PARAMETRIC STUDIES OF SSP PRODUCTION AND MODELING OF SSP REACTION KINETICS

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Abstract

Considering the present scenario of international price hike of rock phosphate and availability of raw materials it is more evident to run the plant in more economic manner for sustainability of the unit. Single Super Phosphate(SSP) is one of the main fertilizer used by farmers. As the price of high grade rock phosphates is very high, it is needed to run the unit with low grade rock phosphates. The conversion of rock phosphate consists two steps. The 2nd reaction is basically a slow reaction because the free H_3PO_4 has to diffuse inside the solid mass to react with unreacted P_2O_5 in the rock and the unreacted DCP to produce MCP. The rate constant appears to increase with increased acid rock ratio upto 0.64 because a higher acid rock ratio means higher H_3PO_4 concentration and hence diffusion rate will be higher. Therefore, rate constant is correlated to acid rock ratio. From the experimental data it is found that 0.64 acid rock ratio gives highest yield of MCP. Rate of reaction during first 6 days appear to be much higher than during rest of the days. These may be due to the reason that the actual reaction is more complex involving in several steps before achieving the final product.

Key Words: *SSP, Acid Rock Ratio, Mixer-Cum-Reactor, Kinetics, and MCP*

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1. INTRODUCTION

Superphosphate, $Ca(H_2PO_4)_2$, also referred as single super phosphate (SSP), is the first chemically man-made commercial chemical fertilizer [1]. It contains P_2O_5 which is the primary nutrient and sulfur is the secondary nutrient in the form of $CaSO_4$. SSP is produced by reacting rock phosphate with sulfuric acid. Simultaneously, some DCP and Phosphoric acid are also produced in the reactor. Beyond the reactor sufficient curing this is allowed for reaction of DCP and unreacted rock with H_3PO_4 to increase P_2O_5 % in the final fertilizer product in the form of monocalcium phosphate (SSP).

Researches have tried different reactor design for maximizing the monocalcium phosphate content in the final product which is water soluble P_2O_5 during the curing time. One such effort has been highlighted in the present work.

1.1 Process Description

Ground rock phosphate is transported from the storage site by a system of belt, screw conveyor and bucket elevator and then fed into the Mixer-Cum-Reactor containing paddles. Rock Phosphate and Sulphuric acid (65% dilutioin) are fed altogether to the reactor to produce DCP, MCP, $CaSO_4$ and H_3PO_4 by two reactions in the 1st stage. These reactions occur in a few minutes and during this period settling and hardening of the superphosphate slurry occurs caused by relatively rapid crystallization of the lower soluble calcium sulphate. [2].

In the next stage, ageing of superphosphate occurs i.e. further production of superphosphate by reaction of H_3PO_4 with DCP and unreacted rock which is a slow process due to diffusion of H_3PO_4 inside the solid followed by crystallsation of MCP in the den. Thus, the slurry is transported to the continuous action den which has a very low travel speed to allow for reaction and solidifying of superphosphate to take place.

The superphosphate powder from the den is transferred for ageing to a storage pile for curing to complete the chemical reaction which takes, 8 to 10 days to get acceptable soluble P_2O_5% to be used as a fertilizer for plant. The raw fertilizer is homogeneously distributed by a scattering device to increase the speed of ageing operation. The superphosphate is agitated by a grab-bucket crane. The final product still contains some amount of phosphoric acid which makes the fertilizer hygroscopic.

