CLAIMS

~~1.~~

1. A process for preparing a synthetic fluorite CaF_2 comprising the following steps:

- preparing a solution of NH_4F, having a concentration comprised from 15 to 30% by weight, by basic hydrolysis, at a pH value comprised from 8.5 to 9.5, of H_2SiF_6, having a concentration comprised from 15 to 30% by weight, with an aqueous solution of NH_3 having a concentration comprised from 10 to 25% by weight, wherein NH_3 is dosed in a stoichiometric excess of about 20-30% by weight on fluorosilicic acid (FSA) relative to the theoretical value;

- filtering said solution of NH_4F so as to yield a substantially silica-free aqueous solution of NH_4F;

- treating said substantially silica-free aqueous solution of NH_4F with calcium hydroxide in an excess amount comprised from 0.01 to 0.5%, relative to the stoichiometric amount, so as to yield a dispersion which is maintained under stirring for a time comprised from 10 to 60 minutes at a temperature comprised from 40 to 90°C; or treating said substantially silica-free aqueous solution of NH_4F with calcium carbonate in an excess amount comprised from 0.01 to 0.5%, relative to the stoichiometric amount, so as to yield a dispersion which is maintained under stirring for a time comprised from 10 to 60 minutes at a temperature comprised from 60 to 90 °C, or

- distilling said substantially silica-free aqueous solution of NH_4F obtained after filtration under reduced pressure so as to transform the ammonium fluoride into ammonium bifluoride according to the following reaction:

$$2NH_4F_{(aq)} \rightarrow NH_4HF_{2(aq)} + NH_{3(gas)}$$

and reacting the ammonium bifluoride obtained with calcium carbonate so as to yield a fluorite CaF_2 dispersion, according to the following reaction:

$$NH_4HF_{2(aq)} + CaCO_{3(solid)} \rightarrow CaF_{2(solid)} + CO_{2(gas)} + NH_{3(gas)}$$

or else with calcium hydroxide so as to yield a fluorite CaF_2 dispersion, according to the following reaction:

$$NH_4HF_{2\,(aq)} + Ca(OH)_{2\,(solid)} \rightarrow CaF_{2\,(solid)} + 2H_20_{\,(aq)} + NH_{3\,(gas)};$$

- filtering the ~~latter solution~~dispersion so as to obtain the synthetic fluorite in the form of a slurry having a moisture content comprised from about 30% to about 50% by weight;

- subjecting said slurry to a drying-granulation step so as to yield an acid grade synthetic fluorite CaF_2 in the form of granules with an average particle size greater than 1 mm for at least the 50% of the same.

2. ~~2.~~ The process according to claim 1, wherein said solution of NH_4F obtained after the first step is treated with an amount of iron nitrate (~~III~~III) comprised from 0.01 g to 0.10 g per 1 g of ~~$Si0_2$~~SiO_2 present in said solution of NH_4F and/or with an amount of magnesium nitrate comprised from 0.01 g to 0.10 g per 1 g of ~~$Si0_2$~~SiO_2 present in said solution of NH_4F, so as to yield a solution of NH_4F purified with the precipitated silica.

3. ~~3.~~ The process according to claim 2, wherein said solution of NH_4F purified with the precipitated silica is subjected to filtration to separate the precipitated silica from the purified solution of NH_4F.

4. ~~4.~~ The process according to any one of claims 1 ~~or 2 or~~to 3, wherein said substantially silica-free aqueous solution of NH_4F obtained after filtration is treated with calcium carbonate in an excess amount comprised from 0.01 to 0.5%, relative to the stoichiometric amount, so as to yield a dispersion which is maintained under stirring for ~~a time comprised from 10 to 60 minutes, preferably~~ 30 minutes at a temperature ~~comprised from 60 to 90 °C, preferably~~of 80°C.

5. ~~5.~~ The process according to claim ~~4~~1, wherein the calcium carbonate has an average particle size distribution comprised from 50 to 400 microns, ~~preferably from 100 to 200 microns,~~ and wherein the ammonia is recovered at a temperature of about 60-70°C and always under ~~slight negative~~pressure which is 6 kPa (60 mbar) below ambient pressure.

