five times on other chemicals. With the exception of borderline cases (1,3,5-trinitrobenzene aniline complex and DRC-1324), the R_{50} of each replicate falls within the permissible statistical limits of the other. Also, the R_{50} values of those chemicals applied to rice fall within the limits of those applied to milo, with the exception of 1-hydroxy-2-pyridine thione disulfide and 9,10-anthraquinone.

In another series of tests, four chemicals were applied to hulled rice, and each treatment was offered to two groups of redwings: group 1 consisted of birds not previously tested or new birds, and group 2 contained birds previously tested one to five times. Both groups included males and females. The results indicated that previously tested birds were more easily repelled than new birds (Table II).

The results of this study show that the concentration-repellent effect method can be used to evaluate the comparative effectiveness of red-winged blackbird repellents. Although the most reliable and reproducible data are obtained using only new blackbirds, in cases where the supply of test birds is limited, for general comparative purposes satisfactory results are obtained using previously tested birds.

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PHOSPHATE ROCK CLASSIFICATION

Phosphate Rock Solubilization by Repeated Extractions with Citrate Solutions

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The potential value of phosphate rock as a supplier of phosphorus can be estimated by any one of three solvents: neutral ammonium citrate, 2% citric acid, or alkaline ammonium citrate. Values for phosphorus solubility of 24 calcium phosphate materials were obtained in single and four consecutive extractions by each of the three solvents. In calcium phosphates of the apatite type, the solubility increased as the acidity of the citrate extractant increased, but the reverse occurred in phosphals and pseudowavellites. The ranking of the material was about the same whether based on a single extractant value or on the total value from the repetitive extractions, but the latter procedure grouped the rocks according to their solubility more effectively, especially with the citric acid and neutral citrate. Among the newer rock discoveries, Peruvian, North Carolina, and sea-bottom rocks compared very favorably with highly soluble rocks from Curacao and North Africa.

World consumption of phosphate rock amounted to about 46 million long tons in 1962. During the past few years, the agricultural usage of phosphate rock, either for direct application to the soil or for the manufacture of commercial fertilizer, has been rising about 8% per year. This demand points to the urgent need for the discovery of new phosphate rock fields and the appraisal of deposits heretofore considered uneconomical for mining. Active exploration calls for practical and reliable procedures for determining the suitability of new deposits for fertilizer purposes.

Earlier investigations have been made with the view of establishing reliable indices of reactivity and agronomic merit of phosphate rocks. They have related to surface area (*7*), solubility in fertilizer solvents, readily exchangeable phosphorus, particle weight and density, composition of the apatite component (*4*), and pore structure (*3*). Inasmuch as the citrate solubility (*4*), determined from single extractions with 2% citric acid and neutral ammonium citrate, gave very good correlation with crop yields in greenhouse cultures, further investigation of this chemical property was pursued. Included in the study were solubility measurements based on single extractions with 2% citric acid, neutral and alkaline ammonium citrate, and the cumulative solubility obtained from four consecutive extractions with these citrate solutions.

Test Materials

Fourteen mineral phosphates, representative of well known varieties or sources of phosphate rock, were used in the study (Table I). Ten of the materials had been well characterized in the earlier studies (*3*, *4*, *7*), while the other materials were added to provide fuller

Table I. Test Mineral Phosphates

Lot No.	Material, Variety or Source	Total P (P_2O_5)	Total CaO
904	Connetable Islands[a]	18.3 (42.0)	0.2
907	Tennessee brown	15.2 (34.9)	48.5
910	Florida pebble	13.4 (30.6)	45.9
985	Curacao	16.6 (38.1)	51.2
1100	Steamed bone	16.8 (38.4)	52.0
1252	Montana, Garrison	16.2 (37.1)	51.7
1253	Idaho, Conda	14.6 (33.4)	48.1
1295	Virginia apatite	17.5 (40.2)	53.7
1446	Florida pebble	14.5 (33.2)	45.6
1484	So. Carolina	12.1 (27.8)	44.9
1551	Tunis, Gafsa	13.2 (30.2)	49.4
2212	Kola apatite	17.5 (40.2)	52.7
2240	Morocco	14.1 (32.4)	52.3
3211	Senegal[b]	15.1 (34.6)	10.3

[a] Aluminum phosphate mineral.
[b] "Phosphal," commercial calcium aluminum phosphate.

Table II. Solubility Position of Several Test Rocks

Lot No.	Material, Source or Variety	Position in Order of Solubility[a] as Determined by[a]: Citric acid, 2%	Neutral ammonium citrate	Alkaline ammonium citrate
1100	Steamed bone	1	1	1
985	Curacao	2	5	6
1551	Tunis, Gafsa	3	2	2
2240	Morocco	4	3	4
910	Florida pebble	5	6	5
1484	So. Carolina	6	4	3
907	Tennessee brown	7	9	8
1446	Florida pebble	8	7	7
1253	Idaho, Conda	9	8	9
1252	Montana, Garrison	10	10	11
1295	Virginia apatite	11	11	12
2212	Kola apatite	12	12	10

[a] Solubility decreases with increasing numerical order.

