International Fertilizer Industry Association

ISMA* Technical Conference

Seville, Spain

20-24 November 1972

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

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

IMPROVED FILTERABILITY OF TUNISIAN PHOSPHATES

by Mr. A. Ben Salah, Compagnie des Phosphates et du Chemin de Fer de Gafsa and Mr. R. Krempff (Cerphos)

1. INTRODUCTION

One of the important features to which manufacturers of phosphoric acid pay attention in selecting phosphate ore is the filterability of the gypsum cake obtained after sulphuric acid attack. Indeed, a gypsum which is highly filterable will mean lower filter investment costs, and as good filterability generally goes with a good yield from washing the cake, the losses of water-soluble P_2O_5 will be lower. These two advantages are far from negligible when calculating the cost of H_3PO_4.

The filtration of the slurry deriving from Tunisian phosphates had hitherto been regarded as mediocre. Systematic studies have recently shown the basic cause of the reduced rate of filtration of Tunisian phosphates to be the presence of a film formed by caking of organic matter at the level of the filter cloth. An accumulation of flat crystals of gypsum may also occur, hindering the flow of fluid through the cake.

Thus any method capable of preventing the caking of organic matter, particularly of bituminous origin, at the level of the filter cloth, and offering the possibility of increased cake permeability, will improve the filtration of Tunisian phosphates.

We directed our research towards the addition of flocculating agents to the phosphoric liquor; indeed, with flocculation, the organic matter should collect in larger lumps which then become distributed evenly through the cake, the filtering effect of which prevents them from reaching the cloth.

I. ACTION OF FLOCCULATING AGENTS

In order that the elementary particles originally making up the organic matter may agglomerate, the forces of mutual repulsion to which they are subject must be overcome. These forces are essentially electrical: identical charges (generally negative) accumulated on the surface of the particles contribute to their dispersal. One way of combining them could therefore be to neutralise these forces and create or increase forces of attraction: this is chemical flocculation, also known as coagulation.

There is another solution: very long macro-molecules with properties of adsorption as regards the fine particles are added to the suspension. The fine particles are then caught, as in a net, resulting in physical flocculation by adsorption (linkage by hydrogen bridge, or Van der Waals forces) of a number of particles on the same chain.

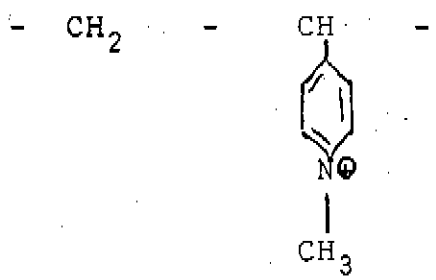
This shows that there are several families of flocculating agents:

- for chemical flocculation, iron or alumina salts were used for a long period. Recently, preference has been given to cationic polyelectrolytes.

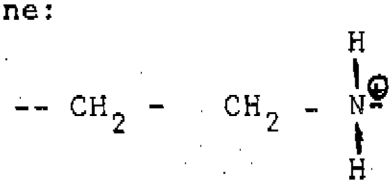
- for physical flocculation, non-ionic or anionic polyelectrolytes are generally used.

By polyelectrolyte we mean a polymer with a high molecular weight (it may be as much as several million) characterised by its solubility in water. In flocculation synthetic polyelectrolytes are normally used.

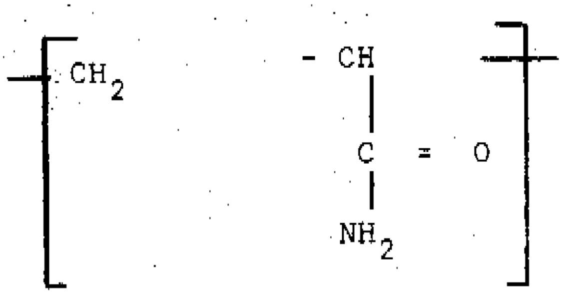
The cationic polyelectrolytes (with positive charges) are often based on vinylpyridine:



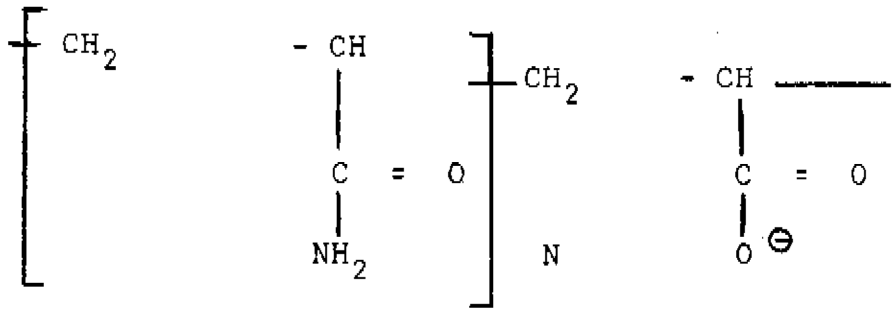
or, polyethylineimine:



Non-ionic polyelectrolytes are generally polyacrylamides with a chain length which may be as much as several microns:



As for the anionic polyelectrolytes (with negative charge), they generally derive from acrylamide/acrylate copolymerisation, or controlled hydrolysis of polyacrylamides:



II. APPLICATION OF FLOCCULATING AGENTS TO THE FILTRATION OF GYPSUM CAKES

Very general patents have been taken out in recent years on the use of flocculating agents in the filtration of phosphoric acid.

As a result of a systematic study of polyelectrolytes in the filtration of gypsum cakes, we have given certain products preference and defined the optimum conditions for use.

