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CRYSTAL HABIT MODIFICATION IN WET PROCESS PHOSPHORIC ACID PRODUCTION (a)

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1. Summary

PRAYON is well known for its knowledge of phosphoric acid technology; for more than 40 years it has studied and developed the process. SEPPIC is a surfactant producer specialized in the production of anti-foaming agent for several industries. Both companies have decided to share their knowledge for the benefit of the phosphoric acid industry and have carried out some specific studies about gypsum crystallisation improvement.

This article shows the positive effects of organic compounds on the crystallisation of gypsum. Impact on crystal shape and the filterability coefficient are developed and discussed through results obtained in laboratory studies, pilot plant tests, and industrial trials. Sedimentary phosphate is considered.

The obtained results confirm that the proper modification of crystal shapes gives a definite improvement of the filterability coefficient together with additional process advantages. This means that by using the appropriate crystal habit modifier, the profitability of the process can be improved.

2. Introduction

Phosphoric acid is an important product for the production of mineral fertilisers. It is mainly produced by a wet process in which phosphate ore reacts with sulphuric acid in order to produce phosphoric acid in addition to calcium sulphate. The latter is considered to be a by-product.

According to the process adopted, the calcium sulphate can be found as gypsum ($CaSO_4$. $2H_2O$) or hemi-hydrate ($CaSO_4.½H_2O$). Whatever the crystal form, this by-product must be removed from the phosphoric acid by filtration. The surface necessary to filter the solid will vary with the type of phosphate, the process parameters, the type of additive eventually used and the form of the calcium sulphate.

In the production of phosphoric acid, filterability of the attack slurry is a key factor. It is a function of the temperature, the sulphate and P_2O_5 content of the liquid and the solids content of the slurry. All these parameters have an impact on the size and shape of the calcium sulphate crystal. In addition to these parameters, crystal shape will be influenced by the origin of the phosphate processed and also the eventual addition of an additive.

The aim of these additives is to change the shape of calcium sulphate crystals. They reduce the length to width ratio, sometimes form aggregates and give a narrower particle size distribution. These additives are called "crystal habit modifiers". They are used in order to

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improve the filterability of the attack slurry, thus improving the phosphoric acid plant economy.

The improvement of the filterability can be justified in different cases. It can be an increase of the production capacity of the unit or a reduction of the filtration losses. Sometimes crystal habit modifiers are used in order to allow the processing of phosphate from different origins in the same unit. These additives are based either on organic chemistry or inorganic chemistry.

This article shows some development done by SEPPIC, with process advice of PRAYON, to find a crystal habit modifier giving a positive impact on the phosphoric acid production. The development of these products was done in SEPPIC's laboratory facilities.

To confirm the effect observed on the laboratory scale, one of the products was tested in PRAYON pilot plant facilities. Industrial data where also collected. Sedimentary phosphates are considered such as K09 and K12 Moroccan phosphate.

Unless specified in the text, all explanation and study presented in this paper are related to the production of phosphoric acid by the dihydrate route.

3. Crystal Habit Modifier

Crystal habit modifiers (hereinafter referred to as CHM) are products able to change particle size and shape of calcium sulphate. From the industrial point of view these products must increase the size of the calcium sulphate crystal but even more important must optimise the distribution of the grain size in order to facilitate the filtration.

The products able to achieve this task come from both mineral and organic origins.

3.1 CHM from mineral origin

The best mineral CHM are alumina or silica based. These are mainly clay and fly ash.

Silica acts as a fluorine complexing agent, the latter has a negative impact on the crystallisation by promoting the formation of needles. This phenomena is inhibited as soon as the fluorine is linked with the silica which is thus considered as CHM.

Alumina has to some extent the same effect, forming a complex with fluorine but also seeming to have a positive effect on the crystal shape by, when present as AlF_5^{2-} , replacing a SO_4^{2-} ion at the fastest growing face, and thus reducing the speed of crystallisation along this face. As a result, crystals grow along the other axis (Martynowicz et al., 1995). Despite being inexpensive aluminium addition for crystal habit modification of gypsum, is not always considered, as it traps fluorine in the acid. This can cause problems when feed grade acid must be produced, as fluorine can not be removed during concentration step.

Other minerals such as Fe^{3+} ions delay the growth in the direction of the preferential axis, converting the gypsum needles into a form close to isometric faceting (Kopilev, 1967). When CHM concentration is increased, the filtration rate passes through a sharp maximum and then decreases. For example, when Palfos is tested, this maximum filtration rate value is observed with particular dissolved ions blend K^+ (at 0.1%) and Fe^{3+} (at 0.05%) (Kruger et al…, 2000).

Fowles et al. (1998) have studied the influence of different inorganic elements on the crystallisation of gypsum produced from Palfos rock.

