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CALCULATION ON MATERIAL BALANCE OF SSP MANUFACTURE

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Material balance has been calculated for SSP manufacture from Jordan phosphate rock based on the mineralogical composition of Jordan rock specific sample. It has been found that by using acid rock ratio of 37.66 to 62.34 Kgs, 105.31 Kgs cured product (SSP) with 6% moisture is obtained.

INTRODUCTION

Single superphosphate (SSP) is being manufactured at NFC Lyallpur Chemicals & Fertilizers Limited, Faisalabad. Jaranwala by using Jordan phosphate rock. Theoretical calculations on The material balance of SSP were undertaken with a view to know the accurate quantities of the SSP being produced and also for a better understanding of the process by knowing the nature of all the chemical reactions occuring during the SSP manufacture.

Jordan phosphate rock of 90% –100 mesh finess is treated with 70% sulphuric acid in a U shaped trough provided with paddle type mixer. The slurry formed in the mixer is then fed to the Moritz Den revolving at the rate of one revolution in 2 hr. Preserving the heat of reaction helps complete the reaction and also helps collect and eliminate the gases evolved during the reaction. The slurry hardens during the slow rotation of Den and is discharged by the shaving action of the rotating cutter on the metallic conveyor. The ex-Den product becomes porous and semi-dry which can be cut, easily handled and stored in the shed for curing.

To start the theoretical material balance calculations it was essential to know the exact mineralogical composition of the Jordan rock i.e. the nature of various components which react with sulphuric acid.

Mineralogical composition of the Jordan rock sample MR–558 is known (taken from TVA un-published data). It is similar in composition to Jordan rock being used in the factory at present. This sample has therefore been selected for the material balance calculations.

Chemical Composition of Jordan Rock (Sample MR-558). CaO 49.20%; P_2O_5 31.50%; CO_2 5.00% F 3.80%; MgO 0.25%; Na_2O 0.70%; SiO_2 6.00%; Al_2O3 0.35%; Fe_2O_3 0.20%; K_2O 0.03%; Cl 0.16%; SO_3 1.05%; Non-sulphate S 0.07%; N.D. matter 2.00%.

The phosphate rock (apatite) is always found substituted to various degrees and differ markedly in the manner in which chemical constitutents are combined. Keeping in view the mineralogical composition of Jordan rock and numerous unpredictable complications during process such as incomplete reaction etc., following assumptions have been made for material balance purposes:

1. (a) All P_2O_5 is present as $Ca_3(PO_4)_2$. (b) All F is present as CaF_2. (c) All CO_2 is present as $CaCO_3$. (d) All SO_3 is present as $CaSO_4$ $2H_2O$. (e) Any CaO not accounted for by the previous assumption is present as such, presumably in the apatite structure.
2. 25% of the CaF_2 present inthe rock reacts with sulphuric acid and SiO_2 to form SiF_4 which is collected in the Scrubber as H_2SiF_2 and precipitates SiO_2 [1].
3. Under ordinary factory conditions where sulphuric acid (65 to 70%) and temperature of reaction is not dissipated by artificial cooling, anhydrite ($CaSO_4$) is the normal form of calcium sulphate in the final product [2].

Average analysis of the product, SSP is as under: Total P_2O_5 20.20% (Equivalent to 64.12 grams of rock); Water soluble P_2O_5 18.10%; Citrate soluble P_2O_5 1.70%; Citrate insoluble P_2O_5 0.4%; Free phosphoric acid 4.0%.

After applying the simplifying assumptions the composition of the rockphosphate therefore becomes as under: $Ca_3(PO_4)_2$ 68.83%; CaF_2 7.80%; $CaCO_3$ 11.36%; $CaSO_4 2H_2O$ 2.26%; S 0.07%; NaCl 0.26%; Na_2O 0.60%; MgO 0.25%; Al_2O_3 0.35%; Fe_2O_3 0.20%; K_2O 0.03%; SiO_2 6.00&; N.D. matter. 2.00%, and their reactions taking place are:

1) $$\underset{310}{Ca_3(PO_4)_2} + \underset{196}{2H_2SO_4} + \underset{18}{H_2O} \rightarrow \underset{252}{CaH_4(PO_4)_2O} + \underset{272}{2CaSO_4}$$

$Ca_3(PO_4)_2$ required for:

15.21%: W.S. P_2O_5 in the product. 33.21%

H_2SO_4 required for the formation of above $CaH_4(PO_4)_2H_2O$.	21.00%
H_2O added.	1.93
$CaH_4(PO_4)_2\,H_2O$ formed.	27.00
$CaSO_4$ formed.	29.14

