

P. A. EMANUEL.

PROCESS OF MAKING ALUMINUM FLUORID AND OTHER ALUMINUM COMPOUNDS.

APPLICATION FILED MAY 29, 1909.

957,754.

Patented May 10, 1910.

2 SHEETS—SHEET 1.

Fig. 1.

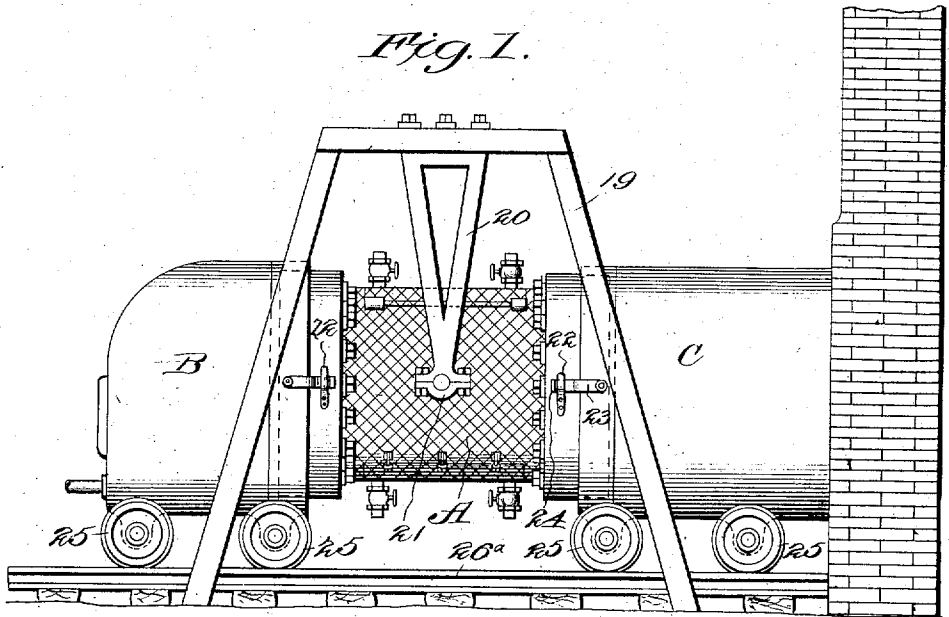
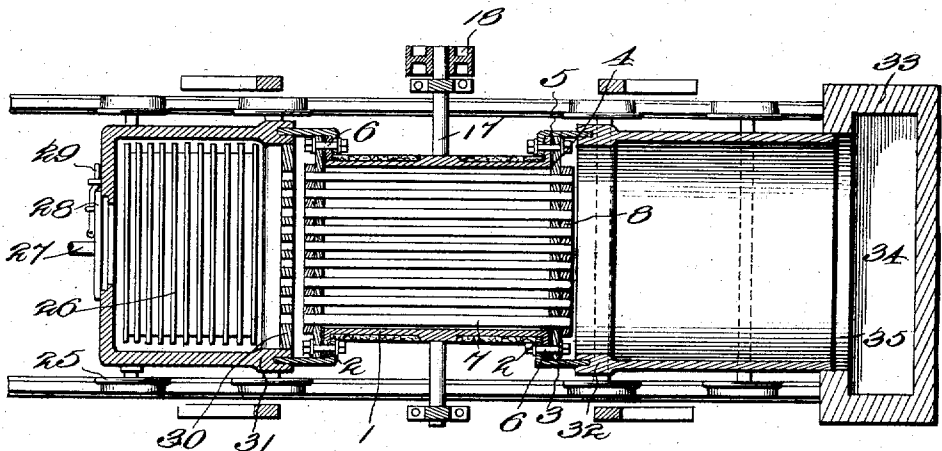


Fig. 2.



Witnesses
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2 SHEETS—SHEET 2.

Fig. 3.

