International Journal of Materials Engineering 2012, 2(4): 32-37
DOI: 10.5923/j.ijme.20120204.01

Experimental Study of the Purification of an Industrial Fertilizer (Mono-Ammonium Phosphate) toLarger Scale Using an Experimental Design

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Abstract $NH_4H_2PO_4$, mono-ammonium phosphate (MAP) has become a leading phosphate fertilizer product worldwide. Ammonium phosphates are produced by reactions of ammonia and phosphoric acid resulting in the formation of the mono-basic salt. A batch crystallizer in a pilot setup was utilized to produce pure MAP crystals using a fractional experimental design 2^{5-2}. The supersaturation level not only influences the growth rate but the crystal shape as well.

Keywords Fertilizer (MAP), Crystallization to Larger Scale, Fractional Experimental Design 2^{5-2} , Supersaturation

1. Introduction

Ammonium phosphates are produced by reactions (neutralization) between ammonia and phosphoric acid resulting in the formation of mono-basic, di-basic or tri-basic salts. When the mole ratio of nitrogen from ammonia and phosphorus from phosphoric acid is 1.0, mono-ammonium phosphate (MAP—$NH_4H_2PO_4$) is formed, and when the mole ratio is 2.0, di-ammonium phosphate (DAP—$(NH_4)_2HPO_4$) is formed. The reaction is exothermic, so the MAP and DAP are produced at an elevated and relatively constant temperature of 110°C. The equations for the neutralization reaction between ammonia and phosphoric acid are as follows:

$$NH_3(g) + H_3PO_4(aq) \rightarrow NH_4H_2PO_4(s)$$
$$NH_3(g) + NH_4H_2PO_4(aq) \rightarrow (NH_4)_2HPO_4(s)$$
$$NH_3(g) + (NH_4)_2HPO_4(aq) \rightarrow (NH_4)_3PO_4(s)$$

The mono-ammonium phosphate (MAP) tends to produce crystals of needle form while the di-ammonium phosphate (DAP) results in more granular forms of crystals. Tri-ammonium phosphate (TAP—$(NH_4)_3PO_4$) is an unstable crystal and less soluble than MAP and DAP. MAP and DAP are used as a main source of phosphorus in fertilizers. Several important characteristics of MAP, DAP and TAP are identified in Table 1[1].

Previous laboratory scale results on purification of industrial MAP were reported earlier[2]. The good results obtained prompted us to continue this work on a larger scale. And to better understand the influence of thermodynamic parameters (temperature and time) on the purification of MAP, we adopted the technique of experimental design.

In this work, the purification of industrial MAP on a larger scale was conducted in a batch crystallization process to improve the product quality. The industrial specifications sought were mainly low heavy metal contents. During this process we determined the solubility of industrial MAP components in two types of solvent (water, water-alcohol) by a 2^{5-2}fractional experimental design. Experimental design is very important in chemometrics to minimize the number of experiments.

The fractional experimental design 2^{5-2} included the five following factors: 1 - Temperature, 2 - dissolution Time, 3 - stirring speed, 4 - type solvent and 5 - addition of charcoal.We present here the physicochemical characterization of MAP fertilizer upstream and downstream of the purification process, aiming at determining the performance of recrystallization. We also compare the recrystallized MAP to the commercial MAP (Fisher).

2. Experimental part

2.1. Crystallization of Industrial MAP

The experiments crystallization of MAP was performed in batch reactor (Fig.1) which is equipped with an electric stirrer. The suspensions were stirred by a propeller at different stirring speeds, ranging from 400 to 600 rpm. Temperature control in the crystallizer was achieved through recycling the water from a thermal basin. The uncertainty of

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temperature control was 0.05 K. In a typical run, a hot and filtered saturated aqueous solution of MAP with high purity was put into the crystallizer. The crystallizer was kept 10K higher than that of the saturated MAP solution in order to assure that no crystal existed in the solution prior to crystallization. After 1h, the temperature of the crystallizer was reduced to the saturation temperature of MAP solution. After a while, an amount of MAP crystal seeds was poured into the crystallizer, and the batch cooling crystallization experiment was started. The experimental conditions are depicted in Table 2. Supersaturation was obtained by slowly cooling.The solid product was dried at 330 K under vacuum.

