

Defluorination of Aqueous Solutions of Superphosphate for use in Animal Nutrition.

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THREE methods are available for supplying additional phosphate to animals on our deficient pastures:

(1) *The Crush Method* whereby individual animals are dosed with the requisite amount of bone meal or other phosphatic substance;

(2) *The Lick Method* in which animals are expected to help themselves to a phosphate-salt mixture in troughs;

(3) *The Drinking-Water Method* requiring the addition of a soluble phosphate to the drinking water in a concentration which will ensure adequate phosphate intake dependent upon daily water consumption.

The drinking-water method has obvious advantages. It eliminates most of the labour necessary for the crush method and all of the waste associated with the lick method. Unfortunately, there have always been difficulties in the way of supplying a suitable water soluble phosphate. Mono-ammonium phosphate, mono-calcium phosphate and mono- and disodium phosphates are all suitable but are either unobtainable or the price is prohibitive.

The possibility of using the common phosphatic fertilizer, superphosphate, as a source of water soluble phosphate was first suggested by du Toit *et al.* (1932, 1939). Unfortunately the high fluorine content of superphosphate constituted a menace to the health of the animals. This danger could, however, be eliminated by making use of an observed depressant effect of high concentrations of phosphates in solution upon the solubility of the fluorides, in addition to the relative insolubility of the fluorides in the crude superphosphate.

Briefly, the procedure suggested was the addition of 40 gallons of water to 50 lb. of superphosphate containing 17 to 20 per cent. phosphoric oxide, vigorous agitation for two periods of 5 minutes with an interval of 15 minutes followed by sedimentation for 12 to 24 hours. The clear supernatant fluid containing all the phosphates in a concentration of about 2.0 to 2.5 per cent. and only a fraction of the fluorides was then siphoned off for dilution at the rate of 1 part in 50 in the drinking water. This drinking water would then contain 0.04 per cent. phosphoric oxide, a concentration considered adequate for supplementary purposes on South African pastures, and not more than 4 parts per million of fluorine, a concentration below the toxic limit estimated at 5 p.p.m.

However, an increase in this ratio of dissolved fluorine to phosphate was observed in subsequent work at this station. This was presumably due to a higher solubility of the fluorine in the superphosphate used. The differences in the

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solubility of the total fluorine in different samples of superphosphate observed by Reynolds and co-workers (1943) are of interest in this connection. These workers also showed that if the ratio of superphosphate to water is increased above 6 gm. per 100 ml. in the preparation of the concentrated solution there is no significant reduction in the amount of dissolved fluorine relative to the phosphate. This observation was confirmed by the present authors.

Further, it is known that temporary hardness of the water causes some precipitation of phosphate from solution. This loss of available phosphate may be counteracted by increasing the ratio of superphosphate to the water but obviously this would result in an undesirable corresponding increase in dissolved fluorine. It was clear, therefore, that a reinvestigation of the problem of utilizing superphosphate as a source of low fluorine, soluble phosphate was indicated. The results of these investigations are reported in this paper.

THE EFFECT OF TEMPORARY HARDNESS OF WATER ON PHOSPHATE AND FLUORINE IN SOLUTION.

Method.—One litre of distilled water was added to each of three flat-bottomed flasks, containing 125, 200 and 250 gm. of 18.5 per cent. superphosphate respectively. These amounts correspond to the addition of 50, 80 and 100 lb. of fertilizer to 40 gallons of water. The mixtures were stirred vigorously for five minutes, allowed to stand for 15 minutes, again stirred for five minutes, and then left to sediment for 24 hours. The clear supernatants were carefully removed without disturbing the sediments. Suitable aliquots of each were diluted 50 times with (a) distilled water and (b) Onderstepoort tap-water. This tap-water showed a temporary hardness equivalent to 7.3 ml. of 0.1 NHC1 per 100 ml. These dilutions, marked A, B and C in ascending order of concentration, were stored in open Erlenmeyer flasks at room temperature, and analysed periodically for fluorine and phosphorus in solution. In the case of dilutions made with tap-water analyses were made 24 hours after mixing and thereafter at daily intervals for four days, the flasks remaining uncovered in the interval.

Results.—The results are shown in Table 1.

TABLE 1.
Phosphate and Fluorine Contents of Dilutions.

Concentrate diluted with	A.		B.		C.	
	P ₂ O ₅ g./litre.	F. p.p.m.	P ₂ O ₅ g./litre.	F. p.p.m.	P ₂ O ₅ g./litre.	F. p.p.m.
Distilled Water.....	0.46	7.3	0.73	11.7	0.92	14.4
Tap Water:						
24 Hours.....	0.31	5.2	0.56	9.1	0.70	11.4
2 Days.....	0.28	5.1	0.53	9.0	0.66	11.3
3 Days.....	0.26	5.1	0.52	8.8	0.64	11.2
4 Days.....	0.25	5.1	0.51	8.8	0.63	11.3
5 Days.....	—	—	—	—	0.63	11.4

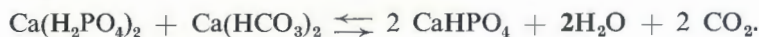
It is seen that over the range of superphosphate concentration investigated the concentration of P₂O₅ and fluorine after dilution with distilled water to meet

the requirements of a supplemented drinking water, were strictly proportional to the original concentration. In other words there was no progressive decrease in the amount of fluorine in solution.

On dilution with the temporary hard water there was a rapid loss of both phosphate and fluorine but stability was attained in about 4 days. The higher the original concentration the higher the final concentration and the proportional loss was fairly constant.

