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

PROCESS AND APPARATUS FOR THE CONTINUOUS MEASUREMENT OF THE FREE
SULPHURIC ACID CONTENT IN THE MANUFACTURE OF WET PHOSPHORIC ACID

(Companhia Uniao Fabril, Portugal).

I. Introduction

In the production of phosphoric acid by the so-called "wet process", a slurry is obtained. The filtrability of this slurry, as is well known, mostly depends on the free sulphuric acid content, in view of the desirability of maintaining a controlled excess of sulphuric acid (say in the range 2-4% by weight).

In the current technique, the control of the excess of sulphuric acid is carried out by removing samples at certain intervals and by analysing them at the Industrial Control Laboratory. The disadvantages of this practice are well known.

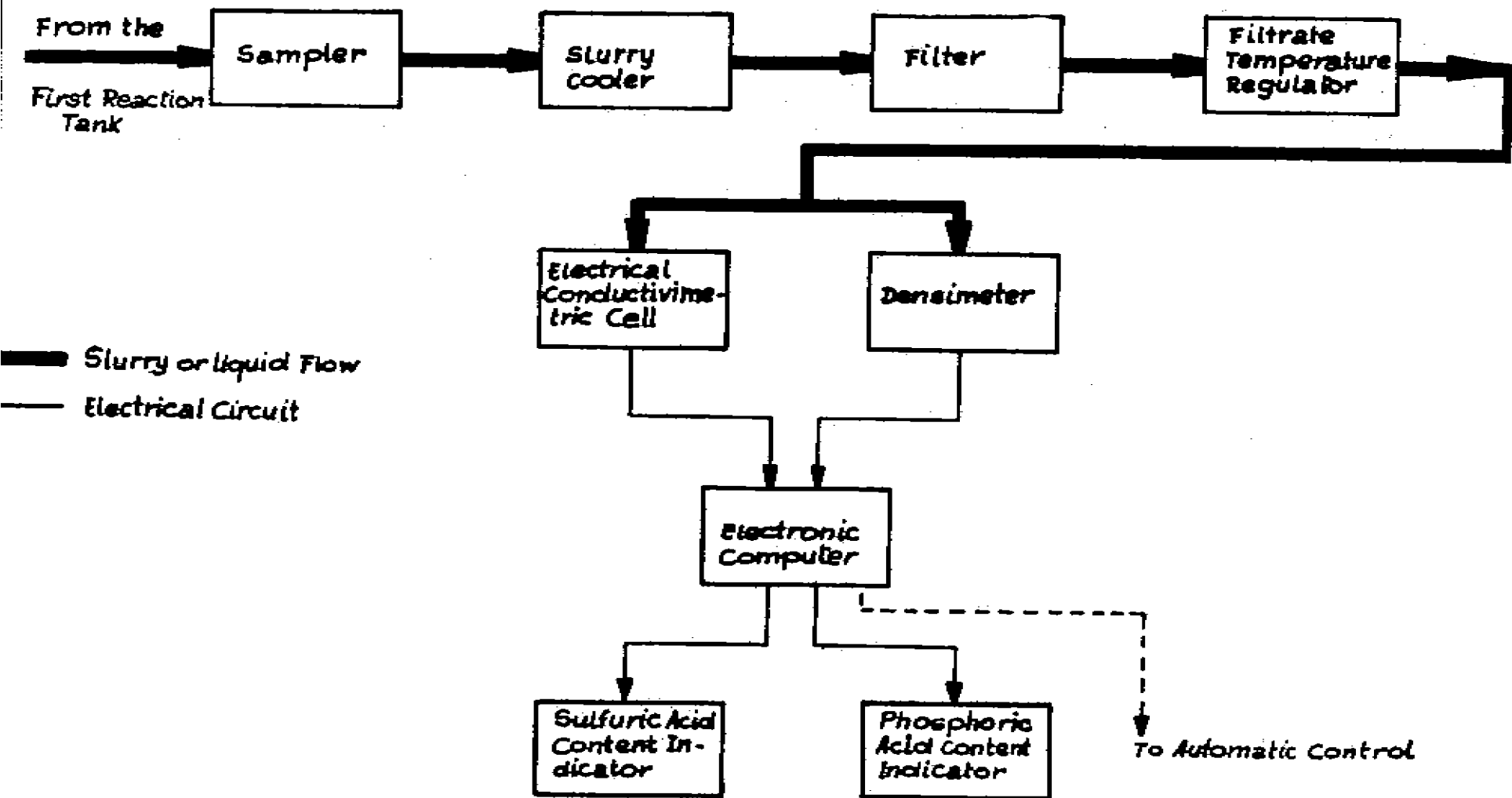
The Research Centre of CUF has carried out a research project designed to achieve a process enabling a continuous measurement of the free sulphuric content in the slurry which results from the industrial chemical reaction.

The results of our research on this subject showed that at least two measurements are necessary for the determination of the free sulphuric acid content. Our experimental work has led us to choose to measure the electrical conductivity and the density of the filtrate obtained from the slurry.

