

NORTH CAROLINA PHOSPHATE CONCENTRATION.
THE TEXAS GULF SULPHUR COMPANY PROJECT
AT THE ASHEVILLE MINERALS RESEARCH LABORATORY

Inno H. Redeker
Mineral Dressing Engineer
NORTH CAROLINA STATE UNIVERSITY
Minerals Research Laboratory
Asheville, North Carolina

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Abstract

Through close cooperation with geophysical and geological test work by Texas Gulf Sulphur Co. in Beaufort County, the Asheville Minerals Research Laboratory assisted in the evaluation of North Carolina's most valuable mineral resource, the Pungo River phosphate deposit. After a core evaluation study, the flotation process for the concentration of North Carolina phosphates was demonstrated in a 500 lb/hr pilot plant in Asheville. Tonnage samples of phosphate concentrate were produced for customer evaluation in USA, Europe and the Far East. Plans for a larger pilot plant to be erected at the plant site at Lee Creek were prepared for TGS. The larger pilot plant was operated by TGS in conjunction with a test dredging operation which led to the adoption of a dragline dry mining method to move 90,000 tons per day of material for the production of 10,000 tons per day of phosphate concentrate in an all flotation phosphate concentrator. Calcining, dry grinding, and by-product studies complimented the construction of one of the world's largest and most modern fertilizer raw material complexes on the Eastern North Carolina Seaboard.

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Introduction

In October of 1961 Texas Gulf Sulphur Company contacted the Asheville Minerals Research Laboratory, of the North Carolina State University, and requested assistance in the development of a phosphate ore body in Beaufort County. The main objectives of the work at Asheville were defined as follows. The Laboratory should try to determine on the basis of drill core samples, submitted by Texas Gulf Sulphur Company, the highest grade of phosphate concentrate that could be obtained with high recoveries from North Carolina ore, the thickness of the ore body that could be treated economically in one section, and the quantity of concentrate that could be obtained per acre. The results should be compared with data obtained from the treatment of Florida ores. It was important to use mineral preparation methods during the initial laboratory work that could be verified later by continuous pilot plant operation and could be scaled-up for a commercial plant.

The writer was in charge of the project at the Asheville Minerals Research Laboratory and participated in the development of one of North Carolina's greatest mineral resources from the first drill core examination to the production of the first poundage and tonnage quantities of flotation concentrates. The Lee Creek phosphate mine and mill was put in operation in early 1966 and can produce three million tons of phosphate concentrate a year. Sulfuric acid, and phosphoric acid plant, diamonium phosphate plant and triple super phosphate plants came on stream in 1967; at that time they were the world's largest.

Now that a phosphate industry has been established in the State, it

seems an opportune time to review developments leading up to this, especially the cooperative efforts of a State supported organization and private company. For a better understanding of North Carolina phosphates, a few words pertaining to the phosphate industry in general, the history of North Carolina phosphates, and the modern approach of Texas Gulf Sulphur Company to the problems of exploration, acquisition and development of the mineral property, which went hand in hand with test work at Asheville, shall precede the project description.

The Phosphate Industry

Almost all commercially produced phosphate in the United States is of marine sedimentary origin. The phosphate granules or pebbles are either in unconsolidated matrix, containing phosphate pebble diluted by quartz sand, calcium carbonate and clay as found in North Carolina, South Carolina and Florida, or in consolidated formations of semi-hard shales as in Idaho, Montana and Utah.

The principal phosphate-bearing mineral in the North Carolina ore has been investigated by Dr. James R. Lehr of the Tennessee Valley Authority at Wilson Dam and by Dr. T. Rooney at Columbia University.⁽¹⁾ The phosphate-bearing mineral is a carbonate fluorapatite or francolite, that is, a fluorapatite in which an excess of fluorine and carbonate replaces phosphate in the apatite lattice. The clean North Carolina phosphate pebble has around 31 percent P_2O_5 content and an inherent CaO/P_2O_5 ratio of 1.59.

In order to produce a commercial phosphate product, the phosphate matrix or ore has to be mined and separated into valuable pebble and wasted sand, clay and calcium carbonate. A phosphate pebble with a high P_2O_5 or BPL content, a low lime to phosphorus ratio (CaO/P_2O_5) and a minimum of other dilutants such as fluorine, iron, aluminum, magnesium and hydrocarbon is desired.

About 70 percent of the phosphate pebble produced in the United States goes into fertilizer production. A small part is still used to produce super phosphate by reacting ground phosphate pebble with sulfuric acid followed by

curing. The trend, though, is towards increased production of wet phosphoric acid and high grade super phosphoric acid from phosphate pebble and sulfuric acid and the production of triple super phosphate by reacting ground phosphate pebble with phosphoric acid. Diammonium phosphate is produced by reacting ammonia with phosphoric acid. Triple super phosphate and diammonium phosphate are concentrated products which are raw materials for mixed fertilizers. Texas Gulf Sulphur Company produces all of the above named phosphate products at Lee Creek, N. C.

History of Development of North Carolina Phosphates

First interest in Beaufort County and surrounding Pamlico and Hyde County phosphates arose, according to Stuckey⁽³⁾ in 1951 when AMCO Exploration Inc., a subsidiary of American Metals Company, started exploration for phosphate and obtained leases from the State for phosphate-bearing minerals for an area underlying the Pamlico River and tributaries from a point six miles upstream from the city of Washington, North Carolina to thirty miles downstream of Washington, N. C. In 1953 AMCO Exploration cancelled the lease with the statement, "...have failed to make any discovery of a commercial ore body of phosphate-bearing minerals. ..." In 1957 Kennecott Copper Corporation through its subsidiary, Bear Creek Mining Company, and Sun Oil Company through its subsidiary, General Crude Oil Company, acquired leases and began to explore for phosphate in Beaufort County. Both companies withdrew from the area in 1958. Texas Gulf Sulphur Company looked at North Carolina phosphates in 1959 but considered the mining cost prohibitive at that time.

The first encouraging report on the phosphate potential in the area was presented by Brown⁽⁴⁾ in 1958, indicating a major phosphate ore body of economic importance together with a theory of the possible origin of the phosphate deposit of Beaufort County, North Carolina.

Two main problems have beset the North Carolina phosphate development

from the beginning. The first problem is mining of a deposit which is below sea level and which is near an ocean-connected water body. It is overlain by 50 to 200 feet of overburden and underlain by a major artesian aquifer, the Castle Hayne formation. The second problem is the production of high-grade phosphate concentrate from the ore or matrix without dilution by coquina, shell and dolomitic limestone which is found in some sections of the ore body. The first problem was solved by TGS during an extensive test mining and test pumping project in 1964. The second problem was solved by the Asheville Laboratory and is described in this paper.

In 1961 A. L. Nash, working for Sun Oil Company, brought the first tonnage quantity of North Carolina phosphate ore to the surface while trying to develop a hydraulic mining technique especially suited to the deeper areas of the Beaufort County deposit north of the Pamlico River. The method was based on the hope of removing large quantities of phosphate ore from the deposit by pumping, without removing or caving the caprock and overburden. The coquina caprock caved in and the venture failed as an economical mining method. However, Nash's work was extremely helpful from another standpoint, as it supplied ore for beneficiation studies at the Asheville Minerals Research Laboratory, for the Texas Gulf Sulphur pilot plant at Lee Creek in 1964, and for an FMC Corporation pilot plant in Asheville in 1965.