During the reaction of phosphate rock with sulphuric acid in the den, hydrogen fluoride is produced which reacts with the silicon oxide contained within the phosphates and forms silicon-tetra-fluoride (SiF_4) and fluosilicic acid (H_2SiF_6). So, the den is enclosed to ensure that fumes of these compounds do not get away into the working place. The fluoride gases, containing H_2SiF_6 vapors are withdrawn through the openings of the den roof through a ventilation pipe and sent an absorption unit.
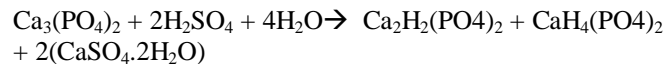
The process of manufacturing [3, 4] depends on reacting phosphate rock which contains minimum 14.50 % min P_2O_5.
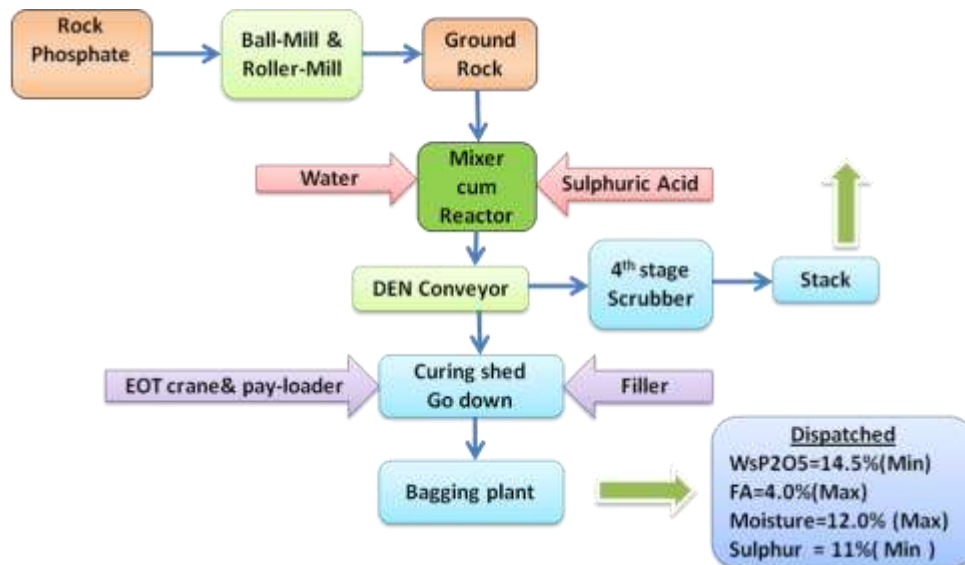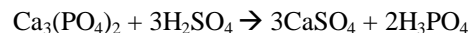
Reactions :

It's a two stage reaction and it proceeds as follows
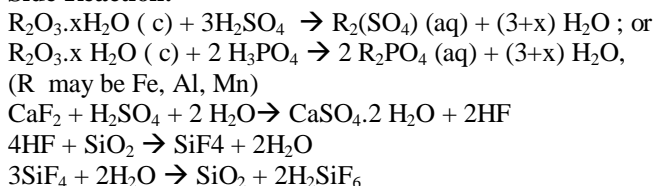
Principle Reaction:

1st stage:

$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow Ca_2H_2(PO4)_2 + CaH_4(PO4)_2 + 2(CaSO_4.2H_2O)$

2nd stage:

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

Process Flow Diagram for Single Superphosphate Manufacturing

Side Reaction:

$R_2O_3.xH_2O$ (c) $+ 3H_2SO_4 \rightarrow R_2(SO_4)$ (aq) $+ (3+x) H_2O$; or
$R_2O_3.x H_2O$ (c) $+ 2 H_3PO_4 \rightarrow 2 R_2PO_4$ (aq) $+ (3+x) H_2O$,
(R may be Fe, Al, Mn)
$CaF_2 + H_2SO_4 + 2 H_2O \rightarrow CaSO_4.2 H_2O + 2HF$
$4HF + SiO_2 \rightarrow SiF4 + 2H_2O$
$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$
Overall reaction:
$CaF_2. 3Ca_3(PO_4)_2 + 7 H_2SO_4 + 3 H_2O = 3CaH_4(PO_4)_2. H_2O + 2HF + 7CaSO_4$

2. MATERIAL AND METHODS

Though low grade rock phosphates are cheaper than high grade rock phosphates, following drawbacks have to be overcome.

- Reactivity of low grade rock is less,
- High specific consumption of Raw materials (Rock phosphates and Acid)
- Conversion efficiency is less.
- Curing time is high.
- Contains high impurities which lead to poor scrubbing performance.

To overcome these constraints, the following points are given more importance.

- Study & mathematical modeling of reaction at Mixer-cum-Reactor.
- Study & mathematical modeling of curing reaction.
- Proposal for some modification of Mixer-cum-Reactor design.

