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RESEARCH REPORT

COMMERCIAL UTILIZATION OF
FLORIDA LEACHED ZONE ORE

D. A. Ellis
and
H. W. Hill

DOW-112-A

February 24, 1954

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Metallurgy-Raw Materials

TOPICAL REPORT

COMMERCIAL UTILIZATION OF
FLORIDA LEACHED ZONE ORE

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by

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February 24, 1954

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Metallurgy-Raw Materials

I. ABSTRACT

TOPICAL REPORT

COMMERICAL UTILIZATION OF
FLORIDA LEACHED ZONE ORE

February 24, 1954

THE DOW CHEMICAL COMPANY
Western Division
Pittsburg, California

Four processes which appear to be economically feasible for the conversion of leached zone ore (a phosphatic ore located in Florida) to marketable products are discussed. A caustic leach process for preparing alumina and sodium phosphates is considered in more detail in an appendix.

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II. SUMMARY

A. Occurrence and Composition of Leached Zone Ore

The northern part of the Florida Bone Valley formation consists of two zones. The lower zone contains the phosphate gravel which is the raw material presently used for fertilizer manufacture. The upper zone, which is known as the leached zone, has been modified by leaching so that the appearance is vesicular and much of the apatite, which is the predominant material of the lower zone, has been replaced by pseudowavellite and wavellite. It ranges in thickness from a feather edge to 60 feet. In present mining operations, the leached zone is stripped with the overburden and discarded.

Analysis of leached zone material indicates that it consists of quartz sand, partially coated with a clay phosphate matrix, and clay particles intimately associated with phosphatic phases. The relative proportions of the phosphate minerals vary from place to place and also with depth and, hence, the chemical composition of the ore varies considerably. It is, in general, lower in phosphate and calcium and higher in aluminum than the normal fertilizer plant feed. Samples containing high proportions of apatite are usually designated as "high lime" ores while those containing a greater proportion of aluminum minerals are designated as "low lime" ores. The uranium concentration ranges from less than 0.01% to 0.04% U_3O_8 . Although this is quite low, the extent of the deposit is such that it represents an important source of uranium.

B. Beneficiation of Leached Zone Ore

Since the phosphate minerals in these ores are softer than the quartz sand, considerable beneficiation can be obtained by preferentially grinding the phosphate minerals and making a size separation. Both wet and dry methods can be used. Recent wet beneficiation studies at the TVA laboratories indicate that no initial grinding is necessary but that the +12 M portion is high in both phosphate and uranium. Thus, if separation is made at 12 M and the -12 M fraction is ground to -35 M and deslimed at 40 microns, most of the phosphate and uranium will appear in the +12 M and -40 micron fractions. The sand fraction can be further beneficiated by flotation of the quartz using an amine collector.

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In dry beneficiation it has been found that about half of the ore is ground readily but the other half is ground only with difficulty. The easily ground portion is high in phosphate and uranium and the difficultly ground fraction can be beneficiated by flotation of the quartz with an amine collector.

C. Manufacture of Saleable Products from Leached Zone Ore

Several processes have been suggested for the conversion of leached zone ore to saleable products. In two processes, a single fertilizer product is produced. The consumption of fertilizer in the United States is sufficiently great that several plants of these types could probably be built without saturating the market. Other processes have been proposed which recover the alumina separately and convert the phosphate into ammonium, calcium, or trisodium phosphate.

Nitric Acid Process

This process has been studied extensively at the TVA laboratories. A pilot plant has been in operation for some time. The ore is crushed, calcined, and leached with a nitric acid solution or a mixture of nitric and sulfuric acids. The slurry is filtered and the filtrate is ammoniated. The dried product is sold as a fertilizer. Potassium chloride is sometimes added in the ammoniation step. This results in an ammonium-aluminum nitrate-phosphate-potassium product.

Products of high citrate solubility have been obtained but the water solubility of the phosphate is sometimes low. Attempts are being made at present to improve the water solubility of the product. Greenhouse tests on experimental fertilizers made from both high lime and low lime ores indicate that they are about as effective as superphosphate and ammonium nitrate.

A preliminary cost estimate has been prepared. This estimate, for a plant in Florida treating 5000 tons of ore per day for a market in Illinois, indicates a return on the investment before taxes of over 50%.

Superphosphate Type Process

This process has been studied only in bench-scale experiments. Calcined ore is extracted with sulfuric acid. The slurry is filtered and the filtrate is used to acidulate rock phosphate. The acidulated product is dried and could be sold as a fertilizer. Products have been obtained which contained over 25% P_2O_5 of which over 90% was citrate soluble.

A preliminary cost estimate has been prepared for this process also. It was estimated that a plant located in Florida, treating 5000 tons of ore per day for a market in Illinois, would give a 16% return on the investment.

Sulfuric Acid Digestion Process

This process has been carried into the pilot plant stage by the International Minerals and Chemical Corporation but only sketchy information is available. Ground, beneficiated ore is digested with sulfuric acid at high pressure and high temperature and the slurry is filtered. The filtration is slow and appears to be one of the biggest problems in the process. Ammonium alum is crystallized from the extract by addition of gaseous ammonia and ammonium phosphate is recovered from the other liquor. The alum is converted to alumina.

A preliminary cost estimate has been made for a process similar to this. This estimate for a plant consuming 720 tons of unbeneficiated ore per day indicated as 11% return on the investment before taxes. However, this estimate was based on very little laboratory data and includes considerable guessing.

