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ENHANCING FILTRATION RATE OF NEW VALLEY OXIDIZED PHOSPHATE CONCENTRATE WITH ADDITIVES

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Abstract: Phosphoric acid is utilized for production of fertilizers. It is mainly produced by wet processes, in which phosphate concentrate, produce by several operations including crushing, scrubbing, classification, attritioning, and desliming, is leached with sulfuric acid with coproduction of calcium sulfate dihydrate (phosphogypsum). The New Valley oxidized phosphate concentrate was processed for phosphoric acid production by addition of certain additives to improve gypsum filtration through modifying its morphology and particle size distribution. The additives used were cetylpyridinium chloride (CPC) as a cationic surfactant, sodium dodecyl sulfate (SDS) as an anionic surfactant and sulfonic acid (SA). The applied dosages ranged from 0.25 to 2.5 kg additive/Mg P_2O_5 in the phosphate concentrate. The filtration rate of the New Valley oxidized phosphate concentrate is 3.6 Mg P_2O_5 /m^2·day without additives. The filtration rate was increased by 33% and 31% with 1 and 0.8 kg/Mg P_2O_5 doses of CPC surfactant and sulfonic acid (SA), respectively. On the other hand, the filtration rate was decreased by 33% with addition of 1 kg/Mg P_2O_5 dose of SDS. The aspect ratios of gypsum crystals were 6:1, 3:1, 3:1 and 12:1 without additive, with CPC, SA and SDS surfactant, respectively. Reaction efficiencies without and with 0.8 kg/Mg P_2O_5 of CPC, SA and SDS dose of additives were 95.0%, 97.9%, 97.9% and 94.7%, respectively. The P_2O_5 recoveries without and with 0.8 kg/Mg P_2O_5 of CPC, SA and SDS dose of additives were 92.6%, 95.5%, 95.8% and 90.8%, respectively.

***Keywords**: New Valley phosphate concentrate, surfactant, filtration rate, gypsum morphology, crystal size distribution*

Introduction

The necessity of securing food for the rapidly increasing human population requires increasing the cultivated area as well as its quality by the application of fertilizers. Phosphatic fertilizers are produced from phosphate rocks which are abundant all over Egypt (New Valley, Nile Valley and Red Sea).

Phosphoric acid (H_3PO_4) is an important intermediate product for production of phosphatic fertilizers and also it used in other areas of chemical industries. In fertilizer

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production it serves as an intermediate material between phosphate ore and major end products such as ammonium phosphates, triple superphosphate, liquid fertilizers and some types of nitric phosphates. Phosphoric acid is mainly produced by a dihydrate process in which phosphate ore concentrates are leached with sulfuric acid (H_2SO_4) and recycled weak phosphoric acid to produce phosphoric acid and gypsum. Each year, more than 25 teragrams (Tg) of P_2O_5 equivalent phosphoric acid is produced by this method in the world (Becker, 1989). The reactions of this process are as follows (El-Shall et. al, 1999):

$$Ca_{10}F_2(PO_4)_6 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2HF$$

$$10Ca(H_2PO_4)_2 + 10H_2SO_4 + 20H_2O \rightarrow 20H_3PO_4 + 10CaSO_4{\cdot}2H_2O$$

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4{\cdot}2H_2O + 2HF.$$

The total reaction is fast. It takes from 2 to 10 minutes, depending on phosphate reactivity and process conditions. However, the crystallization of gypsum extends for a long time (2-8 hours) (Becker, 1989). Productivity of phosphoric acid depends mainly on the gypsum filtration. A high production capacity with low operating costs can be achieved if the filtration rate is increased. It is known that the filtration rate depends on the characteristics of the filter cake such as crystal size, size distribution and morphology of the crystals. Therefore, enhancing the formation of large and uniform gypsum crystals is desired in achieving better filtration rate in the phosphoric acid manufacture (Abdel-Aal, 1984, 1989, 2004).

The basic objective of the phosphoric acid manufacture is to obtain the highest concentration of phosphoric acid possible with the maximum yield (Becker, 1989; Slack, 1968). The yield is dependent on the completeness of the reaction of phosphate concentrate with sulfuric acid, the efficiency of separation of phosphoric acid from calcium sulfate and the quantity of wash water required to remove essentially all P_2O_5 from the calcium sulfate during the filtration (Becker, 1989; Slack, 1968).