The practical value of this process relies upon the possibility of obtaining a clear filtrate, without any traces of solids in suspension. The presence of solid particles gives rise to difficulties in both measurements, but mainly in the electrical conductivity determination. So we have successfully developed a filtration process and apparatus, which gives a very clear filtrate.

The process also permits the simultaneous determination of the phosphoric acid content in the slurry.

The process and the apparatus are protected by the Portuguese Patent No. 39.510 and the exploitation rights of this patent have just been sold to DORR OLIVER, INC (U.S.A.)



FLOW DIAGRAM OF THE PROCESS

FIG.1

II General description of the Process and Apparatus

The process is schematically represented in fig. 1. The slurry is sampled from the first reaction tank, and is then cooled and filtered. The very clear filtrate obtained is passed to a temperature regulator, where the filtrate is heated to about 80°C. This temperature is approximately maintained during the measurement of both the electrical conductivity and the density, in order to prevent the deposition of fine crystals and to enable an accurate measurement to be made.

The measurement component is formed by a conductivimetric cell of suitable material with platinum electrodes and by a densimeter. We have also developed a new type of densimeter (1) in order to achieve the most appropriate and practical measurement conditions. The appropriate temperature correction is incorporated in both measurements.

The electrical signals obtained in the continuous and simultaneous determination of the electrical conductivity and density of the filtrate form the input of an electronic computer. It is possible to use either a commercial computer or, if desired, a computer specially developed for the purpose. There are two or three outputs from the computer: two of these electrical signals correspond to the values of the sulphuric acid and phosphoric acid contents in the industrial slurry. The third signal, if desired, is designed for the automatic control of the sulphuric acid flow rate used in the manufacturing plant.

III Analytical Results and the Influence of Impurities

The composition of phosphate rock varies according to type and source. Experimental research was carried out to determine the influence of the impurities on the final results and to determine a process for calibrating the apparatus. From statistical interpretation of the experimental results we have found that the free sulphuric acid content is conveniently expressed as follows:

$$S = \alpha X^2 + \beta d^2 + \gamma X d + \epsilon d i + \rho \quad (1)$$

where

S free sulphuric acid content
 X electrical conductivity
 d density

(1) Portuguese Patent No. 43.662

1 impurities level

$\alpha, \beta, \gamma, E, \dots$ constants.

The computer is based on this analytical expression. It is easy to adapt the constants of equation (1) to the particular type of phosphate rock.

For the phosphoric acid content we have found an analytical expression of the same type as (1).

DISCUSSION

Mr. A. SALES LUIS (Companhia Uniao Fabril, Portugal): The work described in our paper was part of a complex research project involving a number of different departments in our Research Centre. Moreover, as I am not personally a specialist in the phosphoric acid field, I may not be able to give you all the details you may require. Also, I must make a correction to the general description of the process on page 3 : slurry is sampled from the third reaction tank, not the first.

We believe our process enables us to determine continuously the contents of sulphuric and phosphoric acids in the slurry of a wet process phosphoric acid plant. The physico-chemical basis of our process may be explained in the following way:

Let us suppose that we have a very clear filtrate with a certain level of impurities, e.g.

Fe	0.026	g/kg	of	solution
Cr	0.084	"	"	"
Al	0.031	"	"	"
Na	0.009	"	"	"
Total:	<u>0.150</u>	"	"	"

and also containing 0.4% of fluosillicic acid and 0.3% of arsenic, with calcium sulphate in equilibrium with the H_2SO_4 content at 55°C. For different levels of P_2O_5 content and sulphuric acid content, the electrical conductivity of this filtrate can be plotted against its density. Now let us suppose that the level of impurities is, say, three times higher. There is then a certain displacement of these experimental curves, and we have found that, irrespective of the content of impurities, it is always possible to determine the sulphuric and phosphoric acid contents of such very clear filtrates.

In the development of our process and device we have encountered many difficulties, but we think we have completely overcome them.

The device may be divided into three parts :-

- 1) sampling, cooling and filtration until the very clear filtrate is obtained;
- 2) measuring and traducing of the electrical conductivity and the density of the filtrate;
- 3) the computer device.

The first section is operated in close connection with the industrial plant. Experience may be based not only on experiments undertaken in our Research Centre but also in direct connection with the plant itself. As far as the second section is concerned, the only important thing is the filtrate and its composition. One can

even prepare a synthetic solution with different levels of impurities and study the characteristics of these curves. The operation of this section is practically independent of the plant, if the first section works well; and its performance is irrespective of the composition of the filtrate. Finally, the computer device depends entirely on the composition of the filtrate, i.e. on the level of impurities. The computer must be adapted to a particular filtrate composition. One can use a commercial analogue computer, e.g. as produced by Honeywell, or alternatively a special electro-chemical computer developed in the automation department of our Research Centre. The former is, perhaps, rather expensive.

To conclude, I should like to stress that our process rests on the following hypothesis: in a given plant in a stationary state the impurity levels remain constant. I should point out that with our electro-chemical computer, 5 computing stages can be included, so that if a given plant deals with 5 different kinds of impurities, the changeover from one to another is effected merely by pushbutton.

Mr. S.-E. DAHLGREN (A.B. Föronade Superfosfatfabriker, Sweden): The need for sufficiently accurate and reliable equipment for a steady control of the acid produced in a wet-process phosphoric acid plant is too obvious to be argued.

