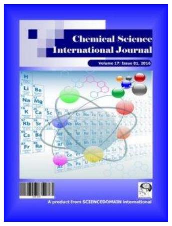

Chemical Science International Journal

24(3): 1-6, 2018; Article no.CSIJ.44167
ISSN: 2456-706X
(Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

Enriched Superphosphate Based on Decomposition of Ordinary Phosphorite Powder with Phosphoric Acid Gypsum Slurry

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AAR and OAB did all of laboratory experiments. Author SSN checked and corrected the main article (in Russian). Author ARS wrote this article. Author UKA translated this article from Russian into English dates. Author BES helped to find literature dates. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2018/44167
Editor(s):
(1) Dr. Nagatoshi Nishiwaki, Professor, Kochi University of Technology, Japan.
(2) Dr. Akmal S. Gaballa, Professor, Faculty of Specific Education, Zagazig University, Zagazig, Egypt.
Reviewers:
(1) Edward Someus, Hungary.
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(3) R. K. Mathukia, Junagadh Agricultural University, India.
Complete Peer review History: http://www.sciencedomain.org/review-history/27072

Original Research Article

Received 28 August 2018
Accepted 23 October 2018
Published 06 November 2018

ABSTRACT

Complex, nitrogen-phosphate fertilisers are applied before seeding, with seeding and extra nutrition, while single phosphoric ones are the most effective under autumn ploughing. In that case, enriched superphosphate, more concentrated than single superphosphate, was obtained using phosphoric acid gypsum slurry semiproduct produced by the interaction of thermo concentrate with sulphuric acid and recycled phosphoric acid in accordingly dihydrate operation (60-80°C). However, the mix of sulphuric and phosphoric acids was not used those are usually applied in conventional ways for enriched superphosphate production. Phosphate raw material (PRM) is dosed into phosphoric acid gypsum slurry (PAGS) upon weight ratio of PAGS: PRM equal from 100: 15 to 100: 40 that provides a condition for slurry fluidity. Interaction of the components was

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performed at 70°C for 60 min. Then the superphosphate mass obtained was downloaded from reactor followed by ripening at 95-100°C, cooling, and obtaining final products. Since optimal weight ratio of PAGS: PRM is 100: 25 and 100:30 respectively depending upon the grades of PAGS in which samples of enriched superphosphate are obtained with high total and assimilated form of P_2O_5 having of water-soluble that of P_2O_5 no less 50%. It should be explained the requirement of agriculture on single phosphoric fertiliser possessing high content total and acceptable form of P_2O_5 and water soluble that of P_2O_5 no less 50% towards to total P_2O_5.

Keywords: Phosphoric acid gypsum slurry; phosphorite powder; decomposition; enriched superphosphate; composition.

1. INTRODUCTION

In Uzbekistan, there is mineral fertiliser being a stable developing branch for the chemical industry of the national economy. Additionally, in 2016 our chemical industry produced 944.7 thousand tonnes of nitrogen, 143 thousand tonnes of phosphate, and 138 thousand tonnes of potassium fertilisers based on 100% nutrients. Whereas, need of the republic is 839.58 thousand tonnes of N, 525.21 thousand tonnes of P_2O_5 and 278.92 thousand K_2O. Therefore, government attempts vigorous actions to satisfy the needs of agriculture in phosphoric and potassium fertilisers. As a result, implementation of wide arrangements considerable performances are reached particularly capacity of Dekhanabad plant for potassium production was increased to 360 thousand tonnes of K_2O or based on 600 thousand those of KCl. In that case, Kyzyl-Kum phosphorite complex rose output of washed and dried phosphoconcentrate from 400 to 716 thousand tonnes in average 26% P_2O_5 (WDC-26).

