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CONCENTRATION OF PHOSPHORIC ACID  
USING THE "PERLOMATIC"

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By :

Y.F. Berquin  
Azote et Produits Chimiques S.A.  
France

Phosphoric acid is playing an increasingly important role in Chemistry.

Its principal use is in the manufacture of phosphate fertilisers, in particular the water soluble form which is most required at present.

But it is also used in other manufacturing processes ; bicalcium phosphate for animal nutrition or toothpaste, detergents etc.

Its most common source at present, at least in Europe, is so called "green" or chemical route acid.

At present, and pending hoped-for results from new methods, the acid so produced is of weak concentration, 28 to 32% normally, exceptionally 40%.

However, for most uses, phosphoric acid must have a higher concentration, of the order of 50 to 55%, sometimes higher. It is therefore normally necessary to concentrate it.

This concentration of phosphoric acid has for a long time been the subject of studies in depth. Numerous methods have been proposed.

Thus there have been introduced in turn processes effected under atmospheric pressure or under a vacuum, using direct or indirect heating, then using heat exchangers of different types.

The multiplicity of proposed methods indicates that no perfectly satisfactory solution has been found to date.

In our turn, we have tried an approach to the problem which, if it is not perfect, at least offers, in our opinion, numerous advantages over its predecessors. The basic idea consists of converting our "Perlomatic" apparatus for this new use.

The Perlomatic has already been the subject of papers in the past, but time has gone by and it is perhaps useful to recall its principle.

It is a granulation apparatus formed from a conical-cylindrical vertical chamber. The lower trunk of the cone, joined to another inverted cone trunk conducting the air, forms with the latter a sort of venturi. A bed of granules in formation occupies the lower part of the chamber. A spraying system leads the liquid (solution or fused product) to be granulated to the level of the venturi. The air blown into the chamber is previously heated (direct combustion, exchanger etc. according to the nature of the product to be granulated). The combination of the jet of air and the bed of granules sucked to the level of the venturi, produces a geyser effect in the center of the chamber which ensures a very rapid renewal of granules in the spraying zone. There is thus a progressive enlargement of the granules by instantaneous evaporation of the film deposited on the granulation starters. An assembly of simple appliances obviously permits a continuous train with overflow, grading of the granules, return of fines and oversize, the latter after crushing.

Analysis of the various phenomena which occur when operating the above gave an expectation that an adaptation could be used for concentrating solutions.

Furthermore, it was already known to use a current of warm air to concentrate acids ; usually, the liquid was dispersed by streaming according to different methods, but also by spraying.

Unfortunately, and particularly in the case of phosphoric acid, the major difficulty of this method of concentration is in the formation of nocuous effluents which are difficult to treat. At present, and we ourselves have used this method in numerous applications, one of the best methods of combating vesicular mists involves the use of the watered venturi, i.e. the gases to be treated pass into a venturi, in the neck of which washing solution injectors are located. In view of the considerable energy resulting from the high speeds achieved at this point, the repulsion effects which act on the small particles are overcome and there is coalescence of the mist on the small drops of injected water.

The mist is thus converted into small drops which it is easy to collect by known means, a cyclone for example.

In addition, the Perlomatic, in its granulation version, has been shown to be an excellent temperature exchanger with a particularly good thermal efficiency.

The internal recycling of liquid which regulates the liquid-gas contact time can be chosen to a large extent by the relative regulation of the delivery of gas and liquid, which allows various results to be obtained ; rapid concentration in certain cases (bodies sensitive to heat) or, on the other hand, sufficient time to obtain certain relatively slower reactions, such as one which will be considered further on.

It has certainly been necessary to modify slightly some parts of the apparatus to take account of new situations, but, fundamentally the apparatus has remained in its initial form.

In particular an internal small collar has been added to the lower part to facilitate the flowback of liquid towards the wall, without being carried along directly by the air towards the overflow.

The system of pneumatic grading in the upper part have been replaced by devesiculating means which retains and condenses most of the droplets formed to lead them again into the liquid circuit.

Concerning the equipment, and because of the rapid cooling of the gases, relatively common and therefore cheap materials can be used. The mechanical simplicity of the apparatus adds to the attraction of the process and results in the investment costs being particularly low.

The performance obtained is of a high standard taking into account the above remarks.