Thus we noted that the anionic polyelectrolytes were more effective than the cationic polyelectrolytes. This may seem surprising, for it is generally accepted that in the working conditions, i.e. with a very low pH, anionic polyelectrolytes lose their activity, and cationic polyelectrolytes tend to be recommended for a highly acid medium.

Certain non-ionic polymers are also useful, but the anionic polyacrylamides have given us more systematically positive results.

Among the anionic polyacrylamides, experience has shown that those with the highest degree of ionicity are best, probably as a result of greater deployment brought about by the presence of charges with the same polarity on the chain, thus allowing for more "bridging". On the other hand, the lengthening of the chains brings about a slight increase in viscosity of the solution, although this does not cause handling problems.

Generally speaking, flocculating agents of the polyelectrolyte type are used in very dilute form: a solution of 0.01% for instance. To prevent any effect on the strength of the acid, we use an 0.5% solution with a viscosity not in excess of 1000 centipoises (Brookfield viscosimeter at 60 rpm with No. 3

spindle body). In these conditions, a few cubic centimetres of solution per litre of acid at 30% P_2O_5 are enough; such an addition does not therefore alter the acid concentration.

Another important factor is the point at which the flocculating agent is introduced. Indeed, once the fines have coagulated, they must not be subjected to violent agitation or the flocs will be destroyed. As the action of the flocculating agent is virtually instantaneous, the addition must be made very shortly before filtration; we have taken a figure of the order of 1 min. before distribution of the liquor over the filter. Introduction of the flocculating agent in the acid tank is much less effective, partly because the flocs are destroyed by prolonged agitation and partly because of the rapid degradation of the polymer.

The flocculating agent may be added directly into the circuit between the reaction tank and the filter, or, preferably, in a small buffer tank with low residence time and gentle agitation, with gravity feed to the filter.

Owing to the very small quantities introduced into the slurry, and the higher than 99% retention of the flocculating agent by the solid phase, there will be virtually no flocculating agent recycled by the acid circuit in the reaction tank; there is therefore no need to fear harmful effects on crystallisation of the gypsum or on the material of which the tank is made.

III. PRACTICAL RESULTS OBTAINED WITH GAFSA PHOSPHATES

Systematic tests have been carried out in the CERPHOS laboratory on a pilot installation for the manufacture of H_3PO_4. Owing to the highly satisfactory results obtained a rapid extrapolation in industrial plants has been possible.

3.1 Pilot Tests

The pilot installation used for this study consisted of a tank with a useful volume of 45 litres, continuously supplied with phosphate, at the rate of 3 kg/hour, 92% sulphuric acid and recycled phosphoric acid. A large circulation of fluid ensures wetting of the phosphate. Regular samples of liquor are kept for measurement of the filtration rate by a filtration test using a Buchner funnel. From these measurements the industrial filterability of the gypsum can be calculated, expressed in tons P_2O_5 per day per square metre for a filter rotation speed of 4 mins/rev.

The addition of an 0.5% solution of a long chain, high ionicity anionic polyacrylamide at the rate of 3 cm3 per kilo of liquor taken from the filter supply gave the following results:-

- an appreciable improvement in filtration: the same phosphate with filterability of 3.4 tons P_2O_5/day/m2 when measured without flocculating agent gave 4.7 tons P_2O_5/day/m2 in the presence of a flocculating agent used in the conditions described above (acid at 29% P_2O_5).

- quality of the acid manufactured: the acid obtained is transparent on emergence from the filter. In fact the very fine particles of organic matter which used to pass through the mesh are collected by the flocculating agent before filtration and held in the cake.

- reduction of foam in the reaction tank: the recycling of a clear acid in the reaction tank reduces the foam and creates favourable conditions for good crystallisation of the gypsum.

3.2 Industrial Tests

Pilot tests have been extrapolated in several phosphoric acid plants with capacities in the region of 200 tons/day.

It has thus been possible to confirm the pilot results. Thanks to the flocculating agent, it has proved possible to increase the production of a certain plant by 50%. Above this figure, bottlenecks were found elsewhere than the filters: cooling of the acid tank, liquor recycling pumps, filter feed pumps, etc.

The acid manufactured was perfectly clear and there was no foam in the vessels at the base of the filter vacuum column.

But the increase in filterability and the clarity of the acid are not the only advantages secured by the use of flocculating agents: the cake is in these circumstances appreciably better drained and the content of free water in the gypsum deriving from the GAFSA phosphate at the outlet from the filter falls from 35-40% to 25-30%. In addition to the effect on water consumption, this means a reduction in water-soluble P_2O_5 losses in the region of 0.5 to 0.7%. These losses - reckoned at the P_2O_5 price of the acid - are known to be very expensive.

The increased production of the plant, without additional investment, the reduction by more than 0.5% of the losses of water-soluble P_2O_5, and the clarity of the manufactured acid bring about savings which are much greater than the expense involved in the use of the flocculating agent, which does not exceed 0.1 dollars per ton of phosphate.

CONCLUSIONS

The use of flocculating agents in the production of phosphoric acid from Tunisian phosphates considerably improves the operating conditions as well as the factors which determine the cost of the acid.

The filterability rates obtained from these products: 4.5 to 5 tons per day per square metre of filter area (4 minutes filtration cycle), and the improved filtration yield (losses in the region of 0.3%) provide the necessary conditions for an excellent profitability threshold.

In addition, the quality of the acid produced is considerably improved in clarity on emergence from the filter: the amount of organic matter in suspension is virtually nil.

The outlay involved in the use of these products (0.10 dollars per ton of phosphate) is negligible as compared with the advantages quoted.