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THE CONTINUOUS RECORDING OF P_2O_5 LOSSES IN DRAINS

By J.S.S. Reay (Scottish Agricultural Industries Ltd., United Kingdom).

1. INTRODUCTION.

The work to be described on continuous measurement of phosphate in drains has been carried out principally at Scottish Agricultural Industries Leith Fertiliser Works which includes a phosphoric acid plant, two phosphoric acid concentrators, one industrial and one fertiliser ammonium phosphate plant and a compound granular fertiliser plant. It was on the main works drain carrying effluent from all these plants that the Company first applied the system of continuous analysis primarily as a measure of works efficiency. While it was realised from the outset that analysis of a composite drain would pose considerable problems of interpretation and diagnosis, the exercise was of considerable value in indicating the magnitude of losses of which various plants were capable and in deciding which individual drains would show greatest benefit from continuous monitoring. In addition, many of the problems associated with the application of the analytical and sampling systems were solved before they were applied to single plants where the operators were expected to act upon the results. The project got a very helpful send-off from Marchon Products Ltd. Whitehaven. That company, on learning of our purchase of a Technicon Auto Analyzer, made available their experience with such equipment on their phosphoric acid plants.

2. PHOSPHORIC ACID PLANT EFFICIENCY.

The P_2O_5 efficiency of a phosphoric acid plant is easily defined as the P_2O_5 produced as acid expressed as a percentage of the P_2O_5 input as rock. In practice, however, it may not be easy to measure the amount of acid produced. Direct gravimetric or volumetric measurement of output cannot allow for the varying relationship between strength and specific gravity. Measurements may be further complicated by return of acid from storage, or usage of acid from the same tank as is fed by the acid plant. For a plant running at 90% efficiency the assessment of plant efficiency to an accuracy of 1% involves product measurement to 1 in 90 whereas the same result can be obtained from effluent measurement to 1 in 10.

It has been recommended in the past, that extraction and

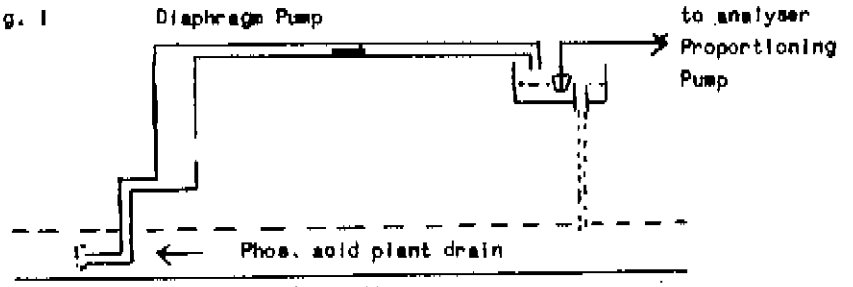
filtration efficiencies on a phosphoric acid plant should be measured from samples of gypsum taken from the filter immediately prior to discharge. In common with other producers we have found this to be practically useless for determination of filtration efficiency, but, at least with a high recycle phosphoric acid plant, the level of insoluble phosphate in the gypsum remains fairly constant and shiftwise analysis of samples is adequate for estimation of extraction efficiency. From the point of view of process control any change in extraction efficiency will normally be reflected in the level of free sulphate in the reaction magma which is measured regularly by the plant operator. With the gypsum insoluble phosphate related to the tonnage of rock fed to the reaction system, it becomes unnecessary to obtain a representative sample from a drain carrying considerable quantities of suspended gypsum since the remaining losses of soluble phosphate from filtration and other operations can be measured on liquid filtered from the drain. From the above it is obvious that wet disposal of filter cake is being assumed. Other typical effluents from phosphoric acid plants are vacuum condenser flows from the filter or slurry coolers and these are frequently combined with the filter slurry in a common drain thus simplifying and cheapening the estimation of overall plant efficiency. It is necessary to ensure that the sampling point is chosen such that the liquid is representative of the soluble phosphate losses of the plant. This requires the efficient mixing of individual streams making up the effluent and the attainment of an even distribution of the soluble phosphate from the gypsum throughout the drain liquid. This latter requires checking if the sample point is chosen, for minimum time lag, very shortly after the point of slurrying of the filter cake. To do this a sample with solids is drawn from the drain and some liquid is extracted immediately as for the auto-analysis. The sample is shaken and further liquid is extracted at intervals. From phosphate determinations on the liquid extracts it can be shown whether there is progressive transfer of soluble phosphate from the filter cake to the liquid. It has been our experience that, in a suitably turbulent drain, transfer is almost complete in less than a minute from the time of slurrying the gypsum.

