

THE EFFECT ON THE CITRIC SOLUBILITY OF 'LANGFOS' WHEN COMPOSTED WITH WASTE PRODUCTS OF THE SUGAR INDUSTRY.

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I.—Introduction.

In 1951, G. C. Dymond, in a communication to the South African Sugar Technologists' Association,¹ showed how the phosphate content of waste organic material could be improved by composting with Langebaan phosphate rock ("Langfos"). Describing a series of experiments carried out in 1950, he gave figures to illustrate that—

- (1) The total phosphoric oxide content of the composting mixtures was considerably increased.
- (2) The citric solubility (referred to as "availability" in his communication) of the "Langfos" itself appeared to increase during the process.

A scrutiny of the results, however, revealed that the samples taken at the beginning of the experiment were not representative and made the analytical figures unreliable. Dymond, therefore, decided to repeat the experiment in 1951, eliminating where possible factors which might vitiate the figures.

One feature of the 1950 experiments which augured well for future tests was the fact that the addition of "Langfos" to the composting materials did not appear to inhibit the breakdown of the organic matter. In no instance did the temperature fall below that of the control, an effect not always observed in the past.

2.—Citric Solubility.

(a) **General.** Before describing Dymond's 1951 experiments, the terms "availability" and "citric solubility" will be elucidated.

It is customary to state the availability of a phosphatic fertiliser in terms of its solubility in a 2 per cent. solution of citric acid. One fertiliser is said to be more available to plants than another if its solubility in citric acid is higher. On these grounds, a basic slag with a citric soluble phosphoric oxide content of 18 to 19 per cent. would be at least two and a half times as available as "Langfos" with 7 per cent citric soluble phosphoric oxide.

The use of citric acid as a criterion of availability was introduced by P. Wagner during the last century, and used by him to detect adulteration in basic slag. As such, nothing against its use has ever been brought forward but, as G. S. Robertson² pointed out in 1914, the subsequent interpretations placed on its use as a test for the availability of rock phosphate are unjustified.

He showed, for instance, that over a period of three years, experimental plots treated with Tunisian phosphate and basic slag gave very similar yields.

Plots 1/20 acre.	Three years' ley.	Average yield of hay for 3 years/ acre.
1.	750 lbs. Tunisian phosphate (total 59.99 per cent. phosphate of lime, trace citric soluble)	37½
2.	1,200 lbs. basic slag (total 35.89 per cent. phosphate of lime), 95 per cent. citric soluble)	38¼
3.	Control (no phosphate))	33¼

Robertson concludes by stating that these figures demonstrate the worthlessness of the citric acid test as a means of judging the relative value of phosphatic manures to the plant.

Experiments in this country on "Langfos" rock phosphate have shown that its citric solubility is not correlated with crop production and substantiate Robertson's conclusions.

It is well known that the citric solubility (so-called availability) test does not take into account—

- (1) Type of crop grown.
- (2) Nature of soil.
- (3) Climatic conditions.

It might be asked, why was the citric acid method retained in the experiments on "Langfos" and compost? The reasons are:—

- (1) It is the legal method in the Union of South Africa for determining the availability of a phosphatic fertiliser, and for this reason very extensive investigations were carried out on "Langfos."
- (2) Increase in citric solubility or citric soluble phosphate indicates a change to a more soluble form (*cf.* manufacture of superphosphate from rock phosphate and sulphuric acid).

2 (b) **Citric Solubility:** A function of the actual amount of rock phosphate taken for determining availability.

In the official method for determining availability the amount laid down is 5 gms./495 millilitres 2 per cent. citric acid.

It was found that when varying amounts of "Langfos" were taken, namely, from 0.25 gm. to 10 gms. the citric soluble/total phosphoric oxide was a function of the actual amount taken for analysis. Table 1 reflects this function.

TABLE 1.

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

These results are shown on the graph.