2) $2\,Ca_3(PO_4)_2 + 6PH_2SO_4 + 3H_2O \rightarrow 4H_3PO_4 + 6CaSO_4\,½\,H_2O$
620 588 54 392 870

$Ca_3(PO_4)_2$ required for: 2.89% W.S. P_2O_5 in the product.	6.32%
H_2SO_4 required for formation of above H_3PO_4.	6.00
H_2O (added).	0.55
H_3PO_4 produced.	4.00
$CaSO_4\,½\,H_2O$ formed.	8.87

3) $Ca_3(PO_4)_2 + H_2SO_4 \rightarrow 2CaHPO_4 + CaSO_4$
310 98 272 136

$Ca_3(PO_4)_2$ + required for 1.7% C.S. P_2O_5 in the product.	7.71
H_2SO_4 required for the formation of above $CaHPO_4$.	1.17
$CaHPO_4$ produced.	3.26
$CaSO_4$ produced.	1.63

4) Unreacted Tri–calcium phosphate

$Ca_3(PO_4)_2$ as such equivalent to 0.40% P_2O_5 the product.	0.87

5) $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$
100 98 136 44 18

$CaCO_3$ present in 64.12 g of the phosphate rock used for SSP manufacture	7.28g
H_2SO_4 required for the decomposition of above $CaCO_3$.	7.13
$CaSO_4$ formed.	9.90
CO_2 evolved (loss)	3.20
H_2O produced.	1.31

6) $Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$
160 294 400 54

Fe_2O_3 present in 64.12 g of phosphate rock used for SSP manufacture.	0.13g
H_2SO_4 required to convert above Fe_2O_3 to $Fe_2(SO_4)_3$.	0.24
$Fe_2(SO_4)_3$ produced.	0.33
H_2O produced.	0.04

7) $Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$
102 294 342 54

Al_2O_3 present in 64.12 g of phosphate rock used for SSP manufacture.	0.22g
H_2SO_4 required to convert above Al_2O_3 to $Al_2(SO_4)_3$.	0.63
$Al_2(SO_4)_3$ produced.	0.74
H_2O produced.	0.12

8) $Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$
62 98 142 18

Na_2O present in 64.12g of phosphate rock used for SSP manufacture.	0.38g
H_2SO_4 required to convert above Na_2O to Na_2SO_4.	0.60
Na_2SO_4 produced.	0.87
H_2O produced.	0.11

9) $K_2O + H_2SO_4 \rightarrow K_2SO_4 + N_2O$
94 98 174 18

K_2O present in 64.12g of phosphate rock used for SSP manufacture.	0.02g
H_2SO_4 required.	0.02
K_2SO_4 produced.	0.04
H_2O produced.	0.004

10) $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$
42.31 98 122.31 18

MgO present in 64.12g of phosphate rock used for SSP manufacture.	0.16
H_2SO_4 required for 0.16 grams MgO.	0.37
$MgSO_4$ produced.	0.46
H_2O produced.	0.07

11) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$
78 98 136 40

$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$
60 80 104 36

CaF_2 present in 64.12g of phosphate rock used for SSP manufacture.	5.0g
According to simplifying assumption No. 2, 25% fluoride takes part in reaction.	1.25
Acid consumption.	1.57

$CaSO_4$ produced.	2.18
HF formed.	0.64
SiO_2 going to stack in the form of SiF_4	0.48
Constituents going as such in the product are:	
1. CaF_2	3.75
2. $CaSO_4$ $2H_2O$	1.45
3. SiO_2	3.37
4. S	0.04
5. NaCl	0.17
6. N.D. Matter.	1.28

End product (SSP) obtained.

$CaH_4 (PO_4)_2 H_2O$.	27.0
Free H_3PO_4	4.00
$CaH PO_4$	3.26
$Ca_3 (PO_4)_2$.	0.87
$Fe_2 (SO_4)_3$	0.33
$Al_2 (SO_4)_3$	0.74
$Na_2 SO_4$	0.87
K_2SO_4	0.04
$MgSO_4$	0.46
CaF_2	3.75
SiO_2	3.37
S	0.04
NaCl	0.17
N.D. Matter	1.28
	46.18
$CaSO_4$	53.17
Total	99.35

Total calculated $CaSO_4$ formation.

From $CaH_4 (PO_4)_2 H_2O$	(Reaction No. 1)	29.14
From H_3PO_4 (Free acid)	(„ 2)	8.87 (Hemihydrate)
From $CaHPO_4$	(„ 3)	1.63
From $CaCO_3$	(„ 5)	9.9
From CaF_2	(„ 11)	2.18
From phosphate rock, as such ($CaSO_4$ $2H_2O$)		1.45
		53.17

Total calculated acid consumption.

