CONVENTION APPLICATION FOR A PATENT

KAISER ALUMINUM & CHEMICAL CORPORATION

300 Lakeside Drive, Oakland, California 94643

UNITED STATES OF AMERICA

hereby apply for the grant of a Patent for an invention entitled:

"MODIFIED PYROHYDROLYSIS PROCESS FOR SPENT ALUMINUM REDUCTION CELL LININGS"

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered 927,084 for a patent or similar protection made in the United States of America on the 24th July, 1978.

Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 26th day of APRIL, 1979

by: [Signature]

(W F. Dancer)
Reg’d. Patent Attorney

To: THE COMMISSIONER OF PATENTS.
In support of the Convention Application made by 1

Kaiser Aluminum & Chemical Corporation

(hereinafter referred to as the applicant) for a Patent

for an invention entitled: 2 MODIFIED PYROHYDROLYSIS

PROCESS FOR SPENT ALUMINUM REDUCTION CELL LININGS

I, 3 Paul Emerson Calrow

of 300 Lakeside Drive, Oakland, California 94643, United States of America
do solemnly and sincerely declare as follows:

1. I am authorized by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in the United States of America on the 24th day of July 1978, by John Nikolai Andersen and Norman Bell.

3. John Nikolai Andersen, 721 Crossbrook Drive, Moraga, California 94556; Norman Bell, 1148 Arroyo Road, Livermore, California 94550, United States of America, respectively

is/are the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of John Nikolai Andersen and Norman Bell.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Oakland, California, United States of America 12th day of February 1979.

Paul Emerson Calrow

To: The Commissioner of Patents.
Abstract

1. In the process of recovering valuable components from carbon and fluoride-containing aluminous spent and waste materials generated in electrolytic aluminum reduction systems by subjecting the spent and waste materials to pyrohydrolysis in the presence of steam in a fluidized bed reactor having a fluidized bed and a freeboard area above the bed at a temperature within the range of about 900°C to about 1300°C, the improvement comprising the combination of steps of

(a) combusting the carbon content of the spent and waste materials in the fluidized bed with an \( \text{O}_2 \)-containing stream having an \( \text{O}_2 \) content of at least about 90% by volume thus generating a hot offgas substantially free of nitrogen and containing HF and vaporized Na-containing compounds;
(b) establishing an extended reaction zone in the freeboard area of the reactor by contacting the hot offgas with a relatively finely divided source of Al₂O₃ having a particle size within the range of about 40 to about 500 microns whereby the Na-containing vapors are converted to HF and Na₂O · xAl₂O₃;

(c) cooling the hot, HF-containing offgas by direct contact with an aqueous HF-containing stream and conducting the cooled offgas to a scrubber for the removal of its HF content by scrubbing with an aqueous medium, while generating a steam and inert gas containing scrubbed offgas;

(d) recovering the aqueous HF from the scrubber and using at least a portion thereof for cooling hot HF-containing offgas generated in the fluidized bed reactor;

(e) recovering an HF-containing side stream from the cooled HF-containing offgas prior to scrubbing of the offgas with the aqueous medium and employing the HF-containing side stream for the production of an AlF₃ product of at least about 85% by weight AlF₃ content in a fluidized bed reactor using as alumina source alumina trihydrate; and

(f) recovering the AlF₃ product and steam from the AlF₃ reactor and recycling the steam to the pyrohydrolysis reactor.
Complete Specification for the invention entitled:

"MODIFIED PYROHYDROLYSIS PROCESS FOR SPENT ALUMINUM REDUCTION CELL LININGS"

The following statement is a full description of this invention, including the best method of performing it known to:  US:
This invention relates to an improved pyrohydrolysis process for spent and waste materials generated in electrolytic aluminum reduction systems. More particularly, it concerns a pyrohydrolysis process wherein fluidization of the fluoridic waste material charge is accomplished by use of an \( \text{O}_2 \)-containing gas having an \( \text{O}_2 \) content of at least about 90% by volume.