Since major phosphorus-containing fertilisers, in the republic, are as follow: ammophos (10% N; 46% P_2O_5), suprefos-NS (8-15% N; 20-24% P_2O_5), PS-Agro (4-6% N; 34-41% P_2O_5), nitrocalciumphosphate (12% N; 16% P_2O_5), simple (1.5% N; 13.5% P_2O_5) and enriched (2.5% N; 18-26% P_2O_5) superphosphate. As regards, an assortment of phosphate fertilisers only two the latter type of products belong to single phosphoric fertilisers, but the rest of ones are complex nitrogen-phosphate. On the other hand, nitrogen-phosphate and complex fertilisers are not included in scientific and based distribution of annual norm of mineral fertilisers on agrichemical terms for their application. Furthermore, those complex fertilisers do not have to introduce under the ploughing and merely with seeding and as additional fertilising. As nitrogen, during the winter, is lost gratuitously with rainy and water from melted snow. On the basis of the agrochemists' recommendation phosphorus must be applied under cotton 60-70%, vegetable cultures 75% and crops all 100% with yearly for application under autumn ploughing [1]. However, the amount of simple and enriched superphosphate produced is a little. For that reason, it is necessary to increase the manufacture of single phosphoric fertilisers.

For kind of single phosphoric fertilisers can be belonged to triple superphosphate [2-4]. That type of fertiliser is one of the most concentrated phosphoric product. For its production, high-quality phosphate raw material and concentrated phosphoric acid must be used. Wet process phosphoric acid from low-grade phosphorite such as Karatau (21% P_2O_5) is not applicable for triple superphosphate production [5]. It is explained that due to high impurity, especially magnesium, therefore the acid obtained from Karatau cannot be concentrated by evaporation until the concentration of P_2O_5 38% and more. In that case, it loses fluidity [6]. Taking into account, low-grade phosphorite from the Kyzyl Kum is not used either to produce triple superphosphate resulting expensive and uneconomic.

As is known that simple superphosphate is manufactured by means sulphuric acid decomposition of natural phosphate while enriched superphosphate with a mix of sulphuric and phosphoric acids by chamber, line or chamber-line production. Unlike simple superphosphate, enriched superphosphate content of P_2O_5 constitutes between the simple and triple superphosphate. Note that production of enriched superphosphate it is possible based on phosphorite containing more than 20% P_2O_5. Additionally, enriched superphosphate can be obtained at sets for production simple superphosphate with a little change of operation as well as including additional accessories for dosing and dilution of acid.

Considering low concentration of P_2O_5 and high content of CO_2 in Kyzyl Kum phosphorite, investigation on obtaining enriched superphosphate should be carried out by decomposition of phosphorite powder with phosphoric acid gypsum slurry produced at JSC “Ammofos-Maxam” based on decomposition thermoconcentrate, WDC-26, in sulphuric acid [7]. Phosphoric acid gypsum slurry mainly contents $CaSO_4{\cdot}2H_2O$ in an aqueous solution of phosphoric acid. The slurry is used to produce fertiliser called "Suprefos-NS" essence of whose concludes in the implementation of its deep ammonisation reaction (until pH=8.5) accordingly the following equation:

$$CaSO_4 + H_3PO_4 + 2NH_3 = CaHPO_4 + (NH_4)_2SO_4$$

We have assured that laboratory studies confirm above-indicated reaction [8-11]. The result, the product obtained – Suprefos-NS is the complex fertiliser that contents to 45% of precipitate, to 35 ammonium sulphate, and 10-15% of mono-and diammonium phosphate. The way was implemented at JSC “Ammofos-Maxam” in 2005.

The fertiliser is produced at equipment of ammophos production. Primarily, phosphorite is decomposed by sulphuric acid simultaneously with reverse wet process phosphoric acid (WPA) in extractor in the dihydrate operation. Then a part of the phosphoric acid gypsum slurry is directed at rotary vacuum filter, which divides the slurry into phosphogypsum and productional WPA. The latter is reproduced in ammophos. And the second part is pumped to saturated where the slurry is neutralised deeply by ammonia. Thus, ammonited slurry is dried and granulated in drum and granulator drier (DGD) by following Suprefos-NS.

In contrast with the above, we offer neutralisation of phosphoric acid gypsum with phosphorite powder instead of synthetic ammonia that leads to obtaining single phosphoric fertiliser. That is, neutralisation reaction will take place between the carbonate mineral of the phosphorite powder and acid in the WPA.

Hence, the aim of the present study is the preparation of samples of enriched superphosphate based on the decomposition of phosphorite powder with the acid gypsum slurry closer to industrial condition, providing upon unthicken slurry.

The process was explored in real industrial phosphoric acid gypsum slurry obtained a decomposition of WDC-26 by sulphuric acid in dihydrate operation.

