ADVANCED SEPARATION TECHNOLOGIES INCORPORATED™

HIGH PROFITS FROM POND WATER

BY

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BACKGROUND

Most of the phosphoric acid industry view pond water as an expense and necessary part of their plant operation. Each day environmental factors are placing greater emphasis on cleaning the ponds and reducing environmental pollution. Those companies which resist change and fight the clean-up program are destined to become defunct.

Contrary to the above, there are a few companies who consider pond water as a valuable source of profitable products. One such company is Advanced Separation Technologies (AST), a subsidiary of Florida Progress Corporation. AST views pond water as a source of almost infinite SiF_6, $P0_4$, and $S0_4$ ions, worth $1 Billion.

MARKET FOR POND WATER IONS

The key to success is finding ways to extract these ions and doing something valuable. For the SiF_6 ion, the logical use is to make $Si0_2$ and Fluorine Compounds. $S0_4$ is a valuable ion in making phosphoric acid and $P0_4$ can be easily employed in the existing phosphoric acid product line.

$Si0_2$ is an interesting product. In crystalline form, it is used in abundant quantity but sold at a low price and normally at minimum profit. In its amorphous form, $Si0_2$ becomes a very valuable product which sells between $800-$4,000/ton. The U.S. market is 150,000 tons valued at $180 Million.

Fluorine is also a widely used chemical species used to make hydrofluoric acid and fluorine compounds. This class of chemicals account for 600,000 tons of product in the U.S. valued at $900 Million.

In the world, there are only two primary sources of fluorine, fluorspar rock and phosphate rock. 99% of Fluorine products are made from fluorspar rock which sells for $150/ton. Only 1% is made from the phosphoric acid by-product, fluorsilicic acid (FSA), which sells for $100/ton. Just think of using the fluorine from pond water and buying it for $0/ton.

Over $1 Billion of chemical products generating $200 Million profit can be made from the SiF_6 ion found in pond water. The challenge is to economically extract the SiF_6 and convert it into amorphous silica and Fluoride compounds.

THE ISEP® CONTACTOR

AST developed the ISEP® Continuous Contactor for adsorption and ion exchange applications. Among its many benefits and features, the ISEP® allows an economical ion exchange for high concentrations (300-150,000 ppm) of chemical species (Figure 1). The ISEP® uses a slow moving carousel arrangement to continuously and simultaneously feed the to-be-treated liquid stream along with ion regeneration. The ISEP® allows ion exchange to be used economically in applications such as extracting SIF_6 for pond water.

HF PROCESS DESCRIPTION

The AST fluoride recovery process is designed to recover fluoride from the acidic pond water circulated in a wet-process phosphoric acid plant. The process employs the use of the continuous "ISEP®" ion exchange system to concentrate the fluoride in the form of fluosilicate ions. The concentrated fluoride-bearing solution exiting the ISEP® is further treated to produce high purity silica, anhydrous hydrogen fluoride, and/or fluoride salts.

Pond water has a pH in the range of 1-2 and generally contains about 0.5-1.2% fluoride, 1.0-2.0% phosphate as P_2O_5, 0.4-0.8% sulfate and lower concentrations of calcium, sodium, potassium, iron, aluminum and magnesium cations. Generally, the fluoride in pond water is all present as fluosilicate ions.

The fluoride recovery facility is divided into the following major areas which are depicted in Figure 2:

- ISEP® SiF_6 Concentration & Purification
- Silica Coproduct Precipitation
- NH_4F Conversion to NaF•HF
- HF Calcination & Purification

The only interface with the phosphate complex required for the operation of the fluoride recovery process is access to the circulating cooling pond as shown in Figure 3. Water is pumped from the pond directly into the adsorption zone of the ISEP® system. The ISEP® continuous ion exchange process consists of a carousel of rotating resin chambers which pass under a series of fixed ports through which flow feed, wash and eluant, or stripping, solutions. The continuous nature of the process optimizes resin site utilization for the desired species while minimizing wash and strip solution volumes.

The ISEP® is used in this application to concentrate fluoride and as the first stage of fluoride purification. Figure 4 shows the 20-port ISEP® configuration. In the first step, pond water is distributed into resin beds through feed ports in the "Adsorption Zone". Fluoride, in the form of the fluosilicate ion (SiF_6), is exchanged onto the resin sites for sulfate ions (SO_4) which enter the water phase that is returned to the pond. Pluggage of the resin beds via filtration of solids present in the pond water is prevented by feeding a portion of the pond water through the ISEP® in the upflow mode as shown in Figure 4 where ports #2 and #3 are configured in this manner.

