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SUPERPHOSPHATE FERTILIZER PLANT OPTIMIZATION[1] [2]

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SUMMARY

PT Petrokimia Gresik (Persero) is a state owned company located in Gresik, East Java, Indonesia. It produces various kinds of fertilizer such as urea, ammonium sulphate, TSP/SP-36 and NPK; and basic chemicals such as ammonia, sulphuric acid, phosphoric acid, aluminium fluoride, cement retarder, oxygen, purified gypsum, liquid CO_2 and dry ice.

The existing TSP plant has been modified to produce double superphosphate (SP-36) since 1995. The reasons for this modification are:

1. Satisfy Indonesian farmers agronomic needs
2. Meet competitive prices
3. Product diversification

The basic principle of this modification is mixing phosphoric acid with sulphuric acid in a system. The mixing will generate heat and the mixed acid at high temperature is then reacted with phosphate rock in a cone mixer. This new process produces superphosphate fertilizers with 36% P_2O_5.

RESUME

Petrokimia Gresik (Persero) est une société nationalisée située à Gresik, East Java, Indonésie. Elle produit différents types d'engrais comme l'urée, le sulfate d'ammonium, TSP/SP-36 et NPK et des produits chimiques de base comme l'ammoniac, l'acide sulfurique, l'acide phosphorique et le fluorure d'aluminium, des retardateurs de prise de ciment, de l'oxygène, du gypse purifié, CO_2 liquide et glace sèche.

L'unité de TSP existante a été modifiée pour produire du superphosphate double (SP-36) depuis 1995. Les raisons de cette modification sont :

1. *Satisfaire les besoins des agriculteurs indonésiens en agronomie*
2. *Atteindre des prix compétitifs*
3. *Diversifier les produits*

Le principe fondamental de cette modification est le mélange d'acide phosphorique avec de l'acide sulfurique dans le système. Le mélange génère de la chaleur et le mélange d'acides à haute température réagit ensuite avec le phosphate dans un malaxeur conique. Ce nouveau procédé donne un superphosphate à 36 % P_2O_5.

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INTRODUCTION

PT Petrokimia Gresik (Persero) has two units of phosphate fertilizer plant: Phosphate Fertilizer Plant I (PF I Plant) and Phosphate Fertilizer Plant II (PF II Plant). Both units use the Tennessee Valley Authority Process, USA and were designed by Barnard & Burke Co., USA with Spie Batignolles, France as contractor.

PFI Plant was designed to produce TSP, DAP and NPK and has been operating since 1979. PF II Plant was designed to produce only TSP and has been operating since 1983.

In order to develop the process so as to make phosphate fertilizer conform to the quality and quantity demanded by the market, PT. Petrokimia Gresik (Persero) has modified and optimized the existing Plant as follows:

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[1] *Optimisation d'une unité de superphosphate*
[2] *The paper will not be presented by the authors*

1. In 1987:
   Optimization of the plant operation by reducing curing time. This process, Run Of Pile (ROP) from the cone mixer was then continuously fed to granulation unit without curing in the ROP storage. The results of the optimization were good with the production capacity increased by 20% of TSP SII fertilizer.

2. In 1990:
   Process modification to produce TSP SII plus Zn fertilizer.

3. In 1992:
   Process modification to produce TSP SNI fertilizer.

4. In 1992:
   Process modification to produce TSP SNI plus Zn fertilizer.

5. In 1995:
   Process modification to produce SP-36 fertilizer.

OPTIMIZATION BACKGROUND

To support the agriculture sector development, the Indonesian government had set aside funds for its annual fertilizer subsidy. From year to year, the fertilizer consumption had been increasing, so together with the rate of national development and limited development funds, the government's policy was to eliminate subsidy gradually.

The elimination of the government subsidy increased the fertilizer price and finally would be a heavier burden to farmers and consumers. Therefore, efficiency on fertilizer usage should be carried out while agriculture productivity be maintained.

Efficiency on fertilizer usage, especially for phosphate fertilizer, is implemented by manufacturing new phosphate fertilizer as substitute for TSP but with a lower price and without reducing agriculture productivity, especially for rice production. This program should be implemented by utilizing the existing plant. To achieve the goal, the P_2O_5 content in the new phosphate fertilizer shall be made lower than TSP. The reduction of P_2O_5 content is acceptable by government and farmers because the phosphate content is high due to TSP usage intensification program previously.

