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WATER MANAGEMENT FOR MINIMUM ACIDITY IN PHOSPHATE COMPLEXES

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**WATER MANAGEMENT FOR MINIMUM ACIDITY
IN
PHOSPHATE COMPLEXES**

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In the 1990 Clearwater Meeting, we had the opportunity to present a paper entitled (reference 8):

"Water Management for Minimum Discharge in a Phosphate Complex".

At that time, the paper did not address the reduction in the acidity of existing cooling ponds or gypsum stacks nor the elimination of the large volumes of acidic cooling water or acidic gypsum.

Since that time, many papers (references 1 thru 7) by others have been written which address wastewater management and minimization. In 1990 and 1991, we had the opportunity to assist EPA,through ICF, in developing information on alteratives for wastewater management (references 6 and 7).

As a result of that work and the opportunity to prepare plant designs for new phosphoric acid complexes we have further studied the water management and gypsum systems to minimize acidity.

This paper presents those new ideas/concepts on approaches to minimization or elimination of acidity in wet process cooling ponds and gypsum stacks. The following will be discussed and summarized (Figure I):

- Non Comingled Gypsum/Cooling Water System
- Neutralization of Gypsum Slurry
- Double Filtration and Maximum P2O5 Efficiency
- Cooling Towers and Heat Exchangers
- Fluorine Recovery and Fluorine Products
- Water Recycle and Management

One of the first paradigms to address is the "Present Comingled Process/Cooling Pond and Gypsum System". For years the comingled concept has been accepted (Figure II). This system results in extensive water soluble P2O5 losses to the gypsum stack that will never be recovered. It also generates large acid ponds that will be here until neutralized.

The distribution of acid pond water and resulting water soluble P2O5 losses in a comingled process are shown in Figure III. Approximately 1.7 tons pond water per ton P2O5 produced reports to the gypsum stack, assuming a 25% filter cake moisture. And, 2.2 tons pond water per ton of P2O5 is recovered in the process. As an example, a 2% P2O5 pond water will reflect an instantaneous soluble P2O5 loss of 7.8% (3.9 times 2%) and the net soluble loss is 3.4% P2O5 (1.7 times 2%). Remember, plants will always resaturate a stack with pond water as they stack gypsum or maintain water balance by evaporation. Therefore, pond water is lost to the stack.

The average instantaneous loss of P2O5 in the acid pond depends on the number of years of operation, the pond volume and acid pond P2O5 concentration. For a 30 year old pond with 2% P2O5 pond water concentration, the average loss to the pond is about 1/25 of the total soluble loss while 24/25 of the soluble loss remains in the stack.

The major soluble P2O5 loss is to the gypsum stack! (Figure IV)

In the Leyshon paper (reference 2), there are 20,000 MTPD P2O5 produced in Florida. With a typical 2% P2O5 pond water, this represents 680 MTPD P2O5 soluble loss to the stacks. At a value of $200 per ton P2O5, this results in a $50 million per year loss to the stacks and, in 30 years, $1.5 billion. (Figure V)

The average P2O5 loss to the cooling ponds is $2 million per year and $60 million in 30 years. Assume 2000 acres at 2 meter depth.

Therefore, it follows that there are economic reasons to examine a non-comingled process.

In most existing plants, the filter is at its full capacity and is the major source of P2O5 loss as stated by Weyers (reference 3). Therefore any retrofitting to improve efficiency will require more filtration area. Rather than operate additional filters in parallel with existing filters, it is envisioned that maximum P2O5 washing efficiency will be achieved by operating filters in series, i.e., double filtration as shown in Figure VI. The gypsum stack has a smaller pond used only for gypsum transport water and possibly for filter wash water. The well washed gypsum from the second filter containing only very little phos acid residuals is neutralized with lime or clays to eliminate acidity. This scheme eliminates the recycle of fluorine from the evolved vapors from flash coolers and evaporators. Also, lime requirements to meet EPA limits are minimized.

Double filtration is not a new concept. Plants that require end use of gypsum will normally have two filters. Also, the hemi-dihydrate process uses two filters. The new concept is to separate phos acid from fluosilicic acid by not comingling cooling water and gypsum slurry.