After being washed with a small stream of fresh water to remove entrained pond water and its impurities, the fluoride-loaded resin then moves to the "Strip Zone" where the above ion exchange is reversed by contacting the resin with ammonium sulfate stripping solution. The fluosilicate ions enter the stripping solution at a concentration 6-12 times greater than that in the pond water. This "loaded strip solution" exits the ISEP® as a mixture of ammonium fluosilicate ($(NH_4)_2SiF_6$) and ammonium sulfate ($(NH_4)_2SO_4$). Stripped resin is then rinsed with a recycle stream of fresh water in order to recover SiF_6, SO_4 and NH_3 species entrained in the resin.

The ammonium fluosilicate (AFS) is separated from the loaded strip solution as a solid and purified via a crystallization process. Mother liquor rich in ammonium sulfate is recycled to the ISEP® stripping process. Sulfuric acid, the only chemical consumed in the entire process, is mixed with recycle NH_3 from a downstream process and added to the mother liquor to replenish the ammonium and sulfate ions removed via crystallization and ion exchange, respectively.

Essentially all of silica is precipitated from the pure ammonium fluosilicate in the next step via pH adjustment. The SiO_2 produced via this process is amorphous in structure as well as being very pure, and therefore, it has high value as a specialty chemical. Amorphous SiO_2 is both physiologically and environmentally safe.

The ammonium fluoride filtrate intermediate produced in SiO_2 precipitation is converted to ammonium bifluoride ($NH_4F \cdot HF$) in an evaporation process. This fluoride salt is reacted with solid sodium fluoride in agitated reactors to produce sodium bifluoride ($NaF \cdot HF$). The filtrate, ammonium fluoride, is recycled to the evaporation step.

Wet sodium bifluoride cake is first dried to ensure complete moisture removal, and then it is fed forward to a calciner where the sodium bifluoride is decomposed to hydrogen fluoride (HF) gas and NaF. The hydrogen fluoride gas is purified by rectification, and transferred to storage as the anhydrous liquid. NaF solids are cooled and recycled to the sodium bifluoride exchange reactors.

The anhydrous HF produced via this process is purer than HF made using the conventional fluospar route because it contains none of the common impurities such as arsenic, heavy metals, sulfur compounds and fluosilicate. Analysis of the HF and silica are tabulated in Table 1.

There are no purge streams or water discharges from the process, and there is no net addition of water to the cooling pond.

COMMERCIALIZATION

Focusing on one project, (i.e. HF) sometimes leads to commercializing a different product. This is the case for AST. We successfully proved the HF process in a 1000 Lb/Day demonstration plant which operated for a 10 month period. Through cooperation with other companies, we expect this process to be commercial in the next 1-3 years. Simultaneously, Fluoride Salts caught our interest. Realizing the high purity and low cost of the Ammonium Fluoride, a research effort began 10 months ago to make fluoride salts. We modified the HF flow chart to look like Figure 5. The results have been exciting from the view of manufacturing costs and chemical purity. Samples tested by customers indicate the AST process can produce the highest purity product. The process reduces the cost of manufacture by 50%.

FUTURE

One of AST's important objectives is commercializing the SiF_6 recovery process. By solely investing, entering into a joint venture, or licensing the technology, AST hopes to begin construction of the first SiF_6 recovery plant in the next six months.

