Crystal Habit Modifiers for Enhanced Filtration of Phosphogypsum

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ABSTRACT

Filtration of phosphogypsum is an important unit operation in wet-process phosphoric acid production. Phosphate mining in Florida is moving towards the Southern region where the rock is of less quality and higher MgO content. Filtration rates of Phosphogypsum obtained from such rock are lower than that obtained from Central Florida region. Therefore, cost effective improvement in filtration rate is desirable by all phosphoric acid producers in general, and Florida's phosphate industry in particular.

In this study, an anionic surfactant has been tested as crystal modifier for phosphogypsum during production of phosphoric acid using phosphate concentrate from South Florida at different sulfate contents. The improvement in filtration rate was up to 31%. In addition, the reaction efficiency was higher by 2.1% to 3.9% and the overall P_2O_5 recovery was also higher by 0.5% to 1.6% in the presence of surfactant.

Observed effects are correlated with crystal morphology and crystal size distribution. Best results are obtained when the crystals from clusters and of narrow size distribution. Effect of surfactant on filtration rate, P_2O_5 recovery, cake moisture content, and both digestion and washing efficiencies are determined. Also, correlations between crystal size distribution and filtration rate are presented in this paper.

INTRODUCTION

The purpose of filtration in wet-process phosphoric acid production is to separate the acid from the phosphogypsum cake. Good crystallization quality of phosphogypsum leads to higher filtration rate. The crystallization quality depends on crystal size, size distribution and morphology of the crystals.

There is no published data about industrial crystallization of phosphogypsum using surfactants. The available data in literature is about nucleation and crystal growth of gypsum from pure chemicals [(1-4)]. Also, the influence of different inhibitors on the growth rate of calcium sulfate dihydrate crystals was reviewed [(5-8)]. In addition, many papers are published explaining effect of additives and impurities on crystallization of calcium sulfate [(9-14)]. There are numerous reports about improving the filtration rate using polymers[(15-25)]. On the other hand, reports dealing with effect of surfactants on filtration of phosphogypsum are limited [(26-28)]. Even in these studies, crystallization of calcium sulfate dihydrate from pure chemicals is reported. For instance, Kopyleva et al.[(28)] tested addition of 1-2% aqueous surfactant solution to the slurry before filtration and found that the specific cake resistance was decreased by 35-40% and the filtration rate was increased by 1.5 - 2.3 times as well as decreasing of washing time by factor of 1.2 - 1.7.

The main objective of this study is to test effect of a nonionic surfactant on the filtration rate of phosphogypsum as well as the reaction efficiency and P_2O_5 recovery. To achieve this goal, a high dolomitic phosphate concentrate is tested for phosphoric acid production with and without surfactant at different (low, medium, high) sulfate contents. Due to high impurities content in this concentrate, its filtration rate is relatively low. For testing the concentrate, the conventional Dihydrate process conditions were simulated [(24,25,29,30)] and material balance program was applied [(30)] for calculations of reactants feeding rates. The wash water was calculated using this program and according to the water balance of the whole process. Size distribution of the produced gypsum crystals was determined to know effect of surfactant on the crystals growth at different sulfate levels and different time intervals.

EXPERIMENTAL

A. Materials Characterization

The phosphate concentrate sample is provided by IMC-Agrico Company. Chemical and sieve analyses of this sample are given in Tables (1 and 2). Table (1) shows that the phosphate concentrate contains high content of MgO (1.58%). MgO increases the acid viscosity and consequently decreases the filtration rate. The accepted industrially limit of MgO in commercial phosphate concentrates is less than 1.0%.

Table (2) shows the sieve analysis of the sample. It contains 51.8 % -100 mesh and 29.7 % -200 mesh, which are required for the Dihydrate process. Most of the particle size of the concentrate (80.5%) ranges between 44-295 μm.

The sulfuric acid used is pure 95.5% acid and has 1.835 g/ml specific gravity. The recycle (return) acid is accumulated while carrying out the tests. It is adjusted to the required P_2O_5 content and recycled. The surfactant used is Crysmod (nonionic surfactant).

