International
Fertilizer Industry
Association

ISMA[*] Technical Conference

Sandefjord, Norway
8-11 September 1970

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[*] *In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

THE CONCENTRATION OF PHOSPHORIC ACID
POSSIBLE VARIATIONS IN THE DESIGN OF THE FORCED-CIRCULATION VACUUM EVAPORATORS

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1. INTRODUCTION

The production of wet process phosphoric acid has undergone tremendous development in the last ten years, particularly as a result of the growing vogue for high-grade fertilisers based on triple superphosphate and ammonium phosphates.

Such a development required considerable technical progress not only in the reaction and filtration stations, but also in the process used for concentrating phosphoric acid. This operation has long been considered as one of the most troublesome in the chemical industry, partly because of the very corrosive nature of the fluid and of the vapours which are evolved, partly because of the precipitation of impurities on the walls and the heating surfaces, and finally, because of the problems of atmospheric pollution. Various processes have been developed to overcome these difficulties - in particular, concentration in a tower by hot gases, direct heating by submerged combustion, vacuum evaporators with both internal circulation by thermosyphon and external circulation through a thickener or an agitated tank (1, 3), falling film vacuum evaporators, and finally, forced circulation vacuum evaporators.

This last method has ultimately prevailed and is used in all recent installations of large capacity.

The success of forced circulation vacuum evaporators is due to a number of reasons :

- the avoidance of any atmospheric pollution

- the use, as heating agent, of the low pressure steam - generally free - provided by the adjacent sulphuric acid plant
- the low temperatures, which reduce the problems of corrosion
- the very small losses of P_2O_5
- the high operating factor as a result of the progress achieved in the prevention of build-up and scaling
- the high unit production capacity with a low space requirement.

This process has been put into effect in various forms, distinguished by the type of heat exchanger used, by the pressure of the heating system, by the recirculation rate and by the materials used. It is these variants which we intend to review. For the sake of clarity, let us begin by recalling some theoretical points.

2. THEORETICAL STUDY

A) Thermal balance

According to the heat of formation of pure phosphoric acid (11, p. 50), the concentration of this acid from 32.6% up to 57.9% P_2O_5 absorbs a quantity of heat equal to :

$$308.01 - 306.00 = 2.01 \text{ kcal per mol g } H_3PO_4$$

or 28.3 kcal per kg P_2O_5.

This roughly corresponds to the concentration of an impure wet process phosphoric acid from 30 up to 54% P_2O_5. Leaving out the release of Si F_4 and HF, this means that per ton of evaporated water we use 0.675 t of P_2O_5 in the form of 2.25 t 30% acid and we obtain 1.25 t 54% acid.

Assuming that boiling is carried out at 80° C under an absolute pressure of approximately 70-75 mm Hg, the thermal balance of the evaporation is established as follows :

OUTPUT	K. calories	
- Phosphoric acid at 54% P_2O_5, 80° C	1250 x 0.52 x 80 =	52,000
- Water vapour released at 80°	1000 x 631 =	631,000
- Heat of concentration	675 x 28.3 =	19,100
- Heating losses (example)		35,500
	TOTAL ...	737,600

INPUT		K. calories
- Phosphoric acid at 30% P_2O_5, 50° C	2250 x 0.69 x 50 =	77,600
- Quantity of heat to be provided	q =	660,000
	TOTAL ...	737,600

It is easy to see that per ton of evaporated water, the quantity of heat to be provided (q) is not greatly affected by the variations in the initial and final concentrations of the acid.

B) Heating surface required

Let :

E = evaporating capacity, in tons of water per hour

Q = q E the quantity of heat to be provided, in kcalories

T = the condensation temperature of the steam (°C)

t = average temperature of the acid circulating in the exchanger (°C)

K = over-all heat-transfer coefficient in $kcal/m^2 x h x ^\circ C$

S = required area of heating surface in m^2 (acid side)

Then :

$$S = \frac{Q}{K(T-t)} = \frac{q\ E}{K(T-t)}\ m^2$$

C) Circulation rate required

Let :

d = the internal diameter of the exchanger tubes (m)

L = the serviceable length of the tubes (m)

v = the velocity desired for the acid in the tubes (m/sec).

The number (n) of tubes in the exchanger is equal to :

$$n = \frac{S}{\pi\ L\ d}$$

The required circulation rate V in m^3/h is equal to :

$$V = 3{,}600\ n\ \pi\ v\ \frac{d^2}{4} = 900\ S\ v\ \frac{d}{L} = 900\ \frac{Q}{K\ (T-t)}\ v\ \frac{d}{L}\ m^3/h$$

When the evaporating capacity and the velocity of the acid are constant, the flow-rate of the recirculation pump varies :

- in proportion to the diameter of the tubes,
- in inverse ratio to their length, and to the mean temperature difference between steam and acid.

Note : We must remember that the over-all heat-transfer coefficient K is itself a function of v, of d, and to a smaller extent of T-t. According to the empirical study of Fragen and Badger (13), at a specified viscosity one would obtain the following formula :

$$K = k \frac{d^{0.57} v^{\frac{1.1}{L}}}{(T-t)^{0.1}} \qquad \text{(k being a constant)}$$

which would yield, for the recirculation rate :

$$V = k' \frac{Q}{(T-t)^{0.9}} v^{(1-\frac{1.1}{L})} \frac{d^{0.43}}{L}$$

However, we must be careful when applying these formulae to graphite exchangers heating phosphoric acid. It is more reliable to determine coefficient K directly in the existing installations.

D) Temperature rise of the acid on passing through the exchanger and resulting increase in concentration

These two factors are generally considered important in controlling the crystallisation of the salts dissolved in the acid, so as to avoid scaling.

Let :

m = the density of the acid entering the exchanger (mixture of the diluted feed acid and of the recycled concentrated acid) in g/cc.

c = the specific heat of the same acid in cal/g/°C

C_o= its concentration in P_2O_5 (mass ratio P_2O_5:acid)

t_o= temperature of the acid when entering the exchanger

t_1= temperature of the acid when leaving the exchanger

With each passage through the exchanger the acid is heated by :

$$t_1 - t_o = \frac{Q}{1{,}000\ Vmc} = \frac{K\ (T-t)\ L}{9 \times 10^5\ vmcd} \quad {}^{o}C$$

Inversely, if we know v, T, t_o and t_1, we can calculate the over-all heat-transfer coefficient K by the formula :

$$K = 9.10^5.v.m.c\,\frac{d}{L}.\,\frac{t_1-t_o}{T-t}\ \text{kcalories/m}^2.\text{h.}^\circ\text{C}$$

After flashing in the vapour head the P_2O_5 concentration of the acid becomes :

$$C_1 = \frac{Vm\ Co}{Vm-e}$$

This is the concentration of the evaporated acid. We deduce from this :

$$C_o = C_1\ (1 - \frac{E}{Vm})$$

$$C_1 - C_o = \frac{C_1 E}{Vm}$$

During passage through the flash chamber, the evaporation of each kg water absorbs approximately 551 kcal of the 660 furnished in all.

The corresponding cooling is shown roughly by the following formula, the boiling temperature being represented by t_e :

$$\frac{t_1-t_e}{t_1-t_o} = \frac{551}{660} = \frac{5}{6}\ \text{therefore}\ t_e = t_o + \frac{1}{6}\ (t_1-t_o) = t_o + \frac{1}{3}\ (t-t_o)$$

The boiling temperature is therefore found between the temperature of the acid when entering the exchanger (t_o) and its average temperature (t) in the same exchanger.

E) Examples of numerical applications

To consolidate these ideas, we show in the Table below the characteristics of the exchanger in 16 different hypothetical situations with a constant evaporating capacity equal to 10 tons of water per hour (i.e., 6.75 t/h. or approximately 160 t/d. P_2O_5 concentrated from 30% to 54%).

