PHOSPHOGYPSUM RECYCLE

DMC/FIPR Phosphogypsum Process Aggregate Production Test Plant

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1. ABSTRACT

The Davy McKee Corporation (DMC) and the Florida Institute of Phosphate Research (FIPR) have cooperated in a phased program to develop a process to economically recover the sulfur values from phosphogypsum and produce a saleable, solid by-product. The encouraging results of the initial phases of this work led to an agreement between DMC and FIPR which established the program for commercialization of the DMC/FIPR process. A key facet supporting this program is the production of relatively large quantities of the solid by-product for qualification of its use as road construction material.

Recently an important announcement, regarding the further development of this process, was made by Freeport McMoRan Incorporated (FMI). FMI will build and operate a test plant, based on the DMC/FIPR process, at their Uncle Sam phosphate complex in Louisiana. The limited amount of solids produced by batch runs have been tested and the results indicated that the solid by-product would be excellently suited as road aggregate. This test plant will produce adequate quantities of solids to allow a full-scale evaluation of its acceptability. The description of the test program for this plant is the subject of this paper.

2. BACKGROUND

Since 1982, the Davy McKee Corporation (DMC) and the Florida Institute of Phosphate Research (FIPR) have been involved in a cooperative program for the utilization of phosphogypsum. The object of this joint effort is to demonstrate a practical process for the thermal decomposition of phosphogypsum for the production of sulfuric acid and a saleable, solid by-product. The innovative application of the commercially proven DMC circular grate, used as the process "reactor" for this phosphogypsum utilization system, has been extensively tested with the support of FIPR. The circular grate system which has been successfully applied to the iron and steel industry, exhibits significant advantages, both technically and economically, when compared to other phosphogypsum decomposition processes.

The DMC/FIPR process has evolved through a number of enhancements since the early work. The results of test work funded by FIPR in conjunction with DMC's experience with circular grate design and construction were used to develop capital and operating cost estimates for the various alternatives to recover sulfur values from phosphogypsum and coproduce other valuable products.

The joint program to date with references to our previous publications can be summarized as follows:

Phase I (1)

Batch testing was completed for various raw material combinations using both pellet-firing and sintering approaches with the goal of producing SO_2 rich gas and a low grade lime. Conclusions included "notional" economics which indicated that the SO_2 gas was least expensive from the sintering operation and that the solid by-product could be considered for use as an aggregate.

Phase II/Pyrites Addition (2)

After producing only marginally acceptable solid by-products with various mixtures of phosphogypsum, silica and petroleum coke, a new feed formulation containing pyrites was tested. The resulting solid by-product was tested both chemically and mechanically and is apparently excellently suited for high quality aggregate use. The pyrites also reduced the carbon requirement and increased the SO_2 in the raw gas to 9%.

Coal/Cogeneration (3)

The coal/cogeneration approach integrated with the circular grate system resulted in a process which could (1) utilize high sulfur coal or coal waste as the carbon source; (2) produce steam/power equivalent or exceeding the energy produced by sulfur-burning, sulfuric acid plants; and (3) produce sulfuric acid at costs lower than acid currently produced from sulfur-burning. A simplified block flow diagram of this system is shown in Appendix (A).

Balanced Plant/Sulfur Coproduct (4)

While pyrites are essential to the process, they do reduce the quantity of gypsum consumed per ton of sulfuric acid produced. A modification of the coal/cogen flowsheet will allow us to convert a portion of the bound sulfur in the phosphogypsum and pyrites to sulfur. The product mix is somewhat changed but as a result the P_2O_5 complex now becomes balanced, with all phosphogypsum recycled. Sufficient SO_2 is produced for H_2SO_4 production, plus excess sulfur value is converted to elemental sulfur not sulfuric acid. Additional test work and economic evaluations to examine this route will be completed over the next few months.

The most significant recent development regarding this process involves the April 15, 1987 announcement (see Appendix (B)) by Freeport McMoRan Inc. (FMI) that they will provide the funding to construct and operate a large scale, test plant based on the DMC/FIPR phosphogypsum process. A cooperative agreement between DMC/FIPR and FMI has resulted in a research/engineering/operating team that is committed to the demonstration of an environmentally acceptable and economically competitive process to recover sulfur values from phosphogypsum. The successful operation of this test unit will provide the necessary technical and economic information required to establish the viability of a commercial facility.

