ISMA* Technical Conference

Wiesbaden, Germany

11-15 September 1961

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

THE INTERNATIONAL
SUPERPHOSPHATE
MANUFACTURERS' ASSOCIATION
TECHNICAL COMMITTEE · COMITE DES TECHNICIENS

LE/61/41
Received: 17th April, 1961

TECHNICAL MEETINGS - WIESBADEN

CONFIDENTIAL

This paper will be presented at the Technical Meetings in Wiesbaden from September 11th to 15th, 1961. It must not be published prior to that date, and in any case it must not be published without the permission of the author.

RECOVERY OF FLUORINE AS A BY-PRODUCT OF PHOSPHORIC ACID MANUFACTURE

by D.J. BREEZE
Fisons Fertilizers Limited

1. INTRODUCTION

Potassium fluosilicate has been manufactured by Fisons Fertilizers Limited for many years, using as a raw material fluorine bearing gases evolved from superphosphate dens. In 1959 a new plant was commissioned at Fisons' Immingham factory to recover the salt as a by-product of phosphoric acid manufacture. The plant is described in this paper.

2. THEORETICAL BACKGROUND

Phosphoric acid (32% P_2O_5) is produced at Immingham by reacting Morocco phosphate rock with a mixture of sulphuric acid (94 - 96%) and recycled phosphoric acid (approx. 22% P_2O_5). Fluorine in the rock, which may be considered to be present as calcium fluoride reacts with the mixed acids, forming in the first instance hydrogen fluoride.

$$CaF_2 + 2H_3PO_4 \longrightarrow Ca(H_2PO_4)_2 + 2HF \qquad .... (1)$$

$$CaF_2 + H_2SO_4 + 2h_2O \longrightarrow CaSO_4\ 2H_2O + 2HF \qquad .... (2)$$

Silica in the phosphate rock is converted by the hydrogen fluoride to fluosilicic acid.

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O \qquad .... (3)$$

Weak phosphoric acid recycled from the gypsum filtration step of the phosphoric acid process therefore contains fluosilicic acid in solution. This acid mixture is heated to drive off fluorine as silicon tetrafluoride, possibly mixed with a little hydrogen fluoride.

$$H_2SiF_6 \longrightarrow SiF_4 + 2HF \qquad ..... (4)$$

The gases are absorbed in water to produce fluosilicic acid, with simultaneous deposition of silica in a hydrated form.

$$3SiF_4 + 2H_2O \longrightarrow 2H_2\ SiF_6 + SiO_2 \qquad .... (5)$$

The silica is filtered leaving an aqueous solution of fluosilicic acid. Recovery of this acid is the first stage in the manufacture of potassium fluosilicate. The final stage is to react the acid with an aqueous solution of potassium chloride, when the potassium salt is precipitated.

$$H_2SiF_6 + 2KCl \longrightarrow K_2SiF_6 + 2HCl \qquad .... (6)$$

As previously mentioned it is necessary at one point of the phosphoric acid process to mix weak recycled phosphoric acid with concentrated sulphuric acid. The heat of dilution of the sulphuric acid can be used to strip fluorine bearing gases from the recycled phosphoric acid as in equation 4. Phosphoric acid is added to the sulphuric acid in two stages, the proportion used for the first stage being adjusted to give conditions for optimum evolution of silicon tetrafluoride.

Graph 1 is a typical curve showing how the temperature of the mixed acids varies with the acid ratio. For a fixed throughput of sulphuric acid, maximum fluorine recovery does not, of course, necessarily occur at the acid ratio which gives maximum mixture temperature.

3. DESCRIPTION OF PLANT

3.1 Manufacture of fluosilicic acid

Essential equipment is shown in the process flowsheet and equipment details are given in the appendix. Items 1 and 2 are stripping tanks operating in parallel. Each receives metered streams of sulphuric acid and recycled phosphoric acid The sulphuric acid flow is governed entirely by the phospho[ric] acid plant operation, since all the sulphuric acid needed for rock digestion is fed through the stripping tanks. The phosphoric acid feed is a proportion only of the total recycle acid available. About 0.6 lbs. of recycled phosphoric acid are used per lb. of sulphuric acid. Higher proportions of phosphoric acid cause the mixture to foam, with consequent losses of acid to the scrubber system.