The lower half of the Table corresponds to a tube length of 9 metres, which could be obtained in practice, by installing two exchangers of L = 4.50 in series or by setting up a three-pass exchanger of 3 m. length between plates, the total number of tubes then being three times the number indicated.

When setting up the Table we assumed that the average temperature of the acid in the exchanger was in all cases maintained at 80° C by suitable adjustment of the absolute pressure between 60 - 75 mm Hg.

We note that the required heating surface and the rate of the recirculation pump vary very widely in accordance with the steam pressure used, the diameter and length of the tubes, and the velocity of the acid (in a 1 to 4 ratio for the surface and a 1 to 12 ratio for the rate). There is no obvious economical solution, however, since we must take account not only of the energy required for pumping, but mainly of the risk of deposition of the precipitated salts on the exchange surfaces - a greater or lesser risk according to the operating conditions chosen and the origin of the rock used for the production of phosphoric acid.

Table I - THEORETICAL CHARACTERISTICS OF THE EXCHANGER IN VARIOUS HYPOTHETICAL SITUATIONS

Constant parameters :

Evaporating capacity : 10 t/h water

Feed phosphoric acid : P_2O_5 % : 30 Rate : 22.5 t/h
17 m^3/h
density : m : 1.32 g/cc

Evaporated phosphoric acid : P_2O_5 % : 54 Rate : 12.5 t/h
7.8 m^3/h
density : m : 1.60 g/cc
spec. heat : c : 0.52 cal/g.°C

Mean temperature of the acid in the exchanger : 80° C

Velocity of the acid	v = 2 m/sec.				v = 3 m/sec.			
Over-all heat-transfer coefficient	K=800 kcal/m^2.h.°C				K=1000 kcal/m^2.h.°C			
Steam : gauge pressure	0 kg/cm^2		4 kg/cm^2		0 kg/cm^2		4 kg/cm^2	
Temperature °C	100		150		100		150	
Heating surface acid side m^2	412		118		330		94.5	
Inside diameter of tubes mm	19	38	19	38	19	38	19	38

Table I (cont)

	Length of tubes : 6 metres							
Number of tubes n	1150	575	330	165	920	460	264	132
Cross sectional area inside tubes dm^2	32.6	65.2	9.35	18.7	26.1	52.15	7.48	14.96
Circulation rate m^3/h	2350	4700	672	1345	2820	5640	805	1610
Temp. rise of the acid °C	3.4	1.7	11.8	5.9	2.8	1.4	9.9	4.9
Increase of the P_2O_5 % content	0.14	0.07	0.5	0.25	0.12	0.06	0.42	0.21
	Length of tubes : 9 metres							
Number of tubes n	768	384	220	110	614	307	176	88
Cross sectional area inside tubes dm^2	21.8	43.6	6.25	12.5	17.4	34.8	5.0	9.97
Circulation rate m^3/h	1570	3140	450	900	1880	3760	537	1074
Temp. rise of the acid °C	5.1	2.5	17.6	8.8	4.2	2.1	14.8	7.4
Increase of the P_2O_5 % content	0.21	0.11	0.75	0.37	0.18	0.09	0.63	0.31

3. PREVENTION OF SCALING

The principal methods used to combat the build-up of scale on the internal surfaces of the evaporators, particularly inside the exchanger tubes, have been repeatedly described by various investigators (1, 2, 3, 4, 5, 6, 10).

They may be summarised as follows :

1) Place the exchanger under an adequate hydrostatic head.
2) Mix the feed diluted phosphoric acid with a large quantity of concentrated acid before passage through the exchanger.
3) Limit to a low value the difference in temperature between the steam and the phosphoric acid in the exchanger.
4) Make the acid in the exchanger tubes circulate at high speed.
5) Limit to only a few degrees the temperature rise of the acid with each passage through the exchanger, so that the increase in P_2O_5 concentration for each cycle is below 2%.
6) Maintain an adequate solids content in the circulating acid.
7) Include in the circuit of the evaporator a capacity aimed at promoting crystallisation.

The purpose of principles 1, 2 and 3 is essentially to prevent the boiling of the phosphoric acid within the exchanger tubes.

The purpose of principle 4 is to prevent the precipitation of solids on the walls, while improving the coefficient of heat transfer.

The purpose of the three final principles (5, 6 and 7) is essentially to control the supersaturation of the acid by dissolved salts, so as to avoid the development of an excessive number of nuclei and to promote the formation of large crystals which do not adhere to the walls and are ultimately more readily eliminated.

We immediately note that some of these principles are not independent. For example, the demand for a high velocity in the exchanger tubes necessarily entails mixing of the diluted acid with a large supply of recycled concentrated acid, as well as a small increase in the temperature rise and a small concentration increase during each pass through the exchanger. This results from the formulae established in the foregoing section.

Only principles 1, 3, 4, 6 and 7 are truly independent.

There is no doubt that simultaneous observation of all these rules will promote good operation. However, it must be noted that some principles, particularly Nos. 3 and 7, involve a not insignificant increase in the cost of the installation ; it is therefore normal for us to consider the relative value of these different principles.

a) Hydrostatic head in the exchanger

For pure phosphoric acid with 58% P_2O_5, which corresponds roughly to a wet process impure acid with 52 to 54% P_2O_5, the vapour pressure is as follows in relation to the temperature (11, p. 45) :

Temperature °C	80	85	90	95	100
Pressure mm Hg	74	95	118	143	170

If with each pass through the exchanger the acid is heated by 5° in the vicinity of 80° C, it is sufficient to establish a hydrostatic head equal to :

$$\frac{21 \times 13.6}{1000 \times 1.6} = 0.18 \text{ m fluid column}$$

at the highest point of the exchanger to prevent flashing during normal operation.

However, it is theoretically desirable (6) to have a sufficient hydrostatic pressure to prevent boiling of the acid even at the temperature of the heating steam, because - were the inlet of a tube blocked by a piece of scale - flashing without circulation would result in complete plugging. This requirement entails a much higher hydrostatic head than that calculated above.

If heating is carried out by means of steam at atmospheric pressure (100°), the required height of the fluid column becomes (assuming a boiling point of 80° C) :

$$\frac{(170 - 74) \times 13.6}{1000 \times 1.6} = 0.816 \text{ metres}$$

In practice this does not present any difficulty, particularly if we take into consideration the pressure drop by friction between the exchanger and the evaporation chamber.

The same does not hold true if we use a higher steam pressure, as for example 4 kg/cm^2 eff. (150° C).

According to the Dühring line, with vapour pressures according to (11) p. 45 and (12) p. 140, pure phosphoric acid with 58% P_2O_5 heated to this temperature has a vapour pressure of approximately 850 mm Hg. To avoid flashing at this temperature, the height of the fluid column must be equal to:

$$\frac{(850 - 74) \times 13.6}{1000 \times 1.6} = 6.60 \text{ metres}$$

If the exchanger has been installed vertically it would be expensive to set the flash chamber this high, particularly as this would involve the risk of problems with the circulation pump seal. The use of a horizontal exchanger is more rational, but although it has its followers (5, pp. 250-251), this arrangement is rarely used.

Another possible solution involves the formation of a constriction between the exchanger outlet and the inlet into the expansion chamber, so as to obtain the required overpressure ; this can be done by setting in an orifice plate or a valve, for example.

The disadvantage of such a device is that it increases the pumping energy and, on the basis of our experience, its practical significance appears doubtful. It seems preferable to use all of the power available from the pump motor to increase the recirculation rate. Of course we must absolutely prevent pieces of scale from obstructing the tube inlets, for example, this can be done by placing a filter with large holes up-stream from the exchanger.

Experience has also shown us that even with a strong pressure on the acid side of the exchanger, scaling of the tubes cannot be avoided if the velocity of the acid is inadequate.