Caustic Leach Process

This process has been studied extensively by both the Virginia-Carolina Chemical Corporation and the Dow laboratories but no pilot plant studies have yet been made. The process developed at Dow consists of leaching calcined ore with a caustic soda solution, filtering while hot, and precipitating alumina and trisodium phosphate separately. Sodium hydroxide is then added to the mother liquor in an amount equivalent to that removed by the products and the solution is recycled. Hydrated alumina products containing 64% Al_2O_3 , 0.02% SiO_2 and 0.05% P_2O_5 and TSP products containing as little as 0.02% Al_2O_3 have been obtained.

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III. OCCURRENCE AND COMPOSITION OF LEACHED ZONE ORE

The Bone Valley formation is found in Polk, Hillsborough, Hardee, and Manatee Counties in Florida. It overlies the Miocene Hawthorne formation, which is a limestone bed containing some phosphate, and is overlain by Pleistocene quartz sand. At the northern boundary of the district, the Bone Valley formation may be underlain by Miocene Tampa limestone or Oligocene Suwanee limestone. The Bone Valley formation is believed to be Pliocene.

In Polk and Hillsborough Counties, which comprise the northern part of the district, the Bone Valley formation consists of two zones. The lower zone contains phosphate gravel and sand, trace amounts of heavy minerals, such as ilmenite, zircon, tourmaline, and staurolite, and some montmorillonite and kaoline. This is the raw material used at the present for fertilizer manufacture.

The upper zone, which is known as the leached zone, consists of a pebbly quartz and phosphate sand with phosphatic cement. The original composition of this zone has been modified by leaching so that the appearance is vesicular and much of the apatite, which is the predominant material of the lower zone, has been replaced by pseudowavellite and wavellite. The leached zone can be distinguished from the rest of the formation by its vesicularity and gray to white color. It ranges in thickness from a feather edge to 60 feet, but over most of the region it is 2 to 13 feet thick. In present mining operations, the leached zone is stripped with the overburden and discarded.

The southern part of the Bone Valley formation, in Hardee and Manatee Counties, does not seem to consist of distinguishable zones but is homogeneous, consisting of quartz and phosphate sand or sandy clay.

Most of the material in the leached zone consists of the following minerals:

Apatite - $\text{Ca}_{10}(\text{X})(\text{PO}_4)_6$, in which $\text{X} = 2\text{F}, 2\text{Cl}, 2(\text{OH}), \text{CO}_3, \text{SO}_4$.

Wavellite - $2\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 9\text{H}_2\text{O}$.

Pseudowavellite - $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$.

Millicite - $\text{Ca}_2(\text{NaK})_2\text{Al}_{12}(\text{PO}_4)_8(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$.

Quartz

Clay minerals - Only kaolinite and kaolinite type minerals have been found.

Microscopic analysis of leached zone material indicates that it is about half quartz sand. The sand particles are partially coated with a clay phosphate matrix which appears to be firmly cemented. The second most abundant fraction consists of clay particles of the kaolinitic type intimately associated with phosphatic phases. Several phosphate minerals can be detected.

At the Homeland Mine of the Virginia-Carolina Chemical Corporation, where the leached zone is 13 feet thick, the following average composition has been found.

Quartz - 58%
Wavellite - 24%
Apatite - 7%
Pseudowavellite - 5%
Kaolinite and misc. minerals - 5%

The relative proportions of the phosphate minerals vary from place to place in the leached zone and vary also with depth. Sampling of the region has been too sparse as yet to determine the typical composition of the zone. Samples containing a high proportion of apatite are usually designated as "high lime" ores, while those containing a greater proportion of aluminum minerals are designated as "low lime" ores.

The chemical composition of leached zone ore varies considerably because of this variation in the proportions of the minerals. It is, in general, lower in phosphate and calcium and higher in aluminum than the normal fertilizer plant feed. Table I shows typical analyses of samples of unbeneficiated ore. The uranium concentration ranges from less than 0.01% to 0.04% U_3O_8 . While this is a very low grade uranium ore, the extent of the deposit is sufficiently great that, since uranium can be recovered as a by-product in the manufacture of fertilizer from the ore, it represents an important source of uranium. For this reason, the Atomic Energy Commission has undertaken considerable research on the manufacture of fertilizer from the ore as well as on the recovery of uranium.