It is obvious, therefore, that the citric soluble/total phosphoric oxide ratio, in the experimental work that follows, is dependent on the actual amount of "Langfos" rock phosphate contained in 5 gms. of each of the mixtures (i)—(vi).

3.—Experimental Work.

Early in 1951 a series of experiments were carried out on the composting of (A) "Langfos" (as marketed) with the following: (B) mixture of cane trash, 18 per cent., and cattle manure 82 per cent. and (C) filter cake.

The composition of A, B and C were as follows:—

TABLE 2.

	A. Per cent.	B. Per cent.	C. Per cent.
Water at 105°C.	1.4	54.0	74.3
Loss on ignition (105-900°C.)	2.5	29.4	12.8
Phosphoric oxide (total)	17.0	0.40	0.50
Citric soluble phosphoric oxide	7.0	0.37	0.43
Calcium oxide (total)	25.8	—	—
Calcium oxide as lime	1.1	—	—
Iron oxide	3.2	—	—
Aluminium oxide	1.6	—	—
Fluorine	1.8	—	—
Insolubles (silica, etc.)	49.2	12.7	3.8
Fineness: retained on 90 mesh	14.0	—	—
retained on 200 mesh	45.0	—	—

The following mixtures were made:—

No.	Mixture Per cent. Per cent.	
(i)	5 A, 95 B	26/4/51 to 26/7/51, 3 months.
(ii)	10 A, 90 B	26/4/51 to 26/7/51, 3 months.
(iii)	20 A, 80 B	26/4/51 to 26/7/51, 3 months.
(iv)	25 A, 75 B	26/4/51 to 26/7/51, 3 months.
(v)	10 A, 90 C	25/5/51 to 9/8/51, 3 months 15 days.
(vi)	20 A, 80 C	25/5/51 to 9/8/51, 3 months 15 days.

In the table below the figures before and after composting are given. For the sake of convenience, the analytical results of each experiment have been calculated on a water-free basis.

TABLE 3A.—BEFORE COMPOSTING.

	P ₂ O ₅ total. Per cent.	P ₂ O ₅ citric soluble. Per cent.	Citric solu- bility. Per cent.	Loss on ignition. Per cent.
Original material B.	0.87	0.80	—	63.9
C.	1.94	1.67	—	49.9
Mixture (i), A+B	1.95	1.61	82.6	56.6
(ii), A+B	3.12	2.34	75.1	49.9
(iii), A+B	4.85	3.05	62.8	39.2
(iv), A+B	6.22	3.64	58.6	38.0
(v), A+C	5.67	3.40	60.0	37.8
(vi), A+C	8.42	4.21	50.0	31.4

TABLE 3B.—AFTER COMPOSTING.

	P ₂ O ₅ total. Per cent.	P ₂ O ₅ citric soluble. Per cent.	Citric solu- bility. Per cent.	Loss on ignition. Per cent.
Original material B.	1.34	1.05	—	48.2
C.	2.52	2.37	—	50.7
Mixture (i), A+B	3.25	2.29	70.5	38.5
(ii), A+B	4.46	3.02	67.6	32.6
(iii), A+B	6.98	4.14	59.4	30.7
(iv), A+B	7.55	4.32	57.2	28.0
(v), A+C	6.42	4.87	76.0	36.0
(vi), A+C	9.18	5.74	62.6	26.2

The apparent increase in the phosphate figures is due to the loss on ignition being lower after composting than before.

From an examination of Table 3 it will be observed that mixtures (i)—(iv) (A+B experiments) show an apparent decrease in citric solubility, whereas in the case of (v) and (vi) (A+C experiments) a substantial increase is noted.

Dymond's 1951 series of experiments were concerned, chiefly, with changes in the citric solubility of A ("Langfos") during composting. It will be shown below that—

- (1) No change in the citric solubility of the "Langfos" itself took place in the A+B experiments.
- (2) The citric solubility of the "Langfos" when composted with C increased from
 - (a) 51 per cent. to 69 per cent. in the case of (v).
 - (b) 46 per cent. to 58 per cent. in the case of (vi).

