

# THE EFFECT ON THE CITRIC SOLUBILITY OF LANGEBAAN PHOSPHORITE (LANGEBAAN PHOSPHATE ROCK) WHEN COMPOSTED WITH FILTER CAKE

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## 1.—Abstract.

Dymond's 1951 compost experiments with filter cake and Langebaan phosphate rock were continued in 1952. Composting increased the citric solubility of the phosphoric oxide in the rock, although not to the same extent as in the 1951 experiments. Citric solubility decreased with increasing quantities of phosphate rock. Field trials on sugar cane in Natal have been initiated to determine the availability of the phosphoric oxide mixtures of Langebaan phosphate rock and filter cake after composting.

The effect of readily-soluble calcium compounds in filter cake on the citric solubility of Langebaan phosphate rock is discussed.

The addition of small percentages of formic acid to the composting mixtures did not increase the solubility of the phosphate rock.

## 2.—Introduction.

Experiments conducted by G. C. Dymond in 1951, showed that the citric solubility of "Langfos" could be increased by composting with filter cake. (Krumm, 1952a). Other waste products of the Sugar Industry, such as cane trash, did not give the same effect. To determine, therefore, whether the results obtained with filter cake could be reproduced, Dymond decided to carry out a further series of experiments in 1952.

The experimental technique employed in 1951 was not changed.

The 1952 experiment, however, was modified as follows:

- (1) Langebaan phosphorite was used instead of "Langfos". Chemically and mineralogically, these two materials are the same, but the phosphorite is lower in phosphoric oxide.
- (2) The number of mixtures was increased from two to four, the additional mixtures containing 15 per cent. and 40 per cent. of phosphorite, respectively.
- (3) Small percentages of formic acid were added to a separate series of three mixtures. Each contained 20 per cent. of phosphorite.

The results of Dymond's 1952 experiments revealed that the increase in citric solubility of the phosphoric oxide was smaller than that obtained in 1951. This cannot be attributed to the use of Langebaan phosphorite in place of "Langfos", but rather to variations in the composition of the filter cake.

The importance of the results, however, lies in the fact that a change did occur, and that it was due almost entirely to an increase in the citric phosphate solubility of the Langebaan phosphorite. It is probable that this change is of more significance than the figures tend to show, particularly in view of the limitations of the citric acid method for determining availability. (Krumm, 1952b). A field trial, recently laid out at Kearsney in Natal, using composted mixtures of filter cake and Langebaan phosphorite, and planted to sugar cane, should help to elucidate this point.

In the formic acid series, the increase in citric solubility of the phosphorite was no larger than that of the control.

In the 1951 experiments, the citric solubility of the "Langfos" "actually found", was lower than the corrected figures. This difference has now been clarified.

### 3.—Materials.

#### (a) Langebaan Phosphorite.

At Langebaan Road, Cape Province, large quantities of phosphate rock occur which cannot normally be marketed as "Langfos", owing to its low phosphoric oxide content. It ranges from 9 to 15 per cent., whereas "Langfos" has been registered at 17 per cent. phosphoric oxide with the Department of Agriculture. It could, however, be classed as a Group II Fertilizer. Dymond used this material, in place of "Langfos", in his 1952 experiments.

#### (b) Formic Acid.

The citric solubility of phosphoric oxide in mixtures of compost and phosphate rock, is stated to increase in the presence of stinging nettles. (Kolisko). Stinging nettles contain formic acid. Dymond decided to include formic acid in a series of mixtures to ascertain whether this could be used as a substitute for stinging nettles.

#### (c) Filter Cake.

TABLE 1.

Composition of the Langebaan phosphorite (A) and filter cake (B) used.

