF on the surface of metallurgical grade alumina, which is then fed to an aluminum reduction cell. Very high conversion rates of fluorine-containing materials are achieved.

Detailed Description of the Invention

This invention relates to the recovery of HF in increased yield from aluminum reduction cell cathodes and linings. More particularly, this invention concerns a process wherein the spent cell materials are reacted at elevated temperatures in a suitable vessel with water, air, and sulfur dioxide. The HF product of this reaction
is subsequently absorbed or reacted to form a fluoride compound, such as aluminum trifluoride. The solid reaction products of the reaction comprise sulfates which are removed in the form of ash and/or clinker.

The carbonaceous reduction cell linings and cathodes utilized in this invention comprise materials recovered from conventional aluminum reduction cells after extended use. Typical compositions of such material are shown in Table 1.

### Table 1

**Chemical Analysis of Ash From Cathode Waste**

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Block</th>
<th>Block</th>
<th>Paste</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>64.4</td>
<td>35.3</td>
<td>55.4</td>
</tr>
<tr>
<td>Ash %</td>
<td>35.6</td>
<td>64.7</td>
<td>44.6</td>
</tr>
<tr>
<td>Analysis of Ash %</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sodium, as Na₂O</td>
<td>40.7</td>
<td>45.4</td>
<td>57.2</td>
</tr>
<tr>
<td>Aluminum, as Al₂O₃</td>
<td>32.93</td>
<td>28.94</td>
<td>8.52</td>
</tr>
<tr>
<td>Calcium, as CaO</td>
<td>6.23</td>
<td>6.54</td>
<td>1.40</td>
</tr>
<tr>
<td>Silica, as SiO₂</td>
<td>1.27</td>
<td>1.58</td>
<td>14.54</td>
</tr>
<tr>
<td>Iron, as Fe₂O₃</td>
<td>1.35</td>
<td>1.50</td>
<td>0.78</td>
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<tr>
<td>Magnesium, as MgO</td>
<td>0.80</td>
<td>0.55</td>
<td>1.20</td>
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<tr>
<td>Titanium, as TiO₂</td>
<td>0.14</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>Nickel, as NiO</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
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<tr>
<td>Vanadium, as V₂O₅</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
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<tr>
<td>Total</td>
<td>83.43</td>
<td>84.66</td>
<td>83.73</td>
</tr>
<tr>
<td>Fluoride by</td>
<td>16.57</td>
<td>15.34</td>
<td>16.27</td>
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<tr>
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Various forms of reaction vessels may be utilized in the present invention. Appropriate reactor designs include such approaches as a multi-stage fluidized bed, a multi-stage Hirschhoff furnace, or a moving packed bed reactor. Examples of packed reactors include vertical furnaces similar to a shaft kiln, or furnaces inclined somewhat from the horizontal in which solid feed material would fill the entire furnace cross section. In addition, it is possible that the reaction could be carried out in a closed refractory-lined furnace operating at temperatures above the melting point of the sulfate materials formed by the reaction. In such cases, solid waste cathode material would be added to a molten sulfate bath and caused to react through the introduction of oxygen or air, sulfur dioxide, and steam to the molten bath via refractory tubes extending into the molten bath. HF enriched exit gases would be withdrawn from the top of such a furnace. Periodically, part of the molten bath would be tapped from the furnace to provide space for the additional sulfate materials produced through the described reactions.

The spent carbonaceous materials are preferrably reacted in a fluidized bed reactor. For such a reactor, the materials are first formed into an easily fluidizable form, and then subjected to fluidization and reaction. Preparation may include crushing to an appropriate size, such as by conventional crushing apparatus. It has been found that for operation of dense fluidized beds, particles should be not less than about 1 mm in size, and preferably in the range of from about 1.3 to 5 mm. Comminuting operations generally result in the generation of fines, e.g. particles having a size below about 1 mm. Accordingly, the waste materials are subjected to a comminuting step, and then the comminuted material is subjected to a classification step to provide a cross section having oversize particles, particles in the preferred range, and fines having a smaller size. Particles
having sizes above the desired range are recycled to the comminuting or crushing step, while the fines may be subjected to a shaping step if so desired. Fluidization is accomplished by provision of sufficient fluidizing gas, i.e. air, to provide the required fluidity.

