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Ammonia-salt methods in the technology of production of chemical and metallurgical products

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Abstract

The problems of industrial waste processing, production of commercial products from them and their use as reagents for creating environmentally friendly efficient technological processes in various industries remain relevant. In this regard, the use of ammonium salts is of great interest. The author of the article develops the fundamental and applied foundations for expanding the scope of the ammonia-salt technology for solving a number of previously unsolved problems. It is proposed to use circulating ammonium bisulfate instead of sulfuric acid, which is a pyrolysis product of ammonium sulfate. The withdrawn ammonia can be widely used in various well-known production processes, such as the purification of gases from sulfur dioxide and carbon, in the production of fertilizers, etc.

Keywords: ammonia technology, ammonium sulfates, melt, fluorides, fluorite

Introduction

Ammonium fluorides are in great demand in various areas of the national economy. They can be used in metallurgy, oil extraction and production of white soot, in the production of glass products, etc. NH_4HF_2 is used as a substitute for hydrofluoric acid because it is less aggressive. Ammonium fluorides are often used as a reagent for the preparation of metal salts of hydrofluoric acid. This makes it advantageous to directly obtain ammonium fluorides, bypassing the stage of obtaining HF.

The only known method of processing natural fluoride raw materials - fluorite concentrate - is based on its "cooking" with concentrated (93%) sulfuric acid at 250-350°C [1-3]. The products of the chemical reaction in the vapor-gas phase are hydrogen fluoride, sulfur trioxide and water vapor, as well as solid calcium sulfate:

$$CaF_2 + 1{,}1H_2SO_4 \bullet nH_2O = CaSO_4 + 2HF\uparrow + 0{,}1SO_3\uparrow + 1{,}1nH_2O\uparrow \quad (1)$$

Ammonium fluorides are obtained by reacting hydrofluoric acid with an ammonia solution.

The need to find more efficient methods for producing fluorides is due to the main disadvantages of the basic technology for producing hydrofluoric acid and its derivatives:

1. The use of an aggressive reagent, leading to premature wear of equipment and frequent downtime due to restoration work;
2. The need for a technologically complex process of purification of hydrofluoric acid from silicon fluoride and sulfuric acid vapors;
3. High loss of thermal energy due to external heating and low thermal conductivity of calcium sulfate;
4. The need for neutralization of hydrofluoric acid with an ammonia solution and evaporation of the solution to isolate ammonium fluorides.

Along with the complexity and high cost of the technology itself, the transportation of these reagents to the place of production leads to additional costs and inconvenience.

This article presents previously unpublished materials related to the creation and justification of an alternative technology for processing fluorite concentrate using ammonium salts. According to the author, the reason for this is the presence of an alkaline ammonium cation and stronger anions of polybasic acids in their composition. Also, an attractive and characteristic property for them is the lower temperatures of their decomposition, the possibility of regeneration of ammonia and the salts themselves. These include ammonium sulfates and phosphates.

In early works, the possibilities of cleaning dirty ammonium sulfate from organic impurities [4-6] and its effective use for the development of a new method for producing soda ash [7, 8] were shown.

According to the same principle, studies of chemical reactions of the interaction of calcium fluoride with ammonium sulfates were carried out [9-11]. It has been established that the primary decomposition of (NH4)2SO4 into ammonia and liquid ammonium bisulfate occurs first. The latter actively interacts with metal fluorides, like calcium fluoride.

Based on these results, experimental tests were carried out (Figures 1 and 2) to verify the possibility of carrying out the reaction:

$$CaF_2 + (NH_4)_2SO_4 = CaSO_4 + 2HF\uparrow + 2NH_3\uparrow = 2NH_4F \quad (2)$$

A fluorite concentrate containing 95% CaF2 and purified ammonium sulfate of ArcelorMittal Temirtau JSC containing 98.9% of the main substance was used as a raw material.