In 1961 interest in North Carolina phosphates was renewed by three companies: Texas Gulf Sulphur Company, Magnet Cove Barium Corporation, and North Carolina Phosphate Corporation (a joint venture of Kennecott Copper Corporation and American Agricultural Chemical Company). The State received bids in 1962 for leases of State-owned river bottoms under the Pamlico River and under the Pungo River. Texas Gulf Sulphur Company was awarded the option to lease 9,200 acres of river bottom north of Lee Creek. Magnet Cove Barium Corporation was awarded options to lease blocks in the Pungo River. The various interested companies have also acquired many thousands of acres of private

land adjacent to the State leases.

The Texas Gulf Sulphur Approach to North Carolina Phosphates - A Text Book
Example of Scientific Geology

Texas Gulf Sulphur Company's bid for the lease on the State owned river bottom and acquisition of surrounding land was preceded by rapid collection of knowledge about the ore body by means of geophysical methods and by a comparison with other producing phosphate deposits in the United States. A major tool in the early work of Texas Gulf Sulphur Company was gamma ray logging of existing water wells. The small amount of radioactive uranium, and possibly thorium, minerals in the North Carolina phosphate pebble, gives a gamma ray count proportionate to the phosphate content of the ore. Gamma ray logging therefore shows the approximate ore grade and also defines the contacts between the Pungo River phosphate formation and the discordantly overlying Yorktown formation and the discordantly underlying Castle Hayne formation.

Through a one man gamma ray logging program of about 50 existing water wells, Dr. Leo Miller of Texas Gulf Sulphur Company gained knowledge about the extent of the ore body, especially south of the Pamlico River, the thickness of the phosphate formation and of the overburden. By March 1962 a map with overburden and ore isopachs was drawn and the limits of an ore body with a minimum thickness of 40 feet, a maximum ratio of overburden to ore of 2 : 1 and with less than 200 feet total depth could be delineated. It was hoped that a deposit meeting these requirements had possibilities for dry, open-pit mining if the amount of water inflow could be determined and controlled. The area around Lee Creek met the above requirements and could be secured by Texas Gulf Sulphur Company partly because not too much was known up to then about the extent of the ore body south of the river. Similar information was made public later through a gamma ray logging project by the North Carolina Department of Conservation and Development, in cooperation with the U. S. Geological Survey. This project started in March 1962, has been on open file since 1963, and was

published in 1965. (5) A map showing overburden thickness and phosphate ore body thickness, as computed from the data given in the report, is presented in Figure 2.

Without drilling, Texas Gulf Sulphur Company gained control over a most valuable part of the North Carolina phosphate ore body. A relatively small number of drill holes, less than one hundred, put down in 1962 provided more exact geologic knowledge and material for studies about the physical quality of the phosphate ore, the amenability to concentration and the quality and quantity of concentrate that could be extracted. These holes can now be called million dollar holes, because at least 100 million dollars have been expended to mine, mill, process and ship North Carolina phosphate products.

The Concentration of North Carolina Phosphates

Because of layers of calcitic and dolomitic limestone in the phosphate matrix, the concentration of North Carolina phosphates presented a problem to earlier investigators and may have contributed to the delay in development. No reliable flotation method to separate phosphate and calcite was known at that time. Especially when the whole phosphate section was treated after grinding by flotation appreciable amounts of free calcite entered the concentrate. This made the concentrate unacceptable for the fertilizer industry because of high sulfuric acid requirements in acidulation. A series of logical steps had to be taken to produce high grade phosphate concentrates with high recoveries from the Pungo River phosphate formation. The steps are as follows.

Step 1: Defining of High Lime and Low P₂O₅ Upper and Lower Low Grade Sections and High Grade Section for Differential Mining - In Table I pertinent analysis data of typical drill core sections are presented. On the basis of high free lime content, low P₂O₅ content, and high optimum ratio of concentration, the upper three footage sections (76'-87') were defined as upper low grade to be removed from the top of the ore bed. This upper low grade section,

in average 10 to 15 feet thick, is easily recognized because it contains a high percentage of light colored coquina limestone indurated through the phosphate sand. (See Figure 3). The upper low grade to be rejected contains in the case of hole 84, only 5.8 percent of the total P_2O_5 in the phosphate section but has 33.2 percent free calcium carbonate.

The footage section 87-132 has an average P_2O_5 content of 14.9 percent, a low lime P_2O_5 ratio of 1.8, a low optimum ratio of concentration of 2.1, contains only 4.5 percent free calcium carbonate and the free calcium carbonate is mainly in the fine sizes as is shown later in Step 3. This 45-foot thick section is defined as high grade phosphate section, it contains 89.2 percent of the total P_2O_5 in the phosphate section, and is to be mined and milled for phosphate recovery.

The footage section 132-136 is lower in phosphate and again high in free calcium carbonate, 38.7 percent, it contains also some magnesium carbonate, and it is to be left in the ground as a barrier against the underlying Castle Hayne Aquifer.

Step 2: Removal of Lime from High Grade Section - The high grade section was to be treated as one section of approximately 40-foot thickness, in spite of a thin layer of hard dolomitic limestone in the upper 10 feet of this section. (See footage 96-97, Table 1). It was discovered that this hard dolomitic limestone could be kept out of the high grade ore matrix by screening even when crushed to minus 1/4-inch for sample composition. The hard lime material could be removed by wet screening on 14 mesh and rejecting of oversize with low P_2O_5 losses, 31.5 percent of the free lime is so removed. (Table 2, Step 2). The large part of the free lime which is fine grained and softer could be removed after wet scrubbing by desliming on 200 mesh. In contrast to Florida phosphate processing experience, the fine montmorillonite type clay slimes of the North Carolina matrix are high in free calcium carbonate

and contain only a very minor amount of phosphate values. Sixty to 90 percent of the free lime in the high grade section is removed with the fine slimes with a low P_2O_5 loss of only around three percent. The lime rejection from North Carolina phosphates consists of physical sizing on 14 mesh after light wet agitation and removal of fine clay slimes and fine lime after scrubbing by desliming on 200 mesh. The removal of 16-18 percent by weight of low P_2O_5 clay slimes upgrades the minus 14 plus 200 mesh flotation feed to about 17-18 percent P_2O_5 .

Step 3: Removal of Quartz from Phosphate Pebble - For the upgrading of the well sized and well deslimed minus 14 plus 200 mesh fraction of North Carolina high grade matrix, containing 85-90 percent of the P_2O_5 in the high grade section or matrix, the physicochemical process of flotation separation was employed.

For the separation of North Carolina phosphate pebble from quartz three flotation methods can be employed. A) First, it is possible to condition the deslimed sands with an anionic, fatty acid-type collector and float the hydrophobic phosphate away from the quartz. A fair-grade rougher concentrate with 26 to 29 percent P_2O_5 and with phosphate recoveries of over 95 percent can be obtained. Quartz particles which have phosphate inclusions or are phosphate stained float in the fatty acid flotation step. By multiple cleaning, a concentrate grade of 29 to 30 percent P_2O_5 can be obtained with a fair recovery (80 to 90 percent). B) Second, it is possible to render the quartz hydrophobic and float it away from the phosphate pebble with a cationic, amine-type collector. Acceptable concentrate grades of 30 to 31 percent P_2O_5 with fair recovery of 80 to 90 percent can be obtained. The amine system is very sensitive to slimes and reagent variations and it therefore causes operation problems. There are also problems involved in floating the coarser quartz without losing fine phosphate in the float waste product. C) The most reliable system for obtaining high concentrate grades, 30 to 31 percent P_2O_5 , with high flotation recoveries, 90 to 95 percent, is a combination of an anionic float followed by dereagentizing and then a cationic float. The cationic float removes the fine silica and

coarse phosphate stained quartz particles from the fatty acid concentrate with little loss of phosphate. This double flotation method is used extensively in Florida where it was developed by Crago⁽⁶⁾ in 1941. It allows more variation in flotation feed and plant conditions than either the single anionic or single cationic flotation procedures. The double flotation procedure was advocated by the Minerals Research Laboratory and a technique was developed to treat the core samples from the Texas Gulf Sulphur Company drill project which consistently gave high grade concentrates with high recoveries. It was also noticed that some times small amounts of free calcite were removed in the cationic flotation step. The acid scrub may not completely remove fatty acid from shells, or calcium sulfate formed on the shell surface during sulfuric acid scrub causes it to float with amine, or possibly the shape factor effect may cause the shell material to be removed with the amine float product which is wasted.

