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Phosphogypsum (PG) crystal size distributions in presence and absence of PG seed crystals and sorbitol surfactant

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Abstract: Leaching of calcium phosphate with sulfuric acid was carried out to study phosphogypsum (PG) crystal growth and size distributions in presence and absence of phosphogypsum seed crystals (PGSC) and sorbitol surfactant (SS) additives. PG crystallization simulates industrial Dihydrate process for phosphoric acid production. PG crystals grow in a medium containing 26±1% P_2O_5 phosphoric acid and 2±0.5 % free sulfuric acid. Better filterability of phosphoric acid can be achieved with large crystals. The formed PG crystals are larger with addition of either 100 ppm Sorbitol surfactant, 5%, 10% or 15% PGSC compared to the baseline (without additives). With addition of surfactant or increasing the % of PGSC from 5% to 15%, both the mean diameter and d_{90} of crystalized PG are increased due to enhancing the crystallization growth rates.

Keywords: crystal growth, crystal size distribution, characterization, calcium sulfate dihydrate, leaching with simultaneous crystallization

1. Introduction

Phosphoric acid is mainly produced by the common dihydrate wet-process in which fluorapatite, $Ca_{10}(PO_4)_6F_2$, in phosphate concentrate reacts with sulfuric acid and recycled weak phosphoric acid to produce phosphoric acid as liquid phase and by-product phosphogypsum cake as a solid phase (Becker, 1989). Crystallization of phosphogypsum occurs simultaneously during phosphate leaching. The slurry is filtered and the filter cake is counter-current washed to separate the produced phosphoric acid from the gypsum (industrially termed as phosphogypsum). The reaction time is very fast from 2 to 10 minutes (Becker, 1989). Size distribution of phosphogypsum crystals has an effect on filtration rate (production rate) of phosphoric acid.

Different types of additives have been used as phosphogypsum-crystal modifier to enhance filterability of phosphoric acid e.g. surfactants (El-Shall, et.al, 1999; Abdel-Aal, 2004; Abdel-Aal et al., 2007), phosphonate (El-Shall et al., 2002), foreign ions (De Vreugd et al., 1994), carboxylic acids (Tadros and Mayes, 1979; Badens et al., 1999; Rashad et al., 2005), EDTA and gelatin (Liu and Nancollas, 1973). These additives alter the crystals' surface properties and change nucleation, growth, shape, and the crystals' aggregation or dispersion behavior. In addition, the additives increase P_2O_5 recovery as a result of decrease the co-crystalized P_2O_5 lattice losses. Rabizadeh et al., (2019) proved that the high molecular weight of Poly(acrylic acid) polymer (PAA) enhanced gypsum crystallization growth; while the low molecular weight of PAA do the opposite effect. Ultra-long α-calcium sulfate hemihydrate whiskers with aspect ratios from 200 to 500 were hydrothermally prepared (Wang et al., 2019). Sudden change of the gypsum interfacial tension can be occurred during changing of the reactant's concentrations (Gayevskii et al., 2020). Also, increasing the reactants concentration leads to increasing the supersaturation ratio and correlated to the available gypsum crystals surface area (Choi et al., 2019). It was reported that addition of alkylbenzene sulfonate increases the gypsum's filtration rate (Rocha and Ciminalli, 1995). Moreover, the mechanism of sodium dodecyl sulfate (SDS) on gypsum crystallization

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was explained (Liu and Nancollins, 1973). Moreover, addition of pure silica and fly ash waste additives enhanced the filtration rate of phosphoric acid from phosphogypsum by-product and increased the rare earth elements transfer from phosphate rock to phosphoric acid during chemical processing of Moroccan phosphate as reported (Arhouni et al., 2022; Hakkar et al., 2021).

The work's main objectives are studying the effects of Sorbitol surfactant, 5%, 10% and 15% seed crystals on both the phosphogypsum (PG) crystal growth and size distributions. In industry, better filterability and high productivity were achieved with large crystals. To the best of our knowledge, sorbitol surfactant was studied for the first time for enhancing phosphogypsum crystallization and hence filtration rate under the applied system.

2. Materials and methods

Chemicals of ultra-pure grade - include phosphoric acid, sulfuric acid, tricalcium phosphate (calcium phosphate or calcium orthophosphate) [$Ca_3(PO_4)_2$], methanol, and sorbitol surfactant (SS): [$C_6H_{14}O_6$] from Fisher Scientific Company - are used. Fig. 1 shows the experimental system including the used tools and apparatus.

2.1. Leaching of calcium phosphate

Calcium phosphate was leached using sulfuric acid and weak phosphoric under simulated conditions of phosphoric acid production. The technique is already described (El-Shall et al., 1999). The crystalized phosphogypsum (PG) was collected to be used as seed crystals. Amounts of Calcium phosphate and Sulfuric acid were adjusted to give 1.502 supersaturation ratio (S). S was calculated by applying the relation as reported elsewhere (El-Shall, et.al, 1999; Abdel-Aal, 2004; Abdel-Aal et al., 2007) with considering 0.83 % the solubility of calcium sulfate dihydrate under the applied conditions (Becker, 1989). Crystallization of PG is occurred simultaneously during leaching. Samples of the crystalized PG were taken after 1, 5, 15 and 35 minutes of leaching time. The PG seed crystals used in this study were collected after 35 minutes leaching and crystallization time. Different % of phosphogypsum seed crystals (PGSC) were applied (5%, 10% and 15%). The PG crystals of about 0.35, 0.62, 0.68 and 1.01 µm mean diameters after 1, 5, 15 and 35 minutes of crystallization times respectively were used as seed crystals.