Pyrohydrolysis of spent and waste materials generated in electrolytic aluminum reduction systems has been described in detail in copending application S.N. 855,506 now U.S. 4,113,832 to Bell et al. The process described involves the pyrohydrolysis of spent aluminum reduction cell linings and other fluoridic waste materials, such as floor sweepings, channel cleanings and spent alumina from reduction cell offgas scrubbing systems.
in a fluidized bed reactor. Fluidization and pyrohydrolysis generates an NaF and HF-containing offgas from which NaF is recovered and the NaF-free gas, containing the HF constituent, is used for AlF₃ manufacture and/or production of anhydrous HF. The clinker product of the pyrohydrolysis is essentially Na₂OₓAl₂O₃, which is utilized as a source of Al₂O₃ and Na₂O, for example by the well-known Bayer process. In this process both NaF and HF are produced, however, the HF content of the offgas is relatively low due to the simultaneous generation of NaF and also since air is used as a fluidizing medium for the spent material charge. Due to the diluteness of the HF in the gas, the AlF₃ product, which is made by contact of HF with Al₂O₃ in a separate fluidized bed reactor, has an AlF₃ content in the neighborhood of about 13-20% by weight.

In copending application S.N. 910,416 to Andersen et al, filed May 30, 1978, an improvement on the above discussed process is described. In the Andersen et al application, the pyrohydrolysis reactor, where the fluidization and pyrohydrolysis take place, is provided with an "extended" reaction zone in the freeboard area of the reactor. The extended reaction zone, in which vapor-phase Na-containing compounds, such as NaF and Na₂O, are contacted with a relatively finely divided source of Al₂O₃ in the presence of steam, allows essentially complete conversion of the vaporized NaF to HF and also the formation of Na₂OₓAl₂O₃ by the extended reaction of the vaporized Na₂O with the Al₂O₃. This improved process provides an essentially NaF-free offgas in which the HF content is significantly increased due to the conversion of the NaF
constituent to HF in the extended reaction zone. This higher HF content in the offgas renders the offgas more suitable for the manufacture of anhydrous HF and/or AlF₃ than previous processes. However, the HF is still considerably diluted due to the CO₂-content of the offgas which has been generated by the combustion of the carbon content of the waste materials, the excess water vapor required to drive the pyrohydrolysis reaction to completion and the large volume of nitrogen introduced with the air used for combustion.

It has now been found that the HF content of the pyrohydrolysis offgas can be further increased by a considerable degree using as fluidizing medium and as a source for combustion of the carbon content of the waste material charge, a stream which contains at least about 90% by volume O₂. Using the essentially nitrogen-free stream for these purposes, in combination with the expanded reaction zone concept where a relatively finely divided source of Al₂O₃ is contacted with the vaporized Na-components of the offgas, results in a more than 300% increase in HF content of the Na-free offgas. This offgas, as will be shown hereinafter, can be readily employed for the production of an AlF₃ product containing at least about 85% by weight AlF₃ and/or a highly concentrated HF with a fraction of the energy required in comparison to prior art processes.

An improved process for recovering fluoridic values from carbon-containing spent and waste materials, such as are generated in electrolytic aluminum reduction system is provided by pyrohydrolysis of these materials in a fluidized bed reactor in the presence of steam. In the

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:
process, the fluidized bed reactor is provided with an expanded reaction zone above the fluidized bed in the reactor freeboard area by contacting the vaporized Na-containing compounds, such as NaF and Na₂O with a relatively finely divided source of Al₂O₃ in the presence of steam. This extended reaction provides an essentially NaF-free offgas having an increased HF content. This HF content can be further increased by the improved process of the invention wherein the medium introduced for the fluidization of the waste material charge and for the combustion of its carbon content is an O₂-containing gas of at least about 90% by volume O₂ content. The reduction of the N₂ diluent from this fluidizing and combusting medium increases the HF content of the offgas by a significant degree and permits the production of an AlF₃ product of at least about 85% by weight AlF₃ content. Due to the significantly increased HF content of the offgas, manufacture of highly concentrated HF can proceed with considerably lower energy input than required for systems employing air as fluidizing and carbon combusting medium.

The Figure schematically shows the pyrohydrolysis of spent and waste materials generated by electrolytic aluminum reduction systems. The HF generated by pyrohydrolysis in the fluidized bed reactor and the extended reaction zone is, after cooling and conventional dust removal, introduced in a tail gas scrubber for purging steam and other inert gases. From this scrubber high concentration HF is recovered which is used as a direct contact cooling medium, thus increasing the HF content of the gas stream. The concentrated HF gas stream is then used for the production

(d) recovering the aqueous HF from the
of an AlF₃ product of 85% AlF₃ content. It can also be used for the preparation of highly concentrated aqueous HF and ultimately anhydrous HF.