The following process reactions are believed to take place:

\[ 2 \text{NaF} + \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HF} \]
\[ \text{CaF}_2 + \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 + 2 \text{HF} \]
\[ \text{AlF}_3 + \frac{3}{2} \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3 + 3 \text{HF} \]
\[ \frac{2}{3} \text{AlF}_3 + \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \frac{1}{3} \text{Al}_2(\text{SO}_4)_3 + 2 \text{HF} \]
\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]

Thus, the solid products of the reaction mode comprise calcium sulfate, sodium sulfate, and alumina (in as much as aluminum sulfate decomposes at 770°C). Minor amounts of Fe_2(SO_4)_3, SiO_2, and sulfates and/or oxides of other metals present in the waste material may also be formed. The principal gaseous product of the reaction are CO_2, HF, and unreacted feed gas materials.

The sulfur dioxide utilized in the reaction of the present invention may be produced externally to the furnace reactor, or produced in the reactor, in situ, by the reaction of sulfur and oxygen at elevated temperatures. If externally produced, the sulfur dioxide gas is added with the air and water fed to the furnace. A particular external source of sulfur dioxide which may be practicable is the primary exhaust gas exiting the dry scrubbers utilized for purification of the exit gases from the reactor. If the SO_2 and SO_3 levels in this dry scrubber exhaust stream are sufficiently high for ensuring complete reaction with the spent cathode material at economical furnace sizes, such gases would be fed with air and water as previously described. Although thermodynamic calculations indicate the SO_2 would be virtually consumed on a stoichiometric basis, if excess SO_2 should be necessary or desirable, it would be possible to recycle a portion of the exit gas through the reactor furnace.
It is also to be noted that other sources of SO$_2$ may be utilized in the present invention. For example, such sources of SO$_2$ as sulfuric acid, ferric sulfate, ammonium sulfate, sulfur trioxide, hydrogen sulfide, and other suitable sulfates or sulfides, as well as sulfur per se, may be utilized. However, sulfur dioxide in the presence of water, and air, has been found to be the most advantageous sulfating material.

It has been found that the reaction may be conducted at temperatures within the range of from about 600°C to about 1200°C, with reaction efficiency improving at higher temperatures. Since the decomposition temperature of Al$_2$(SO$_4$)$_3$ is 770°C, it is preferable to operate above this temperature to maximize Al$_2$O$_3$ formation and minimize ash formation. Similarly, since Na$_2$SO$_4$ melts at 884°C, it is preferred to operate below this temperature to avoid problems of liquid Na$_2$SO$_4$ clogging equipment, inhibiting heat exchange, or interfering with gas flow in a fluidized bed reactor. Thus, a preferred temperature range is from about 770°C to about 884°C, with the most preferred range being from about 850°C to about 880°C.

It has been found that air flow rates can play a very important part in moderating reaction temperature. In actually operations, it is quite likely that the composition of the cathode waste material will vary quite markedly on a sample-by-sample basis. Thus the capability for variable air flow rates will be important for maintaining proper reactor temperature. This can be accomplished through a controlled system wherein the reactor temperature is continuously monitored and compared to a set point or set temperature range. If at any time the temperature were above the desired range, the air flow rate would be increased to provide cooling. Similarly if the temperature were below the desired range, the air flow rate would be reduced to provide heating.

In most reaction vessels, it is desirable to utilize the stoichiometric amount of SO$_2$ required for reaction.
Similarly, the amount of water vapor added is also equivalent to the stoichiometric requirements for reaction with the fluorides. In as much as air is assumed as the source of oxygen, the amount of nitrogen added is equivalent to the normal ratio of nitrogen to oxygen in air. In actual operations, it may be desirable to operate the reactor with excess quantities of air. In such cases, the excess amounts of oxygen and all nitrogen would pass directly through the reactor undergoing no chemical reactions.

However, since it has been found that temperature control of the reaction may be effected by flow rate of reactant gases, it may be found advantageous under certain conditions to utilize minimal amounts of reactant gases, rather than providing large excess. For example, it may be appropriate, under certain operating conditions, to substitute oxygen for air in the inlet gases, so as to reduce the volume of gaseous material while still maintaining the necessary oxygen balance. Similarly, it may under certain conditions, be desirable to provide larger excess amounts of such reactants as sulfur dioxide. For example, geometric considerations, and/or flow/packing densities of a fluidized bed reactor may require extremely high stoichiometric excesses of reactant gas, so as to insure complete reaction of all of the fluoride values in the product feed. Of course, a far more efficient usage of the sulfur dioxide gas may be insured through the use of a properly designed reactor, and control of all operating parameters.