6. ~~6.~~ The process according to claim ~~4 or~~ 5, wherein ~~said substantially silica-free aqueous solution of NH_4F obtained after filtration is distilled under reduced pressure so as to transform~~ the ~~ammonium fluoride into ammonium bifluoride according to the following reaction:~~calcium carbonate has an average particle size distribution comprised from 100 to 200 microns.

~~$2NH_4F_{(aq)} \rightarrow NH_4HF_{2\,(aq)} + NH_{3\,(gas)}$~~

~~7.~~

The process according to ~~claim~~ any one of claims 1-6, wherein the ~~ammonium bifluoride obtained is reacted~~

~~with calcium carbonate so as to yield the synthetic fluorite CaF_2, according to the following reaction:~~

~~$NH_4HF_{2\,(aq)} + CaCO_{3\,(solid)} \rightarrow CaF_{2\,(solid)} + CO_{2\,(gas)} + NH_{3\,(gas)}$~~

~~or else it is reacted with calcium hydroxide so as to yield the synthetic fluorite CaF_2, according to the following reaction:~~

~~$NH_4HF_{2\,(aq)} + Ca(OH)_{2\,(solid)} \rightarrow CaF_{2\,(solid)} + 2H_2O_{(aq)} + NH_{3\,(gas)}$.~~

7. ~~8. The process according to one of the preceding claims, wherein the~~ calcium carbonate ~~must have~~has a moisture content of less than 10% by weight, ~~preferably less than 5% by weight,~~ a $CaCO_3$ concentration greater than 97%, ~~preferably greater than 99%~~ and a low content of inorganic contaminants selected from among SiO_2, $MgCO_3$, metal oxides and metals.

8. ~~9.~~ The process according to claim 7, wherein the calcium carbonate has a moisture content of less than 5% by weight.

9. The process according to claim 7, wherein the calcium carbonate has a $CaCO_3$ concentration greater than 99%.

10. An apparatus for preparing an acid grade synthetic fluorite according to any one of ~~claims1-8~~claims 1-9, comprising:

- a hydrolysis reactor ~~(R-x01),~~ equipped with a ~~heating means (E-x01)~~cooling coil and a stirring means ~~(P-x01),~~ so as to receive ammonia from the storage tank ~~(D-x02)~~ by means of the pump ~~(G-x02),~~ and to receive fluorosilicic acid from the storage tank ~~(D-x01)~~ by means of the pump ~~(G-x01),~~ so as to yield a slurry comprising NH_4F and silica;

- a filter press ~~(F-x01)~~configured for receiving said slurry comprising NH_4F and silica so as to yield an aqueous solution comprising substantially silica-free NH_4F;

- a reactor ~~(R-x02)~~configured for the formation of the synthetic fluorite, for receiving said aqueous solution comprising substantially silica-free NH_4F and receiving the calcium hydroxide $Ca(OH)_2$ or calcium carbonate $Ca(CO)_3$ from a storage silo by means of a rotary valve ~~(T-x01)~~ and a screw conveyor ~~(T-x02)~~ so as to yield a slurry comprising the synthetic fluorite, water and ammonia or synthetic fluorite, water carbon dioxide and ammonia, respectively;

- a filter press ~~(F x02)~~configured for receiving the slurry comprising the synthetic fluorite, water and ammonia or synthetic fluorite, water, carbon dioxide and ammonia so as to yield the synthetic fluorite in the form of a slurry with a moisture comprised from 30% to 50% by weight, which is collected in a storage tank ~~(D x07);~~;

- a rotary oven ~~(B x01)~~ provided with a burner, configured for receiving said synthetic fluorite in the form of slurry from said storage tank ~~(D x07)~~ by means of the screw conveyor ~~(T x03 A/B)~~ so as to yield the acid grade synthetic fluorite in granules.

