

# New Phosphatic Fertilizer from Basic Slag, Hydrochloric Acid, and Rock Phosphate

M. T. SHAFIK and A. F. SABRY  
 Société Financière et Industrielle d'Égypte S.A.E. Kafr El-Zayat (Egypt), U.A.R.

Laboratory scale experiments were carried out to improve phosphate availability and other properties of basic slag. Excessive water washing and treatment with carbon dioxide slightly improved availability, while treatment with hydrochloric acid gave an 80% conversion to citrate-soluble  $P_2O_5$ . On this basis, a new process was developed for the production of a fertilizer containing 23 or 26% available  $P_2O_5$  from basic slag containing 15% citric acid-soluble  $P_2O_5$ , by-product hydrochloric acid, and rock phosphate. The process involves the attack of rock phosphate by hydrochloric acid, neutralization of the resulting solution with basic slag, and precipitating, washing, and drying of the fertilizer.

THE AIM OF THIS INVESTIGATION WAS to study the properties of basic slag produced in Egyptian steel works and to improve these properties, especially with regard to high pH and phosphate availability. Soil in the United Arab Republic is somewhat alkaline (pH 7.5 to 8.5) and thus water-soluble or citrate-soluble phosphatic fertilizers are recommended. Phosphates in basic slag are mostly citric acid-soluble and are associated with considerable free lime.

Studies on a laboratory scale showed that hydrochloric acid, a by-product of our soda works, can be used to convert citric acid-soluble  $P_2O_5$  into citrate-soluble  $P_2O_5$ . The authors were already preparing dicalcium phosphate from rock phosphate and hydrochloric acid. Through amalgamation, a fertilizer containing 23 or 26% citrate-soluble  $P_2O_5$  could be prepared, which combines the advantages of dicalcium phosphate and improved slag.

### Slag Improvement Experiments

These experiments were started on a sample representing the output of the Helwan Steelworks. Its important constituents are listed in Table I.

In spite of the free CaO and the alkalinity, the product contains a certain

amount of citrate-soluble  $P_2O_5$ . The authors decided first to remove the alkalinity to reduce the CaO/ $P_2O_5$  ratio and to study the effect of this upon the citrate solubility of the product. In this connection, experiments were carried out on leaching with water, treatment with carbon dioxide, and treatment with hydrochloric acid. All  $P_2O_5$  determinations were carried out according to the method cited in (1).

**Water Leaching.** Each treatment involved mixing 50 grams of slag with 200 ml. of water for 30 minutes with a mechanical stirrer. The wash water was decanted, another 200 ml. added, and stirring repeated. Each time the wash water was tested with phenolphthalein for the presence of calcium hydroxide. Alkalinity was still present after 20 washings. This fact may throw a light on the hydrolytic decomposition of complex tetracalcium phosphate and other calcium compounds which are said to be present in the slag (3). After the desired number of washings, the sample was filtered and the washed material dried, weighed, and analyzed (Table II).

There was a slight rise in the citrate-soluble  $P_2O_5$  content with an increase in the number of washings. A maximum percentage of 6.19 and a maximum conversion of 33.5% were reached with no further improvement with excessive washing.

**Carbon Dioxide Treatment.** Treatment with  $CO_2$ , dry and in the presence of water, gave less improvement in citrate solubility than water washing. After 6 hours of bubbling gas through the mixture of water and slag, the weight of the product had increased slightly, with a citrate-soluble content of 5.44%, total  $P_2O_5$  content of 17.47%, and 31.1% conversion.

**Hydrochloric Acid Treatment.** Each run involved treatment of 50 grams of slag with 100 ml. of water and the desired amount of hydrochloric acid—sp. gr. 1.146 at 20° C. The mixture was well stirred and filtered, and the residue washed twice with water, dried, weighed, and prepared for analysis. The results of acid treatment are found in Table III.

The percentage of citrate-soluble  $P_2O_5$  increased and a conversion value of about 80% could be reached by this treatment. These encouraging results led to the use of slag instead of lime to neutralize phosphoric acid.

### Preparation of Fertilizer

The preparation of fertilizer started with the usual steps involved in the preparation of dicalcium phosphate (2, 4). These steps may be summarized as follows:

Treatment of rock phosphate with hydrochloric acid to obtain a solution of phosphoric acid.