For the concentration of green phosphoric acid the best operating conditions at present correspond to the following data :

- Air-phosphoric acid ratio : 10 Nm<sup>3</sup>/kg concentrated P<sub>2</sub>O<sub>5</sub>
- Temperature of the acid coming out : 92° C
- Entrance temperature of the gases : 521° C
- Temperature of the gases coming out : 95° C
- Original concentration of the acid : 30.5% P<sub>2</sub>O<sub>5</sub>
- Concentration of the acid obtained : 55.2% P<sub>2</sub>O<sub>5</sub>
- Consumption of calories : corresponding to a thermal efficiency of 75.0%
- Consumption of energy : 22.8 kWh/t. P<sub>2</sub>O<sub>5</sub>
- Concentration of gases after cyclones : 150 to 300 mg P<sub>2</sub>O<sub>5</sub>/m<sup>3</sup>  
i.e. loss : 0.15 to 0.3%

- Level of gases after brief washing in the lined tower :  
50 to 100 mg  $P_2O_5/m^3$   
i.e. loss : 0.09 to 0.1%
- Concentration of fluorine in the acid coming in : 1.2%
- Concentration of fluorine in the concentrated acid : 0.4%

It will therefore be noticed that, in addition to a very competitive consumption of energy and calories, there is a powerful defluorination of the concentrated acid making it suitable for numerous uses.

Furthermore, the phenomenon of coalescence of the mists mentioned above is particularly effective, as the concentration of  $P_2O_5$  in the gases before treatment shows. A simple washing of the latter lowers the level of  $P_2O_5$  in the effluent to a practically negligible value.

The apparatus has other possibilities in connection with phosphoric acid production.

By modification of the operating conditions, it is possible to obtain any desired concentration, both the weakest, for example the production of 40 to 42% acid necessary for certain industries, as well as concentrations going up to the production of superphosphoric acid.

In this respect two points in particular have attracted our attention.

First of all the possibility of producing without difficulty an acid of 60 to 65%  $P_2O_5$ . This acid is not available at present but, with the development of the transport of phosphoric acid over long distances, we are persuaded that there is a substantial improvement in cost prices to come from the use of our apparatus for the superconcentration of commercial acid.

By going further with temperature and thus concentration, the field of superphosphoric acid is entered. There is obviously a complication : that of the corrosion of the apparatus by this particularly aggressive material, but, there again, simplicity in the form of the apparatus and the low temperature permit the use of the most economic solutions.

We have thus been able to produce an acid with 75%  $P_2O_5$  which is well suited, for example, to the preparation of liquid fertilisers.

Incidentally, although it is outside the subject with which we are principally concerned here, it is worthwhile to point out that this same apparatus is well suited to several

other concentration operations, for which an apparatus working under vacuum is not justified : various acids, salt solutions, etc.

We believe therefore that, with this apparatus, we have made, at a time when a considerable increase in the potential demand for phosphoric acid may be expected, an important contribution which will facilitate further the use of the latter and will play its part in the hoped-for development of this industry.

DISCUSSION

Mr. Y.F. BERQUIN (Azote et Produits Chimiques, France) : You are probably familiar with the principle of the equipment which is the subject of the paper, since it is a variation of our "Perlomatic", on which a number of papers have already been given. At the bottom of the plant (see Fig.) you will recognise the double-cone which provides both the propulsive force to the hot air which governs the rate of evaporation, and at the same time maintains the material to be concentrated in suspension and thus prevents it from dropping into the bottom of the vessel. The technique is the same, whether one is dealing with a granular product, or with the concentration of liquids as described in the present paper. However, in the latter case we have found it necessary to modify slightly the base of this piece of equipment in order to obtain a better separation of the liquid phase from the air which contains suspended droplets. The modification comprises a circular baffle or baffles as indicated by 5. Also at the bottom of the plant you will see the atomiser intended to disperse the liquid to be concentrated. Withdrawal of the concentrate is effected by means of an overflow tank fitted with a siphon as shown by 8. The rest of the equipment is quite simple and consists of a cylindrical jacket on top of which is the primary separator in which the large droplets are taken up in the bed. Obviously, this is a typical arrangement which is completed by a number of devices at the bottom of the combustion chamber and finally by the vent to air. The latter can be at the top, although the two systems can be combined. At the outlet the gas is stripped of suspended droplets by means of the conventional arrangement of one or two moist cyclones.

In the case of phosphoric acid with which we are concerned today, we have provided for a washing stage using a packed tower. I shall not quote the essential details since they appear in the paper which is before you. I shall simply refer to the conclusions relating to the problems with phosphoric acid. It appears that costs are of the same order as those obtained with other processes. On the other hand, the simplicity of the construction and operation of this plant seems likely to result in appreciable economic advantages for it. Consequently, a pilot-scale industrial installation is in course of erection, and we shall shortly be able to confirm or refute our provisional conclusions.

