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LABORATORY SCALE APPARATUS FOR THE CONTINUOUS PROPORTIONING OF LIQUID AND POWDER PRODUCTS, AND ITS APPLICATION TO THE STUDY OF WET PROCESS PHOSPHORIC ACID MANUFACTURE

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One of the most intractable problems for the laboratory technician is that of the distribution, at a constant rate of flow, of very small quantities of a solid product in powder form. The difficulty is further aggravated when it is necessary to ensure the flow of a solid and of one or several liquids simultaneously, in ratios fixed in advance; for the errors in each rate of flow can be additive and give a considerable total error.

However, for the requirements of our applied research laboratories, we have been able to construct a simple apparatus enabling us to achieve a strict proportioning of reagents in either solid or liquid form and thus affording us the possibility of studying the continuous manufacture of several products, particularly wet process phosphoric acid.

Distribution of the solid reagent

In the process employed, the hopper which distributes the powder is placed on the platform of a scale or weighing machine which is brought into balance. One then varies the weight of the balancing tare according to a strictly linear relationship as a function of time. As it becomes very slightly unbalanced, the weighing system operates an electrical contact which, by means of a relay, works the discharge mechanism of the hopper and evacuates a small quantity of the powder from the platform. The scale or weighing machine is then restored to equilibrium, breaks the electrical contact and stops the discharge mechanism of the hopper. The tare continues to vary, a second electrical contact is established and a further quantity of powder is distributed, and so on.

In short, the solid product is distributed in very small amounts - about ten per minute - according to the same programme as that of the variation of the weight of the tare.

A particularly convenient way of constructing this programme is to arrange the filling or emptying, at a constant speed, of a container placed on one of the platforms of the weighing system with a liquid, which may be water or an appropriate solution. This can be achieved by means of a

volumetric pump, but it is simpler, more accurate and less expensive to use the classic Mariotte device, which ensures a constant rate of flow for a liquid in a closed container and which consists, as is well known, of a plunger tube which makes the air bubble before it enters the container.

Distribution of liquid reagents

We have succeeded in modifying the classic Mariotte apparatus, so that we can simultaneously obtain the flow of liquid which governs the regular distribution of the solid material, as we have described above, and that of the different liquid reagents necessary for the reaction (x). Figure 1 represents this new system diagrammatically.

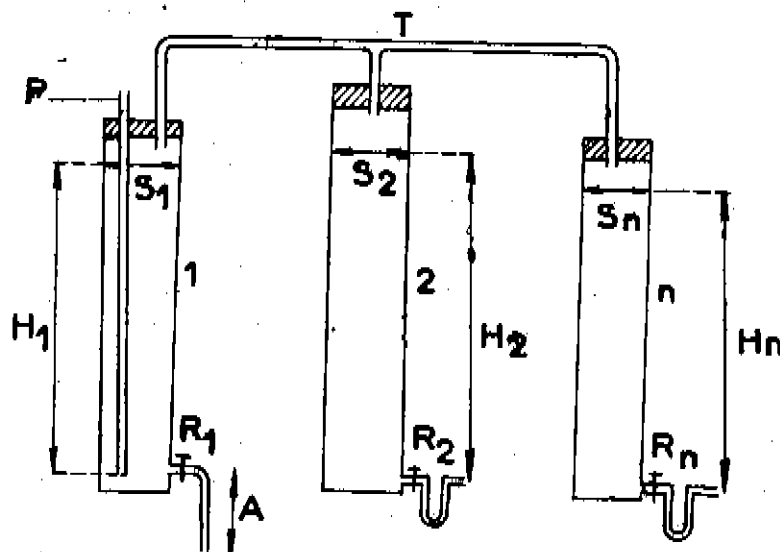


fig 1

Container 1, with a constant horizontal section S_1 is set up as a Mariotte flask, i.e. it is provided with a plunger tube P for the introduction of air and a fitment A, the height and section of which condition the rate of flow. Containers 2, 3 ... n, with horizontal sections $S_1, S_2 \dots S_n$, are linked with container 1 through their upper section by means of tubes T. Outlet taps $R_1, R_2, R_3 \dots R_n$ are closed and the vessels are filled with their respective liquids, of densities $D_1, D_2, D_3 \dots D_n$, so that, approximately, $H_2 D_2 = H_3 D_3 = \dots = H_n D_n$, which is very slightly more than $H_1 D_1$. Taps $R_1, R_2, R_3 \dots R_n$ are opened, and after a few minutes equilibrium is achieved, and at any moment:

$$h_1 D_1 = h_2 D_2 = h_3 D_3 = \dots = h_n D_n$$

(x) For further details see "L'Industrie Chimique", April 1956 and February 1962, as well as French patent No. 1334420, dated 1st July 1963.

It follows that the rates of flow by weight $P_1, P_2, P_3 \dots P_n$ of the distributed liquids are proportional to the horizontal sections of the vessels

$$\frac{P_1}{S_1} = \frac{P_2}{S_2} = \frac{P_3}{S_3} = \dots = \frac{P_n}{S_n}$$

In practice, to regulate the ratio of the rates of flow to some extent, it is possible to decrease the horizontal sections of the vessels by introducing filled tubes into them or, alternatively, it is possible to increase the horizontal sections by tilting the vessels.

Construction of the reagent distribution system

For illustrative purposes, and with reference to figure 2, we give the description and preliminary calculations of our first installation.

The rates of flow to be ensured for twenty hours were as follows:

Phosphate rock	128 to 150 g/h
Sulphuric acid 78%	162 g/h, density 1.71
Phosphoric acid 20.8%	188 g/h, " 1.18

Container No. 1

Reserve for the phosphate rock distribution apparatus, filled with 3 litres of water: tube, 60 cm in useful height or 70 cm in real height, and with an internal diameter of 8 cm, i.e. a section of 50.24 cm².

A set of three full tubes, 10 mm in diameter (section 0.7854 cm²) and two full tubes with a diameter of 20 mm (section 3.1416 cm²), when immersed, enable the weight of phosphate delivered to be varied in successive stages from 150 g to 150 - 2.35, 150 - 2 x 2.35 150 - 11 x 2.35 = 124.2 g.

Container 2 for sulphuric acid

As the horizontal section had to be 50.24 x 162 = 50.24 x 1.08 = 54.21 cm², we took a tube, diameter 8 cm, 150 tilted at 68° (sin i = $\frac{1}{1.08} = 0.926$, hence i = 68°). With a useful height of $\frac{150}{1.08} = 138.9$ cm, we chose a total height of 60 cm. in practice. The very strict adjustment of the proportion of H₂SO₄ used can be obtained by varying the grade of sulphuric acid around 78%.

