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(54) PURIFYING HYDROFLUORIC ACID

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the production of concentrated hydrofluoric acid and more especially for purifying the crude hydrogen fluoride gases evolved during the reaction of fluorite with sulphuric acid.

The starting materials used are, for example, acid-grade fluorite containing $\geq 97\%$ of CaF_2 and the water-and HF-containing charging acid with an H_2SO_4 content of about 90% which is obtained during purification of the crude gases. The crude HF gases evolved from the reaction system at temperatures of 200°C contain as their principal impurities water, sulphuric acid, sulphur dioxide, silicon tetrafluoride, inert gases and dust fractions, for example CaSO_3 and CaF_2 . The dust fractions may be larger than normal if, instead of mixing the reactants in the cold state, the hot fluorite with a temperature of approximately 500°C is reacted with hot charging acid with a temperature of approximately 100°C (for example in accordance with U.K. Patent No. 1,371,790).

U.K. Patent No. 1,414,748 describes a process for purifying and condensing the reaction gases in the production of hydrofluoric acid. In this process, the gases issuing from the reaction system with a temperature of 200°C are subjected in a first stage to countercurrent washing with concentrated H_2SO_4 heated to a temperature of from 50°C to 120°C and are subsequently cooled to a temperature of from 60°C to 130°C .

A preferred embodiment of this known process is illustrated in the accompanying Figure 1 in which a preliminary H_2SO_4 wash is carried out as a two-stage countercurrent wash.

Referring to Figure 1, in a first preliminary

washer 1 the acid issuing from a second preliminary washer 2 is recirculated by pumping without being cooled so that it assumes a temperature of from 100°C to 140°C . The crude HF gases are passed from a reactor 12 to a preliminary washer 1 and leave with a temperature of from 90 to 160°C . A slightly impure concentrated H_2SO_4 6 issuing from a residual gas washer (not shown) following the condensation stages enters the second preliminary washer 2 and the circuit 1—1a from the storage vessel 2a. The washing acid is recirculated from the second preliminary washer 2 by pumping via an indirect water cooler 2b, the acid being cooled to a temperature of from 40 to 70°C . The HF issues from the second preliminary washer 2 with temperatures of from 50 to 90°C . The preliminary H_2SO_4 washers 1, 2 are followed by a first indirect water cooler 14 and a direct HF-washer for further purification and precooling of the HF-gases (not shown). Subsequent condensation takes place in a second indirect water cooler and following brine coolers. The HF—and SiF_4 —containing gases issuing from the condensation stages are further purified with concentrated sulphuric acid in a residual gas washer, followed by further processing of the H_2SiF_6 . The HF-washer consists of a direct HF-cooling stage which is fed with liquid HF from the condensation stages in such a way that all the liquid HF introduced just evaporates.

A washing acid 1a issuing from the preliminary H_2SO_4 washers is combined with the condensates from the first indirect H_2O cooler and the HF washer, followed by the addition of oleum. The resulting product is delivered as charging acid to the reaction furnace.

A concentrated 99.95% pure HF, which still contains up to 0.001% of H_2SO_4 , is obtained by this process according to U.K. Patent No. 1,414,748.

Both for reasons of pollution control and also for the potential value of the end products, there is advantage to be gained in further improving the process with a view to obtaining a purer end product and waste

gases laden to a lesser extent with reactive gases.

One critical parameter of the process described above is the water content of the sulphuric acid and the reaction gases:

In the reaction of fluorite with sulphuric acid, it is necessary, in order to ensure a smooth reaction, to maintain a certain water content in the acid charged to the fluorite reaction. The reaction of sulphuric acid or hydrofluoric acid with the oxygen-containing impurities in the fluorite (for example SiO_2 , Fe_2O_3 , CaCO_3) gives rise to the formation of more water so that the crude HF gases formed enter the first purification stage with different water contents, depending upon the quality of the fluorite. With low water contents in the crude HF gas, the water content in the washing acid of the preliminary H_2SO_4 washer falls to such an extent that the gas leaving the preliminary H_2SO_4 washer entrains with it considerable quantities of H_2SO_4 which can no longer be completely removed in the HF-washer.

Another critical parameter is the fact that CaSO_4 gradually crystallises out on the packing in the first part of the H_2SO_4 washer. This ultimately brings the installation to a standstill and necessitates involved repair work for replacing the packing.

It has now been found that these difficulties can be obviated, firstly, if instead of the total amount of sulphuric acid (washing acid from the residual gas washer), being introduced in countercurrent into the preliminary washer 1 by way of the prewasher 2, the acid is distributed beforehand between both preliminary washers, and, secondly, if instead of the total amount of oleum required for adjusting the charging acid being introduced into the washing acids from the preliminary H_2SO_4 wash which are combined with the condensates of the following stages, the oleum is actually added in portions to the washing circuit of the first preliminary H_2SO_4 washer.