Today, I should like to stress the ease with which the acid can be concentrated to 61 to 62%, since with this acid as the starting point we are going to investigate and develop an extremely simple process for the separation of solutions of ammonium polyphosphate. We hope to be able

largely to short-circuit the rather cumbersome equipment that we use at the moment. The results, as well as those of investigations undertaken by others, seem to indicate that the future of phosphates as fertilisers is likely in the very near future to tend towards much higher concentrations than those which are possible from the ortho form. Therefore, we can expect more new developments from this process, which some years ago appeared to have reached the point of maximum development.

In addition, I should like to indicate some results obtained not from the phosphoric acid route, but from the concentration of salts. We carried out some trials with a 12% solution of calcium chloride (calculated on the anhydrous salt) which we were able to concentrate up to 60% by means of a two-stage operation. The first stage gave excellent results in terms of thermal efficiency, since the gases which entered at 595° C, left the apparatus at 92° C. The second stage enabled us to increase the concentration to 63%. One cannot go beyond this figure on account of the viscosity which interferes with the functioning of the equipment. In the second stage the gases also entered at 590° C, and left at 145° C and the temperature of the concentrated solution was 113° C. I regret that I am not able to give you fuller results. Unfortunately, as I have already stated, our pilot-plant is only in the course of construction and consequently I have not been able to give you the results I had hoped.

Mr. SCURR (Bosveld Kunsmis, South Africa) : The concentration of wet-process phosphoric acid is generally carried out by one of two methods :

- a) at or near atmospheric pressure, using direct heat transfer between heating air and the acid,
- b) at reduced pressure and temperature, using indirect heat transfer, commonly between steam and the acid.

I think it is true to say that the fertiliser phosphoric acid industry in recent years has generally favoured the reduced pressure method despite the necessity of regular downtime to clean the heating surfaces on the acid side, and the inherent lower overall thermal efficiency. However, the fact that we have the present paper and a similar one which was presented at the ISMA Brussels conference in 1968, shows that the reduced pressure method is not accepted as the final answer. At best, it can be regarded as the lesser of two evils except where sufficient waste or cheap steam is locally available for the heating.



The disadvantages of the atmospheric processes, of which there are a number of variations, are mainly connected with plant corrosion and air pollution by phosphoric acid mist. The latter problem is aggravated by the fact that the heating medium, air, becomes mixed with the vapour and results in large volumes of gas with relatively low pollutant concentrations having to be treated before discharge to the atmosphere. Mr. BERQUIN has dealt with these two aspects in his paper but I would like to ask him for some further information.

Firstly, the best heating gas temperature is given as 520° C. Higher inlet gas temperatures than this are used in atmospheric concentrators, and I would like to ask whether higher temperatures have been found unsuitable in this case because of increased corrosion or because of increased P<sub>2</sub>O<sub>5</sub> mist formation ?

Secondly, it is not clear whether the P<sub>2</sub>O<sub>5</sub> losses stated in the gases "after cyclones" also means after the Venturi scrubber. If so, could Mr. BERQUIN say what proportion of the P<sub>2</sub>O<sub>5</sub> fed to the plant is recovered in the Venturi scrubber/cyclones and at what strength ?

Thirdly, it is my experience that atmospheric phosphoric acid concentrators do not lend themselves easily to economic fluorine recovery, because of low fluorine concentrations and phosphoric acid contamination in the scrubbing liquid. Has Mr. BERQUIN any comments on these aspects in the light of his experience with the Perlomatic concentrator ?

Reverting to the principle of the Perlomatic process, there is presumably a quantity of phosphoric acid maintained in the upper part of the unit, corresponding to the bed of granules in the case of a granulator using this principle. If this is the case, is it not true to say that the process as applied to liquids is largely a physical modification of the submerged combustion principle ? Perhaps Mr. BERQUIN would elaborate further on the liquid circuit in this connection ?

Finally, I would like to ask Mr. BERQUIN if his experience so far enables him to say anything about the potential operating time of the equipment. I have in mind regular downtime which could be necessary for cleaning such parts as the "devesiculating means" in the upper part, and removal of scale formed in the unit, particularly at the wet/dry line which must exist somewhere on the internal surface.

Mr. BERQUIN : Mr. SCURR's first question refers to the

temperature of the gas which we chose for our trials. If a higher temperature is used, as is the case in some concentration processes - I have in mind particularly superphosphoric acid - corrosion problems arise and arise progressively. But what has restricted us mainly to this temperature is the development of a mist of the acid that is very difficult to dispel, and which we believe can be minimised, if not completely eliminated, by working at the temperatures we have indicated. This will be a point of major interest if it is confirmed on the large scale.