3.2 CHM from organic origin

There are numerous organic molecules having a crystal habit modification effect. It can be for example the dodecylbenzenesulfonic acid (at concentration up to 5 g/kg of solution , the diisooctylsulfoccinate (Rocha et al., 1995) or alkylarylsulfonate for hemihydrate process (South African patent 725173) or ethylene oxide with tall oil rosin with or without fatty acid (US patent 3,594,123).

Dodecylbenzenesulfonic acid (DDBS) can produce side effects. It has been observed that in a “synthetic acid” containing 28% P_2O_5 and at 70°C at a concentration of 10 g/kg of solution, precipitation of hemihydrate is observed and above 50 g/kg solution the precipitation of calcium sulfate was completely inhibited (Rocha et al., 1995).

Mixture of sorbitan ester have been tested successfully recently (El-Shall et al., 2000). The filterability of a high MgO content Florida phosphate was improved. The improvements were attributed to change in crystal size distribution.

Cocheci et al., (1982) have studied the influence of akylbenzenesulfonic acid on the crystallisation of gypsum produced with phosphate of different origins. Depending on the phosphate origin, the best result were obtained with addition of CHM from 170 to 580 g/T of rock. The shape of the crystal obtained was also a function of the phosphate. For example crystals produced from Togo phosphates were just shorter with the same width while the Jordanian phosphate gave clusters.

The basic mechanism of these products is to delay the crystal growth of the faster growing face of the crystal. The exact mechanism is not fully known. For Roccha et al., crystallisation delay is most likely related to reduction in nucleation associated with surfactant adsorption due to the affinity that calcium has for dodecylbenzenesulfonic acid. Another author, studying other CHMs, suggests that adsorption may involve OH^- bonding to calcium ions on the growth face of the nuclei reducing or preventing the growth of the crystal (Austin et al., 1975).

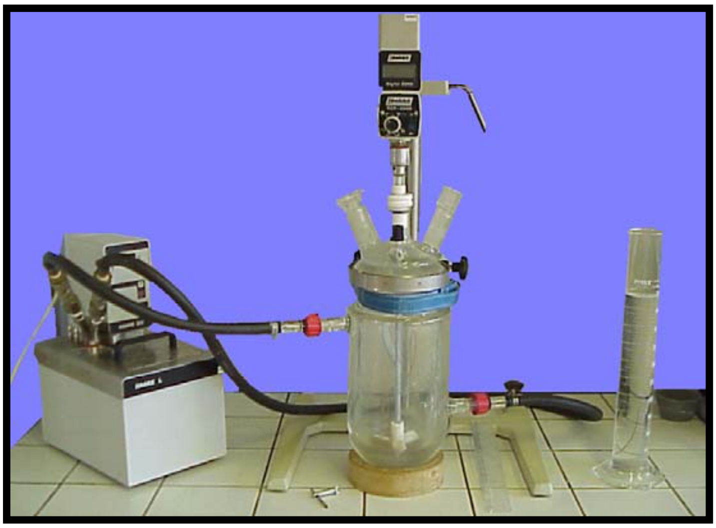
Whatever the mechanism, it has been stated that CHM must be introduced upstream from the nucleation of calcium (El-Shall,1999).

It has often been observed that organic CHM can present other properties such as anti-foaming or scale reduction.

3.3 CHM from SEPPIC S.A.

SEPPIC has developed in collaboration with its customers some specific products for the mineral fertiliser industry classified under the trade name, “Montaline”.
One of the Montaline ranges is dedicated to the phosphoric acid manufacturing in order to solve problems faced by the manufacturers such as foaming or low filtration performance.

Photography of the equipment used for the attack and digestion steps



The CHM grades are based on organic chemistry, they are composed of a complex mixture of surfactants selected in order to meet the phosphoric industry requirements (liquid, easy to pump at room temperature, compatible with rubber linings…)

4. Laboratory Test

Prior to pilot evaluation, the Montaline range has been screened in SEPPIC's laboratory in order to select the most efficient products according to the application test listed below:

- ✓ anti-foaming test
- ✓ filtration test

These application tests are based on dihydrate process technology wherein a sedimentary phosphate from The Kingdom of Morocco is processed (K12 type).
The operations are discontinuously carried out; the sulphuric attack step is performed first then followed by the digestion and filtration steps.

4.1 Operation description

The attack, digestion and filtration operations are briefly described hereunder:

4.1.1 Attack step

It is divided into five cycles so that the obtained slurry at the end of the last cycle presents the characteristics of a dihydrate reaction slurry in terms of temperature, solid contents, slurry density, excess of sulphuric acid and percentage of P_2O_5 in the liquid phase. Furthermore, the operating parameters are adjusted with the chemical analysis and granulometry of the ground phosphate rock.
At this step and during the five cycles, the foams generated are regularly measured then plotted on a graph. The foam profiles reported for each Montaline grade, allows us to select the most efficient anti-foaming product in the range.