ISEP® CONTINUOUS CONTACTOR

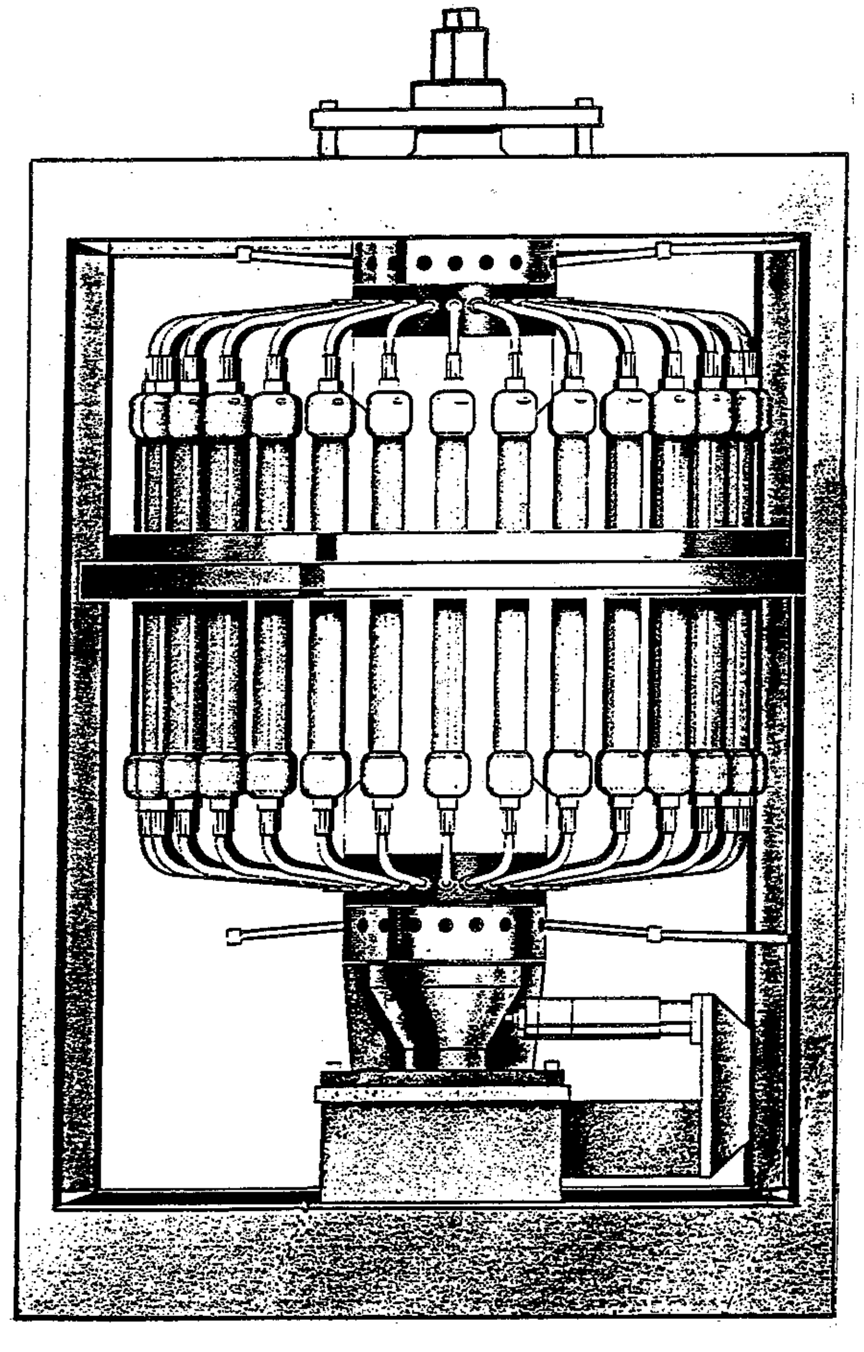