TABLE I

Chemical Composition of Leached Zone Ores

	Percent						
	P ₂ O ₅	Al ₂ O ₃	CaO	Fe ₂ O ₃	SiO ₂	F	L.O.I.
BC-0	15.1	8.8	17.4	1.9	49.8	----	6.6
BC-4	15.3	20.8	1.8	1.9	48.1	----	11.7
BC-5	12.2	18.0	4.9	2.6	51.8	----	9.4
BC-6	5.8	10.0	5.4	2.4	70.0	----	6.7
BC-8	18.4	17.2	4.6	4.5	42.8	----	10.3
BC-9	10.2	13.9	1.6	2.1	62.9	----	7.8
BC-10	15.5	18.1	4.5	2.0	47.3	----	9.6
BC-11	15.0	18.3	2.7	1.1	48.8	----	10.8
BC-12	9.4	16.1	1.8	2.2	56.8	----	8.6
BC-13	9.2	9.9	4.6	0.4	66.5	----	6.4
BC-14	15.3	18.6	6.0	2.2	47.0	----	9.4
V-5	11.8	16.2	2.6	1.6	57.7	0.42	9.2
V-6	10.8	15.1	1.9	1.5	61.8	0.46	8.4
V-10	16.9	13.6	12.1	1.8	45.1	1.4	8.5
V-11	17	13	12	2	46	1.2	8
V-12	14	9	11	4	52	1.2	7
V-13	15.1	9.2	12.3	3.3	57.0	1.2	6.4
V-14	14	10	10	4	54	1.2	6
V-15	15	10	12	4	49	1.3	6
V-16	15	10	11	4	53	1.2	6
V-17	15	10	11	4	52	1.2	6
X-1	6.3	9.0	6.3	1.2	43.0	0.32	11.4
X-2	4.7	6.0	3.4	1.7	42.9	0.18	15.3
X-3	17.3	16.8	17.3	1.1	27.1	0.77	10.4
X-4	7.3	15.3	2.2	1.6	39.6	0.23	12.3
X-5	14.0	23.8	2.4	1.5	30.8	0.10	16.6
X-6	2.5	7.3	1.6	3.0	59.7	0.54	7.2
X-7	11.4	14.1	11.0	5.4	44.2	0.69	8.3
X-8	12.5	17.9	3.2	1.0	35.0	0.46	14.6
X-9	6.8	10.1	2.0	0.7	62.8	0.29	7.6
X-10	6.4	13.3	2.6	0.7	44.1	0.30	12.2
X-11	16.2	20.9	5.1	1.1	30.8	0.42	13.8
X-12	3.2	11.1	1.8	3.2	49.5	0.08	9.0
X-13	6.0	2.9	2.3	1.1	44.2	0.31	12.8
X-14	7.3	13.0	4.7	1.2	42.4	0.25	12.4
X-15	4.4	9.3	1.1	0.4	43.1	0.09	11.2

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IV. BENEFICIATION OF LEACHED ZONE ORE

Since the phosphate minerals in these ores are softer than the quartz sand, which is the major contaminant, considerable beneficiation can be obtained by preferentially grinding the phosphate minerals and making a size separation. Both wet and dry methods have been used. When the ores are wet ground in a rod or ball mill, attrition ground in a centrifugal pump, and separated at 30 to 40 microns in a hydraulic cyclone, about 2/3 of the phosphate and uranium are found in the -30 or -40 micron fraction in concentrations of over 20% P_2O_5 and 0.03% U_3O_8 . Similar results are obtained by dry grinding and air classification.

Recent studies at the TVA laboratories indicate that the initial grinding in wet beneficiation is not necessary but that the +12 M portion is high in phosphate and uranium. Thus, if separation is made at 12 M and the -12 M fraction is ground to -35 M and deslimed at about 40 microns, most of the phosphate and uranium will appear in the +12 M and the -40 micron fractions. The -35 M +40 micron fraction, which consists mainly of quartz sand, can be further beneficiated by flotation of the quartz using an amine collector. A typical collector that has been used for this purpose is Armour's Armac T, a technical grade primary amine acetate derived from tallow fatty acids.

Using this method of beneficiation, a 13-ton sample of ore, which initially contained 16% P_2O_5 and 0.014% U_3O_8 , yielded 3.2 tons of a coarse concentrate (+12 M) containing 20.5% P_2O_5 and 0.016% U_3O_8 and 2.7 tons of slime concentrate (-40 micron) containing 25.2% P_2O_5 and 0.028% U_3O_8 . These two concentrates represent a 66% recovery of phosphate and 70% recovery of uranium. The washed sand fraction (-12 M +40 micron), which contained 10% P_2O_5 and 0.008% U_3O_8 , was further beneficiated by flotation of the quartz with an amine collector. A recovery of 86% of the phosphate and 78% of the uranium in this fraction was obtained in a concentrate containing 31.5% P_2O_5 and 0.019% U_3O_8 .

In dry beneficiation studies, it has been found that increase in the particle size at which separation is made results in increase recovery with only moderate lowering of the grade of the ore. Thus, separation at 18 microns results in only 18% of the phosphate and uranium in the

fine fraction at a grade of 23.5% P_2O_5 and 0.028% U_3O_8 but separation at 90 microns results in 70% of the phosphate and uranium in the fine fraction at a grade of 20.6% P_2O_5 and 0.026% U_3O_8 . However, although about half of the phosphate is ground readily, the other half is ground only with difficulty, probably because it is firmly cemented to the quartz particles. This difficultly ground portion of the phosphate can be easily separated from the quartz by flotation of the quartz with an amine collector. Thus, by removing the coarse fraction (+55 microns) after gentle grinding, and removing the quartz from this fraction by flotation, better recoveries have been obtained in higher grade concentrates than by fine grinding of the whole ore. A typical flotation of a +55 micron fraction resulted in a 97% recovery of phosphate in a 31% P_2O_5 concentrate.

Some recent studies indicate that wavellite can be separated from apatite by magnetic means, since wavellite is magnetic, while apatite is not.

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V. MANUFACTURE OF SALEABLE PRODUCTS
FROM LEACHED ZONE ORE

Several processes have been suggested for the conversion of leached zone ore to saleable products. In two processes, a single fertilizer product is produced. In one, the ore is extracted with nitric acid and the extract is ammoniated. In the other, the ore is extracted with sulfuric acid and the extract is used to acidulate phosphate rock, producing a superphosphate type fertilizer. The consumption of fertilizer in the United States is sufficiently great that several plants of these types could probably be built without saturating the market. The following table compares recent fertilizer consumption and anticipated fertilizer requirements with the estimated production of a plant which consumes 5000 tons of leached zone ore per day.