4.1.2 Digestion step

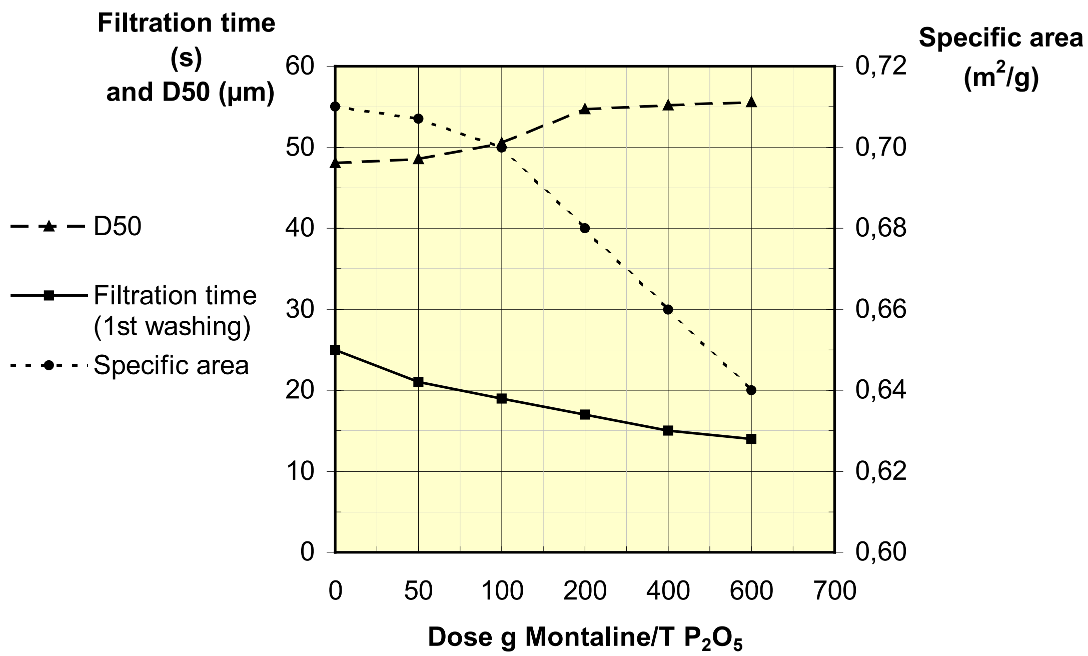
It is simply defined by a curing time at a controlled temperature with low-speed mixing. Then the gypsum crystals are observed by microscopy. The shape and size of the crystals are studied, the presence of twinned crystals (Y or X forms) or clusters is reported. Moreover, the ratio of length to width of the crystals is considered.

4.1.3 Filtration step

It is performed under vacuum. The slurry is filtered with an appropriate filter cloth then washed with weak phosphoric acid then washed again with water.
The gypsum cake is prepared for particle size distribution analysis.
Finally the CHM property of the Montaline grade is quantitatively characterised. To confirm the positive effect on filtration time, the gypsum average specific surface and mean diameter are studied to make sure that trends are similar. Indeed, it has been shown that both values are correlated to filtration time.

The grades are ranked depending on their anti-foaming activities and filtration improvement characteristics. The most promising product is selected for pilot evaluation at PRAYON facilities.

Graph1: CHM profile of the Montaline selected for pilot evaluation



5. Pilot Test

5.1 Introduction

As Montaline is widely used as a anti-foaming agent during the production of phosphoric acid, it was possible to observe its positive effects on filtration of the slurry. It was thus decided to explore in more detail the effect of this additive on production by carrying out pilot plant tests in PRAYON Pilot plant facilities.

The phosphate used for this study is the K09 phosphate. It is a phosphate of sedimentary origin obtained from the Khouribga mine, Morocco. The analysis of the phosphate is shown in the chart below.

Chemical Analysis of K09 phosphate rock

	Analyses (% w/w)
P_2O_5	30.7
CaO	52.33
Mg	0.51
F	3.9
Na	0.6
SO3	1.7
CO2	8.0
Fe2O3	0.15
Al2O3	0.23
SiO2	1.7
C total	0.5

5.2 Test description

The pilot is composed of two reaction vessels in series, fitted with baffles. They are made of W 1.4539 stainless steel (UB6, 904L…)

Each reaction vessel is equipped with a small PRAYON stirrer. The lower turbine is equipped with helical blades, the central turbine with pitched blades and, finally, the upper turbine with anti-foaming blades.