Many materials are tested for enhancing crystallization of calcium sulfate dihydrate including aluminum sulfate, clay, calcined clay (Abdel-Aal, 1989), aluminum hydroxide, pearlite, active silica, active charcoal, manganese dioxide (Ismail, 1997; Abdel-Aal et al., 2004), polymers (Amjad and Hooley, 1986; Kerr et al., 1991; Zhu, 1996), surfactants (El-Shall et al., 1999, 2000, 2005; Mahmoud et al., 2004; Abdel-Aal et al. 2007), phosphonate (El-Shall et al., 2002; Tadros and Mayes, 1997), foreign ions (Rashad et al., 2004; De Vreugd et al., 1994), carboxylic acids (Tadros and Mayes, 1997; Badens et al., 1999; Rashad et al., 2005), and other organic additives such as EDTA and gelatin (Liu and Nacollas, 1973). In addition, studies about crystallization of other calcium salts such as calcium oxalate and calcium phosphate with and without additives at different levels of supersaturation are reported (El-Shall et al., 2004a; 2004b; Abdel-Aal et al., 2008; 2009). The mechanism for enhancing filtration rate by organic additives is discussed elsewhere (El-Shall et al., 1999).

Phosphoric acid production from the New Valley phosphate concentrate suffers from poor gypsum filtration. This problem affects feasibility study for production of phosphoric acid from the New Valley phosphate concentrate of 1 petagram (Pg) estimated potential reserves. The New Valley phosphate rock has a good potential of rare earths metals source (Ismail and Abdel-Aal, 1990; Abdel-Aal and Amer, 1995; Abdel-Aal et al., 1998).

A low filtration rate requires large filter areas which means high capital and operation costs. It is worth mentioning that, generally in phosphoric acid plants, the capital cost of filtration unit is about 50% of the total cost of the plant. So, enhancing the filtration rate of phosphoric acid produced from the New Valley phosphate concentrate is very important for the project to be economically feasible.

The main objective of this paper is to enhance filtration rate of phosphoric acid produced from the New Valley phosphate by addition of different organic additives.

Experimental

Materials and reagents

The chemical analysis of the New Valley phosphate concentrate is given in Table 1.

Table 1. Chemical analysis of New Valley phosphate concentrate

Constituent, %	Phosphate concentrate
P_2O_5	31.6
CaO	44.5
SiO_2	3.2
Fe_2O_3	3.7
Al_2O_3	0.6
MgO	0.1
Na_2O	0.9
K_2O	0.2

The run of mine phosphate ore is concentrated by crushing followed by scrubbing to reject +2 mm oversize, and then by classification at 0.149 mm. Attritioning of the classifier undersize -2.0 +0.149 mm is performed followed by desliming to get primary concentrate. The concentration and density of the used sulfuric acid were 97.99% and 1.825 g/cm^3 while the phosphoric acid concentration and density were 85% (61.58% P_2O_5) and 1.689 g/cm^3, respectively. The phosphoric acid was used to prepare solution containing 20% P_2O_5. Organic additives used in enhancing or retarding the growth rate of gypsum were cetylpyridinium chloride (CPC)

$C_{21}H_{38}ClN \cdot H_2O$ (cationic surfactants), sodium dodecyl sulfate (SDS) $C_{12}H_{25}NaO_4S$ (anionic surfactants) and sulfonic acid (carboxylic acid).

Experimental procedure

The reaction between phosphate concentrate and sulfuric acid was performed in a 1 dm^3 covered reactor. The solution was heated to 80 °C using a water bath. The electric mechanical stirrer speed was 450 rpm. The calculated amount of recycle acid (~20 % P_2O_5) was put in the reaction vessel. The calculated amount of phosphate concentrate was added continuously for 1 hour using a vibrating rock feeder. Sulfuric acid was added continuously for 1 hour using a peristaltic dosing pump. The calculated amount of additive solution was added continuously for 1 hour using a peristaltic dosing pump. The slurry was stirred using an electrical mechanical stirrer with propelling shaft mounted through an opening of the beaker cover to avoid losses of solution by evaporation. The reaction system and the experimental procedures were given in our previous work (El-Shall et al., 1999). The filtration process was performed using a Buchner type filter funnel. The slurry was poured on an 8.5 cm diameter filter funnel with a polypropylene filter cloth. The suction was induced by a vacuum pump. The applied pressure difference was 0.67 Bar. The filtration system was described in our previous work (El-Shall et al., 1999). The filtration time was recorded when the surface of the cake was no longer wetted. The gypsum cake was then washed three times using heated solutions. The times of washing stages were recorded. Chemical analyses of filter acid as well as gypsum were performed according to the standard methods of analysis using a Shimadu UV-VIS recording spectrophotometer UV-160 with a double beam. The produced acid after filtration contained about 28 % P_2O_5 and 2.5 % sulfate. The most important are the P_2O_5 and sulfate contents. The range of P_2O_5 content in the filter acid was from 27 to 29% while sulfate range is from 2.0 to 3.0%. The P_2O_5 content was analyzed using the colorimetric method (Vogel, 1978). This method is applied for the P_2O_5 of filter acid and phosphate concentrate. Different methods for the chemical analysis of phosphates, phosphoric acid and gypsum were reported (Young, 1971).

