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Synthesis of reagents for fluoride technologies

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Abstract: Growing demand for fluorinating reagents to be used in rare-metal industry has stimulated conducting research in the field of production for these reagents. That is why the fluorinating reagents production has recently formed an independent segment of industry. Main industrial fluorinating reagents include hydrofluoric acid, anhydrous hydrogen fluoride, technical ammonium hydrodifluoride, fluorosilicic acid and its salts. To produce technical etching acid, fluor-spar with calcium fluoride content at least 92% is used in most cases. To produce anhydrous hydrogen fluoride, fluor-spar with calcium fluoride content 96%-97% is necessary. The fluorine-containing raw materials refinement from silica by means of flotation makes the fluorinating reagents production substantially more expensive. In this work we have attempted to process unconcentrated raw materials by fluorine removal in the form of volatile silicon tetrafluoride. In this process silicon tetrafluoride was recovered by liquid ammonia with subsequent hydrolysis of the formed ammonia hexafluorosilicate. Hydrolysis occurred according to the reaction:

$$(NH_4)_2SiF_6+4NH_3+2H_2O=6NH_4F+SiO_2$$

The products of the ammonia hexafluorosilicate hydrolysis included ammonia fluoride and amorphous silica gel ("white soot") as by-product. This "white soot" was of high purity-with main component content 99.95% and total admixture content 0.05%. Silica gel is a superfine material with specific surface of 267.6 m^2/g and is recommended as filler in the production of rubber, plastics and for other applications. Ammonia fluoride was transformed into ammonia hydrodifluoride (main processing product) according to the reaction:

$$2NH_4F\rightarrow NH_3+NH_4HF_2$$

It was stated that the $NH_4F:NH_4HF_2$ ratio depends on boiling point temperature-with its increase the ammonia hydrofluoride concentration in solution increases as well.

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Growing demand for fluorinating reagents to be used in rare-metal industry has stimulated conducting research in the field of production of these reagents. That is why the fluorinating reagents production has recently formed an independent segment of industry. Main industrial fluorinating reagents include hydrofluoric acid, anhydrous hydrogen fluoride, fluorine, technical ammonium hydrodifluoride, fluorosilicic acid and its salts. The most widely spread fluorinating agents are fluorine and hydrogen fluoride, however, ammonium hydrodifluoride has also recently acquired a priority in this regard. Ammonium hydrodifluoride is the product of ammonium fluoride decomposition or

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its interaction with hydrogen fluoride:

$$2NH_4F = NH_4HF_2 + NH_3 \quad (1)$$

$$NH_4F + HF = NH_4HF_2 \quad (2)$$

To produce technical etching acid, fluor-spar with calcium fluoride content at least 92% is used in most cases. To produce anhydrous hydrogen fluoride, fluor-spar with calcium fluoride content 96%-97% is necessary. The fluorine-containing raw materials refinement from silica by means of flotation makes the fluorinating reagents production substantially more expensive. In this work we have attempted to process unconcentrated raw materials by fluorine removal in the form of volatile silicon tetfafluoride. In this process silicon tetrafluoride was recovered by liquid ammonia with subsequent hydrolysis of the formed ammonia hexafluorosilicate. Hydrolysis occurred according to the reaction:

$$(NH_4)_2SiF_6 + 4NH_3 + 2H_2O = 6NH_4F + SiO_2 \quad (3)$$

The products of the ammonia hexafluorosilicate hydrolysis included ammonia fluoride and amorphous silica gel ("white soot") as by-product. This "white soot" was of high purity-with main component content 99.95% and total admixture content 0.05% (see Table1).

Silica gel is a superfine material with specific surface of 267.6 m^2/g and it is recommended as filler in the production of rubber, plastics and for other applications. It was stated during experiments that synthesis of ammonium fluoride-hydrofluoride is better to conduct in several stages: (1)Absorption of silicon tetrafluoride; (2) Hydrolysis of ammonium hexafluorosilicate; (3) Separation of solid (SiO_2 n H_2O) and liquid (MH_4F) phases by filtration; (4) Silica gel drying; (5) Evaporation of ammonium fluoride solution with production of ammonium fluoride-hydrofluoride; (6)Separation of liquid phase from product by centrifugation.

Absorption of silicon tetrafluoride (stage 1) should be conducted by recycle solution of ammonium fluoride (containing 6%-10% of NH_4F and 1%-2% of NH_3) with output of 15%-20% solution of ammonium hexafluorosilicate and 0.5%-2% solution of fluosilicic acid.

Hydrolysis of ammonium hexafluorosilicate (stage 2) is conducted by ammonia until silica gel and ammonium fluoride precipitate in the solution.

During evaporation of the ammonium fluoride solution (stage 5), the gaseous phase, that is under constant pressure in equilibrium with liquid phase, can be as two-component (NH_3-H_2O) as three-component (NH_3-HF-H_2O) system depending on the temperature of boiling solution. It was found that the NH_4F/NH_4HF_2 ratio depends on the solution boiling point-its growth results in concentrating ammonium hydrodifluoride in the solution.

To reduce the product humidity, water, that is present mostly as ammonium fluoride solution, is removed by centrifugation. At humidity of 1.7%, the produced ammonium fluoride-hydrodifluoride does not become caked and does not lose its properties at long-term storage as well.

Ammonium hydrodifluoride is a prospective reagent for synthesis of inorganic fluorides and is used in solutions for metal and glass etching and as timber preservative.

Table 1 Admixtures content in amorphous silica gel

Admixtures	Content, %
Al	0.0103
Ca	0.0024
Cr	0.0044
Cu	0.0065
Fe	0.0158
Mg	0.0085
Mn	0.0004
Pb	0.0005
Zn	0.0012