	Tons		Fertilizer consumption in fiscal year ended June 30, 1951		Fertilizer requirements in 1955 as estimated by the U.S.D.A.	
	Annual production from leached zone plant using un-beneficiated ore					
	Nitric Phosphate	Super-Phosphate	E. Central & S.E. States	Continental U.S.	E. Central & S.E. States	Continental U.S.
P ₂ O ₅	164,000	308,000	1,255,000	2,086,000	1,935,000	3,450,000
N	<u>164,000</u>		<u>654,000</u>	<u>1,171,000</u>	<u>1,200,000</u>	<u>2,185,000</u>
Total	328,000	308,000	1,909,000	3,257,000	3,135,000	5,635,000

Other processes have been proposed which recover the alumina separately and convert the phosphate into ammonium, calcium, or trisodium phosphate.

303 011

A. Nitric Acid Process

The nitric acid process has been studied extensively at the TVA laboratories. A pilot plant, using this process, has been in operation for some time. The ore is crushed, calcined, crushed again and fed to the extraction stage where it is treated with 60% HNO_3 and recycled wash water. The slurry is filtered, the extraction filtrate is ammoniated and the product is dried, crushed, sized and bagged. The following diagram shows the flow sheet for this purpose.

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Unbeneficiated ore has been used in most of the studies but a few experiments with beneficiated ore indicate that the process is adaptable to either feed. The ore is calcined at 1800° F. This procedure reduces the amount of acid subsequently consumed and increases the filter rate of the extraction slurry. Slurries of uncalcined ore are almost impossible to filter because of the fine clay particles. After calcining, filter rates of about 0.5 tons/day/ft.² have been obtained in the pilot plant.

In the pilot plant the acidulation is done in three stages. Approximately 90% of the phosphate in the ore and about 50% of the alumina are extracted by the acid. It has been found that the filtration characteristics are improved when a small amount of H₂SO₄ is added to the last extraction stage.

The filtrate is ammoniated in either one or four stages. In some runs, KCl has been added in this step. The ammoniated slurry, which contains 40% to 45% water is mixed with recycled oversizes and fines in a pug mill and dried in a Roto-Louvre drier.

Products of 20-20-0 grade or, when KCl is added, of 15-15-15 grade can be produced in this manner. The citrate solubility of the P₂O₅ in the products is 95% to 99%. The water solubility, however, is a function of the mole ratio of Al₂O₃/P₂O₅, and other variables. In order to increase the water solubility, attempts have been made to remove part of the alumina from the acidulation filtrate by precipitation of ammonium alum. However, this procedure has resulted, so far, in large losses of P₂O₅ to the alum precipitate. Another variation, which is being tested currently, is extraction with a reduced quantity of HNO₃ and an increased quantity of H₂SO₄ to suppress the alumina solubility and then addition of more HNO₃ to the filtrate. Some tests indicate that the water solubility of the P₂O₅ in the product is increased by cooling during ammoniation or by ammoniation in a single stage.

Greenhouse tests have been made with several experimental fertilizers produced in the pilot plant. The grade of these fertilizers was approximately 14-14-14. A mixture of concentrated superphosphate, potassium chloride and ammonium nitrate was used as a control. The results of these tests are shown in Table II. The material of low P₂O₅ water solubility that was prepared from low calcium ore was less effective than the other materials. However, the material with high water solubility prepared from low calcium ore and the material with low water solubility prepared from high calcium ore were about equal in effectiveness and about as effective as the superphosphate.

TABLE II

Summary of Greenhouse Tests
with High-Alumina Nitric Phosphate Fertilizer Materials

Kind of Ore ^(a)	P ₂ O ₅ Water solubil- ity, %	Parti- cle size, mesh	Relative yield ^(b)	
			Unlimed ^(c)	Limestoned ^(c)
Low calcium	10	-10+50	70	54
Low calcium	10	-50	74	52
Low calcium	28	-10+50	91	72
Low calcium	28	-50	92	65
High calcium	5	-10+50	90	69
Concentrated Superphos- phate ^(d)	--(e)	-10+50	100	90
Concentrated Superphos- phate ^(d)	--(e)	-50	86	71
None	--	-----	24	18

(a) Low-calcium ore, V-6; high-calcium ore, V-10.

(b) Relative yield of rye grass based on yield with minus 10- plus 50-mesh concentrated superphosphate on unlimed test - 100.

(c) Average of tests at 40 and 80 pounds of P₂O₅ per acre using Clarksville silt loam and Hartselle fine sandy loam.

(d) Ammonium nitrate and potassium chloride were added in amounts equivalent to the N and K₂O in the experimental materials.

(e) Concentrated superphosphate usually has 80 to 90 per cent of its P₂O₅ in a water-soluble form.

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A preliminary cost estimate (based on laboratory data) of this process has been prepared. A plant producing 20-20-0 fertilizer which treats 5000 tons of unbeneficiated ore per day to be located at Bartow, Florida, was assumed. Because of the high costs of transporting nitric acid, a plant for the production of nitric acid from ammonia was included. It was assumed that the investment would be amortized in a 15-year period. Estimates were made both for a plant producing its own ammonia and for a plant buying ammonia. An estimate for a plant treating beneficiated ore was also made. The following table shows a summary of the investment and production costs.