A proposed retrofit non-comingled operation might look like Figure VII.

To enhance P2O5 recovery from an existing acid pond there are two alternatives (assume wet grinding in place):

1. Maintain existing rock grinding system and add a rock filtration system to permit addition of pond water to the rock slurry feed (reference 9).

2. Convert existing rock grinding system to use all pond water (reference 10). A rock filter is not required.

For a 1000MTPD P2O5 plant with 100 acres acid pond at 2% P2O5,the recovery time is about 2.5 years with about 18,000 tons P2O5 recovered at a value of about $3 million.

Now that the gypsum stack is separated from the cooling circuit, we can address the acidity of the cooling water circuit. Basically, the cooling water is used to condense vapors evolved from flash coolers and evaporators. With proper equipment design (entrainment separators) and operation, there should only be fluorine and water vapor evolved from these equipment. Our experience with evaporators indicate only trace amounts of phos acid in the recovered fluosilicic acid. The method to recover fluorine as fluosilicic acid (H2SiF6 or FSA) is well established (references 13-16). We have designed and installed both single stage FSA and two stage series FSA recovery systems as shown in Figures VIII and IX.

The cooling pond is replaced with a cooling tower. Either direct contact condensing or indirect condensing with heat exchangers can be used (reference 13 and 15). If direct condensing is used, it is our experience that a two stage series operated FSA system will be required to achieve acceptable fluoride concentrations in the cooling water circuit.

If indirect condensing is used, a single stage FSA system should be sufficient if evaporation is done as a single stage (52-54 % P2O5 product acid).

In any case, the ideal system is the indirect condensing, which results in zero fluorides in the cooling water circuit. The condensed water, with a low fluoride concentration can be recycled to the process or neutralized depending on water management/balance in the complex. The cooling tower blowdown can be discharged as is presently done with sulfuric acid cooling tower blowdown or can be reused to maintain water balance.

As can be expected, the water management/ balance is dependent on whether we are retrofitting or designing a new grassroots complex and site specific designs must be done on a case by case basis.

A typical new non-comingled grass roots process might have the water management system as shown in Figure X and basically there is zero discharge as all cooling tower blowdown is used in the process. Also, there is minimal lime required for neutralization.

As a result of all this FSA recovery a typical question is:

"Is there a market for all the recovered FSA ?"

Well, the answer is:

" Not as FSA, but as other fluorine products such as: Aluminum Fluoride and Anhydrous HF, as seen in Figure XI."

Also we doubt that all of this FSA will suddenly appear on the market, and therefore an instantaneous glut is highly unlikely.

We have designed and constructed an ALCOA Aluminum Fluoride plant in Florida which has been in operation over 20 years. In addition we offer the Poznanskie Zaklady Chemiczne (PZC) process for the production of anhydrous HF (AHF). It is the only commercially proven process for AHF from FSA.

In addition, there are other processes that utilize FSA for the digestion of phosphate rock (references 11 and 12).

In a non-comingled process, some of the recovered FSA can replace the fluoride equivalent recycled from the pond in a comingled process. This can be very useful if the FSA is contaminated with P2O5, such as from equipment without P2O5 entrainment separators, i.e., flash coolers. The FSA would be fed directly to the phos acid reactor.

In summary, some of the plant water management alternatives with non-comingled concept can be seen in Figure XII. The resulting concentrations of fluoride are based on experience with FSA systems and cooling water systems. The economics of the alternatives must be done on site specific basis. Remember, there is no better time to eliminate acid cooling ponds and recover the P2O5 than while the plant is in operation!

It is envisioned that in any case, gypsum neutralization is desired to motivate efficient recovery of phos acid, improve recovery potential of gypsum and minimize environmental problems now and in the future.