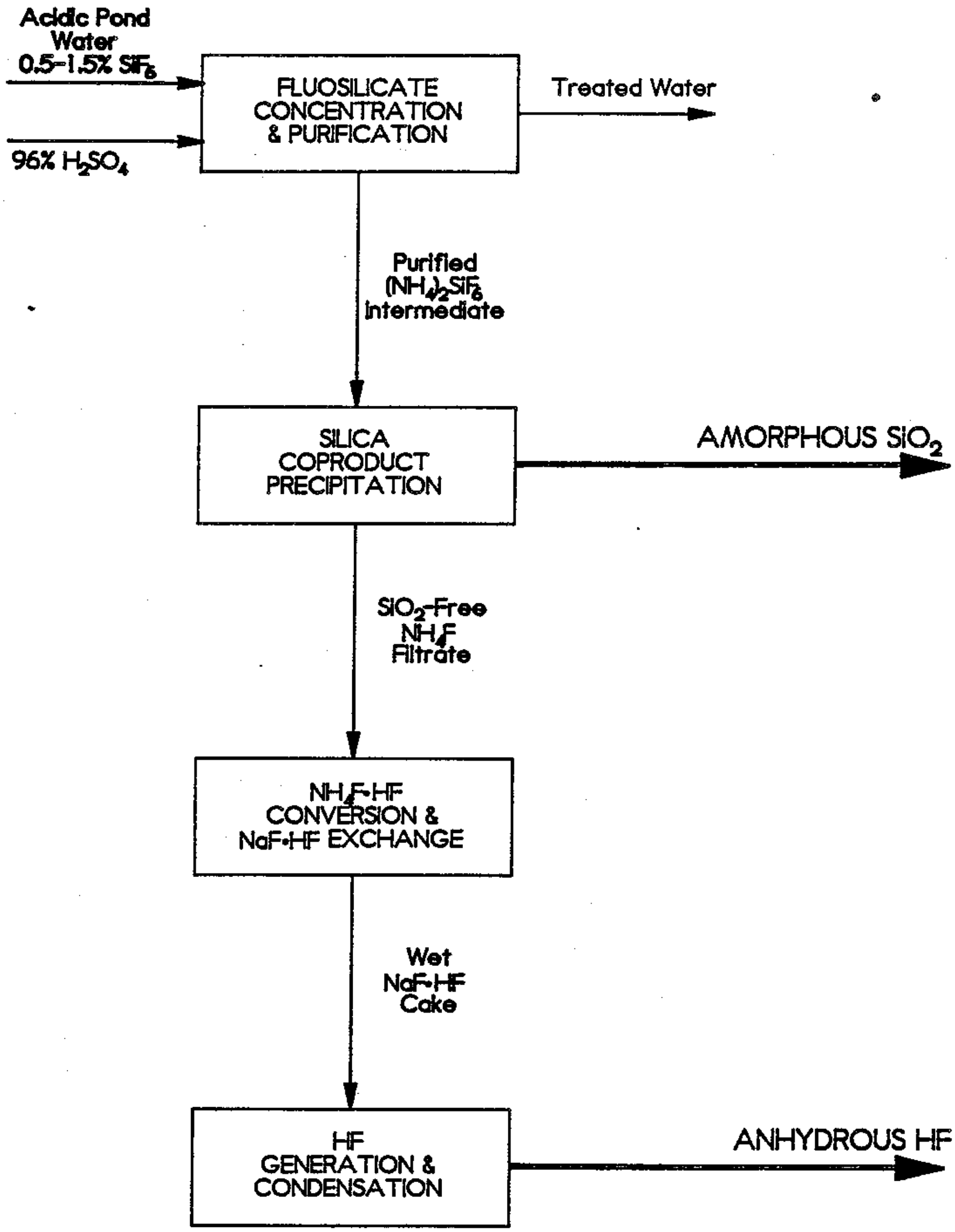


