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A New Complex Soluble Fertiliser - N.P.P.S. - *(Nitro-Phosphate - Potassium Schoenite Complex)*

by

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Introduction: The importance of fertiliser production in the economy of our country with agriculture as the main industry cannot be over-emphasised. Also, self sufficiency in this direction presents itself as a mirage, demand far out-stretching supply. Among many factors, the formidable are the scarcity of raw materials like sulphur and quality rock phosphate at home. Prospects of foreign import are indeed dull involving foreign exchange. It will therefore, certainly be an attractive proposition to hit upon a process to dispense with sulphur altogether and make use of indigenous inferior raw materials like phosphate deposits of Trichy and Singhbhum and also Schoenite, a by-product of salt industry. Success in this direction for the production of phosphatic fertilisers will be hailed as a significant revolution.

The phosphate deposits of Trichy and Singhbhum, containing high amounts of calcium carbonate and oxides of iron and aluminium present great difficulty in their economic utilisation by the conventional method which consists in wasteful but inevitable treatment with sulphuric acid, with the formation of calcium sulphate which is not a significant plant nutrient. Precisely, therefore, the present process enumerated is a distinct improvement in several ways.

In the first instance, use of sulphuric acid is eliminated. Next, indigenous, inferior phosphate is advantageously employed.

Again, to overcome the shortage of sulphur the world over, Nitro phosphate processes have been proposed from time to time and such phosphates are only citrate soluble. Use of a mixture of Nitric acid and sulphuric acid/ or Nitric acid and Phosphoric acid is made in order to render a part of it into water soluble form.

With respect to this too, the new process has a distinct superiority. The water soluble P_2O_5 from the fertiliser prepared in this process can widely be altered by manipulating $CaO : P_2O_5$ ratio, preferably to one or below one.

The process developed by the author is briefly presented here. Nitric acid is employed for treating the phosphate rock with the Potassium Schoenite, separately processed, the objectives being:

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(i) to release the otherwise unavailable P_2O_5 and

(ii) to prepare a complete fertiliser containing both major and secondary elements, with a scope for enriching with micro-nutrients.

Advantage is taken of the dual role of Nitric acid in dissolving the insoluble phosphate and in furnishing plant nutrient nitrate-nitrogen, introduced for acidulation of the phosphate rock. $CaO : P_2O_5$ ratio in the acidulated slurry is reduced by precipitating calcium as $CaSO_4\ 2\ H_2O$ and removing it by filtration.

Review of Literature: Hignett (1951) has observed that global shortage of sulphur will encourage the use of nitric acid instead of sulphuric acid for the manufacture of Phosphatic fertilizers. McKnight *et. al.* (1952) reported a modified method for the manufacture of phosphatic fertiliser by partial replacement of sulphuric acid with nitric acid so that, a certain percentage of water soluble P_2O_5 may be obtained. Nielsson *et. al.* (1953) reported that Nitro-phosphate with certain percentage of water soluble P_2O_5 can be manufactured from Phosphate rock, Nitric acid, Ammonia and Potassium sulphate.

Process: Two samples representing 'Superior' and 'Inferior' phosphate rock – Morocco and Trichy phosphates were analysed (Table I).

TABLE 1

	Percent		Ratio		Percent	
	P_2O_5	CaO	CaO :	P_2O_5	Fe_2O_3	Al_2O_3
Morocco Phosphate	36.6 (± 1.0)	50.1 (± 2.0)	3.46 :	1	0.11	0.50
Trichy Phosphate	27.0 (± 2.0)	47.6 (± 3.0)	4.50 :	1	1.30	0.90

The amount of Nitric acid required to solubilise the phosphate rock stoichiometrically is about 1.6 mole per mole of CaO and is converted into mono-calcium phosphate. At this ratio the desired pH is not attained for precipitation of $CaSO_4\ 2\ H_2O$. When $HNO_3 : CaO$ ratio is altered to 1.8 to 2.2, good results were obtained. The ideal ratio of $HNO_3 : CaO$ is 2.

The reaction may be expressed thus:

$$Ca_{10}\ (PO_4)_6\ F_2 + 20\ HNO_3 = 6\ H_3\ PO_4 + 10\ Ca\ (NO_3)_2 + 2\ HF$$

While maintaining the molar ratio of $HNO_3 : CaO$, a known quantity of Morocco phosphate was decomposed by using 55% HNO_3, whereas with Trichy phosphate it could be accomplished with 30% acid, keeping the slurry temperature not exceeding 60°C during the course of digestion. Through mixing of phosphate was ensured by agitation and digestion was carried out for various duration of time viz., ½, 1, 1½, 2, 2½, 3, 3½ and 4 hours and the corresponding values of P_2O_5 extracted were evaluated. The results are presented in Table 2.

