https://doi.org/10.29321/MAJ.10.A03723

Studies on the Reversion of P_2O_5 and Loss of N When Super is Mixed with Urea

by

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Introduction: The quality of mixed fertilizers, sometimes, suffer due to faulty mixing and also due to unfavourable physical and chemical changes of the fertilizer materials in the mixture, during storage. In recent years, super phosphate is being widely used in the fertilizer mixtures instead of using it as a straight phosphatic fertilizer. In the case of fertilizer mixtures containing urea, super phosphate and fillers like gypsum, it has been observed that there is a reduction in water soluble P_2O_5 on storage. A laboratory study was undertaken to see, how far the super phosphate is affected in its water soluble P_2O_5 content by mixing with urea and storing for a period of six months.

Review of Literature: Matson (1915) has shown that as the concentration of free phosphoric acid in super decreases with cure, the complex mono-basic acid probably changes to a water insoluble but citrate soluble calcium salt of the complex acid. Ross (1934) found that in the ammoniation of super, calcium phosphate more basic than tri-calcium phosphate will be formed and this may result in the loss of available phosphoric acid. Marshall and Hill (1940) concluded that citrate soluble phosphates result from the reaction of mono-basic acid which combines with calcium salts. Hardesty and Davis (1946) found that mixed fertilizers containing super, NO_3 and organic matter may develop high temperature leading to loss of N and reversion of P. Terman *et al* (1960) noted that heavy ammoniation decreased the water solubility of phosphorus from 70% to 14% in ordinary super and from 89% to 57% in concentrated super mainly due to the conversion of $CaHPO_4$ and more basic phosphates. Sirur and Saolapurkar (1962) indicated that prolonged storages of urea, super phosphate mixture leads to the reversion of water soluble phosphates to water insoluble di-calcium phosphotes. Mustafa (1964) observed the reversion of water soluble P_2O_5 and loss of Nitrogen in mixtures containing calcium ammonium nitrate, urea and super. Hardesty as quoted by Gas Ser (1964) stated that mono-hydrate and urea react to form urea phosphate, di-calcium phosphate and water. It also seems possible that urea may hydrolyse giving rise to free ammonia which combines with mono-calcium phosphate, converting it into di-calcic form.

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Received on 17—9—1965.

Material and Methods: Two mixtures of urea, super and gypsum with and without potassium were prepared in the ratios of 12:6:0 and 12:6:6 respectively. The mixtures were stored in polythene lined jute bags and kept under laboratory conditions for a period of six months, *i. e.*, from September, 1964 to February, 1965. Samples were drawn at periodic intervals of one month and analysed for the percentage of moisture, total nitrogen, total P_2O_5, water soluble P_2O_5 and available P_2O_5 and total K_2O as per A. O. A. C. methods and the results were statistically analysed.

Results: The results and data of statistical analysis are given in Table No. I and II.

Moisture: Moisture status during the period of storage varied significantly with the type of mixtures, eventhough the initial moisture status of the two mixtures did not vary significantly. There was a steap increase in the moisture content at 30th day and thereafter, the increase was progressive. The rate of increase of moisture in 12:6:6 mixture was significantly lower than 12:6:0 in the early stages. During 2nd and 3rd month, both the mixtures have shown significant difference in moisture content due to differences in the rate of increase of moisture.

Nitrogen: There were no variations in the nitrogen status in the mixtures. But there was a slight drop in 'N' status due to storage, the trend being equal in both the mixtures. This loss of nitrogen (*i. e.* 0·07%) due to storage for 6 months was significant at 1% level.

Total Phosphoric Acid: The total phosphoric acid in both the mixtures remained constant throughout the storage period of study.

Water Soluble P_2O_5: Both the mixtures showed a decreasing tendency in water soluble P_2O_5 content as the storage period advanced. In both the mixtures, there was a significant drop in water soluble P_2O_5 within 30 days and the rate of drop decreased gradually thereafter. Both the mixtures behaved similarly indicating that the addition of potasium as a K_2SO_4 has no significant effect on the reversion of water soluble P_2O_5.

Citrate Soluble P_2O_5: Citrate soluble P_2O_5 gradually got reduced during the storage period.