FIGURE #1



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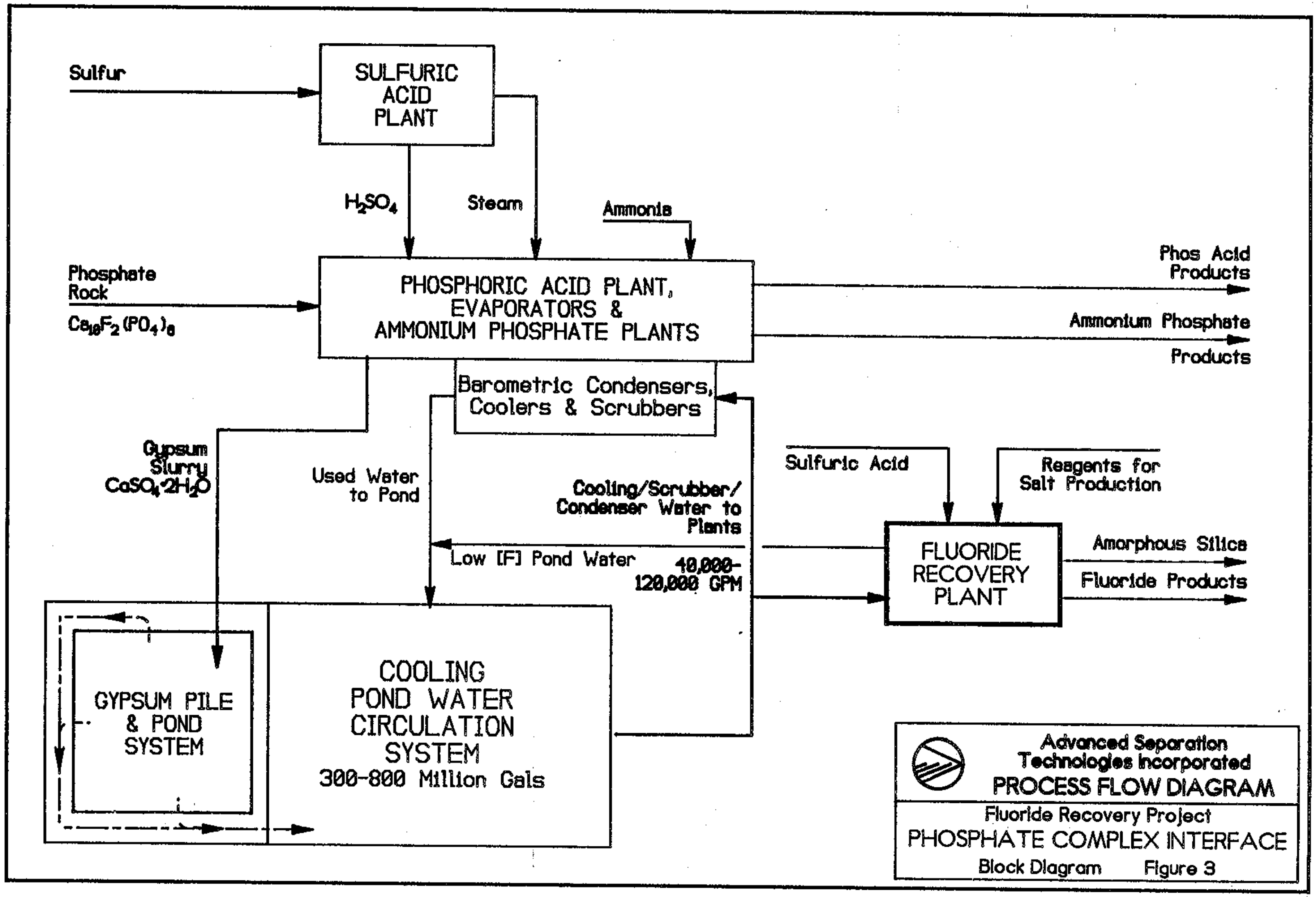
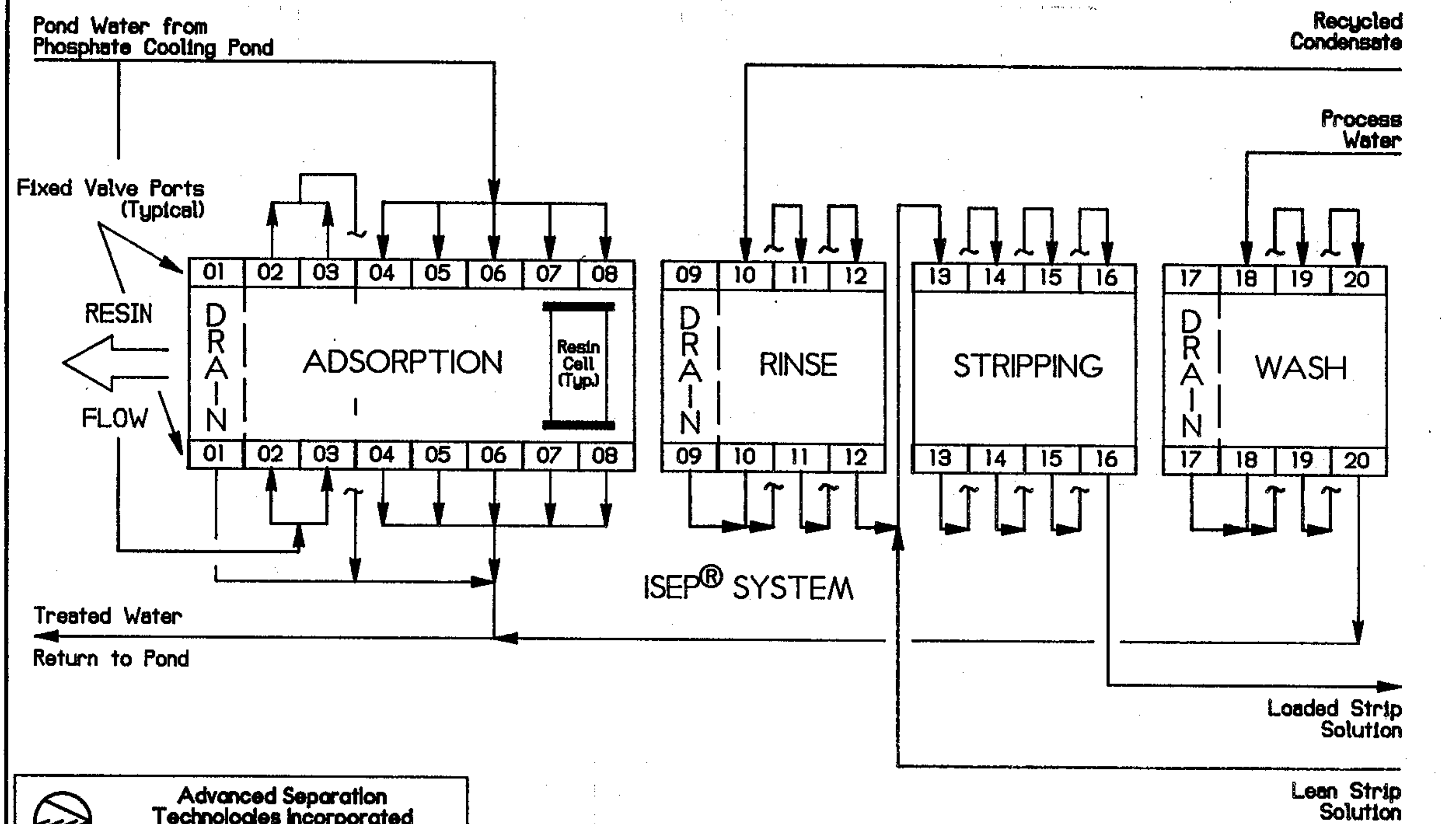
PROCESS FLOW DIAGRAM