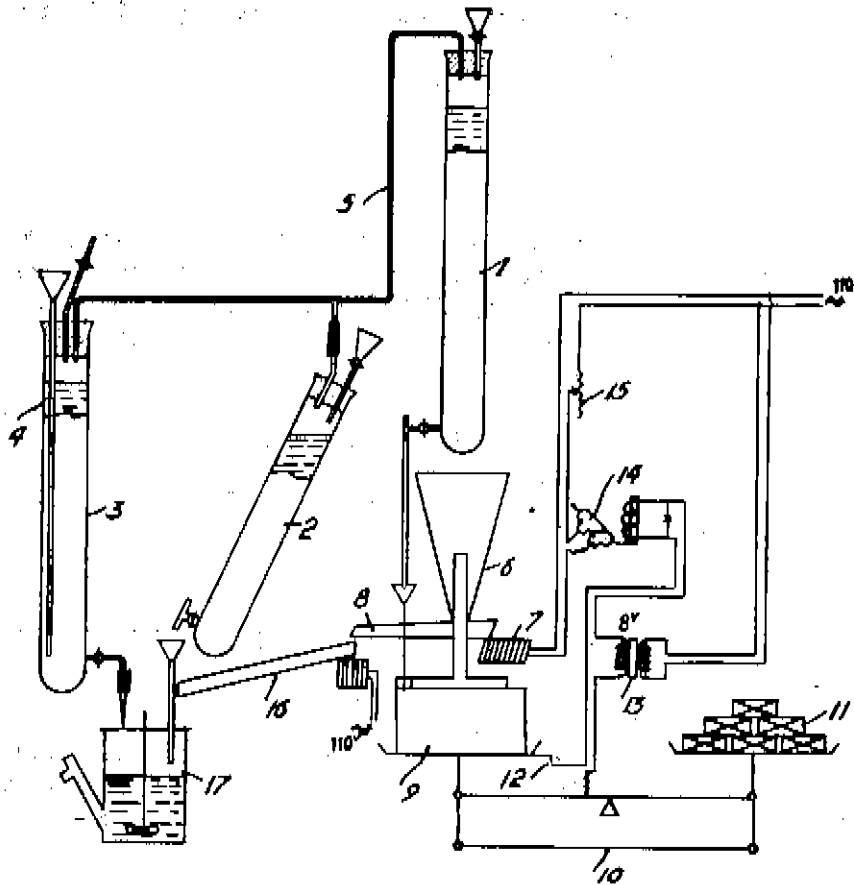


fig 2

Container 3 for phosphoric acid

As the horizontal section had to be $50.24 \times \frac{188}{150} = 50.24 \times 1.253 = 62.95 \text{ cm}^2$ we took a tube of diameter 9 cm, i.e. a section of 63.58 cm^2 . To decrease the surface, we immersed tube 4, with an external diameter of 9 mm, and a section of 0.64 cm^2 , giving a useful section of $63.58 - 0.64 = 62.92 \text{ cm}^2$. In this case, it was convenient to use the 9 mm tube to introduce air into the system. Useful height of the tube: $\frac{1}{1.18} \times 60 = 50$. We chose a total height of 60 cm.

Tubing 5 of diameter 10 mm to connect the atmospheres of the three vessels.

Hopper 6 loaded at commencement with 3 kg of powdered calcium phosphate. It is provided with a discharge mechanism, consisting of a rocker 7 which activates the feed chute 8. This is all placed on a container 9 of 3 litres, itself placed on the platform of a balance 10, with a capacity of 20 kg, balanced by counterweights 11.

Automatic control of the outlet mechanism of the hopper is achieved by means of a contactor 12 in platinised metal, a

transformer 13, a mercury rocker 14, and a box 15 to maintain the flow of powder slightly in excess of the desired rate. A small chute 16, independent of the system and subject to the action of a vibrator, permits a continuous flow of powder fed by pulsations into 8. The two solutions, sulphuric and phosphoric, and the phosphate rock arrive together in the reactor 17.

We subsequently found that it was more practical to mix the sulphuric and phosphoric acid in advance, to maintain the sulphuric acid/phosphate rock ratio a priori slightly low and to make the necessary adjustment (95% of the normal quantity, for example) by running in a small quantity of more or less concentrated sulphuric acid. The maintenance of the P2O5 concentration is obtained by the determination of phosphoric acid density every hour and by the appropriate admission of a small quantity of water.

Reactor

A pyrex beaker of 1.5 to 2.5 litres with overflow pipe. Very energetic stirring is necessary to break the emulsion and permit the rapid exit of reaction gases. We used an agitator of molybdenum stainless steel, consisting of six paddles of 40 mm x 13 mm. Speed: 400-600 r.p.m. An improvement was achieved with the addition of a second co-axial agitator revolving at a lesser speed of 150-200 r.p.m., designed to stir the surface of the slurry to avoid local stagnation of the phosphate in contact with the foam. Temperature is maintained constant by placing the reactor in a thermostatically controlled bath. On the very small scale at which we operate, the problem of a strictly continuous evacuation of the slurry by a small overflow pipe is not entirely resolved. To avoid blockages, we currently prefer to evacuate the slurry through the overflow every 10 or 15 minutes.