The remainder of this paper will describe the test plant program.

3. TEST PLANT DESCRIPTION

The aggregate production test plant will be constructed at FMI's Uncle Sam Facility near Convent, Louisiana. An artist's rendering of the plant is included in the Appendix (C).

The plant is being designed to process phosphogypsum, petroleum coke and pyrites on a continuous basis to produce aggregate and to produce a raw gas which will be scrubbed primarily to remove SO_2 and particulate. Depending on the feed mix used, the plant can be operated to produce about one ton per hour of aggregate and an amount of SO_2 equivalent to slightly over one ton per hour of sulfuric acid. Consumption of phosphogypsum will vary, again depending on the feed mix "recipe", particularly the pyrites percentage, but is projected to be tested in the range of 1.5 to 2.5 tons per ton of aggregate produced.

3.1 Description of Equipment

The equipment to be utilized in the test facility will include new equipment, existing equipment currently owned by FMI, used equipment and modified used equipment. The main component, the straight grate sintering machine, falls in the latter category. The straight grate is an existing grate which was used in the testing of agglomerating processes for the iron and steel industry. It is being modified to provide the operating zones required by our process; i.e. ignition, gas and sinter production and sinter cooling. The configuration is flexible within limits and the current plans include two major modes of operation; Mode 1 will be used during start-up and initial operation and Mode 2 will be used for aggregate production runs. Mode 1 will have four production zones and two cooling zones. Mode 2 will have five production zones and one cooling zone.

Other than the sintering machine, the remaining equipment is fairly standard for:

(1) raw material receiving, storage, reclaim

(2) solids blending

(3) solids nodulization (granulation)

(4) sintered solids handling

(5) hot gas scrubbing for particulate and SO_2 removal

3.2 Description of Operations

Raw Materials Receiving, Storage, Reclaim

Phosphogypsum will be "mined" directly from FMI's gyp stack using a payloader. An existing screening system and truck loading system currently located at the stack will be used to screen any debris from the gypsum and load it into dump trucks for transfer to the plant. The gypsum will be dumped and stored on a concrete pad near the plant. Gypsum will be transferred from this in-plant storage to a feed hopper by payloader. This hopper will be fitted with a positive discharge device to ensure uninterrupted flow from the bin.

The pyrites currently considered for the first series of tests will be fine, flotation material. Due to the moisture level required for transport and dust suppression, the pyrites will be handled in a similar manner to the phosphogypsum.

Petroleum coke will be used as the carbon source. The coke will be purchased sized and ready for use without crushing. It will be received in hopper trucks and pneumatically conveyed to a cylindrical storage bin. Air pads will be used for positive coke removal by screw feeder.

Solids Blending

All of the solids to be blended will be fed in a controlled manner on to a common, sidewall-type conveyor. Phosphogypsum, pyrites, petroleum coke, recycle sinter (returns) and binder (bentonite) will be conveyed to a pug mill. The pug mill will thoroughly mix the materials prior to the nodulizing step. Provisions have been made to allow testing of phosphatic clay as the binder.

Nodulizing

The blended feed mix will be nodulized in an 8 ft. diameter, stepped pan-type granulator. An automatic spray and scraper system will be included to provide additional product size and moisture control. The finished nodules will range from 1/8" to 3/8" in diameter and will be transferred to the feed end of the grate by belt conveyors.

Sintering

The sintering operation will include the same processing steps that are required for the commercial operation; hearth-layer feed, nodule feed, ignition, gas and sinter production and sinter cooling.

The sintering machine will be capable of running various bed depths, to a maximum of about 12" deep and at varying speeds from about .25 fpm to 1.5 fpm. The ignition zone will use natural gas as fuel. The sintering zone will use preheated air from the sinter cooling zone. The sinter will be cooled with ambient air. The cooled sinter will be dumped from the end of the grate and immediately crushed to -3" by a sinter breaker. The crushed sinter will be stored in a surge hopper, intermittently dumped into a skip hoist, elevated and discharged to a storage pile.