In paragraph 2 (b) it was shown that citric solubility is a function of the actual weight taken. In order to assess the true nature of the changes in citric solubility, the individual weights of A ("Langfos"), as well as the composting substances contained in 5 gms. of the mixture, have to be taken into account.

Experiments in the variation of the citric solubility with the weights taken of the two composting substances, B and C have indicated that in both cases this factor is not significant. It is necessary, therefore, to apply this correction only for "Langfos." (See graph.)

When this correction is applied to the actual amount of "Langfos" in the 5 gm. samples taken for the citric solubility in the series (i)—(vi) the corrected figures, before and after composting respectively, were as follows:—

(i) 94.2 and 88.4 per cent.	(iv) 73.0 and 69.6 per cent.
(ii) 86.5 and 82.2 per cent.	(v) 79.0 and 77.4 per cent.
(iii) 79.0 and 72.0 per cent.	(vi) 66.4 and 65.0 per cent.

The amounts actually found, however, were:—

(i) 77.0 and 66.0 per cent.	(iv) 55.5 and 54.8 per cent.
(ii) 70.5 and 65.3 per cent.	(v) 51.5 and 68.8 per cent.
(iii) 59.1 and 56.6 per cent.	(vi) 45.6 and 57.6 per cent.

4.—Conclusions.

The reasons for the differences between the corrected figures and the amounts actually found are not understood, but it is clear that—

- (1) The citric solubility of the "Langfos" remained unchanged when composted with the mixture of cane trash and cattle manure.
- (2) During the composting of "Langfos" with filter cake an increase in the citric solubility of the "Langfos" has been effected.

It is anticipated that experiments will be continued.

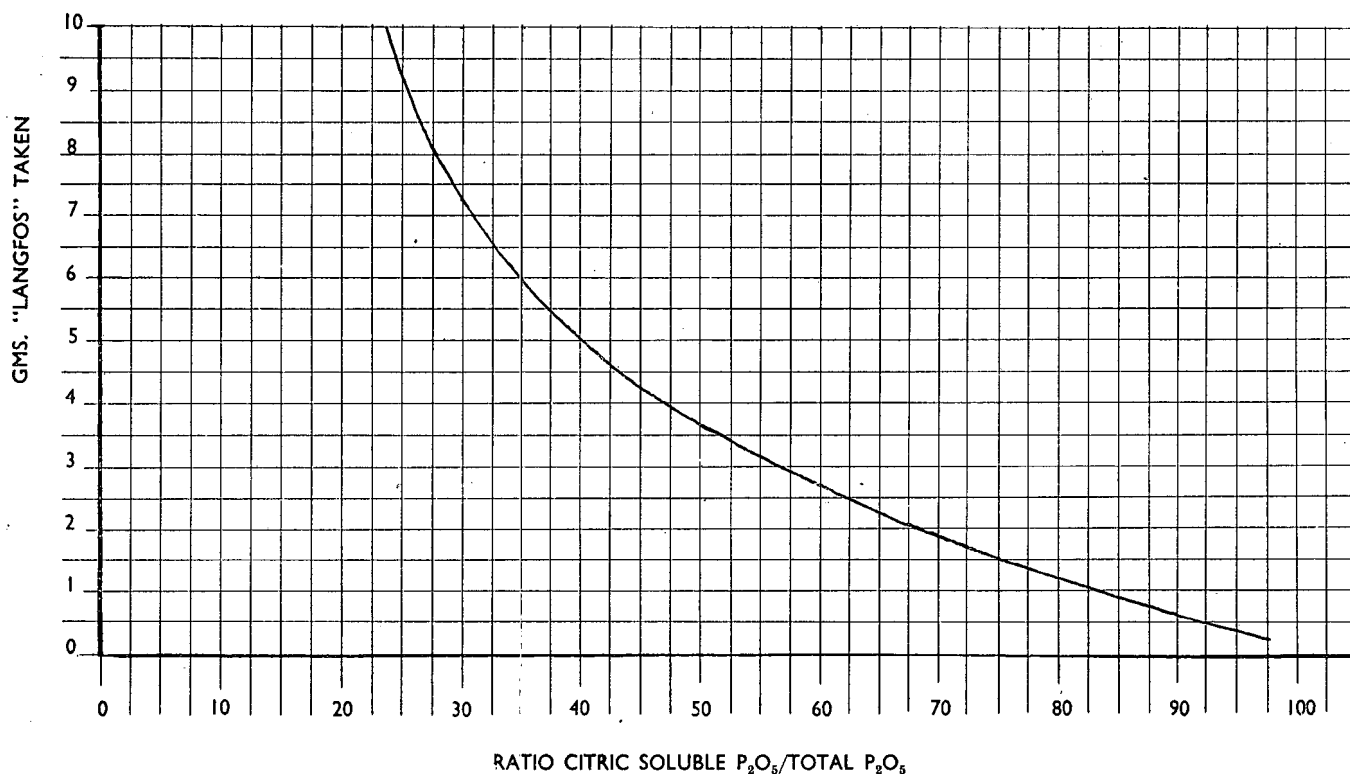
Acknowledgment.