In the present work, we have made 8 experiments according to a fractional experimental design 25-2, using the following matrix (Table 2). During this work we varied the 5 factors (1.Temperature, 2. Stirring time, 3. Speed stirring, 4. Type of solvent, 5. Stirring time with charcoal added) into two levels coded -1 (low level) and +1 (high level). Using statistical software JMP, we optimized two responses that are the % P2O5 and % N of the MAP and the influence of each factor on these two responses.

Figure 1. Pilot plant evaporation-crystallization

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2.2. Analytical and Testing Methods

P_2O_5 content in the solution is determined gravimetrically.

The ammonia to phosphoric acid molar ratio (MR) was obtained by titration with standard 0.5M NaOH and 0.5M HCl solutions. The amount of HCl and NaOH added was used to calculate the MR with MR = 2- (volume of NaOH/volume of HCl) according to the method described in Ref.[3].

1st time: $NH_4H_2PO_4 + NaOH \rightarrow NaNH_4HPO_4 + H_2O$

$(NH_4)_2HPO_4 + NaOH \rightarrow Na(NH_4)_2PO_4 + H_2O$

2nd time: $NaNH_4HPO_4 + HCl \rightarrow NH_4H_2PO_4 + NaCl$

$(NH_4)_2HPO_4 + HCl \rightarrow NH_4H_2PO_4 + NH_4Cl$

A pH Meter was employed to measure the pH values of slurries.

N content in the solutions was determined by the Kejdahl method.

2.3. Methodology of experimental design

Experimental design methodology is used to decide which experiments are needed to carry out to get information about certain chemical process or product. It is used to decide which factors have an influence on the properties of the chemical process or desirable product. Another question is to define the number of experiments that have to be carried out to obtain more knowledge about the system. It is obvious that optimization of chemical process is essential. Main methods of experimental design are factorial design including fractional factorial design. The selection of experiments has an influence on the quality of the system. It is applied to determine the conditions to obtain a product or a process with desirable characteristics. The characteristics of the product or process are optimized. The characteristics are also named responses. The factors are independent and the responses are dependent variables. So the experimental design is a set of carefully planned experiments. The main steps of experimental design are selection of initial factors and responses, selection of experimental domain (extreme values at which factors are studied). With experimental design the response is optimized. After screening design the unimportant factors are discarded and the type of experimental design is chosen. Usually two level factorial design is used for the determination of important factors (variables) and intervals. The optimal response is usually the highest or the lowest value of product or process characteristic. After determining which factors have minimal or no influence on the response (characteristics) the optimum settings of the important factor levels yielding the best characteristics of product or a process, have to be performed[4].

3. Results and Discussion

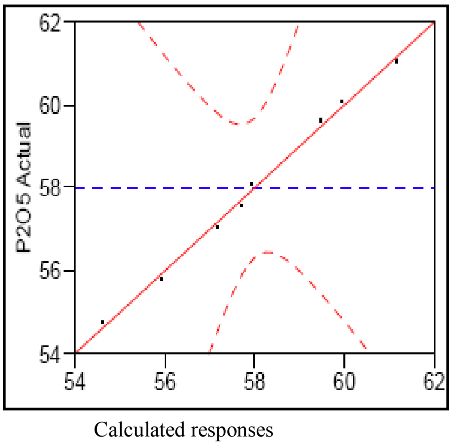
3.1. Optimization of Recrystallization of Fertilizer MAP Using Experimental Design

In the present work, we studied the purification of the industrial MAP at larger scale using a fractional experimental design 2^{5-2}. Using this matrix experiment (Table3) we conducted 8 experiences and we have subsequently determined the % P_2O_5 and % N of each sample (Table 3), which aims to select the best test that allowed us to give pure MAP.