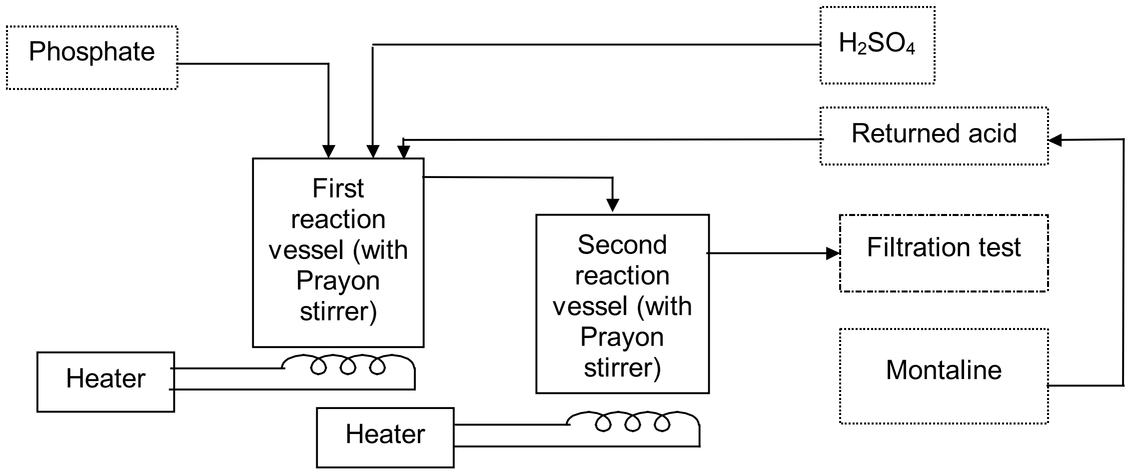
The phosphate is fed automatically into the first reaction vessel by a loss in weight feeder connected to a vibrating channel. Two metering pumps inject sulphuric acid and recycled acid at the same point in the first reaction vessel.

Each reaction vessel is equipped with a heating system to keep the reaction temperature of the slurry constant.

The reaction slurry overflows from the first reaction vessel to the second, which is used as a buffer volume between filtrations, performed in discontinuous mode. From there, the slurry is extracted every 20 minutes to perform the routine filtrations and specific filtration tests.

The routine filtrations produced the amount of recycled acid to be fed back to the first reaction vessel. Due to the size of pilot and thus the low quantity of additive to be added, we have decided to disperse the Montaline with the recycled acid prior to the introduction in the attack tank.

Schematic flow of pilot-unit configuration



The specific filtration tests are conducted on a 1 dm² cell. The filter cloth is comparable to that used in the factory.

The operator first pours the slurry into the filtration cell, then connects it to vacuum and starts the timer. The vacuum is broken and the time recorded when the surface of the cake appears.

The gypsum cake is then washed with a solution with a given weak acid content (d=1.050). To do this, the operator pours a predefined quantity of this acid into the cell and then connects it to vacuum and starts the timer. The vacuum is broken again and the time recorded when the surface of the cake appears.

This operation is then repeated a final time with water. The three liquid passage times are then added. The gypsum cake is then drained for a period equivalent to 20% of this sum. The drainage consists of keeping the cell under vacuum.

During this test, the operating vacuum is recorded.

All the liquids produced (production acid, first and second washes) are collected in separate containers. Their volume and their density are measured. A sample is then sent to the laboratory for analysis.

The final gypsum cake is then removed and weighed. Its thickness is measured. Part of the cake is washed with alcohol. One aliquot of cake as is and another washed with alcohol are then sampled for analysis.

5.3 Presentation and Discussion of Results

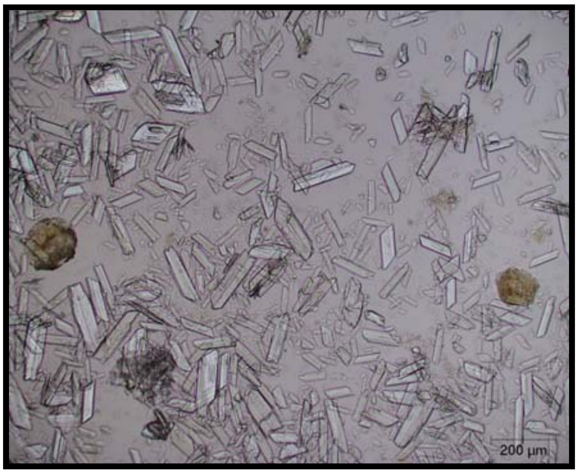
5.3.1 Optimal Point of Addition of the Montaline

As indicated in the test description, we started by adding the whole quantity of Montaline required for the day into a quantity of weak recycled phosphoric acid equivalent used in one day of operation.