Preparation of the foot of the reactor tank

Initially, the foot of the reactor tank is prepared batchwise: the phosphate is introduced into the phosphoric acid, and sulphuric acid is progressively added, followed by stirring for several hours, whilst maintaining the temperature and P2O5 concentration constant by the addition of hot water. The need for sufficient time to set the system in operation has led us to carry out this preparation on the previous day and to maintain the slurry at the chosen temperature in a thermally insulated chamber under refrigeration.

Start-up of the system

We estimate that a minimum of 10-12 hours is required to start-up the system. Only when the crystals have reached a constant size does the slurry begin to be representative and results become valid, particularly with regard to filterability.

The slurry can be left stagnant during the night without any change in the size of the crystals. If one then restarts with the same operating conditions, the same characteristics reappear, but despite this it is preferable to wait for several hours before considering samples as valid. On the other hand, by recommencing with different working conditions, one can observe the crystalline system progressively changing. For example, after obtaining fine crystals of gypsum from a reaction in a slightly sulphuric medium, if one modifies these conditions to work with an acid deficit, one observes after some hours a decrease in the size of the crystals as well as a reduction by a few percent in the rate of solubilisation. Similarly, one has to wait a sufficient time for the new conditions of equilibrium to be attained.

Results

It should be noted that the whole proportioning mechanism is controlled by a true hydraulic clock. Once the operating conditions are established in the desired ratios, the apparatus requires no further attention, except for its adjustment for different products and for bringing it initially into equilibrium. These operations require only a few minutes. But one can easily decrease or increase the rate of production merely by adjusting the flow of the master flask, since the same proportioning will be strictly and automatically respected in all the rates of flow. The accuracy of the flow ratios is better than 0.2% error, i.e. distinctly better than that in industrial plants, and this despite very small levels of production.

We are including certain photographs in this paper to give some idea of the kind of service which such an installation can offer. The first 3 photographs represent crystals of hemihydrate calcium sulphate sampled at one hour, 7 hours and 10 hours after commencement of the continuous experiment at 90°C. One can clearly see the increase in the size and the change in the shape of the crystals as time increases, and one can appreciate the need to wait a sufficient time for equilibrium to be established.

Photograph No. 4 represents a slurry of hemihydrate calcium sulphate in phosphoric acid, obtained after a continuous reaction at 90°C and stirring for twelve hours at 65°C in the presence of 8% gypsum. One can see clearly - and analysis confirms it - that the conversion of the hemihydrate into the dihydrate form has not yet occurred and that one is dealing with a very stable form within the conditions of the experiment.

Photographs Nos. 5 and 6 correspond to an operation with production of gypsum at zero time, i.e. immediately after the preparation of the foot of the reactor tank, and after 36 hours. The corresponding operating conditions were as follows:

ground Moroccan phosphate rock....4.5% oversize at mesh 100

Temperature..... $73^{\circ} \pm 1^{\circ}\text{C}$

retention time in the reactor.....2h. 45 mins \pm 15 mins.

$\frac{\text{H}_2\text{SO}_4}{\text{phosphate rock}}$: 87.5

Filterability under 10 cm of vacuum at 40-45 $^{\circ}\text{C}$

Filter diameter 12 cm - S = 113 cm 2

75 cm 3 - 47 seconds (\pm 10 seconds %)

