

AZEOTROPIC HF ACID FROM  
DEFLUORINATED PHOSPHATE ROCK

BY

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## INTRODUCTION

A need for animal grade, defluorinated phosphate, feed supplement arose during WW-II. The feed industry had found that phosphorus from bone meal was in short supply and imported phosphate (Caracao) was suffering from transportation difficulties. A research program sponsored by the U. S. Government was initiated to develop a process using domestic phosphate rock. High temperature calcination, one of the more successful processes, was developed by the Coronet Phosphate Company, now Smith Douglass Division of Borden Chemical, Inc. Basically, the process consisted of chemical adjustment of the rock followed by calcination at temperatures above 2000°F, producing a fluorine-free biologically available phosphate. Fluorine is evolved during calcination as gaseous hydrogen fluoride, a toxic corrosive compound. Early in the development, it was realized that this gas must be contained. At first, separation was accomplished by scrubbing and neutralizing in a vertical stack using a limestone slurry sprayed into the gas stream. The scrubber effluent was settled and cooled in a pond, then clarified water was recycled.

Since fluorine removal was costly, a market search was initiated to see if fluorides could be produced and sold to offset scrubbing and handling costs. Two fluorides, potassium silico fluoride and potassium fluoborate, were produced to customer specifications and marketed profitably. However, a flood of requests followed, none of which could be produced satisfactorily due to phosphate contamination. Phosphate and other dusts entrained in the calcination flue gas stream were absorbed in the scrubber liquor and reappeared as contaminants in the product fluorides. Satisfactory elimination of these contaminants from the product was found to be impossible. However, one laboratory procedure, distillation, appeared to be promising. Moderate improvement was demonstrated in the laboratory when vapor demisting was used.

A modified pilot plant was constructed, which consisted of two Karbate heat exchangers mounted on an "A" frame, and linked together with a Karbate vane type demister. Steam was applied to the distillation exchanger and feed was admitted at the top. The bottom was closed by means of a liquid seal and the vapors passed out from the top, through the demister, and down through the second heat exchanger, which was cooled with water. About 20 gallons of a pure dilute (3.0%) hydrofluoric acid was collected. A number of high-quality fluorides were made from the acid. Based on the success of this test, a larger pilot plant was approved for further testing. Union Carbide Corporation was chosen to design the plant since they had extensive experience in construction of plants used in the production of halide acids. After considerable study with Union Carbide, a flow plan was accepted, which consisted of three steps: (1) an evaporation step, (2) a vapor separation and demisting step, and (3) a concentration, condensation, and product cooling step.

#### PILOT PLANT DESCRIPTION

Figure 1, page 6, is a flow diagram of the pilot plant which will be referred to in the following text.

#### LIQUOR\* EVAPORATION

The evaporation step consisted of a Karbate falling film evaporator; a vapor disengaging section below the evaporator; a Karbate pot for collecting liquor non-volatiles; a Karbate pump for recirculating the liquor; piping for liquor return back to the evaporator. Feed liquor was introduced into this line just ahead of the evaporator. A metering

\*Impure, dilute HF acid from the calcination scrubbers.

pump (not shown) served to control the feed rate input. The evaporator was a falling film Karbate heat exchanger, in which total flow was not supposed to exceed 4 gpm. The liquid receiving pot was a 5 ft. by 2 ft. ID Karbate tank, which served as a holding area for recirculating liquor. An overflow line established the liquid height within the tank, which, in turn, was fitted with a Karbate bottle to provide a liquid seal. The bottle, likewise, was fitted with an overflow to remove accumulated liquor. A carbon probe was inserted through the top of the pot, which provided an electric alarm for low pot liquid levels. The recirculating pump was installed near the bottom of the pot and had a maximum flow capacity of 25 gpm. A valve at the pump outlet served to control rate of flow.