The second question relates to the  $P_2O_5$  losses. As was indicated briefly in the description of the lay-out of the process, we have a primary splash head, of simple design, at the top of the apparatus to which the liquid resulting from the recovery stage is returned directly without being measured. After this we have one or two cyclones and the  $P_2O_5$  content of the gases as they leave the cyclones is given on page 3 as 250 to 300 mg.  $P_2O_5$  per cubic metre of gas, which corresponds to a loss of 0.15 to 0.30%  $P_2O_5$ . We have tried a subsequent washing in a tower packed with Raschig rings. This is a very simple arrangement at the exit of which the  $P_2O_5$  content of the gas falls to 50-100 mg. per cubic metre, which represents a loss of 0.05 to 0.1% expressed in terms of the  $P_2O_5$  that enters.

The third question concerns the recovery of fluorine, or to put it in more general terms, the problem of pollution due to gaseous effluents. In point of fact, where this problem occurs it is similar, despite appearances to the contrary, to that which is encountered in plants working under vacuum. Such plants do not give rise to gaseous effluents, but to liquid effluents that must be treated. We were reminded of this earlier. This effluent is obtained when the gases are washed prior to condensation, and the process is similar to that used for the treatment of the gaseous effluent from a plant that works at atmospheric pressure and the treatment of the solution resulting from the washing process is the same in both cases. Therefore, there is little difference between the two systems.

I have also been asked if our process is considered to be in the same family as the submerged combustion process. Actually we think that there is a physical difference between these processes which manifests itself in the possible presence of the above-mentioned mist. During submerged combustion, bubbles of hot gas are formed when the gas is injected into the mass of liquid, and they can be considered as an emulsion of a gas in a liquid. The bubbles themselves contain a mist which is due to the evaporation of the liquid into which the gas has been injected. Here we are dealing

with another emulsion, since the mist inside the bubbles is essentially a second degree emulsion. Consequently you will appreciate that it may be formed rather easily and be rather difficult to break. In the case of the "Perlomatic", however, we have from the outset attempted to get droplets of the smallest size possible from the atomiser, so that the "Perlomatic" can be thought of rather as giving a simple emulsion of liquid droplets in gas. This, I believe, corresponds to what actually obtains. Here once more, the evolution of mist, which we produce at will, seems to prove that there is, at all events, a physical difference of some importance between the two processes.

The last question relates to the length of time that the plant can be operated before cleaning down becomes necessary. As I have said we have not yet got the full scale plant that I had hoped, but we have, nevertheless, run the laboratory pilot-plant for long periods. The amount of scale encountered in this plant was very small and was easily removed with hot water. It is difficult for me to give you the actual period between each shut-down for cleaning. I can only tell you that, for internal reasons, we can only run for eight hours continuously in practice, so that we have to restart the plant each morning without exception. Working in this fashion we have been able to run for several days, including the overnight stoppages, without having to clean down.

Mr. SCURR : I should like to put my second question again. It is now clear to me that the  $P_2O_5$  losses in the gases, after the Venturi scrubber, are 0.3 to 0.15, 0.15 to 0.13%, I would still like to know what proportion of the  $P_2O_5$  fed to the plant is recovered in the Venturi scrubber cyclones and at what strength. As I understand it, we have a separate stream of phosphoric acid being recovered in the Venturi scrubber and cyclones. It is not clear to me whether this arises as a weaker product or whether it can be regarded as part of the output of the concentrator.

Mr. BERQUIN : The acid obtained from the cyclone which is right at the end of the plant, is fairly concentrated, about 40%, and it is recirculated to the plant in order to get up to the requisite concentration of 50-55% in the trials using a traditional concentration process, and beyond this figure in certain other tests. On the other hand the liquid effluent obtained after washing, and I stress that this consists of a single washing in a scrubber without a venturi, is a dilute acid, so dilute that in the trials we decided to discard it. In any case it does not amount to much.

Mr. MENIN (Fabricca Perfosfati Cerea, Italy) : I think that in order to increase the mass transport between the liquid and the hot gases, it is necessary to atomise the liquid thoroughly, in which case spherical droplets are formed and therefore the average velocity of the gas in the plant becomes most important. Can you tell me what the velocity is ?