TABLE 2.

Phosphate	% P_2O_5 Total (0.1619 KOH)	% Nitric acid concentration	P_2O_5 extracted at the end of hours of digestion ½	1	1½	2	2½	3	3½	4	% Fe_2O_3 extracted at the end of 4 hour	% Al_2O_3 extracted at the end of 4 hour
Morocco	735	50%	640	675	695	715	725	730	750	750	—	—
	735	55%	635	680	695	720	730	730	730	—	—	—
	735	60%	640	690	700	720	730	730	—	—	—	—
Trichy	540	25%	405	475	495	510	510	520	525	530	0.42	0.23
	540	30%	405	485	500	510	515	625	530	535	0.44	0.25
	540	35%	410	485	505	520	525	530	530	535	0.50	0.25

Note: Tit values corrected to nearest 5 ml

At the end of reaction, the digested phosphate slurry was gently treated with calculated amount of processed potassium schoenite slurry containing about 0.15 g/ml to 0.25 g/ml of sulphate radical to precipitate calcium as calcium sulphate dihydrate (gypsum). The reaction possibly be represented as below:

$$2\,Ca\,(NO_3)_2 + [\,K_2SO_4 + (NH_4)_2\,SO_4 + 4\,H_2O + (Mg\,SO_4)\,] \rightarrow$$

(Processed Schoenite Solution)

$$2\,K\,NO_3 + 2\,NH_4\,NO_3 + 2\,Ca\,SO_4\,2\,H_2O + (Mg\,SO_4)$$

The above reaction can take place and $CaSO_4\ 2\ H_2O$ can be eleminated by maintaining the slurry pH between 1 and 1.6 and at a temperature not exceeding 60°C during the course of reaction.

The reaction was studied under varying conditions of dilution, temperature, concentration of the precipitant as well as its amount and also pH of the slurry. Further to addition of the precipitant, the slurry was allowed to stand for about 3 to 4 hours to permit additional calcium sulphate to precipitate and settle. The analysis of gypsum and filtrate under varying conditions are presented in Table 3.

The filterate containing phosphoric acid, Nitric acid, Ammonium sulphate, Ammonium nitrate and Magnesium sulphate, was neutralised carefully in the first stage till pH range of 2.5 to 3 0 is reached and finally the slurry was ammoniated slowly at pH maintained between 8 0 and 8 5 to yield Ammonium phosphate and Ammonium nitrate. The ammoniated slurry is evaporated to dryness to obtain a complete NPK fertilizer which analysed NO_3-N; NH_4-N; water soluble and citrate soluble P_2O_5, K_2O, CaO and MgO.

TABLL 3. *Analysis of Filtrate and Gypsum*

Temperature=50°C

Tith values corrected to nearest - 5.0 ml.

		Total P_2O_5		Total CaO		Filtrate				Gypsum			
						P_2O_5		CaO		P_2O_5		CaO	
		No. ml. Mor.*	KOH Tri.*	No. ml. Mor.	$KmnO_4$ Tri.	No. ml. Mor.	KOH Tri.	No. ml. Mor.	$KmnO_4$ Tri.	No. ml. Mor.	KOH Tri.	No. ml. Mor.	$KmnO_4$ Tri.
1. Theoritical quantity of sulphate and onepa rt by weight of phosphate and 10 part by volume of the slurry	2.0 pH	735	540	180	170	695	500	15	15	35	40	165	155
	1.5 pH	730	540	180	170	710	510	15	15	20	30	165	150
	1.0 pH	735	545	180	170	720	515	20	25	20	25	160	145
	0.5 pH	735	540	180	170	,730	530	35	35	10	20	145	140
2. Theoriticai quantity of sulphate and constant pH 1.0 with varying dilution	1:10	740	550	180	170	710	515	15	15	20	25	160	145
	1:15	735	535	180	170	720	610	25	25	20	25	155	135
	1:20	735	530	180	170	720	510	30	35	20	20	150	130
	1:25	730	540	180	170	720	510	40	40	20	25	140	125
3. With constant pH at 1.0 and dilution 1:10 and with varying sulphate ion concentration	1.0	735	540	180	170	725	510	20	20	25	20	155	145
	0.75	735	540	180	170	720	515	65	60	20	20	110	100
	0.5	740	530	180	170	720	515	100	95	20	25	75	65
	1.25	735	535	180	170	725	510	35	35	15	20	145	130