An improved process is provided for the pyrohydrolysis of fluoridic spent and waste materials generated in electrolytic aluminum reduction system. More particularly, the process relates to the pyrohydrolysis of carbon-containing, fluoridic spent and waste materials in a fluidized bed reactor, wherein an extended reaction zone is provided in the reactor freeboard area by introduction of a relatively finely divided source of Al₂O₃ into this area, and by using a gas, containing at least about 90% by volume O₂, for the combustion of the carbon content and for the fluidization of the spent and waste material charge.

For the purposes of this invention "pyrohydrolysis" of the fluoridic spent and waste materials of electrolytic aluminum reduction systems refers to the following reactions:

\[
2NaF + H_2O \rightleftharpoons 2HF + Na_2O \tag{1}
\]

\[
2AlF_3 + 3H_2O \rightleftharpoons 6HF + Al_2O_3 \tag{2}
\]

\[
Na_2O + xAl_2O_3 \rightleftharpoons Na_2O_xAl_2O_3 \tag{3}
\]

These reactions take place at elevated temperatures, generally above about 900°C. The water required for pyrohydrolysis reactions (1) and (2) is usually introduced as liquid water, combined water or as steam to the fluidized bed or as a combination of these.

The expression "spent and waste materials of electrolytic aluminum reduction systems" encompass among others carbonaceous cell or pot linings which are recovered after their useful lives have expired. Typical composition aqueous medium.

6. Process according to claim 5, wherein
of such pot linings is shown in Table I.

### TABLE I

**TYPICAL COMPOSITION OF SPENT POT LININGS**

<table>
<thead>
<tr>
<th>Elements</th>
<th>% by Weight</th>
<th>Elements</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>16.1</td>
<td>Ca</td>
<td>1.4</td>
</tr>
<tr>
<td>F</td>
<td>10.5</td>
<td>Fe</td>
<td>0.8</td>
</tr>
<tr>
<td>Na</td>
<td>11.8</td>
<td>Si</td>
<td>0.7</td>
</tr>
<tr>
<td>Li</td>
<td>0.3</td>
<td>CN</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>32.1</td>
<td>O₂,CO₃,Cl, etc.</td>
<td>26.1</td>
</tr>
</tbody>
</table>

10 In addition to the spent cell linings, the charge to the fluidized bed reactor can also contain floor sweepings, trench and channel cleanings, as well as the spent alumina scavenger of reduction offgas scrubbing systems. Typical compositions of these spent and waste materials are shown in Tables II and III.

### TABLE II

**TYPICAL COMPOSITION OF COMBINATIONS OF CHANNEL AND TRENCH CLEANINGS WITH FLOOR SWEEPINGS**

<table>
<thead>
<tr>
<th>Element</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>32.0</td>
</tr>
<tr>
<td>F</td>
<td>25.5</td>
</tr>
<tr>
<td>Na</td>
<td>13.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1.0</td>
</tr>
<tr>
<td>Si</td>
<td>0.4</td>
</tr>
<tr>
<td>Others</td>
<td>Balance</td>
</tr>
</tbody>
</table>

These spent and waste materials are generally admixed prior to charging the materials into the fluidized bed reactor.

In the instant invention an "extended" reaction zone, such as fully described in copending application S.N. 910,416, filed May 30, 1978 (Andersen et al), is
board area of the fluidized bed reactor by introducing a relatively finely divided source of Al₂O₃ in the reactor. As shown in detail in the above-referenced application, the source of Al₂O₃ can be introduced into the reactor by adding it to the charge, or in the vicinity of the fluidized bed surface, or in a split stream or both. The size of the relatively finely divided source of Al₂O₃ is kept in the range of about 40-500 microns, this relatively small particle size allows elutriation or "lifting out" of the Al₂O₃ from the fluidized bed when admixed with the charge. It provides a reactive surface for reaction with the vaporized Na-containing constituents of the pyrohydrolysis offgas and also due to its small size, will be heated rapidly in or in the vicinity of the fluidized bed thus avoiding cooling of the extended reaction zone.

The purpose of the introduction of the relatively finely divided Al₂O₃ source in the freeboard area of the fluidized bed reactor is to react with the Na₂O formed in reaction (1) and thus shift the equilibrium in favor of the formation of HF, with simultaneous formation of Na₂OₓAl₂O₃ according to reaction (3). This provides for the generation of an essentially NaF-free offgas and increased HF yield.

