Patented Apr. 2, 1940

2,196,077

UNITED STATES PATENT OFFICE

2,196,077

METHOD OF PRODUCING SODIUM ALUMINUM FLUORIDE

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No Drawing. Application June 25, 1937, Serial No. 150,260

4 Claims. (Cl. 23—88)

This invention relates to the production of double fluorides of alkali metals and aluminum, and it is particularly concerned with the production of double fluorides of sodium and aluminum.

Various methods have been used in the past for the production of the double fluorides of alkali metals and aluminum, particularly cryolite, a double fluoride of sodium and aluminum having the formula $3NaF.AlF_3$, and chiolite having the reported formula $5NaF.3AlF_3$. These methods depend generally upon an acid decomposition of mineral fluorspar for the production of hydrofluoric acid in gaseous form, which is subsequently absorbed in water and reacted with sodium and aluminum compounds to produce sodium aluminum fluoride. The commercial use of these methods is subject to various objections. The hydrofluoric acid gas produced is difficult and hazardous to handle, relatively expensive acid-resisting equipment must be provided, and the reaction is necessarily carried out at relatively high temperatures. A high grade fluorspar is also necessary as the starting material for an economical operation of these processes.

It is an object of this invention to provide a substantially alkaline method for the decomposition of fluorspar and the production of double fluorides of alkali metals and aluminum. It is more particularly an object of this invention to provide an improved process for the production of sodium aluminum fluoride from fluorspar ores without any intermediate formation of hydrofluoric acid gas. Another object of this invention is to provide a cyclic or continuous method for the production of sodium aluminum fluoride. The term "sodium aluminum fluoride" as used herein and in the appended claims is intended to include cryolite and chiolite as well as double fluorides of sodium and aluminum in which the ratios of sodium fluoride to aluminum fluoride differ from their ratios in cryolite and chiolite.

This invention is predicated upon the discovery that fluorspar can be effectively decomposed and an economical extraction of fluorine can be obtained in the form of a soluble fluoride by the digestion of fluorspar at moderately high temperatures with a solution of an alkali, and that by subsequent treatment of the solution of the alkali metal fluoride thus formed with an alkali metal aluminate and an acid material a double fluoride of the alkali metal and aluminum may be precipitated. Furthermore, by the use of carbon dioxide as the acid reagent in the second step of this process it has been found that a by-product liquor containing an alkali carbonate and bicarbonate may be produced which is readily available for use in the first step of the process for the digestion of further amounts of fluorspar. Thus, by the method of this invention a double fluoride of an alkali metal and aluminum may be produced from fluorspar by a method in which no hydrofluoric acid gas is formed. The various steps of the process are carried out in solutions which are substantially alkaline, and the by-product of the final step of the process may be returned to the first step of the process for reuse in carrying out the process in a cyclic manner.

The method of this invention has the further advantage of being applicable to the production of double fluorides of alkali metals and aluminum from certain types of fluorspar ores heretofore considered to be of little or no commercial value. Fluorspar ores relatively high in calcite cannot be used economically in the acid processes because of the fact that the acid reagents are used up to a large extent by reaction with the calcite. On the other hand, relatively large amounts of calcite may be present in the fluorspar ore used in the method of this invention without interfering substantially with the process.

While the method of this invention is applicable to the production of double fluorides of various alkali metals and aluminum, it will be more particularly described hereinafter in connection with the preferred form of the invention in which sodium aluminum fluorides are produced. It is not intended that this invention shall be limited to, or circumscribed by, the specific details of operation hereinafter set forth, except as they are recited in the appended claims.

In carrying out the method in its preferred form, in which a sodium aluminum fluoride is produced, the fluorspar is reduced to convenient particle size and placed in a suitable digestion vessel with an alkaline solution of a sodium compound, such as caustic soda or sodium carbonate, which will react with the fluorspar to produce sodium fluoride and an insoluble salt of calcium. It is preferred to use sodium carbonate for the fluorspar digestion because it may be recovered as a by-product from the final step of the process and reused in the digestion of further amounts of fluorspar. When sodium carbonate is used in the fluorspar digestion the reaction proceeds according to the equation:

$$CaF_2+Na_2CO_3=2NaF+CaCO_3.$$

The sodium fluoride formed is in solution and

the calcium carbonate is precipitated as a sludge which is readily separated by filtration or other means. While the fluorspar and sodium carbonate may be digested together in substantially any proportions to produce sodium fluoride, it is preferred to use the sodium carbonate in an amount in excess of the stoichiometric quantity required to combine with all of the fluorine of the fluorspar to produce sodium fluoride. The use of an excess of sodium carbonate tends to increase the yield of sodium fluoride produced and thus increases the efficiency of the process.

The reaction will proceed to some extent even at room temperature. It is preferred, however, to carry out the digestion at elevated temperatures in order to effect substantially complete reaction in a reasonable operating time. When the digestion is carried out at temperatures of about 100° C., substantially complete reaction can be effected in about 16 hours, while at a temperature of about 170° C. a digestion period of only 3 hours is required. The separation of the sodium fluoride solution from the calcium carbonate sludge may be effected in any convenient manner. In addition to the sodium fluoride, the solution obtained will contain any excess of sodium carbonate used for the digestion.