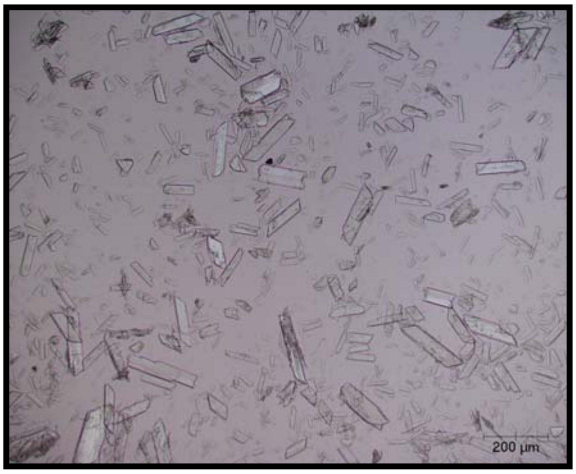
The best filtration was observed a few hours after the addition of the Montaline in the recycled acid. This phenomena has been observed in other studies (Cliford et al., 1999). Introduction point of the CHM is consequently an important factor, it should be as close as possible to the nucleation point. For industrial use, Montaline must be added continuously and directly into the reaction tank at a highly turbulent point to ensure satisfactory dispersion in the acid close to the nucleation point of gypsum.

5.3.2 Effect of Montaline on Gypsum Crystallisation

Pictures of gypsum crystals are done for microscopy studies. Some of them is reported below:



✓ Photo A: without additive



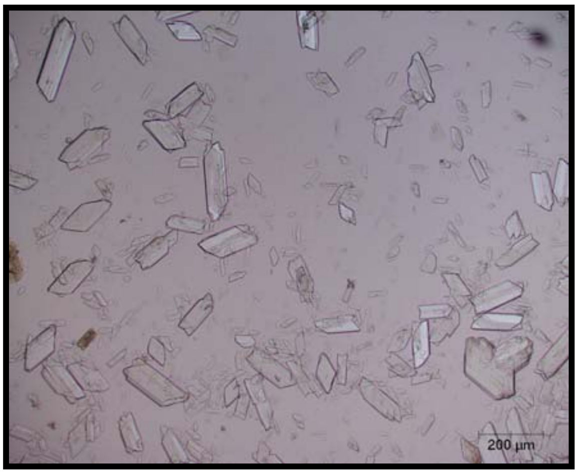
✓ Photo B: with 250 g Montaline/T of P2O5

➢ Photo A: operation without additive

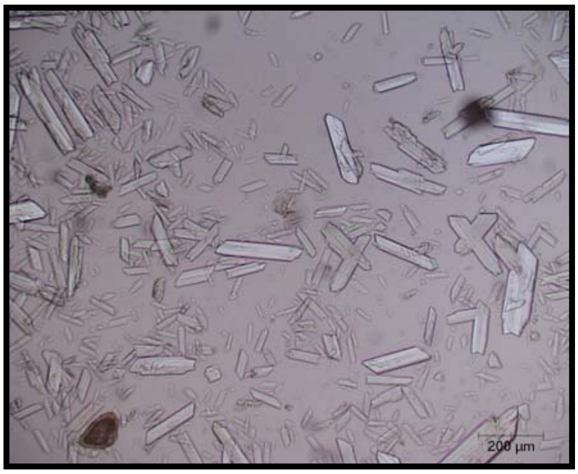
The crystals obtained are flat with "length vs. width" ratios from 2 to 6. The number of twinned crystals is low.

➢ Photo B: operation with 250 g Montaline/T P_2O_5

Introducing 250 ppm of Montaline does not cause any major changes to the shape of the crystals. A similar elongation is observed; however, an increase in the number of fishtailed crystals must be noted.



✓ Photo C: with 350 g Montaline/T of P2O5

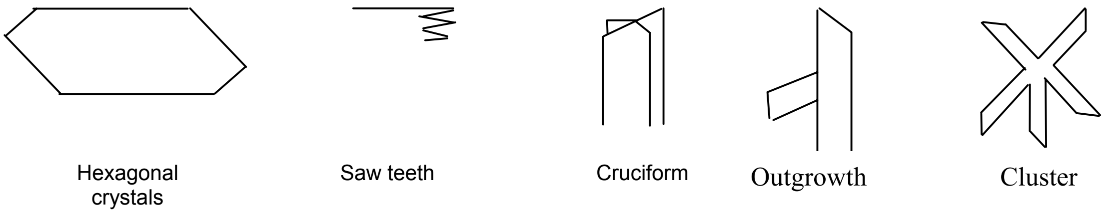


✓ Photo D: with 500 g Montaline/T of P2O5

- Photo C: operation with 350 g Montaline/T P_2O_5

When the Montaline ratio is increased to 350 ppm, an increase in crystal thickness is observed. Some crystals no longer have four sides, as in the blank, but are hexagonal, with a sort of tapered break at the tip of the crystals.
Some crystal is cruciform lengthwise, others have saw-toothed ends or have outgrowths or, finally, have cluster shapes.
A simplified diagram of these different shapes is given below.

