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### THE EVOLUTION OF FLUORINE IN THE COURSE OF SUPERPHOSPHATE MANUFACTURE.

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At the 1955 Technical Meetings of the I.S.M.A. held in Aarhus, M. H. Delomenie presented a very interesting paper on the evolution of fluorine during the manufacture of superphosphate. In particular, he showed that the reactions gave rise to three categories of fluorine derivatives:-

- 1) Volatile derivatives ( $\text{SiF}_4$  and HF)
- 2) Soluble derivatives ( $\text{H}_2\text{SiF}_6$  and its salts)
- 3) Insoluble calcium fluoride, made up partly of unattacked fluorine and partly of re-precipitated salt.

The author also studied the influence of different factors on the liberation and solubilization of fluorine and used as test the corresponding incidence found in the consumption of sulphuric acid.

After reading this paper, we wondered if it would be possible to determine still more accurately the mechanisms which could explain the formation of certain fluorine derivatives rather than others. With this object in mind, and in order to assemble evidence for a possible theory, we conducted a number of additional experiments in the laboratory which we have described below.

#### Operating conditions.

The experiments were carried out using a Moroccan phosphate the analysis of which was as follows:-

$\text{P}_2\text{O}_5\%$	33.45	$\text{SiO}_2\%$	1.80
$\text{CO}_2\%$	4.07	F/ $\text{P}_2\text{O}_5$	0.119
F%	4.0	Fineness:	76% passed through a 0.08 mm. sieve.

The mixing of 200 gm. of phosphate and the corresponding quantity of acid was done by hand either in a narrow vessel which could be closed with a lid, or in an open tray.

After each experiment the total fluorine and the water-soluble fluorine were determined in the product obtained: the water-soluble

fluorine had been separated by means of the technique used to extract water-soluble  $P_2O_5$ . The fluorine was determined by distilling as fluosilicic acid, followed by titration with thoriu

#### The Effect of ventilation.

Two experiments were carried out with the same quantity of acid at the same concentration, one in the practically closed vessel the other in the open tray, and mixed for a long period. The analytical results were as follows:

Experiment No.	1	2
Operating conditions	closed vessel	open tray with ventilation
Conc. Sulphuric Acid ( $H_2SO_4$ %)	65.7	65.7
$H_2SO_4$ (% of phosphate)	65.7	65.7.
% of $H_2O$ in super obtained	16.2	14.15
% of fluorine liberated	0	9.2
% " " solubilised	41.5	46.8
% " insoluble fluorine	59.5	44.0

Ventilation during mixing therefore increases both the liberation and the solubilisation of the fluorine.

#### The Effect of the method of introducing acid and phosphate.

In the fourth experiment, the phosphate was added in four consecutive, equal parts, so that the attack of the first parts occurred in a fluid and concentrated mixture of  $H_2SO_4$ . In the fifth experiment, on the contrary, we began by adding 32% of water to the phosphate, then following that, 67.6% of 99.5% sulphuric acid and also 15% of water to compensate for evaporation due to the dilution of the acid. In this way the liquid phase of the reaction mixture had a much lower  $H_2SO_4$  concentration than in the previous experiment.

The results are given here alongside those of experiment No.

Experiment No.	2	4	5
% $H_2O$ of super obtained	14.15	14.25	10.2
% of fluorine liberated	9.2	10.1	4.7
% " " solubilised	46.8	34.4	41.5
% " insoluble fluorine	44.0	55.5	53.8

The progressive addition of acid to a diluted mixture reduces both the liberated fluorine and the soluble fluorine, while the consecutive addition of phosphate increases the first slightly and reduces the second appreciably.

#### The Effect of adding Boric Acid.

In experiment No. 3, which was carried out under the same conditions as experiment No. 2, 5% boric acid was added to the phosphate, which would give the hydrofluoric acid volatile boron fluoride  $BF_3$  and borofluoric acid  $BF_4$  or its salts, which remain dissolved. The comparative results are as follows:

Experiment No.	2	3
% $H_2O$ of super obtained	14.15	13.55
% of fluorine liberated	9.2	18.9
% " " solubilised	46.8	53.0
% " insoluble fluorine	44.0	28.1

An increase in the amount of fluorine liberated and solubilised can be seen.

Simultaneous effect of factors favouring both the formation and the liberation of SiF<sub>4</sub>.

We tried to liberate all the fluorine contained in the phosphate using the following factors:

- Addition of silica (precipitated dried silica or kieselguhr)
- Successive addition of phosphate
- Concentration of the sulphuric acid
- Quantity of the sulphuric acid.

We compare the results with those of experiment No. 2.