Regardless of the particular furnace reactor design which is chosen, the HF enriched gas exiting the reactor is fed to a second reactor to be reacted with various feed materials for the production of fluorine-containing chemicals. The potential recovery processes include the following.

Aluminum trifluoride may be produced through the reaction of the HF enriched gas with aluminum trihydrate
in a fluidized bed reactor. This process is analogous to the standard industrial method for producing AlF₃. Alternatively, a mixed cryolite/aluminum trifluoride reduction cell bath material may be made by feeding the HF enriched gas to a dry scrubber, capturing the dried HF by chemisorption on the surface of high surface area metallurgical grade alumina, and feeding the fluoride-containing alumina to aluminum reduction cells. The excess bath produced through such additions may be periodically tapped from the reduction cells and stored for subsequent sale or use.

Cryolite may be produced following the standard industrial process of introducing the HF enriched gas stream to a caustic sodium aluminate solution.

Various fluorocarbon materials may be produced through the direct reaction of the HF enriched stream with carbon or various organic feed stock materials such as methane, ethane, or other more complex hydrocarbon materials. In a similar sense, chloro-fluorocarbon materials may be produced through the joint reaction of the HF-containing gas, HCl, and organic feed stock. In the production of fluorinated hydrocarbons, it is critical that the furnace reactor for the treatment of the waste cathode material be operated at air flow rates equivalent to the stoichiometric requirement for oxygen. Any excess oxygen would carry through with the HF enriched exit gas, leading to oxidation losses of organic feed stocks in a fluorocarbon producing reactor.

The HF gas, and the other gaseous products of the reaction, such as CO₂, are discharged from the reactor medium at a highly elevated temperature. Accordingly, such gases must be cooled. Cooling may be accomplished in any apparatus suitably capable of removing substantial heat from the vapors. The type of cooling equipment and/or cooling medium utilized also influence the nature of the recovered fluoridic material. For example, when the hot vapor is contacted with a cooling water spray, an
aqueous HF solution is recovered. When cooling is accomplished by indirect heat exchange utilizing suitable exchange media, the HF content of the gas remains undiluted by the cooling agent and is recovered at a higher concentration.

It is particularly to be noted that the temperature of the process of the present invention is considerably lower than temperatures employed in prior art pyrohydrolysis processes. Due to the presence of the sulfur dioxide in the reaction, resulting in the formation of sulfates, a very large negative (favorable) free energy change occurs. On the other hand, under normal pyrohydrolysis conditions, a large positive (unfavorable) free energy change is encountered. On the basis of calculated free energies for the various species involved in the reactions occurring, either in the presence of sulfur dioxide or in the absence thereof, it is found that the free energy of reaction, in the presence of sulfur dioxide, would be favorable over a wide range of temperatures. As a result, the choice of an optimal operating temperature hinges primarily on reaction kinetics rather than equilibrium conditions. It has also been found, experimentally, that the sulfur dioxide reaction occurs readily at moderate temperatures, whereas 20% or less conversion of sodium fluoride results under normal pyrohydrolysis without the use of SO₂ even at temperatures of 1100°C. Ideally, the maximum temperature within the reactor vessel would be lower than the melting point of the lowest melting temperature constituent of the ash residue, e.g. Na₂SO₄, which melts at 884°C. Under such conditions, there is no formation of a molten slag to enter through, nor are diffusion processes required for gaseous reaction with fluoride constituents. However, optimization of temperatures should be based upon reaction rates which increase at somewhat higher temperatures, in accordance with the specific composition of the cathode waste material being treated.
Example 1

To confirm the possibility of reacting pure sodium fluoride, a major ingredient of cathode waste materials, with a gaseous mixture of SO₂, O₂ and H₂O, an experimental reaction was conducted at 860°C. Sulfur dioxide was present in this reaction at about 380 times the stoichiometric amount of limiting reagent. The conversion of sodium fluoride to sodium sulfate was found to be approximately 97% complete after one hour. Since sodium fluoride is the least reactive component of the cathode waste material, thermodynamically, it was concluded that the SO₂ treatment of cathode waste materials containing sodium fluoride, calcium fluoride, and aluminum fluoride was thermodynamically feasible.