	A per cent.	B per cent.
Water at 105°C. ...	1.54	76.9
Loss on ignition (105-900°C.) ...	2.21	14.9
Phosphoric oxide (total) ...	15.8	0.53
Water-soluble phosphoric oxide...	Nil	Trace
Citric-soluble phosphoric oxide ...	6.9	0.48
Calcium oxide (total) ...	21.5	2.12
Water-soluble calcium oxide ...	Nil	0.70
Citric-soluble calcium oxide ...	10.2	2.01
Calcium oxide as lime ...	0.58	—
Iron oxide ...	1.9	—
Aluminium oxide ...	1.4	—
Fluorine ...	1.7	—
Insolubles ...	52.9	2.34
Fineness retained on 90 mesh		
I.M.M. ...	5.6	—
retained on 200 mesh		
I.M.M. ...	36.0	—

Note.—The phosphoric oxide content of the Langebaan phosphorite used in these experiments was slightly higher than the normal run of this material.

### 4.—Experiments and Results.

The following mixtures were made:

No.	Mixture.		Series I. Period of Composting.
	% A	% B	
(i)	10	90	25/9/52 to 24/12/52, 3 months.
(ii)	15	85	25/9/52 to 24/12/52, 3 months.
(iii)	20	80	25/9/52 to 24/12/52, 3 months.
(iv)	40	60	25/9/52 to 24/12/52, 3 months.

### Series II.—Formic Acid.

20 per cent. A and 80 per cent. B.

No.	Formic Acid Per cent.	Period of Composting.
(i)	Control (No formic acid)	6/10/52 to 23/12/52, 2 mths. 18 days.
(ii)	0.10	6/10/52 to 23/12/52, 2 mths. 18 days.
(iii)	0.26	6/10/52 to 23/12/52, 2 mths. 18 days.
(iv)	0.62	6/10/52 to 23/12/52, 2 mths. 18 days.

In the tables below the figures before and after composting are given. The analysis was carried out on the air-dried samples, but the results of each experiment have been calculated on a water-free basis.

Wagner's method was employed for determining citric soluble. (5 gms. shaken with 495 mls. 2 per cent. citric acid for 30 minutes.)

TABLE 2a.—Series I.

Before Composting.

	P <sub>2</sub> O <sub>5</sub> total Per cent.	P <sub>2</sub> O <sub>5</sub> citric soluble Per cent.	Cit. sol. total P <sub>2</sub> O <sub>5</sub> ratio Per cent.	Loss on ignition Per cent.
Original Material B	2.30	2.08	90.4	64.7
Mixture ...	5.82	3.54	60.8	50.5
(ii) ...	6.85	4.05	59.1	41.2
(iii) ...	7.41	4.35	58.7	35.0
(iv) ...	10.40	5.69	54.7	23.4

TABLE 2b.—Series I.

After Composting.

	P <sub>2</sub> O <sub>5</sub> total Per cent.	P <sub>2</sub> O <sub>5</sub> citric soluble Per cent.	Cit. sol. total P <sub>2</sub> O <sub>5</sub> ratio Per cent.	Loss on ignition Per cent.
Original Material B	3.92	3.61	92.1	42.5
Mixture (i) ...	6.81	4.68	68.7	25.9
(ii) ...	7.66	4.98	65.0	22.4
(iii) ...	8.21	5.24	63.8	19.2
(iv) ...	10.44	5.86	56.1	15.5

TABLE 3a.—Series II.—Formic Acid.

Before Composting.

	Formic Acid Per cent.	P <sub>2</sub> O <sub>5</sub> total Per cent.	P <sub>2</sub> O <sub>5</sub> citric soluble Per cent.	Cit. sol. total P <sub>2</sub> O <sub>5</sub> ratio Per cent.	Loss on ignition Per cent.
(i) Control (No formic acid)		7.45	4.48	60.1	39.9
(ii) 0.10 ...	0.10	7.82	4.97	63.4	35.8
(iii) 0.26 ...	0.26	7.21	4.82	66.9	37.3
(iv) 0.62 ...	0.62	7.50	4.78	63.7	32.7

TABLE 3b.—Series II.—Formic Acid.