Furthermore, research and experiment to manufacture phosphate fertilizer with 36% P_2O_5 content were carried out in laboratories and in the TSP Plant. The product was evaluated for effectiveness and was field tested simultaneously by interrelated government agencies.

The results of the research and field demonstrations of SP-36 fertilizer on rice, palawija (crops planted as second crop in dry season or dry land such as peanut, soybean, etc.), horticulture and industrial plant were good. SP-36 fertilizer is not different from TSP fertilizer. In fact, 56% of the demonstration locations using SP-36 on rice showed greater efficacy compared with TSP fertilizer. The sulphur content in SP-36 is higher than TSP, 0.7% in TSP vs. 5% in SP-36, so SP-36 is better than TSP for sulphur depressed area.

The optimization reduced the production cost by economizing on raw material. And based on crop yield analysis, SP-36 usage raised the income by 0.78% to 1.41% in rainy season and 0.2% to 1.57% in dry season in 1994. One of the causes of income increase was the price difference between TSP and SP-36: SP-36 was 12.5% cheaper than TSP.

SP-36 fertilizer produced by PT Petrokimia Gresik has the following technical specification:

P_2O_5 total	=	36	% (dry basis)
P_2O_5 available	=	34	% (dry basis)
P_2O_5 water soluble	=	30	% (dry basis)
Total S	=	5	% (dry basis)
H_2O content	=	5	%
Free acid as H_3PO_4	=	6	% (dry basis)

Based on the above research and field demonstrations, the existing TSP Plant was modified to manufacture SP-36 fertilizer.

CHEMICAL REACTION

The basic principle in the manufacture of superphosphate fertilizer (SP-36) is the conversion of water insoluble phosphate rock (tricalcium phosphate) into water soluble monocalcium phosphate by acidulation with phosphoric and sulphuric acid:

1. $Ca_3(PO_4)_2 + 4\ H_3PO_4 + 3\ H_2O \rightarrow 3\ CaH_4(PO_4)_2.H_2O$
2. $Ca_3(PO_4)_2 + 2\ H_2SO_4 + H_2O \rightarrow CaH_4(PO_4)_2.H_2O + 2\ CaSO_4$

The reaction between acid (phosphoric acid and sulphuric acid) and phosphate rock can also produce dicalcium phosphate:

1. $Ca_3(PO_4)_2 + H_3PO_4 + 6\ H_2O \rightarrow 3\ CaHPO_4 . 2\ H_2O$
2. $Ca_3(PO_4)_2 + H_2SO_4 + 4\ H_2O \rightarrow 2\ CaHPO_4 . 2\ H_2O + CaSO_4$

Dicalcium phosphate and several other secondary products of side reaction are insoluble in water but are soluble in a neutral ammonium citrate.

Side reaction arises from the presence of impurities in the phosphate rock and phosphoric acid:

1. $CaCO_3 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CO_2 + H_2O$
2. $2\ CaF_2 + 4\ H_3PO_4 + SiO_2 \rightarrow 2\ CaH_4(PO4)2 . H2O + SiF_4$
3. $Al_2O_3 + 2\ H_3PO_4 \rightarrow 2\ AlPO_4 . H_2O + H_2O$
4. $Fe_2O_3 + 2\ H_3PO_4 \rightarrow 2\ FePO_4 . H_2O + H_2O$
5. $3\ Na_2O + 4\ H_3PO_4 \rightarrow 2\ Na_3PO_4 + 6\ H_2O$
6. $3\ K_2O + 4\ H_3PO_4 \rightarrow 2\ K_3(PO_4)_2 + 6\ H_2O$
7. $3\ MgO + 2\ H_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3\ H_2O$
8. $CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 . 2\ H_2O + CO_2$
9. $CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 . 2\ H_2O + 2\ HF$
10. $Al_2O_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2O$
11. $Fe_2O_3 + 3\ H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3\ H_2O$
12. $Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$
13. $3\ K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O$
14. $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$

Calcium sulphate is formed by the reaction of sulphuric acid and $CaCO_3$ or CaF_2 in the phosphate rock.