Table I. Constituents of Sample

Constituents	Per Cent in Sample
$P_2O_5$ soluble in ammonium citrate	4.59
$P_2O_5$ soluble in citric acid	15.15
Total $P_2O_5$	18.11
Calcium oxide total	45.20
$Fe_2O_3 + Al_2O_3$	20.40
Free CaO	4.50
Insoluble matter	8.00
% passing 100-mesh screen	87
% passing 200-mesh screen	76

Table II. Results of Water Washing

Number of Washings	Weight of Product, Grams	Citrate-Soluble $P_2O_5$ , %	Total $P_2O_5$ , %	Conversion, %
0	50	4.59	18.11	25.3
3	49.15	5.30	18.21	29.1
6	48.18	5.58	18.42	30.3
9	47.4	6.19	18.50	33.5
12	47.52	6.16	18.40	33.5
15	47.4	6.19	18.47	33.5

**Table III. Results of Acid Treatment**

Sample Number	HCl Acid, MI.	Weight of Product, Grams	Citrate-Soluble P <sub>2</sub> O <sub>5</sub> , %	Total P <sub>2</sub> O <sub>5</sub> , %	Conversion, %
1	...	50	4.59	18.11	25.3
2	5	49.0	10.26	18.34	56.0
3	10	47.85	12.05	18.75	64.3
4	15	46.77	15.26	19.31	79.0
5	20	45.0	15.97	19.78	80.7
6	25	43.69	16.27	20.19	80.6
7	30	42.12	16.72	20.11	83.1

**Table IV. Rock Phosphate Analysis**

Ingredients	Per Cent in Sample
Moisture	1.9
Total P <sub>2</sub> O <sub>5</sub>	28.95
Tricalcium phosphate	63.22
Calcium carbonate	12.59
Insoluble material	8.60
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	2.91
CaSO <sub>4</sub>	1.86
Cl	0.35
CaF <sub>2</sub>	3.10
Fineness through No. 100-mesh sieve	91.5%

Filtration of this solution and neutralization with lime or limestone until dicalcium phosphate precipitates.

Filtration, washing, and drying of the product.

Dicalcium phosphate, which is superior to basic slag in availability as a fertilizer, is very light and accordingly difficult to handle. Another important disadvantage is the absence of the group of trace elements present in the slag.

Therefore, slag was used instead of lime to neutralize the phosphoric acid solution, to use the lime present in the slag, and to obtain a mixture of

improved slag and dicalcium phosphate.

As a first step, conditions of the reaction between ground phosphate and hydrochloric acid were studied—namely, dilution, temperature, and time of reaction. This study, on a laboratory scale, was essential to obtain good bases for the design of a pilot plant and find the best conditions to give the highest quality sample. The sample of rock phosphate used was obtained from the mines at Sibaiya; its analysis is given in Table IV.

The procedure for the preparation of a sample of fertilizer involved the treatment of a fixed weight of phosphate, with the desired amount of water and hydrochloric acid, digestion, dilution again, and neutralization with slag to the dicalcium phosphate stage.

The product was filtered, washed, dried at 105° C., weighed, and sampled. In each sample, the citrate-soluble and total P<sub>2</sub>O<sub>5</sub> were determined.

According to this procedure, the residue after digestion is retained in the final product which contains 22 to 23% citrate-soluble P<sub>2</sub>O<sub>5</sub>. The solution was filtered after digestion, and the procedure completed by neutralization with slag; the authors obtained a product contain-

ing 26% citrate-soluble P<sub>2</sub>O<sub>5</sub>. The results of study of the factors affecting the quality of fertilizer are found in Table V.

Concerning acid dilution, the ratio 1 to 1 by volume was suitable for digestion. Boiling temperature of digestion was necessary, and 0.5 or 1 minute of boiling gave results near those obtained by 15 minutes of boiling. The digestion, carried out at 75° to 80° C. for 1 hour (sample 6), gave a sample with less conversion than the others.