After Composting.				
Formic Acid Per cent.	P <sub>2</sub> O <sub>5</sub> total Per cent.	P <sub>2</sub> O <sub>5</sub> citric soluble Per cent.	Cit. sol. total P <sub>2</sub> O <sub>5</sub> ratio Per cent.	Loss on ignition Per cent.
(i) Control (No formic acid)	8.37	5.44	65.0	21.4
(ii) 0.10 ...	8.60	5.51	64.1	21.6
(iii) 0.26 ...	8.83	5.71	64.7	21.8
(iv) 0.62 ...	8.29	5.41	65.3	21.6

The concentration of Formic acid used in the above experiment appeared to have had no significant effect on composting.

### 5.—Discussion.

#### (a) Citric solubility changes during composting.

It must be clearly understood that when comparing the results of citric acid soluble phosphate, before and after composting, two important factors have to be taken into account, namely:

- (1) Loss of organic matter during composting. (This is reflected in the "Loss on ignition" figures in the tables.) The percentage of mineral matter is, therefore, increased as the organic matter disappears.
- (2) Citric solubility is a function of the percentage of phosphorite in the 5-gm. samples taken for the determination. (Krumm, 1952a). Table 4 reflects this function.

TABLE 4.

Weight "Langfos" taken Gms.	Phosphoric oxide soluble in 2 per cent. citric acid. Per cent.	Citric soluble total phosphoric oxide ratio. Per cent.
0.25	16.5	97.1
0.50	15.4	90.6
1.00	14.0	82.4
2.00	11.8	69.4
3.00	9.7	57.1
4.00	8.0	47.1
5.00	6.8	40.0
6.00	6.0	35.3
7.00	5.4	31.8
8.00	4.8	28.3
9.00	4.4	25.9
10.00	4.0	23.5

TABLE 5.

Figures are given on a water-free basis.

Mixture.	Wt. phosphorite in 5 gms. mix Gms.	Cit. sol. corrected (Table 4)	Cit. Sol. actually found.	apparent change in Cit. sol.
<i>Before Composting</i>				
(i)	0.8850	87.5	46.6	—
(ii)	1.4435	78.0	49.3	—
(iii)	1.8405	71.5	51.0	—
(iv)	2.6655	60.7	50.6	—
<i>After Composting</i>				
(i)	1.6085	75.0	53.7	+ 7.1
(ii)	2.1221	67.5	53.2	+ 3.9
(iii)	2.3375	64.7	54.3	+ 3.3
(iv)	2.8000	59.2	49.0	— 1.6

The reason for the differences between the corrected Cit. Sol./Total P<sub>2</sub>O<sub>5</sub> ratios (citric solubility) and those actually found will be discussed below.

The citric solubility of mixture (iv) appears to have decreased. This probably represents no change, as the corrected figures clearly show that citric solubility diminishes with increasing weight of phosphorite. Therefore, since the amount of phosphorite is greater in the 5-gm samples after composting, it would appear that:

- (1) The decrease in citric solubility of the phosphoric oxide in the Langebaan phosphorite in mixture (iv) probably represents no change.
- (2) The increase in citric solubility of the phosphoric oxide in the Langebaan phosphorite in mixtures (i), (ii) and (iii) is probably greater than the analytical figures would appear to show.

#### (b) The Effect of Readily-Soluble Calcium Compounds in Filter Cake on the Citric Solubility of Langebaan Phosphate Rock.

Differences between the corrected citric solubility figures and the amounts actually found were first observed in Dymond's 1951 experiments. The reasons were not then understood. Work carried out in 1952, however, showed that the citric solubility of Langebaan phosphate rock is depressed by the presence of readily-soluble calcium compounds in filter cake. This effect will now be described.

It has been shown (Krumm, 1952b), that:

- (1) The addition of calcium ions depresses the citric solubility of the phosphoric oxide in Langebaan phosphate rock.
- (2) Citric solubility is a function of the pH.



TABLE 6.  
Series I.—After Composting.  
24.12.52.

