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Effect of Impurities in Phosphoric Acid on the Granulometery of the Produced DAP(Di-ammonium Phosphate) in Petrochemical Plants

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Abstract−The influence of impurities in phosphoric acid on the granulometery of the produced DAP was experimentally investigated in a petrochemical plant. It was found that DAP granulometery can be substantially improved as the total concentration of aluminum and iron oxides in the phosphoric acid is increased up to 2.2±0.1 wt%. A correlation was proposed for predicting the DAP granulometery in terms of total concentrations percent of (Al_2O_3+Fe_2O_3) in the phosphoric acid.

Key words: DAP, Granulometery, Aluminum Oxide, Iron Oxide, Phosphoric Acid

INTRODUCTION

Di-ammonium Phosphate (DAP) is one of the best chemical fertilizers used individually or in combination with other fertilizers or soil nutrients. It is usually produced through reaction of wet phosphoric acid with ammonia in a pipe or tank reactor followed by the granulation process [Becker, 1989]. When a pipe reactor is used the slurry moisture is lower as compared to the tank reactor. Therefore less water is flowing through the process which results in reducing the dimension and cost of required equipment [Didier Eng. GmbH, 1988]. Effect of impurities on the DAP granulation by using a pipe reactor followed by a drum granulator based on the TVA design (Fig. 1) is the subject of this study.

The reaction between ammonia and phosphoric acid in the reactor leads to MAP (mono ammonium phosphate) or DAP depending on the N/P ratio. The overall reactions can be written as:

$$H_3PO_4+NH_3 \rightarrow NH_4H_2PO_4 \quad (1)$$

$$NH_4H_2PO_4+NH_3 \rightarrow (NH_4)_2HPO_4 \quad (2)$$

When the ratio of N/P is greater than unity, the produced MAP in the first reaction is converted to DAP in the second one. Since both reactions are highly exothermic, DAP is commercially produced in two consecutive steps, which results in lowering the slurry viscosity and reducing the loss of ammonia. In the first step, phosphoric acid with 40 to 42 wt% of P_2O_5 is introduced through the reactor and after reacting with ammonia, the precipitated product with N/P of about 1.3-1.4 is carried to the granulator drum. The second step is then completed by injection of further ammonia into the drum keeping the N/P of the granulated product at about 1.8-2. Recycled seed granules are fed to the granulation drum. Produced slurry in the pipe reactor is sprayed onto the seed granules, and granule growth occurs. Granules leaving the granulator are first dried and then screened to separate out the product size.

Generally, 70 to 80 weight percent of the produced DAP leaving the granulator should be in the size range of 1-4 mm; otherwise the process variables, namely temperature, acid density and recycle ratio, should be changed properly [Didier Eng. GmbH, 1988]. Since controlling the granulation circuit at steady state is difficult, any change in these variables should be in the range of permitted design values.

It should be noted that the required phosphoric acid for DAP production is usually provided by acidulation of phosphate rock (wet process) in the phosphoric acid unit. Since the levels of impurities in different phosphate rocks are not the same, the produced phosphoric acid will also contain different amounts of these impurities. The concentrations of these species may have a strong effect on granulometery of the product. In some cases, too fine or too coarse DAP granules far from the optimum range of 1-4 mm are obtained [ZareNezhad, 2001].

Effects of temperature and moisture content on DAP granulation were previously investigated [Adetayo et al., 1993; Ennis et al., 1990]. Although the influence of impurities such as iron, aluminum and magnesium on the phosphoric acid viscosity and DAP composition have been evaluated [Becker, 1989; Handley, 1984], but the effects of impurities on the DAP granulometery are not presented in the literature. Therefore a series of experimental investigations is carried out to determine the influence of impurities in plant scale. The parameter Z(=1/C.V) is used to express the granulation quality of the produced DAP. The coefficient of variations (C.V) of granules (around the mean size) in a collected sample at the granulator outlet can be written as:

$$C.V = [\sum (L_i^* - L_m)^2 w_i]^{0.5} / L_m \quad (1)$$

where L_m is the weight mean size defined as:

$$L_m = \sum (L_i^* w_i) \quad (2)$$

where L_i^* represents the average diameter of the granules collected between the sieves i and i+1, in the size interval L_i to L_{i+1} and in weight fraction w_i defined as $(L_i+L_{i+1})/2$. As the granule sizes in an assembly become more uniform, the C.V gets smaller. In this study the parameter Z(=1/C.V) is more convenient to use, since a higher Z value implies more uniform granules and hence a better