For the production of sodium aluminum fluoride from the sodium fluoride solution thus obtained, the solution is treated with sodium aluminate and an acid reagent to precipitate the sodium aluminum fluoride. Substantially any acid reagent may be used, including a solution of an acid or acid salt or an acid gas, such as sulfuric acid, hydrofluoric acid, sodium bicarbonate, sulfur dioxide, and carbon dioxide. It is preferred, however, to effect the precipitation by means of carbon dioxide, in which case the reaction proceeds according to the equation:

$$6NaF+NaAlO_2+4CO_2+2H_2O=Na_3AlF_6+4NaHCO_3$$

The sodium aluminate is used in an amount equal to or slightly less than the stoichiometric quantity required to combine with all of the sodium fluoride. The acid material is preferably used in an amount sufficient to effect substantially complete precipitation of the sodium aluminum fluoride.

In commercial operation it has been found particularly advantageous to carry out the process of this invention in a cyclic or continuous manner in which the sodium fluoride solution is formed by digestion of the fluorspar with an excess of sodium carbonate solution, preferably at a temperature of about 170° C. The sodium fluoride solution containing sodium carbonate thus formed is separated from the calcium carbonate precipitate and is treated with a solution of sodium aluminate in an amount somewhat less than the amount required to combine with all of the sodium fluoride and with sufficient CO_2 to convert about 80 to 100 per cent of the soda present to sodium bicarbonate. The sodium aluminum fluoride precipitate thus formed is separated from the sodium carbonate-sodium bicarbonate solution and this solution is returned to the digestion step of the process where it is digested at 170° with additional amounts of fluorspar, and if necessary additional sodium carbonate. During this digestion the sodium bicarbonate decomposes into sodium carbonate and carbon dioxide. The carbon dioxide may be bled off and reused in the sodium aluminum fluoride precipitation step. As the sodium bicarbonate content of the digestion liquor is reduced the reaction of the sodium carbonate with the fluorspar proceeds to form sodium fluoride. The subsequent steps of separation of sodium fluoride solution and the precipitation of sodium aluminum fluoride are carried out as before. This cyclic method of operation effects very substantial economies in materials, heat consumption and handling.

It is, of course, to be understood that whether or not a cyclic process is carried out, the sodium carbonate-sodium bicarbonate liquor resulting from the precipitation of the sodium aluminum fluoride may be decarbonated by heating at temperatures of 170 to 175° C. for the recovery of sodium carbonate and carbon dioxide.

The following example illustrates the operation of the process of this invention in its preferred form. 18 grams of fluorspar containing approximately 73.5 per cent CaF_2, 10.4 per cent $CaCO_3$, and 13.8 per cent SiO_2 were placed in an autoclave, and there were added 2.18 liters of a solution containing total Na_2O equivalent to 91.7 grams per liter sodium carbonate, 81.4 per cent of which was in the form of sodium bicarbonate. This mixture was heated to a temperature of about 170° C. and the temperature was maintained for a period of about 3 hours. During this time CO_2 was removed through a reflux condenser. The mixture was then filtered and the temperature of the filtrate adjusted to about 50° C. While maintaining this temperature carbon dioxide was added until about 50 per cent of the total soda content was converted to sodium bicarbonate. 100 cubic centimeters of a solution of sodium aluminate containing 2.79 grams of Al_2O_3 was added to the carbonated filtrate with stirring. Additional carbon dioxide was then added until about 85 per cent of the total soda content had been converted to sodium bicarbonate. The resulting slurry was filtered to separate the precipitated cryolite. This filtrate was then returned to the autoclave and sufficient fluorspar and sodium carbonate added to make up the proportions used in the original digestion. The mixture was heated at a temperature of 170° and the carbon dioxide formed by the conversion of the bicarbonate to carbonate during this heating was vented off. The subsequent steps of separation of sodium fluoride solution and precipitation of sodium aluminum fluoride were then repeated as before.

We claim:

1. A method for the production of sodium aluminum fluoride which comprises digesting fluorspar at a temperature of about 170° C. with a solution containing sodium carbonate, treating the sodium fluoride solution thus formed with sodium aluminate and carbon dioxide, separating the sodium aluminum fluoride thus precipitated, and returning the resulting filtrate to the digestion stage for decomposition of additional amounts of fluorspar.

2. A method for the production of sodium aluminum fluoride comprising digesting fluorspar with a hot solution of sodium carbonate, treating the resulting solution of sodium fluoride with sodium aluminate and carbon dioxide, separating the sodium aluminum fluoride thus formed, decarbonating the filtrate to convert at least part of its sodium bicarbonate content to sodium carbonate, and returning the decarbonated filtrate to the digestion stage of the process for the decomposition of additional amounts of fluorspar.

3. A method for the production of sodium aluminum fluoride which comprises digesting fluor-

spar at a temperature of about 100° C. to about 170° C. with a solution containing sodium carbonate, treating the sodium fluoride solution thus formed with sodium aluminate and carbon dioxide, separating the sodium aluminum fluoride thus precipitated, and returning the resulting filtrate to the digestion stage for decomposition of additional amounts of fluorspar.

4. A method for the production of sodium aluminum fluoride which comprises digesting fluorspar at an elevated temperature with a solution containing sodium carbonate, treating the sodium fluoride solution thus formed with sodium aluminate and carbon dioxide, separating the sodium aluminum fluoride thus precipitated, and returning the resulting filtrate to the digestion stage for decomposition of additional amounts of fluorspar.

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