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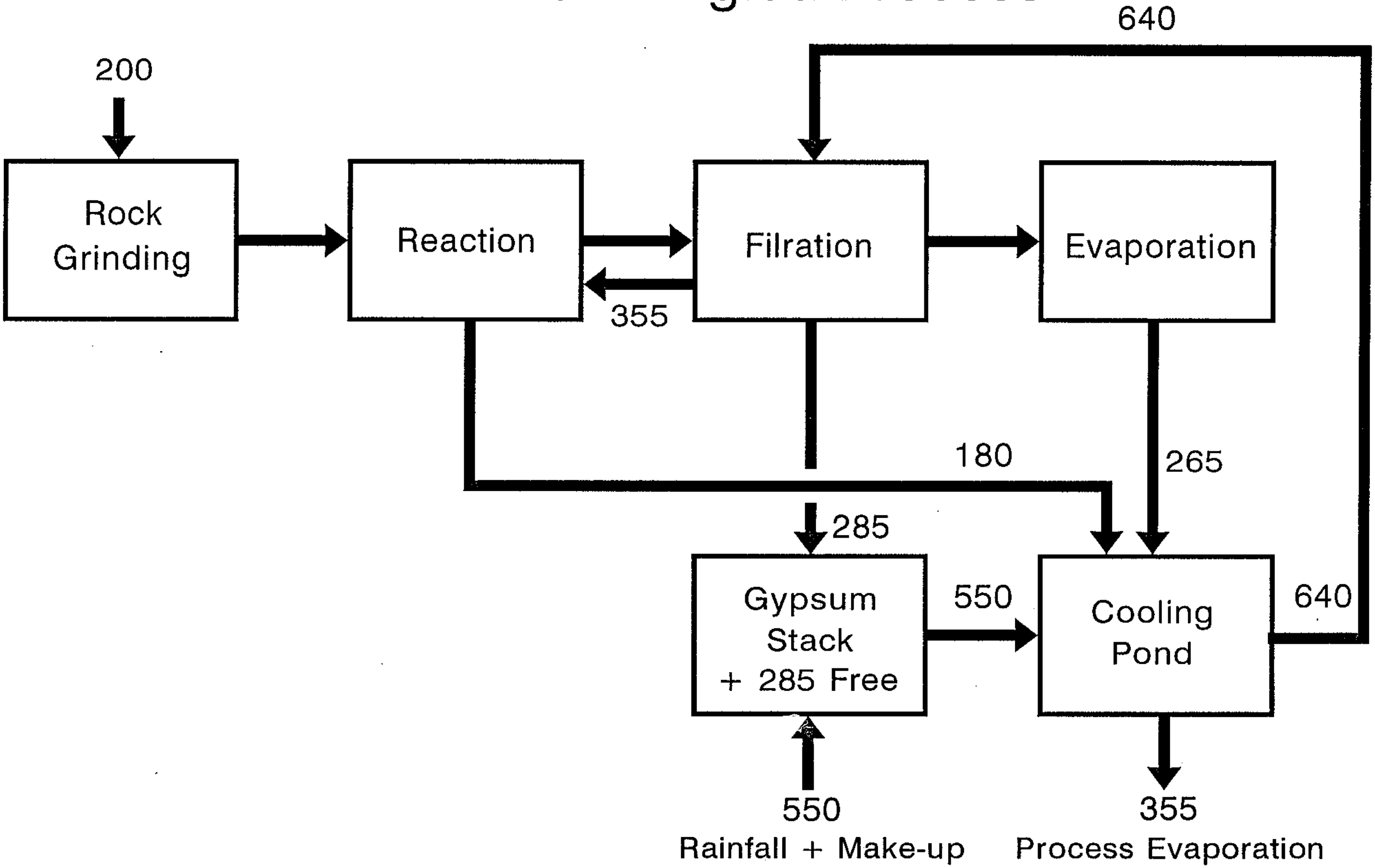
Figure I

Water Management for Minimum Acidity in Phosphate Complexes

- Separate Gypsum Stack and Cooling Water System
- Neutralization of Gypsum Slurry
- Cooling Towers with Indirect Heat Exchangers
- Maximum P2O5 Washing Efficiency in Filtration
- Maximum Fluorine Recovery
- Recovery and Recycle of Acid Spills and Wash Solutions