In Table 2, Step 3, the results of flotation separations are presented.

Step 4: Drying and Calcining of Flotation Concentrates - The flotation concentrates are further upgraded by drying to remove free process water and by calcining at 1500-1750° F. under controlled conditions. Calcining removes hydrocarbons and CO₂ from the phosphate pebble and reduces foaming problems in the digester of phosphoric acid plants. Calcining also reduces the weight by 10 percent and effects a freight savings and an increase in P₂O₅ content from 30.5 to 33.0 percent. Calcining does not change the CaO/P₂O₅ ratio. The grade of super phosphoric acid obtained when treating North Carolina calcined phosphate concentrate is of such quality that animal feed grade phosphate products can be produced from it.⁽⁷⁾ Texas Gulf Sulphur Company operates now the world's largest phosphate calciner at Lee Creek.⁽⁸⁾ Table 3 shows analysis and properties of North Carolina phosphate concentrates before and after calcining.

Phosphate Core Evaluation Procedure

Representative core composites from high grade and low grade sections were prepared from the cores by crushing to 1/4-inch and riffing. Six-hundred gram samples were then used for evaluation of million dollar holes.

Feed Preparation

Tumble 600 grams of wet sample at 40 to 50 percent solids in 8" x 9" laboratory mill with 440 gram rubber rod for 15 minutes.

Screen out plus 14 mesh material.

Wash remaining mud balls, if any, through screen with water spray.

Decant minus 14 mesh material on 200 mesh screen to 60 to 70 percent solids.

Save minus 200 mesh slimes.

Scrub minus 14 mesh material at 60 to 70 percent solids for 10 minutes with 4-bladed, 3-inch impeller at 1200 rpm.

Screen out plus 28 mesh material.

Deslime minus 28 mesh twice on 200 mesh after diluting to 10 percent solids.

Settle minus 28 mesh material to about 60 to 65 percent solids.

Flotation of Minus 28 Plus 200 Mesh Material

Condition at 60 to 65 percent solids for 5 minutes with 4-bladed, 3-inch impeller at 700 rpm after adding saponified fatty acid (0.3 to 0.8 lb/ton of feed) and fuel oil (0.5 to 1.0 lb/ton of feed).

Float in Denver 500-gram laboratory flotation machine.

Clean float product once.

Scrub cleaned concentrate with H_2SO_4 (2 to 4 lb/ton of feed) at high solids for 5 minutes.

Wash twice after diluting to about 10 percent solids.

Float remaining quartz after conditioning for 15 seconds in cell with amine acetate (0.15 to 0.3 lb/ton of feed).

Agglomeration of Minus 14 Plus 28 Mesh Material

Condition this coarse fraction with saponified fatty acid and fuel oil for 5 minutes.

Agglomerate float with water spray.

The results of a typical hole are presented in Table 4.

Comparison of North Carolina Practice With Florida Practice - Texas

Gulf Sulphur Company was very encouraged when concentrate grades of up to 31 percent P_2O_5 with high recoveries were produced at the Asheville Laboratory from the first drill core in January 1962 and from succeeding drill cores during the following month.

A comparison of the assay procedures and flotation methods by other laboratories verified the high grade concentrate and high recoveries obtained at the Asheville Laboratory.

The Asheville flotation method for North Carolina phosphate ores differs from Florida practice in that partially saponified, tall oil fatty acid of definite quality and rosin acid content is used instead of crude tall oil and NaOH. The apparent advantages over Florida practice are mentioned here in order of importance.

1. Percent solids in the conditioner can be kept lower when using saponified fatty acid than when using crude tall oil and NaOH, thereby saving wear and power and minimizing slime formation.
2. Less fatty acid is necessary because of better dispersion and higher fatty acid content. This more than compensates for the higher cost of refined tall oil of uniform quality.
3. Less NaOH is necessary and conditioning and flotation pH can be held below 9.
4. Less H_2SO_4 is needed in the following fatty acid removal step because of uniformity of the Ca-fatty acid salt coating on the phosphate pebble. A

special reagent tank farm was erected at Lee Creek and the reagent system was found to be very reliable under varying feed conditions.

Results of Core Evaluation - In the first phase of the drill core program, 67 drill holes were evaluated and TGS was informed that from a large part of their property approximately 30,000 tons of high grade concentrate could be recovered from each acre by treating only the 40-foot high grade ore zone. The hard layers of high calcium carbonate and high magnesium carbonate content in the high grade ore body could be separated from the bulk of the material by simple screening, scrubbing and desliming methods. A very good picture about the uniformity of the ore body was obtained.

The core evaluation also included calcining of the concentrates.

Samples from nine Florida phosphate pits, representing eight operating companies, were processed in the Minerals Laboratory in 1962. To make comparisons with North Carolina results the same laboratory procedures were used to process the Florida samples. The comparison of Florida and North Carolina data looked very encouraging. The area Texas Gulf Sulphur Company was interested in would yield more than five times the amount of phosphate concentrate per acre than was obtained in Florida. The amount of overburden and matrix to be mined per ton of concentrate was the same as in Florida. The reagent amounts necessary to up-grade the ore by flotation were much less per ton of concentrate than in Florida. The North Carolina phosphate pebble is not weathered and is harder than Florida pebble. The amount of phosphate lost in the slimes is only a tenth as great as the loss in Florida per ton of ore treated. Less favorable factors are that the bulk of North Carolina phosphate concentrate contains only 30.5 to 31 percent P_2O_5 whereas the average Florida concentrate grade is 33 percent P_2O_5 . North Carolina phosphate concentrate has a slightly higher CaO to P_2O_5 ratio than Florida phosphate pebble, which means that slightly more sulfuric acid is necessary in producing of super phosphate or phosphoric acid, but some of the lime is in the form of non acid consuming calcium sulfate. A

lower alumina and iron content in the North Carolina phosphate concentrate, about half the amount generally found in Florida phosphate material, is favorable. Also, the reaction rate of North Carolina phosphate with sulfuric acid in the conversion process is faster than with Florida phosphates, and the grade of phosphoric acid and other fertilizer products such as diammonium phosphate, and triple super phosphate produced now at Lee Creek compares favorably with Florida products. (7)

The TGS Phosphate Flotation Pilot Plant at the Asheville Minerals Research Laboratory - Pilot Plant Objective and Operation

Samples of concentrate weighing up to 50 pounds were produced by batch procedures during the drill core evaluation for shipment to prospective customers. Tonnage quantities of concentrate were needed for super phosphate and phosphoric acid test work. In November 1962 Texas Gulf Sulphur Company requested rapid erection of a pilot plant at Asheville that could produce tonnage quantities of phosphate concentrate from ore which was pumped to the surface at Gum Point on the northern shore of Pamlico River. The pilot plant later treated a number of large diameter drill cores.