* Mor. Merocco - Phosphate   * Tri. Trichy - Phosphate

Chemical analysis of the fertiliser apart, the efficacy is best judged by its relative effect in out-yielding by a test crop, the test crop in this case being Ragi Co. 7. A pot culture experiment was conducted with NPK straight fertilizers (Ammonium sulphate, Super Phosphate and K_2SO_4). New complex N P K Fertiliser against NO fertilisers control. Significant superiority of the fertilisers in general and significance of New complex fertilisers over the rest in effecting grain yield was established in Table 4.

TABLE 4. *Yield of grain (g/pot.)*

Treatment	Grain (Average of 8 pots)	Percent increase over control	Percent increase over St. fertilisers
1. Control	10.5	100%	—
2. St. fertilisers	21.6	205%	100%
3. New complex soluble fertiliser (N.P.P.S.)	25.1	239%	112%

Statistical analysis conclusion

New complex fertiliser, St. fertiliser, Control

Results and Discussion: The Morocco and Trichy phosphates taken in this investigation contain 3.5 and 4.5 moles of CaO per mole of P_2O_5 respectively. The end product to contain water soluble P_2O_5, the CaO : P_2O_5 ratio must be held below two preferably below one to obtain nearly 100% water soluble P_2O_5. Hence approximately 60 to 100% CaO must be fixed and eliminated to obtain proportionate water soluble P_2O_5 in the final product. It is neither possible nor necessary to eliminate 100% calcium to obtain water soluble P_2O_5. The best results can be obtained, if the molecular ratio between the calcium and phosphate ions in the filtered slurry is maintained below one.

The isolation of calcium sulphate is an instance of fractional precipitation. Processed potassium Schoenite, an industrial by-product of salt industry contains a mixture of sulphates of Potassium, Ammonium and Magnesium, which when added to Acid Nitro-Phosphate slurry precipitates the sparingly soluble $CaSO_4$ – the salt of a strong acid. The precipitation of sparingly soluble sulphates should be rather less complete in strongly acid solutions than in neutral and alkaline solutions. This means that the solution pH cannot be ignored in precipitation of sulphates.

Similarly, the precipitation of phosphates – the salt of a weak acid is also determined by pH of the solution. Under an experimental condition of the above type actual pH at which, which of the sparingly soluble salt could be precipitated and others suppressed, can be calculated based on solubility product. Therefore, the need for a compromise pH range under the above situation, arises for suppressing phosphate prescipitation and precipitating $CaSO_4 2H_2O$. It was considered the final pH of 1 to 1.6 is optimal and not below 0.8 and not more than 1.8. At not too low concentration of sulphate ion and low pH (below 0 8) the formation of HSO_4 anion is favoured, resulting in incomplete precipitation of $CaSO_4 2H_2O$. If the pH is above 1.8, the chances of precipitation of di-and tri-calcic phosphates are high. Under these circumstances therefore, it is worth considering to keep HNO_3 to CaO ratio at 2 or within the range of 1.8 to 2.2.

When the acid strength was more than 55% as in the case of Morocco phosphate there is considerable loss of valuable oxides of N. It was then decided to have 55% HNO_3 In the case of Trichy phosphate, it was found that 30% gave the best results. This dilution is necessary because it helps to dissolve most of the calcium phosphate compounds but comparatively little of the undesirable oxides of iron and aluminium. In the case of Morocco phosphate more than 99% P_2O_5 was extracted within 2½ hours, whereas in the case of Trichy nodules only 98% of P_2O_5 could be extracted at the end of four hours.

The sulphate ion concentration is very important. Insufficient sulphate precipitant gives thin plate like crystals which are difficult to filter. About 1 to 2% above the optimum encourages good crystal formation which filters and washes well.

From relatively concentrated phosphate slurry, large crystals are formed and most of the calcium ions are fixed as $CaSO_4 2H_2O$.

When the slurry temperature goes above 60°C, the gypsum crystals start losing water of crystallisation and they do not filter and wash well. The ideal temperature for the formation of desirable quality gypsum is found to be 45°C to 55°C.

The precipitant must be added slowly in small instalments especially, at the start of precipitation to prevent super saturation by local high concentration of sulphate ions and accordingly precipitate must not be filtered for at least 2 to 3 hours after formation. The amount of unprecipitated Ca^{++} in the slurry depends on the concentration of the final Nitro-phosphate slurry. Higher the concentration, smaller the amount of Ca^{++} left behind.