Most efforts aim at automation of the chemical analysis using the Auto Analyser technique with spectrophotometric determination. In the presented paper the problem has been attacked in quite a different way - by continuous direct determination of two physical quantities related to the concentrations of the sulphuric acid and the phosphoric acid-quantities which are converted into electrical signals and which via a computer may be fed back for process control.

Some physico-chemical aspects of this technique might be of interest. The SO_4 as well as the PO_4 groups have tetrahedral configurations and are almost of the same size and shape. Further, since the molecular weights of H_3PO_4 and H_2SO_4 are very close to each other, it follows that a partial replacement of H_3PO_4 by the same amount of H_2SO_4 causes almost no change in volume and thus no change in density. Within the concentration range of interest for a dihydrate process acid, there is a nearly linear relationship between density and phosphoric acid concentration. The conclusion is that the sum of H_3PO_4 + H_2SO_4 must be a nearly linear function of the density. A change of 1% P_2O_5 gives a change in the density of about 0.010 g/ml.

A useful physical quantity not mentioned in the paper but in the French patent is viscosity. A rather simple additivity rule has been established for the influence on the viscosity of sulphuric acid and other impurities common in wet process phosphoric acid (S-E Dahlgren: The influence of impurities on viscosity and density in water solutions of phosphoric acid. Acta Polytech. Scand., Ch 19, 316/1962).

An increase of the phosphoric acid concentration strongly reduces the molar conductivity resulting in a maximum of the specific conductivity at about 37% P_2O_5 at room temperature. A similar

situation is expected at 80°C. Only a very small fraction of the phosphoric acid is dissociated at the actual concentrations, while the sulphuric acid is present almost entirely as HSO_4^- ions. The conclusions must be that conductivity is rather insensitive to changes in the phosphoric acid concentration but sensitive to changes in the sulphuric acid concentration. A change of 1% P_2O_5 at 30% P_2O_5 gives approximately 1% relative change in the conductivity at room temperature. This may be compared to a change of 1% H_2SO_4 at the same P_2O_5 level, which gives nearly 10% relative change in the conductivity. In this connection I would like to draw the attention to a new commercial process meter introduced by the Danish firm Kemotron. It is specially designed for solutions with high conductivity and is insensitive to scale formation.

Recently the development of a selective reversible electrode for SO_4 was reported (E. Pungor et al.: Anwendung von Membranelektroden in der chemischen Analyse. Z. Chem. 5 (1965) 9-14). Whether further work in this direction will make an application to phosphoric acid possible is an open question. It illustrates, however, that there is potentially more than one way of direct measurement.

If all the practical problems with the technique of direct measurement of physical quantities find their appropriate solutions, this technique seems to me to offer a more attractive way for automatic process control than automation of chemical analysis.

Finally I would like to ask a few questions.

1. Have you any unit of this kind in continuous use at any phosphoric acid plant and what is your experience?
2. How accurately can you measure the sulphuric and phosphoric acid concentrations?
3. Is the equipment now sufficiently developed for marketing?
4. What is the approximate price of the equipment?
5. Would you like to give the numerical values of the constants in the expression for sulphuric acid content given in the paper as well as the expression for phosphoric acid content?

Mr. SALES LUIS: At present, we have no such unit in use at a phosphoric acid plant, but as I mentioned earlier, our device may be divided into three parts, only the first of which is directly connected with the plant. As far as this first part is concerned, we now have had it in operation for more than 6 months at our Barreiro phosphoric acid plant.

With regard to accuracy, we have carried out an intensive study of the error propagation involved in our process and device. I cannot remember the exact figures resulting from this study, but I can tell you that the final indication of the sulphuric acid content is known to within an absolute error of roughly 0.1%, and the phosphoric acid content is known to within an absolute error

of roughly 0.025%. Secondly, we have developed a densimeter specially for this process, in order to obtain a better error distribution. Thirdly, in our study of error propagation we found that one must select a compromise between time delay and the margin of error. As far as we can tell, it seems better for the instruments to indicate a trend of a sudden variation in sulphuric acid content than to give the real value of this variation with a large error, but more rapidly.

I think our equipment is now sufficiently developed to be marketed. I cannot give details of price, but these can be obtained on request to my company or to Dorr-Oliver.

As far as your question on the value of the constants in our equation is concerned, these constants depend entirely on the level of impurities in the filtrate. They vary from case to case.

Mr. P.R. GLIKIN (Simon-Carves Ltd., U.K.): What is the time delay between sampling and analysing? Am I right in assuming that the reason for cooling the slurry is to maintain a constant degree of supersaturation? If this is so, is it not necessary to allow the slurry to stand for a certain period of time?

Mr. SALES LUIS: The delay between sampling and the final indication is 10 - 15 minutes.

The residence time in the cooler is about one minute. Cooling is required to stabilise the calcium sulphate content, and we have had no difficulty with regard to supersaturation. Our filtration operates at about 50°C. and we heat the filtrate to about 80°C, and the final results obtained are quite satisfactory with a cooling time of one minute.