#### VAPOR SEPARATION AND MIST ELIMINATION

Vapor separation occurred in an enlarged area immediately below the evaporator. This was an 8 in. square section having a 3 in. inlet and outlet for recirculating liquor. The vapor outlet, at right angle, led the vapors to the demister. This 3 in. line was cut diagonally, with the longer cut facing into the stream and extending approximately 5 in. into the square section. While this arrangement served to separate the liquor, a residual mist still entrained in the vapor stream had to be removed. A vane type Karbate demister was used to remove these mists. Later in the tests, a severe mist problem developed and a second demister was installed in the 3 in. line leading from the Karbate demister to the adiabatic tower. The second demister was a "York" teflon mesh type enclosed in a 4 in. square section by 1 ft. in length.

## CONDENSATION-CONCENTRATION AND PRODUCT COOLING

Vapor condensation and concentration was conducted in a packed tower. The tower, called an adiabatic concentrator, consisted of four cylindrical sections, each 6 ft. long by 1 ft. ID. Each cylinder was filled to the 5 ft. level with polypropylene "pall" rings supported by a perforated plate at the foot. The cylinders formed a sealed column when erected due to a recessed area at the top which received an extension at the foot of the cylinder installed above it. Two 2 ft. long identical closure sections were used as cap and base for the tower. Each had two openings, one on the side and one in the closure plate. The lower support section used these openings for reboiler liquor circulation while the upper section outlets were used for water vapor escape and reflux. The reboiler concentrator was a 6 ft. long Karbate heat exchanger with a steam heat capacity of about 70 psig. As the concentrated liquor absorbed heat, recirculation back to the tower was maintained by convection. The heated liquor at a boiling point commensurate with its concentration released a vapor lower in concentration. Boiling and condensation continued as vapors progressed to the top of the tower, where water was released to the atmosphere. The tower operated on an adiabatic cooling line with some loss in efficiency due to radiation losses at the uninsulated Karbate tower-air interface. A "Tee" at the base of the reboiler served as a product bleed to a Karbate heat exchanger-cooler. Well water at 70°F cooled the liquor product for storage. A stand pipe at the cooler outlet was used to maintain a liquid level in the reboiler. The acid product was stored in plastic lined 55 gallon steel barrels.

## PLANT OPERATION AND TEST DESCRIPTION

At start-up, water was used instead of plant liquor to familiarize personnel with procedures and to debug the plant. Then, on a Monday morning, plant liquor was charged into the plant and steam was applied. Following is a typical liquor analysis:

### Weight % Analysis

<u>HF</u>	<u>H<sub>2</sub>SiF<sub>6</sub></u>	<u>P<sub>2</sub>O<sub>5</sub></u>	<u>Na<sub>2</sub>O</u>	<u>SO<sub>4</sub></u>
4.75	0.08	1.86	0.49	0.145

Feed input was about 1 gpm with a 3 gpm recycle rate; thus, total evaporator throughput was 4 gpm. A 31% HF product was made towards the end of the first week. Early in the following week, the recycle pump began to labor and liquor flow became erratic. About 5:00 PM the third day, a gasket at the top of the evaporator blew out. The plant was shut down and the evaporator was opened for inspection. Each of the 1 in. ID Karbate tubes was plugged solid with a white crystalline material later identified to be sodium silico fluoride. The recycle was removed and stored for reuse. A small hole was drilled through the scale and the pot was charged with 98% sulfuric acid. The pump was started and steam was applied to the evaporator. The scale dissolved in the hot acid, breaking down into sodium sulfate and volatile silicon tetra fluoride. The pot was then drained of acid and washed with water.

