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PROCESS FOR PRODUCING A SODIUM FLUOALUMINATE COMPOSITION HAVING PREDETERMINED NaF/AlF_3 RATIO

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The present invention relates to a process for the preparation of sodium fluoaluminates having a NaF/AlF_3 molar ratio fixed at a value between 2.65 and 1.67.

By the term "sodium fluoaluminates" it is intended to denote, in the present description, those compounds in which the fluorine, aluminum and sodium are chemically bound to one another, that is, in each molecule of which, are always present all three of the elements, as occurs, for example with the known cryolite and chiolite compounds.

In order to characterize hereinafter such compounds, for the sake of simplicity, the NaF/AlF_3 molar ratio, will be adopted, even if said ratio is not in any way related to the actual structure of the molecules.

During long operation periods of a furnace for aluminum electrolysis, the NaF/AlF_3 ratio in the bath tends to vary due to losses deriving from decomposition and volatilization of the various constituents of the bath, losses which are normally higher for the aluminum fluoride than for the sodium fluoride, whereby the NaF/AlF_3 molar ratio in the electrolysis baths is evidences an increase, and is therefore re-established and maintained at the value required by the practice of each plant, by means of periodic additions of aluminum fluoride, in addition to cryolite.

The drawbacks derived from the necessity of adding free aluminum fluoride to the baths are many and commonly known; they are in relation to the different melting point and the different solubility in the baths of the aluminum fluoride and cryolite, and to its high volatility and easy decomposition. In addition the relatively low titer of the products mainly on the market (in which often the AlF_3 content does not reach 90%), the considerable moisture content of these products, and the inconvenience of the operation itself are also disadvantages.

An object of the present invention is to provide a process for the preparation of a sodium fluoaluminate having a definite NaF/AlF_3 molar ratio fixed at a value comprised in the range between 2.65 and 1.67, that is, in other words, wherein the percentage of AlF_3 is higher than that of the normal types of natural and synthetic cryolites. For clarity of explanation it is stated that these new fluoaluminates have a pre-established excess of aluminum fluoride varying from about 5.3 to 35% with respect to the standard reference formula Na_3AlF_6 depending on the type of the desired fluoaluminate, but wherein the aluminum fluoride is not free nor in mechanical mixture, but is all chemically combined with the sodium fluoride in the fluoaluminate molecule; within this molecule the aluminum fluoride thus acquires the heat stability, solubility and other well known properties, positive as far as the electrolysis of a chemically bound substance is concerned.

Said fluoaluminates may thus be advantageously used in the aluminum industry for a more regular operation of the electrolysis baths instead of the usual cryolite and aluminum fluoride, because, by means of their use, the drawbacks already mentioned, deriving from the separate use of cryolite and free aluminum fluoride, are completely or partially eliminated, as are particularly the

drawbacks deriving from the ready decomposition of the aluminum fluoride by the heat, a fact which always leads to considerable losses, and the considerable difference between the solubilities and the melting point of the aluminum fluoride and the solubility and melting point of the cryolite.

Numerous processes have been heretofore proposed and adopted for the preparation of synthetic cryolite; the difficulties of obtaining a product having a high NaF/AlF_3 molar ratio that is close to 3, and therefore proximal to the molar ratio of the natural cryolite, are well known above all when the preparation of synthetic cryolite occurs in the presence of free acid. It is also known that the synthetic cryolite, tends during preparation, to degenerate toward the formation of compounds which have in fact a lower NaF/AlF_3 ratio; this is due to the presence of free aluminum fluoride whose quantity, furthermore is not controllable, and varies within very wide ranges depending upon a great number of factors, such as the temperature and concentration of the various components of the solution from which the product is being precipitated, in relation to the complicated phase diagram of aluminum fluoride and the different crystalline forms under which the aluminum fluoride may precipitate; precipitation of free aluminum fluoride, i.e. that which is not bound to the sodium fluoride, gives rise as a direct consequence, to a considerable decrease of the reaction yields, precisely in relation to the sodium fluoride not bound which remains in solution and is then eliminated with the mother liquors. Furthermore, during drying and calcination of the product, the water which crystallizes with aluminum fluoride at the rate of from 3 to 9 moles for one mole of AlF_3, causes an hydrolysis of the products with a consequent loss of hydrofluoric acid, loss which is the higher the greater is the quantity of unbound aluminum fluoride in the product.