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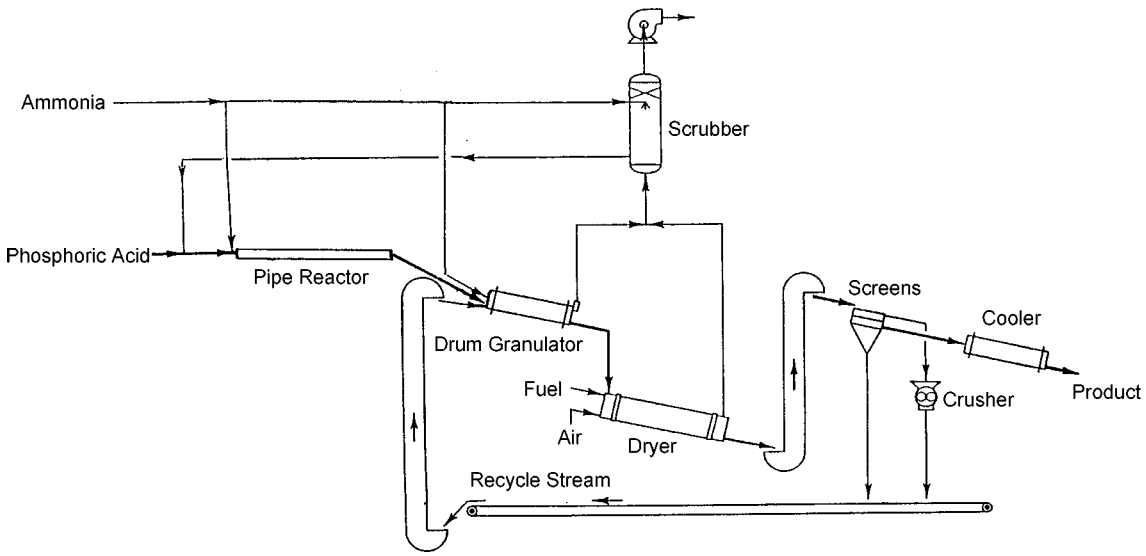

Fig. 1. Process flow diagram for production of granular DAP.

granulation quality.

PRELIMINARY STUDIES

Three set of experiments were initially carried out in a DAP plant at similar operating conditions [ZareNezhad, 2001]. The analysis of phosphoric acids, namely A, B and C, produced from digestion of three different phosphate rocks in sulfuric acid is given in Table 1. When acid A is used, the size range of produced DAP granules is mostly within 1-3 mm, whereas for type C acid, too coarse granules are produced which overloads the crushers resulting in too fine particles in the recycle stream. Regarding the granulometery of the product, the quality of the acid of type B is better than type C but not as good as type A. According to Table 1, as the phosphoric acid changes from type C to A, the C.V of the DAP granules reduces significantly from 159.3% to 24.6%. It is quite clear that the main difference between the three analyses is the weight percent of suspended solid, Al_2O_3 and Fe_2O_3 in the phosphoric acid solution. Therefore, a series of experiments is performed in real scale to find out the effect of these three species on the DAP granulometery.

Table 1. Analysis of three types of phosphoric acid produced by acidulation of different phosphate rocks and the corresponding C.V% of produced DAP granules

Item	Acid A (wt%)	Acid B (wt%)	Acid C (wt%)
P_2O_5	50.50	52.14	51.29
SO_4^{2-}	2.600	2.630	2.710
Susp. solid	0.881	0.473	0.320
Cl^-	0.015	0.013	0.012
Fe_2O_3	1.250	0.580	0.120
Al_2O_3	0.981	0.714	0.200
F^-	0.640	0.610	0.630
CaO	0.090	0.083	0.104
MgO	0.610	0.570	0.552
C.V.%	24.62	45.87	159.3

EXPERIMENTAL SECTION

All required chemicals were provided from Merck, Ltd. The purity of Al_2O_3 and Fe_2O_3 powders was about 99.5 and 99.7% with mean particle sizes of about 1 μm and 2.5 μm, respectively. A series of experiments were carried out in the DAP plant of Razi Petrochemical Complex of Iran at similar operating conditions. The level of impurities was the only changing variable. The pipe reactor was 2.5 m long with ID of 27 cm. The slurry at the reactor outlet was conducted to a drum granulator (ID=4 m, Length=8 m) with 4% slope and rotational speed of 6 RPM. Run R1 was done with low quality phosphoric acid (Acid C in Table 1). Other runs were performed by adding different amounts of Al_2O_3, Fe_2O_3 and Suspending solids (gypsum and inerts similar to the real case) to this acid (acid C) to observe any subsequent change in the DAP granulometery. The mixed acid was then pumped toward the reactor inlet.