	Unbeneficiated Ore		Beneficiated Ore
	<u>NH₃ produced in plant</u>	<u>NH₃ bought</u>	<u>NH₃ bought</u>
Prod'n., tons/yr.	820,000	820,000	570,000
Total Plant Investment	\$59,800,000	\$30,100,000	\$24,000,000
Total Production Cost/Yr.	26,000,000	37,000,000	25,500,000
Total Value of Product/Yr.	59,600,000	59,600,000	41,600,000
Profit before Taxes/Yr.	33,600,000	22,600,000	16,100,000
Return on Investment (before taxes)	56%	75%	67%

This estimate indicates a return on the investment, before taxes, of over 50% for a plant located in Florida and a market in Illinois. For sales nearer a centrally located plant, the return on the investment should be higher.

New estimates based on extended pilot plant studies are now being prepared by both TVA and Blaw-Knox.

303 015

B. Superphosphate Type Process

The superphosphate type process has been studied only in bench-scale laboratory experiments. In this process, calcined ore is extracted with sulfuric acid and the filtrate from the extraction slurry is used to acidulate rock phosphate. The acidulated product is dried, sized and bagged.

The amounts of the various components of the ore extracted with sulfuric acid are about the same as the amounts extracted with nitric acid. Final products contained over 25% P_2O_5 . The P_2O_5 availability varied considerably but a number of products were prepared in which over 90% was available. The products were not hygroscopic. Samples dried over dehydrite adsorbed only 2% to 5% by weight of water and were in good condition after exposure for one hour in an atmosphere at 70% relative humidity and 86° F.

A preliminary cost estimate has been made for this process also. A plant consuming 5000 tons of unbeneficiated ore per day to be located at Bartow, Florida, was assumed. The estimate includes a plant for manufacture of sulfuric acid from elemental sulfur. A summary of the investment and production costs is shown in the table below. It was assumed that the investment would be amortized in a 15-year period.

Production, tons/year	1, 180, 000
Total Plant Investment	\$25, 800, 000
Total Production Costs/Yr.	18, 900, 000
Total Value of Product/Yr.	23, 070, 000
Profit Before Taxes/Yr.	4, 170, 000
Return on Investment (before taxes)	16%

A return on the investment, before taxes, of 16% is indicated for the plant located in Florida and a market in Illinois. For markets closer to a centrally located plant, the return should be higher. However, on this basis, the nitric acid process looks considerably more attractive.

303 016

C. Sulfuric Acid Digestion Process

This process has been carried into the pilot plant stage by the International Minerals and Chemical Corporation. However, only very sketchy information is available to us on the process. The leached zone ore is ground and beneficiated and fed to the digesters as a slurry containing 20% solids. It is digested with sulfuric acid and the slurry is filtered. The filtration is very slow and appears to be one of the biggest problems in the process. Ammonium alum is crystallized from the extract by addition of gaseous ammonia, and ammonium phosphate is then recovered from the mother liquor.

The alum is recrystallized twice and a fairly pure alumina is then precipitated by addition of the alum to aqueous ammonia. The ammonium sulfate remaining in the solution is then converted to ZnSO_4 and NH_3 by reaction with ZnO and the ammonia is recycled. The ZnSO_4 is converted to ZnO and SO_3 by calcining and the SO_3 is converted to H_2SO_4 and recycled. The ammonium phosphate product can be sold as a fertilizer.

A preliminary cost estimate for a process similar to this has been calculated. In this estimate, however, the ammonium sulfate was not converted to H_2SO_4 and NH_3 . Thus the final products were alumina, ammonium sulfate, and ammonium phosphate. A plant consuming 720 tons of leached zone ore per day was considered. The following values were computed. It was assumed that the investment would be amortized in a 10-year period.

Total Plant Investment/Yr.	\$21,000,000
Total Production Costs/Yr.	7,850,000
Total Value of Products/Yr.	10,300,000
Profit Before Taxes/Yr.	2,450,000
Return on Investment (before taxes)	11%

This estimate was based on very little laboratory data and includes considerable guessing. The value of the products was computed on the basis of products of quite high purity but it is not known whether the process is capable of producing such purity.

D. Caustic Leach Process

The caustic leach process has been studied extensively by both the Virginia-Carolina Chemical Corporation laboratories and the Dow laboratories but no pilot plant studies have yet been made. Some experiments have also been done at the TVA laboratories. The process developed at Dow consists of leaching calcined ore with a caustic soda solution, filtering while hot, and precipitating alumina and trisodium phosphate separately. Sodium hydroxide is then added to the mother liquor in an amount equivalent to that removed by the products and the solution is recycled.

It is necessary to calcine the ore because filter rates with uncalcined ore are too slow to be practical. With calcined ore, rates of 1/2 ton/day ft.² have been obtained. This process is most applicable to low lime leached zone ores, since an amount of phosphate equivalent to the calcium content cannot be extracted. The remaining phosphate, however, is almost completely extracted by leach solutions containing 3 moles of NaOH per mole of phosphate dissolved. From 5 to 15 minutes are required for extraction. The extraction is made at about 80° C. but the effect of variation in the temperature has not been studied. About one mole of aluminum is dissolved per mole of phosphate dissolved.

The alumina precipitates on standing. It may be removed either before or after precipitation of TSP. The order of precipitation has little effect on either the grade or physical characteristics of the alumina. The best grade of product that has been produced contained 64% Al₂O₃, 0.02% SiO₂ and 0.05% P₂O₅. About half of the alumina in the solution is precipitated each cycle and the remainder is recycled.