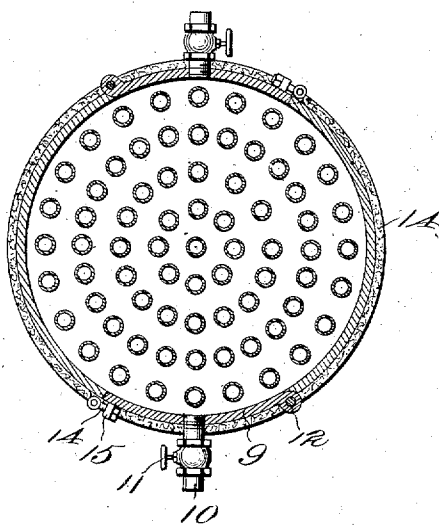


Fig. 5.

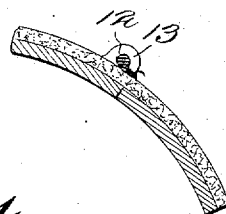
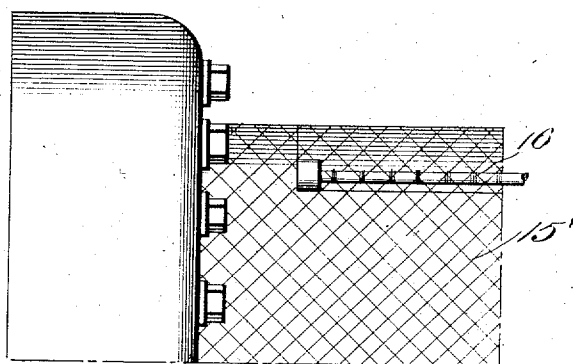


Fig. 4.



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PHILIP A. EMANUEL, OF AIKEN, SOUTH CAROLINA.

PROCESS OF MAKING ALUMINUM FLUORID AND OTHER ALUMINUM COMPOUNDS.

957,754.

Specification of Letters Patent.

Patented May 10, 1910.

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To all whom it may concern:

Be it known that I, PHILIP A. EMANUEL, a citizen of the United States, residing at Aiken, in the county of Aiken and State of South Carolina, have invented certain new and useful Improvements in the Process of Making Aluminum Fluorid and other Aluminum Compounds; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

My invention relates to the process of making aluminum fluorid and other aluminum compounds, and is designed to treat ordinary clays in such a manner as to save all their valuable constituents and at the same time make use of the by-products. It is also applicable to the treatment of bauxite and corundum for the making of soda, a double sulfate of soda and aluminum, silica, aluminum fluorid, sodium sulfate, metallic sodium, and aluminate of soda.

I carry out my process by an apparatus a part of which is shown in the accompanying drawings, and in which—

Figure 1 is a side elevation showing an apparatus for carrying out the process constituting my invention. Fig. 2 is a horizontal cross section thereof. Fig. 3 is a cross section through the retort. Fig. 4 is a side elevation on a larger scale, showing part of the retort and part of the furnace, and Fig. 5 is a partial section showing part of the retort and the manner of securing the wire netting thereon.

Referring to the drawings, A represents the retort, B the furnace portion, and C the portion connecting the retort with the smoke stack.

The retort is composed of a cylindrical body portion 1, having at each end an extended portion 2, forming a ridge on which the portion 3 is bolted. The part 3 is cylindrical, and open at both ends, but having one end bent inwardly to embrace the portion 2, both ends of the retort being exactly similar.

4 represents a perforated plate fitting tightly against the end of the retort, a suitable packing 5 of asbestos or similar material being used if desired. Bolts 6 pass through the bent-in end of the part 3 through the part 2 and through the plate 4, uniting the whole firmly together.

7 represent tubes which pass through the

end plates 4, the ends of which are secured in perforations in the plate 8, secured to the plate 4.