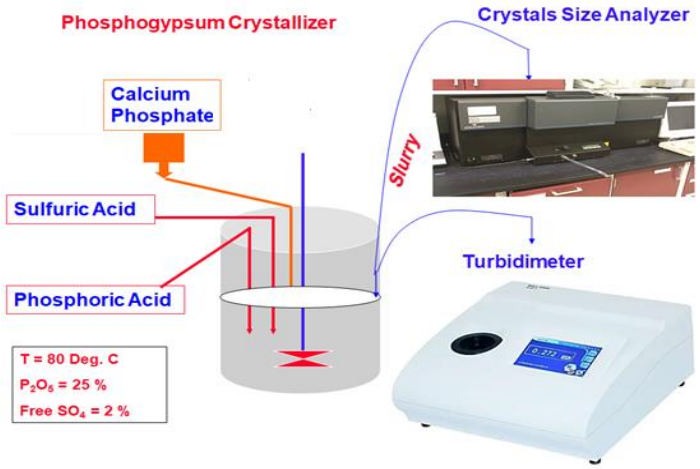

Fig. 1. Diagram indicated the experimental technique as well as turbidity and crystal size distribution (CSD) measurement apparatuses

2.2. Crystal size distribution measurement (El-Shall et al., 1999)

Coulter Laser Diffraction Analyzer model LS230 was used to determine the size distribution of the crystalized PG crystals as reported in the cited reference. Crystal size distribution tests were carried out by taking 3.0 ml slurry sample at different time intervals, and dispersed in 100 ml methanol, then conducting size analysis.

2.3. Calculation of crystal growth efficiency and growth rate (EL-SHALL et al., 1999)

Growth efficiency (E) and growth rate (G) were calculated by applying the relations as reported down. From the crystal size distribution data, d_{90} of the crystals at 1.502 supersaturation ratio and after various crystallization time intervals without additives and with additives are obtained. These additives (100 ppm sorbitol surfactant (SS), 5%, 10% and 15% phosphogypsum seed crystals: PGSC) were individually applied. Moreover, crystal growth rate (R) and crystal growth efficiency (E) are calculated by the following equations: R = d_{90}, µm (at Time T/T) in µm/min, where: d_{90} is 90 % of the crystals less than the size that measured at the crystallization time T in µm., T is crystallization time in minutes. E = (R with additive – R without additive) * 100/R without additive in % (at Time T), where E is crystal growth efficiency, % and R is crystal growth rate, µm/min.

3. Results and discussion

PG was crystallized according to the following chemical reaction equation:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3CaSO_4.2H_2O$$

The PG crystals grow at 80 °C in solution containing phosphoric acid (26±1 % P_2O_5) and 2±0.5 % free sulfuric acid with presence and absence of additives. This PG is different than regular chemically precipitated gypsum or naturally occurring gypsum as it contains co-crystalized P_2O_5.

3.1. Crystal size distribution (CSD) with and without additives

3.1.1. CSD without additives

The CSD without additives is measured and presented in Fig. 2 and Table 1 at 1.502 supersaturation ratio. Table 1 shows the values of mean diameter, median, mode, d_{10}, and d_{90} of the crystals at 1.502 supersaturation ratio and after various crystallization time intervals without additives.