Calculations of filtration rate, reaction efficiency and P_2O_5 recovery

The total filtration time is defined as a sum of the filtration time of product acid and washing time of gypsum. Reaction efficiency (digestion or process efficiency, in percent of extraction or conversion) is defined as the percent of P_2O_5 removed from the phosphate concentrate into solution, because some of P_2O_5 is lost with incompletely washed gypsum. The reaction efficiency is calculated from the following equation (El-Shall et al., 1999):

$$\text{Reaction efficiency} = 100 - 94 \cdot (A - B) \cdot C / (D \cdot E)$$

where A is the total P_2O_5 in gypsum cake, B water-soluble P_2O_5 in gypsum cake, C CaO in phosphate concentrate used to make the acid, D P_2O_5 in phosphate concentrate used to make the acid and E CaO in gypsum cake. Parameters from A to E are given in percent. Also P_2O_5 recovery (either overall or plant efficiency, or yield) is defined as the percent of P_2O_5 passing from the phosphate concentrate into the produced phosphoric acid. It can be calculated as follows (El-Shall et al., 1999):

$$P_2O_5 \text{ recovery} = 100 - (94 - A \cdot C) / (D \cdot E) .$$

The filtration rate (FR) is calculated as follows:

$$F.R. = \frac{X \cdot P_2O_5\%.K_{re} \cdot 10^4 \cdot 86400}{100 \cdot 100 \cdot 10^6 \cdot A \cdot T}$$

where FR is filtration rate, Mg $P_2O_5/m^2 \cdot$day, X weight of concentrate used, g, P_2O_5 in phosphate concentrate, K_{re} P_2O_5 recovery, 10^4 conversion factor from cm^2 to m^2, 86400 conversion factor from seconds to day, 10^6 conversion factor from g to Mg, A active filter area, cm^2 and T total time of filtration and washing, in seconds.

Results and discussion

Chemical processing without additives

Leaching and filtration data

Tests were carried out under the optimum leaching and filtration conditions (El-Shall, 1999). The obtained results are given in Table 2. The average filtration rate, reaction efficiency and P_2O_5 recovery, are 3.6 Mg $P_2O_5/m^2 \cdot$day, 95.0 % and 92.6 %, respectively.

Table 2. Results of leaching and filtration of New Valley phosphate concentrate without additives (Ismail, 1997)

Experiment Number	Filtration Rate, $MgP_2O_5/m^2 \cdot$day	Reaction Efficiency, %	P_2O_5 Recovery, %
1	3.6	95.7	93.2
2	3.5	94.7	92.4
3	3.8	96.7	94.3
4	3.5	94.2	92.0
5	3.5	93.7	91.0
Average	3.6	95.0	92.6

Gypsum quality and morphology

The chemical composition and density of co-produced gypsum is given in Table 3. This table shows that the quality of gypsum is good as it contains low levels of impurities. A scanning electron microscope picture of gypsum crystals in the absence of additives is given in Fig. 1 which indicates that the shape of obtained crystals are needle type crystals with average aspect (length to width) ratio about 6:1. These crystals are difficult to filter and wash during phosphoric acid production (Rashad et al., 2003).

Table 3. Chemical analysis and physical properties of New Valley gypsum cake

Constituent	Gypsum cake, wt. %, dry basis
Total P_2O_5	0.83
Water-Soluble P_2O_5	0.38
Citrate-Soluble P_2O_5	0.40
CaO	31.7
SO_4^{2-}	49.6
SiO_2	1.60
Fe_2O_3	1.01
Al_2O_3	0.16
MgO	0.04
Na_2O	0.22
K_2O	0.015
Density, g/ml	2.29

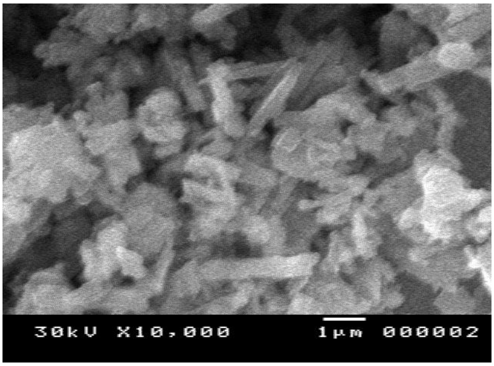

Fig. 1. SEM of gypsum crystals in absence of additives

Chemical processing with cetylpyridinium chloride (CPC)