Shape and type of encountered crystal



- Photo D: operation with 500 g Montaline/T P_2O_5

With a dose of 500 ppm the number of twinned crystals and outgrowth crystals increases.

- Operation with 1.00 kg Montaline/T P_2O_5

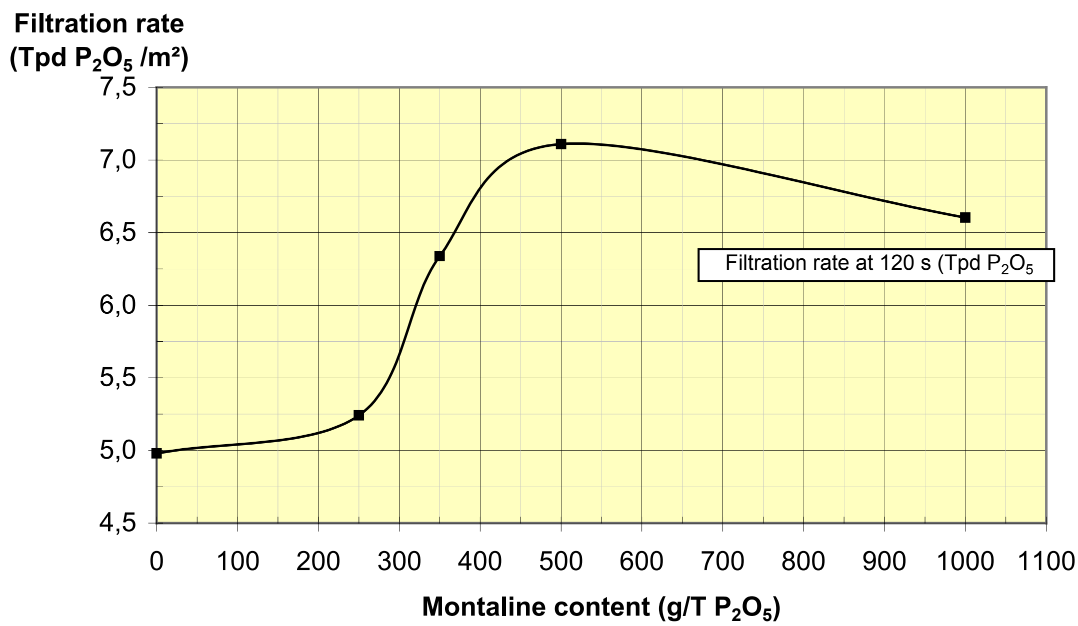
For a content of 1,000 ppm the crystallisation is similar to the previous one.

5.3.3 Progression of filtration rate

To be able to compare the different tests, all the filtration rates obtained in the tests are extrapolated on the basis of 120 s cycles and a 450 mm Hg vacuum. The interpretation of the results remains similar.

Graph 2 gives the results. It is observed that the filtration rate increases while the Montaline content is less than 500 g/T P_2O_5. For contents greater than 500 g/T P_2O_5, the filtration rate decreases again but remains greater than that of the reference (with no additive). However, this decrease is moderate and progressive. This presents an advantage over products such as DDBS which improve the filtration rapidly but also induce a sudden degradation of the gypsum crystallisation as soon a maximum dosing threshold is exceeded.

Graph 2: Effect of Montaline on filtration rate



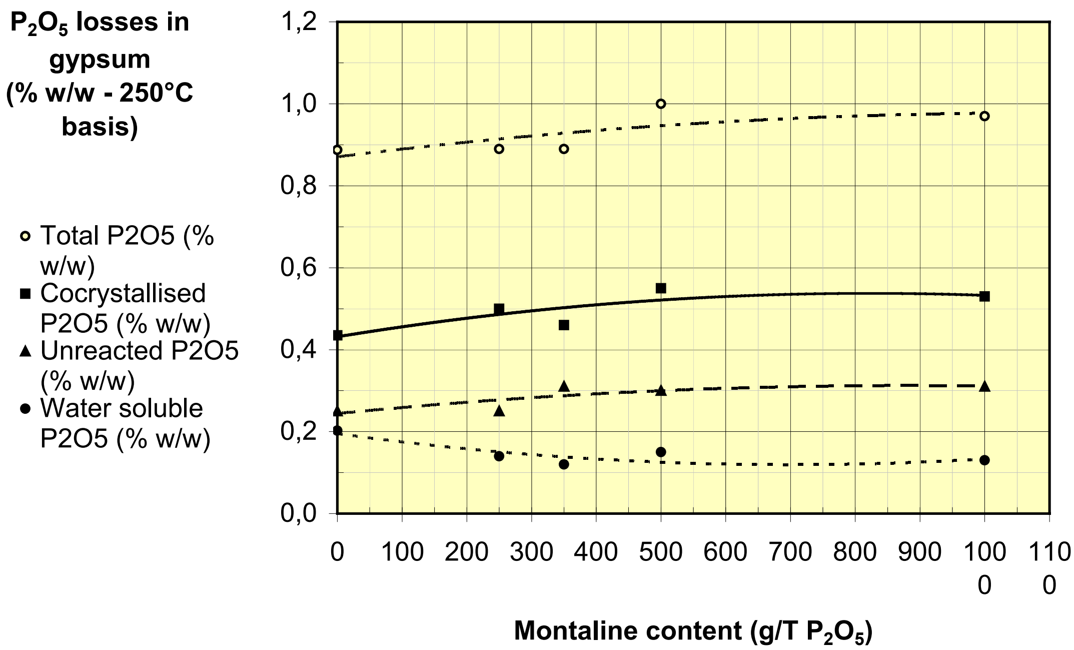
If the extreme values are compared, an increase in the filtration rate of up to 38% can be expected. This value must be considered with caution given the low number of tests taken into consideration. However, a 30% increase in the filtration rate can reasonably be estimated.