In view of this, we may conclude that a certain hydrostatic charge in the exchanger is a precaution which is probably useful, but is certainly insufficient in itself to prevent build-up and scaling.

b) Steam pressure

The steam pressure within the calandria directly controls the temperature difference between the saturated steam and the acid. For example, if the mean temperature of the latter is 80° C, the following differences are found :

Steam gauge pressure, kg/cm^2	0	1	2	3	4	6	8
Temperature difference T-t	20°	39°	53°	63°	71°	84°	90°

The required transfer surface may thus vary in an approximate ratio of 1 to 4, depending on the pressure of the steam admitted.

If low pressure steam from a steam turbine is available (used, for example, to drive the blower of a sulphuric acid plant), we are certainly justified in giving priority to the use of this steam. However, in practice it is very rare that steam is transported in a factory at a pressure of less than 3-4 kg/cm^2. Moreover, it is entirely possible to set up steam turbines functioning at a much higher counter-pressure (8 to 16 kg/cm^2).

It therefore appears that numerous plants operate with a very low steam pressure in the calandria (atmospheric pressure, and sometimes less) for an entirely different reason : it is probably due to the fear of local flashing points inside the tubes and the resulting scaling. Our own experience does not confirm these fears. With the rock phosphates which we usually use we have observed no appreciable difference in the scaling rate in relation to the steam pressure, and we commonly use a gauge pressure between 3 and 4 kg/cm^2.

It may be that other phosphates give a different result.

In exchangers with tubes made of Karbate, the use of low pressure steam might be justified because of the fragility of the tubes.

The heat released by the condensation of the steam decreases with its pressure : 503 kcal/kg for the steam at 4 kg/cm^2 gauge pressure compared to 539 kcal for the steam at atmospheric pressure. However, it is easy to recover the latent heat of the condensate (or of the vapour which it releases by flashing at atmospheric pressure) by using it either in a separate compartment of the exchanger, or to heat the water used for washing the gypsum cake on the filter. In this way the total steam consumption is independent of the pressure at which it is used.

c) Velocity of the acid in the tubes

It is generally thought that the velocity of the acid in the tubes is certainly a prevailing factor in the battle against scaling. In our own industrial trials we have found that whatever other precautions are taken, it is impossible to avoid rapid scaling and blockages if the velocity of the acid in the tubes is less than 1.5 m/sec.

S.M. Janikowski (5, p. 251) recommends the choice of the highest velocity which does not lead to abrasion of the tube walls, despite the high pressure drop which requires the use of centrifugal pumps. Indeed, it is obvious that if erosion began at a certain exact velocity, the use of this specific velocity would suffice to prevent all difficulties, since where there is erosion, there can be no scaling - and as soon as the diameter of the tube had increased slightly, the erosion would stop because of the reduction in velocity.

However, the reality is unfortunately somewhat more complex.

There is scarcely any indication in the literature of the velocities used in the exchangers made of impervious graphite. F.W. Edwards (4, p. 46) mentions a velocity of 7 to 8 ft/sec (2.13 to 2.44 m/sec) and states that he observed no erosion under these conditions.

It would seem that a velocity of the same order is used in most industrial installations.

There is one important factor which technical papers relating to multitubular exchangers generally do not mention : the inequality of the velocity of the liquid in the various tubes. For example, if the feed is axial, the velocity is greater in the centre tubes than in the peripheral tubes. If the feed is lateral, the velocity is greater in the tubes on the side opposite the feed. In practice it is very difficult to know the true velocities obtained in the various tubes, and this is probably the reason for the frequently observed differences in scaling of the tubes in relation to their position in the exchanger. This also explains the difficulty in obtaining by theoretical calculation a transfer coefficient in agreement with experience.

To obtain a uniform velocity in the tubes is not a simple problem since upstream and downstream from the exchanger there are necessarily bends and changes of section which create turbulences interfering with good distribution. If a better solution to this problem were found, the average circulation velocity of the acid might perhaps be reduced without disadvantage.

Must we, on the contrary, go further in the direction of high velocities ?

The hesitation of equipment manufacturers and of users in view of the risk of erosion and the increase in motive power is understandable, but if successful, such an option would allow a reduction in the investments.

d) Control of the crystallisation of impurities

When we first designed forced circulation vacuum evaporators in 1961, we decided on the installation of an agitated tank in which the diluted feed acid was mixed with the recycled concentrated acid before passing through the exchanger. The aim was to reduce the supersaturation of the acid and to promote the precipitation of the impurities ($CaSO_4$, Na_2SiF_6, K_2SiF_6) on the pre-existing crystals so as to reduce the risk of precipitation within the exchanger.

In subsequent installations we omitted this crystallisation tank, which increased the investment and the pumping energy.

In the new version, the flash chamber, which is provided with an overflow for the evacuation of the concentrated acid produced, retains a large volume of acid, whereas in the previous version, this chamber acted simply as a separator and remained virtually empty. We have estimated that the hold-up created in this manner would be sufficient to decrease supersaturation.

We did not observe, in fact, any difference either in the dimensions of the crystals or in the sealing rate of the exchanger. It must be stated we simultaneously increased the velocity of acid inside the tubes.

Other manufacturers have followed a similar course (4, p. 28).

Recently the idea of a crystallisation zone has been taken up again in a much more advanced design by a manufacturer specialising in the construction of crystallisers of the "OSLO KRYSTAL" type (5, pp. 627-634 and 10, p. 28, pp. 31-32). Several high-capacity units have been built, particularly in the United States, and have been successfully put into operation. For example, in an installation in Florida where the concentration of phosphoric acid is carried out in three stages from 29% to 52.5/54% P_2O_5, the regular schedule for boil wash-out is as follows :

1st stage : 14 days (product : 34/35% P_2O_5)
2nd stage : 21 days (product : 42% ")
3rd stage : 28 days (product : 52.5/54% ")

This result is excellent.

However, the following points may be made :

- complete avoidance of regular wash-out, which was the initial aim, was not possible.
- evaporation is carried out in three stages, which decreases the risks of scaling, as will be seen in the following section.
- heating is carried out by means of steam at atmospheric pressure (100°), the temperature difference between steam and acid is small (18° C), recirculation is intense, the velocity of the acid in the tubes is 7 to 8 ft/sec. (2.13 to 2.44 m/sec.), the heating of the acid with each pass through the exchanger is limited to 2.2° C.

Thus the optimal conditions for reducing the risk of deposits on the surfaces have all been met without exception. It is consequently difficult to establish what part in the success of the operation should be attributed to the crystalliser incorporated in the circuit, and to know whether the required supplementary investment (25% according to the manufacturer) is justified. Perhaps this technique should be reserved for the rock phosphates, which present particularly difficult problems.

An additional advantage of this technique is that ultimate separation of the solids from the evaporated phosphoric acid is facilitated as a result of the formation of large crystals. However, until now producers do not appear to have been successful in appreciably enlarging the precipitated fluosilicates.

Another method has recently been proposed for controlling supersaturation and the crystallisation of impurities

(5, p. 622). In this "sludge recirculation" process the diluted feed acid receives a part of the precipitate impregnated with acid, separated after evaporation in a static or centrifugal clarifier. If the solids content in the circulating acid is kept at about 10%, it is possible, as in the preceding procedure, to space out the periodic wash-out considerably.

This technique requires little extra equipment, but does increase the load on the clarification facilities and would require a slightly larger evaporator heater. The process has the advantage of great flexibility : according to the characteristics of the acid treated, one can regulate at will, or entirely omit, the recycling of solid matter. It is also possible to check accurately in each case the efficiency of the method.

This process is not applicable if clarification facilities for evaporated acid are not available, unless an additional amount of gypsum in the acid does not present a disadvantage for its final use.

e) Evaporation in several stages

It is well known that the concentration of phosphoric acid up to 36 - 40% P_2O_5 presents far fewer difficulties than concentration to 52 - 54% P_2O_5 (leaving aside corrosion). It is because of this favourable circumstance that it was originally possible to use vacuum evaporators with natural circulation obtained by thermosyphon for concentrating up to 39% P_2O_5, which is sufficient for the production of granulated triple superphosphate or diammonium phosphate.