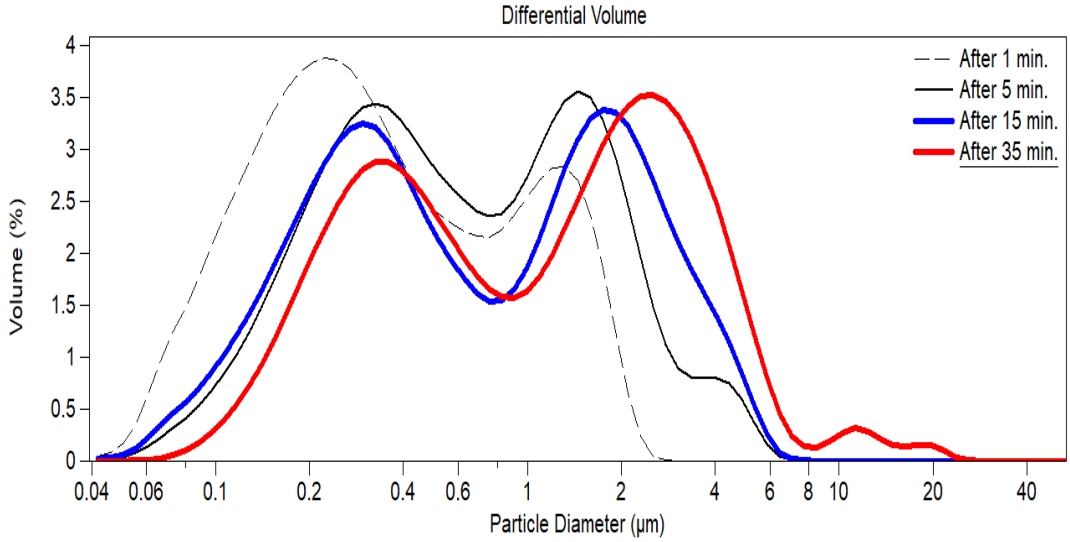

Fig. 2. Crystal size distribution (CSD) of phosphogypsum without additives at 1.502 S

Table 1. Effect of time on phosphogypsum crystal size distribution (CSD) without additives at 1.502 S

Item	Crystallization Time, min			
	1	5	15	35
Mean Diameter, µm	0.351	0.621	0.680	1.011
Median, µm	0.316	0.601	0.655	1.158
Mode, µm	1.106	1.451	1.749	2.539
d_{10}, µm	0.107	0.172	0.158	0.220
d_{90}, µm	1.346	2.167	2.902	4.038

d_x : diameter of crystals passing x vol. %

3.1.2. CSD in presence of 100 ppm sorbitol surfactant (SS)

The CSD with 100 ppm SS additive at 1,502 supersaturation ratio is measured and presented in Fig. 3 and Table 2. This table shows the values of mean diameter, median, mode, d_{10}, and d_{90} of the crystals at 1.502 supersaturation ratio and after various crystallization time intervals with 100 ppm SS additive.

Crystal growth rates and growth efficiencies are calculated with and without SS as shown in Table (3). It is clear that, the crystal growth rates are enhanced with SS. In contrast, the crystal growth rates and growth efficiency are decreased with increasing the retention time. The growth efficiency was decreased from 140.3 % to 80.9 % with increasing the retention time from 1 to 35 minutes. This is attributed to availabilities of Ca^{2+} cations and SO_4^{2-} anions are decreasing with time. On the other hand, the ions availabilities are higher with the additive due to increasing the localization of ions around the crystals (in case of SS) or increasing the number of crystals (in case of addition 5%, 10% and 15% PGSC).

The mechanism of action of the sorbitol surfactant on the enhancing phosphogypsum crystallization is related to increasing the localized supersaturation ratio around the new born crystals. Sorbitol molecule has 6 hydroxyl groups that adsorbed on positive site of crystals and helping to increase the localized supersaturation around the crystals.

It is worth mentioning that, both crystal growth and the growth efficiency decrease as a function of the time of crystallization due to decrease of available soluble ions for crystallization with time.

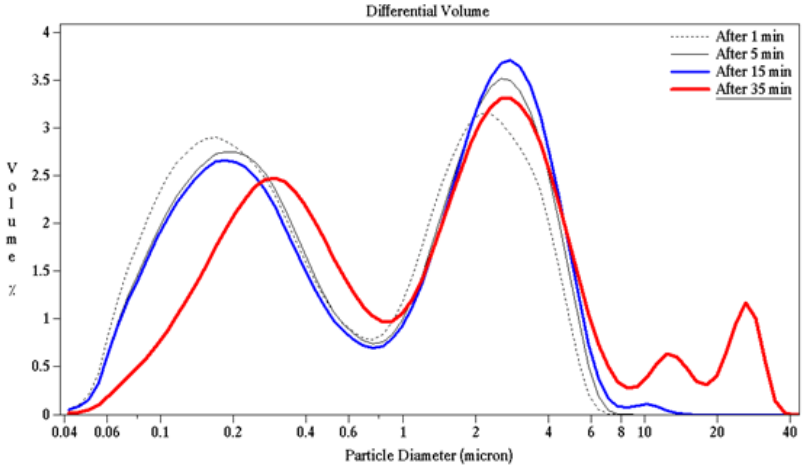

Fig. 3. CSD of phosphogypsum with 100 ppm SS at 1.502 S

Table 2. Effect of 100 ppm SS on phosphogypsum CSD at 1.502 S and different crystallization times

Item	Crystallization Time, min			
	1	5	15	35
Mean Diameter, μm	0.561	0.651	0.710	1.864
Median, μm	0.465	0.630	0.877	1.457
Mode, μm	2.106	2.539	2.780	2.787
d_{10}, μm	0.099	0.108	0.110	0.172
d_{90}, μm	3.235	4.585	5.910	7.280

d_x : diameter of crystals passing x vol. %

3.1.3. CSD in presence of 5% PGSC

The CSD in the presence of 5% PGSC at 1.502 supersaturation ratio is measured and presented as given in Fig. 4 and Table 4. This table shows the mean diameter, median, mode, d_{10}, and d_{90} of the crystals after various crystallization time intervals with 5% PSC. These data show that the mean diameter, median, mode, d_{10}, and d_{90} of the PG crystals are increased with increasing the retention time.