In order for the pyrohydrolysis reaction to proceed rapidly and to a high degree of completion, it is necessary to meet a series of interrelated criteria. Favoring the reaction rate and the degree of completion of the pyrohydrolysis reaction are (1) elevated temperature (above about 900°C, generally in the range of about 900°C-
11300°C), (2) efficient gas to solids contact, (3) the length of time the reactants are in the reaction zone, (4) the removal of intermediate reaction products (such as the combination of Na₂O with Al₂O₃ in the form of Na₂OₓAl₂O₃), and (5) the maintenance of a high partial pressure of water vapor in the reaction zone. Copending application S.N. 855,506 employs a fluid reactor using air for combustion of the carbon in the criteria. Copending application S.N. 910,416, provides an improved means of extending the reaction zone residence time, bettering the gas to solids contact efficiency and significant reduction of the volatile sodium compounds in the offgases.

It has now been found that a further, significant improvement in the pyrohydrolysis process can be achieved by the use of a high oxygen content stream in place of air for combustion. This improvement of the process, in conjunction with the use of an HF scrubber for the removal of excess steam and combustion products and the utilization of the generated aqueous HF for the cooling of the offgas by direct contact, can generate, as will be discussed in detail hereinafter, a gas stream with an HF content sufficiently high to produce an AlF₃ product of at least about 85% by weight AlF₃ content.

The use of a stream containing at least about 90% by volume O₂, for combustion of the carbon content of the charge eliminates the diluent effect of the nitrogen associated with the common use of air for this purpose. In addition, the heat load required to bring the nitrogen content of the air to reaction temperature is eliminated, thus reducing the heat input required for maintaining reactor
temperature. Consequently, this use of a gas of high O\textsubscript{2} content also reduces the total combustion offgas volume and allows the partial pressure of water vapor be increased in the fluidized bed reactor. This enhances the pyrohydrolysis reaction, thus substantially increasing the HF concentration in the offgas and also permitting the pyrohydrolysis reaction to proceed at lower operating temperatures. In turn, the increase in offgas HF concentration results in increased fluidized bed reactor capacity which improves the operational efficiency of the entire pyrohydrolysis process.

The advantages obtained by the use of a fluidizing gas containing at least about 90\% by volume O\textsubscript{2} are manifold. Thus, for example, the hydrogen fluoride content of the offgas generated and removed from the pyrohydrolysis reactor, can be approximately 6-10\% by volume. This high HF content offgas, particularly if it is directly cooled with a liquid of about 25\% HF content such as is obtainable in the novel system of the invention and as is shown hereafter, allows preparation of an AlF\textsubscript{3} product of more than about 85\% by weight AlF\textsubscript{3} content. This product can be made by contacting the HF-containing gas with alumina trihydrate (Al\textsubscript{2}O\textsubscript{3}·3H\textsubscript{2}O) in a fluidized bed reactor. The utilization of alumina trihydrate in the production of AlF\textsubscript{3} not only produces the desired product, but it also generates steam which can be readily employed for the pyrohydrolysis of a fresh charge of spent pot lining. This additional feature of the invention results in significant energy savings since the steam requirement for pyrohydrolysis can be generated in the system without the necessity
The operation of the novel pyrohydrolysis system, using oxygen as the fluidizing and combustion medium, will be further explained with reference to the Figure.

As shown in the Figure, the spent pot lining charge is introduced into the pyrohydrolysis reactor where upon charging of oxygen (at least about 90% by volume O\textsubscript{2} content) and steam, combustion of the carbonaceous constituents, and generation of hydrogen fluoride containing offgas is achieved at temperatures in excess of about 900°C, usually within the range of about 900°C - 1300°C. In order to convert the volatilized Na-containing components of the offgas, a relatively finely divided source of Al\textsubscript{2}O\textsubscript{3} is introduced either in the fluidized bed, or in the "extended reaction zone" or into both places. The offgases generated by the combustion and pyrohydrolysis of the spent pot lining will contain besides HF, also steam and CO\textsubscript{2}, as well as entrained solids. Due to the use of O\textsubscript{2} for combustion, the diluting effect of nitrogen is minimized and the HF-content of the offgas will be about 6-12% by volume. After removal of the entrained solids the offgas is cooled. In an advantageous embodiment of the invention the hot gases exiting from the reactor can be cooled directly with a cold stream of HF-containing gas, such as shown by the dotted lines in the Figure. Since this is a recycle stream and there is no heat removal from the system, the quantity of cooling gas used affects the intermediate concentration of HF, but has no effect on the HF concentration in the product gases. Subsequent cooling in a direct contact cooler, such as also shown in the Figure, with a highly concentrated HF
gas scrubber, can increase the concentration of the gas, for example up to about 13-16% by volume. The cooled HF-containing stream is then introduced into a scrubbing unit where water is employed as a scrubbing medium. The scrubber offgas will be free of HF and will contain mainly water vapor and CO₂. The aqueous HF stream recovered from the scrubber will have an HF content of about 25% by weight. A portion of the steam discharged from the scrubber unit may be recycled to the pyrohydrolysis unit as shown.