These results show after purification, the % P_2O_5 and % N were increased knowing that the industrial MAP is characterized by a % P_2O_5 which varies between 52-54 % and a % N equal 11 %[3].

According to the statistical software JMP, we have interpreted our results (% P_2O_5 and % N) using the method of least squares[5].

The graphical comparison between the measured responses and calculated responses is given in Fig.2.



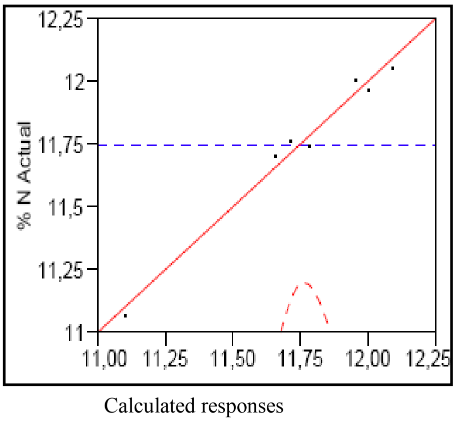


Figure 2. Graph comparing the measured responses and calculated responses

From these results we note that the calculated responses and measured responses are on the same bisector which shows that the model fully explains the measured responses, the numerator and denominator is equal to the coefficient of determination R^2 is equal to 0.99 for % P_2O_5 and equal 0.98 for % N.

With JMP software, were determined the isoreponses curves (Fig.3), which determine the effect of these factors that influence the % P_2O_5 and % N.

Table 1. Properties of ammonium phosphates salts (MAP, DAP and TAP)

Properties	$NH_4H_2PO_4$ (mono-ammonium phosphate)	$(NH_4)_2HPO_4$ (d-iammonium phosphate)	$(NH_4)_3PO_4$ (Tri-ammonium phosphate)
Molar mass (g/mol)	115	132	149
Specific gravity at 20 °C	1.803	1.619	N/A
Heat of formation (cal)	29.000	48.500	58.400
Solubility at 25 °C (g/100g water)	40	69.5	17.7
Ammonia vapor pressure	0.00 and 0.05	5.00 and 30.0	643 and 1177
at 100 °C and 125 °C (mmHg) pH of 0.1M solution	4.4	8.0	9.4
Crystal form	Tetragonal	Monoclinic	Orthorhombic

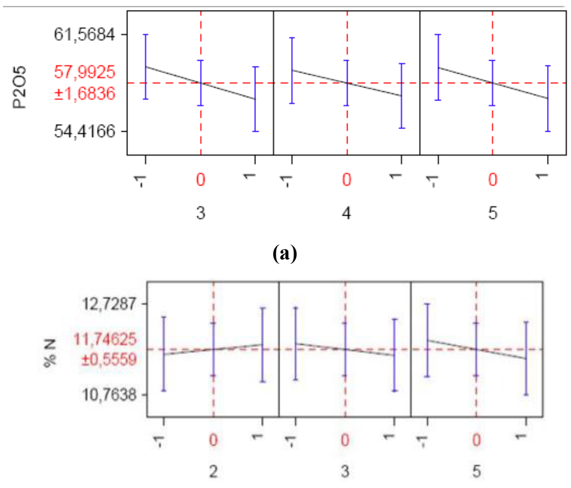
Table 2. Desing matrix in the screening design (2^{5-2})

N Experiences	1	2	3	4	5
1 - - - - +	-1	-1	-1	-1	+1
2 + - - + -	+1	-1	+1	-1	-1
3 - + - ++	-1	+1	+1	-1	+1
4 + + - - -	+1	+1	-1	-1	-1
5 - - + + -	-1	-1	-1	+1	+1
6 + - + - +	+1	-1	-1	+1	+1
7 - + + - -	-1	+1	-1	+1	-1
8 + + + + +	+1	+1	+1	+1	+1