Crystal growth rates and growth efficiencies are calculated with and without 5% PGSC as shown in Table (5). It is clear that, the crystal growth rates are enhanced with addition of 5% PSC. In contrast, the crystal growth rates and the growth efficiencies are decreased with increasing the retention time. The growth efficiency was decreased from 90.9 % to 12.2 % with increasing the retention time from 1 to 35 minutes. The interpretations of the results are reported in the previous paragraphs.

Table 3. Effect of time and 100 ppm SS on the Phosphogypsum crystal growth rate and growth efficiency at 1.502 S

Crystallization Time, min	Crystal Growth Rate, μm/min		Growth Efficiency, %
	Without SS	With SS	
1	1.346	3.235	140.3
5	0.433	0.917	111.8
15	0.194	0.394	103.1
35	0.115	0.208	80.9

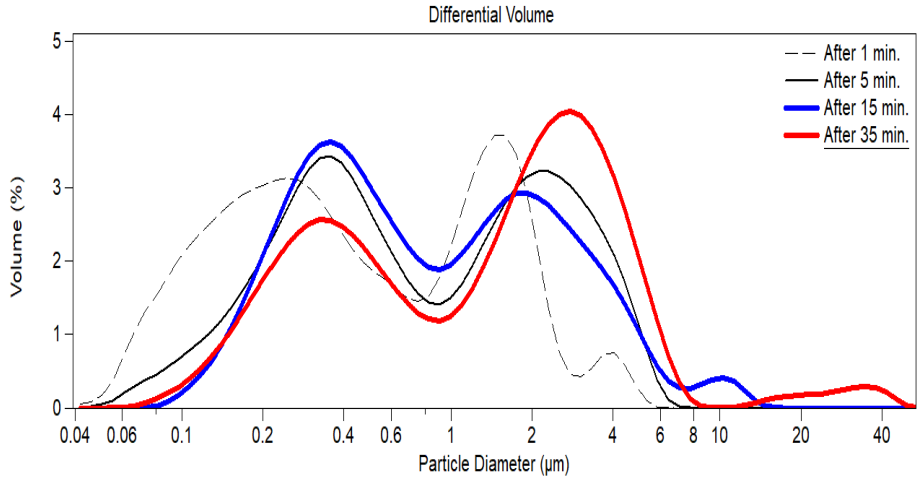

Fig. 4. CSD of phosphogypsum with 5% phosphogypsum seed crystals (PGSC) at 1.502 S

Table 4. Effect of time on phosphogypsum CSD with 5% GSC at 1.502 S

Item	Crystallization Time, min			
	1	5	15	35
Mean Diameter, μm	0.453	0.774	0.847	1.193
Median, μm	0.398	0.726	0.765	1.559
Mode, μm	1.593	1.939	2.180	2.787
d_{10}, μm	0.108	0.181	0.222	0.225
d_{90}, μm	2.570	3.369	3.561	4.499

d_x : diameter of crystals passing x vol. %

Table 5. Effect of time and 5% phosphogypsum seed crystals on the crystal growth rate and growth efficiency at 1.502 S

Crystallization Time, min	Crystal Growth Rate, μm/min		Growth Efficiency, %
	Without Seed Crystals	With 5% Seed Crystals	
1	1.346	2.570	90.9
5	0.433	0.674	55.7
15	0.194	0.237	22.2
35	0.115	0.129	12.2

3.1.4. CSD in presence of 10% PGSC

In the presence of 10% PGSC, the CSD at 1.502 supersaturation ratio is measured and presented as given in Fig. 5 and Table 6. This table shows the mean diameter, median, mode, d_{10}, and d_{90} of the crystals after various crystallization time intervals with 10% PSC. These data show that the mean diameter, median, mode, d_{10}, and d_{90} of the PG crystals are increased with increasing the retention time. Crystal growth rates and growth efficiencies are calculated with and without 10% PGSC as shown in Table (7). It is clear that, the crystal growth rates are enhanced with addition of 10% PGSC. In contrast, the crystal growth rates and the growth efficiencies are decreased with increasing the retention time. The growth efficiency was decreased from 129.2 % to 34.8 % with increasing the retention time from 1 to 35 minutes. Again, the interpretations of the results are reported in the previous paragraphs.