The investigation was conducted using industrial phosphoric acid - gypsum slurry obtained by the decomposition of WDC-26 by sulphuric acid in the dihydrate process.

2. METHODS AND MATERIALS

To carry out experiments the following starting materials were used (mass.%):

Phosphoric acid gypsum slurry with three grades is as follow:

1) liquid (L) and solid (S) L : S = 2 : 1 – P_2O_{5total} 12.19; P_2O_{5water} 12.04; $CaO_{total.}$ 12.47; SO_{3total} 16.61; pH= 0.59;
2) L : S = 2.5 : 1 – $P_2O_{5total.}$13.13; P_2O_{5water} 13.08; $CaO_{total.}$ 10.07; SO_{3total} 14.55; pH= 0.28;
3) L : S = 3 : 1 – $P_2O_{5total.}$14.33; $P_2O_{5water.}$ 13.56; $CaO_{total.}$ 8.75; SO_{3total} 13.65; pH= 0.20;

Phosphorite powder: 17.76 P_2O_{5total}; $P_2O_{5assimilated}$ by citric acid : P_2O_{5total}= 17.74; 47.51 CaO; 1.79 MgO; 0.73 Fe_2O_3; 0.95 Al_2O_3; 3.27 SO_3; 17.02 CO_2; 5.27 insoluble residue; $CaO_{total.}$: P_2O_{5total} = 2.68.

Stoichiometric norm was calculated according to the formula below:

$$N = \frac{\omega(P_2O_5)_{WPA} \cdot 100}{\dfrac{\omega(CaO)_{PRM} \cdot M(P_2O_5)_{FA}}{M(CaO)_{FA}} - \omega(P_2O_5)_{PRM}}$$

Where N- stoichiometric norm for decomposition of phosphorite powder, %; $\omega(P_2O_5)_{WPA}$ – mass fraction of P_2O_5 of wet process phosphoric acid in PAGS; $\omega(CaO)_{PRM}$ and $\omega(P_2O_5)_{PRM}$ – mass fraction CaO and P_2O_5 in initial phosphorite raw material respectively; $M(P_2O_5)_{FA}$ and $M(CaO)_{FA}$ – mole mass of P_2O_5 and CaO in fluorine apatite ($Ca_5(PO_4)_3F$), respectively.

Laboratory experiments were conducted in a glass vessel with volume 200 mL equipped by a stirrer, where the estimated amount of phosphoric acid gypsum slurry was fed in advance. Meanwhile, the calculated amount of phosphorite powder (that is, weight ratio the slurry to phosphorite is from 100: 15 to 100: 40) was added gradually in the vessel during the stirring. Interaction of the components was at 70°C for 60 min. Further superphosphate mass was downloaded from the vessel and was placed in the oven to ripen at 95-100°C. Thus, resulting product was ground and analysed on the diverse form of P_2O_5 and CaO, MgO, SO_3, $A1_2O_3$ and Fe_2O_3 according to the procedure in [12]. P_2O_5 was defined by a photocalorimetric method on yellow vanadic-molybdenum complex using KFK-3 (Russia) at wavelength 440 nm. An assimilated form of P_2O_5 determined on solubility both 2% solution of citric acid and 0.2 M that of EDTA.

Determination of calcium and magnesium oxides were carried out by a volumetric complexometric method using EDTA as a titrant in presence of fluorexon and chrome dark blue respectively. Measurement of pH was conducted at ion meter И-130M (Russia).

SO_3^{2-} was defined by the gravimetric method using barium sulphate while Al_2O_3 and Fe_2O_3 were determined by complexometric technique.

3. RESULTS AND DISCUSSION

Results obtained are summarised in Table.

The table shows that increase in the mass fraction of phosphate raw material regarding phosphoric acid gypsum slurry does not impact strongly on total P_2O_5 , but considerably reduces relative assimilated and water-soluble forms of P_2O_5 versus total P_2O_5. So, when using PAGS with a ratio of L : S = 2 : 1 with increasing weight ratio of PAGS: PRM from 100: 15 to 100: 40 in products content of P_2O_{5total} is varied in a range 22.52-22.75%, and conversion extent $P_2O_{5assemilated}$: $P_2O_{5total.}$ by citric acid is from 91.25 to 73.22% while $P_2O_{5assimilated.}$: $P_2O_{5total.}$ on EDTA is from 88.97 to 64.92% and P_2O_{5water}: P_2O_{5total} from 83.56 to 17.41% respectively.