3. SAMPLE EXTRACTION AND INSTRUMENT SITING.

The continuous and reliable extraction of the liquid sample is the heart of the auto-analytical system. For minimum time lag between drain sampling and presentation of analysis, the instrument should be as near the drain as possible. If significant separation is inevitable it is preferable to divert suitably a substantial fraction of the drain flow to a point near the instrument where the liquid sample is then extracted. The solids-carrying effluent should be transferred with a glandless or diaphragm pump for reliability in the presence of abrasive materials. The nature and position of the liquid extraction filter has been

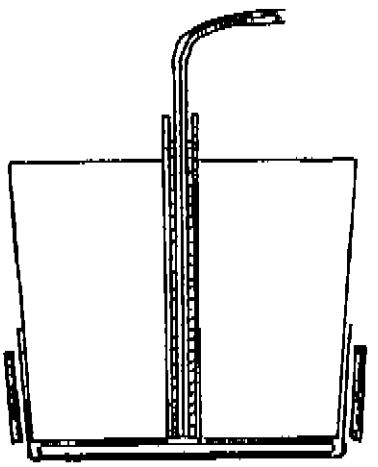
the subject of considerable experiment. Designs involving the insertion of the filter element into a rising pipe on the delivery of the pump involved shut-down of the pump for servicing of the filter. To avoid frequent servicing a self-actuating filter cleaning system was fitted which also produced discontinuities in the analytical record unless an intermediate buffer of liquid was kept, which decreased the instantaneous sensitivity of the system owing to sample mixing. The most satisfactory design has been found to be one in which the delivery from the pump is broken as in Fig. No. 1 and the filter element is suspended in an overflowing

Fig. 1



basin in which the turbulence is adequate to avoid build up of solids below the filter. The advantages are that the state of the main drain pumping system can be seen at a glance and the filter can be examined and serviced with the minimum interruption. The filter design, Fig. No. 2, is

Fig. 2



simple and has been generally trouble free on the Company's Leith Works. A sintered glass disc, porosity 2 or 3, is held to the face of a rubber bung by a piece of terylene filter cloth gripped by a rubber collar. With the volume of liquid through the filter limited to that required for auto analysis and cumulative sampling, the filter may need cleaning weekly, and the disc lasts several months before clogging with fine material, which resists even acid washing.

The sample is drawn through the filter by the Technicon Auto Analyzer's proportioning pump along a very narrow tube to reduce time lag and minimise mixing. We have designed our system to obtain the maximum detail on instantaneous drain conditions. This is assisted by the absence of a mixing tank for the gypsum slurry which is present in some plants. Such a tank is usually of capacity great enough for the effluent produced by at least one revolution of the filter and therefore any differences in the performance of various segments of the filter are lost.

The distance from the filter to the Technicon Auto Analyzer pump of about seven feet is dictated by the layout of the equipment but should be shorter if possible. Since the trace of the Technicon Auto Analyzer is not readily integrated, the liquid sample is split before the proportioning pump into two streams, one for auto-analysis and one for accumulation to give a daily average sample. A large tube is used for the cumulative sampling merely to decrease the time lag from the sample filter. We achieve an overall time lag between gypsum disposal from the plant filter to presentation of analysis of just over eight minutes.

At an early stage in our work trouble was experienced with slugs of gypsum passing the filter into the analysed stream. Solution of the gypsum in the acid reagents released otherwise unsoluble phosphate and produced anomalous 'blips' in the trace. Prior to improvement of the filter this difficulty was overcome by positioning the split of the sample before the proportioning pump so that the unwanted gypsum gravitated into the larger line leading to the cumulative sample. With the present filter arrangements the sample is more frequently contaminated with air bubbles which would apparently reduce the drain losses if passed through the Technicon Auto-Analyzer. The air is removed by inverting the sample divider so that the bubbles may rise into the limb to the cumulative sample, now above the limb to the Analyzer.