	Original Material B Per cent.	Mixtures of A + B			
		(i) Per cent.	(ii) Per cent.	(iii) Per cent.	(iv) Per cent.
Total calcium oxide ...	15.10	15.12	14.77	15.66	17.99
Calcium oxide from filter cake ...	15.10	10.24	9.01	8.04	6.64
Calcium oxide from phosphorite ...	—	4.88	5.76	7.62	11.35
Total Citric soluble calcium oxide ...	14.43	12.19	11.89	11.51	11.75
Citric soluble calcium from filter cake oxide	14.43	9.79	8.61	7.68	6.35
Citric soluble calcium oxide from phosphorite	—	2.40	3.28	3.83	5.40
pH of citric acid after shaking ...	2.55	2.55	2.60	2.60	2.60

Table 6 shows that:

- (1) Calcium contained in the filter cake was readily soluble in 2 per cent. citric acid.
- (2) The citric solubility of the Langebaan Phosphate Rock was inhibited when the concentration of calcium oxide in solution reached 11.8 per cent. and the pH rose to 2.55—2.60.

It would appear, therefore, that when a mixture of filter cake and Langebaan phosphate rock is shaken with 2 per cent. citric acid, readily-soluble calcium compounds in the filter cake pass rapidly into solution. A relatively high concentration of adventitious calcium ions as this established, and the solubility of the calcium compounds of phosphorus in Langebaan phosphate rock is, therefore, suppressed.

#### 6.—Conclusions.

The citric solubility of Langebaan phosphorite increased when composted with filter cake. The change was small, but was probably greater than the analytical figures would tend to indicate. The Wagner method (citric solubility) was used to determine the solubility of the phosphorite before and after composting, but it would appear to have very definite limitations in this respect.

The increase in citric solubility was not as great as in the 1951 experiments. This could be ascribed to variations in the composition of the filter cake.

It is anticipated that experiments will be continued, probably along new lines. It would appear that a more reliable method for determining changes in solubility of the phosphate is indicated.

#### Acknowledgments.

I have to thank Mr. C. W. Sharp, General Manager, African Metals Corporation, and Mr. C. F. Muller, Works Manager, Bellville Fertilizer Works, for permission to publish this paper.

#### REFERENCES.

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<sup>2</sup>Krumm, H. E. The effect on the citric solubility of "Langfos" when composted with waste products of the sugar industry. Proc. 26th Congress S.A.S.T.A., 1952, 100-105.

<sup>3</sup>Krumm, H. E. The limitations of the Wagner method (citric solubility) when applied to rock phosphate. S.A. Journal of Science, 49, 1953, 197-204.

#### APPENDIX.

by G. C. Dymond.

Two series of composting experiments with low grade rock phosphate have now been completed and the results analysed by Mr. Krumm.

Observations on the behaviour of filter cake under aerobic and anaerobic conditions necessitate the continuance of these experiments before any finality can be reached.

In the experiments reviewed by Mr. Krumm the following figures are of interest:—

The amount of filter cake taken for each experiment was 1,800 lb.

No.	Wt. of Lang-fos lbs.	Total Wt.	After 3 mths.	Moisture Free.		Moisture Free.		% Wt. ost l
				% organic matter original	% ash	% organic matter after 3 months	% ash	
1.	Nil	1800	1008	64.65	35.58	42.50	57.51	44.0
2.	176	1076	1278	50.50	49.50	25.93	74.10	35.3
3.	264	2064	1443	41.15	58.83	22.37	77.55	30.1
4.	352	2152	1532	34.97	65.12	19.23	80.85	38.8
5.	704	2504	1930	23.42	76.60	15.50	84.65	22.9

During the period of three months the heaps were turned four times. Monthly averages showed a regular trend in the loss of organic matter and slow drop in temperature and pH values.

The range of temperature was from 58°C. to 38°C. and the pH from 8.0 to 6.8.

It was obvious that in general the decomposition was mostly anaerobic, except in the top layers.