The TSP precipitates when the solution is cooled. Precipitates containing as little as 0.02% Al₂O₃ have been obtained by recrystallization. Some studies have been made of the conversion of TSP to calcium phosphate for use as fertilizers or cattle feed supplements. However, it is believed that the market for the various sodium phosphates would be adequate for the present.

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A few studies have been made of leaching with KOH solutions. About the same amounts of the various constituents of the ore are extracted as with NaOH. However, filtration rates are slower and separation of the phosphate from the aluminum is more difficult as tri-potassium phosphate does not precipitate completely except at quite low temperatures. Some experiments indicate that a separation can be obtained by ammoniating the leach filtrate under pressure. A two-phase system is obtained, one phase containing most of the phosphate and the other most of the aluminum.

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VI. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Four processes which are considered feasible for the utilization of leached zone ore have been discussed. Some work has been done on several other processes, such as HCl leaching, direct production of fertilizer by roasting and grinding, etc., but these processes do not appear economically profitable at the present time.

2. Of the processes presented, the nitric acid process and the caustic leach process indicate the greatest return on the investment.

3. The nitric acid process works equally well with either high or low lime ores but much of the plant consists of the equipment necessary for the production of NH_3 and HNO_3 and much of the profit corresponds to that which would be obtained from an ammonium nitrate plant. It is somewhat difficult to determine what part of the profit is derived from the treatment of the leached zone ore. Thus, this process depends, to a great extent, on the economics of ammonium nitrate, a product which has no direct connection with the leached zone.

4. The caustic process is applicable mostly to low lime ore. If high lime ore is used, phosphate equivalent to the calcium content is not recoverable and, hence, a greater amount of ore must be treated to obtain the same amount of product. The proposed process, at the present state of development, is promising, however, and the cost estimate indicates that TSP can be produced at lower cost than by the present processes. It is believed that it can be produced cheaply enough for use as a raw material for the production of other phosphate compounds which have a considerably larger market.

Recommendations

1. That further process development work be done on the caustic leach process, at least to a bench scale test of the complete process.

2. That further economic evaluation of the caustic process be made, particularly as regards market potential for the possible products.

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VII. SOURCES OF INFORMATION

The information in this report was obtained from the following sources, most of which are classified.

Geology and Minerology

1. U. S. Department of the Interior Geological Survey Reports, TEI-102, -212 and -270.
2. Virginia-Carolina Chemical Corporation Research and Development Reports, RMO-2937.
3. Oak Ridge National Laboratories, Y-12 Division Report, ORNL-1500.

Beneficiation, Nitric Acid Process, Superphosphate Type Process

1. Tennessee Valley Authority Reports, TVA-2706, et seq.
2. Correspondence with the TVA laboratories.
3. Virginia-Carolina Chemical Corporation Research and Development Report, RMO-2938.

Sulfuric Acid Digestion Process

1. Virginia-Carolina Chemical Corporation Research and Development Report, RMO-2938.
2. Trip through the International Minerals and Chemical Corporation pilot plant by Dow personnel.

Caustic Process

1. Virginia-Carolina Chemical Corporation Research and Development Reports, RMO-2935 and RMO-2938.
2. Tennessee Valley Authority Reports, RMO-2706, et seq.
3. The Dow Chemical Company A.E.C. Progress Reports, DOW-88, et seq.

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VIII. APPENDIX

DETAILED ACCOUNT OF THE CAUSTIC LEACH PROCESS

A. Leaching of the Ore

In leached zone ores, only the phosphate associated with aluminum can be extracted by caustic leaching. Thus, an amount of phosphate stoichiometrically equivalent to the calcium is not extractable. Calcining has no appreciable effect on the phosphate recovery but considerably less aluminum is extracted from calcined ore than from uncalcined ore. This is probably because a considerable amount of clay is dissolved from uncalcined ore while only the aluminum associated with the phosphate is dissolved from calcined ore.

The filtration rates of leach slurries of uncalcined ore are extremely slow. Rates less than 0.05 ton/day ft.² are typical. Hence, calcining is a necessary step in the process. Filtration rates of 0.5 ton/day ft.² have been obtained with slurries of ore calcined at 1000° C. for one or two hours. The solutions must be kept hot during filtration to prevent crystallization of TSP.

The extraction of phosphate and aluminum from calcined ore has been studied as a function of NaOH concentration, slurry density, and time. Most of the leaches have been made at 80° C. A few experiments at the boiling point (~105° C.) did not indicate any appreciable difference in extraction but the effect of temperature has not been studied further. Table III shows the extraction of phosphate in a number of leaches under various conditions at 80° C. The data are somewhat erratic but the extraction of phosphate seems to increase with solid density at low mole ratios of Na₂O/P₂O₅ while it is fairly constant with solid density at high Na₂O/P₂O₅ ratios. A slight increase in extraction with increased leaching time is indicated but, even with only 5 minutes, almost all of the extractable phosphate is leached. In only one case was the extraction better in 15 minutes than in 10.

The mole ratio of Na₂O used/P₂O₅ in the ore is not a good criterion for determining comparable conditions with ores of different lime content since the phosphate associated with the calcium does not enter the reaction. The mole ratio of Na₂O used/P₂O₅ dissolved is probably better for this purpose. From the above data it can be seen that 3 moles of NaOH per mole of phosphate dissolved are sufficient to recover essentially all of the extractable phosphate.

TABLE III

Percent of P_2O_5 Extracted from Ore

Low lime leached zone ore V-6.

Temperature of leach, 80° C.

Time of leach in minutes indicated by figure in parenthesis.