A 500-pound-per-hour pilot plant was designed around the equipment available at Asheville and was set up within one month. In December 1962 the first experimental run produced acceptable concentrate. By March 1963 about 35 tons of ore had been processed. The final pilot plant run on April 3, 1963 was made on drill core material in order to verify the process on ore like that which would be obtained by dry mining methods. Representatives of Texas Gulf Sulphur Company were satisfied that the process could treat North Carolina phosphate ore reliably. In all pilot plant runs acceptable concentrate grades of plus 30 percent P_2O_5 were obtained. The recovery was very high in a few runs, but was lower in others depending on variables studied, such as reagent quantities and screening methods.

The flowsheet of the Texas Gulf Sulphur Company pilot plant at Asheville

is presented in Figure 4.

Pilot Plant Description

Feed Preparation - The ore was fed on a belt feeder at a constant rate of 500 pounds per hour into an impeller-type scrubber, was diluted and pumped onto a 28 mesh trommel or stationary Wedge Wire screen. The small amount of screen oversize was kept separate. The screen undersize was diluted to about five percent solids and deslimed in the first cyclone. The overflow from the first cyclone contained all slimes removed. Slime samples were kept for settling characteristics and thickener requirement determinations. The cyclone underflow was densified in a screw classifier and scrubbed at 65 percent solids in a Wemco-type attrition scrubber. The scrubbed material was deslimed in a second cyclone after dilution. The second cyclone overflow was recirculated to the first cyclone. The second cyclone underflow was densified to 75 to 80 percent solids in the second screw classifier.

Fatty Acid Flotation - The sized, deslimed and densified material was fed to the fatty acid conditioner where the percent solids was adjusted by adding water in metered quantities. The flotation feed was conditioned with saponified fatty acid and fuel oil. The feed was then diluted to flotation density and fed to the Denver pilot plant flotation machine. A rougher float was followed by two cleaner steps. The tailings from the cleaners were circulated to the rougher machine. The fatty acid tailings were sampled and discarded. Ninety-six to ninety-eight percent of the P_2O_5 in the flotation feed was recovered in a fatty acid concentrate containing five to ten percent insolubles. The type concentrate produced in the fatty acid float alone could be used for the production of phosphoric acid in a captive plant. Open market sales would require upgrading by the amine float.

Acid Scrub and Amine Flotation - The fatty acid concentrate was conditioned in an impeller-type scrubber with sulfuric acid. The concentrate was then washed in a fluid-bed-type, V-box washer to remove the fatty acid-

sulfuric acid reaction products. In the next float the remaining silica was floated away from the phosphate concentrate by an amine acetate collector. Ninety-five to ninety-six percent of the P_2O_5 in the flotation feed was recovered in a concentrate containing 30 to 31 percent P_2O_5 and less than three percent insolubles. The final concentrate was dried in a rotary dryer before shipment to prospective customers in the United States and as far away as Japan and Europe.

Pilot Plant Control - All feed streams into the pilot plant, such as ore, water, and reagents, were metered continuously. The product streams out of the pilot plant were sampled at intervals by taking timed samples on a routine schedule. Material balances were made on the basis of sample weights and P_2O_5 assays. The assay method employed is based on the color intensity of molybdivanadophosphoric acid which is measured in a colorimeter. A number of samples were sent out to other laboratories for checks and standardization of the method.

The pilot plant circuit ran very reliably and could be operated by one engineer, two technicians and one utility man.

Pilot Plant Results - In Table 5 the material balances for pilot plant runs on pumped ore are presented together with the amount of reagent used.

The Larger Pilot Plant Operated by Texas Gulf Sulphur Company at Lee Creek

In early 1964 Texas Gulf Sulphur Company tested the feasibility of wet, and dry mining by experimental dredging at Lee Creek. With a conventional cutter-head dredge the water table could be lowered by 95 feet in a test pit to reach the ore body. It was desirable to determine if the recommended concentration process would give satisfactory results with freshly-mined ore and ore contaminated with overlying material, using local water.

Based on the experience and data obtained in Asheville, a proposal for a larger pilot plant was presented to Texas Gulf Sulphur Company in May 1963. It recommended a 12-ton-per-hour feed preparation circuit, stockpiling

facilities for the flotation feed, and a 2.7-ton-per-hour flotation circuit. The proposal contained a flowsheet, equipment size and cost, estimated construction and operating cost, and a construction and start-up time plan. A general layout for the larger pilot plant was also presented. It was recommended that the equipment be unitized so that quick changes could be made and minimum equipment needs determined. The plans presented were based on equipment available through Denver Equipment Company which specializes in flotation pilot plant equipment. Most of the equipment used in batch work and in the smaller Asheville pilot plant was Denver Equipment Company type.

To expedite the construction of the larger pilot plant, Denver Equipment Company was recommended to assist in the detailed design and to furnish the equipment. The pilot plant was erected at Lee Creek in the fall of 1963. During 1964 the Lee Creek phosphate pilot plant was operated with assistance by the Asheville Laboratory and objectives were fulfilled. In July of 1964 Texas Gulf Sulphur Company awarded Brown and Root of Houston, Texas and Rea Construction Corporation of Charlotte, North Carolina the contract to erect a phosphate mill, with all supporting facilities, that can produce 3,000,000 tons of phosphate concentrate per year from North Carolina ore. This plant was designed and erected in 1965 and it began operation in March 1966. Texas Gulf Sulphur Company's Lee Creek phosphate mine, mill, and fertilizer plants are described in different mining magazines. (9) (10)

Additional Metallurgical Studies at the Asheville Laboratory

For support of the pilot plant work at Lee Creek, studies of important variables in the concentration circuit were made at Asheville. The influence of the different possible water sources at Lee Creek on the flotation results was tested. The influence of dilution of high grade ore by low grade ore was studied. Methods to up-grade the low grade ore sections of the ore body were worked out. Further flotation test work with saponified fatty acid established that a very wide range of conditions, such as conditioning percent solids,

conditioning time, and saponification ratios, would give high concentrate grades and recoveries. Variables in the flotation feed preparation were studied especially with respect to amount of slimes that could be tolerated in the flotation circuit. A differential grinding method was tested that could recover a fair percentage of the phosphate values in the plus 14 mesh oversize which was rejected in earlier work.

By-Products of Phosphate Mining

When the Lee Creek pilot plant began to operate successfully in 1964, the attention of the Asheville Laboratory shifted from phosphate concentration studies to evaluation of possible by-products. Excellent samples of overburden and low grade ore for use in by-product investigations had been made available by the experimental mining.

On the basis of physical properties, chemical analysis and concentratability, the main by-product sources were defined. Each is described below.

The Shells - In the upper 25 feet of the overburden in the upper Yorktown formation there is a 10 to 15-foot layer of shell matrix. This layer contains calcium carbonate in the form of fossil clam, oyster and coral shells. Laboratory tests showed that a part of the calcium carbonate material could be obtained, free of clay and sand contamination, by simple washing and screening methods. Since North Carolina has no commercial production of high-calcium limestone, this possible source is of special interest.