At steady state condition, three 10 cm^3 samples were taken from the reactor exit and transferred quickly to the filtration equipment. The solid particles collected on the 0.2 μm filter paper were kept in an electrical oven at 50 °C for 24 hours. The obtained dried particles were then used for particle size analysis by a Coulter counter (Model Multisizer II) [Coulter Electronics Ltd., 1988]. The collected solution samples were analyzed for determination of N/P by pH titration using 0.5 N sulfuric acid and 0.5 N sodium hydroxide. The atomic spectrophotometer was used to determine the different chemical compounds in the solution samples [Jeffery et al., 1989]. Also 2 kg of produced DAP granules was collected at the granulator outlet and the corresponding C.V was determined by sieving analysis in each experiment. The run numbers and experimental conditions are summarized in Table 2.

RESULTS AND DISCUSSION

Chemical analysis of the solid and solution phases [Arthur, 1990; Jeffery, 1989] indicates that as the reaction of ammonia with phosphoric proceeds, Al_2O_3 and Fe_2O_3 participate in the reaction and produce aluminum and iron compounds such as $AlPO_4$. $2H_2O$, NH_4Al

Table 2. Ranges of species concentrations in different runs

Runs	Fe_2O_3, wt%	Al_2O_3 , wt%	Susp. Solid, wt%
R1-R6	0.12	0.2-1.2	0.32
R7-R12	0.37	0.2-1.2	0.32
R13-R18	0.62	0.2-1.2	0.32
R19-R24	0.87	0.2-1.2	0.32
R25-R30	1.12	0.2-1.2	0.32
R31-R36	1.37	0.2-1.2	0.32
R37-R42	1.12	0.2-1.2	0.62
R43-R48	1.12	0.2-1.2	0.92
R49-R54	1.12	0.2-1.2	1.22

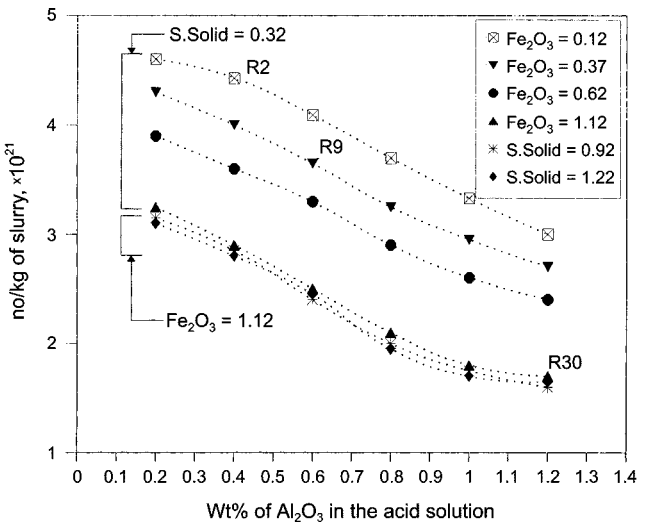

Fig. 2. Effect of impurities on the number of fine particles produced at the reactor outlet.

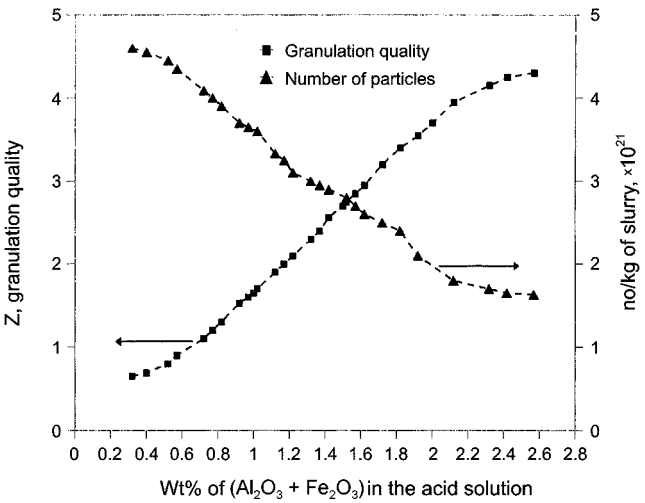

Fig. 3. Comparison of the effects of impurities on the number of fine particles at the reactor outlet and granulation quality of produced DAP.