The water soluble P_2O_5 can be controlled to vary widely by manipulating $CaO : P_2O_5$ ratio in the final product. Even when the ratio is kept low, other factors deserve special consideration. Under somewhat different conditions present here, for the precipitant carries a small percentage of divalent Magnesium, with the result Magnesium is converted into non-characteristic phosphates of varying compositions; when the slurry is ammoniated. This results in a portion of P_2O_5 remaining in a form rather not readily soluble in water. In reality the solubility in water is raised because of extensive hydrolysis of Magnesium phosphates.

As seen from Table 3, pH, determines $CaSO_4$ precipitation. As the pH decreases more and more calcium comes in the filtrate. This would suggest that a higher pH is to be preferred. But, again at pH value of 2.0, more phosphate coprecipitates along with gypsum. Similarly, as the dilution increases, the calcium concentration in the filtrate gradually increases. Finally by varying the concentration of sulphate ions, it is noticed, in-sufficient sulphate ion causes not only incomplete precipitation but gives thin plate like crystals which are difficult to filter. Excess sulphate ions cause the formation HSO_4^- ions and precipitation is incomplete. Not only that, excess sulphate ions also cause the formation of needle like clusters which are difficult to wash free of acids. One other interesting observation is that coprecipitation of phosphate is more in the case of Trichy phospoate, probably due to the presence of high percentage of oxides of iron and aluminium.

The preneutralisation of the slurry till a pH range of 2.5 to 3.0 is reached, helps to have highly buffered slurry and thus preventing the reversion of phosphate. Ammoniating, finally at pH range of 8.0 to 8.5 helps to have good quality product.

The pot-culture experiment has indicated the significant superiority of the fertiliser so prepared, in effecting grain yield. This superiority of the new fertilizer may at least, in part be ascribed to the presence of magnesium, an important secondary essential plant nutrient element, and also to the combined beneficial effects of readily available Nitrate-nitrogen, relatively slow acting Ammonical-nitrogen and water soluble phosphate for immediate response and citrate soluble phosphate for gradual release of phosphoric acid, all being present in the new complex fertilisers.

The process is flexible and with a few modifications a high analysis N : P : K fertiliser may be prepared. By adding H_3PO_4 acid to neutralise the processed schoenite slurry, a product with low $N : P_2O_5$ ratio is obtained, Advantage is taken of the fact that calcium can be removed from Nitro-phosphate slurry by the reaction of $SO_4^{=}$ ions of schoenite slurry. In fact, the removal of calcium sulphate forms the criteria of water soluble P_2O_5 in the final product.

Summary : In principle, this complex fertiliser production is based upon an initial decomposition of phosphae rock by diluted nitric acid to produce phosphoric acid and calcium nitrate. The original high Cao : P_2O_5 ratio is reduced by precipitating calcium as calcium sulphate by using processed

K schoenite, a double sulphate of potassium and magnesium; keeping the pH between 1.0 and 1.6 and filtered The filtrate is ammoniated in two stages. in the first stage till a pH range of 2.5 to 3 0 is reached and finally it is ammoniated till the pH range falls between 8.0 and 8.5. The ammoniated slurry is evaporated to dryness to obtain a complete N : P : K fertilizer. The fertiliser thus prepared contains the following :

Primary elements : (1) Water soluble phosphate for immediate response. (2) Citrate soluble phosphate for gradual release of phosphoric acid. (3) Quick acting Nitrate-nitrogen (4) Relatively slow acting ammonia-nitrogen (5) easily available potash.

Secondary elements : (1) Calcium (2) Magnesium and (3) Sulphur.

It is also possible to enrich fertiliser with micronutrients.

The above composition of the fertiliser renders it eminently suitable for short and long duration crops on acid, neutral and alkaline soils.

As can be seen from the above, this process has the following outstanding merits to recommend it.

(i) It saves a great deal of foreign exchange by dispensing with the use of sulphuric acid.

(ii) It renders possible the utilisation of low grade phosphate rock with high CaO : P_2O_5 ratio as in Trichy nodules.

(iii) The process is capable of producing high analysis complete fertiliser with varying degrees of water soluble P_2O_5.

(iv) All the raw materials including phosphate and schoenite required for the process are available indigenously.

Additionally the by-product gypsum obtainable from this process can be readily converted by the known methods into ammonium sulphate which independently by itself is a very valuable fertilizer. This also results in saving foreign exchange.