Figure II
Present Comingled Process



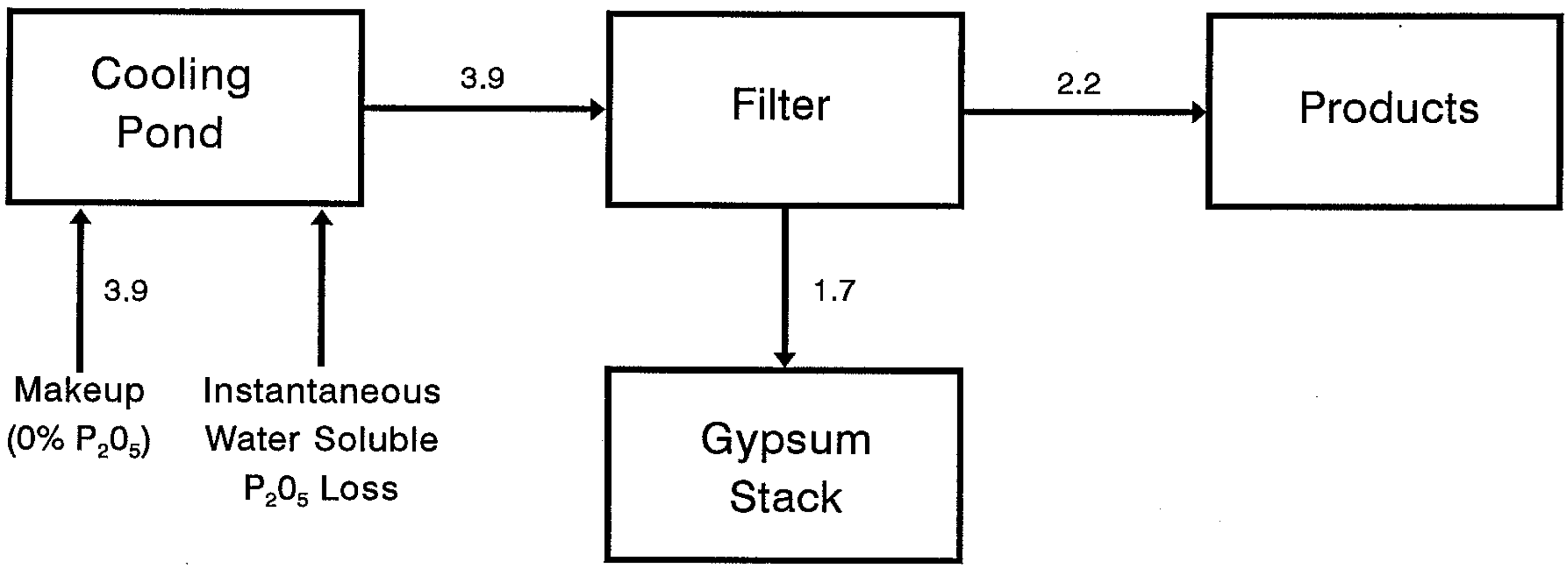
Net Flows in GPM Free Water for 1000 STPD P2O5 Feed @ 92% Efficiency

Assume: Rainfall = Evaporation in Cooling Pond, No Seepage from Gyp Stack or Cooling Pond

Figure III

Pond Water Distribution in Comingled System

Net Ton H2O / Ton P_2O_5 Produced



Water Soluble Loss, $\%P_2O_5$ Instantaneous Loss (Gypsum Slurry)	Water Soluble Loss, $\%P_2O_5$ Net (To Stack)	%P2O5 in Pond Water
1.15	.5	.3
2.3	1.0	.6
3.4	1.5	.9
5.7	2.5	1.25
6.9	3.0	1.75
8.0	3.5	2.06
9.2	4.0	2.35