Table 3. Desing matrix and response values in the screening design (2^{5-2})

N Experiences	1	2	3	4	5	% P2O5	% N
1 - - - - +	333K	2h	400rpm	Water	30min	61.04	12.00
2 + - - + -	353K	2h	400rpm	Water-alcochol	15min	59.61	11.96
3 - + - ++	333K	4h	400rpm	Water-alcochol	30min	60.08	12.05
4 + + - - -	353K	4h	400rpm	Water	30min	55.79	11.76
5 - - + + -	333K	2h	600rpm	Water-alcochol	15min	58.06	11.70
6 + - + - +	353K	2h	600rpm	Water	30min	57.04	11.06
7 - + + - -	333K	4h	600rpm	Water	15min	57.57	11.74
8 + + + + +	353K	4h	600rpm	Water-alcochol	30min	54.75	11.70

(-): low level, (+): high level



(a)

(b)

Figure 3. Isoreponses curves of% P_2O_5 (a) and % N (b) based on factors

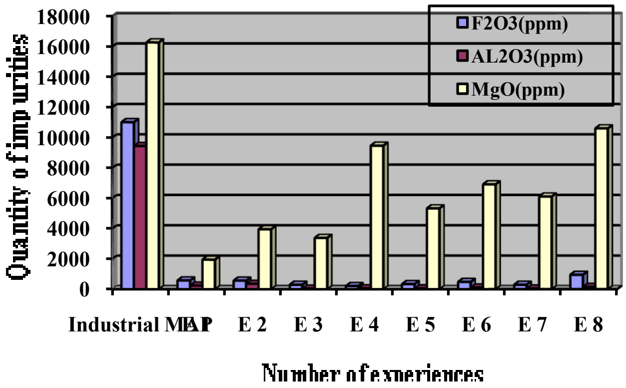


Figure 4. Variation of impurities in the various compoundsof MAP recrystallized

These curves show that the solubility of P_2O_5 in water (Factor 4) is larger than in water-alcohol mixture. We also note that the temperature factor (1) does not affect the solubility of P_2O_5 and N during recrystallization. To the stirring speed (factor 3), we note that the solubility of N and P_2O_5 increases when using a stirring speed level (-1) that is to say 400 rpm. The stirring time (Factor 2) does not affect the solubility of P_2O_5 and a slow affect for solubility of N. The % P_2O_5 and % N increase when the stirring time with the charcoal (Factor 5) equals 15 min.

The change of major impurities (Fig.4) shows that the best test to eliminate the maximum impurity which to obtain the pure MAP is trial number one.

3.2. Physicochemical Characterization of MAP Upstream and Downstream of the Purification

The principal chemical compositions of the MAP upstream and downstream from the recrystallization in condition of number one experience, are presented in Table 4. After purification, the % P_2O_5 and % N were increased while keeping the molar ratio (MR) ranging between 0.9-1.10. Also, after purification, the percentage of H_2O and value of pH are not changed.

Table 4. Chemical compositions of the MAP upstream and downstream from the recrystallization