The gas produced will be collected in alloy ductwork and piped to the scrubbing unit. The entire gas handling side of the sinter machine including the hood, windboxes and discharge hoppers will be maintained at negative pressure to prevent external leakage of gases.

Sintered Solids Handling

The sinter solids will be removed from the storage pile by payloader and transferred to a sizing unit. The sizing unit will include a dump hopper, feeder, screen feed conveyor, a double deck screen and stacking conveyors for returns, hearth layer and product. Product will be shipped out of the plant by trucks.

Gas Scrubbing

The hot, raw gas produced during sintering will be treated by a venturi scrubber to cool and remove particulate followed by a spray tower scrubber to remove SO_2. The SO_2 in the gas will be removed by circulation of a slurry of lime. Forced oxidation will be used to convert any calcium sulfite or calcium bisulfite in the scrubber purge stream to calcium sulfate.

4. PROGRAM GOALS

4.1 Description

The use of a modified, existing straight grate offered the most cost effective method to produce relatively large amounts of gypsum-based aggregate in a short timeframe with minimal capital cost. The current schedule targets a September, 1987 (mechanical completion/precommissioning) in the field, with start-up and initial operation in October, 1987. An important parallel program, in support of the further development of the this process and the aggregate production tests, will be the operation of the batch test unit by FIPR. Recently FIPR purchased a sintering batch test unit and will install and operate the unit in Florida.

The batch unit will provide a cost effective method to check and screen "what-if" alternatives prior to testing in the aggregate production plant. Changes such as different raw materials sources or other chemistry-related modifications can be tested prior to any field runs. This unit will also provide the capability to thoroughly test the other process developments such as balanced plant/sulfur production route, SO_2 gas strength improvement, solid-product modifications, and cogeneration-related tests.

The inherent differences between the straight grate and a circular grate place certain limitations on the data collected from the straight grate unit concerning gas analysis, but the few remaining questions will be answered with successful straight grate operation coupled with an extensive batch test program.

By far the majority of the questions raised regarding the DMC/FIPR circular grate process center around the aggregate; its variability of quality, its mechanical and chemical stability, its marketability. The batch tests produced a solid by-product material which exhibited great promise (2, 3) but as one major highway constructor said "you have to build a section of road to convince the non-believers and officials in charge of acceptance".

The following are the major goals of our program at FMI:

1. Demonstrate the continuous production of a solid by-product material (aggregate) which is both mechanically and chemically suitable for road construction.

2. Produce sufficient quantities of aggregate which would be used to run a complete battery of tests which are required by the various governmental agencies to establish acceptability of the solid by-product for commercial use. This test work would be targeted for a minimum of two Gulf Coast States and would concentrate on the higher valued uses, keeping in mind the quantities to be produced in commercial operations. A test section of road in each prospective state will most probably be required.

3. Develop steady state "solids-side" data which would be applicable for the scale-up to commercial unit.

   This data would include but not necessarily be limited to:

   a) Impact of feed mix "recipe" variations

   b) Parameters for nodule preparation by pan granulation

c) Sinter Cooling data

d) Cooled sinter handling and processing parameters

e) Verification of "grate factor"

Other useful data will obviously will be collected but may not be directly applicable to scale-up due mainly to the sealing limitations, and interzone and side wall effects inherent in a straight grate unit of this capacity. This data will include:

1. Raw gas characteristics with special attention to particulate, SO_3 content and other contaminants.

2. Sample coupons will be installed at key locations to provide data on materials of construction.

3. Taking into account leakage measurements or estimates and observed side wall effects of the straight unit, limited data will be available to predict certain other "gas-side" parameters for the scale-up to commercial unit. These parameters include:

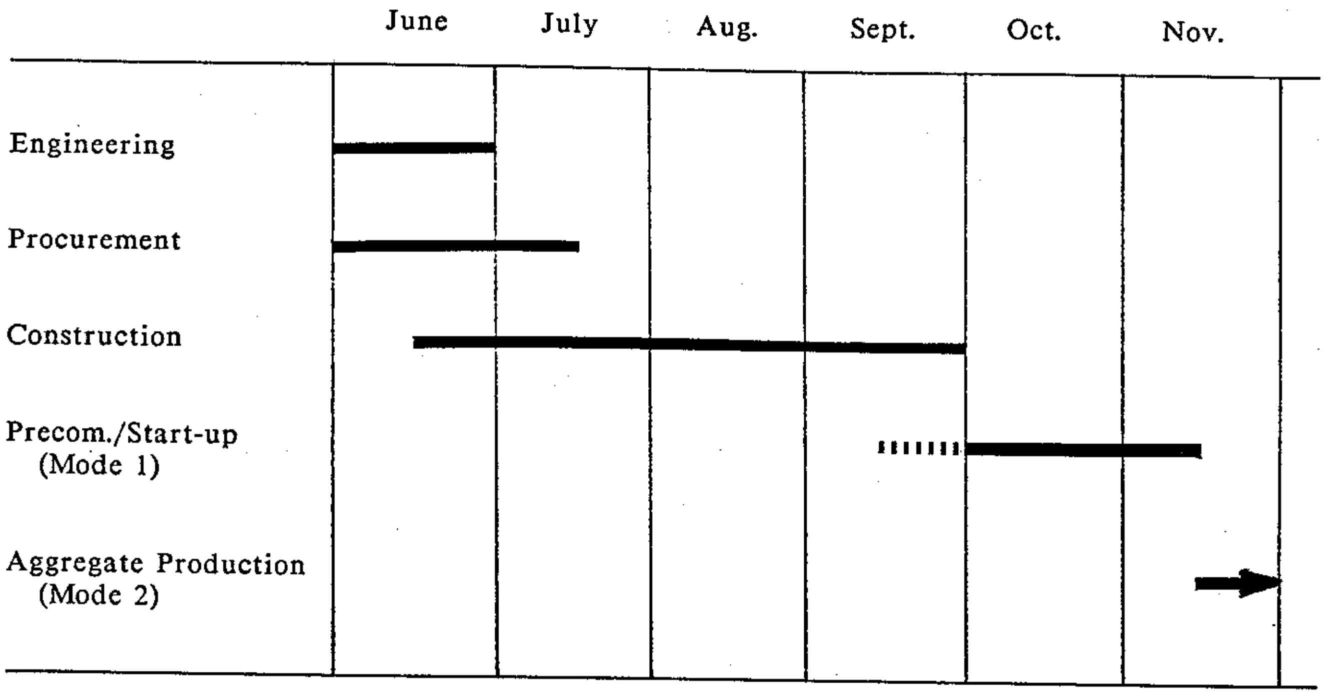
    a) Air/sinter heat exchange data

    b) Gas temperature profiles in ignition and gas production zones

A complete battery of tests is currently planned for the aggregate. A "Plan for Acceptance" for Florida has been drafted and is summarized in Appendix (D). In addition to the standard tests, an environmental monitoring program for our test road(s), similar to the program developed by the University of Miami for the phosphogypsum road section in Polk County (5), could be conducted.

4.2 Schedule

The current target schedule for the program is as follows:



The critical path activity for construction is the modification, shipment and installation of the straight grate.

Mode 1 operation is scheduled for the first weeks after mechanical completion and will provide operator training, equipment shakedown and continuous operating data to establish the best conditions for Mode 2 (Aggregate Production) operation.

The remainder of the operating program will concentrate on Mode 2 runs and will have targeted aggregate product specifications and quantities for specific road construction applications. The production rates of aggregate will be sufficient to provide amounts adequate for the priority road tests to begin in early 1988. The final results of these tests will not become available during the following months but probability of acceptance should be identifiable early in the program.

5. SUMMARY

Clearly, the aggregate production test plant is a significant step toward commercialization of the DMC/FIPR phosphogypsum technology. FMI has committed significant financial, technical and operational resources to this next step. We trust that the successful operation of the test plant and positive results from subsequent road material test programs will allow us to announce, by next year at this time, that a contract has been received for a full scale, circular grate plant.