Comment.—Dilutions made with the distilled water represent the position that would obtain from the use of natural water, showing no temporary hardness. No precipitate was formed and the concentrations of fluorine and phosphorous, therefore, might be expected to remain unchanged.

Directly after mixing the concentrated solutions with tap-water, a precipitate of insoluble calcium phosphate started to settle, presumably according to the following equation:—



Since the carbon dioxide formed would escape from the open vessels, the reversible reaction would move to the right until equilibrium was established. The loss of fluorine could be accounted for by adsorption onto the insoluble precipitate.

The daily consumption of water by grazing animals is a factor which varies within wide limits. Accurate figures are not available but it is assumed that 5 gallons per day is a fair average. It has been estimated (du Toit *et al.* 1940) that the daily phosphate requirement for growth of a bovine is about 23 grams, expressed as P_2O_5 , and that the pasture seldom contributes less than half of this amount. Based on these assumptions and given a supply of water devoid of temporary hardness solution A would meet the requirements for phosphatic supplementation but the maximum permissible concentration of fluorine estimated at 5 p.p.m. (Steyn 1950) would be exceeded. Solutions B and C would be well within the toxic range. If a temporary hard water was used solution A would not meet the phosphate requirements but would be non-toxic. Adequate phosphates could be provided by increasing the initial quantity of superphosphates used (c.f. solutions B and C) but the final drinking water would be well above the toxic limit.

Conclusion.—The proposed method of preparing a water extract from superphosphate, consisting of the initial preparation of a concentrated solution, sedimentation of the insoluble fraction and suitable dilution of the supernatant in the drinking water, was found to be impracticable with the brand of fertilizer used. When an adequate concentration of phosphate was obtained the fluorine was found to be within the range of toxicity. Should a temporary hard water be the only supply available for drinking purposes the position would be further aggravated in that portion of the phosphates would be precipitated as insoluble calcium phosphate. Any attempt to remedy the deficiency by increasing the original superphosphate concentration would again bring the final solution within the limit of fluorine toxicity.

DEFLUORINATION OF CONCENTRATED SOLUTIONS OF SUPERPHOSPHATE.

From the results discussed above it is obvious that the successful utilization of superphosphate in the feeding of farm animals through their drinking water is dependent upon finding a suitable method of defluorinating solutions of this fertilizer.

DEFLUORINATION OF AQUEOUS SOLUTIONS OF SUPERPHOSPHATE.

Method.—In the course of investigations on this problem it was observed that a flocculent precipitate forms when a concentrated solution of superphosphate is heated, the precipitate starting to make its appearance at about 55° C. Subsequent analysis of the filtrate revealed a significant reduction in the concentration of fluorine accompanied by a negligible loss of phosphate from solution. Superphosphate solutions of varying strengths were, accordingly, prepared as before and subjected to different heat treatments. The results presented in Table 2 are typical of the effects produced. They were obtained with a solution prepared by using 275 grams of 18.5 per cent. superphosphate per litre of water.

Results.—The outstanding feature was the marked reduction in solute fluorine coinciding with only minor changes in phosphate concentration. Thus a simple calculation reveals that boiling the concentrated solution for 20 minutes depressed the phosphate content by only 4 per cent. as against a reduction of about 84 per cent. in soluble fluorine. The defluorination was, admittedly, only partial. Nevertheless, it has great practical significance judging from the data in the last two columns of Table 2 relating to the composition of solutions suitable for drinking purposes. The small reductions in solute phosphate due to the heat treatments have no significance in practical nutrition. These heat treatments, however, caused the loss of so much fluorine from solution that the resultant dilutions were rendered safe for animal consumption. Furthermore, these low-fluorine dilutions contained about double the accepted minimum level of solute phosphate. In the event of dilutions being made with water exhibiting temporary hardness some phosphate and fluorine would naturally be lost from solution, more or less in accordance with the data described in Table 1. However, it should not be difficult to make the adjustments necessary for ensuring dilutions from heat-treated concentrates fulfilling all requirements.

TABLE 2.

The Influence of Heat Treatment on Fluorine and Phosphate in Superphosphate Solutions.

Treatment.	CONCENTRATED SOLUTION.		DILUTED 60 TIMES WITH DISTILLED WATER.	
	P ₂ O ₅ g./litre.	F. p.p.m.	P ₂ O ₅ g./litre.	F. p.p.m.
None.....	50.5	810	0.842	13.5
Brought to boil.....	50.0	342	0.833	5.7
Boiled for 5 minutes.....	49.0	158	0.817	2.6
Boiled for 20 minutes.....	48.5	126	0.808	2.1
On steam bath for 30 minutes (± 85 C.).....	49.0	230	0.817	3.8

The precipitate formed on heating superphosphate solutions, containing mainly monocalcium phosphate, calcium sulphate and a fluorine compound, had the following elementary percentage composition: Ca, 30.75; P, 8.85; F, 23.50; Fe, 1.90 and Cr, 0.84. The molecular composition is not definitely known. Since

monocalcium phosphate is known to react with water at temperatures between 25° C. and 100° C. to form phosphoric acid and dicalcium phosphate (Elmore and Farr, 1940) it was probably composed largely of the latter and calcium fluoride.

SUMMARY.

A method of preparing low-fluorine water solutions of superphosphate as a source of phosphate for farm animals is described. It consists of the preparation of a concentrated solution, sedimentation of the insoluble fraction, boiling of the clear supernatant, and suitable dilution of the new supernatant in the drinking water.

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