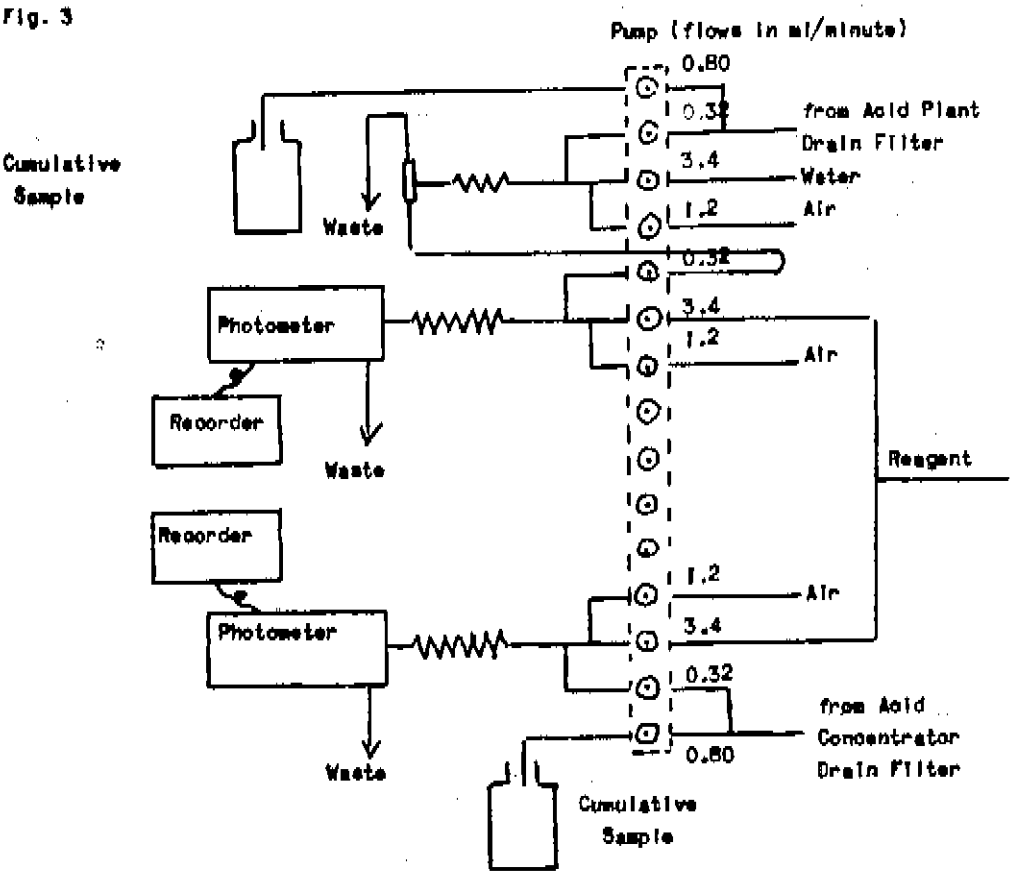
4. DETAILS OF THE TECHNICON AUTO ANALYZER SET-UP.

Within the proportioning pump, the manifold (Fig. No.3) follows standard procedure with an initial dilution and subdivision to minimise reagent requirements and reduce colour density. It has not been found necessary to have a dialysis stage.

For the accuracy required for plant operation, daily standardisation of the Analyzer is adequate except perhaps when a new manifold is being run in and throughput is altering more rapidly. Standard solutions representing drain phosphate concentrations over the range 100 to 2000 p.p.m. are made up in sea water since this is used for gypsum disposal and for condensers. The standards are

introduced by breaking the line from the sample filter. The cumulative sample may also be run on the same Analyzer provided its value is calculated from standards quite close in concentration since wide extrapolation seriously reduces the accuracy of measurements.

Fig. 3



The Analyzer is taken off stream for an hour or more once a week when the manifold is checked and its tension altered. Lines are washed through with sodium EDTA solution to dissolve any gypsum deposits and the photometer cell is rinsed with detergent to remove any oil or grease. The rare accidental introduction of oil from the drain causes blinding of the cell wall and serious drifting of the recorded trace.

The proportioning pump and photometer have been sited near the drain in a hut at constant temperature. The information is most suitably presented in the acid plant control room. However, at least an instantaneous reading of instrument output is necessary beside the photometer for the presetting of transmission limits. Closed circuit television transmission to the control room of the recorder trace from the hut has been replaced by taking the primary

room, and retransmitting the instantaneous recorder readings to a meter in the hut. The acid plant operator can therefore observe short term trace form and have access to previous records for the recognition of longer term trends. A chart speed of two inches per hour allows the recording of a sufficiently detailed trace for routine operation while reversing gear wheels to give eighteen inches per hour clarifies fine detail for special plant measurements.