After cleaning the circuit, the water was replaced with the recycle liquor. Following is the liquor analysis:

Weight % Analysis

<u>HF</u>	<u>P<sub>2</sub>O<sub>5</sub></u>	<u>Na<sub>2</sub>O</u>
8.10	17.40	2.10

Note the uneven increase in concentrations. Phosphate increase rose as expected; HF increase indicated that a soluble fluoride salt was present, over and above the solubility product of sodium silico fluoride. However, the increase was much less than phosphate, due, of course, to the volatile fraction reporting as HF product; sodium increase represented the soluble fraction of sodium silico fluoride. At start-up, recycle was increased to 15 gpm. It was felt that the shearing effect of higher liquid velocity would reduce tube scale. This supposition appeared to be correct during the following extended plant run, but another factor, which will be discussed later, was changing the scale problem. However, in the meantime, the evaporator was operating as a forced flow heat exchanger, which did not affect heat transfer but did create a severe mist carryover problem. The demister was flooded, and a second demister installed in the vertical portion of the vapor line to the adiabatic tower did not completely prevent product contamination. The test was continued, however, for approximately one day more when the overflow bottle became plugged and the test was stopped. The evaporator was inspected and found to be clean. The overflow bottle, however, was about half full of sodium silico fluoride crystals, which had precipitated when cooled in the lower bottle area. Following are laboratory results of the recycle liquor and product:

Weight % Analysis

	<u>HF</u>	<u>P<sub>2</sub>O<sub>5</sub></u>	<u>Na<sub>2</sub>O</u>
Recycle Liquor	12.39	28.87	5.64
Product	31.10	0.74	

The product cooler was inspected and found to have a considerable deposit of the same crystalline material found in the bottle. Apparently, the solubility in high concentration HF was low since no contaminate was found in the product. Two changes were made before test resumption. First, the evaporator was moved to a spare opening on the pot and the original line was used for vapors exclusively (See Figure 2, page 8). Now vapor separation occurred in the more spacious area above the liquid level in the pot. Secondly, a crystallizer circuit was installed on the evaporator circuit. Hot liquor, bled from the bottle overflow, was cooled and the troublesome crystals separated. Cooled liquor was returned to the circuit. The solubility of these crystals in 30% phosphoric acid came as a welcome surprise solution to evaporator tube scale problems. The test was resumed and run for a full week without incident. The free space at the top of the pot proved adequate for mist separation and the crystallizer solved the bottle plugging problem. Following are analyses of the final product, crystals, and liquor:

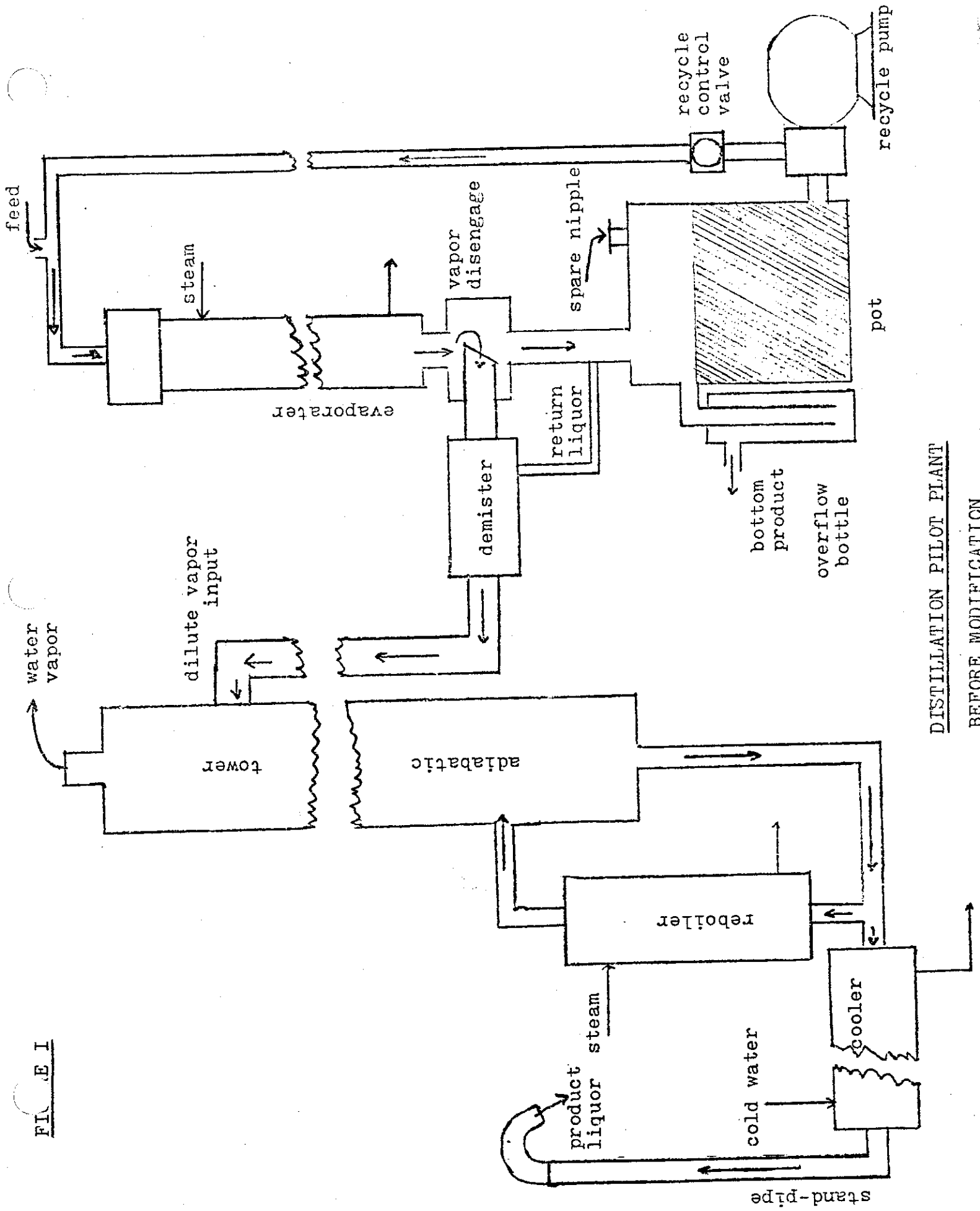
Weight % Analyses

	<u>HF</u>	<u>P<sub>2</sub>O<sub>5</sub></u>	<u>Na<sub>2</sub>O</u>	<u>Temp. °F</u>
Recycle Liquor	5.03	39.56	5.00	241
Product	31.02	0.00	0.00	235
Crystals	59.00	0.30	43.60	175

This plant test series proved the feasibility of producing high purity HF acid up to azeotropic strength.