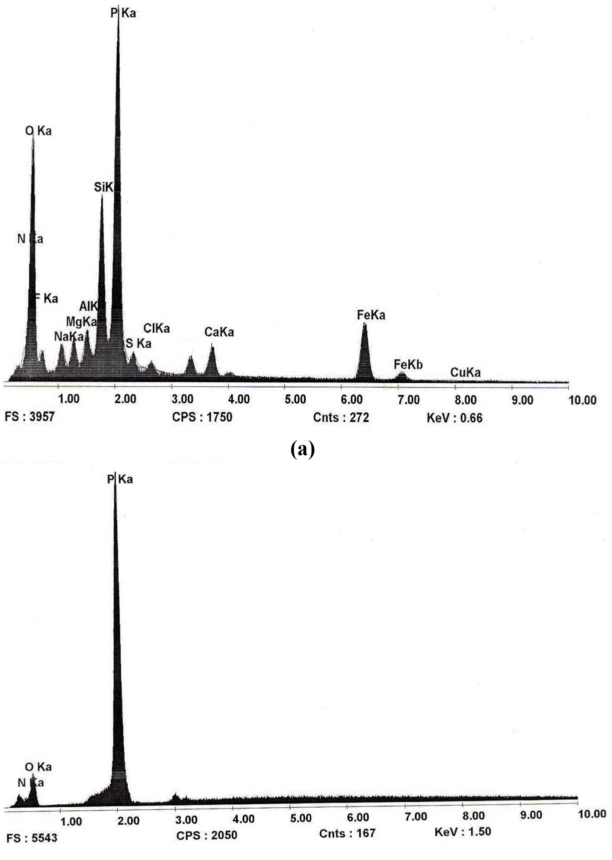
Samples	% (Wt)P_2O_5	%(Wt) N	% H_2O	N/P	pH
Industrial MAP	53.17	10.77	1.68	1.03	4.80
MAP recrystallized	61.04	12.00	1.68	1.06	4.80

The MAP contains toxic elements such as Cd, Zn ect., which are toxic for plants and have the potential for adverse effects on human health due to the transfer of metals from soils to food corps. Thus, it is important to eliminate or reduce these toxic elements in MAP. The analysis of the MAP by ICP spectroscopy after purification is given in Table 5, and shows that the quantity of impurity decreases. The results are comparable to those of the pure commercial MAP (Fisher) this justifies the performance of the crystallization.

Table 5. .Determination of the impurity present in MAP upstream and downstream from the recrystallization

Sample	Fe	Al	Mg	Cr	Zn	Cd	Mn	V (ppm)
Plant MAP	7705	5000	9815	240	275	29	65	65
Plant MAP Recrystallize	401	125	774	32	23	2	4	3

The analysis by scanning electron microscope (SEM) of the industrial MAP downstream recrystallization also showed that several impurities such as (Fe, Al, Mg, Cl, Si, Na, ect…) were eliminated (Fig.5).



(a)

(b)

Figure 5. Analysis by scanning electron microscope (SEM) of the industrial MAP upstream (a) and downstream(b) recrystallization

The curve solubility of recrystallized MAP, that was determined following a standard procedure described by Mullin[6], is show in (Fig.6). The solubility of a solute is most conveniently stated as the parts by weight per part (or 100 parts) by weight of solvent.

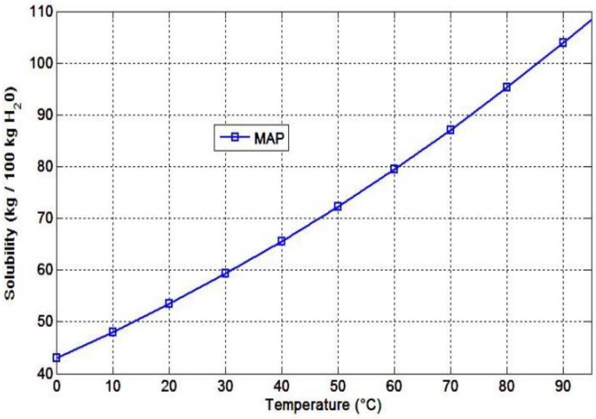


Figure 6. Curve solubility of MAP

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Figure 7. Morphology of MAP in α and β –stage