With increase in the quantity of acid used, more slag will be required for neutralization and a product with less citrate-soluble P<sub>2</sub>O<sub>5</sub> will be obtained. This is shown in Table V (samples 11, 12, and 13), where sample 12 is best in percentage of citrate-soluble P<sub>2</sub>O<sub>5</sub> and conversion. The low conversion in sample 11 is due to less digestion of rock phosphate, while in sample 13, it is due to the application of more slag. Sample 14 is obtained by filtering the solution after digestion; less fertilizer is obtained, 146 instead of 165 to 170 grams, containing 26.6% citrate-soluble P<sub>2</sub>O<sub>5</sub>.

**Results**

In the light of the results of laboratory studies, the authors conclude that a higher efficiency phosphatic fertilizer can be obtained from basic slag by the application of by-product hydrochloric acid and rock phosphate.

The fertilizer has a more acceptable color for farmers, higher efficiency, and improved availability, which will save transport costs and suitability to the alkaline soil of the United Arab Republic (the alkalinity being removed), and it can be mixed with organic fertilizers, farmyard manure, and ammonium salts with no danger of the loss of nitrogen.

**Table V. Treatment of 100 Grams of Phosphate with Hydrochloric Acid (Sp. Gr. 1.151 at 20° C.)**

Sample Number	Acid, MI.	Water, MI.	Digestion <sup>a</sup> Time, Minutes	Slag Used, Grams	Product, Grams	Citrate-Soluble P <sub>2</sub> O <sub>5</sub> , %	Total P <sub>2</sub> O <sub>5</sub> , %	Conversion, %
Effect of Acid Dilution								
1	140	70	0.5	98	168	21.96	28.56	77.0
2	140	105	0.5	98	168	22.14	28.62	77.4
3	140	140	0.5	98	168	22.64	28.52	79.4
4	140	175	0.5	99	176	21.62	28.42	76.1
5	140	210	0.5	99	176	21.06	28.16	74.8
Effect of Temperature and Time of Digestion								
6	140	140	60	99	168	20.91	27.40	76.3
7	140	140	1	98	165	22.64	28.34	79.9
8	140	140	5	98	166	23.0	28.70	80.1
9	140	140	10	98	170	23.16	29.06	79.7
10	140	140	15	98	160	22.23	28.02	79.3
Effect of Quantity of Acid								
11	120	120	10	70	150	22.50	29.0	77.6
12	140	140	10	98	170	23.16	29.06	79.7
13	160	160	10	120	188	21.26	27.66	77.0
Filtration after Digestion								
14	140	140	5	98	146	26.64	31.52	84.5

<sup>a</sup> Digestion of samples was at boiling temperature, except sample 6, at 75° to 80° C.

## Literature Cited

- (1) Kassner, J. L., Krammer, H. P., Ozier, M. A., *Anal. Chem.* **20**, 1052 (1948).
- (2) Strauchen, A., Paper No. LE/61/44, International Superphosphate Manu-

facturers' Association Technical Conference, September 1961.

- (3) Sulphuric Acid and The Manufacture of Phosphatic Fertilizers, pp. 56-58, The Organization for European Economic Co-operation, Paris, 1953.
- (4) Waggaman, W. H., "Phosphoric

Acid Phosphates and Phosphatic Fertilizers," 2nd. ed., pp. 372-4, Reinhold, New York, 1952.

Received for review October 26, 1965. Accepted August 27, 1966.

## PROCESSING CHANGES

# Xanthophyll and Carotene Stability during Alfalfa Dehydration

A. L. LIVINGSTON, R. E. KNOWLES, M. ISRAELSEN,<sup>1</sup> J. W. NELSON, A. C. MOTTOLA, and G. O. KOHLER  
Western Regional Research Laboratory, Western Utilization Research and Development Division, U. S. Department of Agriculture, Albany, Calif.

The xanthophyll content of dehydrated alfalfa meal was greatly reduced as the outlet temperature was increased and the moisture content of the meal decreased. Although total carotene was relatively unaffected by temperature of dehydration or moisture of meal, the beta-carotene isomers increased with the higher outlet temperature and lower moisture levels.