Cryolite Na_3AlF_6 is prepared by reacting, for example, a sodium salt solution with a fluoaluminic acid solution in a small volume, mixing intimately together the two solutions then removing the slurry containing the cryolite precipitate just formed and finally maintaining the product obtained, under agitation for at least one hour to effect a digestion. The synthetic cryolite thus obtained has a NaF/AlF_3 molar ratio equal to about 3 and physical characteristics (e.g. heat stability) very close to those of natural cryolite, and in addition the precipitation yields are high even if chloride is used as sodium salt, that is, even if the cryolite is precipitated in an atmosphere containing at the free state the hydrochloric acid, which, as known, is formed by the reaction between sodium chloride and fluoaluminic acid; the fluoaluminic acid solution, prepared for example by dissolving aluminum oxide or hydrate in hydrofluoric acid, has an HF/AlF_3 molar ratio equal to 3, that is, not lower than the NaF/AlF_3 molar ratio which it is desired to obtain in the synthetic cryolite.

According to the inventive process, the reaction is carried out with the above-mentioned modalities, between a sodium salt solution, for instance chloride, and a solution containing hydrofluoric acid and aluminum fluoride, said solution having however an HF/AlF_3 molar ratio lower than 2.65, more precisely, fixed to one of the values comprised between 2.65 and 1.67, having thus a predetermined excess of AlF_3 with respect to the quantity which corresponds to the fluoaluminic acid formula (H_3AlF_6). It has been found that, by carrying out the reaction between the two solutions it is possible to avoid the presence of aluminum fluoride in the obtained precipitate, by blocking the Na-Al-F-compound in the initial ratio preestablished as desired, though the precipitate is constituted of a sodium fluoaluminate having an NaF/AlF_3 molar

ratio lower than that of cryolite, that is lower than 3, or approximately equal to an HF/AlF_3 molar ratio which was in the aluminum fluoride and hydrofluoric acid solution used for the precipitation. As already said, and as illustrated in the following examples, in the obtained precipitate free aluminum fluoride is not present. Instead, in said precipitate two components coexist: one having the formula Na_3AlF_6 (cryolite) and the other having the formula $Na_5Al_3F_4$ (chiolite), in different proportions depending on the pre-established ratio. The same result is attained by carrying out the reaction still with the same reaction and conditioning modalities, between an aluminum fluoride and hydrofluoride acid solution having an HF/AlF_3 molar ratio even higher than NaF/AlF_3 molar ratio which it is desired to obtain in the product, and a sodium salt solution, always added, however, in a quantity such that Na^+/AlF_3 molar ratio is equal, and in any case not higher than NaF/AlF_3 molar ratio which it is desired to obtain in the product. Similarly, it is possible to operate by reacting a solution containing aluminum and sodium with a solution containing fluorine, or a solution containing sodium and fluorine with a solution containing aluminum, always complying, however, with the fact that Na^+/Al^{+++} molar ratio should never be higher than NaF/AlF_3 molar ratio which it is desired to obtain in the product, and that the quantity of F must be at least stoichiometrically equal and not lower than the sum of Na^+ and Al^{+++} used.

Example 1

100 kgs. of a solution containing 10 kgs. of HF and 15.85 kgs. of AlF_3, in which HF/AlF_3 molar ratio is equal to 2.65, are reacted with a sodium chloride solution comprising 25% NaCl.

The slurry obtained is conditioned for 1 hour at the temperature of 50° C. 36.85 kgs. of sodium fluoaluminate are collected. The chemical analysis carried out on said fluoaluminate has given the following results:

	Percent
NaF	57
AlF_3	43

NaF/AlF_3 molar ratio of the product obtained is therefore 2.65 (NaF/AlF_3 weight ratio=1.325) whereby this compound corresponds to a cryolite with 5.3% of AlF_3 in excess with respect to the standard formula of comparison Na_3AlF_6. A roentgenographic analysis carried out on the product has given the following results:

	Percent
Cryolite	79.3
Chiolite	20.7

Example 2

250 kgs. of a solution containing 25 kgs. of HF and 39.6 kgs. of AlF_3, in which the HF/AlF_3 molar ratio is equal to 2.4 are reacted with a sodium chloride solution comprising 25% NaCl.