Mole Ratio, Na_2O/P_2O_5 in Ore	% Solids									
	15	20	25	30	33	36	39	40	45	50
2.0	40(5) 55(10) 60(15)									
2.4										69(5)
2.6										70(5)
2.7						61(5) 65(15)				
2.8										71(5)
2.9		70(5)		64(5)				74(5)		72(5)
3.0	65(5) 74(10) 70(15)									73(5)
3.2										74(5)
3.6							65(5) 71(15)			
4.0	83(5) 75(10) 68(15)			66(5) 77(15)						
4.5			71(5) 71(15)		71(5) 78(15)					
5.0	74(5) 86(10) 78(15)									
6.0	66(5) 75(10) 74(15)									

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The data above were obtained with leach solutions which, initially, contained no aluminum. Under actual plant conditions, the leach liquor would be recycled and, since only part of the aluminum is precipitated each cycle, the aluminum concentration in the recycled leach would be considerable. To determine the effect of this recycle aluminum, a number of leaches were performed in which sodium aluminate was added. Table IV shows the data obtained.

TABLE IV

Percent of P_2O_5 Extracted from Ore

Low lime leached zone ore V-6.

Sodium aluminate added to simulate recycle solution.

Temperature: 80° C.

Time of leach in minutes indicated by figure in parenthesis.

Mole Ratios		% Solids			
Na ₂ O added / P ₂ O ₅ dissolved	Al ₂ O ₃ added/ P ₂ O ₅ dissolved	27	32	35	37
3.4	1.3			72(60)	
3.5	1.3			69(120)	
3.5	1.7			71(60)	
3.4	1.8			70(120)	
3.6	2.2			69(60)	
3.6	2.2			68(120)	
3.9	1.4				76(5)
3.9	1.3				78(15)
5.2	1.4		77(5)		
5.3	1.4		75(15)		
6.5	1.4	77(5)			
6.5	1.4	77(15)			

The extraction seems to be slightly poorer with the one- and two-hour leach times. The extractions for the short leaching times are about the same as those shown in Table III. In these leaches the effective amount of base present in the leach solution is greater than that indicated in the Na₂O/P₂O₅ column because some is obtained from the sodium aluminate.

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In all of the above leaches the mole ratio of Al_2O_3 dissolved to P_2O_5 dissolved was very close to 1.0. While this ratio is probably constant with variation in the ore, the percentage of aluminum extracted from the ore will vary widely as the relative proportion of clay to aluminum phosphate minerals in the ore varies.

As the sodium loss to the residue is of great significance in the economics of this process, it was determined in most of the leaches described above. The sodium loss is defined as the percent of the sodium required to convert the dissolved phosphate to TSP assuming that the total amount of sodium lost is equal to that found in the residue plus that stoichiometrically equivalent to the silica dissolved. The sodium loss found in the leaches with NaOH alone is shown in Table V; that found in the leaches in which sodium aluminate was added, in Table VI.

At 15% solids, there seems to be a minimum of 2.7% loss. This minimum does not seem to appear, however, at higher solids content. With the higher solids densities, the loss seems to be fairly constant at 4% to 6%, although it was higher in a few instances. There seems to be a slight increase in sodium loss with increased leaching time or increased NaOH concentration. The losses would probably be expected to increase in both cases because of increased opportunity for reaction with the siliceous materials and tests in which leaches were sampled at various time intervals also indicate increased sodium loss with time. The amount of dissolved silica in the leach solutions is negligible in leaches where the mole ratio of Na_2O added to P_2O_5 in the ore is 4 or less. With larger amounts of caustic, however, the silica in solution becomes appreciable and increases with increasing NaOH concentration and increasing leach time.

Several leaches were made with beneficiated ore. The leaching characteristics were not found to be appreciably different from those of unbeneficiated ore. The slurries made with uncalcined ore had impossibly slow filter rates but those made with ore calcined at 1000°C . to 1100°C . filtered readily.

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TABLE V

Percent Sodium Loss

Low Lime leached zone ore V-6.

Temperature of leach: 80° C.

Time of leach in minutes indicated by figures in parenthesis.

Mole Ratio, $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ in Ore	% Solids									
	15	20	25	30	33	36	39	40	45	50
2.0	4.6(5) 3.9(10) 3.3(15)									
2.4										
2.6										
2.7						4.5(5) 5.0(15)			4.6(5) 5.0(15)	
2.8										
2.9										
3.0	3.3(5) 3.1(10) 5.0(15)									
3.2										
3.6				6.1(5) 4.7(15)			4.7(5) 5.5(15)			
4.0	2.7(5) 2.7(10) 2.7(15)									
4.5			5.4(5) 5.5(15)		5.0(5) 5.1(15)					
5.0	4.1(5) 2.6(10) 4.5(15)									
6.0	5.9(5) 6.1(10) 6.1(15)									

TABLE VI

Percent Sodium Loss

Low lime leached zone ore V-6.

Sodium aluminate added to simulate recycle solution.

Temperature of leach: 80°C.

Time of leach in minutes indicated by figures in parenthesis.