Table (1)
Chemical Analysis of High Dolomitic Phosphate Concentrate Sample

Constituent	%	Constituent	%
P_2O_5	27.22	Al_2O_3	0.95
CaO	42.79	Na_2O	0.73
MgO	1.58	K_2O	0.12
Fe_2O_3	1.56	Insolubles	8.05

Table (2)
Sieve Analysis of High Dolomitic Phosphate Concentrate Sample

	Particle size		Cumulative wt. %
Mesh*	**Inch**	**Mm**	
-10	0.0650	1.651	100
-48	0.0116	0.295	87.5
-65	0.0082	0.208	68.1
-100	0.0058	0.147	51.8
-150	0.0041	0.104	40.1
-200	0.0029	0.074	29.7
-270	0.0021	0.053	18.6
-325	0.0017	0.044	7.0

* Tylor standard

B. Apparatus

The reaction was carried out in 1L reactor fitted with stirrer and placed in water bath adjusted at 80 ^oC. The phosphate concentrate was added continuously using a vibrating rock feeder, whereas the sulfuric acid was added continuously by using the peristaltic pump with Viton tubing. The surfactant suspension was added continuously by using a small graduated separating funnel. The filtration was performed by using the Buchner type filter of 4.6 inch diameter. The filter cloth used was polypropylene which has 80 mesh opening size. The vacuum pump was used to give the required vacuum (20 inch. Hg). A laser diffraction analyzer was used to determine the size distribution of produced phosphogypsum crystals.

C. Procedure

For the first test (start-up), the required amount of recycle acid (about 18% P_2O_5) was prepared by double-stage acidulation. The first stage with sulfuric acid and water and the second stage with sulfuric acid and phosphoric acid solution (about 10 % P_2O_5) produced from the previous run. For routine tests, add the required amount of the return (recycle) acid to the reactor. After attaining the required temperature (80 ^oC), add continuously the phosphate concentrate, the sulfuric acid and the surfactant suspension for 30 min. Continue the reaction for another 2.5 hours. Then, filter and wash 3 times with wash liquors (10 and 5% P_2O_5) and wash water. The temperature of wash liquors is 60 ^oC.

In industry, the filtration rate is expressed in tons P_2O_5 produced per square meter per day. So the same expression was used. The filtration rate was calculated applying the following equation [24,25,29,30] :

$$\textbf{F.R.} = \frac{\textbf{SW * SC * F}}{\textbf{T}} \quad \textbf{Ton } \mathbf{P_2O_5 /m^2.day}$$

where,

F.R. : Filtration rate, ton P_2O_5 /m^2.day — SW : Slurry weight, g
SC : Solid content, % — F : Filtration factor
T : Total time of filtration, washing and drying, sec

During the experiment and after 0.5, 1, 2 and 3 hours from the start-up, take 3ml slurry and disperse in 100ml methanol. Then sieve using 106μm sieve and determine the size distribution of obtained phosphogypsum crystals.

RESULTS AND DISCUSSION

High dolomitic phosphate concentrate is tested for phosphoric acid production with and without surfactant at different sulfate contents (low, medium, and high). The results of filtration rates, reaction efficiencies, P_2O_5 recoveries, washing efficiencies and size distribution of formed phosphogypsum crystals are obtained at each sulfate level. These results are considered exploratory data. These results are as follows:

A. Testing of the Concentrate at Low Sulfate Content (1.5-1.8%)

Tests have been carried out, with and without surfactant addition. The amount of applied surfactant corresponds to 1.5 kg/ton P_2O_5. The results are given in Table (3&4) and Fig. (1).

The filtration data of the samples at relatively low sulfate contents of about 1.5% and 1.8% with and without surfactant, respectively are given in Table (3). The obtained filtration rate is 4.24 ton P_2O_5 /m^2.day without surfactant and improved to 5.54 ton P_2O_5 /m^2.day with the addition of surfactant. This corresponds to about 31% improvement. This is attributed to modification and growth of produced crystals upon surfactant addition. The size distribution of gypsum crystals which is given in Table (4) and Fig. (1) show that, the volume percentage of fine produced gypsum crystals (<10μm) is decreased to about 31% upon addition of surfactant while it is about 64% without surfactant.

The obtained reaction efficiencies, P_2O_5 recoveries and washing efficiencies of the phosphate concentrate with surfactant compared with the phosphate processed without surfactant (baseline) are given in Table (3). It is important to note that the reaction efficiency is increased with the addition of surfactant. This may be attributed to decrease of lattice (co-crystallized) P_2O_5 which represents about 60% of the total P_2O_5 losses [31]. Torocheshnikov et al.[32] have stated that, presence of a surfactant led to reduction of P_2O_5 in the precipitated calcium sulfate. They have concluded that [32], surfactants do have a definite effect in reducing the capture of phosphate ions from solution by crystallizing crystals. Also, addition of surfactant increases the phosphate concentrate solubility and consequently increases reaction efficiency. Kopyleva [33] has stated that presence of surfactant increase the solubility of calcium phosphate in thermal and wet-process phosphoric acid of 10-40% P_2O_5 concentration and at temperature range of 40-75 ^oC.