By virtue of these measures, the water content in the second preliminary washer can be raised to such an extent that a hydrogen fluoride with very low H_2SO_4 content is obtained. At the same time, the water content in the first preliminary washer is reduced.

Furthermore, it has surprisingly been found that by this method, hardly any calcium sulphate crystallises out.

Optimum conditions are obtained when the distribution of oleum and sulphuric acid between the preliminary washers is arranged such that the water content in the washing acids of each of the at least two preliminary washers is kept in a range of 6% to 10% by weight.

The preliminary sulphuric acid washers are then followed in known manner by HF

washers, water coolers and brine coolers for condensing the purified gases. The residual gases (substantially SiF_4 -containing inert gases which still contain a little HF) are washed with concentrated sulphuric acid and further processed as H_2SiF_6 .

Accordingly, the present invention provides a process for the production of pure concentrated hydrofluoric acid wherein crude HF gases obtained from the reaction of fluorite with sulphuric acid are purified in at least two preliminary H_2SO_4 washing stages, followed by an HF-wash, at least one water cooler, at least two brine coolers and an H_2SO_4 residual gas wash, wherein hydrofluoric acid is condensed out of the at least one water cooler and at least two brine coolers, wherein the acid overflowing from a second preliminary washing stage is recycled to a first preliminary washing stage and wherein a desired concentration of H_2SO_4 in the preliminary washing stages is maintained by addition of oleum, wherein the sulphuric acid required for reaction with the fluorite is passed through the H_2SO_4 residual gas wash and subsequently distributed between the at least two preliminary H_2SO_4 washing stages, wherein at least part of the quantity of oleum required for adjusting the acid charged to the reaction with fluorite is introduced to the first preliminary washing stage in such proportions that the water content in the at least two preliminary H_2SO_4 washing stages is kept in the range from 6% to 10% by weight.

The process is preferably carried out by introducing into the washing circuit of the second preliminary H_2SO_4 washer from 25 to 75%, and most preferably from 40 to 60%, and into the washing circuit of the first preliminary washer from 25 to 75%, and most preferably from 40 to 60% of the total quantity of sulphuric acid used, by introducing the overflow from the second preliminary H_2SO_4 washer into the washing circuit of the first preliminary H_2SO_4 washer and by additionally introducing into the washing circuit of the first preliminary H_2SO_4 washer from 25 to 100% and most preferably from 50 to 75% of the quantity of oleum required for adjusting the acid charged to the fluorite reaction.

In cases where the water contents of the crude gases are subject to considerable fluctuations, the water content of the washing acids may be checked at regular intervals, for example hourly, according to the homogeneity of the fluorite used, and the distribution of acid regulated accordingly.

The sulphuric acid used is preferably introduced into the preliminary washers in a ratio of substantially 50:50 and the water content of the washing circuits regulated by

the quantity of oleum additionally introduced into the first washer.

A hydrogen fluoride with a very low H_2SO_4 content, of the order of a few ppm, is obtained by the process according to the invention, in addition to which the service life of the installation is considerably lengthened. For example, in an installation operated in accordance with the present invention, the packing in the H_2SO_4 washers did not show any sign of requiring replacement even after continuous operation for 6 months.

The process according to the invention is described in more detail in the following with reference to the accompanying drawings, wherein:

Figure 1 is a flow diagram which illustrates the known process and is included for the purpose of comparison and

Figure 2 is a flow diagram which illustrates the process according to the present invention.

Referring to Figure 2, crude gases leaving a reaction furnace 12 (fed with fluorite from source 11 and acid 10) with a temperature of approximately 150 to 250°C are largely freed from dust-form compounds (CaSO_4 , CaF_2) and substantially non-volatile gaseous compounds (H_2SO_4 , H_2O) in a first sulphuric acid washer 1. The washer 1 is sprayed with H_2SO_4 washing acid from a receiver 1a through a pump-operated circuit. In a second sulphuric acid washer 2. The prepurified gas is further cooled to approximately 50–110°C and freed from remaining dust particles and other substantially non-volatile gaseous compounds. The second washer 2 is sprayed from the receiver 2a with H_2SO_4 washing acid through a pump-operated circuit. For cooling the washing acid, a water cooler 2b is incorporated into the circuit. The gases thus prepurified then enter the reservoir for liquid HF 13 after passing through a HF washer 3 and after condensation in an H_2O -cooler 4 and two or more brine coolers 5. The residual gases issuing from the condensation stages 4, 5 enter a H_2SiF_6 further processing stage 7 after a sulphuric acid residual gas wash 6.

The acid overflowing from the receiver of the second sulphuric acid washer 2a together with 25 to 75% of the total quantity of concentrated sulphuric acid 9, coming from the residual gas washer 6 and 25 to 100% of the quantity of oleum from source 8 required for adjusting the concentration of the acid 10 charged to the fluorite reaction, are introduced into the receiver 1a for the washing acid of the first sulphuric acid washer 1.