Mr. BERQUIN : The velocity of the gas, as measured at the base of the plant is about 100 metres per sec., i.e., at the neck of the venturi. In fact we get efficient atomisation, and due also to the supernatant bed of liquid, coalescence of the mist which forms in the bottom of the plant probably occurs. Thus, although we are sometimes dealing with extremely fine droplets, we do not get any mist. A proof that the plant is not working correctly is given by the formation of a geyser, as we call it, which rises and becomes a mist. This tells us that the height of the liquid bed is insufficient. There was a question earlier about another process that was introduced two years ago. In point of fact the two processes are different, since, if I am not mistaken, this works on a single pass, whereas we use a closed circuit above the bed and only the overflow comes out of the plant.

Mr. L.K. RASMUSSEN (Dansk Svovlsyre-og, Denmark) : Mr. SCURR was comparing the Perlomatic process with submerged combustion. I should like to mention that perhaps it is more correctly compared with spray-drying. There is, however, one thing that is striking in the presentation. Mr. BERQUIN mentioned a velocity at the base of 100 m/sec. I should like to ask what is the terminal velocity in the wider diameter of the evaporators and secondly if there is a bed of droplets, how does one actually control the droplet size ?

Mr. BERQUIN : Actually, I believe that the process can be compared with spray-drying, although I think that I indicated where they differ a moment ago. Spray-drying corresponds exactly with the process mentioned two years ago and to which I have made reference. Our case is slightly different in the sense that, even if there is a spray-drying effect during the few centimetres immediately after atomisation, a different result ensues because of the meeting with the bed of material at the bottom of the plant. This leads me directly to the third question since it is connected with it. This plant does not, in fact, work quite like a granulator, as it does not embody a bed of separate droplets, but a

truly mobile liquid which is visible beyond the central section of the plant where the geyser effect may occur. Thus there is no question of droplets being present in the bed itself, these occur solely in the region where splashing takes place, and, as I said earlier, this is determined both by the depth of the bed and the velocity of the gas. Too high a velocity produces an excessively fine degree of atomisation. The velocity of 100 metres per sec. has been calculated between 50 and 100 metres depending on the densities and on the circumstances, and corresponds to the true velocity when the temperature is taken into account. This is important, since if there is a substantial drop in temperature in the apparatus, the volume of the gases, despite the water vapour present, will be greatly reduced at the top of the plant. Furthermore, since the diameter of the pipework is much larger, the velocity is further reduced to level at which the droplets begin to separate out, at least in part. I cannot call to mind the exact velocity, but I should say that it is in the region 10 metres per sec.

Dr. B. RAISTRICK : I think we should consider Mr. BERQUIN's paper in one particular way with regard to this question of  $P_2O_5$  loss in the off-gases. If the temperature of the input gas is low, surely any carry over of  $P_2O_5$  will be mechanical carry over. But at very high temperatures it is known that there is volatilisation of  $P_4O_{10}$  molecules. Indeed, so much so that pure phosphoric acid can be made by operating a unit of this kind at very high temperatures. Thus one goes from one extreme, where it is mechanical carry over at low temperatures, to  $P_4O_{10}$  volatilisation at high temperatures. I think a merit of Mr. BERQUIN's process is that it does use quite low temperatures at which volatilisation of  $P_4O_{10}$  is probably quite low, and therefore the scrubbing problem that has to be faced is simply that associated with mechanical carry over. On the other hand, in some of the other submerged combustion processes I feel sure that the problem of scrubbing is largely due to  $P_4O_{10}$  molecules which are actually being volatilised.

Mr. BERQUIN : Dr. RAISTRICK is perfectly correct in his remarks, and, at least we in France can speak from experience with one of our important specialities, the concentration of phosphoric acid to yield superphosphoric acid. In this process we have to contend with an extremely fine mist of  $P_2O_5$ , which results rather from sublimation than mechanical carry over, or at least from a combination of these two effects. Thus being cognisant of the problem, we have sought to avoid it or at least to minimise it by using a single concentration stage, since the equipment, the operating temperatures and the concentration required enable us to do this.

Mr. A. DAVISTER (Prayon, Belgium) : Even with a powerful air stream, the problem of achieving a relatively fine degree of atomisation does not seem to me to be all that easy, since, as is well known, wet-process phosphoric acid has a tendency to form deposits of scale. Can you describe to us something of the type of atomiser that you use ?

Mr. BERQUIN : At the moment I cannot call to mind the trade name of the actual model of atomiser that was used, but it is merely an atomiser in which the atomisation is mechanically produced by the acid pressure. As you yourself remarked, the presence of the high-velocity air stream surrounding the jet of acid undoubtedly greatly facilitates its dispersion.

A P C C O N C E N T R A T O R

1. Body of the apparatus
2. Gas introduction
3. Injection tube
4. Liquid outlet
5. Baffle
6. Double cone
7. Circular recovery spout
8. Siphon
9. Gas extraction
10. Demister