Whereas, upon application of PAGS with ratio of L : S = 2.5 : 1 these figures vary in spans 24.21-25.6%, from 92.46 to 74.06%, from 89.14 to 65.55% and from 86.44 to 22.22%, when L : S = 3 : 1 data are 26.3-28.81%, from 93.09 to 75.39%, from 89.31 to 67.11% and from 86.84 to 28.59% respectively.

The more amount of liquid part of slurry regarding solid the more concentrated P_2O_5 is in fertiliser. Also, the more phosphorite powder is added in the PAGS the higher CaO_{total} is in the products. Since for L : S = 2 : 1 and with changing PAGS: PRM from 100: 15 to 100: 40 in the products, content of CaO_{total} enhances from 29.91 to 36.72%, for L: S = 2.5: 1 it is increased from 27.91 to 34.79%, and L: S = 3: 1 from 26.92 to 34.11%. At that $CaO_{assimilated.}$: CaO_{total} decreases from 86.99 to 61.22%, from 87.53 to 61.54%, as well as from 95.28 to 66.75% respectively. Should be noted that in all products free $H_3PO_4$is absent except ratio of PAGS: PRM = 100: 15 (0.72-1.21% P_2O_{5free}).

The moisture of the phosphate's slurry is in ranges 32.24-42.53% depending upon the L: S and PAGS: PRM. As a result of which the slurry was easily produced, was not thickened even when stopping the process, and easy involved for granulation. Moreover, there are not anomalous phenomena, as well as fluoride compound emission during the drying. In order to raise the strength of the product granules a little amount of acid drain is recommended to input.

On the basis of the requirement of agriculture single phosphoric fertiliser has to have high content total and acceptable form of P_2O_5 and water soluble that of P_2O_5 no less 50% towards to total P_2O_5.

Hence, for ratio of L : S = 2 : 1 optimal that of PAGS : PRM is 100 : 25, while for L : S equal to 2.5 : 1 and 3 : 1 – 100 : 30. In that case, for the first grade enriched superphosphate with content (mass. %): P_2O_{5total} 22.66; $P_2O_{5assimilated}$: P_2O_{5total} by citric acid = 84.82; $P_2O_{5assimilated}$: P_2O_{5total} on EDTA = 78.51; P_2O_{5water} : P_2O_{5total} = 59.13; for L : S = 2.5 : 1 – P_2O_{5total} 24.7; $P_2O_{5assimilated}$: P_2O_{5total} by citric acid = 82.06; $P_2O_{5assimilated}$: $P_2O_{5total.}$ on EDTA = 75.87; P_2O_{5water} : P_2O_{5total} = 49.15; for L : S = 3 : 1 – P_2O_{5total} 27.21; $P_2O_{5assimilated}$: P_2O_{5total} by citric acid = 82.87; $P_2O_{5assimilated}$: P_2O_{5total} on EDTA = 76.07; P_2O_{5water} : P_2O_{5total} = 52.74. It is necessary to note that calcium is acceptable form. Additionally, calcium is as nutrient element for plants that holds the fifth place after nitrogen, phosphorus, potassium and sulphur.

Thus, conducted investigations convincingly create a background to develop the technology of enriched superphosphate by mean of phosphoric acid gypsum slurry and low-grade phosphorite powder to be produced granular enriched superphosphate in-line production at working equipment of JSC “Ammofos-Maxam” for the manufacture of Suprefos-NS.