In this work sample data was collected from existing operation covering the following points.
- ✓ Ex Mixer-cum-reactor
- ✓ Ex Den
- ✓ Before bagging

Ex-Mixer analysis (present)

FA	w/s P_2O_5	Total P_2O_5	Moisture	Citrate insoluble P_2O_5
14	11.02	16.2	17.67	3.48

Ex-DEN analysis (present)

FA	w/s P_2O_5	Total P_2O_5	Moisture	Citrate insoluble P_2O_5
7.2	13.85	17.8	11.12	2.73

Bag product analysis (present)

FA	w/s P_2O_5	Total P_2O_5	Moisture	Citrate insoluble P_2O_5
3.8	15	17.5	10.22	0.75

Rock	100
P2O5 in the rock (%)	30
Conversion	0
Ex mixer	185.19
P2O5 in the ex mixer(%)	16.20
Unreacted rock	21.48
Actual conversion	**68.02**
Total conversion of rock	78.52

Ex den   168.54
    P2O5 in the ex den(%)   17.8
    Unreacted rock   15.34
    Actual conversion   **77.81**
    Total conversion of rock   84.66
Bag product   171.92
    P_2O_5 in the bag p(%)   17.45
    Unreacted rock   4.30
    Actual conversion   **85.96**
    Total conversion of rock   95.70

3. RESULTS

Experiment carried out with varying acid rock ratio ranging from 0.56 to 0.68 and analyzed in the Laboratory through the span of 60 days. The dilution ratio and the temperature are maintained at constant level. One sample data set is given in table 1.
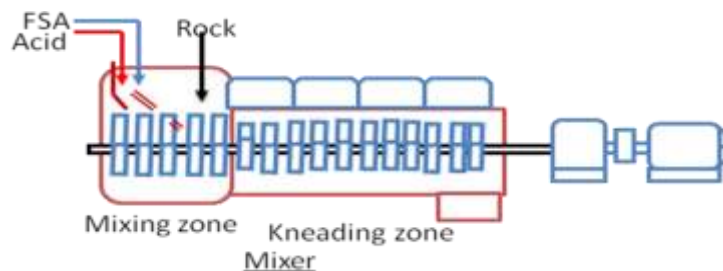
Fig -1: Schematic of Mixer cum Reactor

Table- 1: Acid /Rock ratio: 0.64, Dilution=65% TEMP OF EX-DEN: 113- 115^{0}C

	EX-DEN	1 - day	3 day	6 day	9 day	12 day	15 day	18 day
Free Acid	11.50	6.38	5.70	4.52	4.42	4.15	4.11	4.01
W/S P_2O_5	13.48	15.32	16.26	16.31	16.42	16.53	16.55	16.63
Total P_2O_5	16.54	16.85	17.38	17.47	17.48	17.58	17.60	17.66
Moisture	15.07	14.24	13.81	13.50	12.36	12.28	12.28	12.16
Conversion	81.52	90.92	93.56	93.36	93.94	94.03	94.03	94.17
P_2O_5 (UR+DCP)	3.04	1.53	1.12	1.16	1.06	1.05	1.05	1.03

	21 day	24 day	27 day	30 day	37 day	44 day	52 day	60 day
Free Acid	4.00	3.97	3.95	3.97	3.93	3.79	3.54	3.40
W/S P_2O_5	16.66	16.68	16.71	16.70	16.70	16.75	16.77	16.85
Total P_2O_5	17.86	17.89	17.90	17.90	17.93	17.97	18.01	18.08
Moisture	12.11	12.06	11.43	11.37	11.04	11.00	10.84	10.38
Conversion	93.28	93.24	93.35	93.30	93.14	93.21	93.11	93.20
P_2O_5 (UR+DCP)	1.20	1.21	1.19	1.20	1.23	1.22	1.24	1.23

3.1 Data correlation for 2nd reaction

This stage represents diffusion of phosphoric acid into the pores of unreacted rock particles and its reaction with both the unreacted rock and DCP formed during the 1st stage reaction.

$$Ca_2H_2(PO_4)_2 + 2H_3PO_4 = 2\ CaH_4(PO_4)_2$$

Mechanism used to find out the rate constant:
- Finding out the best rate equation which has high correlation value, tending to 1. (From the data of time vs unreacted P_2O_5 containing in Rock Phosphates and non water soluble P_2O_5 containing DCP))

$$Cur=a/(1+b*exp(-c*time))$$

- Differentiate at each point to find out the slope (-dCur/dt).
- Formation of the equation by following step
- $-dCur/dt = k*Cur^m*Ca^n$ Where,

Cur, represents concentration of unreacted & non water soluble P_2O_5.
Ca, represents concentration of free P_2O_5 (H_3PO_4).