Since the Analyzer indicates the concentration of phosphate in the drain, the rate of loss of soluble phosphate in the effluent is directly proportional to this concentration only for a fixed liquid flow in the drain. Where a variable flow is inevitable, some form of flow indication is necessary for interpretation of the results. An average flow rate derived from a recording indicator will allow estimation of daily losses from the cumulative sample. In principle, the output from the flow indicator may be made to provide a variable shunt to the Analyzer recorder so that the trace provides directly a true record of drain losses. In practice we have found it easier for 90% of the time to keep the drain flow constant to within 5%. At shut-downs the operator is aware if his drain flows are reduced and can modify his interpretation of the trace accordingly.

5. USE OF THE AUTO-ANALYTICAL RECORD IN IMPROVING PLANT CONTROL.

Under normal running conditions with no phosphate disposal except from the filter, the Analyzer registers the efficiency of washing of the gypsum cake. This washing is affected by the desired strength of product acid which largely controls the amount of wash water used. In addition, the positions of the various countercurrent washes can affect the overall removal of acid as does the speed of the filter, which fixes the total time spent over the removal of the successive lots of liquid. Finally, all the above factors are related to the gypsum crystal form, which governs the porosity of the filter cake, and to the rate of delivery of gypsum to the filter, which is directly proportional to the production rate.

The interdependence of these parameters in phosphoric acid manufacture has been realised for a long time, but any experiments involving adjustments of filter conditions have been difficult to assess rapidly since reliance had to be placed on visual assessment of the filter and on the slowly changing specific gravities in the vessels receiving the various filtrates.

While these filtrate specific gravities are useful they do not tell the whole story of filtration unambiguously. For instance, the same performance can be achieved by a series of small washes efficiently removed from the cake or larger washes less completely extracted.

While some alterations can still be fully felt only after some hours owing to the slow effect of feed back on the great mass of the reaction system, the Technicon Auto Analyzer responds rapidly to changes in overall filtration efficiency when any of the above parameters are changed. In particular the operator can more accurately control his primary wash water feed to give a pre-determined efficiency and alter his wash positions to give a desired range of specific gravities in his receiving vessels while knowing how his cake washing is being affected.

One important piece of information which the analytical trace has spotlighted is the full effect of slurry load on the filter for a given crystal condition. Over a wide range the disposal of soluble phosphate is more or less proportional to production rate. As the filter becomes overloaded the loss of phosphate rises more and more rapidly. While previous discontinuous drain monitoring had given a rough indication of the limiting load, it was not fully realised by the operators that, on lower loads, temporary increases in the feed of slurry to the filter to reduce levels in the reaction system could produce very high short term losses. Significant savings can be made by spreading a lower excess load over a longer period.

Something similar occurs in start-up technique. It was realised that for the first revolution of a vacuum filter the slurry feed should be low until the vacuum is fully applied, but thereafter it was difficult to establish the feed rate exactly equivalent to the input of fresh raw materials. Control was by measurement of cake depth or by observation of levels in the reaction system. On high basic loads, overfeeding of slurry produced excessive losses while underfeeding for a period raised levels and had to be compensated for with a spell of overfeeding. The Analyzer can indicate shortly after start-up whether the disposal to drain is consistent with the plant load.

With a multi-section filter the deterioration, through blinding or other means, varies from section to section. One or more sections will become obviously less efficient than the others but, prior to the introduction of continuous analysis, the point at which the plant was stopped for cloth replacement was decided on a largely personal assessment. Now the loss in production time can be related to the measured rise in inefficiency of the filter and a level of loss chosen at which cloth replacement is done. The deterioration of individual sections becomes obvious in the analytical trace before it is noticed by visual inspection and this can be utilised in the comparison of various makes of filter cloth. Half of the sections (consecutive) can be clad in one make and the remainder in another. Their performance can then be observed both for initial porosity and longer term deterioration. The relationship of the filter revolution to the analytical trace can be indicated

by tipping a small quantity of phosphoric acid on to a known section when the cake is to be ejected.