This occurence is perhaps due to the differences in the crystalline state of calcium sulphate. Up to approximately 45% P_2O_5, this salt tends to crystallise in the form of dihydrate, and beyond this in the form of semihydrate followed by anhydrite (5, pp. 609 and 632). The rate of crystal growth varies in accordance with the different forms ; anhydrite produces much smaller crystals which adhere more readily to the surfaces. But most of the crystallisation of calcium sulphate, in a stepwise concentration, takes place below 45% P_2O_5, that is, in the first and second stages of a three-stage system.

Be that as it may, it is generally recognised that evaporation in several stages, first proposed in 1955 by Dorr-Oliver (5, p. 233), reduces scaling problems. Unfortunately, from an economic point of view this solution can only be used for large-scale production, above 250 t/d P_2O_5, or when doubling an existing unit, despite the accessory advantages which it offers (4, p. 29 ; 5, pp. 611 and 632). In particular, the water consumption can be reduced because of a lower vacuum in the first stages : for example, the water can be made to circulate in series successively in the condensers of the third stage, then of the second stage, then of the first stage.

If only one evaporator is available, concentration may be carried out in two successive stages in the same equipment, as for example first from 30 to 39%, then from 39 to 54% P_2O_5. This requires an extra storage tank for the acid of intermediate concentration, unless, as occurs in some plants, 39% P_2O_5 is normally used.

It must be noted that this process, like evaporation in several stages, is only applicable if the problem of corrosion by phosphoric acid containing 38 - 45% P_2O_5 (the zone of concentration where maximum attack occurs) has previously been resolved in a satisfactory manner.

f) Periodic wash-out of the installation

Whatever the precautions observed, there always comes a time when the heat exchange is inhibited by a film of salts deposited on the inside of the tubes. Fortunately it is generally possible to eliminate this scale by a simple wash-out with hot water. Some producers prefer to use a weak (5%) solution of H_2SO_4 or H_2SiF_6 (4, p. 28 ; 5, pp. 622, 787, 790).

Washing is carried out as follows : after complete evacuation of the phosphoric acid, the water - which is kept at a temperature of 85° C by admitting a small quantity of steam - is allowed to circulate at a high speed, generally without the use of a vacuum. The water is renewed at an output of a few cubic meters per hour only.

The wash-out schedule depends on :

- the rock used in the process of phosphoric acid production ;
- the storage conditions of the filter acid and the ageing time before evaporation ;
- the design of the unit and on the operating conditions, as seen in the preceding chapter ;
- the dimensions of the exchanger, which allows a larger or smaller reduction of the heat transfer coefficient before production is affected ;
- the organisation used.

Some producers prefer to carry out frequent wash-out two or three times a week, or even every day, for a very brief period (1 to 1½ hours) so as to avoid the risk of a thick deposit of blockages which can no longer be eliminated by simple washing with water. To avoid losses of time it is indispensable for the installation to be so set up as to allow emptying and filling in only a few minutes. Washing then becomes a routine operation in the same way as normal operation.

Other manufacturers prefer to carry out a longer wash-out (8 to 16 hours) every week, every fortnight or every month only. This is possible if the exchanger is over-powerful. However, there is a greater risk of thick scale-formation and of blockages, and mechanical cleaning, for instance with water at a very high pressure (200 kg/cm^2) is necessary from time to time.

4. RECOVERY OF FLUOSILICILIC ACID

Phosphoric acid with 30% P_2O_5 contains, in the form of fluosilicilic acid, 25% to 75% of the fluorine, present in the phosphate, depending on the origin of the rock and the operating conditions.

During concentration of the phosphoric acid, a greater or lesser part of this fluosilicilic acid is evolved :

$$H_2SiF_6 \text{ (solution)} \longrightarrow SiF_4 \text{ (gas)} + 2\ HF \text{ (gas)}$$

If the final acid contains 54% P_2O_5, the fluorine evolution attains 60% to 80% of the fluorine present in the initial acid.

Before the development of vacuum evaporators for phosphoric acid, the recovery of fluosilicilic acid was a standard operation, both during the production of the superphosphate (which releases SiF_4) and during concentration of phosphoric acid by hot gas or by submerged combustion (5, pp. 582, 587-588, 592, 599, 604, 605).

In vacuum evaporators, the problem of fluorine recovery does not differ, in principle : instead of being mixed simultaneously with air and water vapour, the fluorine gases to be extracted are simply mixed with water vapour, which rather simplifies the problem. Taking into account the low operating pressure, the volume of gas to be treated is of the same order as when concentration by hot gases is carried out.

Thus, the principle of recovery is the same : it consists of spraying the gases with a recycled solution of

H_2SiF_6, which is maintained at the desired concentration either by the addition of water, or by partial condensation of the water vapour (for example, by means of a cooler on the recirculation), or by a combination of these two means.

This process was first proposed in 1936 by a Russian investigator, I.I. Zahring (8) who, in his pilot tests on the concentration of phosphoric acid under vacuum, interposed a "hot condenser" with external recirculation by pump between the flash chamber and the final "cold condenser". The author gave detailed figures on the release of the fluorine in both his laboratory and his pilot tests. It would seem that the work of I.I. Zahring remained unknown or was forgotten, since in 1963, at these same ISMA technical meetings (7), a similar process was presented as new. A patent has even been granted in the United States and elsewhere (9).

We must admit that we ourselves knew nothing of the Russian paper when, in 1961, we designed our first unit for vacuum evaporation of phosphoric acid with fluosilicilic acid recovery. Our device was based directly on our experience in the scrubbing of the gases from superphosphate, without the problems presented by the precipitation of the silica.

When a solution containing 10-12% H_2SiF_6 is produced, a very simple gas scrubber makes it possible to obtain a high fluorine yield (about 95%). For higher concentrations it appears advisable to install several scrubbers in series, to take into account the vapour pressure of fluorine compounds (5, p. 772).

One investigator (15) has suggested that commercial fluosilicates should be produced directly in the scrubbers by spraying the vapour with a saline solution (NaCl, KCl, $BaCl_2$). This process would have the advantage of nullifying the vapour pressure of the fluorine compounds, but we do not know whether it is used industrially.

5. EQUIPMENT

A standard forced circulation vacuum-evaporator consists essentially of :

- 1 circulation loop with : 1 flash chamber
  1 or several heat exchangers
  1 or several circulation pumps
- 1 condenser
- 1 vacuum system

The following may be added as required :

- 1 entrainment separator after the flash chamber
- 1 fluorine recovery installation in one or several stages.

a) Flash chamber

This is a vessel whose lower part is occupied by the boiling acid, the vapours being evacuated through the top. All of the intermediate section acts as a vapour-liquid separator because of the relatively slow velocity of the vapours in this zone. The vessel is a vertical cylinder, frequently conical at the bottom, although a domed bottom is generally less expensive. The acid level is maintained either by an overflow device or by a level-controller.

The recirculating acid is often fed in through a tangential inlet which sets the liquid mass into motion. This way of introducing the acid allows greater thermal uniformity in the liquid and avoids scaling at this level. However, it has the disadvantage of creating acute angles in the rubber lining of the chamber, which is often one reason for the failure of this lining. Further, the relative position of the acid inlet and of the acid level are important. If the acid is fed in above the liquid or slightly below the level, two dangers may develop, depending on the velocity at which the liquid is fed in and the diameter of the chamber :

- a whirling motion of the liquid towards the top, with risk of a serious increase in P_2O_5 losses.
- the creation of a vortex in the liquid, the tail of which may reach the circulation pump and result in dispriming.