$(HPO_4)_2$, $FePO_4.2H_2O$ and $NH_4Fe(HPO_4)_2$ in addition to the ammonium phosphate particles. These together with the suspending solids entering the reactor may have considerable effect on the nucleation rate of ammonium phosphates in the reactor.

The effect of acid impurities on the total particle concentrations of the slurry at the reactor outlet is shown in Figs. 2 and 3. In this figures the number of particles per kilogram of slurry is plotted against the weight percent of Al_2O_3 at different Fe_2O_3 and suspending solid concentrations. In Fig. 3, the resulting DAP granulation quality expressed as Z(=1/C.V) is plotted versus wt% of Al_2O_3+Fe_2O_3 in mixed phosphoric acid.

Three different runs, namely R2, R9 and R30, are shown in Fig. 2. It is clear that increasing the Al_2O_3 concentration from 0.4 to 1.2 wt% and Fe_2O_3 concentration from 0.12 to 1.12 wt% results in a 62 percent decrease in particle number concentration from 4.5×10^{21} (in R2) to 1.7×10^{21} particles/kg of slurry (in R30). It can be concluded that increasing the aluminum and iron oxides in the phosphoric acid solution decreases the rate of ammonium phosphates nucleation; thus the number of fine particles entering the granulator is reduced. This in turn may inhibit the rate of excessive agglomeration, and thus more uniform DAP granules with low C.V (high Z) are produced as shown in Fig. 3. Conversely, the generation of a large number of fine particles due to deficiency of Al_2O_3 and Fe_2O_3 in the reactor may speed up the adhesion and coalescence of the DAP granules in the granulator, and thus large amounts of weak big lumps of the product are obtained. When these lumps pass through the crushers a large amount of dust and fine particles in the recycle stream is produced, which leads to serious operational problems and reduces the production rate.

According to Fig. 3, increasing the Al_2O_3+Fe_2O_3 concentration from 0.4 to 2.3 wt% results in a 62% reduction in the number of generated particles at the reactor exit slurry and a 80% reduction in C.V (4-fold increase in Z) of produced DAP granules. As shown in Fig. 2 the effect of suspending solid entering the reactor on the product particle concentration at the reactor outlet and granulometery of the produced DAP is negligible. According to Fig. 3 there is always a direct correspondence between reduction of fine particles in the slurry at reactor outlet and increasing the DAP granulation quality (Z), as the concentration of Al_2O_3+Fe_2O_3 in the mixed phosphoric acid is increased. Overall, these results confirm the strong

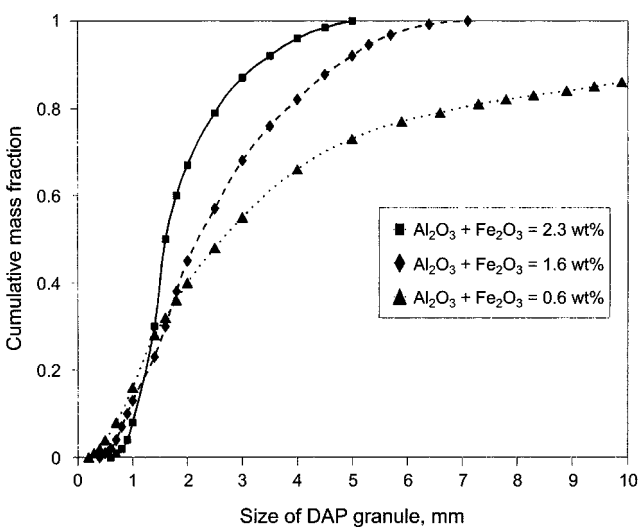

Fig. 4. Effects of concentrations of aluminum and iron oxides on the size distributions of granular DAP.