Iron and aluminium oxides in the rock may react with acid to form hydrated phosphate compounds, such as ferric phosphate monohydrate and may react with sulphuric acid to form hydrated sulphate compounds such as ferric sulphate trihydrate.

The phosphates formed are citrate soluble and contribute to the available phosphate content of the product.

Calcium fluoride and silica from the rock react with phosphoric acid yielding silicon tetrafluoride and monocalcium phosphate and calcium fluoride also react with the sulphuric acid to form calcium sulphate and HF gas.

The initial reactions occur very quickly in the cone mixer with residence time of 1 to 2 seconds. Furthermore, continuous reactions occur on setting belt conveyor, which are followed by changes of physical properties (slurry, paste and solid).

BASIC PRINCIPLE OF MODIFICATION

The rate of raw material consumption in phosphate fertilizer manufacturing is determined by two approach methods: total attack acidulation and partial attack acidulation, and is supported by experiments in the laboratories.

Total attack acidulation is calculated on stoichiometry of acid consumption to convert completely all the compounds in the phosphate rock. But the partial attack acidulation is not. The acid consumption is dependent on the grade of phosphate fertilizer to be produced.

The result of the above methods is then used to determine the ratio of P_2O_5 content in acid and P_2O_5 in rock. This ratio is called acidulation ratio.

Based on the theoretical calculation and experiment in laboratories, in order to produce SP-36 with 36% total P_2O_5 and 30% water soluble P_2O_5, it is necessary to phosphoric acid (54% P_2O_5) and sulphuric acid (98.5% H_2SO_4) with a ratio of 65% and 35%. This will produce a mixed acid with 35.1% P_2O_5 and 34.5% H_2SO_4.

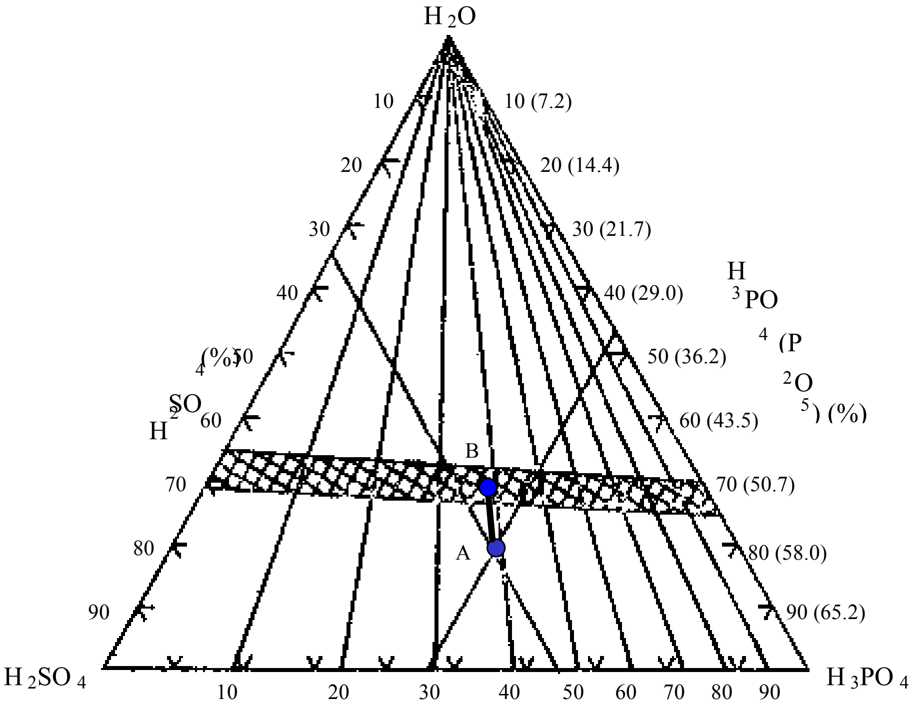
Acid mixing occurs in an additional facility in TSP Plant. During the mixing process (assumed: there is no chemical reaction) heat will be generated. Based on theoretical calculation and experiment in laboratories, the mixing of both acids will produce mixed acid at 105°C and is very corrosive.