6. REFERENCES

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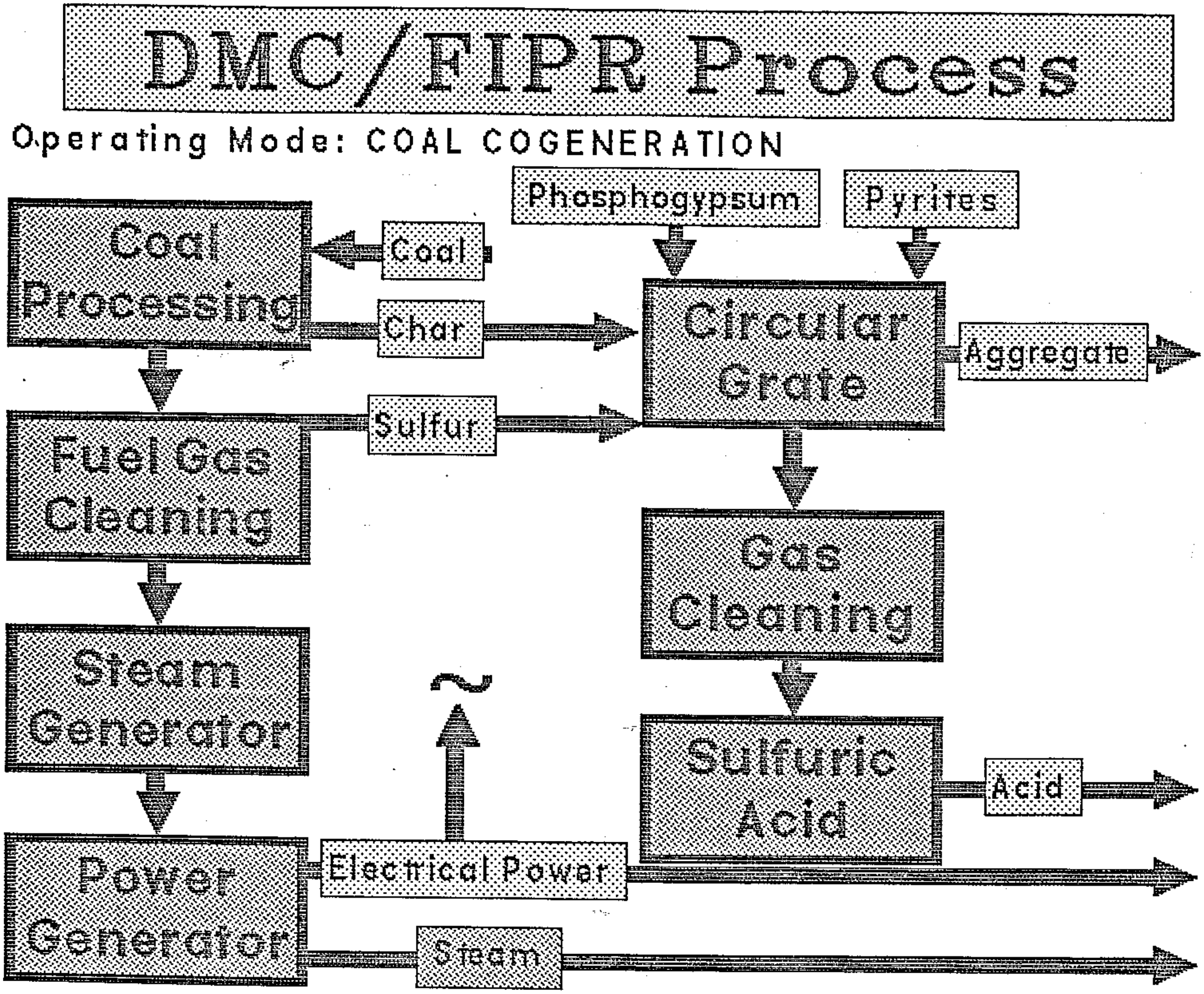
APPENDIX A