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REFERENCES.

¹ Dymond, G. C.: A Preliminary Note on the Increase of Available Phosphate in Rock Phosphate by Composting. Proc. S.A. Sugar Tech. Assn. 1951, 84-85.

² Robertson, G. S.: J. Soc. Chem. Ind. 1914, 33, 9-11.



The general expression for this curve is— $A = R - K \log q$.

Citric Solubility.—A function of the actual amount of "Langfos" taken.

10 divisions = 1 gm. "Langfos."

2 divisions = 1. per cent. ratio citric soluble/total P_2O_5 .

For 5 gms. and under, $R = 2$, $K = 0.0809$.

Above 5 gms., $R = 1.809$, $K = 0.044$.

A is availability, K constant, q quantity taken.

Mr. du Toit thanked Mr. Dymond for reading Mr. Krumm's paper and said that the problem of phosphate was a complex one. He asked Dr. Dodds for his views on the subject.

Dr. Dodds said that he thought it would be advantageous if some way could be found to make rock phosphate available to sugarcane. He said that it was not for nothing that the superphosphate industry had been built up over the last century. It had been found that the conversion of rock phosphate to superphosphate was worth while in every country. He added that, owing to the shortage of sulphur, we now had to make the best use possible of raw rock phosphate.

Dr. Douwes Dekker said that he was not sure that Mr. Williams' results, which had been obtained with a crop other than sugarcane, could be accepted as also being valid for this plant. One should be careful in drawing far-reaching conclusions. Experiments similar to those made by Mr. Williams should be made with sugarcane.

Mr. Dymond said the old yardstick was of no use and further work should be done on the crop. He felt that the costs were so wide and so different and that from the information so far obtained it seemed that by applying rock phosphate with an organic matter one would get a better product at a lower price than by using superphosphate at a high price. He said that there was need for experimenting with sugarcane.

Mr. Lintner asked if there were any reason to suspect that the phosphate in filter press cake could become unavailable, as in the case in sewage containing high quantities of heavy metals.

Mr. Dymond replied that, from the figures he had, there did not appear to be much fixation in the soil. He said it was known that filter cake gave returns in the soil, but why was not quite clear.