The ground shell was also evaluated as a calcium source in poultry feed supplements and it proved to be equal to material now imported into the State. The Laboratory prepared the samples for the test work conducted by the North Carolina State University Poultry Science Department and also the samples sent to various poultry-feed mills.

Shell material can also be used as a cement raw material and as aggregate for road building and concrete block products.

There is a potential of about 350,000 tons-per-year of clean shell product at the planned phosphate production rate.

The Coquina - In the upper low grade section of the phosphate horizon there are layers of hard, cemented coquina containing some phosphate. Tests showed that this material was suitable for aggregate after washing, crushing and sizing. A portion of the material meets the State abrasion specifications. This potential by-product is interesting because sources of hard rock for aggregate are scarce in the coastal area. The tonnages available, in the range of 700,000 tons-per-year, make it an attractive raw material for an aggregate plant.

The finer, softer coquina material, containing high calcium lime and low grade phosphate ore, can be used for agricultural liming purposes after drying and grinding. Tonnage samples of this material were prepared by the Laboratory for testing on eastern Carolina soils.

The Dolomitic Limestone - In the upper ten feet of the high grade ore section there occurs an irregular layer of very hard, dolomitic limestone which can be used, after crushing and sizing, as an aggregate source. It also makes a good agricultural liming material when dried and ground to North Carolina ag-lime specifications.

It is difficult to estimate the quantity of this material available because of the non-uniformity of this layer.

The Ilmenite - The top part of the Texas Gulf Sulphur Company overburden is a sand layer containing 0.97 percent by weight of heavy minerals, mainly ilmenite, and it analyzed 0.47 percent TiO_2 . Ilmenite concentrates containing 52.6 percent TiO_2 were produced in the Asheville Laboratory by gravity separation followed by magnetic separation. In 1968 additional heavy mineral test work was done by the Asheville Laboratory on the amine flotation tailings. There is a potential of 15,000 tons-per-year of heavy minerals mainly ilmenite and some zircon if the amine tailings are processed. (11)

Sand-Lime Bricks From Shell Lime and Flotation Tailings - One possible use for two of Texas Gulf Sulphur Company's by-products is the manufacturing of sand-lime bricks. Sand-lime bricks or calcium silicate building products consist of high-quartz sand bonded with hydrated calcium silicates. These hydrated calcium silicates, similar to the bonding agents in Portland cement, are formed by the reaction of lime and silica under steam pressure. Sand-lime bricks can be made with high compressive strength, low absorption, and freeze and thaw resistance, in colors of natural silver gray or colored as desired. The colors are weather resistant and reproducible. The brick can be split for a textured surface.

The general manufacturing process consists of mixing of ground quicklime or hydrate with high-silica sand, in ratios of 85 to 90 percent sand to 15 to 10 percent lime, and adjusting of moisture for easy pressing and forming. The mixture is pressed at 4000 to 8000 psi and steam-cured in autoclaves at pressures of 150 to 250 psi for four to five hours. The bricks retain their exact dimensions during curing and can be shipped immediately after removal from the pressure vessel. The sand-lime brick manufacturing process can be completely automated so that the bricks are never touched by human hands.

Quicklime produced from Texas Gulf Sulphur Company's shells and flotation tailings sand was tested in the Asheville Laboratory for sand-lime brick production. Preliminary testing showed that an attractive silver gray sand-lime brick can be produced from these by-products of phosphate mining. The test bricks met the requirements of minimum compressive strength for individual bricks of grade SW of ASTM C-73-51.

Summary and Conclusions

Through close cooperation with Texas Gulf Sulphur Company, the Asheville Minerals Research Laboratory assisted in the evaluation of one of North Carolina's most valuable mineral resources, the phosphate in Beaufort County. A process

for the concentration of North Carolina phosphate ores was developed at the Laboratory and tonnage samples for customer evaluation were produced in a pilot plant. Based on the Asheville results, plans for a larger pilot plant were presented to Texas Gulf Sulphur Company. This pilot plant provided larger samples from dredged ore using local water and it also provided design data for the production plant.

Studies on by-products from the phosphate mining operation outlined possible uses for high-calcium shells as lime raw material, coquina as aggregate, dolomitic limestone for agricultural liming purposes or aggregate, and flotation tailings and lime for the production of sand-lime bricks. (12)

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Table 1

Analysis of Drill Core Footage Sections (Hole No. 84)
Pungo River Formation - 76 to 136 Ft. Depth

| <u>Footage</u> | <u>TPA</u> | <u>% P₂O₅</u> | <u>CaO/ P₂O₅</u> | <u>Free CaCO₃</u> | <u>% Pebble^A</u> | <u>Opt. P.C.^{**}</u> | <u>% of Total P₂O₅</u> | <u>Section Designation</u> |
|----------------|---------------|-------------------------------------|--|----------------------------------|---------------------------------|-----------------------------------|--|--------------------------------|
| 76-82 | - | 2.6 | 6.4 | 21.4 | 8 | 12.2 | 2.4 | |
| 83-85 | - | 7.0 | 4.6 | 37.8 | 23 | 4.4 | 1.9 | Upper lowgrade |
| 85-87 | - | 5.8 | 8.3 | 69.9 | 19 | 5.3 | 1.5 | |
| <u>76-87</u> | <u>21,560</u> | <u>4.8</u> | <u>4.3</u> | <u>33.2</u> | <u>19</u> | <u>5.3</u> | <u>5.8</u> | <u>Upper lowgrade</u> |
| 87-96 | - | 16.8 | 1.9 | 8.6 | 54 | 1.9 | 20.1 | |
| 96-97 | - | 14.6 | 2.2 | 14.5 | 47 | 2.1 | 1.9 | |
| 97-110 | - | 15.9 | 1.8 | 4.5 | 51 | 2.0 | 27.5 | |
| 110-111 | - | 14.3 | 1.6 | 0 | 46 | 2.2 | 1.9 | Highgrade |
| 111-124 | - | 13.9 | 1.6 | 0.7 | 45 | 2.2 | 24.1 | |
| 124-132 | - | 12.8 | 1.8 | 3.7 | 41 | 2.4 | 13.6 | |
| <u>87-132</u> | <u>88,200</u> | <u>14.9</u> | <u>1.8</u> | <u>4.5</u> | <u>48</u> | <u>2.1</u> | <u>89.2</u> | <u>Highgrade</u> |
| <u>132-136</u> | <u>7,840</u> | <u>9.3</u> | <u>4.0</u> | <u>38.7</u> | <u>30</u> | <u>3.3</u> | <u>5.0</u> | <u>Lower lowgrade</u> |
| 76-136 | 117,600 | 12.5 | 2.1 | 12.0 | 40 | 2.5 | 100.0 | Tot.Phos.Formation |