Example 2

A bench scale reaction apparatus for the removal of fluoride from cathode waste was constructed for experimentation. This apparatus comprised sources of air, SO₂, and steam, joined to a preheating tube for initial temperature elevation, joined to a furnace for superheating, followed by a high temperature furnace for reaction of the sample. Upon exit from the high temperature furnace, the gaseous product was passed through a condensor, with the condensate collected, followed by an absorption flask and subsequent condensors for cooling of remaining gases. In this apparatus, the current of air, steam, and SO₂, was superheated and passed over the cathode waste sample, which was itself heated to temperatures in the desired range. Under these conditions, carbon constituents of the waste sample were oxidized while the steam and SO₂ reacted with the fluoride compounds and released hydrogen fluoride. Following combustion and reaction, the hot gases were cooled, condensed, and passed through aqueous solutions to absorb entrained fluorides, and finally stored in large bottles containing saturated salt solutions for volume measurement. The fluoride content of the condensate was determined using a fluoride ion activ-
ity electrode. The gas flow through the apparatus was controlled by flow meters located prior to the steam generator. The steam generator was adjusted to yield 0.1 to 2.0 ml of condensate per minute. The mixture of gases was preheated prior to entering the alumina reaction tube containing the sample of cathode waste. The reaction tube was 50 inches long by 1 inch in diameter, and was heated by two electric furnaces; the first to superheat the mixture of gases, and the second to control the temperature of the sample of cathode waste, retained in an alumina boat.

One gram of reagent grade NaF (0.0246 moles) was placed in the alumina boat in the tube furnace, and 2.33 moles of O₂, 10.8 moles of SO₂, and 16.7 moles of H₂O were passed over it during 1 hour at temperatures between 850 and 870°C. The weight of the material in the boat was found to be 1.71g after the reaction time, corresponding to 97% conversion, assuming all of the product was Na₂SO₄. Moreover, the material in the boat was found to contain 61.8% SO₄, and 2.5% NaF by weight from direct chemical analysis. This corresponds to 97% conversion of NaF to sulfate compounds.

Example 3

Samples of typical cathode waste, taken from the stockpile of an operating aluminum plant, were reacted with SO₂, O₂, and H₂O, at temperatures of 850°C, 925°C, and 1,000°C. The reactions were found to be 93.6, 97.7 and 98.8% complete, respectively, after 1 hour of reaction with about 380 times the stoichiometric amount of SO₂.

The cathode waste was analyzed and found to contain 8.72% F (19.3% NaF) and 0.56% SO₃ as received. Approximately 2.8g of cathode waste was ground and placed in the alumina reaction both in the tube furnace and 2.33 moles of O₂, 10.8 moles of SO₂ and 5.56 moles of H₂O were passed over it during 1 hour. Results are shown in Table 2.
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<th>Sample</th>
<th>Reaction Temp., °C</th>
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<th>925</th>
<th>1000</th>
</tr>
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<tr>
<td>1</td>
<td>Total initial wt. (g)</td>
<td>2.8025</td>
<td>2.8157</td>
<td>2.8041</td>
</tr>
<tr>
<td></td>
<td>g NaF final wt. (g)</td>
<td>0.5409</td>
<td>0.5434</td>
<td>0.5412</td>
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<tr>
<td></td>
<td>% S03 after reaction (final)</td>
<td>23.48</td>
<td>97.7</td>
<td>98.8</td>
</tr>
<tr>
<td>2</td>
<td>Total initial wt. (g)</td>
<td>l.2893</td>
<td>l.3509</td>
<td>l.4971</td>
</tr>
<tr>
<td></td>
<td>g NaF final wt. (g)</td>
<td>0.0348</td>
<td>0.01256</td>
<td>0.00629</td>
</tr>
<tr>
<td></td>
<td>% S03 after reaction (final)</td>
<td>93.6</td>
<td>97.8</td>
<td>98.8</td>
</tr>
<tr>
<td>3</td>
<td>Total initial wt. (g)</td>
<td>1.2893</td>
<td>l.3509</td>
<td>l.4971</td>
</tr>
<tr>
<td></td>
<td>g NaF final wt. (g)</td>
<td>0.0348</td>
<td>0.01256</td>
<td>0.00629</td>
</tr>
<tr>
<td></td>
<td>% S03 after reaction (final)</td>
<td>93.6</td>
<td>97.8</td>
<td>98.8</td>
</tr>
</tbody>
</table>

**TABLE 2**
For purposes of the experiment, all of the fluoride in
the cathode waste was assumed to be in the NaF form, and
the "percent reacted" was calculated by subtracting the
grams of NaF after reaction from the grams before reac-
tion and dividing by the grams of NaF before the reaction.
However, in view of the very high reaction completion
obtained, the experiment clearly illustrates the feasi-
bility of the invention.