These drawbacks can be avoided by introducing the acid well below the level of the liquid, and by extending the bottom of the vessel by a cone with a slight angle at the top.

However, to decrease the height of the chamber and to avoid problems with the lining, it seems preferable to feed the recycled acid through an inlet which is perpendicular to the wall, or slightly oblique.

b) Heat exchangers

It may be said that these are now virtually all of the "tube" type.

With regard to corrosion, the most customary material is impervious graphite ; however, exchangers in stainless steel or in special alloys can still be found, the choice of these materials being, in some cases, determined by the nature of the phosphate used, or imposed by the acid concentrations required (superphosphoric acid).

There are two main types of exchangers of impervious graphite :

1) Standard tubular exchangers : graphite tubes mounted on tubular plates, one of which is floating, within a steel shell.

Disadvantages :

- These tubes are relatively fragile ; they therefore require much care during cleaning and when starting up, to avoid hydraulic shocks and vibrations.
- Should breakage of tubes occur during operation, acid may be introduced into the condensed water.

Advantages :

- It is relatively easy to plug the ends of a broken tube and to start up again after a minimum stopping period.
- This type of exchanger readily lends itself to virtually unlimited extrapolation.

2) Exchangers with graphite blocks : these are compact blocks perforated in one direction for circulation of the acid, and perforated in a perpendicular direction for circulation of the steam. All of these holes are arranged so as to minimise the distance travelled by the heat in the graphite. The blocks are piled on top of each other in such a manner that the acid moves in continuous channels, similar to the tubes of the preceding exchangers.

- Obvious advantage : this type of equipment is far less fragile than the tubular exchangers.

- Disadvantage : extrapolation is limited by the dimensions of the graphite blocks which can be produced industrially ; it appears that at present we are limited to approximately 300 m^2, whereas we can go beyond 350 m^2 with tubular exchangers.

These block exchangers are themselves of two main types :

a) the first type consists of parallelepipedal or cubic blocks, each pressed between two cast iron plates which form steam chambers. The steam chambers connect from one block to the next by an external pipe.

- Advantage : there is no internal gasket between acid and vapour, and therefore no risk of polluting the condensed water.

- Disadvantage : these blocks are compressed by stay-bars in two directions only, and the steam pressure tends to extend them in the third direction. Steam pressure is therefore limited with regard to these blocks (we generally do not exceed 4 kg/cm^2 with this type of exchanger).

b) the other type of exchanger consists of cylindrical blocks piled within a steel envelope, the space between the graphite and the wall being used for the circulation of the steam. The graphite is thus entirely under compression. The steam pressure is only limited by the temperature which can be tolerated by the resin impregnating the graphite. Some constructors go up to 15 kg/cm^2.

- Disadvantages : circular internal gaskets separate the steam from the acid, but the construction of these gaskets is now reliable.

- Advantage : the required exchange surface can be reduced considerably and more concentrated acids can easily be obtained, since the temperature of the heating steam may be higher.

  We should also note that recovery of the calories from the high-pressure condensed water is possible by flashing it at atmospheric pressure and feeding the steam thus released into a separate compartment of the same exchanger ; this reduces steam consumption.

c) <u>Circulation pumps</u>

Depending on the production capacity and the type of exchanger used, the circulation flow rate is generally between 200 and 5000 m^3/h.

The total dynamic head may vary from 4 to 5 metres of liquid column in tubular exchangers, and may reach 20 m when perforated blocks with holes of a small diameter are used. Further, to obtain an adequate circulation rate, a multipass heater is sometimes used, which reduces the output of the pump but appreciably increases the pressure drop.

This diversity of characteristics explains why two types of pump are used :

- centrifugal pumps for moderate flow-rates and relatively high heads ;

- propeller pumps for high flow-rates and low heads.

It may be said that in both cases manufacturers have succeeded in supplying reliable equipment.

The seal of centrifugal pumps may be completely pressure relieved, so it is possible to use a standard packing without any injection of water.

With propeller pumps, however, expensive double mechanical seal involving injection of water is required ; this entails a risk of introducing water into the acid, so that a water flowmeter must be mounted in the water feed to disclose any inward flow.

Note that some manufacturers install vertical centrifugal pumps.

d) Condensers

For reasons of economy and because of corrosion problems, barometric condensers are used ; their disadvantage is that they pollute water, which leads to well-known problems with regard to disposal or recycling in the plant.

In practice, every type of barometric condenser has been used : cascade type, spray type, jet type, etc. Each of these designs has its advantages and its disadvantages.

The condenser is sometimes placed directly on the top of the flash chamber. This arrangement has the advantage of a slight gain in investment and of a definite gain in space. However, it involves a risk of dilution in case of partial blockage of the barometric column of the condenser, as for example with precipitated CaF_2, or in case of a failure in the rubber lining of the bottom of the condenser.

e) Vacuum

An absolute pressure between 50 and 70 mmm Hg in the flash chamber is the general rule ; this may be obtained :

- either by means of a two stage steam jet ejector system with intercondensor ;

- or by means of a motor driven vacuum pump preferably of the water-ring type.

The choice depends on the availability of high pressure steam and the relative cost of steam and power.

With regard to the ejectors it must be remembered that their efficiency depends very greatly on the steam pressure ; one must therefore either be sure of the uniformity of this pressure, or provide for its control.

f) Entrainment separator

With a flash chamber of adequate dimensions, the P_2O_5 loss does not exceed 2 to 3/1000. However beyond nominal evaporating capacity, this loss rapidly increases. Moreover, for fluorine recovery in the form of fluosilicilic acid it may be important to avoid pollution of this acid by phosphoric acid.

In certain cases, the installation of a separator allows a considerable increase in the output of an existing unit without excessive losses, or an increase in the purity of the fluosilicilic acid.

The separator may be external to the flash chamber. Various types are used : impingement separators, cyclones, corrugated plates.

An internal cyclonic separator is sometimes placed inside the top section of the flash chamber. Mesh-type separators made of polypropylene have also been used.

g) Fluorine recovery

As previously seen, the vapour must be scrubbed with a solution of recycled fluosilicilic acid.

The equipment generally consists of an empty scrubber, irrigated by a series of sprays, of a circulation tank (hydraulic seal), and of a high-capacity pump. Like the condenser, the absorber may be either installed separately or be placed on the top of the flash chamber.

In some plants we even find the flash chamber, the fluorine absorber and the condenser on top of each other.

If, for its final use, the concentration of fluosilicilic acid must be above 15%, it is preferable to carry out recovery in several stages set up as described previously.

6. MATERIALS

Hot phosphoric acid being highly corrosive, the minimum possible of metallic materials is used in contact with the acid inside the evaporating units.

The only piece of equipment generally built of stainless steel is the circulation pump ; either alloys of the "20" class are used, or special alloys with a high chromium and molybdenum content.

However, although some evaporators have heat exchangers made of alloy 20 or Ni-o-nel (for the production of superphosphoric acid in particular) impregnated graphite has been the most commonly used material until now. It tolerates temperatures up to 200° C.

Rubber lining is used inside the other parts of the equipment. This material resists corrosion perfectly in normal operating conditions, both for phosphoric acid and fluosilicilic acid. However it has the disadvantage of a certain fragility, and it is difficult to apply, which explains the failures which frequently occur at start-up.

Finally we must mention the circulation pumps for fluosilicilic acids ; metallic alloys being rapidly corroded by this acid, either soft or hard rubber-lined steel is used, or impregnated graphite.

Recently, fibreglass-reinforced polyester has been used for the piping, the tanks under atmospheric pressure, the condensers, and even - in some cases - the flash chamber.

7. CONTROL SYSTEM

The operation of an evaporator is very steady, so that very simple controls are sufficient. However, there do exist highly automatised installations.

Usually control of product strength is obtained indirectly by controlling the absolute pressure and the liquid temperature together.