Experiment No.	2	6	10	9
Concentration of acid (% of H <sub>2</sub> SO <sub>4</sub> )	65.7	69.0	75	78.9
H <sub>2</sub> SO <sub>4</sub> (% of phosphate)	65.7	65.7	69	69
% of material added to phosphate	nil	5% of porous silica N.D.A.	1.6% of precipitated dried silica	2.5% of precipitated dried silica
Operating conditions			Added to acid. Phosphate added in 3 parts, (1/4, 1/4, 1/2)	Added to acid. Phosphate added in 3 parts, (1/4, 1/4, 1/2)
% H <sub>2</sub> O of super obtained	14.15	9.35	9.75	5.85
% of fluorine liberated	9.2	23.2	40.3	66.5
% " " solubilised	46.8	44.6	34.1	18.3
% insoluble fluorine	44.0	32.2	25.6	12.2

The addition of silica and the use of excess acid at an unusually high concentration thus bring about a considerable liberation of SiF<sub>4</sub>. There remains nevertheless, an appreciable quantity of insoluble calcium fluoride.

Comparison between the behaviour of phosphate rock and a "synthetic" phosphate rock made from pure products.

In experiment No. 11 we treated with sulphuric acid, using the same conditions as for experiment No. 9, a mixture of pure products Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, CaF<sub>2</sub>, CaCO<sub>3</sub>, SiO<sub>2</sub> (3% of precipitated dried silica reproducing apart from an excess of silica, the composition of the natural phosphate rock used previously. The results are as follows:-

Experiment No.	9	11
% H <sub>2</sub> O of super. obtained	5.85	3.65
% of fluorine liberated	66.5	12.9
% " " solubilised	18.3	8
% " insoluble fluorine	12.2	79.1

Although precipitated calcium fluoride was used in experiment No. 11, it appears to be much less reactive than the fluorine compounds contained in the phosphate rock.

The Effect of drying.

Finally we examined how the fluorine was distributed when superphosphate was dried moderately and intensively. The results with four of the products previously obtained are given below:-

<u>Super No. 1.</u>	% of H <sub>2</sub> O in super	% of fluorine liberated	% of fluorine solubilised	% of insol. fluorine
Before drying	16.2	0	41.5	58.5
After moderate drying	8.42	0	40.5	59.5
After intense "	2.95	22	29.6	48.4
<u>Super No. 2.</u>				
Before drying	14.15	9.2	46.8	44.0
After moderate drying	7.8	22.9	28.4	48.7
After intense "	1.3	30.8	21.0	48.2
<u>Super No. 10. (SiO<sub>2</sub> added)</u>				
Before drying	9.75	40.3	34.1	25.6
After moderate drying	4.1	53.3	19.7	27.0
<u>Super No. 3 (H<sub>3</sub>BO<sub>3</sub> added)</u>				
Before drying	13.55	18.9	53.0	28.1
After intense drying	1.95	48.8	30.9	20.3

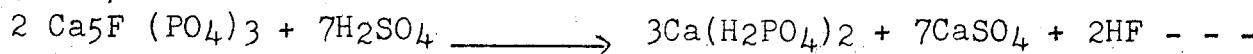
It appears that drying considerably increases the liberation of fluorine and reduces the soluble portion, while the insoluble portion at first increases and then decreases to an appreciable extent.

Interpretation of Results.

In order to find a comparative basis for the results of the previous tests, in spite of their very diverse natures, we decided to consider the following explanatory scheme:

(1) The fluorine contained in phosphate rock occurs in two distinct forms, each of which behaves in an entirely different way when treated with sulphuric acid.

The larger part (74.6% in the phosphate used in the above experiments) occurs as apatite Ca<sub>5</sub>F(PO<sub>4</sub>)<sub>3</sub>. The solubilisation by sulphuric acid of the P<sub>2</sub>O<sub>5</sub> in the latter, which is the actual basis for the manufacture of superphosphate, results in a temporary generation of hydrofluoric acid.



The other part of the fluorine (24.4%) is present as calcium fluoride. This latter is practically never attacked in normal conditions of superphosphate manufacture. It is known that the following reaction

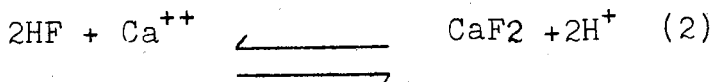


requires a hot and concentrated acid for its completion. Nevertheless this reaction is facilitated by the presence of silica

Thus it is possible to explain the considerable difference between the percentage of fluorine liberated and solubilised in experiments No. 9 (with phosphate rock) and No. 11 (with "synthetic phosphate rock") which were carried out with an excess of silica and an acid of unusually high concentration. We can also understand why the proportion of insoluble fluorine remains just little higher than 24.4%, although coming very close to it when using an acid of a normal concentration, provided we prevent, to

an appreciable extent, the re-precipitation of calcium fluoride by adding boric acid (experiment No. 3) or silica (experiment Nos. 6 and 10).