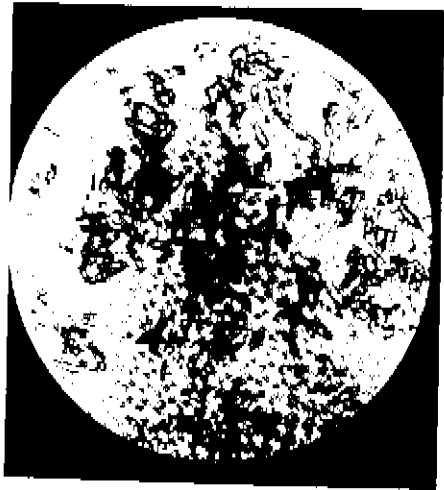
{ P $_2$ O $_5$ % : 29.5 + 0.5

{ total SO $_4$ (after desupersaturation) : 1.0 \pm 0.2

Solubilisation yield : 97.1 \pm 0.3

Our paper shows that the laboratory chemist who hitherto proceeded merely with batch trials and could not claim to reproduce industrial conditions, can, by the simple means we have described, get much closer to them. He is thus able to answer a certain number of questions raised by the manufacturer and, to some extent, he can obviate the need to have recourse to semi-industrial or industrial trials, which are probably more instructive but are certainly longer and much more expensive. The equipment is particularly suited for comparative trials, by varying one factor at a time to study the influence of it. For example, it enables one to estimate the relative value of proposed new phosphates and to study the effect of certain additives or of certain systematic departures from the controlled conditions of manufacture. It can thus indicate the advisability, or otherwise, of certain industrial experiments.

The size of the apparatus that we have chosen is, in our opinion, well suited to the prospecting work which can be carried out in a central laboratory with a minimum of raw materials at the disposal of the chemist. For certain types of trial, however, if we were able to install ourselves next to the phosphoric acid plant, we would preferably choose an installation of the same type but with a balance capable of taking a flow of 3 to 5 Kg per hour of calcium phosphate. This would not afford more accurate ratios of rates of flow but would offer more diverse mechanical facilities, particularly for the proper study of the phenomena occurring in the reactor.



G-740



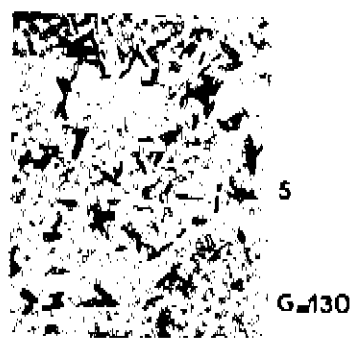
G-740



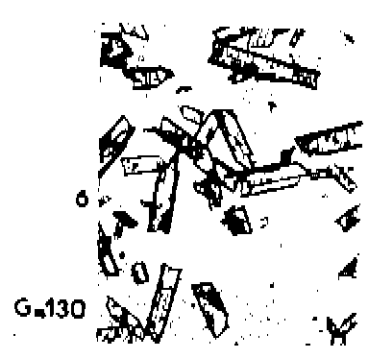
G-740



G-300



G-130



G-130

Figure 3 :

- Nos. 1 - 3 : Crystals of calcium sulphate hemihydrate.
- 4 : Slurry of calcium sulphate hemihydrate in phosphoric acid.
- 5 - 6 : Operation with production of gypsum at zero time and after 36 hrs. (see text for explanation).

DISCUSSION

MR. R. BAUWENS (Ets. Kuhlmann, France) : In our paper, we describe a simple foolproof apparatus for the strict proportioning of reagents in either solid or liquid form, which has enabled us to study on a very small scale the manufacture of several products, particularly phosphoric acid.

As far as the distribution of the said reagent is concerned, the distributing hopper containing the powder is placed on the platform of a balance or scale. It is brought into equilibrium. The weight of the balancing tare is then varied as a strict linear function of time. As the weighing system becomes slightly unbalanced, it makes an electrical contact which, by means of a relay, sets the discharge mechanism of the hopper in operation and takes a small quantity of powder off the platform. The balance or scale is then restored to equilibrium, breaks the electrical contact and stops the discharge from the hopper. As the tare continues to vary, a second electrical contact is made, a further quantity of powder is evacuated, and so forth. Thus the solid product is distributed in very small quantities - about ten per minute - according to the same programme as that of the variation of the weight of the tare.

In practice we achieve the variation of the weight of the tare, as a function of time, by means of the flow of a liquid at a constant rate, using either a volumetric pump or, preferably for small rates of flow, a Mariotte flask.

As far as the distribution of liquid reagents is concerned, we have now been using for more than ten years an apparatus which has given us much good service, particularly for solvent extraction studies, but also for analytical separation. It consists in the use of vessels with a constant horizontal section, calculated in advance, for the different solutions. The various vessels are associated with each other as indicated in figure 1. They are initially filled with their respective liquids. All the taps are then opened, and after a few minutes the liquids achieve a constant rate of flow, these rates being strictly determined by weight in relation to the ratios of the horizontal sections. If with this proportioning system for solutions one of the vessels is used to give the necessary flow for the operation of the powder distributor described above, a mechanism is then achieved which ensures the strict proportioning of a solid product and of one or several liquid products.