* Based on 31 % P₂O₅ content

** Optimum ratio of concentration at theoretical 100 % recovery of pebble

Table 2

High Grade Core Section Phosphate Concentration Results
Average Hole No. 5 to 25 - 38.8 Ft. Thickness

| <u>Fraction</u> | <u>% Wt</u> | <u>TPA</u> | <u>% P₂O₅</u> | <u>CaO/ P₂O₅</u> | <u>% Free CaCO₃</u> | <u>% of Total P₂O₅</u> | <u>% of Total Free CaCO₃</u> |
|--------------------------------------|--------------|---------------|-------------------------------------|--|------------------------------------|--|---|
| <u>Step 2 - Sizing and Desliming</u> | | | | | | | |
| +14 | 7.0 | 5,300 | 20.6 | 2.21 | 22.7 | 9.6 | 31.5 |
| -14+200 | 76.8 | 58,400 | 17.2 | 1.60 | 0.8 | 87.3 | 3.9 |
| -200 | 16.2 | 12,300 | 2.8 | 5.63 | 20.0 | 3.0 | 64.6 |
| Total | 100.0 | 76,000 | 15.1 | 1.78 | 5.0 | 100.0 | 100.0 |

| | | | | | | | |
|---|-------------|---------------|-------------|-------------|------------|-------------|-------------|
| <u>Step 3 - Flotation Concentration</u> | | | | | | | |
| -14+28 Conc. | 2.2 | 1,700 | 27.6 | 1.79 | 6.6 | 4.0 | 2.9 |
| -14+28 Tail | 0.8 | 600 | 2.6 | 1.92 | 1.4 | 0.1 | 0.2 |
| -28+200 Conc. | 38.4 | 29,200 | 30.4 | 1.59 | none | 77.2 | none |
| -28+200 F.A.Tail | 33.3 | 25,300 | 1.7 | 1.47 | none | 3.7 | none |
| -28+200 Am. Tail | 2.1 | 1,600 | 16.5 | 1.68 | 2.1 | 2.3 | 0.8 |
| Total Conc. | 40.6 | 30,900 | 30.2 | 1.60 | 0.4 | 81.2 | none |

Total Concentrate Flotation Recovery 93.0 %

Total Concentrate Ratio of Concentration 2.46 %

Table 3

Chemical & Size Analysis of North Carolina
Phosphate Flotation Concentrate & Calcine

| | <u>N. C. 67 BPL Concentrate</u> | <u>N. C. 72 BPL Calcine</u> |
|-----------------------------------|-------------------------------------|---------------------------------|
| % P ₂ O ₅ | 30.8 | 33.1 |
| % CaO | 49.1 | 53.2 |
| % CO ₂ | 5.1 | 1.8 |
| % Fe ₂ O ₃ | 0.7 | 0.8 |
| % Al ₂ O ₃ | 0.4 | 0.4 |
| % F | 3.5 | 3.9 |
| % SO ₄ | 2.7 | 3.0 |
| % Organic | 1.5 | 0.1 |
| % Cl | 0.05 | 0.05 |
| Acid Insoluble | 2.3 | 2.1 |
| CaO/P ₂ O ₅ | 1.59 | 1.60 |
| <u>Size Analysis</u> | <u>% Weight</u> | <u>% Weight</u> |
| -14 Mesh Tyler | trace | 0.0 |
| -14+35 Mesh | 6.9 | 4.0 |
| -35+65 Mesh | 54.5 | 35.4 |
| -65+100 Mesh | 26.5 | 29.3 |
| -100+200 Mesh | 11.8 | 28.2 |
| -200 Mesh | 0.3 | 4.0 |
| Moisture | 2.0 max. | 0.5 |
| Bulk Wt. lb/cu. ft. | 99-104 | 102-107 |

Table 4

Flotation Test Results of Hole 23-B - 106 to 142 Ft.

| | <u>% Wt</u> | <u>% P₂O₅ *</u> | <u>CaCO₃ % Free</u> | <u>CaO/ P₂O₅</u> | <u>% P₂O₅ of Total</u> | <u>% CaCO₃ of Total</u> |
|--|-------------|---------------------------------------|------------------------------------|--|--|--|
| Phosphate Matrix | 100.0 | 15.32 | 5.05 | 1.78 | 100.0 | 100.0 |
| +14 Mesh Pebble | 3.4 | 27.40 | 19.1 | 2.06 | 5.1 | 9.1 |
| -14+28 Mesh Conc. | 2.2 | 28.65 | 0.5 | 1.61 | 4.1 | 0.2 |
| -28+200 Mesh Conc. | 43.0 | 30.60 | none | 1.59 | 86.0 | none |
| Total Flot. Conc. | 45.2 | 30.4 | none | 1.59 | 90.1 | none |
| Waste Tailings | 32.8 | 1.6 | | 1.63 | 3.4 | none |
| Slimes, -200 Mesh | 18.6 | 1.2 | 24.6 | 13.02 | 1.4 | 90.7 |
| Total Concentrate Flotation Recovery | | | | 96.2 % | | |
| Total Concentrate Ratio of Concentration | | | | 2.2 % | | |

* P₂O₅ analyses by Southern Testing & Research Laboratories

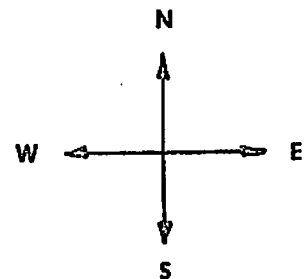
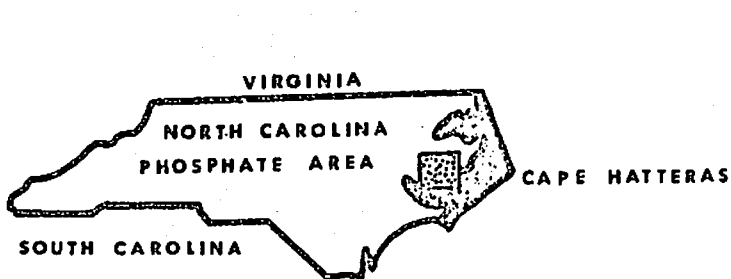
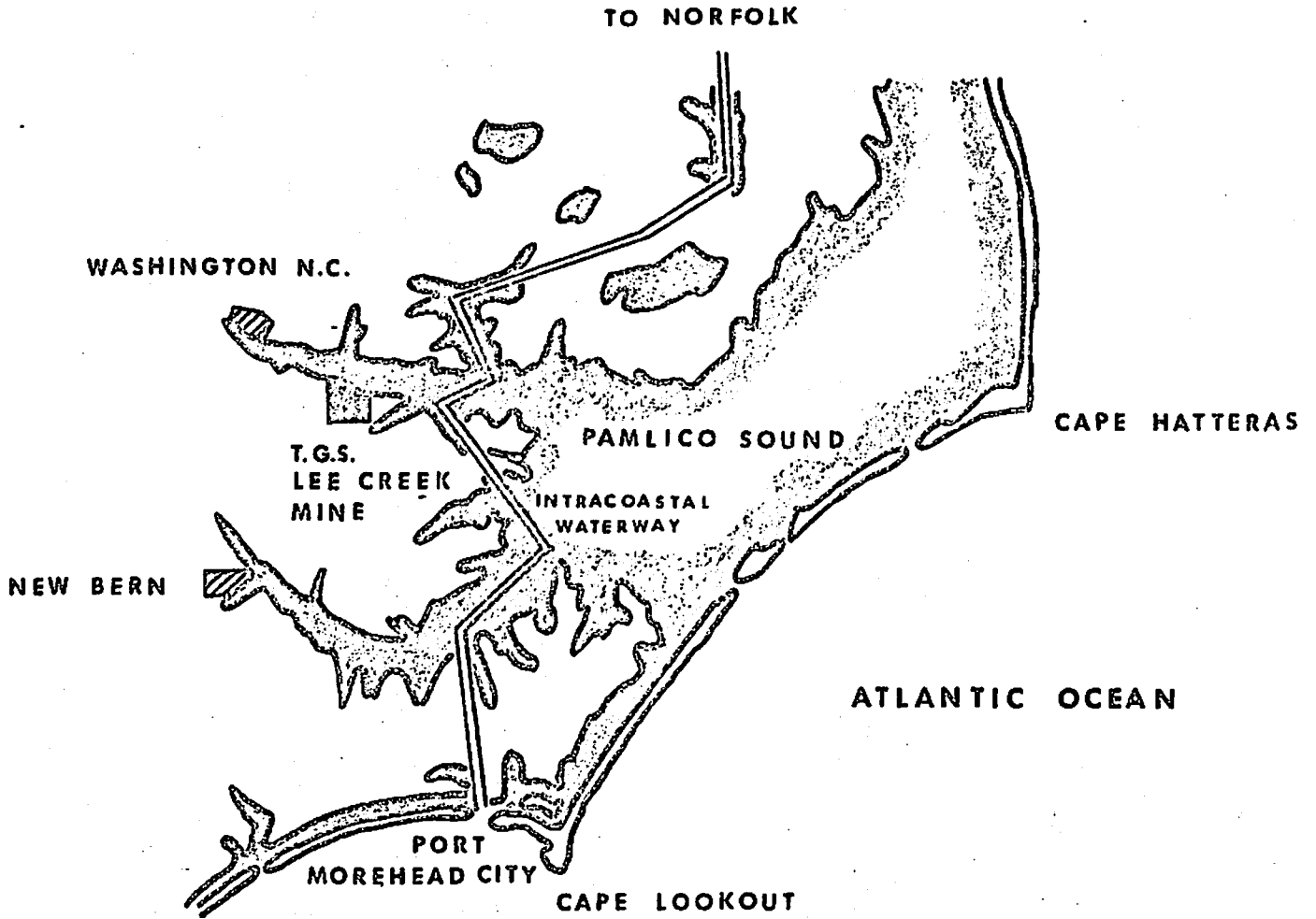
Table 5