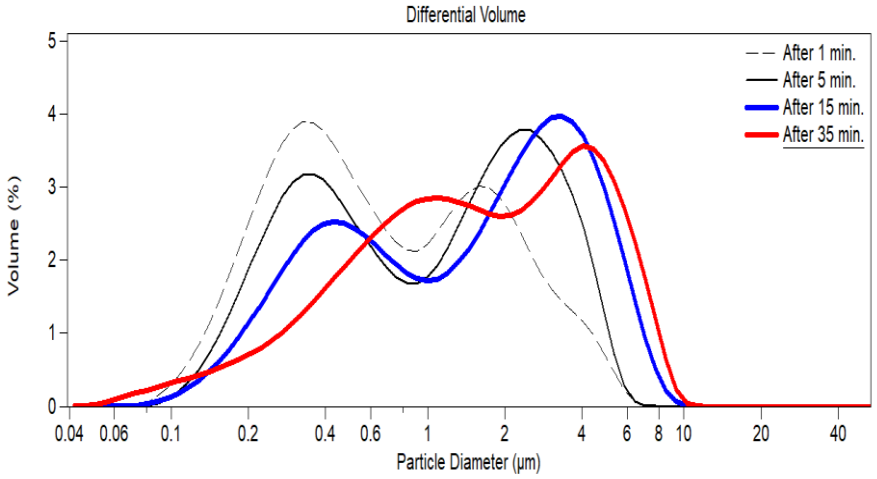

Fig. 5. CSD of phosphogypsum with 10% PGSC at 1.502 S

Table 6. Effect of time on phosphogypsum CSD with 10% PSC at 1.502 S

Item	Crystallization Time, min			
	1	5	15	35
Mean Diameter, µm	0.686	0.949	1.305	1.448
Median, µm	0.605	1.079	1.630	1.593
Mode, µm	1.935	2.312	3.505	4.047
d_{10}, µm	0.203	0.236	0.284	0.328
d_{90}, µm	2.638	3.985	4.769	5.427

d_x : diameter of crystals passing x vol. %

Table 7: Effect of time and 10% phosphogypsum seed crystals on the crystal growth rate and growth efficiency at 1.502 S

Crystallization Time, min	Crystal Growth Rate, µm/min		Growth Efficiency, %
	Without Seed Crystals	With 10% Seed Crystals	
1	1.346	2.638	129.2
5	0.433	0.797	84.1
15	0.194	0.318	63.9
35	0.115	0.155	34.8

3.1.5. CSD in presence of 15% PGSC

With addition of 15% PGSC, the CSD at 1.502 supersaturation ratio is measured and presented as given in Fig. 6 and Table 8 that shows the mean diameter, median, mode, d_{10}, and d_{90} of the crystals after

various crystallization time intervals. These data show that the mean diameter, median, mode, d_{10}, and d_{90} of the PG crystals are increased with increasing the retention time. Crystal growth rates and growth efficiencies are calculated with and without 15% PGSC as shown in Table (9). It is clear that, the crystal growth rates are enhanced with addition of 15% PGSC. In contrast, the crystal growth rates and the growth efficiencies are decreased with increasing the retention time. The growth efficiency was decreased from 161.1 % to 70.1 % with increasing the retention time from 1 to 35 minutes.

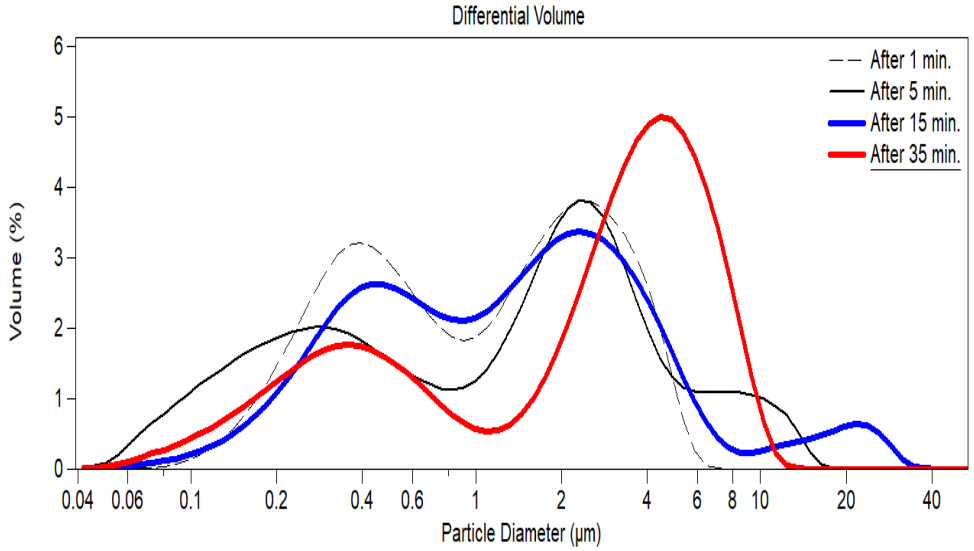

Fig. 6. CSD of phosphogypsum with 15% PGSC at 1.502 S

Table 8. Effect of time on phosphogypsum CSD with 15% PSC at 1.502 S

Item	Crystallization Time, min			
	1	5	15	35
Mean Diameter, µm	0.991	1.033	1.288	1.618
Median, µm	1.115	1.439	1.375	3,026
Mode, µm	2.312	2.592	3.599	4.444
d_{10}, µm	0.256	0.147	0.280	0.239
d_{90}, µm	3.514	5.580	5.020	6.848

d_x : diameter of crystals passing x vol. %

Table 9. Effect of time and 15% phosphogypsum SC on the crystal growth rate and growth efficiency at 1.502 S

Crystallization Time, min	Crystal Growth Rate, µm/min		Growth Efficiency, %
	Without Seed Crystals	With 15% Seed Crystals	
1	1.346	3.514	161.1
5	0.433	1.116	157.7
15	0.194	0.335	72.5
35	0.115	0.196	70.1

3.2. Correlation between PG crystal size and filtration rate

Table 10 shows with increasing d_{90} (90 % of crystals less than the size), the filtration rate and the crystal growth rate after 35 minutes crystallization time are increasing. Moreover, the % increases in both filtration rate as well as crystal growth rate are increased with increasing seed crystals % and with surfactant addition. Similar results were achieved using phosphate rock with different additives (Rashad et al., 2005).