The vacuum is controlled by automatic adjustment either of an air bleed or of the flow of cooling water to the condenser, this second system allowing the minimum consumption of water.

Several different systems are used to hold the recirculating acid temperature constant and to adjust the output of the unit. The principal ones are as follows :

A) the steam pressure is maintained constant, which determines the output. The acid temperature controller adjusts the feed rate to the evaporator.

B) the quantity of steam fed to the heat evaporator is held at a fixed value which determines the evaporating rate. The acid feed-rate is controlled as in A.

C) the acid feed-rate is kept constant. The acid temperature controller operates the steam control valve to the heat exchanger.

D) the quantity of steam fed is kept constant. The level in the flash chamber is controlled by adjusting the acid feed-rate. The acid temperature controller operates the evaporated acid control valve to storage.

System D is theoretically the most satisfactory because :

- on the one hand, the evaporation rate is kept at a fixed value, which determines the P_2O_5 vesicular losses from the flash chamber.
- on the other hand, one can be certain that the product acid sent into storage is at the desired concentration, even on restarting the plant.

This system has, however, the disadvantage of being fairly complicated and expensive. In practice, on condition that a few simple precautions are observed when the installation is restarted, it is possible to obtain equally satisfactory results with the other systems. The least expensive is system A, which does not require any flowmeter and involves only two pressure controllers and a temperature controller.

It is of course possible to elaborate each of the above-mentioned systems by setting up cascade controllers. For example, in system A, instead of having the temperature controller operating the feed acid control valve directly, it may be made to adjust the set point of a feed-rate controller. Considering the large quantity of acid retained in the evaporator and of the corresponding inertia, the advantage of such sophisticated systems appears doubtful.

8. THE PECHINEY-SAINT GOBAIN PLANTS

In the last eight years, Pechiney-Saint Gobain has built (in France and abroad) some 20 phosphoric acid concentrators, with an evaporating capacity ranging between 2 and 15 t/h water per unit.

All these plants have the following characteristics in common :

- the exchangers are made of graphite blocks ;
- the steam is used at a relatively high pressure (3 to 4 kg/cm^2 gauge pressure), so as to reduce the required transfer surface ;
- the pumps are centrifugal, of entirely metallic construction (Uranus B6, cast chromium, stainless steel etc.).

Performances

Below are found performances of two PSG plants, one of which is older (built in 1963) and the second more recent (1967). We may add that plants presently under construction incorporate improvements on the plant of 1967.

Year of construction	1963	1967
Exchanger : type of blocks	cubic	cylindrical
Number of parallel exchangers	1	2
Total heating surface m^2	30	147
Acid : feed concentration product concentration	30% 50-52%	32% 52%
Evaporating capacity in t/h water	3.4	15
Electrical power in kWh/t evaporated water	50	20
Corresponding heat-transfer coefficient in kcal/h.m^2. °C	1290	1150

Wash-out down time : the schedule of periodical shut down differs in the two plants, in accordance with the locally preferred procedure :

- the older plant operates for a week without stop ; this is followed by a washing period of some 8 hours.
- in the more recent plant, taking into account the arrangements allowing rapid emptying and filling of the installation, a daily washing period of 1½ hours is preferred, so

that the installation may always be used at its maximum production capacity.

In both cases, the operating factor is above 92%.

In the new plants at present under construction, additional improvements should allow an operating factor of at least 95% (percentage of on-stream time).

Investments

For a modern PSG plant, the capital cost in France in 1970 within battery limits (excluding storage and clarification), is approximately 1.6 million francs for one concentration unit - without fluorine recovery - involving an evaporating capacity of 15 t/h water. This price does not include the process licence or the engineering costs, which, taking into account the low cost of equipment and erection represent a high percentage.

High-concentration acid

The use of graphite blocks for the exchanger has allowed us to set up installations yielding a final concentration well above 54% P_2O_5.

For our own needs we therefore have a small installation which upgrades the acid up to 61/62% P_2O_5. This installation operates strictly under the same conditions as the conventional concentration units, without any special problem.

It should be mentioned that, at present, acid strength is limited only by the temperature resistance of the rubber-lining inside the flash chamber. Were another material to be used, it would therefore be possible to get a higher strength.

9. CONCLUSIONS

The recent improvements achieved in the design of phosphoric acid evaporators up to 54% P_2O_5 and even beyond has made it possible to space out greatly the periodical washings of the equipment and to obtain a high operating factor, of the order of 95%. In certain plants, one or two monthly washings with water or with weak acid are sufficient.

Unfortunately, these results have been obtained by markedly increasing the cost of installations, because of the large transfer surfaces required (30 to 35 m^2 per t/h evaporated water), because of the high circulation flow of the acid (500 m^3 per ton of evaporated water), and because of the crystallisation chambers which have been added in some cases.

If shorter but more frequent washings (once or twice a week) are accepted, a 3 - 4 times smaller transfer surface is sufficient, and a circulation flow which is 5 - 8 times smaller. The operating factor remains high (above 90%) if the unit has been correctly designed for this purpose.

Under these conditions one may wonder whether the search for long on-stream periods is in itself justified.

It is certainly not an economical aim if the phosphoric acid is only for captive use, which reduces the requirements for ultimate purification. Insofar as expensive designs improve crystallisation of the impurities and facilitate their separation, they are perhaps justified when a large part or the totality of the acid produced must be shipped a long distance.

We have shown in this paper that a fairly large range of means is available for combating build-up and scaling. With new combinations of these means and the changing of certain parameters, we can still hope to improve performances and to space out washings in the low-cost installations with high productivity.

Progress is also possible in the field of materials. The failure of Ni-o-nel, which has now been explained (14), should not cause us to give up definitively the use of metallic exchangers.

As regards the various vessels (evaporation chambers, gas scrubbers, condensers) and the piping system, synthetic materials will one day replace rubber-lining. It is certainly still possible to leave the beaten path.

Some recent processes allow the direct manufacture of phosphoric acid with a P_2O_5 content between 40% and 50%, and the function of the evaporation station may become of lesser importance, or even dispensed with. However, these processes have only just been introduced on a commercial scale, and it is advisable to foresee eventualities or problems (blinding of filter cloth, cooling during shut-down, accidental dilution, corrosion, change of phosphate etc.) whereby an acid substantially less concentrated than required may be temporarily produced, or even whereby it is necessary to return to the conventional gypsum process. Consequently, it seems particularly advisable to choose a concentration process involving low capital cost and having enough flexibility to cope with any eventuality.

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DISCUSSION

Mr. P. MORAILLON (Péchiney-Saint Gobain) : For a long time the concentration of phosphoric acid obtained by the wet process has been considered one of the most difficult problems in the chemical industry. Long and laborious trials and errors were necessary before today's sure and reliable operation of the installations was achieved.

For a number of reasons, most phosphoric acid producers prefer the forced-circulation vacuum evaporation technique. The installation consists in the main of a large flash chamber and an external graphite exchanger heated by steam, acid circulation being provided by a high capacity pump.

Although all existing installations make use of the same principles to prevent the acid from boiling and to limit the precipitation of impurities such as calcium sulphate and sodium and potassium fluosilicates inside the exchanger tubes, there are considerable differences in the design of the equipment, depending on the importance which the designer attached to one principle or another. Most equipment consists of Karbate tubular exchangers with tubes of a fairly large diameter, i.e. 38 mm or 1½".

Steam pressure inside the exchanger is kept at a low level, around atmospheric pressure and sometimes below. In consequence it is necessary to have a large exchange surface (30 to 35 m^2 on the acid side per t/h of evaporated water) and a high circulation rate of the order of 500 m^3 per tonne of evaporated water.

When the acid is concentrated up to 54% P_2O_5, a number of evaporators are often installed in series. For these reasons the cost of the capital investment is high.