Results and Discussion

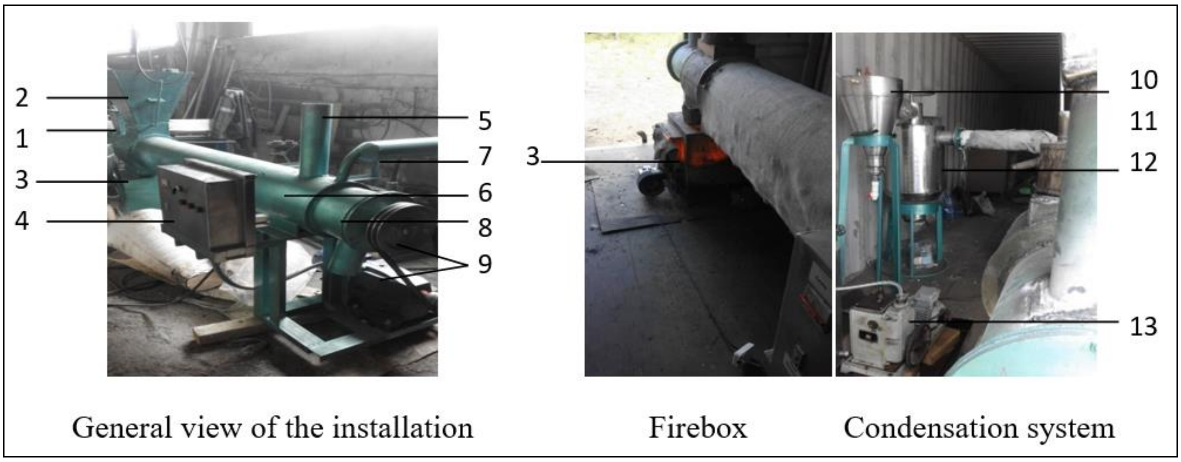
Experimental tests

The purpose of the pilot trials was to test the feasibility of reaction 2.

The installation is shown in Figure 1. Hopper 1 was loaded with a mixture consisting of fluorspar concentrate (34.8%) and ammonium sulfate (65.2%). The content of calcium fluoride in the mixture was 33.0% or 19.84 kg in a 60 kg sample of the mixture. Coal was loaded through hopper 2, which entered furnace 3. Flue gases entered the gas duct between two pipes (Fig. 1, pos. 6 and 8) and thermal energy was transferred to the charge through the walls of the reaction pipe 6 with an inner diameter of 300 mm. The temperature inside the reactor and the gas duct was measured with a sensor with chromel-alumel thermocouple.

The mixture was mixed and the lead was removed by a screw feeder (Fig. 2, pos. 16), which was rotated by a motor with a gearbox connected to a belt drive using 9 (Fig. 1). The minimum number of revolutions of the screw was about 2.5 rpm and the step of moving the material was 150 mm per revolution. With one-sided rotation of the screw, the time for the charge to overcome the distance from the hopper to the exit from the furnace, according to the calculation, was: 2700mm: 150mm: 2.5 rpm = 7.2 min.

This time was clearly not enough. In practice, according to the basic technology, the material is in the furnace for 10–15 hours. Therefore, to increase the residence time of the mixture in the reaction zone, it was necessary to work in the mode of reverse rotation of the screw and complete unloading of the hopper.



General view of the installation Firebox Condensation system

Fig 1: 1- bunker for charge; 2-bunker for coal; 3-furnace for coal; 4-control panel with time relay; 5-chimney; 6- outer pipe (casing); 7-gas duct; 8-inner reaction tube (unheated section shown); 9-motor with gearbox and belt drive

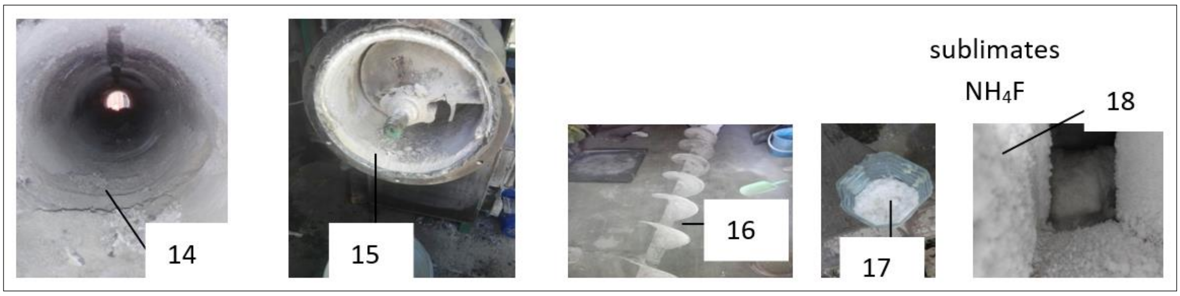


Fig 2: After testing: 14-garnissage; 15-charge and sublimates from the side of the bunker; 16 screw; 17-sublimes from the condenser; 18 - sublimates in an empty bunker for charge