PREVIOUS STUDIES have shown the xanthophyll, carotene, and fat-soluble vitamins of dehydrated alfalfa to be subject to oxidation losses during storage (6, 8, 11, 15-17). Treatment of the alfalfa meal with antioxidants and oils or storage at a low temperature or under an inert atmosphere has eliminated much of these losses (4, 5, 7, 10, 12, 13). However, both xanthophyll and beta-carotene form stereoisomers during dehydration (2, 3, 14) with a resulting loss of the provitamin A activity of the beta-carotene as well as possible loss of the pigmentation potency of the xanthophyll. Since dehydrated alfalfa is used in poultry rations primarily as a source of xanthophyll pigments and fat soluble vitamins (carotene, vitamin E, and vitamin K), the prevention of isomer formation is desirable. Furthermore, high temperatures during dehydration may not only enhance isomerization but could also cause oxidative and destructive losses of these labile compounds.

The present study presents data obtained with a pilot scale alfalfa dehydrator, showing the temperature effect, during dehydration, upon the carotene and xanthophyll content of the alfalfa meal. This information is correlated with the moisture content of the alfalfa meal and the extent of beta-carotene isomerization.

## Materials and Methods

A pilot scale Arnold alfalfa dehydrator was employed at the site of an industrial plant so as to utilize the fresh plant

material being commercially dehydrated. The input temperature of the pilot dehydrator was regulated by controlling gas flow to the burner. The stack gas or outlet temperature was regulated by controlling the feed rate of fresh alfalfa to the dehydrator.

Samples of the fresh plant material were collected as it passed from the loading platform onto the dehydrator elevator. An average fresh sample was obtained by collecting three samples at 5-minute intervals. Then, after allowing ample retention time, two resultant dehydrated samples were collected (after grinding in a hammer mill) at 5-minute intervals.

The fresh plant material was thoroughly and rapidly chopped in a Hobart food chopper. The samples were placed in sealed plastic bags and aliquots taken for analyses and moisture determination within 10 minutes following chopping. Moisture of the fresh and dried alfalfa was determined by drying in a forced draft oven at 110° C. for 24 hours. Carotene and xanthophyll were extracted by mixing 50 grams of fresh alfalfa in a Virtis high speed electric blender for one minute with 175 ml. of acetone. The extract was filtered and the residue washed with 50 ml. of acetone and re-extracted by blending with 125 ml. of acetone. The combined extract was made to volume (500 ml.) and used for determining both the ratio of beta-carotene isomers and the total carotene and xanthophyll content. Extracts of the dehydrated alfalfa meal were prepared by soaking 2-gram portions overnight at room temperature with 30 ml. of Skellysolve B-acetone (7:3).

The method of Bickoff and Thompson (3) was used to separate and determine

the stereoisomers of beta-carotene. Total apparent carotene and xanthophyll of the fresh and dehydrated alfalfa were determined by the procedure of Kohler, Knowles, and Livingston (9), which consists of treating the extract with alkali to saponify the chlorophyll prior to chromatography and eluting the xanthophyll fraction from the chromatographic column with a mixture of Skellysolve B-acetone-methanol (85:10:5). The xanthophyll mixture eluted contains cryptoxanthin, lutein, zeaxanthin, violaxanthin, and neoxanthin, and their main isomers.

Yellow pigments remaining on the column after elution of the xanthophyll pigments were eluted with a mixture of Skellysolve B-acetone-methanol (80:10:10). This more polar fraction is referred to as "polyoxy" carotenoids and consists largely of oxidation products of naturally occurring carotenoids.

## Results and Discussion

As shown in Table I, the total carotene was relatively constant during dehydration. In only one instance was there an appreciable loss (inlet temperature 1200° F., outlet temperature 320° F.), and this may have been due to the variability of the carotene content of the fresh plant material.

The carotene and xanthophyll content of the fresh alfalfa varied from day to day and also varied during any particular day. However, the ratio of the beta-carotene isomers in fresh alfalfa was constant; neo-B, 7% all trans, 84%; neo-U, 9%. The formation of cis isomers of beta-carotene during dehydration is apparently a function of the outlet temperature and the moisture

<sup>1</sup> Present address, Forskaingsinstituttet for Handels-og Industriplanter, Holbergvej 10, Kolding, Denmark.