3.2 Analysis

The 2nd reaction is basically a slow reaction because the free H_3PO_4 has to diffuse inside the solid mass to react with

unreacted P_2O_5 in the rock and the unreacted DCP to produce MCP. The rate constant appears to increase with increase in acid rock ratio upto 0.64. Therefore, rate constant k can be correlated to acid rock ratio. It is also noted that the exponent 'n' at first decreases and then increases with acid rock ratios whereas 'm' decreases with acid rock ratios. These may be due to the reason that the actual reaction is more complex involving in several steps before achieving the final product.

Since the main objective is to get highest amount of water soluble P_2O_5 i.e. MCP, 0.64 Acid / Rock ratio should be used. This corresponds to 'm' equal to 1.88 and 'n' equal to 0.133 and corresponding 'k' is 2.221.

Up to 6 days curing time, there appears a quick decrease in unreacted rock & DCP, beyond which the decrease is gradual because of substantial decrease in H_3PO_4 concentration after 6 days.

The kinetics for data up to 6 days is more or less similar to that from beginning to 60 days except that the magnitude of 'm', 'n' and 'k' are slightly different due to rapid reaction upto 6 days in presence of higher H_3PO_4 concentration.

3.3 Modeling of Mixer-cum Reactor

Basis
- Conversion is a function of RPM of paddles.

i.e. Xws, P_2O_5 =f (N),

Where, Xws, P_2O_5= Conversion of P_2O_5 of the rock.

N = RPM of paddles.
- Conversion is a function of residence time which varies with holdup volume and can be measured indirectly from total volumetric flow rate of Rock and Acid.

Hence,

Xws, P_2O_5 = f (F),

Where, F=((Fr/Dr)+(Fa/Da)),

  Fr = Rock mass flow

  Dr = Rock density

  Fa = Acid mass flow

  Da = Acid density

Conversion is a function of fraction of rock flow

i.e. Xws, P_2O_5= f (Cp_2o_5),

where, $C_{P_2O_5}$ =Fr/(Fa+Fr)
- Conversion is a function of fraction of acid flow

i.e. Xws, P_2O_5= f (Cl_0),

Where, Cl_0=Fa/(Fa+Fr)

Correlation Development:

Xws, P_2O_5 = f (N, F, V, $C_{P_2O_5}$, Clo)

          = K' (F/NV) $^{\alpha'}$ ($C_{P_2O_5}$/Clo)$^{\beta'}$ (1)

% water soluble P_2O_5 depends on the above mentioned variables due to the following reasons.
1. It depends on the RPM of paddle because at higher RPM the holdup volume (V) will be less and hence, the residence time for reaction will be less.
2. It depends on volumetric feed rate of rock plus acid because at higher rate holdup volume in the reactor will be more at a given RPM of paddle and hence, residence time in the reactor changes.

3. Conversion depends on rock to acid ratio because as acid flow rate increases for a given rock flow rate more acid attacks the rock and hence more reaction to produce more water soluble P_2O_5.

Since there is no provision for measurement of holdup volume in the reactor the dimensionless group of equation (1) given above is modified as follows:

Note that V depends on both F & N. So,

V = f (F, N)

  = K'' $F^{\alpha''}$ $N^{\beta''}$ (2)

Therefore, substituting for V in equation (1) we can write

Xws, P_2O_5 =K $(N)^\alpha$ $(F)^\beta$ $(C_{P_2O_5}/Clo)^\gamma$ (3)

Using the experimental data (Table-2 & 3) values of 'K', 'α', 'β, and 'γ' have been determined as follows:

  where, K, α, β, γ are constant.