5.3.4 Effect on yield

Graph 3 shows the progression of P_2O_5 losses as a function of the Montaline content in the reaction medium. The three types of P_2O_5 losses in the cake are indicated separately:

1. Water soluble P_2O_5 losses, which consist of the phosphoric acid remaining in the cake which is evacuated with it.
2. Co-crystallised P_2O_5 losses, which are produced by only partially reacted phosphate ores.
3. Un-reacted P_2O_5 losses. Phosphate ores which have not reacted.

Graph3: Gypsum losses versus Montaline content



Once the Montaline content reaches 300 g/T P_2O_5, it is observed that the co-crystallised and un-reacted losses increase slightly with the Montaline content. On the other hand, water soluble losses decrease. However, the overall results are penalized since the improvement in water soluble losses does not compensate for the un-reacted and co-crystallised losses, which increase and stabilise in parallel.

As from 300 g/T P_2O_5, Montaline induces a decrease in the total P_2O_5 yield between 0.3% and 0.5% max. related the water soluble P_2O_5 gain obtained.
This decrease is progressive, unlike with other products with the same characteristics. At the industrial stage, the reduction in the yield will therefore be limited and there is no need to fear disastrous results in the event of a Montaline over-dosage.

5.4 Economics

Considering the following assumption:

1. the production limitation is the filter
2. maintenance and labour costs are not affected by the increase in capacity
3. the plant runs with K09 type phosphate
4. the process yield loss related to the use of Montaline is 0.5%
5. the plant operating rate remains unchanged
6. increase of the capacity has a slight negative impact on the overall recovery of the attack filtration

We have a done an economic evaluation of the use of Montaline. The results demonstrated that the additional cost of Montaline may be compensated by the reduction of maintenance costs and manufacturing cost.

The expected profits following the use of Montaline are directly related to the increase in capacity that can be obtained, cost of raw materials, overall plant performances.

Each case is unique. The operational benefit should first be considered by an industrial trial. Economical profit can then be calculated with the support of SEPPIC specialists.

5.4.1 Pilot test conclusion

▪ The use of Montaline demonstrates an effect on the crystallisation of gypsum for the phosphate considered. The "length over width" ratio of the crystals decreases when the Montaline content increases in the reaction medium. Similarly, as this content increases, the number of twinned crystals increases in the reaction slurry.

Note: On an industrial scale, the specific features of the reaction system (single-compartment, multi-compartment, vacuum or air cooling, slurry re-circulation of varying intensity, etc.) may or may not reinforce the gypsum crystal twinning phenomenon. The twinning phenomenon is generally low in pilot tanks. Therefore, Montaline can be reasonably expected to have a higher efficiency at the industrial stage.

▪ For a K09 phosphate, the effect of these modifications on filtration is positive irrespective of the dose; however, an optimum efficiency is observed.
This type of behaviour is identical to that of other crystal habit modifiers such as DDBS (dodecylbenzenesulfonate) or additives of the same family. However, the dosing of Montaline are below those used for DDBS for the same result; in addition, in event of an over-dosage, no degradation of filtration is observed as for DDBS over-dosages for example.

▪ The increase in the filtration rate observed is of about 30% for a content of
500 g Montaline/T P_2O_5 produced.

▪ Montaline has a positive effect on the free water of the residual cake, which decreases as the CHM (crystal habit modifier) content increases, up to an optimum level before returning to its initial level. For relatively low CHM contents, this allows to decrease water soluble P_2O_5 losses.

- Montaline has a slightly penalizing effect on the overall yield. This effect increases in intensity as the additive content increases, but due to the low decrease (0.3 to 0.5%) and the tolerance of the analyses, this penalising effect is quite limited.
Under the test conditions and for the Montaline contents giving the best results, i.e. between 500 and 1,000 g/T P_2O_5, the yield decrease is about or below 0.5%.