11. ~~10.~~ The apparatus according to claim ~~9~~10, wherein there is an intermediate tank ~~(D x05)~~configured for receiving the slurry comprising NH_4F and silica from the hydrolysis reactor ~~(R x01)~~ by means of the pump ~~(G x04)~~ and for receiving the magnesium nitrate and the iron nitrate from the tanks ~~(D x03 and D x04)~~ by means of the pumps ~~(G x05 and G x06)~~ respectively, so as to yield said solution of NH_4F purified with the precipitated silica to feed the filter press ~~(F x01).~~

12. ~~11.~~ The apparatus according to claim ~~9~~10 or ~~10~~11, wherein a reactor ~~(not shown)~~ is provided at the outlet of the storage tank ~~(Fig. 8, D x07) or (Fig. 6, D x09)~~ in order to receive said synthetic fluorite in the form of slurry from said storage tank ~~(D x07)~~ and to receive an aqueous solution of acids, ~~preferably 5% or 10% HCl or H_2SO_4,~~ and a filtering unit to remove the excess of oxides, carbonates or calcium hydroxide.

13. ~~12.~~ The apparatus according to claim 12, wherein the aqueous solution of acids is HCl or H_2SO_4.

14. The apparatus according to claim 13, wherein the aqueous solution of HCl or H_2SO_4 has a concentration of 5% or 10%.

15. An acid grade synthetic fluorite CaF_2 in the form of granules with an average particle size greater than 1 mm for at least the 50% of the same, said fluorite being obtained by the process for the preparation thereof in accordance with any one of claims 1-~~8.~~9.

16. ~~13.~~ The acid grade synthetic fluorite in accordance with claim ~~12~~15, wherein said fluorite has:

- a LOI value ~~(~~measured ~~in accordance with the procedures and the techniques known to the person skilled in the art, in samples from the outlet side of D x08 and D x10)~~at 800°C comprised from 0.3 to 1.2~~, preferably comprised from 0.5 to 0.8, even more preferably from 0.6 to 0.7;~~ wt%; and/or

- a BET value ~~(measured in accordance with the procedures and the techniques known to the person skilled in the art, in samples from the outlet side of D x07 or D x09~~ measured in samples after drying at 800°C in

a laboratory) comprised from 20 m2/g to 100 m2/g, preferably comprised from 40 m^2/g to 80 m^2/g, even more preferably from 50 m^2/g to 60 m^2/g; and/or; and/or

- average particle size (measured in accordance with the procedures and the techniques known to the person skilled in the art) as follows in % by weight relative to the synthetic fluorite:

- greater than 10 mm, zero ;

- greater than 5 mm, comprised from 1 to 10, preferably from 1 to 5, even more preferably from 1 to 3;;

- greater than 1 mm, comprised from 40 to 80, preferably from 50 to 70, even more preferably from 55 to 65;;

- greater than 0.05 mm, comprised from 10 to 30, preferably from 15 to 25, even more preferably from 20 to 25;;

- less than 0.05 mm, comprised from 1 to 20, preferably from 5 to 15, even more preferably from 5 to 10.

17. 14. The acid grade synthetic fluorite in accordance with claim 12 15 or 13 16, wherein said fluorite has:

- a concentration of silica SiO_2 of less than 1%, preferably less than 0.7%, even more preferably less than 0.35% (% measured in accordance with the procedures and the techniques known to the person skilled in the art, in samples calcined at 800°C);; and/or

- a concentration of MgO of less than 0.5%, preferably less than 0.3%, even more preferably less than 0.2% (%measured in accordance with the procedures and the techniques known to the person skilled in the art, in samples calcined at 800°C).

18. 15. A use of the The acid grade synthetic fluorite in granules according to any one of claims 12-14 for the production of hydrofluoric accordance with claim 17, wherein said fluorite has:

- a concentration of silica SiO_2 of less than 0.7% measured in samples calcined at 800°C; and/or

- a concentration of MgO of less than 0.3%measured in samples calcined at 800°C.

19. The acid. grade synthetic fluorite in accordance with claim 17, wherein said fluorite has:

- a concentration of silica SiO_2 of less than 0.35% measured in samples calcined at 800°C; and/or

- a concentration of MgO of less than 0.2% measured in samples calcined at 800°C.