At the top and bottom the retort is provided with curved doors 9, hinged thereto, and with two pipes 10, each provided with a cock, such as 11, screwed into the cover. Each of the doors is mounted on a rod 12, in ears 13, projecting from the body of the retort, and on the retort are mounted swinging bolts 14, adapted to swing down behind projections 15 on the cover, thus firmly locking the covers in position. Any desired means, however, may be adopted for fastening the covers to the retort. The top and bottom covers are precisely similar.

14 represents a layer of asbestos, or similar refractory material, placed over the outer side of the retort, including the covers, and held in place by the wire netting 15, the ends of said netting opposite the cover portion being secured to the rods 12 by having the ends of the wires wrapped around it, as shown at 16.

The retort is thickened at the center, and from these thickened portions run shafts 17, one of which is provided with a pulley 18, to which power may be applied to rotate the retort, as hereinafter described. Ordinarily, the retort is suspended from a triangular frame 19, by means of depending supports 20 therefrom, terminating in bearings 21, engaging the rods 17. When it is desired to move the retort, the lower half of each bearing is removed.

To hold the parts A, B and C firmly bound together, in case the bearings 20 are moved, I provide two stout upwardly-extending brackets 22, a little below the center of the outside of the parts 3. These brackets are firmly fastened to the parts 3 by being bolted thereto, or made integral therewith, and have their upper parts bent outwardly for engagement with the latches hereinafter mentioned. With each of the brackets 22 a pivoted latch is adapted to engage, two of these latches being pivotally mounted on the part B, and two on the part C. Each latch 23 has its end thickened, as shown at 24, to pass down around the corresponding bracket 22, so that when the latches are in the position shown in Fig. 1, the parts A, B and C are prevented from longitudinal movement, except as a whole, being firmly locked together, with the ends of the parts 3 fitting into corresponding grooves in the

parts B and C. To the parts B and C are attached wheels 25, in the usual manner, which are adapted to run on tracks 26, so that the whole apparatus, consisting of the parts A, B and C may be moved as a whole from one part of the plant to another, the latches being in the position shown in Fig. 1, or whereby when the latches 23 are thrown up, the parts B and C may be separated from the retort A, whereupon the latter may be rotated by means of power applied to the pulley 18 for a purpose hereinafter described. The part B is the furnace portion, and is provided with a grate 26, pipe 27 for the admission of gaseous or liquid fuel, and door 28, provided with a latch 29. Of course, any desired form of fuel could be used in the part B.

The rear end of the part B is closed by a perforated plate 30, the perforations being located opposite the tubes 7 in the retort A. Around this perforated plate, the rear open end of the part B is thickened, as shown at 31, and is provided with a circular groove, into which groove the part 3 carried by the retort is adapted to fit.

The part C simply serves to carry the waste products of combustion after they have passed through the tubes 7 of the retort into the chimney. It consists of a flue, preferably cylindrical in form, having one end thickened, as shown at 32, said thickened end having a groove therein for the reception of the part 3 on one end of the retort A. 33 represents a chimney, and 34 the flue thereof.

35 represents a cylindrical opening, into which the open end of the part C is adapted to telescope. This arrangement is adapted so that the parts B and C may be moved along the track out of engagement with the retort A, leaving the latter free to rotate.

The operation is as follows:—The apparatus being in the position shown in Fig. 1, if it is desired to make gas, coke, and gas retort carbon, for example, the upper door of the retort is opened, and a suitable charge of soft coal introduced into the interior of said retort into the space between the pipes 7. The upper door is then firmly closed, and connections made between the discharge pipes 10 at the top of the retort leading to the gasometer, or to any place where gas is to be used. A fire is then started in the furnace B, and the hot products of combustion pass through the tubes 7, distilling the coal in the retort A, the gases passing out through the discharge pipes 10. After this operation has been continued for a sufficient time to distil about half of the coal, the latches 23 are disengaged from the brackets 22, and the parts B and C moved along the track 26 out of contact with the retort A. All the cocks in the pipes 10 being closed, the upper pipes are disconnected from the pipes leading to

the gasometer, and by means of power applied to the pulley 18, the retort is rotated 180°. The parts B and C are then brought back into connection with the retort A, and the latches 23 moved down into the position shown in Fig. 1. The pipes at the top of the retort are then connected to the gas delivery pipes, and the cocks therein opened. The distillation process is then carried on to its close, and at the end the upper pipes are disconnected from the gas delivery pipes, and both the upper and lower doors are opened. By means of iron rods, the coke between the pipe 7 is forced down, out through the lower door, leaving the pipes 7, and in fact the whole interior of the retort, coated with an even layer of gas carbon.