Table III. Index of Solubility Based on Four Repetitive Extractions with 2% Citric Acid

Index Value	Representative Varieties or Source of Mineral Phosphates
10	Steamed bone
9	Curacao and Tunis
8	Morocco
7	South Carolina land Florida pebble
6	Tennessee brown Idaho, Conda
5	
4	Montana, Garrison
3	
2	Virginia apatite
1	Kola apatite
0	Connetable Islands ($AlPO_4$)

coverage of the range of mineral phosphate compounds. The additional test materials were an aluminum phosphate from the Connetable Islands, steamed bone, an apatite from the Kola Peninsula of U.S.S.R., and a commercial calcium aluminum phosphate from Senegal, Africa.

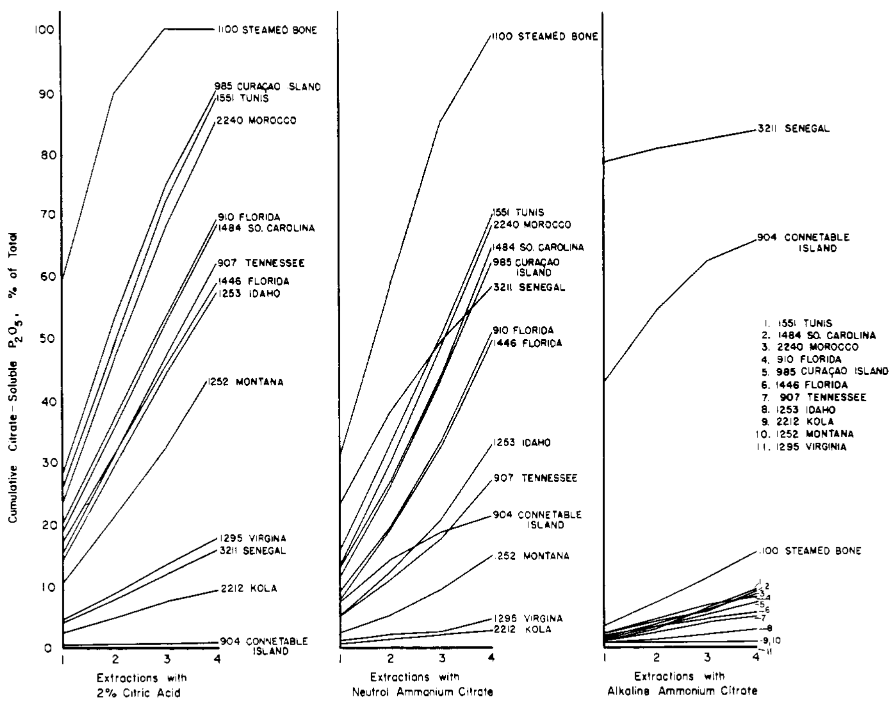

Figure 1. Citrate-solubility distributions of several mineral phosphates

Experimental Procedures

2% Citric Acid Solubility. The solubility in 2% citric acid was determined by a modification of a former official A.O.A.C. method (*1*). Two and one-half grams of sample were agitated for 30 minutes at room temperature in 250 ml. of the citric acid and filtered.

Neutral Ammonium Citrate Solubility. The solubility in neutral ammonium citrate was determined by the official A.O.A.C. method (*2*). One gram of sample was agitated continuously in 100 ml. of the citrate solution for 1 hour at 65° C. and filtered.

Alkaline Ammonium Citrate Solubility. The procedure used was patterned after the official method of the Netherlands (*8*). The soluble phosphorus was extracted by agitating 1 gram of material with 100 ml. of alkaline ammonium citrate (sp. gr. 1.082 and pH of about 9.0) for 30 minutes, allowing the solution to stand for 18 hours at room temperature and 1 hour at 40° C., and filtering.

Repetitive Extractions. The extraction procedure was repeated three times on the insoluble residue from the previous extraction for each of the citrate solutions.

Analytical Methods. Phosphorus was determined in the citrate-soluble solutions by the Dahlgren (*5*) modification of the quinoline molybdate method. The EDTA titration method of Graham *et al.* (*6*), modified to include an ultraviolet detection of the calcine end point, was used for the estimation of calcium. All determinations were made on the 100- to 150-mesh fractions of the rock.

Solubility in Citrate Solutions

The citrate-soluble phosphorus values, as measured by single and repeated extractions by each of the citrate solutions, are shown in Figure 1. The positions of the individual apatite-type phosphate rocks in order of solubility did not change appreciably from one citrate solution to the next (Table II). The greatest changes were shown by the Curacao and South Carolina rocks.