The effect of different dosages of cetylpyridinium chloride (CPC) from 0.25 kg/Mg P_2O_5 to 2.5 kg/Mg P_2O_5 on filtration rate, reaction efficiency and P_2O_5 recovery were studied as shown in Table 4. The obtained results revealed that with increasing dose of CPC, the filtration rate increased from 3.6 Mg $P_2O_5/m^2{\cdot}day$ to 4.8 Mg $P_2O_5/m^2{\cdot}day$. Also, it was found that with increasing dose of CPC, the reaction efficiency increased from 95.0% to 97.6% and the P_2O_5 recovery was increased from 92.6% to 95.9. The optimum CPC dose is 1 kg/Mg P_2O_5, which gives the highest filtration rate of 4.8 Mg $P_2O_5/m^2 \cdot day$.

The SEM of the gypsum crystals in the presence 1 kg/Mg P_2O_5 of CPC is given in Fig. 2. The majority of these crystals are tabular and are not uniform crystals. The average aspect ratio decreased to about 3:1, compared to the ratio of 6:1 without additives. This means that relatively thicker and larger crystals were formed. CPC increases both the mean diameter, nucleation rate and the crystal growth rate of gypsum (El-Shall et al., 2005). CPC may be adsorb on 101 plane of gypsum crystals enhancing filtration rate as Al ions do (Abdel-Aal, 1989).

Table 4. Results of leaching and filtration of New Valley phosphate concentrate with cetylpyridinium chloride (CPC) surfactant

Experiment Number	Dose of CPC surfactant, kg/Mg P_2O_5	Filtration rate, $MgP_2O_5/m^2 \cdot day$	Reaction efficiency, %	P_2O_5 recovery, %
1	0	3.6	95.0	92.6
2	0.25	4.3	97.4	95.5
3	0.5	4.5	97.6	95.5
4	0.8	4.6	97.9	95.5
5	1.0	4.8	97.6	95.9
6	1.25	4.4	97.7	95.8
7	1.5	4.2	97.9	95.6
8	2.5	3.7	97.9	96.0

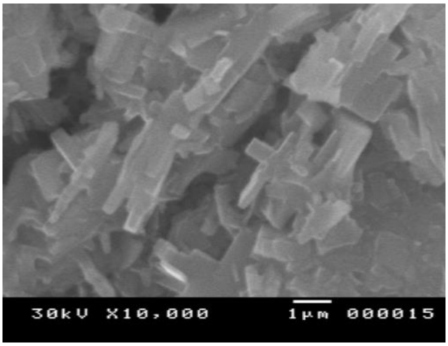

Fig. 2. SEM of gypsum crystals with 1 kg/Mg P_2O_5 of cetylpyridinium chloride

Chemical processing with sulfonic acid (SA)

The effect of different dosages of sulfonic acid from 0.25 kg/Mg P_2O_5 to 2.5 kg/Mg P_2O_5 on filtration rate, reaction efficiency and P_2O_5 recovery were studied as shown in Table 5. The results revealed that with addition of 0.8 kg/Mg P_2O_5 SA the filtration rate was increased from 3.6 to 4.7 Mg $P_2O_5/m^2 \cdot day$. At this dose of SA the reaction efficiency was increased from 95.0% to 96.5% and the P_2O_5 recovery was increased from 92.6% to 95.8%. A further increase of sulfonic acid leads to a decrease of the filtration rate.

Table 5. Results of leaching and filtration of New Valley phosphate concentrate with sulfonic acid

Experiment number	Dose of sulfonic acid, kg/Mg P_2O_5	Filtration rate, Mg $P_2O_5/m^2 \cdot$day	Reaction efficiency %	P_2O_5 recovery %
1	0	3.6	95.0	92.6
2	0.25	4.0	97.8	95.7
3	0.5	4.4	97.8	96.2
4	0.8	4.7	97.9	95.8
5	1.0	3.7	98.1	96.0
6	1.25	3.4	98.1	96.3
7	1.5	3.1	98.2	96.6
8	2.5	3.0	98.2	96.6

The SEM of the gypsum crystals with 0.8 kg/Mg P_2O_5 of sulfonic acid is given in Fig. 3. The majority of these crystals are tabular and their shapes are mostly uniform. The average aspect ratio decreased to about 3:1 compared to the ratio of 6:1 without additives. This means that relatively thicker and lager crystals are formed. It appears that SA has a similar mechanism as CPC. This is apparent from the average particle size of baseline (without surfactant), with CPC and with SA as 5.9, 8.9 and 8.2 micrometer, respectively. So, sulfonic acid increases both the mean diameter, nucleation rate and crystal growth rate of gypsum crystals. Also, SA may be adsorbed on 101 gypsum plane enhancing filtration rate as Al ions do (Abdel-Aal, 1989).