The mixed acids attain a temperature of about 135°C, and return by overflow pipes to the phosphoric acid plant. Steam and SiF_4 evolved from the tanks pass into a Venturi scrubber Item 3 co-currently with a slurry of silica in fluosilicic acid, which removes the SiF_4. Slurry and scrubbed gas separate in a disengagement tank Item 4, from which the slurry is recirculated by pump Item 7 over the scrubber. Formation of fluosilicic acid by absorption of SiF_4 in water is exothermic. To ensure deposition of silica in a form which is readily filterable at a later stage, the slurry temperature is kept below 50°C by controlled admission of cooling air into the scrubber through adjustable dampers Items 5 and 6.

Air and steam containing traces of SiF_4 are vented from the disengagement tank to the phosphoric acid plant wash-towers by fan Item 8. The slurry of silica in aqueous fluosilicic acid, (strength 16 - 18%) is pumped continuously or batchwise to an agitated storage tank Item 9. Make-up water is added as required to the disengagement tank. After filtration in a vacuum filter nutsche Item 11, acid of about 16% strength is stored in tank Item 13.

3.2 Manufacture of potassium fluosilicate

A 20% aqueous solution of potassium chloride is prepared from fertilizer grade material in an agitated dissolving tank Item 15. The solution is heated to 25°C, and impurities are allowed to settle. The supernatant solution is pumped to a head tank Item 17, from which it is metered to an agitated reactor Item 18. This reactor also receives a controlled flow of fluosilicic acid from metering pump Item 14, and a metered flow of water. Potassium chloride and fluosilicic acid are used in stoichiometric proportions.

Potassium fluosilicate is formed continuously as finely divided white crystals. The resulting slurry of the salt in hydrochloric acid solution is filtered continuously on a rotary vacuum filter Item 19 and washed free of chlorides. Filtrate is discarded to sewer. The product is charged batchwise to either of two driers Items 23 and 24, and finally discharged to 112 lb paper sacks through automatic weighing machine Item 25.

4. PLANT CAPACITY AND EFFICIENCY

(i) Recovery of fluorine from the stripping and scrubbing operations is about 140 lbs/hr. using 0.6 parts of recycled phosphoric acid per part of sulphuric acid (by weight).

(ii) The capacity of the reactor section (shown in the lower half of the flowsheet) is about 5.7 tons per 24 hour day of potassium fluosilicate. Supplies of fluosilicic acid for this section of the plant are available from superphosphate manufacturing operations as well as from the phosphoric acid plant.

(iii) The fluorine content of the recycled phosphoric acid is about 1.5%. Between 50% and 65% of the fluorine is recovered in the stripping operation. It has been found that residence time variations within a stripper in the range 6 - 15 minutes do not significantly affect fluorine recovery.

(iv) The efficiency of fluorine absorption in the Venturi scrubber is difficult to determine, but is believed to be better than 97%. The efficiency is independent of the fluosilicic acid strength over the range 0 - 16% H_2SiF_6.

(v) Usage of fluorine (as H_2SiF_6) is 0.61 lb. per pound of potassium fluosilicate produced. This is equivalent to a fluorine efficiency of 85%.

(vi) Usage of muriate of potash (60% K_2O) is 0.8 lb. per pound of potassium fluosilicate produced. This is equivalent to a potassium efficiency of 85%.