Any sudden changes in filter performance caused by faults, such as failure or choking or washing systems, are rapidly indicated. If all the effluent of the plant is being monitored, defects elsewhere in the plant are shown. For instance carry-over from the filter vacuum system or from a vacuum evaporative cooling system, owing to too high a vacuum or choking of the slurry pumping system, will be superimposed on the normal filter losses. The recorder can be fitted with an alarm set to a predetermined maximum so that the operator can be warned of excessive loss while on tour of the plant. The nature of the high loss trace can itself be highly indicative of the type of defect which has developed, and experience shortens the time required for accurate diagnosis. Several of the points of possible loss can alternatively be covered by conductivity or pH measurements, although the latter can be notably misleading where there is substantial carry over of hydrofluoric acid. The Technicon Auto-Analyzer readily covers these points in addition to monitoring filtration and is specific for phosphate.

We have made no attempt to utilise the Analyzer for on-line control, firstly since it measures only one item, variations in which may be connected with several factors. More important, the plant has only one operator whom the Analyzer could not displace and therefore no substantial saving would accrue from cutting out the human link in the control chain.

6. MONITORING PHOSPHORIC ACID CONCENTRATORS.

Adjacent to the phosphoric acid plant at Leith are two Swenson phosphoric acid evaporators with a common hot well from which the fairly constant flow of sea water used in the condensers discharges to drain. Spillage from pumps etc. associated with the evaporators is also fed to the hot well. It was, therefore, a simple matter to lead a pipe from the hot well to a mono-pump beside the Analyzer hut and to sample from the delivery side of the pump through a crude filter to the same proportioning pump used for the phosphoric acid plant. The simple manifold, Fig. No. 3, which requires no dilution stage, is easily accommodated by the pump. A separate photometer is required, feeding a remote recorder which, as before, retransmits to a locally sited meter. The range 20 to 400 p.p.m. is covered with adequate accuracy.

Monitoring of the evaporators has produced useful information relating to conditions throughout the operational cycle. Carry-over of acid mist can be related to vacuum and evaporative load; and the material efficiency during emptying and boil-out can be checked against running

time between boil-outs. At S.A.I.'s Aberdeen Works a Technicon Auto-Analyzer has been applied to a submerged combustion evaporator. Considerable information has been obtained on the relationship of atomisation and burning to the extent of carry-over of acid fume past the cyclonic separator and work is to be done on the alteration of conditions for the efficient usage of various grades of fuel.

7. OTHER APPLICATIONS AND GENERAL CONSIDERATIONS.

A question, that has been raised about continuous process monitoring, concerns the necessity for its long term use. It is accepted that the introduction of the system can point the way to improved operation but it has been suggested that once this has been accomplished it may not be justifiable to retain relatively expensive equipment on continuous monitoring. For a phosphoric acid plant we have no doubt that the Analyzer should be retained since the improvements to be made in operating conditions and control are not of a once-for-all type. In the case of evaporators it is arguable that once an operational routine has been introduced on the basis of analytical findings the monitor may be withdrawn. However, its retention not only provides a warning in the event of unexpected loss, but a round-the-clock superintendent of operator performance. It is temptingly easy to take wasteful short cuts in producing or handling a liquid which can disappear down a drain with no obvious trace.

Where several processes involving phosphate are being operated within a works it is useful to have a mobile unit for individual investigation. It might initially be sited on a composite drain where we have found it easy, with a little practice, soon to distinguish trace shapes characteristic of the operations of various plants. With simple modifications this mobile unit can be made to register the concentration of materials other than phosphate thus increasing its versatility. For specific estimations one can devise continuous systems without recourse to the commercial Technicon Auto-Analyzer but its reliability and adaptibility are to be recommended highly.

8. ACKNOWLEDGEMENT.

The Author wishes to thank the Directors of Scottish Agricultural Industries Ltd., for permission to publish this paper.

DISCUSSION

Mr. J.S.S. REAY (Scottish Agricultural Industries Ltd., U.K.): I make no apology for the detail in my paper, since the principle of the application of continuous analysis is quite obvious. The difficulties lie in practical details. The work reflects the attitude of my company, which believes that, as far as automation in fertiliser manufacture is concerned, one should always learn to crawl before one walks. Many chemical firms could buy a computer, but could they make effective use of it? Firstly, the link with the process parameters may be difficult to achieve with any accuracy and reliability. It is not by accident that the first chemical processes, to which complete automation has been applied, have been those where control lies in the measurement of liquid or gas flow rates and pressures, and of temperature. In most stages of fertiliser manufacture, important items are solid, slurry or fluid flow rates and the chemical analysis of these streams. When the problems associated with these measurements have been solved, study of the process in terms of these parameters can commence.