The aqueous HF recovered from the scrubber unit can be employed for making anhydrous HF in addition to, as shown in the Figure, for the direct cooling of the HF-containing offgas stream. The higher than usual HF-content of the aqueous stream allows its ready conversion to anhydrous HF by conventional means. When the aqueous stream is used primarily for direct cooling of hot offgas, a gaseous product which has an increased HF content is obtained, for example about 13-16% volume.

This stream, containing about 13-16% by volume of HF, is utilized if desired for the production of AlF₃. While the prior art generally avoided the use of alumina trihydrate for the manufacture of AlF₃, the instant process prefers the use of this starting material. In the prior art processes the water content of the hydrate would have posed problems since the heat of reaction generated by the low HF content of the gas stream is insufficient to vaporize the water content of the hydrate and to maintain the required temperature of the gaseous and solid reactants.

In the present process the by-product steam of
the AlF₃ production is also utilized. The steam discharged from the AlF₃ fluid bed reactor is used to provide a major portion of the steam requirement for the pyrohydrolysis reaction, thus providing a favorable heat and energy balance, surpassing the effectiveness of prior art systems. Use of the offgas from the AlF₃ fluidized bed reactor as the source of steam for the pyrohydrolysis reactor recycles trace quantities of unreacted HF. This increased the overall HF recovery and eliminates a possible environmental problem. In addition, the aluminum hydrate starting material is less costly than calcined alumina; also the AlF₃ product, due to its high, more than about 85% by weight, AlF₃ content, is an economically more valuable product than the prior art AlF₃ products of about 15% AlF₃ content.

Thus, it can be observed from the system shown that by using a fluidizing and combustion promoting gas of at least about 90% O₂ content, the entire pot lining recovery process can be made more efficient both from a technical and an economical point of view.

The following example will provide further insight in the operation of the novel system.

Spent pot lining, having a composition shown in Table III was mixed with miscellaneous spent and waste materials from the electrolytic aluminum reduction system. These materials included floor sweepings and channel cleanings and the composition of the combined charge is shown in Table IV.
TABLE III
COMPOSITION OF SPENT POT LINING

<table>
<thead>
<tr>
<th>Elements</th>
<th>% by Weight</th>
<th>Elements</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>14.8</td>
<td>Ca</td>
<td>1.3</td>
</tr>
<tr>
<td>F</td>
<td>13.8</td>
<td>Fe</td>
<td>0.7</td>
</tr>
<tr>
<td>Na</td>
<td>15.5</td>
<td>Si</td>
<td>0.7</td>
</tr>
<tr>
<td>Li</td>
<td>0.5</td>
<td>CN</td>
<td>0.3</td>
</tr>
<tr>
<td>C</td>
<td>29.6</td>
<td>O₂, CO₃, Cl, etc.</td>
<td>22.8</td>
</tr>
</tbody>
</table>

TABLE IV
COMPOSITION OF FEED TO PYROHYDROLYSIS UNIT

<table>
<thead>
<tr>
<th>Elements</th>
<th>% by Weight</th>
<th>Elements</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>19.0</td>
<td>Ca</td>
<td>1.2</td>
</tr>
<tr>
<td>F</td>
<td>16.2</td>
<td>Fe</td>
<td>0.6</td>
</tr>
<tr>
<td>Na</td>
<td>14.8</td>
<td>Si</td>
<td>0.6</td>
</tr>
<tr>
<td>Li</td>
<td>0.3</td>
<td>CN</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>24.2</td>
<td>O₂, CO₃, Cl, etc.</td>
<td>22.9</td>
</tr>
</tbody>
</table>

The pyrohydrolysis reactor, operating at about 1200°C was charged with the feed at the rate of 4.61 t/h. In addition, a relatively finely divided source of Al₂O₃, containing 86.4% by weight Al₂O₃ (as determined after heating to 1000°C for about three hours) was also added to the reactor at the rate of about 0.30 t/h. The particle size of the Al₂O₃ source was in the range of about 200 to 400 microns.

A fluidizing and combustion supporting gas, containing about 95% by volume O₂ was charged to the reactor at the rate of about 2440 m³/h together with steam which was introduced at the rate of about 14,400 m³/h. The offgas generated by the pyrohydrolysis was conducted
A portion of the steam effluent from the scrubber
was introduced into the pyrohydrolysis reactor.