Mr. du Toit pointed out that Williams' figure of 20 per cent. of phosphate utilised was widely quoted. He was not sure that this was quite correct, although in general it probably was. He said that experiments using superphosphate and rock phosphate had been carried out and invariably it was shown that superphosphate was superior to rock phosphate. In one experiment where the crop cycle had continued for 10 or 12 years superphosphate had still shown itself superior. He had little doubt that superphosphate would continue to be the best source of soluble phosphate. He said that experiments were being carried out to compare the superphosphate with imported rock phosphate and mixtures of rock phosphate. Other phosphatic materials were also being experimented with. He felt that the citric solubility basis was perhaps not ideal, but it did serve its purpose. Its value had been shown by tests made

actually on the plants themselves. He felt that the proportion of heavy metals in filter cake was possibly lower than in sewage. Filter cake seemed to be an excellent method of adding phosphate to the soil. He asked Mr. Dymond whether his paper last year indicated a greater conversion to citric solubility by composting than was mentioned in Mr. Krumm's paper.

Mr. Dymond said his paper last year indicated a much larger increase in phosphate availability. Temperatures were high and composting was intense, so the figures obtained were the result of intense activity in the compost heaps. He did not think that any of the experiments to which Mr. du Toit had referred had been carried out on the lines of the work done by himself and Mr. Krumm. Phosphate supplied in a large mass of enveloping material had less possibility of becoming fixed in the soil. He would welcome experiments to take further the work that he and Mr. Krumm had already done. He said that factors in the P_2O_5 content of filter cake were the amount of phosphate used in the factory processes, and the amount naturally occurring in the juice.

Mr. Pearson said that it was general practice to allow filter cake to lie for about 12 months before using. He asked whether any change took place in the compost during this period.

Mr. Dymond replied that in general it did not, because of the method of storing filter cake so that air did not penetrate.

Dr. McMartin referred to Mr. Williams' statement that 20 per cent. of phosphate was taken up from supers, thereby implying that 80 per cent. was wasted. He said that if this process was repeated in successive years, then theoretically at the end of 50 years we should be in the same position as in virgin soil as far as a crop response is concerned. He asked if this actually worked out in practice.

Mr. Dymond suggested that Dr. McMartin should be able to answer the question better than he could.

Dr. Dodds said that the early experiments to which Mr. du Toit referred were done when there was no world shortage of superphosphate. It was hoped to find local alternative materials which would lessen the amount of superphosphate importation. He said that superphosphate remained on top all the time throughout the experiments, not only in yield of cane per acre but in the amount of phosphate taken up by the cane. He said they had not tried mixing rock phosphate with organic matter, but they had done similar experiments in a highly fertile soil at Empangeni and found that superphosphate was again ahead of the rest, but the margin was not as great as in the poorer soils, deficient in organic matter. He felt that the organic matter probably had some effect on the less soluble forms of phosphate. He suggested that

more work could be done with radio-active phosphorus to test the amount of phosphate taken up by the plants.

Mr. Lintner asked Dr. Dodds about the experiments with various types of phosphate and wanted to know which was the oldest experiment carried out. He said he understood that experiments at Potchefstroom lasted 26 years and showed the eventual advantage of rock phosphate where superphosphate had been in the lead for many years.

Dr. Dodds said the oldest experiments had lasted about 10 years.

Mr. Dymond said that as far as he knew there was no evidence to show exactly the amount of phosphate taken up. In long-term experiments the important question of fixation again arose. He said that once the phosphate became fixed it was of comparatively little value. He felt that experiments should be carried on to test the views expressed by Mr. Williams and himself. In other words, phosphate should be wrapped in an organic matter in such a way that it became available steadily and over a long period.

Mr. du Toit questioned whether it was right to assume that the so-called insoluble phosphates were entirely unavailable and contended that there were experiments which indicated that they were available.

Mr. Dymond: The complexity of phosphate fixation in the soil and its absorption into plants, has been rendered even more complex by Mr. Krumm's discovery that the yardstick of citric solubility is open to serious inaccuracy.

Applying corrections to this present standard of determining P_2O_5 availability, he concludes that a series of compost experiments using cane trash and cattle manure with increasing quantities of Langfos, gave no increase in availability.

It is interesting to note at this stage that the organic matter used was cane trash, a difficult composting material, and old cattle manure as an activating medium.