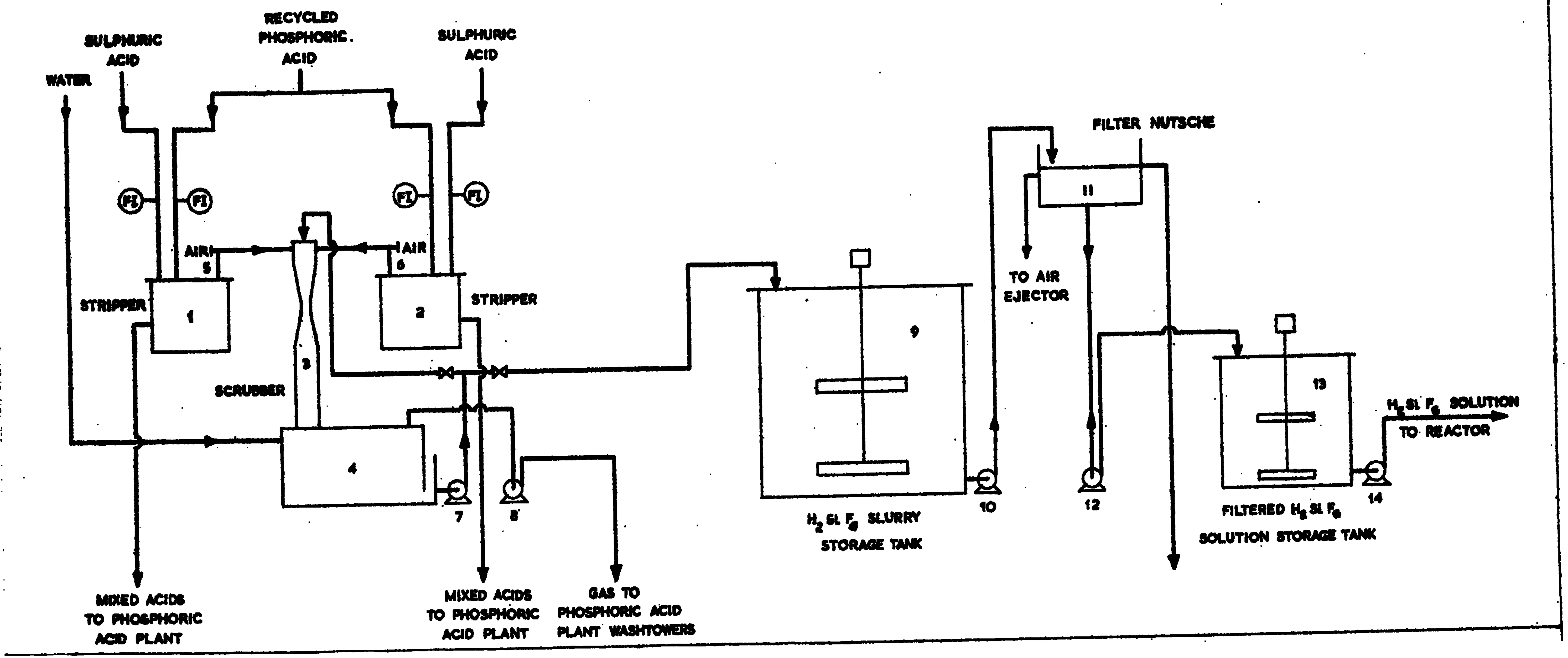
5. ACKNOWLEDGEMENTS

The author wishes to express thanks to colleagues at Immingham, who have assisted in the preparation of this paper, and to the Directors of Fisons Fertilizers Limited and Whiffen & Sons Limited, for permission to publish it.