One of the most important factors affecting the filtration rate is gypsum morphology (size and shape of the crystals). For best filtration and washing, crystals of uniform size are most desirable. At low sulfate contents, the shape of the crystals is changed from tabular crystals to clusters by addition of the surfactant.

Table (3)
Filtration and Reaction Data at Low Sulfate Content (1.5-1.8%)

Item	Without Surfactant	With Surfactant
Filtration rate, ton P_2O_5 /m^2.day	4.24	5.54
Moisture %	28.4	27.5
Change in filtration rate, %	**-**	**+ 31**
Reaction efficiency, %	93.2	97.1
P_2O_5 recovery, %	92.5	94.1
Washing efficiency, %	99.3	97.0

Table (4)
Comparative Size Analyses of Gypsum Crystals
(At Low Sulfate Content and After 3 hr)

Size, µm	Size, mesh*	Cum. Volume % Passing	Cum. Volume % Passing
		Without Surfactant	**With Surfactant**
106	140	100.00	99.91
90	170	100.00	99.05
75	200	99.99	95.68
63	230	99.82	89.70
53	270	99.15	82.11
45	325	97.93	74.91
38	400	96.21	68.12
10	-	64.28	30.75

* ASTM standards

B. Testing of the Concentrate at Medium Sulfate Content (2.2-2.4%)

Experiments have been performed, in presence and absence of surfactant. The amount of surfactant corresponds to 1.5 kg/ton P_2O_5. The data are given in Tables (5 & 6) and Fig. (2).

The filtration results of the samples at medium sulfate contents of about 2.2% and 2.4% with and without surfactant, respectively, are given in Table (5). The obtained filtration rate is 5.13 ton P_2O_5 /m^2.day without surfactant and improved to 6.42 ton P_2O_5 /m^2.day with the addition of surfactant. This corresponds to about 25% improvement. This is related to the growth of produced crystals upon surfactant addition and formation of low volume % of fines (<10 μm). The size distribution of gypsum crystals which is given in Table (6) and Fig. (2) show that, the volume percentage of fine produced gypsum crystals (<10 μm) is decreased to about 10% upon addition of surfactant while it is about 22% without surfactant.

The obtained reaction efficiencies, P_2O_5 recoveries and washing efficiencies of the phosphate concentrate with surfactant compared with the phosphate processed without surfactant (baseline) are given in Table (5). In this case also, that the reaction efficiency is increased with the addition of surfactant. This may be attributed, as mentioned above, to decrease of lattice (co-crystallized) P_2O_5 losses, which represent the majority of the total P_2O_5 losses.

Table (5)
Filtration and Reaction Data at Medium Sulfate Content (2.2-2.4%)

Item	Without Surfactant	With Surfactant
Filtration rate, ton P_2O_5 /m^2.day	5.13	6.42
Moisture %	28.3	27.8
Change in filtration rate, %	**-**	**+ 25**
Reaction efficiency, %	95.8	98.6
P_2O_5 recovery, %	95.0	96.4
Washing efficiency, %	99.2	97.9

Table (6)
Comparative Size Analyses of Gypsum Crystals
(at medium sulfate content and after 3 hr)

Size, µm	Size, mesh*	Cum. Volume % Passing	Cum. Volume % Passing
		Without Surfactant	**With Surfactant**
125	120	100.00	99.85
106	140	99.88	99.18
90	170	98.95	98.06
75	200	95.63	95.65
63	230	89.86	90.55
53	270	82.47	80.54
45	325	74.98	66.31
38	400	67.09	49.95
10	-	22.06	10.38

* ASTM standards

C. Testing of the Concentrate at High Sulfate Content (3.2-3.5%)

Tests have been conducted to study effect of surfactant addition at thses high levels of free sulfate. As in previous tests, surfactant is added at alevel of 1.5 kg/ton P_2O_5. The results obtained are given in Tables (7 & 8) and Fig. (3).

The filtration data of the samples at relatively high sulfate contents of about 3.2% and 3.5% with and without surfactant, respectively, are given in Table (7). The obtained filtration rate is 6.77 ton P_2O_5 /m^2.day without surfactant and improved to 8.33 ton P_2O_5 /m^2.day with the addition of surfactant. This corresponds to about 23% improvement ton P_2O_5/m^2.day). This is related to the growth of produced crystals upon surfactant addition and formation of high volume % of coarse crystals (>75 μm). The size distribution of gypsum crystals which is given in Table (8) and Fig. (3) shows that, the volume percentage of coarse produced gypsum crystals (>75 μm) is increased to about 15% upon addition of surfactant while it is about 10% without surfactant.