Fig. 7 shows the mean diameter and d_{90} of crystalized PG with and without additives (d_{90}: diameter of crystals passing 90 vol. %). These results show that, d_{90} of the PG crystals with the surfactant is higher than other additives. However, with increasing the % of PGSC, both the mean diameter and d_{90} of crystalized PG are steadily increased. In industry, various techniques and design of reactors are applied to maintain the % of PGSC high depending on the type of phosphate. Fig. 8 shows the % increase in filtration rate and crystal growth efficiency of crystalized phosphogypsum with and without additives. Increases in both filtration rate and crystals growth efficiency are achieved with surfactant and with additives comparing to the baseline.

Fig. 9 shows with increasing the d_{90} of crystalized PG, the filtration rate is increased. It is known that, d_{90} of the crystalized PG is increased with increasing the % of added phosphogypsum seed crystals and much increase with addition of the surfactant.

Table 10. Relation between d_{90} and both filtration rate and crystal growth rate of phosphogypsum produced from calcium phosphate with and without additives

Additive	d_{90}, µm	Filtration rate, ton P_2O_5/m^2.day	Crystal Growth Rate @ 35 min, µm/min	% Increase in	
				Filtration Rate	Crystal Growth Efficiency @ 35 min
Base line	4.038	2.6	0.115	-	-
5% PGSC	4.499	2.8	0.129	8	12.2
10% PGSC	5.247	3.4	0.155	31	34.8
15% PGSC	6.848	4.3	0.196	65	70.1
With Sorbitol surfactant	7.280	4.6	0.208	77	80.9

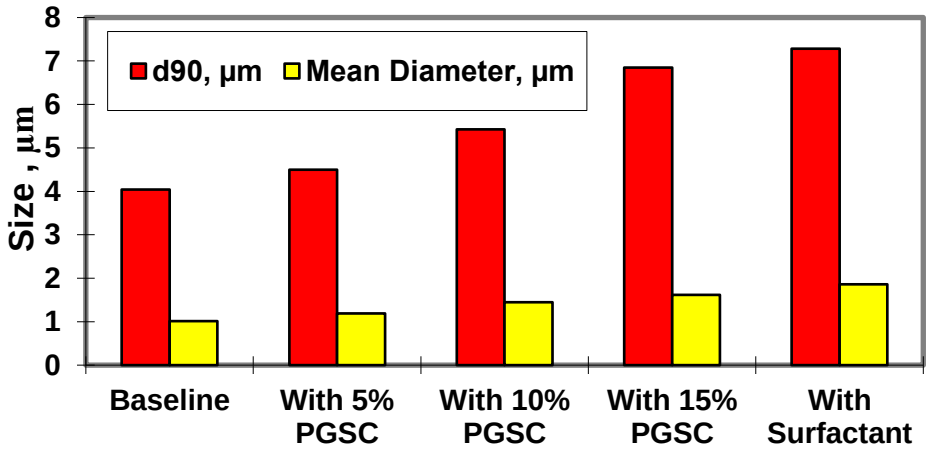

Fig. 7. Mean diameter and d_{90} of crystalized phosphogypsum with and without additives (d_{90} : diameter of crystals passing 90 vol. % , PGSC: phosphogypsum seed crystals)

3.3. Effect of additives on crystalized PG morphology

Fig. 10 shows the photomicrographs of calcium sulfate dihydrate crystals formed in the presence and the absence of 100 ppm SS, 5%, 10% and 15% PGSC. The formed crystals are larger with all the additives compared with the baseline (without additives). The aspect ratios (width to length ratios) of the obtained crystals were larger with the additives. This behavior may be due to increasing the regular crystal rates on the expense of increasing nucleation rates. Different mechanisms about inhibition and

growth of calcium salts are reported with calcium sulfate dihydrate as scales or powders (Nyvlt and Ulrich, 1995; Abdel-Aal et al., 2016), for calcium sulfate hemihydrate as scales (Tanquero et al., 2022) and for calcium oxalate monohydrate (Georgiev et al., 1995; El-Shall et al., 2004).