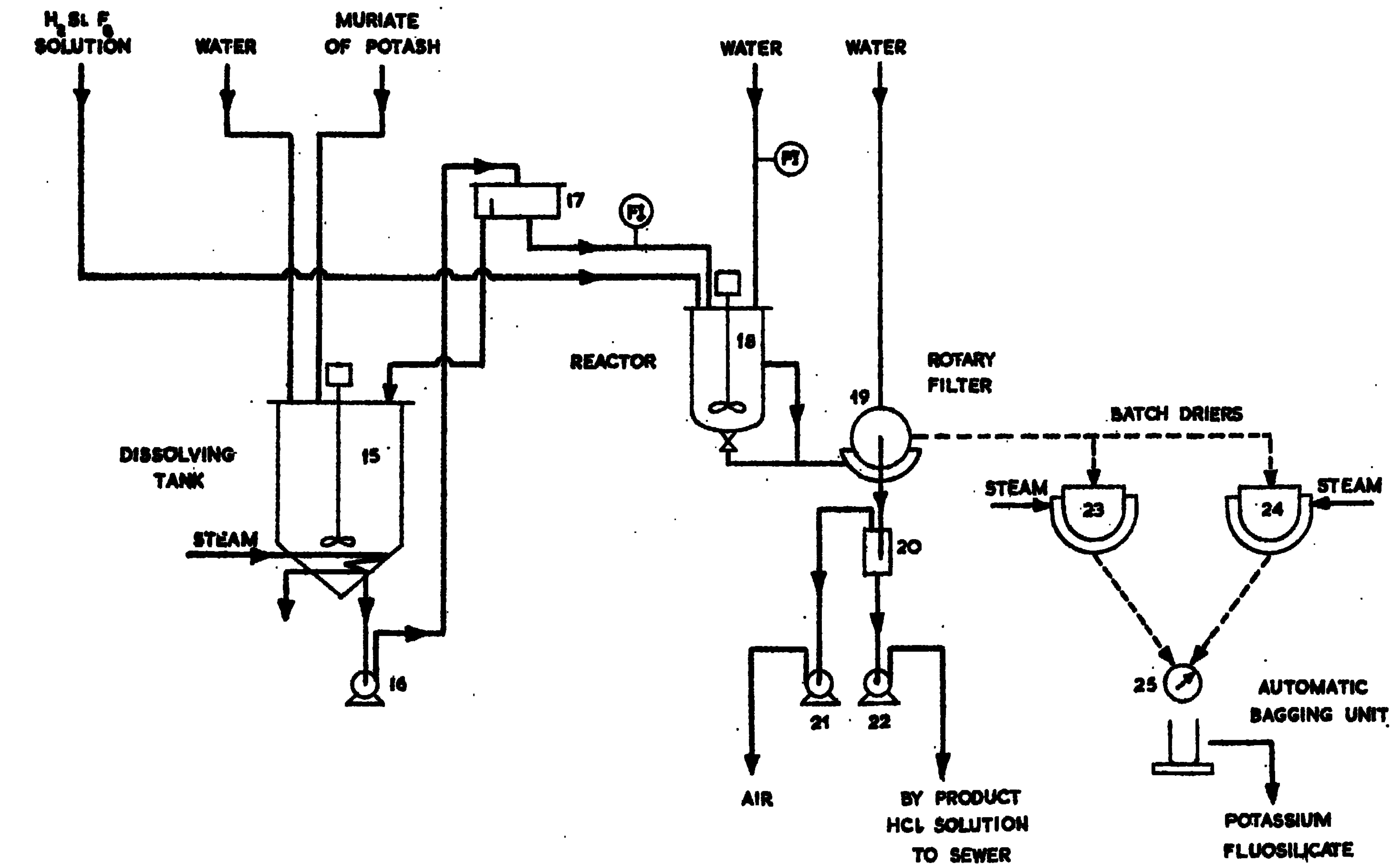
6. APPENDIX

Equipment details

Items 1, 2.	Stripping tank, vertical, cylindrical. Mild steel lined with lead and carbon bricks. Cover lead lined mild steel. Fitted with internal brick baffle.
Item 3.	Venturi type scrubber. Rubber lined mild steel.
Item 4.	Disengagement tank, rectangular section. Rubber lined mild steel.
Item 7.	Scrubber circulation pump. Stainless steel.
Item 8.	Exhaust fan. Stainless steel.
Item 9.	Storage tank for H_2SiF_6 slurry. 16' diam. x 16'-8" deep. Rubber lined mild steel. Fitted with agitator (2 tanks installed).
Item 11.	Wooden filter nutsche, 8' diam. x 5'-5" deep. (2 nutsches installed).
Item 13.	Storage tank for H_2SiF_6 solution. 10' diam. x 10'-10" deep. Rubber lined mild steel. Fitted with agitator. (2 tanks installed).
Item 14.	Metering pump for H_2SiF_6 solution. Ebonite.
Item 15.	Potash dissolving tank. 7'-6" diam. x 8'-6" deep. Mild steel. Fitted with agitator and steam coil (2 tanks provided).
Item 18.	Reactor. 3'-6" diam. x 7' deep. Rubber lined mild steel. Fitted with agitator.
Item 19.	Continuous rotary vacuum filter 20 sq.ft. Monel.
Item 23, 24.	Steam jacketed batch drier with worm type agitator. Mild steel or stainless steel. Capacity 1200 lbs. filter cake.