**Example 4**

A Hirschoff furnace, a multi-stage reactor with
gas/solids flow, having a number of rabbles at each level
of the furnace rotating about the central axis of the
furnace for directing the inward/outward flow of solids
from level to level, is utilized to carry out the process
for recovering fluorides from waste cathode materials.
Gas velocities and the mechanics of gas flow from level
to level are controlled such that the solids at each
level are in a semi-fluidized state. Crushed cathode
waste, mixed with sulfur, is introduced at the top of
the furnace while a gas mixture composed of air and
steam is introduced at the bottom. The ash residue
resulting after the combustion of carbon and the sulfa-
tion of the fluoride components of the waste leaves
through the bottom of the furnace. The gas stream,
enriched with HF resulting from the sulfation reaction
exits the top of the furnace. The exit gas stream may
then be treated as previously discussed. At the various
levels of the furnace, the following reactions occur.
In the lowest levels of the furnace, the introduction
of gases at ambient temperatures causes simultaneous
cooling of the ash residue with heating of the gases.
As the gases become heated there is combustion of the
waste carbon material, leading to the formation of carbon
dioxide and carbon monoxide. In the middle level of the
furnace, sulfation of the fluoride constituents in the
waste cathode materials occurs through the combined
reaction of sulfur, mixed with the cathode waste solid
feed material, oxygen, steam, and fluoride components. Principal reactions include:

\[
2 \text{NaF} + H_2O + S + 3/2 O_2 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HF}
\]

\[
\text{CaF}_2 + H_2O + S + 3/2 O_2 \rightarrow \text{CaSO}_4 + \text{HF}
\]

\[
\frac{2}{3} \text{AlF}_3 + H_2O + S + 3/2 O_2 \rightarrow \frac{1}{3} \text{Al}_2(\text{SO}_4)_3 + 2 \text{HF}
\]

\[
\text{Al}_2(\text{SO}_4)_3 \rightarrow \text{Al}_2\text{O}_3 + 3 \text{SO}_3
\]

In the top level of the furnace, the hot gases resulting from the combustion and sulfation reactions contact the solids fed to the top of the furnace at ambient temperature, resulting in the simultaneous heating of the solids and cooling of the gas stream before the gases exit from the top of the furnace.

It will be recognized by those skilled in the art that various equivalences and alternatives are to be considered within the scope of the present invention. The examples herein are merely for exemplary purposes, and are not meant to define the scope of the invention, which is set forth by the following claims.
We Claim:

1. A process for the recovery of fluoride values from carbonaceous materials, which process comprises liberating the fluorine as gaseous hydrogen fluoride by heating the carbonaceous materials in the presence of oxygen, water, and sulfur dioxide.

2. A process as set forth in claim 1, wherein said heating is conducted in a fluidized bed reactor.

3. A process as set forth in claim 2, wherein said fluidized bed reactor is a multiple-stage reactor.

4. A process as set forth in claims 2 or 3 wherein said carbonaceous materials are particles ranging in size from about 1 mm to about 5 mm.

5. A process as set forth in claims 2 or 3 wherein said heating is within the temperature range of from about 600°C to about 1200°C.

6. A process as set forth in claims 2 or 3 wherein said heating is to a temperature below about 1100°C.

7. A process as set forth in claims 1 or 2, wherein said sulfur dioxide is produced in situ.

8. A process as set forth in claims 1 or 2, wherein said sulfur dioxide is produced by the addition of sulfur to the heated carbonaceous materials.

9. A process for the decomposition of carbon cathode waste material containing cryolite, aluminum fluoride, calcium fluoride, and sodium fluoride which comprises heating the waste material in the presence of water, oxygen, and sulfur dioxide to a temperature at which hydrogen fluoride is generated.

10. A process as set forth in claim 9, wherein said temperature is within the range of from about 770°C to about 884°C.

11. A process as set forth in claim 9, wherein said decomposition takes place in a reactor selected from the group consisting of fluidized bed reactors, packed bed reactors, and closed furnace reactors.
12. A process as set forth in claim 9, wherein said sulfur dioxide is formed in situ.