Figure IV

Water Soluble P_2O_5 Loss - Comingled System

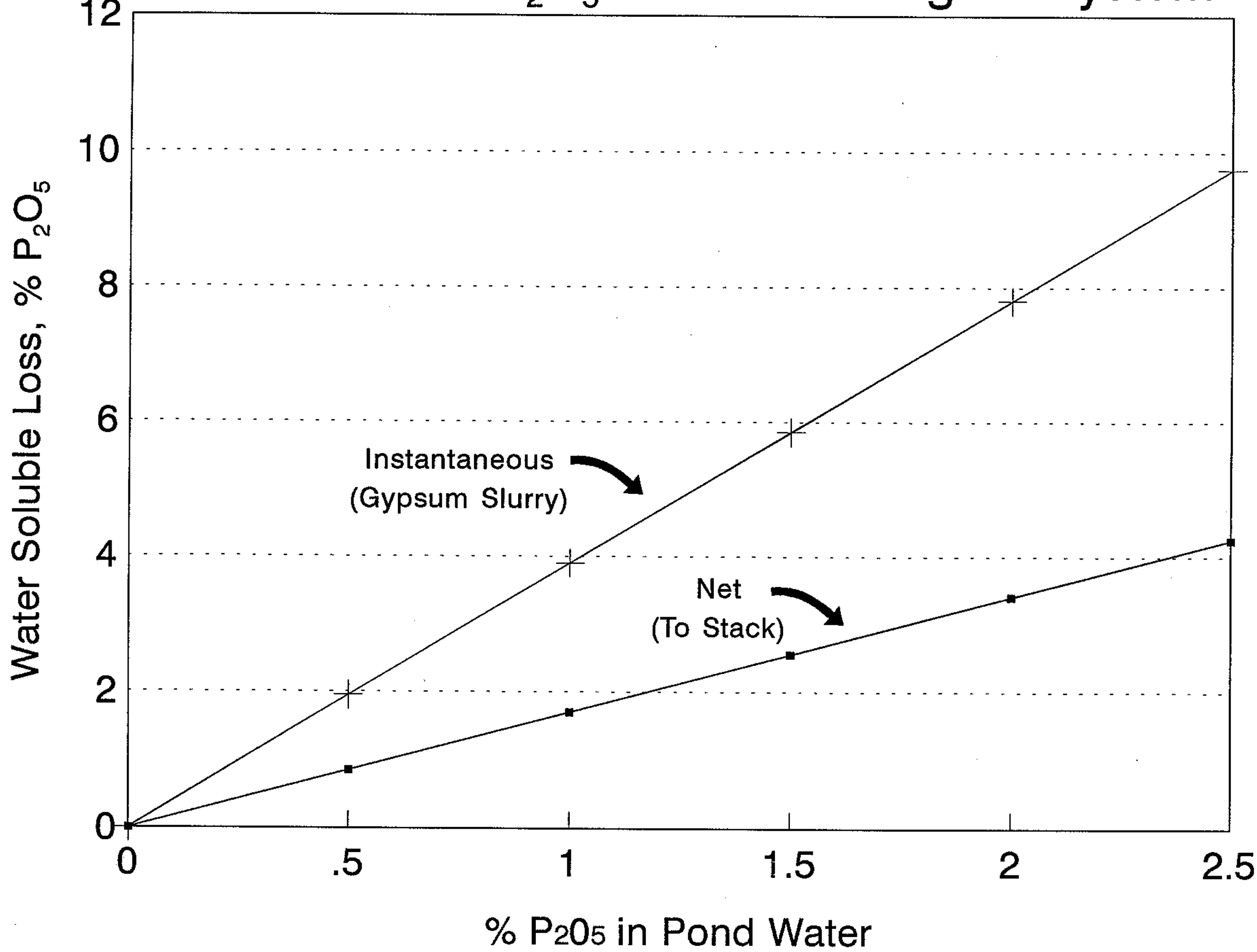


Figure V

P205 Losses and Costs - Comingled Process

Basis: 20,000 MTPD P_2O_5, 2% P_2O_5 Pond Water

$50 x 10^6/yr
680 MTPD P_2O_5

Gypsum Stack

$2x$10^6$/yr
28 MTPD P_2O_5 (30 year basis)

Pond

Basis: 2,000 MTPD P_2O_5, 2% P_2O_5 Pond Water

$5 x 10^6/yr
68 MTPD P_2O_5

Gypsum Stack

$0.2 x 10^6/yr
2.8 MTPD P_2O_5 (30 years basis)