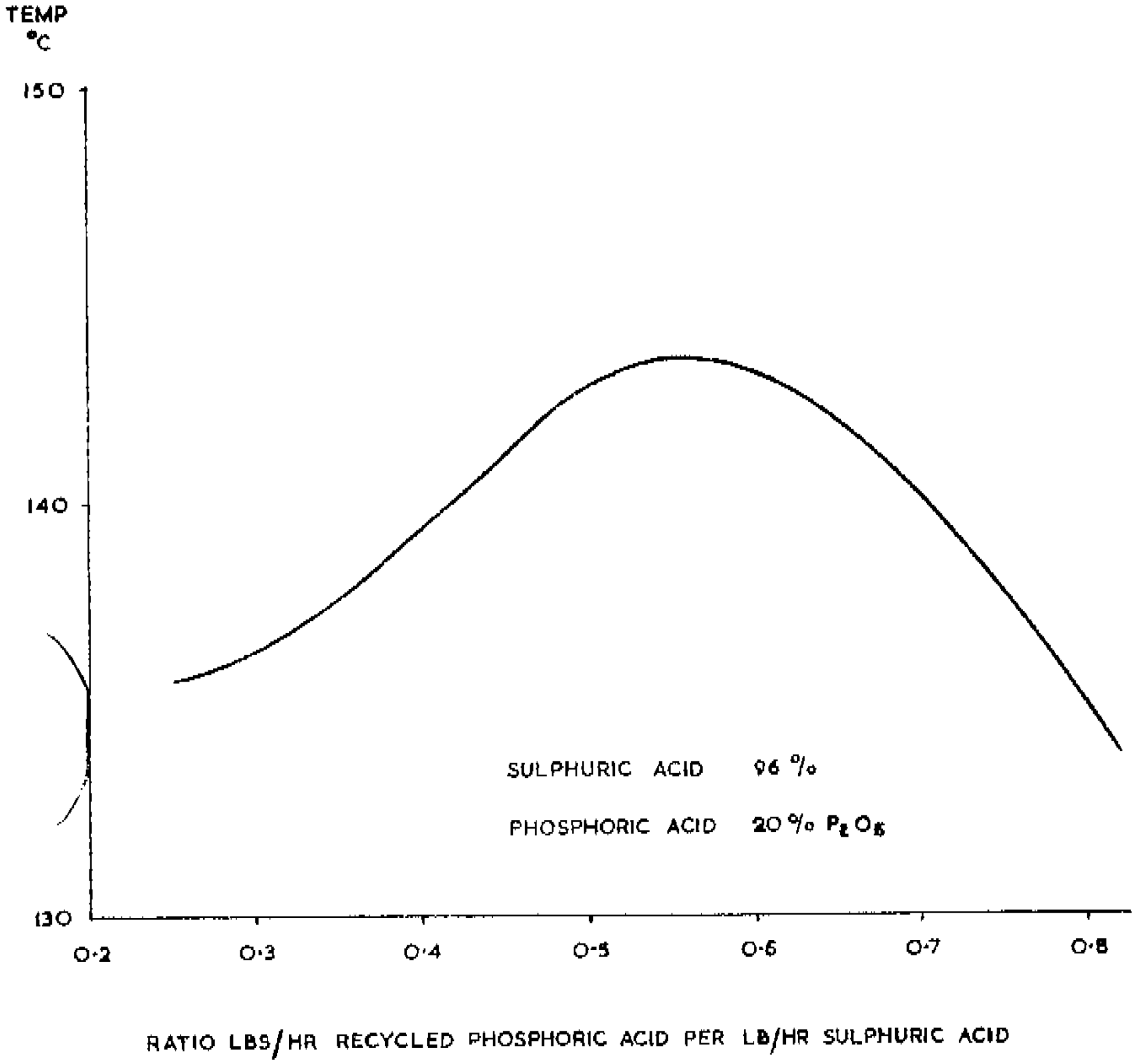


RECYCLED PHOSPHORIC ACID
SULPHURIC ACID
SULPHURIC ACID
WATER
FI
FI
FI
FI
AIR
5
AIR
6
STRIPPER
1
2
STRIPPER
3
SCRUBBER
4
7
8
MIXED ACIDS TO PHOSPHORIC ACID PLANT
MIXED ACIDS TO PHOSPHORIC ACID PLANT
GAS TO PHOSPHORIC ACID PLANT WASHTOWERS
9
H2 Si F6 SLURRY STORAGE TANK
10
FILTER NUTSCHE
11
TO AIR EJECTOR
12
13
FILTERED H2 Si F6 SOLUTION STORAGE TANK
14
H2 Si F6 SOLUTION TO REACTOR



PROCESS FLOWSHEET

RECOVERY OF FLUORINE AS POTASSIUM FLUOSILICATE FROM PHOSPHORIC ACID MANUFACTURE


TEMP
°C
150
140
130
SULPHURIC ACID 96 %
PHOSPHORIC ACID 20 % P2 O5
0·2
0·3
0·4
0·5
0·6
0·7
0·8
RATIO LBS/HR RECYCLED PHOSPHORIC ACID PER LB/HR SULPHURIC ACID