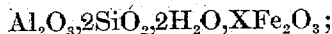
The fact that the whole interior of the retort, including the pipes, is coated with an even layer of gas carbon, makes the retort highly useful in the production of soda, for example, in which it is necessary that the substances under treatment should be subjected to the action of carbon under heat, and in which it is desirable that the retort should be frequently rotated. These retorts may be used either with or without carbon and are arranged in sets so that they can be moved from one part of the plant to another.

For some of the reactions hereinafter mentioned, it is necessary to have a certain amount of carbon in the retort and for other reactions there must be no carbon. To obtain this carbon, I charge the retort with soft coal and heat the same, up to the distillation point, by burning gas, coke, coal, or any desired kind of fuel in the furnace B. As the retort A becomes heated up, the gases from the fuel pass out of the upper pipes 10 in the usual manner, the cocks 11 being open, which gases are collected and either used to run another retort or stored for future consumption.

As described in the description of the apparatus, the retort is revolved 180° one or more times during the distillation process, so that the deposit of gas carbon within the retort on the tubes and walls thereof may be substantially uniform. There is left in the retort coke and a deposit of gas carbon. The former may be removed by opening the top and bottom doors 9 of the retort and pushing out the coke from between the horizontal flues 7, leaving the deposit of gas carbon on the tubes and on the inside of the end plates and on the walls of the retort. This retort may be then used where it stands or conveyed away to another portion of the plant by latching the three parts A, B and C together and releasing the bearing around the rods or shafts 17.

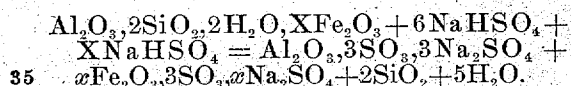
The South Carolina clays, which my process is primarily designed to treat (although it is by no means restricted to the

treatment of these clays) consist of the following parts chemically combined—



that is to say, one molecule of oxid of alumina, two molecules of silica, two molecules of water, and 1 to 3 per cent. of ferrous or ferric oxids or both, approximately stated.

After determining the amount of alumina in the clay, I mix with one part of clay six times the amount of bi-sulfate of sodium, as compared with the alumina in the clay, basing the weights used upon the atomic weights of the alumina and the bi-sulfate of sodium, so that the latter salt may furnish enough sulfuric acid to give up 3 molecules of said acid to the alumina. In place of clay, I may, of course, use other ores of alumina, such as bauxite or corundum. The quantity of bi-sulfate of sodium used should, of course, be sufficient to furnish whatever iron is present with a sufficient amount of sulfuric acid, as well as the alumina, based upon the molecular weights of the oxids of iron and the bi-sulfate of sodium. This mixture is then heated in one of my retorts, producing a double sulfate of aluminum and sodium represented by the formula $\text{Al}_2(\text{SO}_4)_3, 3\text{Na}_2\text{SO}_4$, ferric alum, sulfate of soda, and free silica, according to the following reaction:—