The remaining 25 to 75% of the sulphuric acid coming from the residual gas washer 6 are introduced into a receiver 2a for the

washing acid of the second sulphuric acid washer 2.

The acid 10 charged to the fluoride reaction is adjusted with the overflow from the receiver of the first sulphuric acid washer 1a and with a condensate 3a of the HF washer 3 together with any remaining oleum 8. The HF-containing gases 10a evolved are returned to the first sulphuric acid washer 1.

The HF-washer 3 is preferably operated with liquid HF 13 in such a way that all the HF used just evaporates.

The invention will be further described in the following illustrative Example with reference to Figure 2 and wherein all parts are by weight unless otherwise expressed:

EXAMPLE

The crude HF gases, which contain H_2O , SO_2 , SiF_4 , S and dust (CaF_2 , CaSO_4) leave the reaction furnace 12 with a temperature of 190°C and enter the first sulphuric acid washer 1 which is sprayed with pump-recirculated washing acid from the receiver 1a. The volume of the crude gases is about 3800³/h and that of the wash liquids about 10–20 m³/h. It is mainly dust-form CaSO_4 , H_2SO_4 -droplets and also SO_3 - and H_2O -vapours which are separated off in the first washer 1. The HF gas then enters the second H_2SO_4 washer 2 with a temperature of 140°C. The second H_2SO_4 washer 2 is sprayed with pump-recirculated washing acid from the receiver 2a by way of the water cooler 2b. The HF-gas leaves the washer with a temperature of 90°C, is delivered to the HF-washer 3 for further purification and cooling and subsequently condensed in several stages.

50% of the total quantity of sulphuric acid used (98% H_2SO_4) is introduced into each of the washer receivers (1a, 2a). The sulphuric acid was previously used for washing the residual gases 6 and therefore already contains HF and has a temperature of 35°C. In addition to 50% of the sulphuric acid, the overflow from the washer receiver 2a and 50% of the total quantity of oleum 8 used are introduced into the washer receiver 1a.

The acid charged to the fluorite reaction is prepared in the mixing vessel 10 from the overflow from the receiver 1a, the condensate 3a from 3 and the remaining 50% of the oleum 8. The acid charged to the fluorite reaction flows off to the furnace at a temperature of 120°C.

The water content in the first H_2SO_4 washer 1 is substantially equal to the water content in the washing acid of the second H_2SO_4 washer 2 and amounts to between 7% and 9%. In the first H_2SO_4 washer, no deposits of CaSO_4 are observed even after operation for several months. The hydrogen

fluoride condensed out contains approximately 0.0005% of H_2SO_4 .

WHAT WE CLAIM IS:—

- 5 1. A process for the production of pure, concentrated hydrofluoric acid wherein crude HF gases obtained from the reaction of fluorite with sulphuric acid are purified in at least two preliminary H_2SO_4 washing stages, followed by an HF-wash, at least one water cooler, at least two brine coolers and an H_2SO_4 residual gas wash, wherein hydrofluoric acid is condensed out of the at least one water cooler and at least two brine coolers, wherein the acid overflowing from a second preliminary washing stage is recycled to a first preliminary washing stage and wherein a desired concentration of H_2SO_4 in the preliminary washing stages is maintained by addition of oleum, wherein the sulphuric acid required for reaction with the fluorite is passed through the H_2SO_4 residual gas wash and subsequently distributed between the at least two preliminary H_2SO_4 washing stages, wherein at least part of the quantity of oleum required for adjusting the acid charged to the reaction with fluorite is introduced to the first preliminary washing stage in such proportions that the water content in the at least two preliminary H_2SO_4 washing stages is kept in the range from 6% to 10% by weight.
2. A process as claimed in Claim 1, wherein from 25 to 75% of the total quantity of sulphuric acid used is introduced into each of the first two preliminary sulphuric acid washing stages.
3. A process as claimed in Claim 1 or

2, wherein the water content in the preliminary H_2SO_4 -washing stages is monitored at regular intervals and the addition of the acid to the preliminary washing stages is regulated accordingly.

4. A process as claimed in any of Claims 1 to 3, wherein from a part of the quantity of oleum required for adjusting the concentration of the acid charged to fluorite is introduced to the first preliminary H_2SO_4 washing stage and wherein the remainder of the quantity of oleum is introduced to the acid charged to the fluorite reaction.

5. A process as claimed in any of Claims 1 to 4, wherein 50% to the total quantity of the sulphuric acid is introduced into each of the first two preliminary H_2SO_4 washing stages.

6. A process as claimed in any of Claims 1 to 4, wherein from 40 to 60% of the total quantity of the sulphuric acid is introduced into each of two preliminary H_2SO_4 washing stages and wherein from 50 to 75% of the quantity of oleum required for adjusting the acid charged to the preliminary washing stages is introduced to the first preliminary H_2SO_4 washing stage.

7. A process for the production of pure, concentrated hydrofluoric acid substantially as herein described with reference to the accompanying Figure 2 and/or the specific Example.

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