(2) What happens to the hydrofluoric acid which is set free by the reaction (1)? It is certainly not possible for it to escape as such into the gases. In fact, on the one hand, it is very soluble, and, on the other hand, it occurs in the presence of a considerable quantity of calcium ions, causing the following reversible reaction:-



By reason of the pronounced insolubility of calcium fluoride, even in acid solutions, one can assert that, in normal conditions of superphosphate manufacture, in the absence of silica, the whole of the fluorine of the apatite would be precipitated in an insoluble state.

The presence of silica will greatly modify the phenomena. Two reversible reactions will be superimposed on the previous one:



$\text{SiF}_4$  is a gas which distils, while  $\text{H}_2\text{SiF}_6$  occurs in a dissolved state in the liquid phase.

In what relative proportions will the hydrofluoric acid be distributed according to the reactions (2), (3) and (4) as it is successively liberated by the progress of reaction (1)? At first sight, it might be thought that it is almost entirely converted to insoluble calcium fluoride. There is, in fact, a disproportion between the quantities of calcium and silica which are usually present in a phosphate (30 molecules of  $\text{CaO}$  for one of  $\text{SiO}_2$  in a Moroccan phosphate).

In actual practice matters are different. If calcium fluoride is precipitated it is, nevertheless, present in the reacting mixture, while the silicon tetrafluoride is liable to disappear completely, either by being liberated, or by transformation to fluosilicic acid by reaction (4). According to the Law of Mass Action, it is normal that reaction (3) in the direction from left to right could be the most important, if not the only reaction, given certain favourable conditions.

Let us try to analyse the influence of several factors on the formation of different fluorine compounds.

- (a) the presence of the excess of "attackable" silica obviously facilitates the formation of  $\text{SiF}_4$  and  $\text{H}_2\text{SiF}_6$  at the expense of  $\text{CaF}_2$ . It will be noted that only part of the silica in the phosphate is likely to react and that it is present in Moroccan phosphate in small quantities compared with fluoro apatite.
- (b) High acidity and high temperature in the liquid phase, obtained, for example, by using a hot and concentrated sulphuric acid, favour the generation of  $\text{SiF}_4$ . In these conditions the speed of reaction (2) is very slow, even its direction may be reversed and the initial free calcium fluoride may be attacked, as in experiment No. 9. With regard to the reaction (4) it is obvious that the equilibrium concentration of  $\text{H}_2\text{SiF}_6$  in the liquid phase, which increases with the pressure of  $\text{SiF}_4$  in the gaseous phase, decreases with the temperature and acidity of the mixture.

The total quantity of  $H_2SiF_6$  formed, being equal to the product of its concentration by the mass in the liquid phase being related to the total quantity of water present, it can be easily seen that in the conditions under consideration little fluosilicic acid is formed.

- (c) The fluidity of the reaction mixture, strong mixing and good ventilation also favour the evolution of  $SiF_4$ . In the opposite conditions a pressure of this gas develops in the interior of the mass which opposes the reaction (3) and which favours both reactions (2) and (4). This is especially the case in continuous dens, where the superphosphate is obtained in thick layers.

Conditions of acidity and fluidity favourable to the evolution of silicon tetrafluoride only occur during the first instants of superphosphate manufacture, which explains why only small quantities are obtained industrially.

What happens when superphosphate is dried? In the liquid phase there is produced a concentration of residual free phosphoric acid and fluosilicic acid which causes the latter to be dissociated:



HF is converted to  $SiF_4$  and at the beginning a simultaneous increase is observed in the amount of fluorine liberated and of insoluble fluorine at the expense of soluble fluorine, and this was verified when the samples used in experiments Nos. 2 and 10 were moderately dried. If the drying is continued, the acid concentration in the liquid phase reaches such a degree that the precipitated calcium fluoride is attacked and at the same time the dissociation of  $H_2SiF_6$  continues, which results in the increase of liberated fluorine and a simultaneous decrease in the soluble and insoluble fractions (cf. intense drying of samples 1, 2 and 3).

### CONCLUSIONS.

The complex conversions which give rise to the fluorine derivatives during the manufacture of superphosphate become more comprehensible if we realise that, in the initial phosphate the fluoride occurs in two distinct combinations, free calcium fluoride and apatite, which are affected by the sulphuric acid attack to different extents.

Our laboratory experiments have shown that, by adding silica, the evolution and solubilisation of fluorine can be considerably increased. This fact, if it can be proved in industrial production, could be of interest to manufacturers of superphosphate who recover fluorine as sodium fluosilicate. It should be particularly noted that during the washing of hydrated silica with water, gases containing  $SiF_4$  are precipitated. In order to effect this, the best process would doubtless be to disperse the silica suspended in the sulphuric acid.

### SUMMARY.

The mechanism of the reactions which concern fluorine during the manufacture of superphosphate was up to the present something of a mystery. In the very comprehensive paper presented to the last Conference of the I.S.M.A., Mr. Delomenie pointed out that the insoluble calcium fluoride found in superphosphate was not principally unattacked calcium fluoride, but that it was mainly formed as a result of a series of simple or complex reactions.