A nauseous smell of putrefaction with sulphuretted hydrogen was very noticeable on each turning.

A further series of experiments on filter cake, given in the paper on Clarification showed that an intensive aerobic treatment gave essentially different results from a similar experiment under strictly anaerobic conditions.

Under the former there was a progressive but slow drop in moisture and organic matter with temperatures rising to 75°C. The loss of cane wax under these conditions was over 70 per cent.

Under anaerobic conditions, there was no loss in either moisture or organic matter; temperatures never rose above 55°C. and the loss in wax was less than 20 per cent.

Unfortunately no pH values were recorded, but as Mr. Krumm points out, "a relatively high concentration of adventitious calcium ions is established and the solubility of the calcium compounds of phosphorus in Langebaan phosphate rock is, therefore, suppressed."

It appears probable, therefore, that the high calcium content of filter cake is a major factor influencing the pH values during composting and therefore the increase in availability.

Future work will be conducted along the lines indicated above.

**Mr. Dymond** said he thought the experiments he had started with Mr. Krumm were worth continuing. When one considered the vast amount of filter cake available and the equally vast amount of low grade phosphate, it might be possible to improve the availability of supplies that would give a greater amount of  $P_2O_5$  to planters. There was ample literature to indicate how quickly available  $P_2O_5$  became fixed in the soil and he felt that this question of fixation might be overcome by the series of experiments he and Mr. Krumm had conducted. Mr. Dymond said they were indebted to the Experiment Station for taking up this work and co-operating with the author and himself. He hoped the results would be made available in due course.

**Mr. Rault** asked whether Mr. Dymond had had occasion to use filter cake from the carbonatation process. This cake contained a certain amount of free alkalinity and its pH was decidedly higher than that of the filter cake of sulphitation factories—namely, about ten.

**Mr. Dymond** said he had not. He added that he had made the point already that the pH of filter cake was high. He had unfortunately not kept the pH values of the tests on filter cake under aerobic and anaerobic conditions, but he felt this point was well worth investigating.

**Mr. Pearson** expressed doubt whether any marked yield results would be obtained from the experiments being conducted by the Experiment Station. Various trials had been laid down including the ones with Langebaan phosphate. He gave details of some results obtained on plant cane. The tonnages of cane per acre suggested that the results obtained

from raw rock and Langfos did not measure up to the results obtained from super phosphate. He doubted whether any material difference would be found between the results from filter cake and from composted rock phosphate.

**Mr. Main** asked where Mr. Pearson had got the filter cake for his experiments. His point was that filter cake varied considerably in composition. Filter cake from the carbonatation process at Natal Estates near the Experiment Station would be totally different from that of a sulphitation process mill. Here also there would be different filter cake analysis where raw sugar was being produced without phosphates as against that from a sulphitation mill producing White Sugar where there would be, probably, a high  $P_2O_5$  content.

**Mr. Pearson** replied that the filter cake came from the Gledhow-Chaka's Kraal mill and was rather high in pH.

**Mr. Dymond** said the type of filter cake used must, in his view, affect the yields obtained in the field. The object of this experiment was to take an insoluble material and increase the availability from a non-soluble to a more soluble material surrounded by organic matter.

**Mr. Palairt** asked whether the composting was done with filter cake only or with other materials.

**Mr. Dymond** said that concentration had been on the use of filter cake.

**Mr. Palairt** said that according to recent experiments, fixation was prevented and phosphates again rendered available in the soil by the addition of compost. As a result of these experiments he had applied phosphates mixed with compost on a soil rich in iron. Although this was not done under experimental conditions, the increase in the yield under these conditions was tremendous. He felt that press cake alone made too alkaline a compost and if trash was used as well the lower pH would help to remove calcium ions and so increase the availability of the phosphates.

**Mr. Dymond** said the experiment was still in an early stage and he hoped that results at Kearsney would throw further light on the work being done. He asked for a vote of thanks to Mr. Krumm for his paper.