- The active substance responsible for the gypsum crystal habit modifying property of Montaline appears to deteriorate over time in the presence of phosphoric acid or sulphuric acid. At the industrial stage, Montaline must be introduced continuously in the reaction zone.

- The use of Montaline offers financial benefits to manufacturers since it enables an increase in the phosphoric acid production capacity.

- Montaline, in parallel with its crystal habit modifying role, has good anti-foaming and scaling reducing properties acknowledged by industrial manufacturers (filtration circuits are found cleaner and filtering cloths have a longer life). These advantages were not above and should be added to the cost savings in using Montaline.

6. Industrial Observations

Montaline grade is injected in a phosphoric acid production unit based on a Mark IV PRAYON process using a K09 phosphate. The following observations are done:

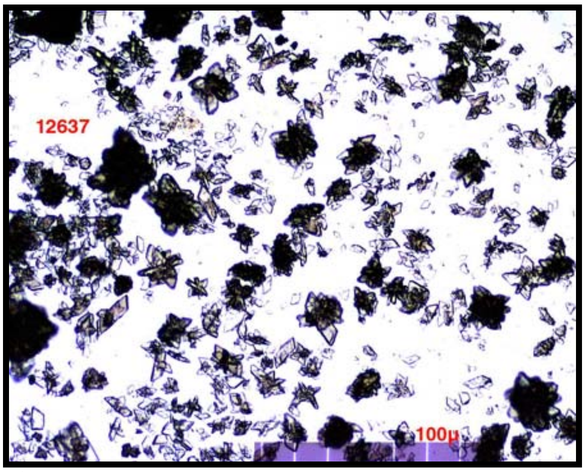
✓ The slurry appears more homogeneous, the small crystals disappeared whereas the biggest ones present a length vs. width ratio closer to 1

✓ The crystals tend to agglomerate to form larger clusters

✓ The particle size distribution of gypsum is narrower

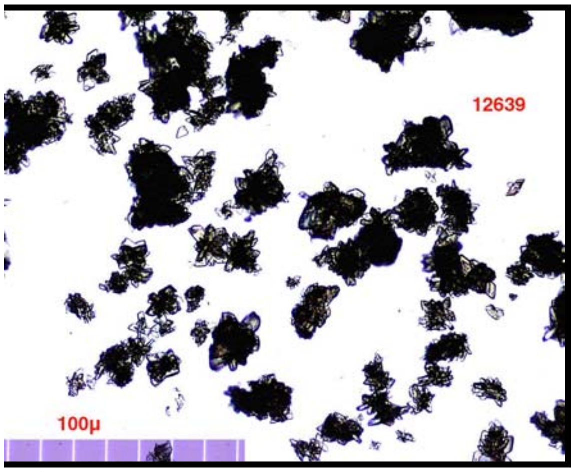
✓ The average specific area is reduced by 24.7% versus reference (without additive)

✓ The mean gypsum crystal diameter is increased by 23.9% versus reference



✓ Without additive as reference

➪ average specific area: 0.639 m^2/cc
➪ average diameter: 68.90 µm



✓ With 250 g Montaline / T of P_2O_5

➪ average specific area: 0.487 m^2/cc
➪ average diameter: 85.35 µm

Montaline is approved at the industrial level and presently used as crystal habit modifier in that plant. Further features such as antifoaming and scaling reduction properties are appreciated as well by the manufacturer.

7. Conclusion

From the recent test and development performed by SEPPIC with the process advice of PRAYON one new product has been developing in order to improve filterability of gypsum slurry.
These crystal habit modifiers have a positive effect on the speed of filtration by modifying the shape of calcium sulphate crystals. It results in an improvement of the shape of the gypsum crystal giving a ratio of length to width closer to one but also a narrower distribution of the crystals.
To be efficient CHM must be added to a point very close to the nuclei formation of crystals.
These products allow in some cases a significant increase of the filterability, allowing existing units to run at a higher capacity. The cost of these products are more than easily justified by the benefit coming from the increase of the capacity on one side but also reducing of scale build up and elimination of foam are the main side benefits. Some producers observe a larger flexibility in process parameter follow-up when Montaline is used. Exact benefits can easily be determined by an industrial test.
Although this paper concerned sedimentary phosphates, preliminary studies on igneous ones have shown the same trends.

SEPPIC permanently optimises Montaline formulations in order to meet the specific requirements of the producers and will continue CHM additives development. A new generation of Montaline are on the verge of being launched in the fertiliser industry.

Thanks to its knowledge of the phosphoric acid technologies, PRAYON has helped the process additive industry to optimise specific formulations. It has been demonstrated one more time that PRAYON is a valuable key in phosphoric acid industry development.

8. Thanks

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