After a time of 2.05 hours from the moment the temperature of the sublimates in the gas duct reached 220°C, calcium sulfate was released through the unloading unit. The approximate yield of calcium sulfate cinder from 60 kg of charge was 45.32 kg, and the residual content of calcium fluoride in it corresponded to 27.98% (5.55 kg). The opening of the reactor at the end of the experiment showed that part of the ammonium fluoride was condensed in the empty bunker for the charge (Fig. 2, item 18), despite the vacuum created by the condenser (Fig. 1, item 13). Part ended up in the condenser (Fig. 2, pos. 18). The total yield of sublimates was 13.45 kg. The difference in weight of charge and products was 1.23 kg. It seems that partially sublimates of ammonium fluoride mixed with the mixture in the colder section of the reactor from the side of the bunker, creating a dense molten mass (Fig. 2, pos. 15). The iron screw was not deformed and there was no significant weight loss (Fig. 2, pos. 16).

Conclusions

So, despite the not very successful test results, they showed the fundamental possibility of carrying out technological processes using ammonium sulfates instead of sulfuric acid. However, the improvement of technological processes in this direction requires taking into account the following factors:

1. To save thermal energy, processes with using ammonium bisulfate, based on chemical reactions:

$$CaF_{2(k)} + NH_4HSO_{4(L)} = CaSO_{4(k)} + NH_{3(g)} + 2HF_g = CaSO_{4(k)} + NH_4F{\bullet}HF_k \text{ (конденсат)} \quad (3)$$

$$CaF_{2(k)} + NH_4HSO_{4(L)} + NH_{3(g)} = CaSO_{4(k)} + 2NH_{3(g)} + 2HF_g = CaSO_{4(L)} + 2NH_4F \text{ (конденсат)} \quad (4)$$

2. The process should be carried out in a vertical cylindrical unit with a device PTO for intensive mixing of the reaction mass in a liquid medium, by using a recycled excess of the ammonium bisulfate melt in relation to the fluorite concentrate;

3. Taking into account these factors, the following technological scheme is proposed (Fig.3) [11]:

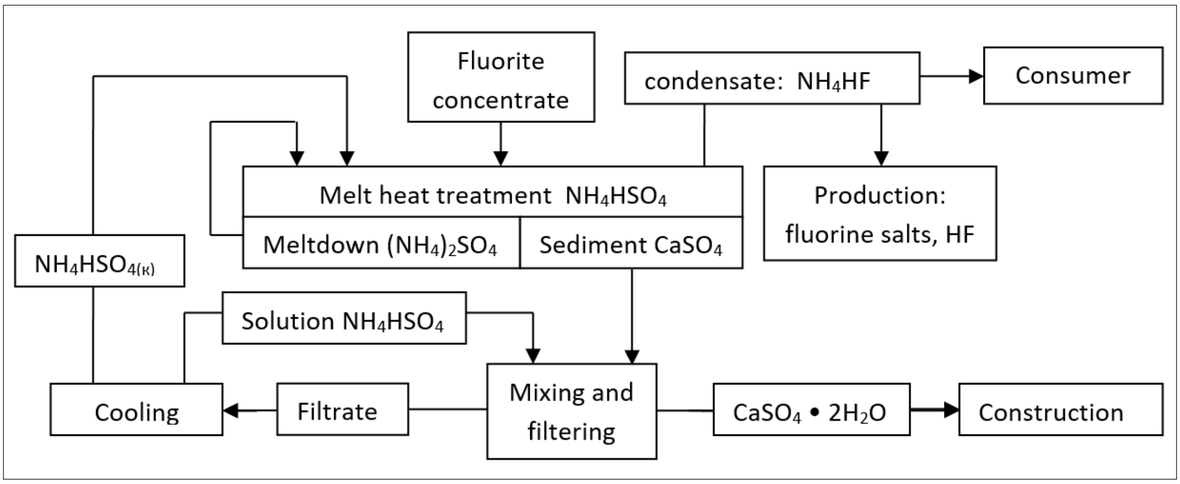


Fig 3: Schematic block diagram of the processing of fluorite concentrate and man-made waste in the melt NH_4HSO_4

4. Principles for obtaining any other fluorine compounds from ammonium fluorides, are well known.

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