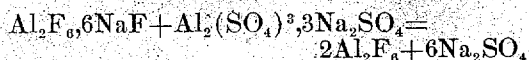


It should be mentioned that the retort should only be charged so that it is about two-thirds full and before heating the retort it is separated from the furnace B and chimney connecting portion C and revolved, thus thoroughly mixing the materials together. Then the three parts A, B and C are reunited, as shown in Fig. 1, and the retort is heated by the furnace B. Sulfuric acid is set free from the bi-sulfate of sodium and attacks the clay, the mass becomes of a dark blue color and boils rapidly, and there is a rapid evolution of steam. Ferric alum is formed and also a new compound consisting of a double sulfate of aluminum and sodium, but having 3 molecules of sulfate of soda combined with 1 molecule of sulfate of aluminum. During the same reaction silica is also formed in an anhydrous condition, and when the reaction is ended, the mass assumes a dirty yellowish white color. As soon as the reaction is ended, the lower bearings of the retort A are removed and the whole apparatus being then free to move is rolled off the track to another portion of the plant. The upper and lower pipes in the retort are then opened and steam or hot water is passed in through the pipes at the top and is discharged through the pipes at the bottom, carrying out with it

the contents of the retort. The double sulfates are dissolved out of the fused mass, leaving the silica in an insoluble form. The mass of material obtained by washing out the retorts is then filtered, separating the silica, which is washed again, if necessary, and is then in a fine white condition, admirably suited for making glass and other purposes for which silica is commonly used.

If clay is fused with acid sodium sulfate, NaHSO_4 , the iron in solution is precipitated with sodium prussiate. The precipitated ferric prussiate is treated with caustic soda, and the prussiate of sodium recovered to be used over and over again.

It will be noted that by my process the sulfate of alumina is united chemically with 3 molecules of sulfate of soda instead of with 1 molecule, as in ordinary alum, and by making use of this new double sulfate, I have devised an improved soda process. This double sulfate is fused in one of my retorts with cryolite in the proportions indicated by the following reaction, no carbon being present in the retorts:

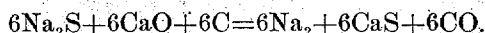


Fluorid of aluminum is produced, which is insoluble. Sulfate of soda is also produced, which is soluble. The mixture is allowed to partially cool and while still hot is lixiviated and the fluorid of aluminum separated from the solution of the sulfate of soda by filtration. The fluorid of aluminum, after being allowed to dry, is heated to about redness and showered down upon melted metallic sodium, whereupon the following reaction takes place:



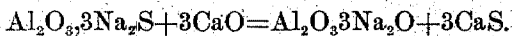
This reaction results in the production of metallic aluminum and cryolite. At the same time a slag is formed which may be used to fuse with the product obtained from clays after fusing them with bi-sulfate of sodium, as mentioned above.

I obtain metallic sodium as follows: The sulfate of soda already obtained is placed in one of the retorts A, which has been lined with gas carbon, as previously described. Coke, finely pulverized, may then be added, if necessary, and the retort is then heated, whereupon sulfid of soda is produced, there still being an excess of carbon left in the retort. Caustic lime is then added and the retort heated to about 800°C ., when metallic sodium commences to distil over and is condensed in the usual manner, the reaction being as follows:



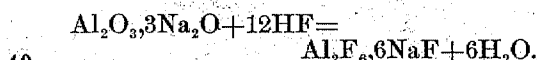
In other words, I produce metallic sodium indirectly from the sulfate of sodium or directly from the sulfid. I use lime to take

the sulfur from the sodium, forming sodium
oxid, which is immediately reduced to metal-
lic sodium by the carbon present in the re-
tort. I also manufacture aluminate of soda,
5 $\text{Al}_2\text{O}_3, 3\text{Na}_2\text{O}$, in a similar manner; that is,
I place the double sulfate of soda and alu-
mina already obtained in one of my carbon
lined retorts, and heat it until the sulfate
of alumina is decomposed, forming the oxid.
10 Sulfurous acid gas is driven off, passes over
carbon monoxid and dioxid into a discharge
pipe, which leads into a sulfuric acid cham-
ber, where the usual treatment for making
sulfuric acid takes place. There is left in
15 the retort alumina either mixed or chemi-
cally combined with 3 molecules of sulfid of
sodium, $\text{Al}_2\text{O}_3, 3\text{Na}_2\text{S}$. I then add caustic
lime in sufficient quantities to take up the
sulfur, whereupon the following reaction
20 takes place:



The aluminate of soda thus produced is
soluble while the sulfid of calcium is insol-
25 ble. The mass is allowed to cool and treat-
ed with water, whereupon the aluminate of
soda dissolves and the sulfid of calcium can
be separated from the solution by filtration
or decantation.