It is this principle that we have applied, amongst others, for the laboratory study of the continuous manufacture of phosphoric acid. Figure 2 is a diagrammatic representation of our experimental apparatus and, as an example, we give the calculations necessary to set up an installation for a given problem. But each one of you can imagine many variants to suit

your own particular problems.

Since our first installation, we have constructed others which are more compact, because the hopper is placed on a balance with a single rectangular platform. Similarly, we have replaced the electrical contact by a photo-electric eye. But all the apparatuses have been entirely satisfactory.

In our paper, we also describe the means we have used to operate the apparatus in the case of phosphoric acid. We should like to draw particular attention to the need to allow a sufficient time for the slurry to achieve equilibrium.

We also quote - solely as an example - certain experimental results which we can obtain in our small installation. In this regard, we draw your attention to the photographs of crystals. As the photographic reproduction is on a reduced scale, the linear dimensions of the crystals shown in the paper should be multiplied by 1.3.

DR. R. F. McFARLIN (Armour Agricultural Chemical Co., U.S.A.)

All who have worked on a laboratory scale realise the difficulty of metering liquids and solids - but particularly solids - on a small scale. We also realise the necessity of studying the variables in wet process phosphoric acid manufacture and usage on a continuous basis, so that equilibrium conditions can be realised, particularly in the growth of the gypsum crystals.

I should like to ask Mr. Bauwens a number of questions.

First, has he considered metering the liquid control stream in a flow-rater to give absolute flow rate of the system ?

Secondly, how can he be sure that the system does not experience in-leaking of air during the operation ?

Thirdly, under actual conditions of flow is there any significant pressure drop through tube T in Figure I ?

Is bridging of the solids in the hopper ever a problem ?

Lastly, is vapour pressure of various gases over the phosphoric acid a factor in affecting the flow rate ?

MR. R. BAUWENS : The Mariotte flask is an apparatus which works even if there are slight leaks in the stoppers towards atmospheric pressure. As long as the liquid flow is greater than the flow of air arriving in the system, i.e. as long as you see the air bubbling in the Mariotte flask, the system is valid. The only thing to be watched is the air bubbling. The air should arrive through the tubing, but if part of it comes through the stoppers the system will nevertheless continue to operate.

As far as metering is concerned, we can do this with test tubes during operation. We see that proportioning is quite exact. The Mariotte flask - the device which I added - works exactly like a hydraulic clock.

You asked me whether vapour pressure affected the addition of liquids into the reactor. This has no influence; it is a way of arranging the apparatus.

MR. M. ROUBINET (Péchiney-St. Gobain, France) : In the conclusion of your paper you consider it necessary "particularly for the proper study of the phenomena occurring in the reactor" to transfer to a distinctly larger scale than that of your laboratory (a tank of about 2 litres). Do you not think that an intermediate capacity of, say, 10 litres might be satisfactory? We chose this capacity for our own continuous test of phosphoric acid manufacture which has proved entirely satisfactory for the past ten years.

Secondly, do you not think that by carrying out your laboratory trials in a single tank you will be automatically led by simple extrapolation to the industrial use of a single reactor - a process which has, in any case, already proved itself ?

MR. R. BAUWENS : As mentioned in our paper, it does indeed seem to us desirable, for mechanical reasons, to avail ourselves of a semi-industrial tank of 30 - 40 litres. However, we believe you quite unreservedly when you say that you make satisfactory use of a 10 litre tank for your own test of continuous manufacture. This naturally implies that you have resolved the problem of good proportioning of the reagents on this scale. As far as we are concerned, the more our experience develops, the more we tend to think that a capacity of 2 litres is largely sufficient, precisely because of the strict, fool-proof proportioning apparatus described in our paper.