Table- 2: Samples collected from the existing field at RPM = 46

Acid Rock Ratio	0.58	0.60	0.62	0.64
Fr	18	18	18	18
Fa	10.44	10.8	11.16	11.52
Dr	1.48	1.48	1.48	1.48
Da	1.84	1.84	1.84	1.84
F=((Fr/Dr)+(Fa/Da))	17.84	18.03	18.23	18.42
N=(paddles RPM)	46	46	46	46
Cl_0=Fa/(Fa+Fr)	0.367	0.375	0.383	0.390
Cp_2o_5 =Fr/(Fa+Fr)	0.633	0.625	0.617	0.610
Cp2o5/Cl0	1.724	1.667	1.613	1.563
Xws,p_2o_5	73.97	76.57	78.85	81.62

Table- 3: Samples collected from the existing field at RPM = 42

Acid Rock Ratio	0.62	0.64
Fr	18	18
Fa	11.16	11.52
Dr	1.48	1.48
Da	1.84	1.84
F=((Fr/Dr)+(Fa/Da))	18.23	18.42
N=(paddles RPM)	42	42
Cl_0=Fa/(Fa+Fr)	0.383	0.390
Cp_2o_5 =Fr/(Fa+Fr)	0.617	0.610
Cp2o5/Cl0	1.613	1.563
Xws,p_2o_5	79.75	82.36

Calculation:

Using the data of table: 2, the following equations are generated

$$73.97 = K*(46)^{\alpha} (17.84)^{\beta} (1.724)^{\gamma} \quad (4)$$

$$76.57 = K*(46)^{\alpha} (18.03)^{\beta} (1.667)^{\gamma} \quad (5)$$

$$78.85 = K*(46)^{\alpha} (18.23)^{\beta} (1.613)^{\gamma} \quad (6)$$

$$81.62 = K*(46)^{\alpha} (18.42)^{\beta} (1.563)^{\gamma} \quad (7)$$

Using the data of table: B, following equations are generated.

$$79.75 = K*(42)^{\alpha} (18.23)^{\beta} (1.613)^{\gamma} \quad (8)$$

$$82.36 = K*(42)^{\alpha} (18.42)^{\beta} (1.563)^{\gamma} \quad (9)$$

Dividing by equation (4) to (5) and taking log,
$\text{Ln}(76.57/73.97) = \beta \ln(18.03/17.84) + \gamma \ln(1.667/1.724)$
Or, $0.0346 = 0.0106 \beta - 0.0336 \gamma \quad (10)$

Similarly, from (6) & (7),
$\text{Ln}(81.62/78.85) = \beta \ln(18.42/18.23) + \gamma \ln(1.563/1.613)$
Or, $0.0345 = 0.0104 \beta - 0.0315 \gamma$
Or, $\beta = (0.0345 + 0.0315 \gamma)/(0.0104) \quad (11)$
Substituting β to equation (10), we get,
$0.0346 = 0.0106((0.0345 + 0.0315 \gamma)/(0.0104)) = 0.0336 \gamma$
Or, $\gamma = -0.40$
  From equation (11),
        $\beta = (0.0345 + 0.0315 (-0.40))/(0.0104)$
        or, $\beta = 2.106$
From equation (7) by (8)
$\text{Ln}(81.62/79.75) = \alpha \ln(46/42) + \beta \ln (18.42/18.23) + \gamma \ln (1.563/1.613)$
        Or, $0.0232 = 0.09097 \alpha + 0.02184 + 0.0126$

        Or, $\alpha = -0.124$

From equation (9) we get,
$K = 82.36/(42)^{\alpha} (18.42)^{\beta} (1.563)^{\gamma}$
  $= 82.36/(42)^{(-0.124)} (18.42)^{2.106} (1.563)^{(-0.40)}$
        Or $k = 0.3388$
Hence the final co-relation is
$\text{Xws}, P_2O_5 = 0.3388*(N)^{-0.124} (F)^{2.106} (C_{P2O5}/Clo)^{-0.40} \quad (12)$

4.0 CONCLUSION

The correlation shows that conversion of water soluble P_2O_5 decreases with increase in RPM because residence time of reaction decreases due to decrease in holdup, and this is evident from experimental data. (Table 2&3).

Conversion increases with increase in volumetric feed rate because holdup increases at a given RPM of paddles and hence, residence time increases and more reaction to take place.

Conversion decreases with increase in rock to acid flow as given by the correlation which is as per the explanation given.

The production data of SSP Mixer-cum-Reactor have been successfully correlated to system parameters and hence, system parameters can be chosen for maximizing the conversion of rock P_2O_5 to water soluble P_2O_5 in the existing plant.

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