To reduce the threat of corrosion, the mixing unit had a cooling system that brings down the mixed acid temperature to 50-60°C. The mixed acid from the cooling system is then recycled to mixing tank with the operation temperature in the mixing tank (inlet cooler) at 80-85°C. The mixing process is shown on Figure 1 Process Flow Sheet.

In anticipation of corrosion caused by mixed acid, PT. Petrokimia Gresik has done research to select the proper materials of construction. From research, the materials of construction which are corrosion resistance is Hastelloy pipe in up-stream of cooling system, and in the down-stream the cooling system uses stainless steel or plastic pipe; mixing tank uses carbon with rubber lining and tube side of cooler uses carbon/graphite. The other material for cooler is stainless steel completed with a cathodic protection.

The flowrate of phosphoric acid and sulphuric acid is adjusted and controlled by the flow ratio control. This ratio is not stable because of fluctuation in P_2O_5 content of the phosphoric acid. To maintain the composition of the mixed acid, on-line P_2O_5 analyzer was installed to measure P_2O_5 content in the phosphoric acid. The output from this device is then used for calculating sulphuric acid flowrate. And finally the sulphuric acid from the calculation is used as a set point of sulphuric acid flow controller.

Differences of process condition in TSP and SP-36 manufacturing are fluidity and rate of reaction. The first, fluidity is influenced by water content in reactant (mixed acid), so to achieve a good reaction, the water content shall be observed. In an other word, the water content will influence the physical properties of produced Run Of Pile (ROP). With the ratio of 65% phosphoric acid and 35% sulphuric acid, dry ROP will be formed, so it must be injected with water at about 15-20% of mixed acid flowrate. The second, sulphuric acid is a very reactive, so it will react with phosphate rock quickly to form gypsum. The gypsum is a compound that harden easily (according the reaction equation no. 2). The influence of the addition of sulphuric acid is shown on the following triangle diagram:



Shaded area is acid composition, which gives satisfactory reaction between acid and phosphate rock. The upper part of the shaded area is wet zone (high water content), while the lower point is dry zone (low water content). The SP-36 process has a composition of 35.1% P_2O_5 and 34.5% H_2SO_4, and if this is drawn on the triangle diagram, it will be found at point A (dry zone). To reach the shaded area, water must be injected, so point A will move to point B.

THE PROBLEMS

Mixing Unit

High temperature of mixed acid causes formation of SiF_4 and HF gas. They are formed from reaction between sulphuric acid or phosphoric acid with impurities in the phosphoric acid such as CaF_2, $CaCO_3$ and SiO_2. To eliminate these gases, the mixing unit is completed with the scrubbing system, which uses sea water scrubbing media.

The other problem in this unit is scaling in the cooler and pipe caused by the solid content (sludge) within the phosphoric acid. To overcome this problem, periodic cleaning is needed.

Reaction Unit

There is much gas produced from the side reaction during SP-36 fertilizer manufacturing. Based on laboratory experiments production, it is 7.03 times more than the gas produced during TSP fertilizer manufacturing. A large part of this gas occurs at outlet of the cone mixer and upon the long setting of the belt conveyor. But in TSP fertilizer manufacturing, a large part of gas occurs in curing storage. To overcome this problem, PT Petrokimia Gresik has redesigned and optimized the existing scrubbing system and will install a new scrubbing system in the future.

Due to the properties of chemicals that can easily become hard, the cone mixer often plugs caused by caking of ROP. It needs control and adjustment of the mixed acid and phosphate rock ratio and the increase of anti caking injection.

Other Units

In other units such as granulation unit, drying unit, screening unit, etc. serious problems are not found. They only need periodic cleaning as preventive action.

CONCLUSION

Elimination of government subsidy increased the fertilizer price, so efficiency on fertilizer usage must be improved. The result of research, demonstration trials of SP-36 fertilizer showed that it is not different from TSP fertilizer. To economize phosphate fertilizer usage, SP-36 fertilizer can be used as a substitute of TSP fertilizer.

The chemical reactions during SP-36 fertilizer manufacturing are quicker than the ones in TSP fertilizer manufacturing.

During SP-36 fertilizer manufacturing, water should be injected at about 15-20% of the mixed acid flow rate in order to maintain fluidity in the reaction.

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