Pond

DJ1773

Figure VI

Wet Process Phosphoric Acid Filtration

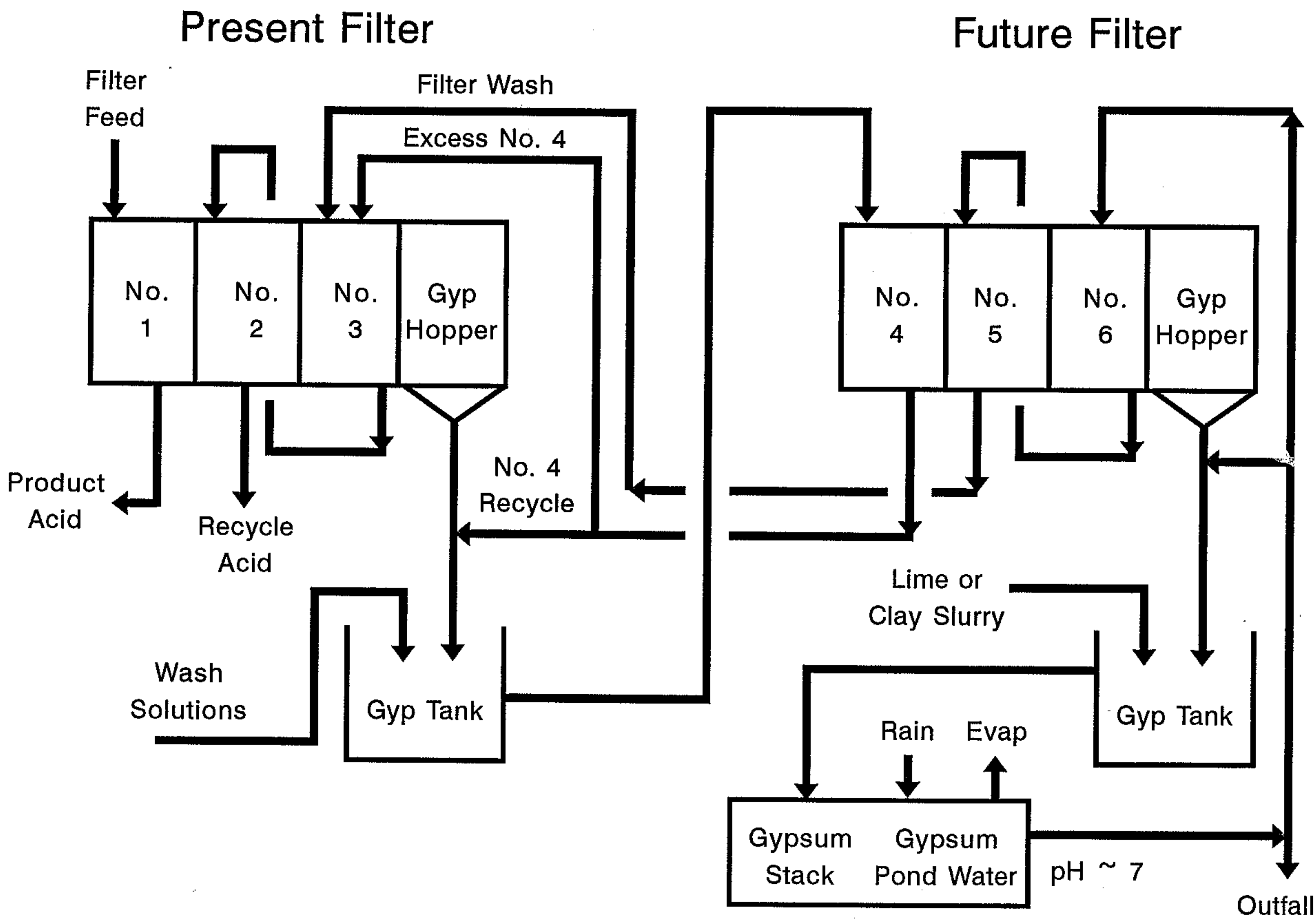


Figure VII