Citrate insoluble P_2O_5: Citrate insoluble P_2O_5 content gradually increased in both the mixtures as the storage period advanced.

Total Potasium: The potassium content of the mixture II (12:6:6) remained almost constant throughout the period of study.

TABLE I

Average Analytical data

Particulars	12:6:0 Mixture I (average for 4 replications)							12:6:6 Mixture II (average for 4 replications)							Mean for Two Mixtures
	Months							Months							
	0	1	2	3	4	5	Mean	0	1	2	3	4	5	Mean	
Moisture	3·49	8·01	8·21	8·25	8·34	8·38	7·44	3·46	7·62	7·85	8·21	8·31	8·37	7·30	7·37
N	13·47	12·47	12·45	12·44	12·43	12·41	12·45	12·47	32·46	12·44	12·42	12·41	12·39	12·43	12·43
TP	6·188	6·188	0·188	9·187	6·187	6·188	6·10	6·188	6·188	6·188	6·188	6-188	6 188	6·19	6·19
WSP	5·725	1·668	1·273	0·908	0·835	0·657	1·84	5·685	1·662	1·269	0·909	0·839	0·657	1·83	1·83
CSP	6·031	5·995	5·957	5·906	5·851	5·756	5 91	6·042	6·010	5 964	5·910	5 856	5 757	5·92	5·91
CIP	0·157	0 191	0·231	0·281	0·336	0·431	0·27	0 147	0 178	0·224	0·378	0·332	0·430	0·26	0·26
TK_2C	...	...	...	...	...	...	...	5·946	5·944	5·943	5·948	5 944	5·945	5·94	...

N = Total Nitrogen
TP = Total P_2O_5
WSP = Water soluble P_2O_5

C. S. P. = Citrate soluble P_2O_5
C. I. P. = Citrate insoluble P_2O_5
TK_2O = Total potash.

TABLE II

Results of Statistical analysis

Particulars	Significance at 1%			S. E.			C. D. (P = 0·05)		
	Between mixtures	Between period of storage	Interaction	Between mixtures	Between period of storage	Interaction	Between mixtures	Between period of storage	Interaction
Moisture	Yes	Yes	Yes	0 0277	0·0482	0·0682	0 0816	0·1421	0·2009
Nitrogen	No	Yes	No	0·0071	0·0123	0·0173	...	0 0363	...
Total P	No	No	No	0·0001	0·0003	0·0004	...	...	...
W. S. P.	No	Yes	No	0·0100	0·0179	0·0255	...	0 0528	...
C. S. P.	No	Yes	No	0·0071	0·0123	0·0173	...	0·0363	...
C. I. P.	No	Yes	No	0·0074	0.0123	0.0173	...	0·0363	...

Since citrate soluble P_2O_5 includes water soluble P_2O_5 also; the analysis of these two components is given in table below:

Month	Citrate soluble P_2O_5			Citrate insoluble P_2O_5	Decrease in water soluble P_2O_5	Increase in water insoluble P_2O_5	Increase in citrate insoluble P_2O_5
	WSP %	WISP %	Total %				
1.	5·70	0·34	6·04	0·15	...	...	...
2.	1·67	4·33	6·00	0·18	4·03	3·99	0·03
3.	1·27	4·69	5·96	0·23	0·40	0·36	0·05
4.	0·91	5·00	5·91	0·28	0·36	0·31	0·05
5.	0·84	5·01	5·85	0·33	0·07	0·01	0·05
6.	0·66	5·10	5·76	0·43	0·18	0·09	0·10

The water soluble fraction (WSP) decreased from 5·7 to 1·7% in the first month amounting to 70% reversion. Almost the same amount increased in the water insoluble fraction (WISP) of citrate soluble P_2O_5. The conversion of citrate soluble P_2O_5 to citrate insoluble, occurring side by side was a very slow reaction.

Discussion: Super mixed with urea, therefore, reduces the critical relative humidity and enhances the moisture absorption by urea. Gypsum and potasium sulphate have no effect on critical relative humidity. The results of experiment also show that in super-urea mixtures, there is greater absorption of moisture.