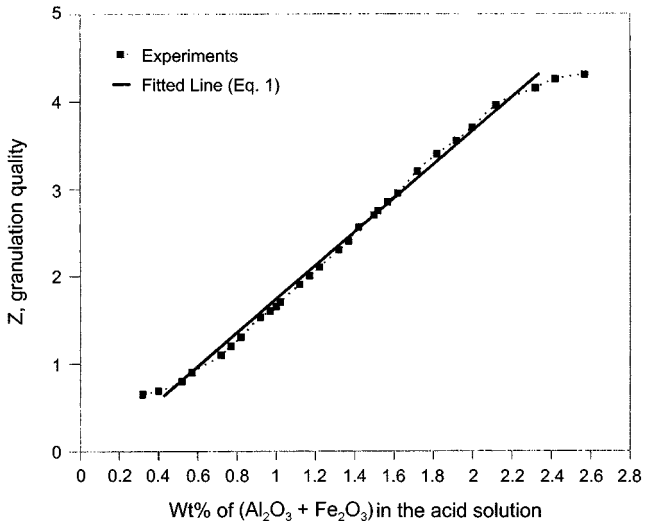

Fig. 5. Comparison of the measured DAP granulometery with Eq. (1) at different total concentrations of aluminum and iron oxides.

effects of Al_2O_3 and Fe_2O_3 concentrations on the ammonium phosphates nucleation rate in the reactor, which in turn influencse the granulometery of the produced DAP in the granulator.

Fig. 4 shows that by increasing the Al_2O_3+Fe_2O_3 concentration in the acid from 0.6 to 2.3 wt%, C.V of the produced DAP granules reduced from 112% to 25%, such that more uniform DAP granules are obtained. When the summation of aluminum and iron oxide concentrations in the phosphoric acid is about 2.3 wt%, about 80% of produced DAP granules are in the size range of 1-3 mm with C.V of about 25% which is quite desirable.

For the wide range of $0.4<Al_2O_3+Fe_2O_3<2.3$ wt%, the measured DAP granulation quality can be correlated as:

$$Z=(2\pm0.01)C-(0.3\pm0.02) \quad (3)$$

where C is the total weight percent of Al_2O_3+Fe_2O_3 in the mixed phosphoric acid entering the pipe reactor and Z is the granulation quality (=1/C.V) of the produced DAP measured at the granulator outlet.

Values of the parameters were determined by linear regression analysis of 34 data points. Eq. (3) as shown in Fig. 5 is well represented. The standard error in parameter estimates was determined at 95% confidence interval.

According to Figs. 3 and 5, when the concentration of Al_2O_3+Fe_2O_3 in the acid is out of the range of 0.4-2.3 wt%, there is no significant effect on the number of fine particles at the reactor outlet and granulometery of produced DAP. The results obtained in this study suggest that the reactive precipitation process in the reactor plays an important role in the subsequent DAP granulation process. Close examination of the results reveals that when the total concentration of Al_2O_3+Fe_2O_3 in the mixed phosphoric acid is gradually increased to 2.2±0.1 wt%, the amount of lumps at the granulator outlet and the DAP fine volume in the recycle stream decreased such that the C.V of the produced granules in the size range of 1-4 mm decreased to about 25%, which is quite desirable.

CONCLUSIONS

Based on experimental measurements, a correlation was found between the total concentrations of Al_2O_3+Fe_2O_3 in the phosphoric acid entering the pipe reactor and DAP granulometery as shown in Eq. (3) and Fig. 5. In order to enhance the granulation quality without operational difficulty, the total concentration of aluminum and ferric oxides in the phosphoric acid entering the reactor should be increased up to 2.2±0.1 wt%. This is an interesting result which can be used for improvement of the operational condition of DAP plants having a PFD similar to Fig. 1. Applying this to the DAP plant of Razi petrochemical complex in Iran resulted in an 80% decrease in C.V of the produced DAP granules and 65% increase in production rate.

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NOMENCLATURE

$Z=1/(C.V)$: granulation quality [-]
$C.V=\sigma/L_m$: coefficient of variation [-]
σ : variance [m]
i : Sieve number [-]
L_i^* : average size of granules between sieve i and i+1 [m]
L_m : mean size of DAP granules collected with n sieves [m]
n : number of sieves [-]
w_i : weight fraction of granules between sieves i and i+1 [-]
C : Al_2O_3+Fe_2O_3 in the mixed acid [kg(kg acid)$^{-1}\times100$]

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