DMC/FIPR Process
Operating Mode: COAL COGENERATION
Phosphogypsum
Pyrites
Coal Processing
Coal
Char
Circular Grate
Aggregate
Sulfur
Fuel Gas Cleaning
Gas Cleaning
Steam Generator
~
Sulfuric Acid
Acid
Power Generator
Electrical Power
Steam

The Times-Picayune
No. 74 New Orleans Wednesday, Apr

APPENDIX B

April 15, 1987

Plant to recycle waste gypsum planned by Freeport-McMoRan

By JAMES O'BYRNE
Staff writer

Freeport-McMoRan will build an experimental $3 million recycling plant that could help solve the environmental riddle posed by millions of tons of contaminated waste gypsum piled along the Mississippi River, company officials said Tuesday.

The plant will be built at the Freeport Chemical fertilizer plant near Convent in St. James Parish. Gypsum is a byproduct of phosphorous fertilizer production.

The project will involve combining the waste gypsum with other products to make a rocklike substance that could be used for construction in place of shells, gravel or rocks. The process also will yield sulfuric acid, which will be used in fertilizer production.

Freeport-McMoRan was one of four companies that waged a losing fight to dump 12 million tons of gypsum waste a year into the Mississippi River. The waste is contaminated with radioactive radium and uranium, toxic heavy metals and other pollutants. The dumping proposal drew fire from environmental groups and downstream communities that drink water from the river.

The dumping plan was scuttled earlier this year by Martha Madden, secretary of the state Department of Environmental Quality.

Madden's decision left the plants with huge mountains of gypsum, which has no current commercial value.

Freeport's announcement came at the first meeting of a special panel named by Gov. Edwin W. Edwards to study potential uses for the waste.

The group of state officials, environmentalists and industry representatives was appointed to find alternatives to dumping the gypsum into the river or heaping it on land. Pollutants from the gypsum mounds are seeping into

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Gypsum

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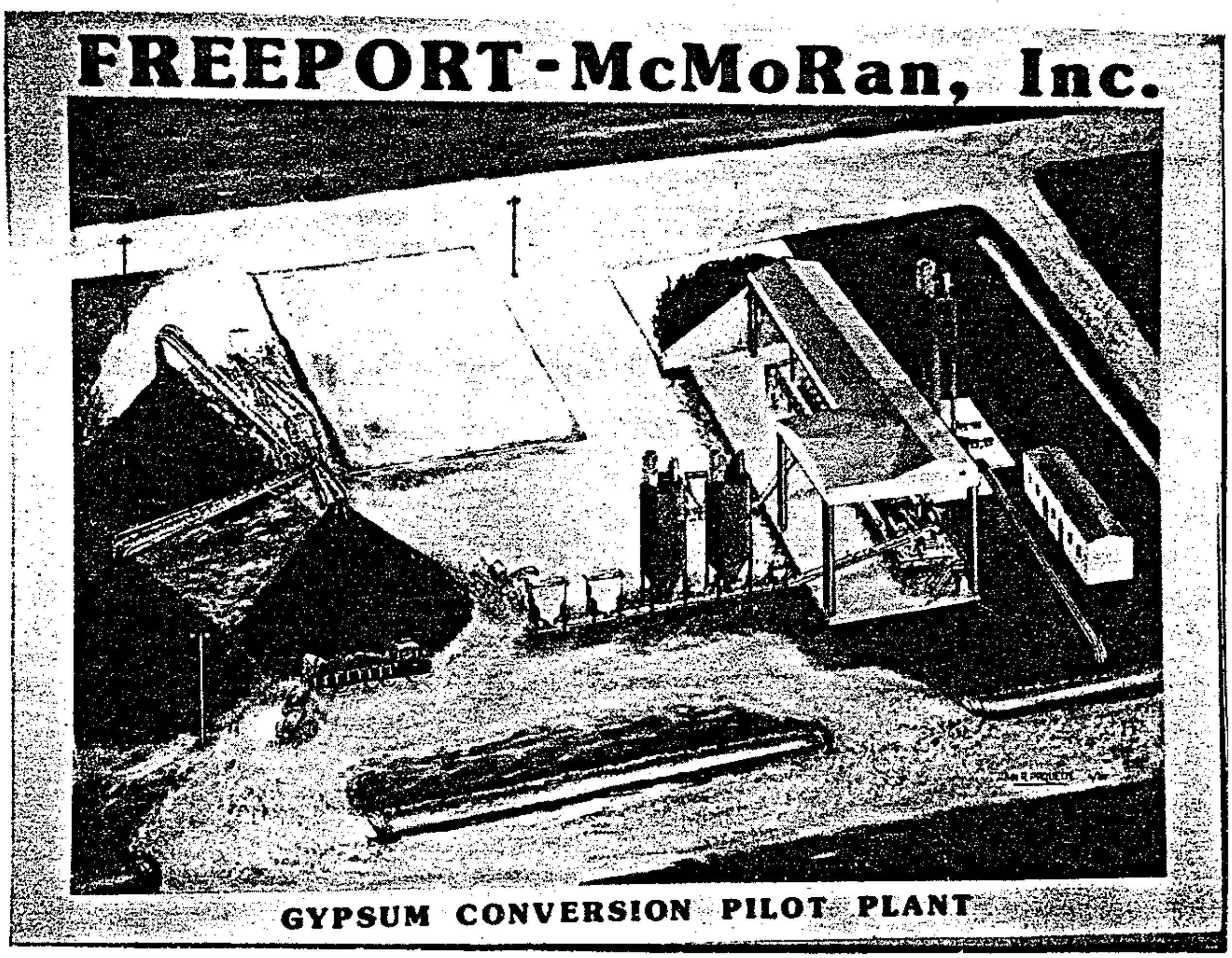
groundwater, state officials said, and the gypsum poses a threat of collapsing into nearby wetlands.