For $CaH_4 (PO_4)_2 H_2O$.	(Reaction No. 1)	21.0
For H_3PO_4	(„ 2)	6.0
For $CaHPO_4$	(„ 3)	1.17
For $CaCO_3$	(„ 5)	7.13
For Fe_2O_3	(„ 6)	0.24
For Al_2O_3	(„ 7)	0.63
For Na_2O	(„ 8)	0.60
For K_2O	(„ 9)	0.02
For MgO	(„ 10)	0.37
For CaF_2	(„ 11)	1.57
		38.73

Loss calculated as volatile material.

CO_2	(Reaction No. 4)	3.20
HF	(„ 11)	0.64
SiO_2	(„ 11)	0.48
		4.32
H_2O Volatilized as steam.		9.82

Calculated water formed during reaction.

From Carbonate	(Reaction No. 5)	1.31
From Fe_2O_3	(„ 6)	0.12
From, Al_2O_3	(„ 7)	0.12
From Na_2O	(„ 8)	0.11
From K_2O	(„ 9)	0.004
From MgO	(„ 10)	0.07
		1.654

Water added for dilution of 38.73 g of H_2SO_4	=	16.6 g

Total input.

Rockphosphate	64.12
Sulphuric acid 100%	38.73
Water for dilution of acid up to 70%	16.60
	119.45

Process losses.

Loss due to evolution of gasses	4.32
water loss	9.82
	14.14

End product.	
Ex-den product having 10% moisture	109.28
Cured product having 6% moisture	105.31

According to calculations sulphuric acid and phosphate rock ratio = Acid : 37.60
Rock : 62.34

The rated capacity of NFC Lyallpur Chemicals & Fertilizers Limited, Faisalabad SSP Plant is 60 tons / 24 hr, i.e. 2500 kg/hr Material balance of the SSP produced has been worked out on the basis of the above theoretical calculated ratios and one hour's production of SSP (2500 kg) as follows:

Rockphosphate required per hour (for 2500 kgs SSP).	1613.49 kgs
Sulpuric acid 100% required " " "	974.58 kgs
Water required for dilution of acid to 70% " " "	417.68 kgs

MATERIAL BALANCE

Components	Dilution tank	Mixer	Den	Gas washer and stack	Finished product kgs
H_2SO_4	974.58	974.58			
H_2O	417.68	417.68	250.00	247.40	150.00
$Ca_3(PO_4)_2$		1110.56	21.89	(Loss during	21.89
$CaCo_3$		183.19		denning and	
CaF_2		125.82	94.36	curing)	94.36
$CaSO_4\ 2H_2O$		36.46	36.46		36.46
S		1.01	1.01		1.01
NaCl		4.28	4.28		4.28
Na_2O		9.56			
MgO		4.03			
Al_2O_3		5.53			
Fe_2O_3		3.27			
K_2O		0.50			
SiO_2		96.81	84.80	12.08	84.80
N.D. Matter		32.21	32.21		32.21
$CaH_4(PO_4)_2\ H_2O$			679.42		100.65
Free H_3PO_4			100.65		82.03
$CaHPO_4$			82.03		82.03
$FO_2\ (SO_4)_3$			8.30		8.30
$Al_2\ (SO_4)_3$			18.62		18.62
Na_2SO_4			21.89		21.89
K_2SO_4			1.00		1.00
$MgSO_4$			11.57		11.57
$CaSO_4$			1301.49		1301.49
HF				16.10	
CO_2				80.52	
Total:		3005.56	2749.98	356.10	2649.98
Working temp.	50^oC	120^oC	90^oC		
Moisture.			10 %		6 %

Appendix A. Model analysis sample No. MR - 558

	Apatite	Calcite	Quartz & chert	Halite	Gypsum	Amorphous Fe oxides	Amporphous Al and K silicates	Non sulfate S	Total
CaO	47.01	1.45			0.74				49.20
P_2O_5	31.50								31.50
CO_2	3.86	1.14							5.00
F	3.80								3.80
MgO	0.25								0.25
Na_2O	0.43			0.27					0.70
SiO_2			5.60				0.40		6.00
Al_2O_3							0.35		0.35
Fe_2O_3						0.20			0.20
K_2O							0.03		0.03
Cl				0.16					0.16
SO_3					1.05				1.05
Non-sulfate S								0.07	0.07
OH	0.20								0.20
H_2O					0.47				0.47
O ∿ F	−1.60								−1.60
O ∿ Cl				−0.04					−0.04
Total	85.45	2.59	5.60	0.39	2.26	0.20	0.78	0.07	97.30

With the courtesy of : Tenessee Valley Authority, U.S.A.

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