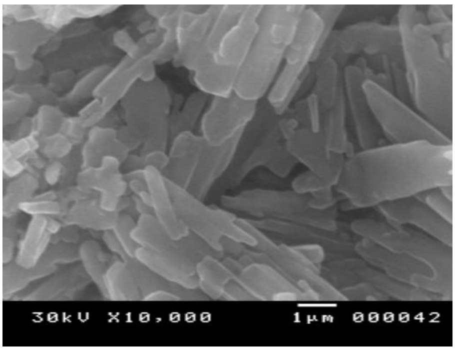

Fig. 3. SEM of gypsum crystals with 0.8 kg/Mg P_2O_5 of sulfonic acid

Chemical processing with sodium dodecyl sulfate (SDS)

The effect of different dosages of SDS from 0.25 kg/Mg P_2O_5 to 2.5 Kg/Mg P_2O_5 on filtration rate, reaction efficiency and P_2O_5 recovery were studied as shown in Table 6. The obtained results reveal that with increasing the dose of SDS, the filtration rate decreased. Also, it was found that with increasing the dose of SDS, the reaction efficiency and the P_2O_5 recovery decreased.

Table 6. Results of leaching and filtration of New Valley open-cast phosphate concentrate with sodium dodecyl sulfate (SDS) surfactant

Experiment number	Dose of (SDS) surfactant, kg/Mg P_2O_5	Filtration rate, Mg P_2O_5/m^2·day	Reaction efficiency %	P_2O_5 recovery %
1	0	3.6	95.0	92.6
2	0.25	3.3	95.3	90.9
3	0.5	2.7	95.1	90.6
4	0.8	2.7	94.7	90.8
5	1.0	2.4	93.9	90.0
6	1.25	2.4	94.0	90.7
7	1.5	2.3	93.8	89.3
8	2.5	2.2	93.7	89.7

The SEM of the gypsum crystals with 1 kg/Mg P_2O_5 of SDS is given in Fig. 4. It is apparent that SDS surfactant helps to form needle–type and some plate-like crystals. The nonuniform mixture of crystals gives relatively low filtration rate. The average length to width ratio was decreased to about 12:1 compared to the ratio of 6:1 without additives.

It appears that SDS works by an opposite mechanism as the CPC surfactant. The average particle size without surfactant, with CPC and with SDS were 5.9, 8.9 and 4.8 μm, respectively. So, SDS decreases the mean diameter, nucleation rate and the crystal growth rate of gypsum crystals.

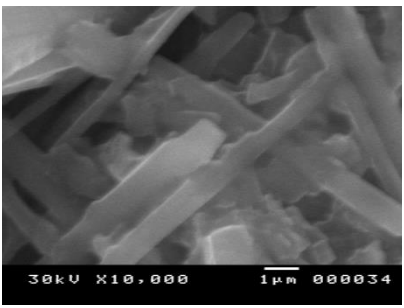

Fig. 4. SEM of gypsum crystals with 1 kg/Mg P_2O_5 of sodium dodecyl sulfate

Conclusion

The filtration rate of the New Valley oxidized phosphate concentrate is low (about 3.6 Mg $P_2O_5/m^2 \cdot day$). The filtration rates were calculated without and with different dosages ranging from 0.25 to 2.5 kg additive/Mg P_2O_5 in phosphate concentrate from cetylpyridinium chloride surfactant (CPC), sodium dodecyl sulfate surfactant (SDS) and sulfonic acid (SA). The filtration rate was increased by 33% and 31% with 1.0 and 0.8 kg/Mg P_2O_5 doses of CPC and SA, respectively. On the other hand, the filtration rate decreased by 33% with addition of 1 kg/Mg P_2O_5 of SDS.

The aspect ratios of gypsum crystals were 6:1, 3:1, 3:1 and 12:1 without additive, with CPC, with SA and with SDS, respectively. Reaction efficiencies and P_2O_5 recoveries increased with CPC and SA in comparison without the additives. Addition of SDS decreased the reaction efficiencies and P_2O_5 recoveries.

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