The slurry obtained is conditioned for 1 hour and 30 minutes at the temperature of 52° C. 92.1 kgs. of fluoaluminate are collected. The chemical analysis carried out on said fluoaluminate has given the following results:

	Percent
NaF	54.5
AlF_3	45.5

The NaF/AlF_3 molar ratio of the product obtained is therefore 2.4 (NaF/AlF_3 weight ratio=1.2) so that this compound corresponds to a cryolite with the 10.2% of AlF_3 in excess with respect to standard formula of comparison Na_3AlF_6.

A roentgenographic analysis carried out on the product has given the following result:

	Percent
Cryolite	62.1
Chiolite	37.9

Example 3

200 kgs. of a solution containing 20 kgs. of HF and 38.2 kgs. of AlF_3 in which the HF/AlF_3 molar ratio is equal to 2.2, are reacted with a sodium chloride solution comprising 25% NaCl.

The slurry obtained is conditioned for 2 hours at the temperature of 51° C. 80.2 kgs. of fluoaluminate are collected. The chemical analysis carried out on said fluoaluminate has given the following results:

	Percent
NaF	52.4
AlF_3	47.6

The NaF/AlF_3 molar ratio of the product obtained is therefore 2.2 (NaF/AlF_3 weight ratio=1.1), so that this compound corresponds to a cryolite with 14.6% of AlF_3 in excess with respect to the standard formula of comparison Na_3AlF_6. A roentgenographic analysis carried out on the product has given the following results:

	Percent
Cryolite	47.6
Chiolite	52.4

Example 4

300 kgs. of a solution containing 30 kgs. of HF and 44.7 kgs. of AlF_3, in which the HF/AlF_3 molar ratio is equal to 2.82, are reacted with 298 kgs. of a sodium chloride solution containing 74.5 kgs. of NaCl (stoichiometrically deficient). The slurry obtained is conditioned for 1 hour at the temperature of 53° C. 98.2 kgs. of fluoaluminate are collected. The chemical analysis carried out on said fluoaluminate has given the following results:

	Percent
NaF	54.5
AlF_3	45.5

The NaF/AlF_3 molar ratio of the product obtained is therefore 2.4 (NaF/AlF_3 weight ratio=1.2), so that this compound corresponds to a cryolite with the 10% of AlF_3 in excess with respect to the standard formula of comparison Na_3AlF_6.

A roentgenographic analysis carried out on the product has given the following results:

	Percent
Cryolite	62.1
Chiolite	37.9

Example 5

150 kgs. of a solution of HF at 70% are reacted with 660 kgs. of a solution obtained by mixing 153.4 kgs. of NaCl and 211.4 kgs. of $AlCl_36H_2O$.

The slurry is conditioned for 1 hour and 30 minutes at the temperature of 49° C. 183.8 kgs. of sodium fluoaluminate are collected. The chemical analysis on said fluoaluminate has given the following results:

	Percent
NaF	45.78
AlF_3	54.22

The NaF/AlF_3 molar ratio of the product obtained is therefore 1.69 (NaF/AlF_3 weight ratio=0.845) whereby this compound corresponds to a cryolite with 31% of AlF_3 in excess with respect to the standard formula of comparison Na_3AlF_6.

A roentgenographic analysis carried out on the product has given the following results:

	Percent
Cryolite	1.8
Chiolite	98.2

We claim:

1. A process for producing a sodium fluoaluminate composition with a predetermined sodium fluoride/aluminum trifluoride molar ratio between 1.67 and 2.65 having substantially all of its aluminum trifluoride con-

tent chemically combined with sodium fluoride, comprising the steps of intimately and rapidly mixing together a first solution containing two compounds selected from the group which consists of a sodium halide, an aluminum halide and hydrofluoric acid, and a second solution containing the third compound, thereby forming a suspension, said sodium halide being present in an amount not exceeding the stoichiometric equivalent of sodium in said sodium fluoaluminate and being in a molar ratio with the aluminum of said aluminum halide substantially equal to said predetermined molar ratio, said hydrofluoric acid being present in an amount selected so that the total quantity of fluoride ion in said solutions is substantially equal to the stoichiometric amount of fluoride in the sodium fluoaluminate composition of predetermined sodium fluoride/aluminum trifluoride molar ratio; and

conditioning the suspension by continuously stirring it for a period of at least one hour at a temperature on the order of 50° C.

2. A process as defined in claim 1 wherein said aluminum halide is selected from the group which consists of aluminum fluoride and aluminum chloride.

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