The rate of reversion is not influenced by addition of K_2SO_4 indicating that the reversion mainly takes place as homogenous reaction phase consisting of saturated liquid phase created by the absorption of moisture. There are good evidences for the formation of urea phosphate at temperature above 30°C and relative humidity 64·5 per cent, which hastens the reversion of water soluble phosphorus. The reactions involved are:

$$\mathrm{Ca\,(H_2PO_4)\,H_2O \rightleftharpoons CaHPO_4 + H_3PO_4 + H_2O} \qquad (1)$$

$$\mathrm{H_3PO_4 + CO\,(NH_2)_2 \longrightarrow CO\,(NH_2)_2\,H_3PO_4} \qquad (2)$$

$$\mathrm{Ca\,(H_2PO_4)_2\,H_2O + CO\,(NH_2)_2 \longrightarrow CaHPO_4 + CO\,(NH_2)_2\,H_3PO_4 + H_2O}$$

The step (1) involving the equilibrium of two phosphates occur in a saturated solution of super. At temperature of about 30°C the equilibrium composition is about 53 per cent of mono-hydrogen phosphate. In presence of urea the equilibrium is shifted towards left. The time for half reversion is studied and hence the step (1) is not a rate determining step. A bimolecular reaction rate is fitted and found to agree with the rate of reversion.

Fitting bimolecular reaction equation,

Relative molar concentration of urea as N/2% = 6·0

Relative molar concentration of Super as P_2O_5% = 9·0

Time in months	P_2O_5% (a−x)	x	$K = \frac{1}{at}$	$\frac{x}{a-x}$	% of water soluble P_2O_5
22 hrs.	5·7	0·3	0·29		100
1·3	1·7	4·3	0·32		30
2	1·3	4·7	0·30		23
3	0·9	5·1	0·32		15
4	0·8	5·2	0·27		14
5	0·7	5·3	0·28		12

Average = 0·30

a = initial concentration of Super

x = fraction which has undergone change

t = time

K = Reaction constant.

Time required for different percentage of reversion :

% of reversion	5%	10%	25%	50%	75%
Time required	16 hours	44 hours	6 days	17 days	50 days

For five per cent reversion, the time needed is calculated and it is found to be about 16 hours, and therefore, the urea super mixture has to be used immediately and the reversion is difficult to be controlled at the relative humidity and temperature prevailing in the tropical conditions. The reversion of citrate soluble to insoluble fraction takes place slowly but the reaction seems to be complicated, perhaps with many side reactions as the rate goes on increasing with the period of storage. The mechanism is therefore, complicated, but within the period of storage studied, the reversion amounts only to 1·7 per cent which amounts 0·1 per cent of P_2O_5 in a mixture containing 6 percent P_2O_5. Therefore, the reversion of citrate soluble to citrate insoluble portion is not a problem in the mixture studied.

Summary and Conclusion: The reversion of super when mixed with urea was studied in polythene lined jute bags. The following results are obtained:

1. The moisture increased rapidly at 30th day and thereafter progressively. K_2SO_4 has no effect on moisture absorption.

2. The decrease in water soluble P_2O_5 to C. S. P. is more than the reversion of C. S. P. to insoluble form. Five per sent reversion to C. S. P. form occurs within 16 hours of mixing and 50 per cent reversion occur within 17 days.

3. The reversion of water soluble P_2O_5 to citrate soluble P_2O_5 appears to occur through the formation of urea phosphate on a bimolecular reaction. It appears also to be difficult to control reversion of water soluble phosphate at the relative humidity and temperature prevailing in the tropical condition in urea-super mixture. Therefore, the degree to which concentrate form like urea can be substituted for ammonium sulphate or mixtures with super requires further studies.

4. The reversion of citrate soluble P_2O_5 to insoluble phosphorus takes place slowly and amounts to only 1·7 per cent and hence not a problem under the conditions prevailing during the storage.

So, the results indicate that the urea-super mixture cannot be stored without reversion and such reversion will be minimised, if the mixture is used soon after it is made. The reversion may be minimised by changing the fillers or by adding urea in small proportions in the mixture.

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