The dust-free offgas stream of about 14% by volume HF content which was divided out of the main stream going into the scrubber was preheated to about 425°C in the superheater by indirect contact with incoming offgas from the reactor, then it was used to make AlF₃ product in a fluidized bed unit consisting of at least one and preferably of three series connected fluidized beds. The fluidized bed reactor was operated at about 550°C and Al₂O₃·3H₂O was charged to the reactor at the rate of about 1.20 t/h to provide for the above-mentioned production rate. The steam discharged from the reactor, after removal of entrained solids, was utilized for the pyrohydrolysis of the spent pot lining while the produced AlF₃ of about 85-90% by weight AlF₃ content was employed in the electrolytic aluminum reduction system as electrolyte.

The AlF₃ production unit does not have to operate continuously during the entire pyrohydrolysis process and production of AlF₃ can be made optional. If the AlF₃ production unit is operating at a reduced rate or does not operate, more, or all of the HF-containing offgas can be utilized for the generation of highly concentrated aqueous anhydrous HF. Thus, the instant system provides a highly desirable operating flexibility.

While there have been shown and described herein-above possible embodiments of the invention, it is to be understood that the invention is not limited thereto and that various changes, alterations and modifications can be made thereto without departing from the spirit and scope thereof as defined in the appended claims.
In the process of recovering valuable components from carbon and fluoride-containing aluminous spent and waste materials generated in electrolytic aluminum reduction systems by subjecting the spent and waste materials to pyrohydrolysis in the presence of steam in a fluidized bed reactor having a fluidized bed and a freeboard area above the bed at a temperature within the range of about 900°C to about 1300°C, the improvement comprising the combination of steps of

(a) combusting the carbon content of the spent and waste materials in the fluidized bed with an O₂-containing stream having an O₂ content of at least about 90% by volume thus generating a hot offgas substantially free of nitrogen and containing HF and vaporized Na-containing compounds;

(b) establishing an extended reaction zone in the freeboard area of the reactor by contacting the hot offgas with a relatively finely divided source of Al₂O₃ having a particle size within the range of about 40 to about 500 microns whereby the Na-containing vapors are converted to HF and Na₂OₓAl₂O₃;

(c) cooling the hot, HF-containing offgas by direct contact with an aqueous HF-containing stream and conducting the cooled offgas to a scrubber for the removal of its HF content by scrubbing with an aqueous medium, while generating a steam and inert gas containing scrubbed offgas;
(d) recovering the aqueous HF from the scrubber and using at least a portion thereof for cooling hot HF-containing offgas generated in the fluidized bed reactor;

(e) recovering an HF-containing side stream from the cooled HF-containing offgas prior to scrubbing of the offgas with the aqueous medium and employing the HF-containing side stream for the production of an AlF₃ product of at least about 85% by weight AlF₃ content in a fluidized bed reactor using as alumina source alumina trihydrate; and

(f) recovering the AlF₃ product and steam from the AlF₃ reactor and recycling the steam to the pyrohydrolysis reactor.

2. Process according to claim 1, wherein the temperature in the fluidized bed reactor is kept within the limits of about 1000°C and about 1200°C.

3. Process of claim 1, wherein at least a portion of the aqueous HF-containing stream is used for making anhydrous HF.

4. Process according to claim 1, wherein all of the aqueous HF stream recovered from the scrubber is employed for cooling hot HF-containing offgas by direct contact.

5. Process according to claim 1, wherein the HF content of the hot offgas generated in the pyrohydrolysis reactor is about 6-10% by volume and after direct cooling with the aqueous HF-containing stream from the scrubber the HF content of the offgas increases up to about 13-16% by volume and this gas is subjected to scrubbing with an
6. Process according to claim 5, wherein scrubbing of the offgas with an aqueous medium generates an aqueous HF containing up to about 25% by weight HF.

7. Process according to claim 1, wherein the HF-containing side stream, used for the production of an AlF₃ product of at least 85% by weight AlF₃ content in a fluidized bed reactor, is preheated to the temperature required for production of AlF₃ by heat exchange through indirect contact with the hot offgas generated in the fluidized bed reactor.

DATED THIS 11th DAY OF APRIL, 1979
KAISER ALUMINUM & CHEMICAL CORPORATION

EDWD WATERS & SONS
PATENT ATTORNEYS
50 QUEEN STREET
MELBOURNE
AUSTRALIA