Table. Composition of enriched superphosphate's samples obtained based on decomposition of phosphorite powder with phosphoric acid gypsum slurry

Weight ratio of PAGS: PRM	Humidity %	Chemical composition. mass. %								$\frac{P_2O_{5assimilated}}{P_2O_{5total}}$ by 2% citric acid, %	$\frac{P_2O_{5assimilated}}{P_2O_{5total}}$ on 0.2M EDTA, %	$\frac{P_2O_{5water}}{P_2O_{5total}}$ %	$\frac{CaO_{assimilated}}{CaO_{total}}$ by 2% citric acid, %
		pH 10 % - solution of product	P_2O_5 total	P_2O_5 free	P_2O_5 assimilated by 2% citric acid	P_2O_5 assimilated on 0.2M EDTA	P_2O_5 water	CaO_{total}	CaO assimilated by 2% citric acid				
L:S=2.0:1													
100:15	36.79	2.83	22.75	0.72	20.76	20.24	19.01	29.91	26.02	91.25	88.97	83.56	86.99
100:20	35.70	3.03	22.73	-	20.01	18.85	16.29	31.63	25.65	88.03	82.93	71.66	81.09
100:25	34.81	3.27	22.66	-	19.22	17.79	13.40	33.03	24.72	84.82	78.51	59.13	74.84
100:30	34.14	3.40	22.59	-	18.39	16.74	9.58	34.45	23.61	81.41	74.10	42.41	68.53
100:35	33.38	3.53	22.57	-	17.50	15.70	6.92	35.64	23.14	77.54	69.56	30.66	64.93
100:40	32.24	3.64	22.52	-	16.49	14.62	3.92	36.72	22.48	73.22	64.92	17.41	61.22
L:S =2.5:1													
100:15	41.39	2.83	25.60	0.75	23.67	22.82	22.13	27.91	24.43	92.46	89.14	86.44	87.53
100:20	40.27	3.0	25.28	-	22.51	21.42	19.31	29.64	24.13	89.04	84.73	76.38	81.41
100:25	39.15	3.18	25.00	-	21.35	20.07	16.56	31.22	23.43	85.40	80.28	66.24	75.05
100:30	38.25	3.36	24.70	-	20.27	18.74	12.14	32.50	22.34	82.06	75.87	49.15	68.74
100:35	37.35	3.45	24.45	-	19.23	17.44	8.69	33.75	22.00	78.65	71.33	35.54	65.18
100:40	36.33	3.54	24.21	-	17.93	15.87	5.38	34.79	21.41	74.06	65.55	22.22	61.54
L:S=3.0:1													
100:15	42.53	2.82	28.81	1.21	26.82	25.73	25.02	26.92	25.65	93.09	89.31	86.84	95.28
100:20	41.16	2.89	28.18	0.53	25.23	23.89	21.62	28.66	25.00	89.53	84.77	76.72	87.23
100:25	39.93	3.12	27.65	-	23.81	22.22	18.34	30.41	24.82	86.11	80.36	66.33	81.62
100:30	39.08	3.25	27.21	-	22.55	20.70	14.35	31.83	24.16	82.87	76.07	52.74	75.90
100:35	38.06	3.41	26.76	-	21.17	19.15	10.61	33.07	23.61	79.11	71.56	39.65	71.39
100:40	37.19	3.50	26.30	-	19.83	17.65	7.52	34.11	22.77	75.39	67.11	28.59	66.75

4. CONCLUSION

To sum up, enriched phosphoric fertiliser is more effective product applying under autumn ploughing. Usually, it is produced based on a mix of sulphuric and phosphoric acid so-called conventional method. However, that approach requires qualitative phosphoric acid that is more concentrated.

Kyzylkum phosphorite is the major raw material for phosphate fertiliser production in Uzbekistan. Wet processing phosphoric acid obtained made of Kyzylkum phosphorite is low concentrated and at present used in the form of acid gypsum slurry for production complex fertiliser called Suprefos –NS. That kind of fertiliser is produced based on neutralisation of phosphoric acid gypsum slurry with ammonia at pH 8.5 followed by granulation and drying at existing equipment.

In that case, the acid gypsum slurry, semi-product of Suprefos –NS, can be used by neutralisation of calcareous phosphorite powder. This way is one of the suitable to neutralise the phosphoric acid with gypsum slurry with further enriched superphosphate preparation. For that weight ratio of the acid gypsum slurry to phosphorite powder, PAGS: PRM, was from 100: 15 to 100: 40 ensuring unthickened slurry during the process. It was established that optimal ratio is PAGS: PRM equalling to 100: 25 and 100:30 respectively that depends on the grades of PAGS. As a result, enriched superphosphate is obtained with high total and assimilated form of P_2O_5 having of water-soluble that of P_2O_5 no less 50% that well agreement by agriculture.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history/27072