Pilot Plant Flotation of Pumped Ore From Gum Point -
Material Balance and Reagent Schedule

| <u>Material</u> | <u>% Weight</u> | <u>% P₂O₅</u> | <u>% Insol.</u> | <u>% P₂O₅ Distr.</u> | <u>Flotation Recovery</u> |
|----------------------|-----------------|-------------------------------------|-----------------|--|-------------------------------|
| +28 Mesh Oversize | 10.8 | 20.9 | - | 11.4 | - |
| -28 Mesh Concentrate | 55.5 | 30.5 | 3.2 | 82.6 | 96.3 |
| Fatty Acid Tailings | 23.8 | 1.1 | - | 1.6 | - |
| Amine Tailings | 3.2 | 8.6 | - | 1.4 | - |
| -200 Mesh Slimes | 3.7 | 15.9 | - | 3.0 | - |
| Feed Sample | 100.0 | 19.8 | - | 100.0 | - |

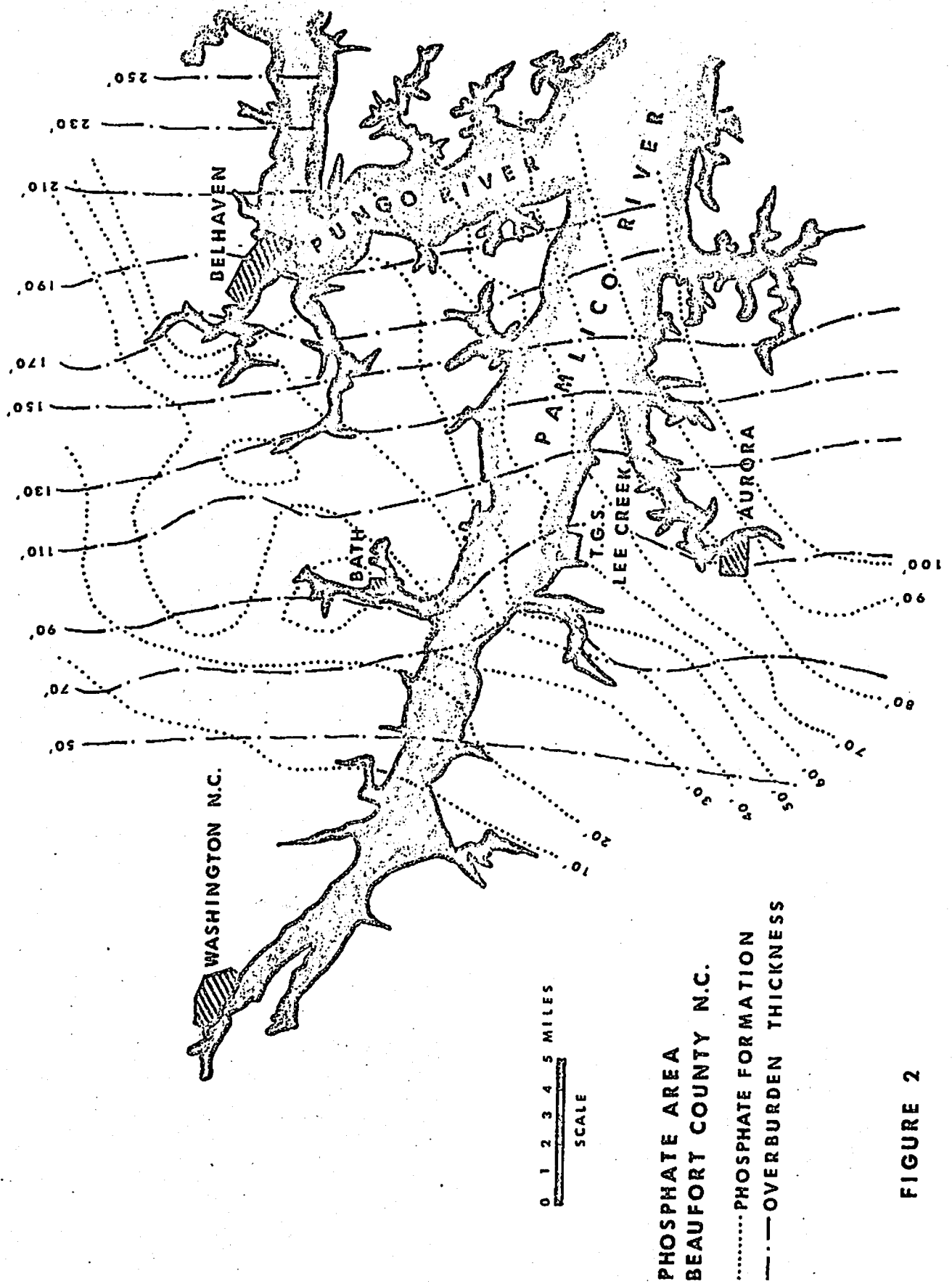
Reagent Consumption
(lbs/Ton of Feed)

| | |
|--------------------------------|------|
| Tall Oil | 0.4 |
| Fuel Oil | 0.8 |
| NaOH | 0.04 |
| H ₂ SO ₄ | 2.4 |
| Amine Acetate | 0.18 |