Mole Ratios					
Na ₂ O added/ P ₂ O ₅ dissolved	Al ₂ O ₃ added / P ₂ O ₅ dissolved	% Solids			
		27	32	35	37
3.4	1.3			5.5(60)	
3.5	1.3			7.1(120)	
3.5	1.7			6.4(60)	
3.4	1.8			5.8(120)	
3.6	2.2			7.9(60)	
3.6	2.2			4.2(120)	
3.9	1.4				7.2(5)
3.9	1.3				4.3(15)
5.2	1.4		10.5(5)		
5.3	1.4		7.0(15)		
6.5	1.4	6.2(5)			
6.5	1.4	5.6(15)			

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B. Precipitation of Trisodium Phosphate

The leach filtrates contain approximately 60 grams P_2O_5 /liter and 90 grams Al_2O_3 per liter. TSP crystallizes from the filtrate on cooling to 20°C. or 30°C. As the crystals are quite large, the slurry filters rapidly. Products containing as much as 93% of the amount of phosphate initially in the leach filtrate have been obtained. The yield depends on the temperature of crystallization, higher yields being obtained at lower temperatures. The yields obtained from leaches which initially contained no aluminum are lower than those from leaches to which aluminum had been added to simulate the composition of plant recycle liquors. For example, a leach containing no added aluminum gave a 72% yield of TSP at 20°C. but only 41% at 25°C., while a leach containing added aluminum gave a 91% yield at 30°C.

In a number of experiments, the TSP products were purified by dissolving in hot water and recrystallizing. Products containing as little as 0.02% Al_2O_3 were obtained in this manner. In a recycle test, where this procedure was followed, the Al_2O_3 concentration in the final TSP increased with recycle of the leach liquor. However, a few experiments indicated that the residual Al_2O_3 can be easily removed by washing with water.

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C. Alumina Precipitation

Alumina precipitates spontaneously from the leach filtrate on standing for a number of hours. This precipitation will take place either before or after TSP precipitation. That is, if the solution is kept at 50°C., which is slightly above the TSP crystallization point, the alumina will precipitate and, after filtration, the solution can be cooled to crystallize the TSP. If the solution is cooled first, the TSP crystallizes and the alumina will precipitate from the filtrate on standing.

The order of precipitation, i.e., whether the aluminum is precipitated before or after TSP crystallization, has little effect on the grade or physical characteristics of the alumina product. The amount of alumina precipitated, however, averages higher in the case where TSP is crystallized first. Thus, it is estimated that about one mole of aluminum would be recycled per mole of aluminum dissolved if the alumina were precipitated after TSP crystallization but about two moles of aluminum would be recycled per mole of aluminum dissolved, if it were precipitated before TSP crystallization.

Since only part of the aluminum precipitates from the solution and since the recycle liquor thus contains a significant aluminum concentration, the aluminum precipitation experiments were made with leaches to which sodium aluminate had been added to simulate the concentrations in plant recycle liquors. In the resulting leach filtrates, about 1/3 of the aluminum was derived from the ore.

When TSP is crystallized first, by cooling rapidly to 20°C. or 30°C., the alumina begins to precipitate during or shortly after the TSP crystallization. This could result in a difficult product separation, although, even in those cases where the alumina precipitates before the TSP is removed, the fine alumina precipitate easily passes through the coarse filters used for TSP filtration. However, the fact that the time of separation between TSP crystallization and alumina precipitation is difficult to control if TSP is crystallized first, makes the reverse procedure appear more favorable in spite of the higher aluminum recycle.

The best grade of alumina hydrate, which has been produced, contained 64% Al_2O_3 , 0.02% SiO_2 and 0.05% P_2O_5 . Alumina precipitation times in excess of 20 hours lead to increased silica content in the alumina. The significance of the phosphate content in the alumina is doubtful, since the amount of phosphate which can be removed by washing has not been determined.

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Dilution of the liquor, from which alumina is precipitated, is undesirable, since this decreases the amount of alumina precipitated. Agitation during the alumina precipitation seems to favor large crystals of alumina. The largest average crystal size obtained was about 70 microns. The crystals appear to be aggregates of smaller units.

There are no doubt a number of other factors affecting the alumina precipitation but these have not yet been determined. The effect of temperature, for example, has not been studied.

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D. Market Possibilities for Products

Some preliminary study has been made of the conversion of TSP to other saleable products. When calcium carbonate is digested with a TSP solution, citrate soluble calcium phosphate is produced. Precipitated calcium carbonate yielded products containing 31% P_2O_5 of which 91% to 96% was citrate soluble. Ground limestone gave somewhat poorer products with 15% to 19% P_2O_5 of which 71% to 79% was citrate soluble. Hydrated lime gave products containing 27% to 31% P_2O_5 but only 35% to 48% was citrate soluble. While the TSP may be too costly to produce a fertilizer by this process, it may be possible to produce a cattle feed supplement in this manner.

It may also be feasible to use TSP produced by this process in place of Na_2CO_3 for the production of mono and disodium phosphates from phosphoric acid. In this way the caustic value of the TSP is used while the phosphate value is preserved.

While the present production of TSP in the United States is only about 50,000 tons/year and is declining because the polyphosphates are preferred for many of its former applications, the demand for both dicalcium phosphate and sodium tripolyphosphate are increasing. Although the production of the present plants is being increased to meet this demand, it is estimated that by 1955 the demand for sodium tripolyphosphate will be over 400,000 tons/year while that for dicalcium phosphate (mostly for use as feed supplements) will approach 275,000 tons/year. Thus, if TSP produced from leached zone ore by the caustic process can be converted to other sodium phosphates or calcium phosphates, there will be ample market for the capacity of any reasonably sized plant.

It is believed that an alumina product of reduction grade can be obtained from the leached zone process. If this can be done, there will be no problem in marketing the product, since there is a shortage of high-grade alumina deposits in this country and the aluminum producers must import from abroad.

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