The frequency of hot water wash-outs depends on the kind of phosphate used, on the concentration of the acid produced, and on the operating conditions. When the acid obtained has a concentration of 52-54% of P_2O_5 12 to 16 hours of down time are generally allowed every 5-7 days.

It has been possible to increase considerably the time interval separating two successive wash-outs (two weeks to one month and even more), by including in the loop of the evaporator a crystallisation chamber in which the supersaturation of the acid is discharged on a crystal bed kept in suspension. Unfortunately this improvement increases the installation cost by about 25%.

The equipment installed by our company is based on an entirely different design. The exchanger consists of a pile of impregnated graphite blocks which have small diameter acid channels of diameter 16-20 mm. The effective steam pressure inside the equipment is 3 to 4 kg/cm^2 and sometimes more. In this way the necessary exchange surface is only of the order of 10 m^2 per t/h of evaporated water and the circulation rate is less than 100 m^3 per ton of evaporated water.

The investment costs are therefore substantially reduced.

Experience has shown that in these circumstances, with a judiciously chosen acid velocity in the tubes, the operating factor is the same as in the installations described previously, as long as these do not incorporate a crystalliser. As a result of current improvements we hope to improve the operating coefficient even more.

One of the advantages of this design is that it is easily possible to obtain concentrations higher than 54% P_2O_5 eg. 60 to 62%, due to a higher steam pressure.

Naturally this type of evaporator, like the others, makes easy recovery of fluorine possible in the form of fluosilicic acid in the desired concentration.

Mr. A. DAVISTER (Société de Prayon) : In introducing the excellent paper by Messrs. MORAILLON and ROUBINET I must state that the wet process for obtaining phosphoric acid remains one of the main preoccupations of fertiliser producers. Once again this time, an entire session of our Technical Meetings is devoted to it.

Two years ago, during the Brussels meeting, the emphasis was mainly on the reaction conditions between the phosphate and the sulphuric acid. This is a subject in which developments continue to be made and I am quite sure that is will reappear on the agenda of later meetings.

The filtration itself seems to be considered as a problem that has been adequately solved so that it is not of much interest. Available equipment has long been well developed and its technological improvement easily meets users needs.

It is therefore logical that in this year of 1970, our preoccupation should be with the concentration of phosphoric acid, which is normally the third operation in the production of this acid.

After a well-presented theoretical study, the authors introduce us very quickly and abruptly to the core of the problem, with the little phrase "but the economic solution is not obvious". Those of us who are concerned with phosphoric acid know that it never behaves like straight-forward liquids. It separates out dissolved salts, depositing them on everything it touches, whether warm or cold walls, in the form of removable deposits or hard scale.

This problem is dealt with very thoroughly by the authors in the section devoted to the prevention of scale. The solutions they have decided to apply to the problems raised in this section impose naturally the choice of equipment and operating techniques subsequently described.

The first question to the authors concerns the type of exchanger chosen, i.e. the one with perforated cylindrical graphite blocks.

Attracted by the robustness of this type of equipment we tried it out in 1961/62 and did not retain it, because we considered that the risk of blockage of these small channels was too great.

If you gentlemen have chosen it you must have been able to overcome this problem.

I would therefore like to ask :

1. What is the diameter of the channels which transport the acid ?
2. What is the minimum frequency of wash-out and is it dependent on the diameter of these channels ? In other words, is there a minimum frequency of wash-out as a function of the diameter of the channels, below which you cannot go without risking blocking the tubes to the point where they are no longer washed out and have to be cleaned mechanically ?
3. Which phosphates are used to obtain the phosphoric acid which you are concentrating with these exchangers ?

My second main question concerns the phosphoric acid produced and especially its content of solids. For the operator of a plant these solids are a nuisance, not only in relation to concentration but also as regards its use, and they must be reduced to less than 0.5% when acid has to be transported, even by pipe to a consumption point in the same plant. I should therefore like to ask the following questions :

1. What is the solids content of acids obtained in your anticipated concentrations without involving the possibility of separation of precipitated salts ?

2. How much time is required in order to clarify these acids to a solids content of 0.5%, which is necessary for transport or simply to prevent the dilution of the final fertiliser with the ballast of these solids ?

I would like to raise one more point in respect of your paper, namely the frequency of wash-out. Of course, in theory, frequent wash-outs, which maintain the coefficient of heat exchange at its maximum, is the ideal solution. On the other hand, from the point of view of the operator, any down time is a source of various kinds of difficulties. There is the loss of time, the risk of mishandling, the loss of calories, the risk of dilution of the acid and so on. Naturally one can limit these drawbacks by an appropriate study of the equipment and mechanisation or better still by advanced automation of the processes. But all these measures incur a cost which is probably of the same order as that of a supplementary exchange surface in anticipation of more widely spaced wash-outs.

May I therefore ask how the cost of equipment allowing rapid and reliable emptying before wash-out compares in your case with the cost of the exchanger itself ?

Mr. P. MORAILLON : As regards the first question concerning the type of exchanger selected and the difficulties encountered by Mr. DAVISTER's company in using graphite blocks or carbon blocks, when we started our first industrial trials with carbon blocks we did in fact have some trouble, as I pointed out in my text. These were due to the recommendations of the constructors who recommended a very low acid velocity. We found that whatever precautions we took to avoid boiling in the tubes there were still scaling and blockages, in spite of the fact that the solubility of all the salts which are precipitated increases with temperature. Thus this precipitation was not due to concentration within the equipment, because there was no possibility of flashing, but simply due to excessive supersaturation and to the fact that at low velocity these precipitations adhere to the tubes. We therefore increased the velocity and as soon as we reached an adequate velocity the precipitations disappeared. These velocities are no higher than those used in Karbate tube exchangers with a bigger diameter. As regards the diameter it is of the order of 16 to 20 mm, i.e. $\frac{3}{4}$".

The second question was about the minimum frequency of washing and whether this was linked to the diameter of the channels. To answer this question it would be necessary to have both types of exchangers in the same plant, working in parallel. It might be thought that if there were a tube of 38 mm diameter it might be possible to allow the scale to reach a thickness of 10 mm. There would still be an 18 mm passage but the exchange would be very poor. It might be possible to carry on for a long time but it would get worse and worse. With 20 mm tubes you must evidently not exceed a thickness of 5 mm scale and in fact we consider that this is much too much and that it is much better to take action earlier. It is much easier to get rid of scale 1/4 mm thick than several mm thick, with which there is the risk of complete blockage.

Mr. DAVISTER : I should like to put my question more precisely. The theory that you should not let scale develop is perfectly sound, but I was not talking so much about scaling as such but about the risk of blockage of the tubes by solids circulating with the acid. Solids of a certain size can develop in this acid and therefore there is a much greater danger of blocking a small tube than a large one.

Mr. MORAILLON : Naturally the risk is greater because quite large pieces might detach themselves from the evaporation chamber and these might come to block the entrance of a tube. Then there would be boiling, accumulation of fragments, then complete blockage. This risk also exists in the case of larger tubes but obviously the risk is not as great. I think that in all installations, however small or large the tubes, up stream of the exchanger you always have a filter or a strainer to catch fragments big enough to cause blocking of the exchanger tubes. In all the plants I know these may not have been provided for in the original design but the users have always installed a grill or filter of some kind.

The next question concerned the phosphates used. We have experience of concentration with a number of different phosphates, Moroccan, Senegal, Togo, Florida, Jordanian.

The next question related to the content of solid matter in the phosphoric acid produced. The level is very variable from one installation to another, and even over time within the same plant, since the level of solids in 30% acid is also very variable, according to operational conditions and the phosphate used. When we use the acid in the same plant where it is produced, we usually do not decant it and the quantity of impurities is tolerable for the concentration of fertiliser we manufacture. Naturally we try to have as little as possible. As to the actual figure, I would say a maximum of 3-4%. Obviously this is very much more than the figure of 0.5% which you recommend for transport purposes but it is tolerable for the concentration of fertilisers which we manufacture such as triple 17. As regards transport, you say one must have less than 0.5% solid matter. I agree when it is a matter of long distance transport by, for example, rail but within a plant there is no trouble with higher levels provided the phosphoric acid vessels have a means of agitation and there is a sufficient velocity in the acid flow conduits.

