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PRODUCTION OF SYNTHETIC FLUOR-SPAR FROM WASTE FLUOSILICIC ACID
(Paper delivered during the Conference)

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The fluoride released when processing fluorine-bearing phosphate rock would seriously pollute the environment if it were not recovered in some harmless form which should preferably be such that it can be put to good use. Calculations based on the amount of phosphate rock processed throughout the world show that the quantity of fluoride obtained in the digestion process is about the same as the quantity of fluor-spar mined, this being the actual fluorine-bearing raw material. In view of the fact that minable fluor-spar is only available in relatively small quantities (the ratio of mined fluor-spar to certain and probable resources being only about 1:25), no effort has been spared to find ways and means of utilizing fluosilic acid as a raw material.

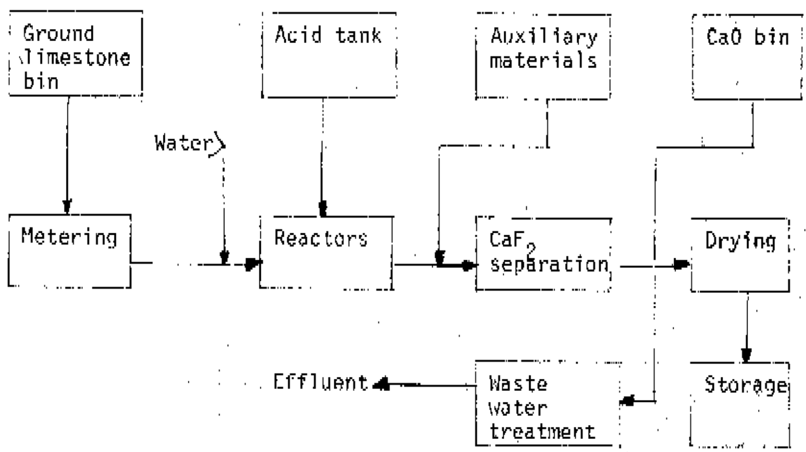
Processes for the production of aluminium fluoride and cryolite, these being the fluorides required most, have already been realized in practice. However, a look at the consumption figures for these fluxing agents of the aluminium industry shows that the market is very limited. It is estimated that the world production of primary-aluminium pig was 13 million tons in 1975. This means that, on the basis of maximum 30 kg per ton of aluminium, 390 000 tons of fluorine were used at the most. Moreover, in view of the increasing use of recycling, the fluorine consumption will probably become considerably less in future.
The major portion of fluorine is used in the form of metallurgical fluor-spar by the metallurgical industries and obtained in the form of hydrogen fluoride, the raw material for the production of fluorine compounds. In spite of all the efforts in this respect, no practicable way has so far been found to produce synthetic fluor-spar on a commercial scale from H_2SiF_6 direct.

We should now like to introduce a process, with the aid of which synthetic fluor-spar can easily be produced from fluosilic acid. Although earlier proposals for doing this are indeed known, it was found that they are either impracticable because of the high cost or that the product is not sufficiently pure. The process introduced here was jointly developed by BAYER AG and KALI-CHEMIE AG. On the basis of the results obtained in a pilot plant operated by BAYER, a production plant was designed jointly with FRIEDRICH UHDE GMBH.

The process is characterized by the following reaction equation:

$$H_2SiF_6 + 3\ CaCO_3 = 3\ CaF_2 + SiO_2 + 3\ CO_2 + H_2O$$

The basic principle of the process is illustrated by the block diagram:



Production of synthetic CaF_2 from H_2SiF_6 and $CaCO_3$

Fluosilicic acid and an aqueous suspension of ground limestone are continuously fed to a system of series-connected reactors. Providing the reaction is properly controlled, CO_2 will be released while SiO_2 remains in solution as a metastable sol. After a short residence time, auxiliary materials are added to improve the filtration efficiency and the solids are separated from the sol. The CaF_2 sludge, which contains about 30% water, is dried. The finished product consists of over 90% CaF_2 and, in

addition, it contains 2.5 - 3.5% SiO_2, calcium carbonate and other impurities originating from the limestone and fluosilicic acid. The fluorine yield is over 99%, so that only a few ppm of fluoride remain in the SiO_2 sol. The sol is then flocculated with CaO, as a result of which the portion of dissolved fluoride is reduced further still.
The synthetic fluor-spar is obtained in a form that is suitable for the production of hydrogen fluoride. Tests conducted by BAYER substantiate this. As a result of the higher SiO_2 content, more H_2SiF_6 is formed during the production of HF. On the other hand, owing to the better reactivity of the synthetic fluor-spar, the fluorine yield is higher.
A further advantage of the process is that even diluted fluosilicic acid may be used.
As already mentioned, it is further possible to use the synthetic fluor-spar in steel production in a similar way to compacted natural fluor-spar such as is used for the production of H_2F_2.
A calculation of the production cost for synthetic fluor-spar suggests that this can compete with a number of qualities of natural fluor-spar.
As an example, let us examine a plant designed to handle 12 000 tons H_2SiF_6 per year. This quantity of fluorine is roughly equivalent to that obtained in a 500 tons-per-day P_2O_5 plant and will render 19 500 tons of 100% CaF_2 per year.

Capital expenditure	approx. DM 7 million
Personnel	2 men per shift

Feedstocks per ton CAF_2 100%:

H_2SiF_6	0.615 t
Ground $CaCO_3$ 98%	1.36 t

The cost of auxiliary chemicals is equivalent to about 10-15% of the ground limestone cost, incl. the CaO required for waste water treatment.

Consumption figures per ton CaF_2 100%, estimated:

Thermal energy	2.300 MJ (550 000 kcal)
Electric power	130 kWh
Water	10 m^3

Summary

The production of CaF_2 from H_2SiF_6 by the process described constitutes a simple, non-polluting and economical way to utilize the H_2SiF_6. The capital expenditure is relatively low, the process being reasonably simple. The synthetic fluor-spar can be used for the production of HF and by the steel industry. On the other hand, if it cannot be put to immediate use, it constitutes a means of storing fluorides without causing pollution.