3.3. Crystallization Kinetics

The supersaturation level not only influences the growth rate but the crystal shape as well. The course of the crystallization (MAP) by slow cooling of the flowing solution can be divided into four stages named α, β, γ and δ stage. At the α-stage, the growth rate is the smallest and independent of flow velocity. The crystal habit is not affected by the flow velocity and the flow direction. The β-stage is characterized by the development of needle- like crystals with curved surfaces. At the γ –stage, prismatic crystals with tapered flat surfaces and twinned crystals appear transiently. The δ –stage is characterized by a large growth rate, pronounced spontaneous nucleation and the development of equidimensional crystal form. The effects of flow velocity and flow direction on the growth rate and the crystal habit become more prominent, as the cooling from the β to the δ- stage[7]. The morphology of crystals obtained after slow cooling was controlled by scanning electron microscope (SEM) and we concluded that in the first crystallization, the growth rate is small and the supersaturation is law .Various habits such as prismatic, tabular and blocky forms appear on the growing crystals (Fig.7). In the second crystallization which includes γ to the δ stage, the degree of supersaturation and the growth rate increases. The crystals are obtained in conical shapes (Fig.8).

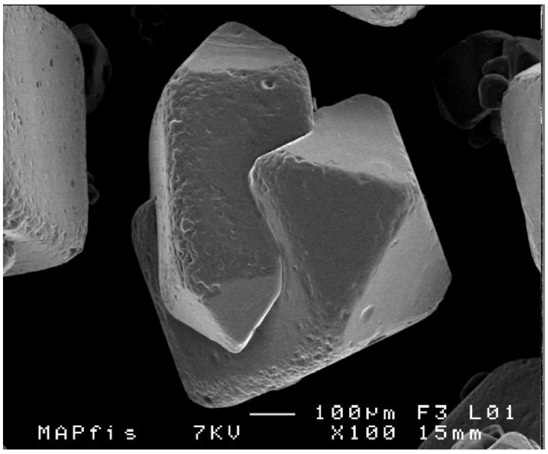

Figure 8. Morphology of MAP in γ and δ-stage

4. Conclusions

After purification, the % P_2O_5 and % N were increased while keeping the molar ratio (MR) range between 0.9 – 1.10 and the products obtained contain 1.5- 2% H_2O and pH of 4-5.

In our case, the use of experimental design help as to determinate the optimal conditions (1.Temperature, 2. Stirring time, 3. Speed stirring, 4. Type of solvent, 5. Stirring time with charcoal added) of recrystallization.

The analysis by ICP and scanning electron microscope (SEM) shows that the major toxic impurities are eliminated after recrystallization especially.

The course of crystallization by cooling of flowing solution of MAP can be divided into four stages. These stages are characterized by the growth rate and the crystal habit which change successively on cooling depending on supersaturation.

REFERENCENCES

[1] W.H. Ross, A.R.Merz, K.D. Jacob, Preparation and properties of the ammonium phosphates, Ind.Eng.Chem.21 (1929) 286-289.

[2] M.Gargouri, C.Chtara, P.Charock, A.Nzihou, H.Elfeki. Synthesis and Physicochemical Characterization of Pure Monoammonium Phosphate (MAP) from industrial Fertilizer. Journal chemistry and Chemical Engineering, ISSN1934-7375, 49, 2010.

[3] Benhe Zhong, Junli, Yun Xiang Zhang and BinLiang « principle and technology of ammonium phosphate production

from middle –quality phosphate ore by a slurry concentration process ».Ind.Eng.Chem.Res.38, 4504 - 4506, 1999.

[4] Massart DL, Vabdeginste BGM, Buydens LMC, De Jong S.Lewi JP, Smeyers-Verbeke J. Handbook of chemometrics and qualimetrics: part A. Amsterdam: Elsevier; 1997

[5] GOUPY Jacques (2001), introduction aux plans d'expériences, Dunod, Paris, 2ème édition.

[6] Mullin, J. (2001). Crystallization. Oxford, GB : Butterworth-Heinemann.

[7] Hiroshi Takubo and Shoichi Kume, Relationtion Ships between supersaturation, solution velocity, crystal Habit and growth rate in crystallization of NH4H2PO4, Journal of crystal growth 67 (1984) 217-226, North-Holland, Amesterdam.