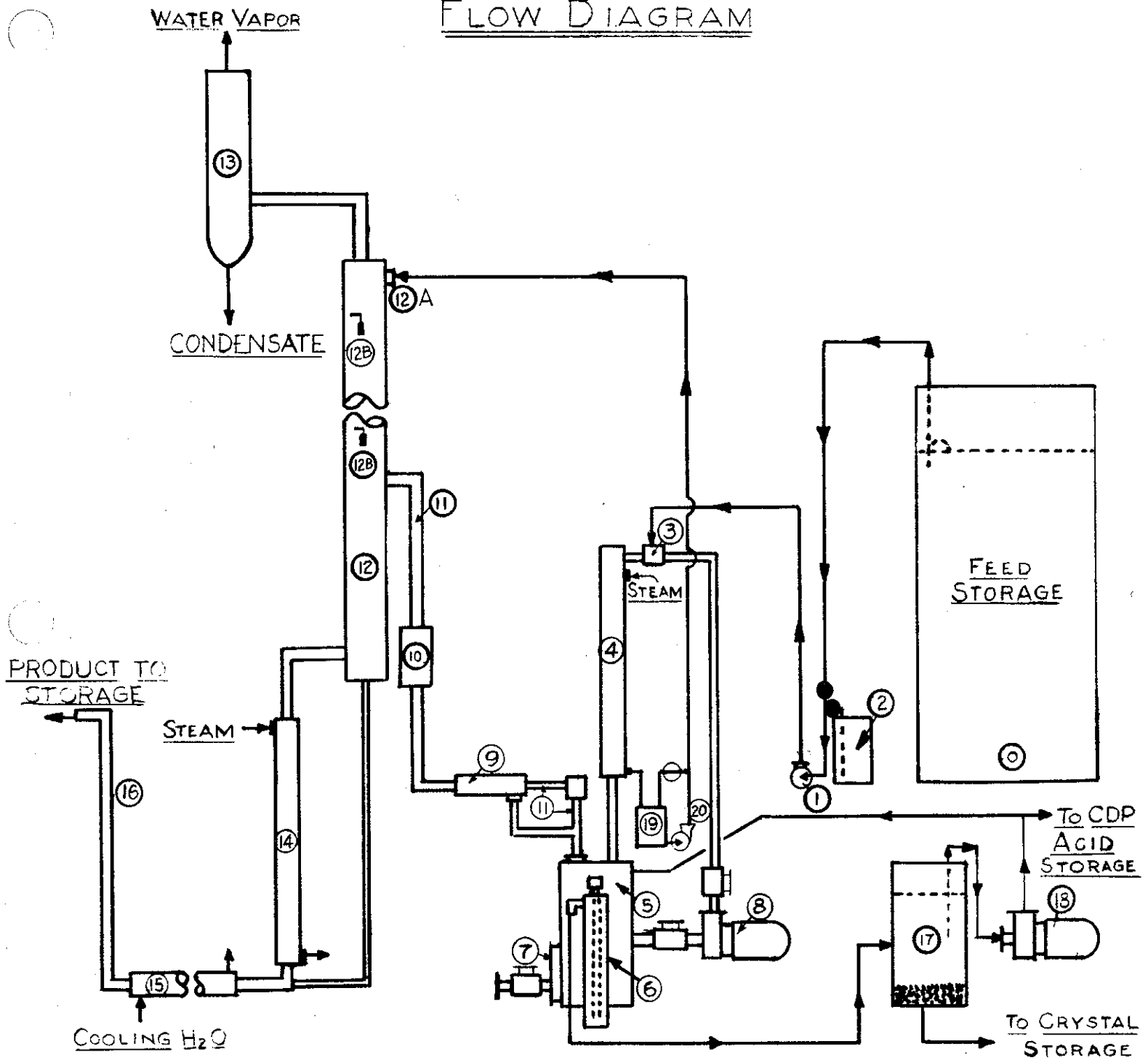
FIG. E I



DISTILLATION PILOT PLANT

BEFORE MODIFICATION

FIGURE 1  
HF DISTILLATION PILOT PLANT  
FLOW DIAGRAM



- |                                 |                              |                                 |
|---------------------------------|------------------------------|---------------------------------|
| <u>0 FEED STORAGE TANK</u>      | <u>8 RECYCLE PUMP</u>        | <u>14 REBOILER</u>              |
| <u>1 METERING PUMP</u>          | <u>9 KARBATE DEMISTER</u>    | <u>15 PRODUCT COOLER</u>        |
| <u>2 FEED MEASURING TANK</u>    | <u>10 YORK DEMISTER</u>      | <u>16 PRODUCT STAND PIPE</u>    |
| <u>3 FEED 'T' ASPIRATOR</u>     | <u>11 3" VAPOR LINE</u>      | <u>17 CRYSTALLIZER</u>          |
| <u>4 KARBATE EVAPORATOR</u>     | <u>12 ADIABATIC TOWER</u>    | <u>18 CRYSTALLIZER PUMP</u>     |
| <u>5 KARBATE POT</u>            | <u>12A TOWER WATER INLET</u> | <u>19 STEAM CONDENSATE TANK</u> |
| <u>6 PRESS. SEAL O'FLOW BTL</u> | <u>12B SAMPLE VALVES</u>     | <u>20 TOWER WATER PUMP</u>      |
| <u>7 POT MANHOLE</u>            | <u>13 TAIL GAS SCRUBBER</u>  |                                 |