The obtained reaction efficiencies, P_2O_5 recoveries and washing efficiencies of the phosphate concentrate with surfactant compared with the phosphate processed without surfactant (baseline) are given in Table (7). As in the previous tests, it is obvious that the reaction efficiency is increased with the addition of surfactant. This may be attributed to decrease of lattice (co-crystallized) P_2O_5 losses.

Table (7)
Filtration and Reaction Data at High Sulfate Content (3.2-3.5%)

Item	Without Surfactant	With Surfactant
Filtration rate, ton P_2O_5 /m^2.day	6.77	8.33
Moisture %	27.9	28.4
Change in filtration rate, %	**-**	**+ 23**
Reaction efficiency, %	96.9	99.0
P_2O_5 recovery, %	96.4	96.9
Washing efficiency, %	99.5	97.8

Table (8)
Comparative Size Analyses of Gypsum Crystals
(At High Sulfate Content and After 3hr)

Size, µm	Size, mesh*	Cum. Volume % Passing	Cum. Volume % Passing
		Without Surfactant	**With Surfactant**
125	120	99.91	99.70
106	140	99.01	97.75
90	170	96.15	92.97
75	200	89.76	84.77
63	230	81.11	76.14
53	270	71.31	68.25
45	325	62.10	61.57
38	400	53.26	55.06

10	-	64.28	30.75

* ASTM standards

D. Correlation between Crystal Size Distribution and the Filtration Rate

The correlation between the crystal size distribution and the filtration rate are given in Table (9). These results show that, with decreasing the % volume fraction of fine crystals and/or increasing the volume % of the coarse crystals, the filtration rate is increased at each sulfate level.

Table (9): Relation between Crystal Size Distribution and Filtration Rate

Item	Phosphogypsum Fines (-10 μm), vol. %	Phosphogypsum Coarse (+75 μm), vol. %	Filtration rate, ton P_2O_5/m^2.day
Low sulfate content:			
Without surfactant	64.3	0.0	4.24
With surfactant	30.8	4.3	5.54
Medium sulfate content:			
Without surfactant	22.1	4.4	5.13
With surfactant	10.4	4.4	6.42
High sulfate content:			
Without surfactant	18.0	10.2	6.77
With surfactant	20.1	15.2	8.33

E. Mechanism of Improvement in Filtration Rate

The data and observations obtained in this study suggest possible mechanism for the effect of surfactant on phosphogypsum filtration as given below:

1. The used anioinc surfactant modifies the shape of the produced calcium sulfate dihydrate crystals e.g. at low sulfate content the crystals change from tabular to small clusters and at medium and high sulfate contents, the crystals change from small clusters to large clusters.
2. The surfactant decreases the nucleation at the same sulfate or calcium contents [27]. Consequently, this leads to growth of the crystals (both fine and coarse). It is obvious that, the volume % of fine crystals (<10 µm) is decreased and/or the volume % of coarse crystals (>75 µm) is increased with addition of surfactant.

3. Narrow size distribution is obtained upon addition of the surfactant. This could be attributed to the reported observation that the surfactant decreases the hydration of Ca^{2+} ions and consequently increases the growth rate of crystals [26].

CONCLUDING REMARKS

High dolomitic phosphate concentrate from the South Florida area was tested for phosphoric acid production. The obtained filtration rate at high sulfate content was 6.77 ton P_2O_5/m^2.day, which was improved to 8.33 ton P_2O_5/m^2.day by addition of 1.5kg surfactant/ton P_2O_5. The % improvement in filtration rate is about 23%. Also the size of produced gypsum crystals was increased. The experimental results show that 10.2% and 15.2% of the produced gypsum crystals were more than 75 μm without and with surfactant, respectively.

The reaction (digestion) efficiencies, P_2O_5 recoveries (overall efficiencies) and washing (filtration) efficiencies achieved were 96.9%, 96.4% and 99.5% without surfactant and were 99.0%, 96.9% and 97.8% with surfactant, respectively. The P_2O_5 in the filter (product) acids are 27.9% and 28.4% without and with addition of the surfactant, respectively.

Similar results are obtained at low sulfate (1.5-1.8%) and medium sulfate (2.2-2.5) contents. The data show that the filtration rate, size of the gypsum crystals, reaction efficiency and P_2O_5 recovery are increased with addition of the surfactant.