Fluoride Recovery Project

ANHYDROUS HF PRODUCTION

Overall Block Flow Diagram Figure 2


Sulfur
SULFURIC ACID PLANT
H_2SO_4
Steam
Ammonia
Phosphate Rock
$Ca_{10}F_2(PO_4)_6$
PHOSPHORIC ACID PLANT, EVAPORATORS & AMMONIUM PHOSPHATE PLANTS
Phos Acid Products
Ammonium Phosphate Products
Barometric Condensers, Coolers & Scrubbers
Gypsum Slurry $CaSO_4 \cdot 2H_2O$
Used Water to Pond
Cooling/Scrubber/ Condenser Water to Plants
Low [F] Pond Water
40,000-120,000 GPM
Sulfuric Acid
Reagents for Salt Production
FLUORIDE RECOVERY PLANT
Amorphous Silica
Fluoride Products
GYPSUM PILE & POND SYSTEM
COOLING POND WATER CIRCULATION SYSTEM
300-800 Million Gals
Advanced Separation Technologies Incorporated
PROCESS FLOW DIAGRAM
Fluoride Recovery Project
PHOSPHATE COMPLEX INTERFACE
Block Diagram
Figure 3



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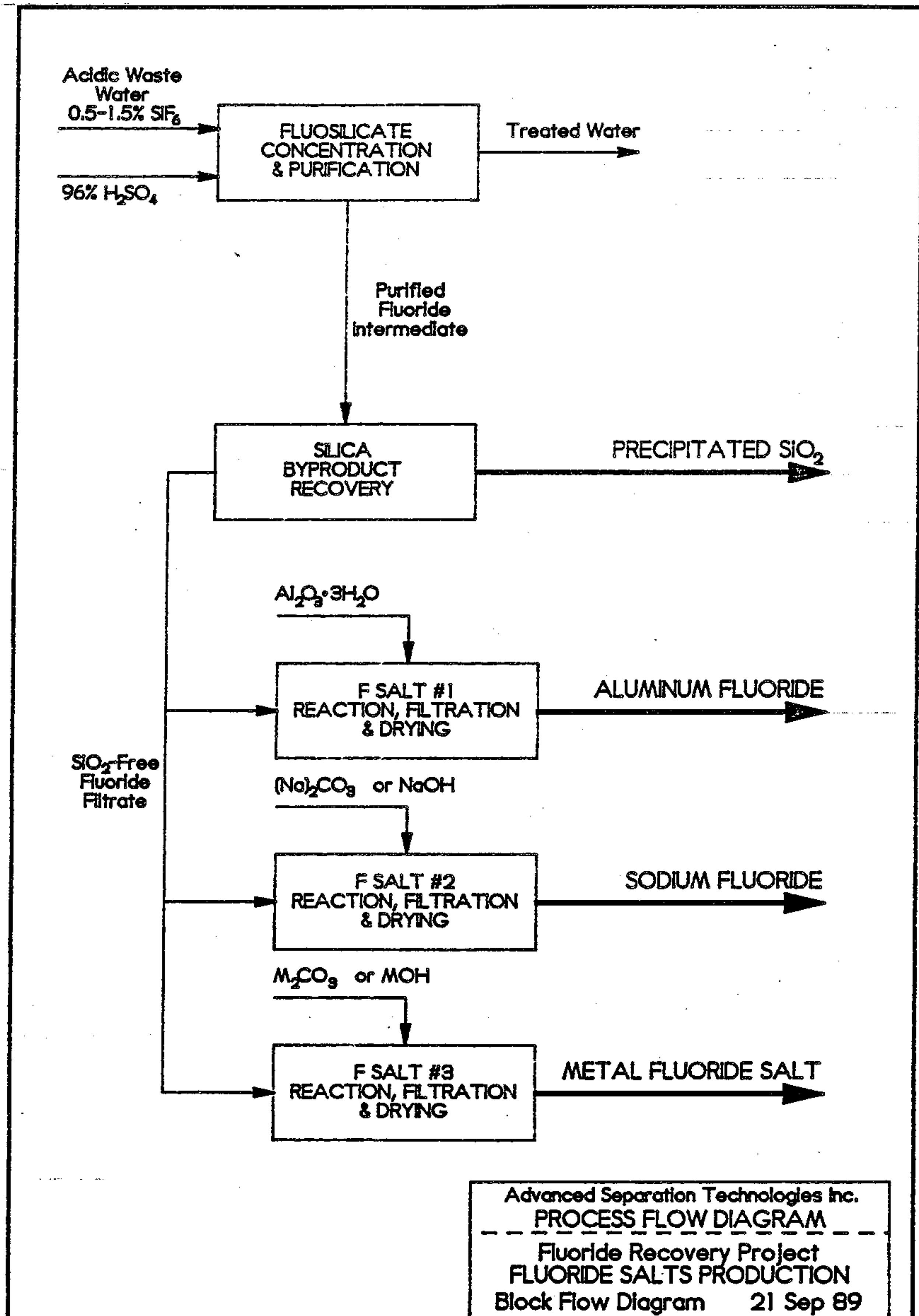
PROCESS FLOW DIAGRAM

Fluoride Recovery Project

ISEP® FLUOSILICATE ION EXCHANGE

Process Schematic Figure 4



Acidic Waste Water 0.5-1.5% SiF_6
96% H_2SO_4
FLUOSILICATE CONCENTRATION & PURIFICATION
Treated Water
Purified Fluoride Intermediate
SILICA BYPRODUCT RECOVERY
PRECIPITATED SiO_2
$Al_2O_3 \cdot 3H_2O$
F SALT #1 REACTION, FILTRATION & DRYING
ALUMINUM FLUORIDE
SiO_2-Free Fluoride Filtrate
$(Na)_2CO_3$ or NaOH
F SALT #2 REACTION, FILTRATION & DRYING
SODIUM FLUORIDE
M_2CO_3 or MOH
F SALT #3 REACTION, FILTRATION & DRYING
METAL FLUORIDE SALT
Advanced Separation Technologies Inc.
PROCESS FLOW DIAGRAM
Fluoride Recovery Project
FLUORIDE SALTS PRODUCTION
Block Flow Diagram 21 Sep 89

FIGURE #5

Fluoride Recovery Process
Product Assays
Table 1

Anhydrous HF

Hydrogen Fluoride	99.98% Minimum
Water	<100 PPM
Heavy Metals (as Pb)	0.0 PPM
Arsenic (As)	0.0 PPM
Calcium (Ca)	0.0 PPM
Iron (Fe)	0.0 PPM
Fluosilicic Acid (H_2SiF_6)	<1.0 PPM
Phosphate (P_2O_5)	<0.3 PPM
Sulfate (SO_4)	<1.0 PPM

Amorphous Silica

Silica (SiO_2)	93.0%
Moisture (H_2O)	1.2%
Loss on Ignition (400 °C)	4.3%
Fluoride (F)	500 PPM
Phosphate (P_2O_5)	95 PPM
Sulfate (SO_4)	<250 PPM
Calcium (Ca)	350 PPM
Iron (Fe)	0 PPM
Magnesium (Mg)	26 PPM
Sodium (Na)	8 PPM