The behavior of the Connetable Island and Senegal phosphate rocks is of particular interest (Figure 1). These rocks are mainly aluminum phosphates, and as the alkalinity of the citrate solutions increased, the citrate solubility of these materials also increased. As shown in Figure 1, the alkaline ammonium citrate solubility of the aluminum phosphate-type rocks was so great compared to that

Table IV. Chemical Composition and Solubility Index of Ten Phosphate Rocks

Lot No.	Variety or Source of Rock	Total P (P_2O_5)	Total CaO	Citrate-Soluble P_2O_5, % of Total: 2% Citric acid, extractions: 1st	Sum of 4	Neutral ammonium citrate, extractions: 1st	Sum of 4	Alkaline ammonium citrate, extractions: 1st	Sum of 4	Index of Solubility No.
3467	Christmas Island	16.8 (38.5)	53.3	21.7	72.6	10.6	37.4	2.4	9.7	7
3498	Peru	12.9 (29.6)	46.4	31.0	98.7	19.3	75.5	0.7	8.0	10
3499	Peru[a]	15.1 (34.7)	53.6	15.5	63.3	12.6	53.9	1.0	8.8	6
3509	Utah black	13.9 (31.8)	46.7	13.1	55.2	4.3	26.3	0.5	2.2	6
3513	Florida pebble[b]	16.0 (36.7)	52.3	16.8	62.3	6.6	27.1	0.9	2.3	6
3521	Florida pebble	15.6 (35.7)	50.8	18.8	68.5	7.8	35.0	1.2	3.7	7
3540	Sea floor phosphorite[c]	12.4 (28.4)	45.7	26.9	91.7	19.0	67.6	2.4	11.5	9
3541	Togoland	16.4 (37.7)	53.1	15.5	56.7	6.4	28.6	0.6	2.2	6
3546	So. Africa, Phalaborwa	16.9 (38.8)	55.2	2.0	13.4	0.4	3.0	0.0	0.0	1
3548	North Carolina	13.2 (30.3)	48.3	23.6	81.4	17.0	62.6	1.4	8.2	8

[a] Lot No. 3498 after calcination.
[b] Lot No. 3521 after calcination.
[c] Obtained at 700-foot depth, 40 miles west of San Diego, Calif.

of the apatite-type rocks that this citrate solution could well serve as an excellent method of differentiating between rocks composed of different mineral phosphates.

With each of the citrate solutions, the order of solubility was about the same whether based on a single extraction value or on the total value of the four repetitive extractions. When 2% citric acid and neutral ammonium citrate solutions were used, the increased solubility from the repetitive extractions resulted in a more effective grouping of rocks according to their reactivity. With the alkaline ammonium citrate solution, the increased solubility was not great enough to merit the use of this solution for the evaluation of phosphate rocks, except as noted earlier.

Even though neutral ammonium citrate is used officially in the United States for the evaluation of available phosphorus and its application has been extended to phosphate rock, the authors feel that repetitive extractions with 2% citric acid are a better criterion of the reactivity of phosphate rocks. By using well known rocks from among the test materials, a solubility index is proposed in Table III. The index ranges from 0 to 10, with 10 (the greatest solubility) represented by steamed bone and 0 (the lowest solubility) by aluminum phosphate.

Classification of Phosphate Rocks

The citrate solubility results on 10 other phosphate rocks by single and repetitive extractions by each of the three citrate solutions are shown in Table IV. These samples represent either the ore presently being mined from well known deposits or that of possible mining locations of recently discovered deposits. The positions of these materials in the proposed index of solubility are also listed in this table.

Christmas Island rock, which the Australian mining companies propose to use after the depletion of the Nauru deposits, ranks slightly above Florida pebble rock.

Peruvian rock, from the newly discovered deposit in the Sechura Desert, with an index number of 10 was the most soluble rock tested. After calcining, the solubility dropped to 6, which is slightly below the solubility of Florida pebble.

The material representing present-day output from Utah and Florida compares quite closely with the test rocks from these domestic fields. Calcining the Florida pebble did not affect its solubility appreciably.

The sea floor phosphorite obtained from the ocean floor off the coast of California had an index of 9 which is higher than the solubilities of the North African rocks.

The index of 1 measured for the Phalaborwa rock from South Africa indicates that this rock is probably similar to Virginia or Kola apatite. Its low solubility in alkaline ammonium citrate solution indicates that it is not an aluminum phosphate type of rock.

Phosphate rock from the North Carolina deposits had an index number of 8, which classifies it between the North African and the Florida pebble rocks.

Conclusions

The proposed index of solubility appears to be a handy method for classifying phosphate rocks. It may likely prove useful in evaluating rocks for direct application or possibly for acidulation in the manufacture of phosphatic fertilizers. However, the results of this study indicate a need for future research aimed at correlating the index number with the results of existing laboratory and agronomic methods of evaluating phosphate rock minerals.

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