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Fig. (1)
Comparative Size Analyses of Gypsum Crystals
(at low sulfate content and after 3 hr)

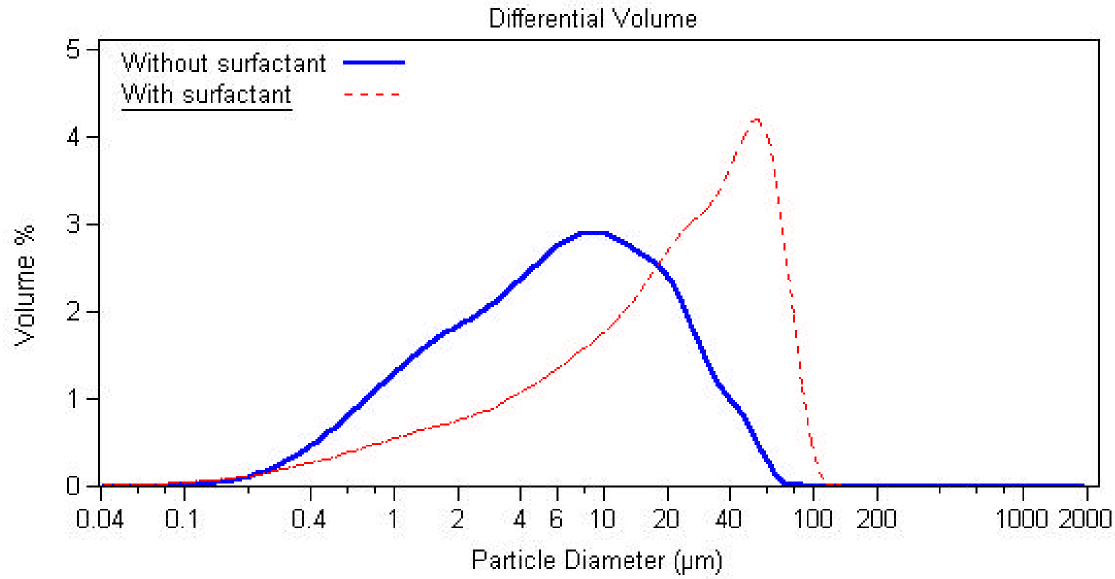

Fig. (2)
Comparative Size Analyses of Gypsum Crystals
(at medium sulfate content and after 3 hr)

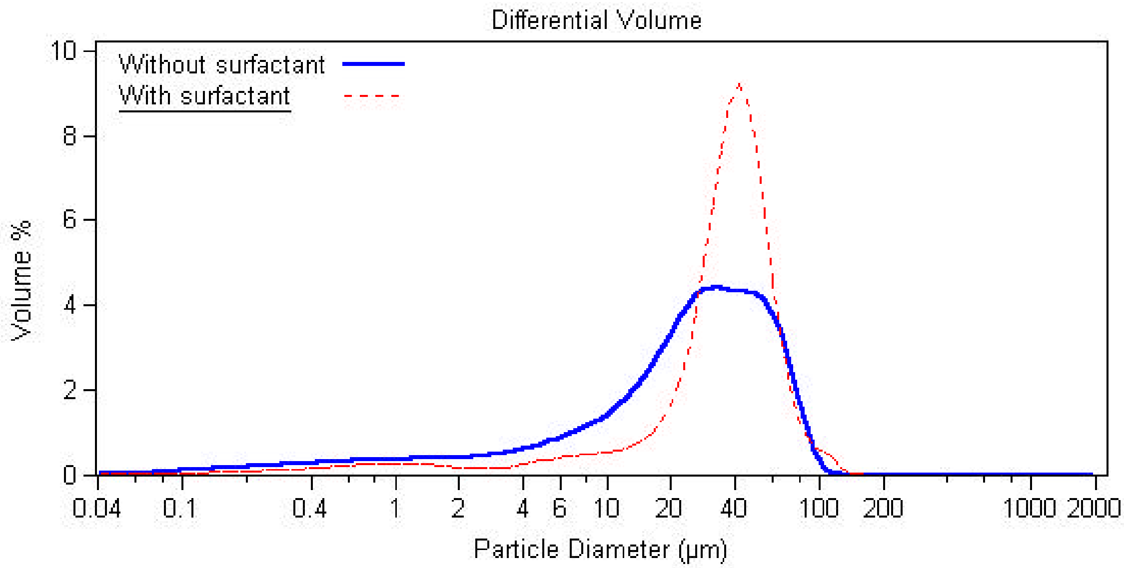

Fig. (3)
Comparative Size Analyses of Gypsum Crystals
(at high sulfate content and after 3 hr)