PAMLICO TIDEWATER ESTUARY AROUND
NORTH CAROLINAS LEE CREEK PHOSPHATE MINE

FIGURE 1



GEOLOGIC SECTION N.C. PHOSPHATE AREA

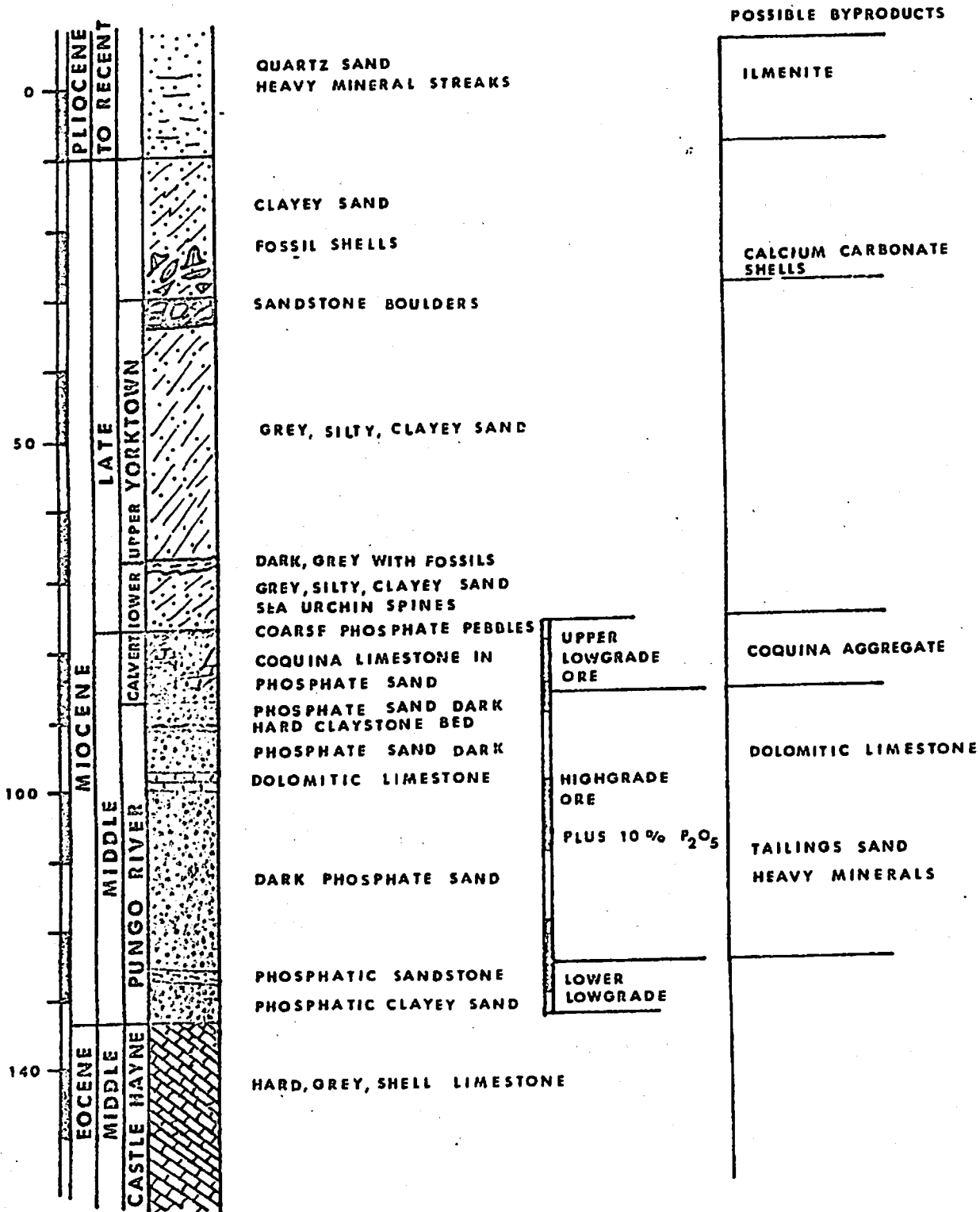


FIGURE 3

TEXAS GULF SULPHUR COMPANY PHOSPHATE PILOTPLANT AT ASHEVILLE MARCH 1963

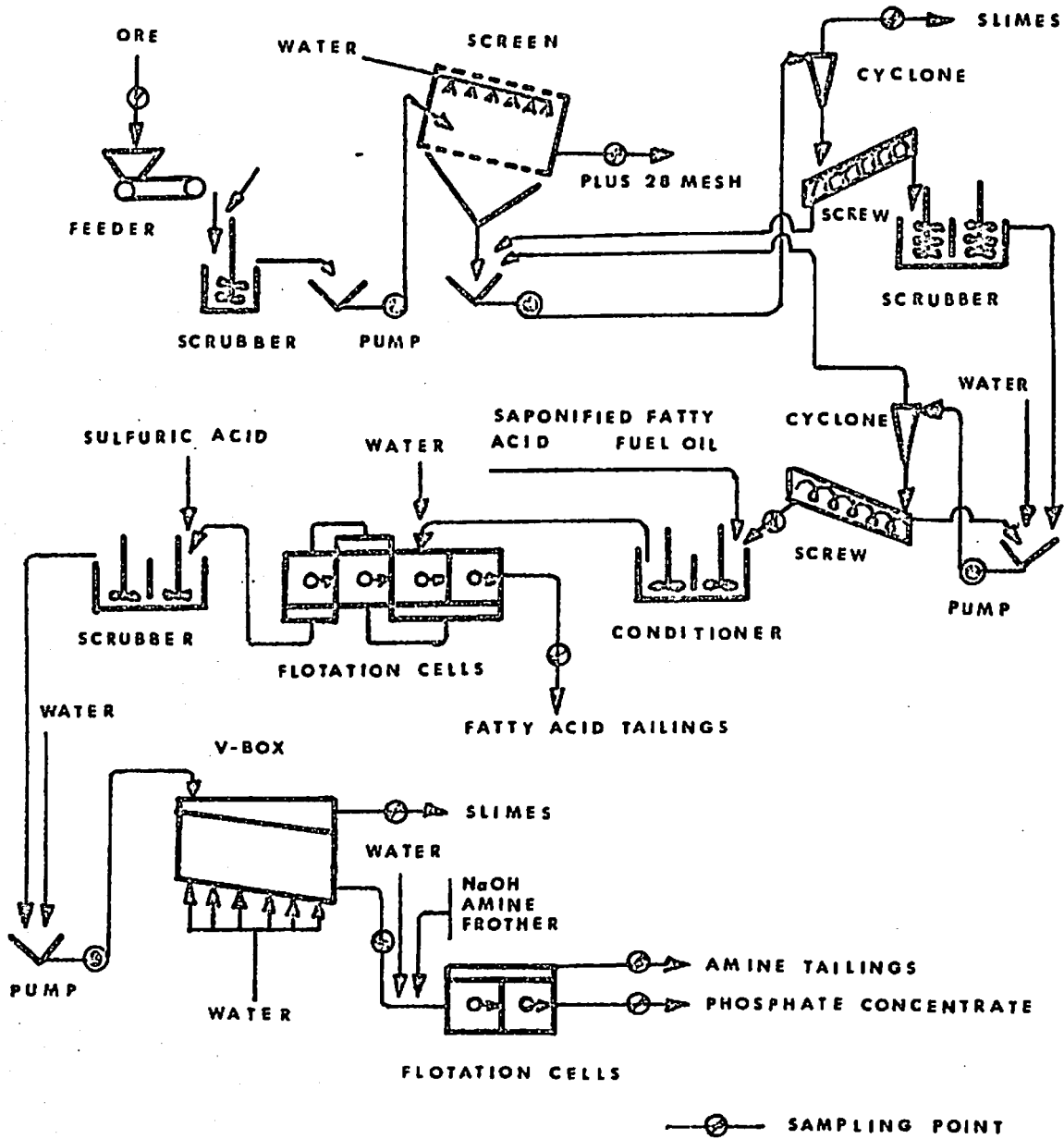


FIGURE 4