As for the second question, the fact of working on a laboratory or semi-industrial scale with a single tank, in either simple or compartmented form, does not necessarily lead, as far as we are concerned, to industrial extrapolation with a single tank. Indeed, it may be advantageous for the manufacturer to have several reactors which are easy to empty and maintain.

If, for example, one wants a very flexible plant where production is ensured for 365 days of the year, one should reflect that it is necessary to work in the reactor with the most homogeneous slurry possible. This can be obtained either by sufficient agitation in a single reactor or by a substantial pumped circulation of the slurry through one or several reactors in series. The very important question of the introduction of the reagents and their immediate dilution in the medium at the

place where they arrive is easily resolved if there is sufficient agitation to ensure their immediate diffusion. This is the case with small reactors : they always have sufficient agitation. In large reactors, where agitation has to be paid for in kilowatts consumed, one has to have recourse to the more or less classic devices for the preliminary dilution of reagents in the slurry put into circulation, either by an appropriate system of agitation or by pumps, or by both. It is up to the chemical engineers and process technicians to select the most economic solution to this problem.

MR. A. M. BRZOZOWSKI (Mathew Hall Engineering Ltd., U.K.) : I should like to ask Mr. Bauwens what was the concentration of P2O5 in the slurries from which the photographs of the crystals shown in his paper were taken.

Secondly, the $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ crystals were presumably obtained after filtration. What was Mr. Bauwens' experience of filtering these crystals ?

MR. BAUWENS : As we have previously indicated, the details we quote represent no more than one example amongst several. In this example, the acid strength was about 30% P2O5. But in our trials we have worked with acid strengths of 30%, 35%, 36% and sometimes 40% P2O5, and we have also used semi-hydrate process going up to 42% P2O5.

The semi-hydrate is obtained at about 30-32% P2O5, but we know very well that a semi-hydrate obtained in a 40% medium is not so good. For us, it comes in the form of agglomerates, and we shall be very interested in hearing the next author tell us of his experience with the semi-hydrate process, to see whether his industrial observations coincide with our own observations.

MR. B. CARLSEN (A/S Danak Svovlsyre- og Superphosphat Fabrik, Denmark) : Your photograph No. 4 represents a slurry of calcium sulphate hemihydrate in phosphoric acid obtained after a continuous reaction at 90°C and stirring for 12 hours at 65°C in the presence of 8% gypsum. Photograph No. 5 relates to a production of gypsum immediately after preparation of the reactor tank and at 73°C. Photograph No. 6 relates to the same slurry 36 hours later, keeping the temperature constant at 73°C. This means that the retention time relating to Photograph No. 4 is only 12 hours whilst in Photograph No. 6 it is three times longer. I wonder if you have had an opportunity of comparing the two experiments using a retention time of 36 hours for both. If so, did you notice any change in the hemihydrate crystals to the dihydrate form ?

MR. BAUWENS : After 10 hours the gypsum is roughly the same. Thus one must wait 10-12 hours before the gypsum is of the size shown in Photograph No. 4. We took a photograph after 36 hours merely to see whether there was any change; but, in fact, the size

of the crystals was almost the same since 10-12 hours after the start of the experiment. Experimental conditions were such that the semi-hydrate obtained was extremely stable, very well formed and very coarse. We suppose that because of this it was not easily susceptible to rehydration. It was because of this that we show you an experiment in which we have tried to prime the semi-hydrate with gypsum, and after 12 hours it was still in the semi-hydrate state. In other experiments, it required only 3 hours, more or less, for the semi-hydrate to become gypsum.

MR. A. C. VAN ES (Albatros Superfosfaatfabrieken, Holland)

On page 5, you say that you add a certain amount of the sulphuric acid and adjust afterwards. It is not quite clear whether you adjust with 5% or 95% of the acid.

MR. BAUWENS : In order to make our trials more flexible, i.e. in order to be able to carry out several trials with the same apparatus, we work with a sulphuric acid deficit in the general flask and we make the small necessary addition with another Mariotte flask in order to achieve the exact flow required.