30 Artificial cryolite can also be made from
the aluminate of soda so obtained by treat-
ing fluorid of calcium (fluorspar) in a lead
tank with sulfuric acid, whereupon hydro-
fluoric acid is formed, in the usual manner,
35 which acid is led into a solution of alumi-
nate of soda through a lead pipe. The fol-
lowing reaction takes place:



The hydro-fluoric acid is rapidly con-
densed and artificial cryolite is precipitated.

Carbonate of soda may also be produced
as follows: Carbonate of lime is heated in
45 one of my retorts and the carbonic acid pro-
duced is led away and stored up for use.
Aluminate of soda in solution is then treated
with this gas, whereupon the hydrate of
alumina is precipitated, while carbonate of
50 soda remains in solution. Whenever car-
bonates or caustic alkalies are heated at a
red heat, the difficulty has been to keep the
carbon, which is lighter than the material
treated, always in contact with the entire
55 mass of the melted material.

In my retort, the gas carbon is fixed
around the flues and outer portion of the
retort and held there immovably, according
to the reactions already set forth. Accord-
60 ing to my method, a new double sulfate
of alumina and soda, ferric alum, and free
silica may be produced, as well as fluorid
of aluminum, sulfate of soda, metallic alumi-

num, artificial cryolite, metallic sodium,
aluminate of soda, besides various others. 65

In a complete plant I design to use one
series or battery of my retorts without dis-
tilling coal in them at all, and in another
series, where it is desirable to use a carbon
lined retort, coal is distilled, forming gas 70
and a fresh lining of graphite or fresh car-
bon at every distillation, taking care in
every distilling operation to tip the retort
over, so that the bottom door is on the top
and vice versa. The retort is preferably 75
suspended from above by hanging supports,
the bottom half bearings being lifted up to
the shaft by bolts and screws, as shown in
the drawing. The retort is detachably fixed
to the furnace and chimney connecting por- 80
tions by means of cylindrical projections
fitting into circular grooves, and these with
the latches support the retort A when it is
released from its bearings, so that the whole
structure, consisting of the three parts A, B 85
and C may be rolled away to another part
of the plant.

I claim:—

1. In the herein described process of treat-
ing ores containing alumina, silica and iron, 90
the step which consists in heating them in
a closed retort with an excess of bi-sulfate of
soda, producing thereby a double sulfate of
alumina and soda, containing three mole-
cules of sulfate of soda to one molecule of 95
sulfate of alumina, a ferric alum and free
silica, substantially as described.

2. In the herein described process, the step
which consists in heating clays in a closed
retort with an excess of bi-sulfate of soda, 100
producing a double sulfate of soda and
alumina, having three molecules of sulfate
of soda to one molecule of sulfate of
alumina, and free silica, and separating said
double sulfate from said silica, substantially 105
as described.

3. The herein described process of making
aluminum fluorid, which consists in heating
clay in a closed retort with an excess of bi-
sulfate of soda, forming a double sulfate of 110
alumina and soda, having three molecules of
sulfate of soda to one molecule of sulfate of
alumina, separating out said double sulfate,
heating it in a carbon-lined retort, heating
the resulting product with lime, dissolving 115
out aluminate of soda from the product and
leading into the solution thus formed a
stream of hydrofluoric acid gas, substan-
tially as described.

In testimony whereof, I affix my signa- 120
ture, in presence of two witnesses.

PHILIP A. EMANUEL.

Witnesses:

S. SUBOSKY,

J. P. McNAIR.