In the second case, fresh filter cake from a sulpho-defecation factory was used. In this an interim analysis after six weeks showed no increase in availability, but after three months when the temperature had dropped, there was a decided increase from 51 per cent. to 69 per cent. when 10 per cent. Langfos had been applied, and from 46 per cent. to 58 per cent. when 20 per cent. had been used.

All this conjures up some interesting speculations, but before attempting any possible explanations or planning further experiments, it is advisable to go over the ground of what we know of phosphate availability or solubility.

The following points are based on a paper published in the N.A.A.S. Quarterly Review No. 4 by E. G. Williams, Macaulay Institute of Soil Research, Aberdeen, in 1949. Mr. Williams differentiates between a decrease in availability and a decrease in solubility. "The difference and also the confusion," he says, "between these two definitions, arises from the fact that the actual availability of phosphate in soils, which can be measured only by growing a crop, depends on factors other than solubility." For this and other reasons he prefers to use the word "fixation" to denote decrease in solubility.

Fixation and Availability.

It would appear that Mr. Williams is already aware of the unsuitability of citric solubility as a guide, as no mention is made of it in his article. The crop itself is the only true guide and "on many acid soils treated with phosphate, the extra phosphate recovered in crops, before it becomes necessary to add more to maintain yields, is equivalent to about 20 per cent. of that applied. If no more were added, some of the remainder would gradually be utilised, but at the price of low yields."

"The availability of phosphate in soils is therefore determined primarily by the degree of solubility and rate of solution and may be greatly reduced by fixation." From a practical point of view, it is important to make the following distinction: "fixation in easily available form" and "fixation in difficultly available form."

The aim of the agriculturalist should, therefore, be to present such conditions in the soil that when phosphates are applied, they will remain in an easily available form for the longest time.

This can be achieved by incorporating the phosphate with dung organic mixtures, such as filter cake or compost. Recent experiments in Sweden and America indicate that the efficiency of superphosphate can be increased considerably by mixing it with dung before applying it to the soil.

The co-operative experiments conducted by Dymond and Krumm not only provide such conditions whereby superphosphate would remain in an easily available form, but in the case of filter cake, provide an increase in availability of a rock phosphate.

Fixation.

Mr. Williams states that "when a soil is shaken up with a phosphate solution under laboratory conditions, fixation takes place very rapidly and is generally about 90 per cent. complete in about an hour." "If the phosphate is added in solid form the rate of fixation is determined in the first place by the rate at which it dissolves. The time necessary for more or less complete fixation to take place under

field conditions, is difficult to establish with certainty, but solubility measurements suggested that in one type of acid Scottish soil 20 per cent. moisture, ordinary superphosphate was extensively fixed in about a week and basic slag in about six weeks."

Mr. Williams depicts the several different reactions in fixation in the attached table.

Application of Rock Phosphate in the Sugar Industry.

The Sugar Industry provides approximately 300,000 tons of filter cake annually.

The P_2O_5 content of the filter cake in the experiments was 1.94 per cent., giving a total of 5,820 tons for the season. If 10 per cent. of Langfos were added, giving a P_2O_5 percentage of 5.67 per cent., the total would rise to 17,010 tons. This increase of 11,190 tons at £4 per ton would cost £44,760.

On the other hand, super, if it could be bought, would cost £11 10s. 6d. a ton. The super rock 4 : 1 mixture costs £10 10s. 6d., so that the 78,000 tons requirements for the Sugar Industry cost £810,950.

According to Mr. Williams, only 20 per cent. of this will be taken up by the crop. The matter now resolves itself into the following important question, which can be answered by experimentation.

What amount of rock phosphate intimately mixed in the filter cake, will equal in crop yield the present application of superphosphate in the soil. From Mr. Williams' statements, the savings should be enormous.

Mr. du Toit then asked the meeting to accord a hearty vote of thanks to Mr. Dymond for reading Mr. Krumm's paper, and to Mr. Krumm for preparing the paper.

PHOSPHATE FIXATION