Freeport's plant will be built using technology developed by the Florida-based Davy McKee Corp. and the Florida Institute of Phosphate Research. Researchers in Florida, which has most of the nation's phosphorous fertilizer plants, have been developing the process for five years.

Freeport's plant will combine gypsum with an oil refinery waste product known as petroleum coke, clay and other additives. The mixture will then be heated to form the rocklike solid. Sulfur dioxide gas formed during heating will be processed into sulfuric acid, which is used to make the phosphorous fertilizer that produces the gypsum waste.

Freeport plans to complete construction of the plant in the fall. Officials said a decision on whether the process will be economical should be made by mid-1988.

APPENDIX C



APPENDIX D

AGGREGATE TESTING

Plan for Acceptance - Florida

General Aggregate:

Preliminary Testing for Aggregate Control Engineer of the Soils Materials and Research Section of the Bureau of Materials and Research

ASTM C88	Sodium and Magnesium Sulfate Soundness test
ASTM C29	Unit weight of aggregate
ASTM C131	Resistance to Abrasion of Aggregate by use of the Los Angeles Machine
ASTM C136	Sieve or Screen Analysis of Fine and Coarse Aggregates
ASTM D423	Liquid Limit of Soils
ASTM D424	Plastic Limit and Plasticity Index of Soils

Asphaltic Concretes:

Performed through the Bituminous Materials and Research Section of Bureau of Materials and Research

MS-2	Asphalt Mix design
ASTM 2726} ASTM 1188}	Bulk specific Gravity of Bit. Mixtures
ASTM D1559	Resistance to Plastic Flow of Bituminous Mixtures using Marshall Apparatus
ASTM D1075	Effect of Water on Cohesion of Compacted Bituminous Mixtures

And Florida Test Methods:

FM 1-T202, FM 1-T011, FM 1-T019, FM 1-027, FM 1-T037, FM 1-T084, FM 1-T085, FM 1-T096, FM 1-T104, FM 5-510, FM 5-512, FM 1-T166, FM 1-T209, FM 1-T245, FM 1-T099, FM 5-515, FM 5-521, FM 5-520, M 5-517

Demonstration/Test Road Project

Test Section of Road(s) - Individual categories or Various Combinations:

Subgrade Stabilization
Base Course
Structural Course
Friction Course

Estimated Minimum/Maximum Material Requirement:

250/5000 tons/lane mile