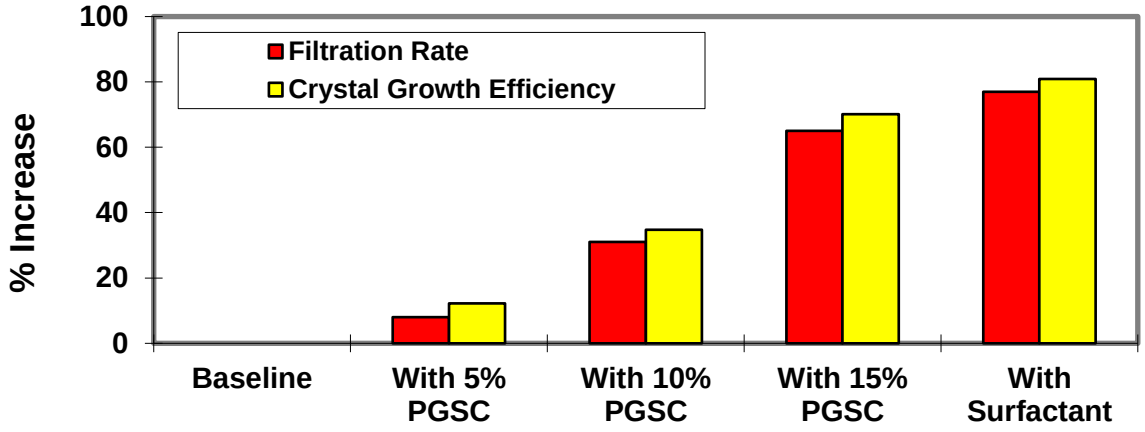

Fig. 8. % Increase in filtration rate and crystal growth efficiency of crystalized phosphogypsum with and without additives (PGSC: phosphogypsum seed crystals)

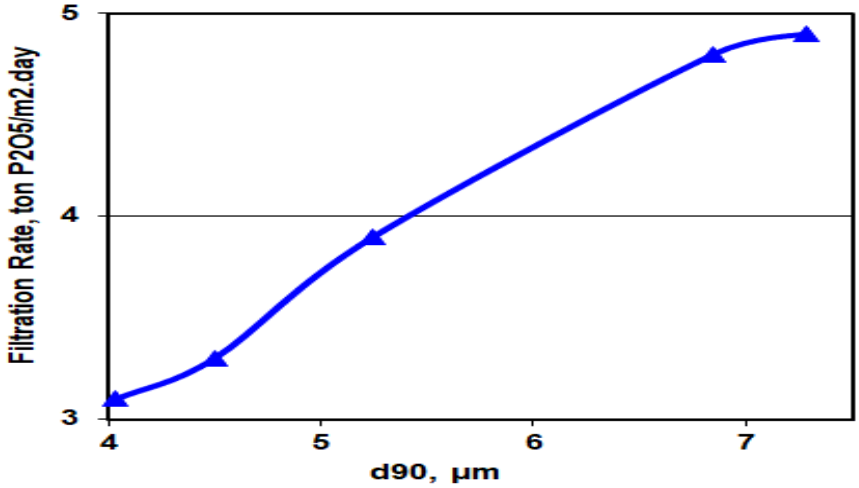

Fig. 9. Correlation between d_{90} of crystalized phosphogypsum and filtration rate (d_{90}: diameter of crystals passing 90 vol. %)

4. Conclusions

The effect of sorbitol surfactant (SS) on phosphogypsum crystallization is studied. The results reveal that, addition of 100 ppm Sorbitol surfactant helps for formation of larger crystals with high (d_{90}) size that 90% of the crystals are less than this size. The crystal growth rates are higher with sorbitol surfactant than without additive. The crystal growth rate and the growth efficiency are decreased with increasing the retention time at 100 ppm SS concentrations and 1.502 supersaturation ratio. Interestingly, the addition of 100 ppm SS gives high mean diameter, median, mode, d_{10}, and d_{90}. The same behavior was obtained with the other additives but to lower extents. The formed crystals are larger with addition of either 100 ppm SS, 5%, 10% or 15% phosphogypsum seed crystals compared to the baseline. With increasing the % of seed crystals from 5% to 15%, the sizes of the crystals are increased. Formation of high mean diameter and high d_{90} crystals are related to the increasing of the regular crystal growth rates compared to nucleation rates due to addition of either surfactant or phosphogypsum seed crystals.