13. A process as set forth in claims 10, 11, or 12, wherein said hydrogen fluoride is reacted with aluminum trihydrate to form aluminum trifluoride.

14. A process as set forth in claims 10, 11, or 12, wherein said hydrogen fluoride is reacted with sodium aluminate to form cryolite.

15. A process as set forth in claims 10, 11, or 12, wherein said hydrogen fluoride is utilized for the production of a fluorinated hydrocarbon.

16. A process as set forth in claims 11 or 12, wherein said temperature is within the range of from about 770°C to about 884°C.

17. A process as set forth in claims 11 or 12, wherein said temperature is within the range of from about 850°C to about 880°C.

18. A process which comprises heating carbonaceous waste material containing absorbed fluoride compounds to a temperature between about 600°C and about 1200°C in the presence of oxygen, steam, and sulfur dioxide, and recovering the hydrogen fluoride reaction product.

19. A process as set forth in claim 18, wherein said heating takes place in a reactor selected from the group consisting of fluidized bed reactors, packed bed reactors, and closed furnace reactors.

20. A process as set forth in claim 18, wherein said sulfur dioxide is formed in situ.

21. A process as set forth in claim 20, wherein said sulfur dioxide is produced by the addition of sulfur to the heated carbonaceous materials.

22. A process as set forth in claim 18, wherein said sulfur dioxide is externally formed.

23. A process as set forth in claim 18, wherein the temperature is no higher than about 1100°C.

24. A process as set forth in claim 18, wherein said hydrogen fluoride is reacted with aluminum trihydrate.
25. A process as set forth in claim 18, wherein said hydrogen fluoride is reacted with sodium aluminate.

26. A process as set forth in claim 18, wherein said hydrogen fluoride is further reacted to produce a fluorinated hydrocarbon.

27. A process as set forth in claims 19, 20, 22, 24, 25, or 26, wherein said temperature is within the range of from about 770°C to about 884°C.

28. A process as set forth in claims 19, 20, 22, 24, 25, or 26, wherein said temperature is within the range of from about 850°C to about 880°C.
INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 82/00540

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 2

According to International Patent Classification (IPC) or to both National Classification and IPC
INT. CL. C01F 7/22, C01F 7/50, C01F 7/54
US. CL. 423/116, 465, 484, 495

II. FIELDS SEARCHED

Minimum Documentation Searched 4

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<td>US</td>
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Documentation Searched other than Minimum Documentation to the extent that such documents are included in the Fields Searched 4

III. DOCUMENTS CONSIDERED TO BE RELEVANT 4

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, 4 with indication, where appropriate, of the relevant passages 7</th>
<th>Relevant to Claim No. 14</th>
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<tbody>
<tr>
<td>A</td>
<td>US, A, 1,871,723, Published, 16 August 1932, Morrow</td>
<td></td>
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<tr>
<td>A</td>
<td>US, A, 2,732,283, Published, 24 January 1956, Clukey</td>
<td></td>
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<tr>
<td>A</td>
<td>US, A, 3,073,676, Published, 15 January 1963, Mollard et al</td>
<td></td>
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<tr>
<td>A</td>
<td>US, A, 4,113,832, Published, 12 September 1978, Bell et al</td>
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<td>A</td>
<td>US, A, 4,158,701, Published, 19 June 1979, Anderson et al</td>
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<tr>
<td>A</td>
<td>US, A, 4,160,808, Published, 10 July 1979, Anderson et al</td>
<td></td>
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<tr>
<td>A</td>
<td>US, A, 4,160,809, Published, 10 July 1979, Anderson et al</td>
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<td>A</td>
<td>GB, A, 2,056,422, Published, 18 March 1981, Gnyra</td>
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* Special categories of cited documents: 13

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 2

<table>
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<td>28 JULY 1982</td>
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<td>04 AUG 1982</td>
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International Searching Authority 1

ISA/US

Signature of Authorized Officer 10

EARL C. THOMAS

Form PCT/ISA/210 (second sheet) (October 1981)
### FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

| A | GB, A, 2,056,425, Published, 18 March 1981, Gnyra et al |
| A | GB, A, 2,059,403, Published, 23 April 1981, McGeer et al |

### V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claim numbers __________, because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim numbers __________, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

### VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

**Remark on Protest**

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.