The purchase of a computer at this stage can be considered for its data logging and analytical facilities; but this may be regarded as presupposing that the improvements which automatic process control brings are going to justify the expense of the installation. We prefer to utilise human examination of the records of process variables to determine what improvements can be made in process technique and what advantages automatic control might bring.

In restricting myself to the topic of phosphoric acid manufacture, I should merely like to stress the following requirements. There must be constant drain flow or proportional linking of the flow rate to the recorded trace, since the analysis indicates concentration and not overall quantity. Secondly, there must be certainty of the extent of transfer of soluble phosphate from the filter cake to the drain liquid, as well as good mixing of this liquid, so that sampling is representative. A constant volume of liquid must be presented at all times to the analyser, free from solids and air bubbles. I have indicated in the paper simple means of dealing with either of these latter difficulties. The analytical instrument must be satisfactorily standardised with phosphate in a medium equivalent to the drain liquid.

With these points in mind, it should be possible to obtain a reliable record of plant efficiency. But if it is intended to use the system for detailed study of the process and, possibly, for eventual control, efforts must be made to obtain a low time lag and a high degree of detail of resolution of drain concentrations over a short period. In the paper, I have therefore stressed the use of short, narrow tubes with high flow rates, a low-volume filter element and a low-volume measuring cell for the final coloured solution, in order to minimise the smearing of short-term fluctuations. These help materially in the use of the instrument for diagnosis of the causes of excessive loss. For example, deterioration of filtration on a rotary multi-element filter will always produce an increasing cyclic fluctuation related to differences between elements. If the

resolution of the analytical equipment is adequate to distinguish events within a revolution of the filter, such deterioration in filitration can be differentiated from aperiodic sources of loss.

I have also mentioned the usefulness of the detailed trace in measuring filter cloth performance, and the advantages of low time lag between an event and the presentation of the record of that event are obvious.

On processes other than the straight manufacture of phosphoric acid, I have mentioned the use of continuous analysis on phosphoric acid concentraters of two types. On both of these, analysis has yielded much useful information.

Elsewhere in the fertiliser works, the concurrent use of several analytical systems on several drains has been very helpful in arriving at accurate mass balances.

Altogether, the experience gained in 21 months of continuous automatic analysis has made a useful contribution to our present effort to provide continuous analysis of the products of our compound fertiliser works.

Mr. J. J. PORTER (Fisons (Pty) Ltd., South Africa): In 1950, I was associated with a phosphoric acid plant, and we found that, after a few months' operation, our idea of filter efficiency bore no relation with recorded results. We sampled right across the filter and were still unable to account for our losses. We then sampled from the gypsum slurry pump and found that P_2O_5 analysis took too long; and therefore, on the assumption that the relation between H_2SO_4 and P_2O_5 would be fairly constant in the plant, we carried out a simple analysis for free acidity and related this with the suspended gypsum in the slurry. We had a shock! We found P_2O_5 losses where we had never suspected. If we had had the system described by Mr. Reay, we would have been saved a lot of anxiety!

Mr. Reay's system analyses only for soluble P_2O_5. There is, however, a considerable quantity of P_2O_5 which becomes tied into the crystal lattice, and I wonder whether sampling only the liquid really gives the true answer. Should one not detain the gypsum sufficiently long to extract the P_2O_5 from the lattice?

I was pleased to see that Mr. Reay still values the human element in recording : I think the examination of plant records helps to maintain the interest of the operator in the plant.

I wonder whether you are taking into account the application of your device to nitrogen - involving gas analysis - and potash.

Mr. REAY: We measure only the soluble P_2O_5 quite intentionally, since the insoluble P_2O_5 - either as unreacted rock or phosphate substituted in the gypsum lattice - is estimated separately in

the laboratory and remains remarkably constant, irrespective of filtration conditions.

As far as the human element is concerned, my remarks were purely in the context of the possible use of a computer. Plant records must be very complete, and we must have continuous and accurately recorded measurements of all parameters in which we are interested.

We are, indeed, interested in extending our methods of automatic control to nitrogen and potassium as well. We have already done this on a discontinuous basis and intend to extend our technique to continuous monitoring of solid products.