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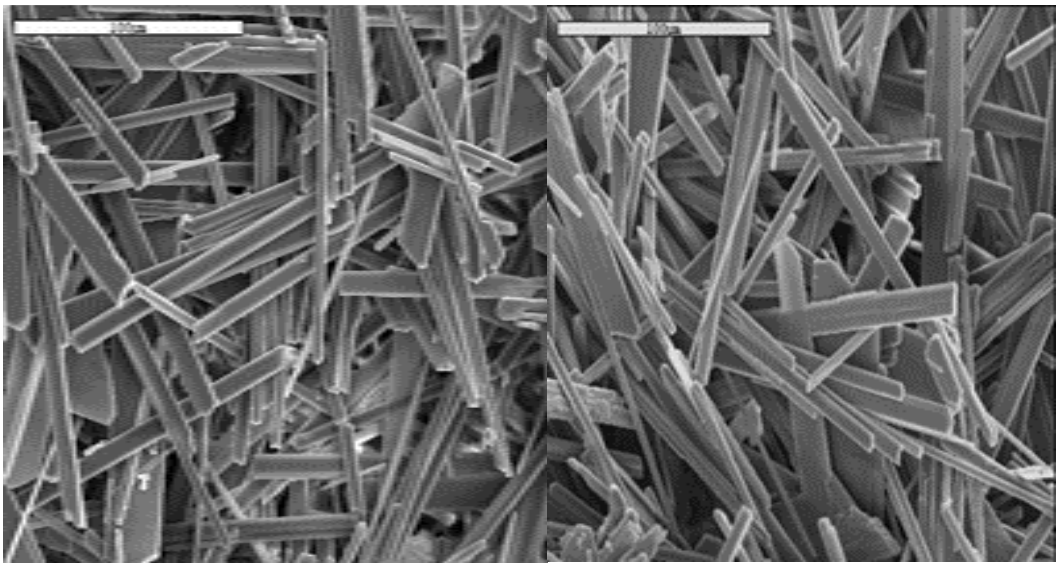
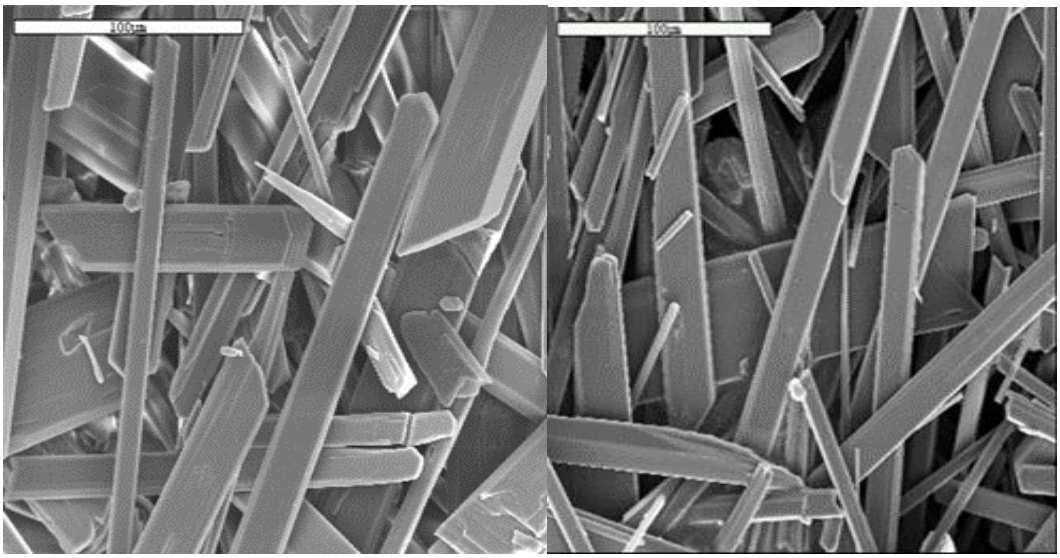
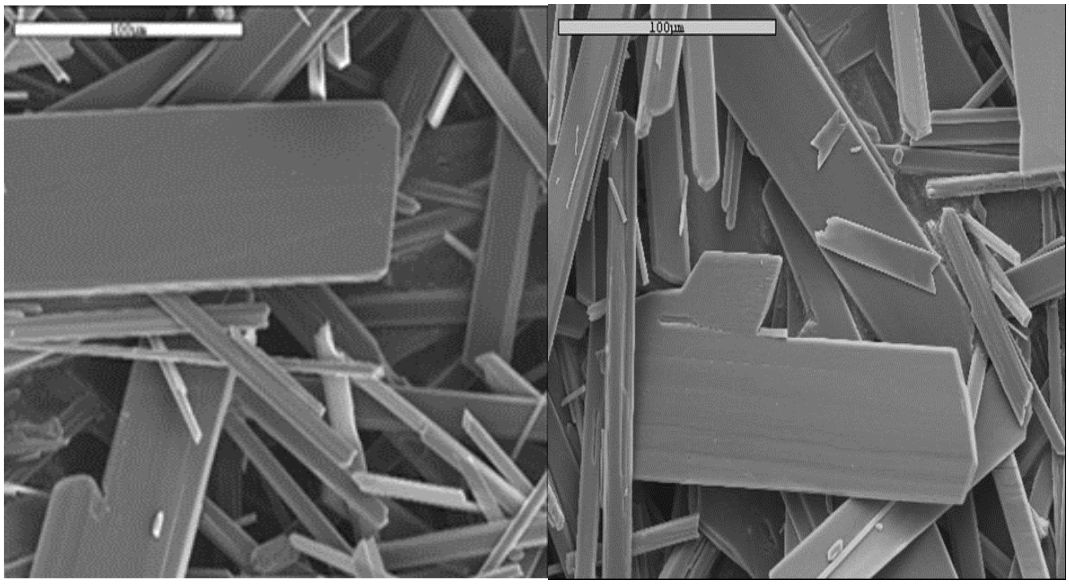


(A) Without additives (A) Without additives



(B) With 100 ppm sorbitol surfactant (C) With 5% PGSC



(D) With 10% PGSC (E) With 15% PGSC

Fig. 10. Photomicrographs of phosphogypsum crystals with and without additives

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