The last question related to the frequency of wash-out and the comparison between the additional cost of the facilities for frequent wash-outs and the cost of greater heat exchange surfaces. I do not really know if you can put the question in this form, because if you allow the exchange coefficient to fall too low there is also the risk that a too thick deposit may develop in the exchanger. In spite of everything, deposits are not regular and you have the risk of blockage. Even with the most sophisticated installations, with crystalliser incorporated, the only solution is to empty completely for wash-out purposes. I think therefore that one should be equipped to carry out a wash-out in a rapid manner so as to give a minimum loss of P_2O_5, subject of course to the need to have a very slight rinsing by water spray in order not to lose P_2O_5. Naturally it is of interest to space the wash-outs as far apart as possible and we are working in that direction. We hope soon to make progress in this respect.

Dr. PEARCE (Fisons Ltd.) : I would like to make a comment on a remark made by Mr. MORAILLON on page 11 of his paper in which he suggests that the problems of scaling and erosion cannot co-exist. I do not think this is so. The erosion occurs essentially at the entrance to the tube and this is where the damage occurs. It is quite possible for this to happen and for scaling to occur in the body of the tube at the same time. My other point is to ask how the availability of 92% mentioned on page 26 is defined. Is it defined as a % of 365 days in the year and does it only include the actual evaporating time or does it include the washing time also ?

Mr. MORAILLON : When I mentioned the relationship between scaling and velocity on the one hand, and erosion on the other, I pointed out myself that this theory seemed to be over simplified and that one cannot wait until there should be a determined velocity at which there is neither erosion nor scaling. You are quite right that there is more erosion at the inlet of the tubes, but it is one of the advantages of the carbon blocks that this erosion does not cause trouble. The extremity of the tubes can be widened and you still get an equilibrium profile which allows one not to worry too much about this kind of erosion. I do not know what happens with Karbate tubes and perhaps someone here can tell us.

The second question concerned the operating time. We indicated an operating coefficient of 92%. This operating coefficient applies in relation to the operating time in the evaporator but excludes annual down time from maintenance. It is the operating time for normal periods, including small down times for washing and also for maintenance but not long down times for periodic maintenance.

Mr. G. MENIN (Fabbrica Perfosfati Cerea) : According to you, the concentration of H_3PO_4 should be carried out in crystalliser-evaporators under vacuum with forced circulation, and for that, it is necessary to avoid flashing within the tubes of the exchanger. This is true. But why have you used the empirical formula of Fragen and Badger for the overall coefficient of transfer K, a formula which, according to Perry, is valid when most of the liquid is boiling inside the tubes ?

Using Fragen and Badger formula :

$$K = 490 \frac{d^{0.57}\ v^{3.6/L}}{\mu^{0.25}\ \Delta T^{0.1}} = \text{BTU/hr ft}^2\ {}^{\circ}\text{F}$$

d = internal diameter of the tubes (in.)
v = velocity in the tubes (ft/sec.)
L = length of the tubes (ft)
μ = viscosity of the liquid (lb/hr ft)
ΔT = $(T - t)$ = temperature difference at the inlet of the exchanger (°F)

Since in the case of table 1 : ΔT, μ, L and v are constants, in changing the internal diameter of the tubes from 19 to 38 mm, the value of K increases by 49%.

In my opinion, the formula of Dittus-Boelter should be used for the partial internal coefficient :

$$h = f'\rho\ c\ v\ Pr^{-2/3}\ 3{,}600 \qquad (\text{Cal/m}^2\text{h}\ {}^{\circ}\text{C})$$

$f' = \varphi(Re) = 0.0027\ Re^{-0.2}$
ρ = liquid density (Kg/m^3)
Re, Pr = Reynolds and Prandtl numbers

and then the overall coefficient can be evaluated according to the formula :

$$\frac{1}{K} = \frac{1}{h_{Nu}} = \frac{1}{h}$$

h_{Nu} = Nusselt's partial condensation coefficient =
5,000 Cal/m^2h °C for the vertical tubes =
8,000 Cal/m^2h °C for the horizontal tubes.

Since $\underline{h}_{Nu}$ is quite high, one can write :

$$K \simeq h = \alpha\ \rho^{0.8}\ v^{0.8}\ c^{0.33}\ \mu^{-0.47}\ \lambda^{0.67}\ d^{-0.2}$$

c = specific heat (Cal/Kg °C)
λ = thermic conductibility (Cal/mh °C)

and thus one can see that, when all the other conditions are constant, by changing the diameter from 19 to 38 mm, the value of $\underline{K}$ falls by 15%.

As regard the hydrostatic charge in the exchanger, one has to remember that with a velocity of 2 m/sec. the system is very turbulent. In consequence, even with very high values of $\underline{\Delta T}$, the liquid temperature is constant throughout the flux section.

In the case of an increase of temperature from 80 to 85°, a hydrostatic charge of 0.18 m of liquid is sufficient to avoid flashing in the tubes. It seems to me that this may confirm what you say on page 11, namely that you did not find any appreciable difference in the speed of scale formation as a function of steam pressure.

<u>Mr. MORAILLON</u> : Your first comment relates to the formula that I mentioned on page 3 of the paper. I only quoted this formula in order to say that in my view the transfer coefficient was not independent of a number of factors, particularly velocity, and diameter of the tubes, and I took the first formula I could find. I do not attach much importance to it, but I am grateful to Mr. MENIN for giving me a much more correct formula and one which certainly favours reducing the diameter of the tubes.

I do not know whether practical experience confirms this increase in the transfer coefficient with the reduction in the tube diameter - I have no experimental results on this subject.

The second question. It is certain that, given a velocity of more than 2 m/sec., you get a very turbulent system and the velocity is the same throughout the interior of the tubes. But can one be sure that one has cut out all risk of flashing in contact with the walls of the tubes, especially with irregular tubes like those of graphite which are not absolutely smooth.

As regards the hydrostatic charge, a static charge of 0.18 m liquid is certainly enough to avoid flashing if the temperature of the acid does not exceed 85° locally, but is one really sure that the local temperature of the acid does not exceed 85° ? Especially if you have a bad distribution of acid flow between the various tubes you may have an average output temperature of 85° but you may have a mixture of streams with very different temperatures, some reaching 100°. It is certain that if special precautions are not taken, one does not have the same acid flow in all the tubes of the exchanger and that is why a lot of the difficulties have occurred.

Mr. J. FROCHEN (Pierrefitte) : On page 22 of the French text Mr. MORAILLON points out that you can install a polypropylene separator. Can he give us more details about the working of this separator, its maintenance and the possibility of blockage by fluorides or other substances.

Mr. MORAILLON : I mentioned the possibility of using a polypropylene separator but we have not tried it ourselves. We have used the shock or centrifuge separators but I just mentioned this as one possibility which I have read about in the literature. I do not know whether there is anybody present who has already tried a polypropylene device.

Mr. J.P. GARDINIER (Ets. Gardinier) : I read in your report in the conclusion a most interesting sentence relating to the future. You say there is a possibility of progress in the field of materials. Should one not in fact abandon metallic exchangers ? If you think that one can go back to metallic exchangers with what kind of metal do you think you could find a solution ?

Mr. MORAILLON : I think that is a question the metallurgists should answer. It is up to them to develop new metals which would be suitable for phosphoric acid. There was the example of nionel which was very promising at one time, but which unfortunately failed for a number of reasons which have now been explained to some extent. However it seems that it is not out of the question that one day we may get better alloys. In any case the main point is that one must not abandon research along these lines.