Proposed Non-Comingled Process
Retrofit Existing Operation

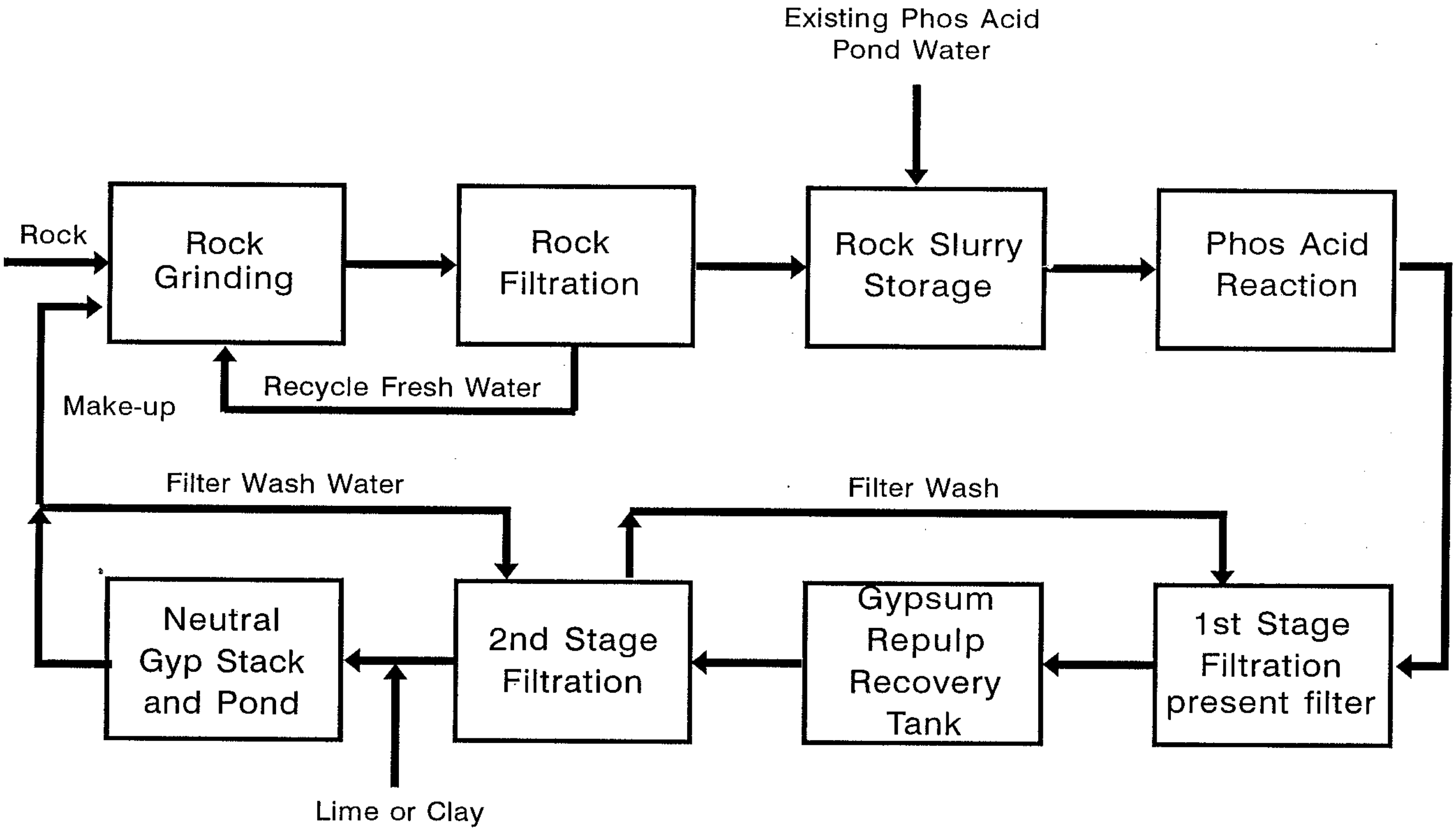
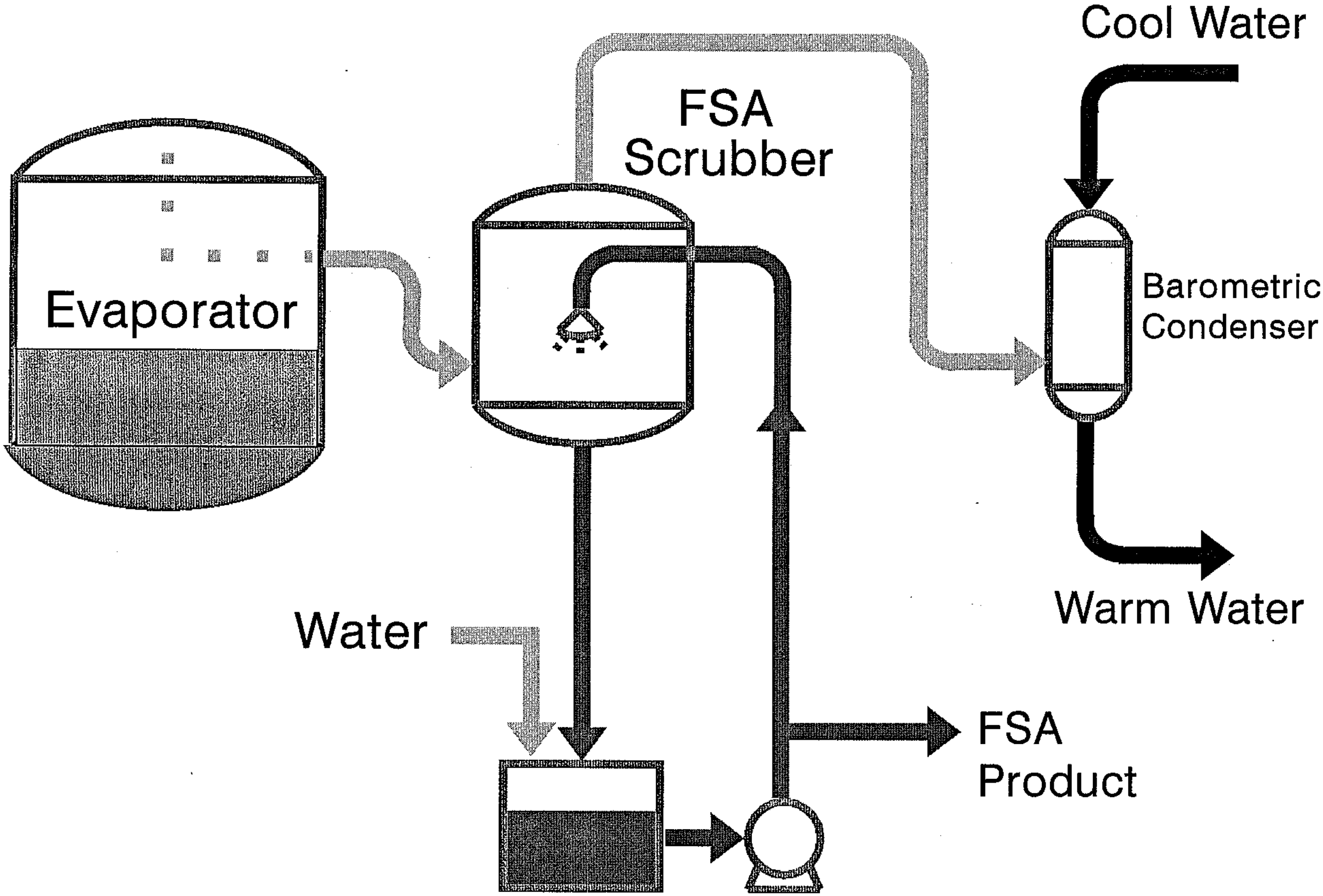


Figure VIII



Cool Water
FSA
Scrubber
Evaporator
Barometric
Condenser
Warm Water
Water
FSA
Product

Figure IX
2 Stage FSA Recovery

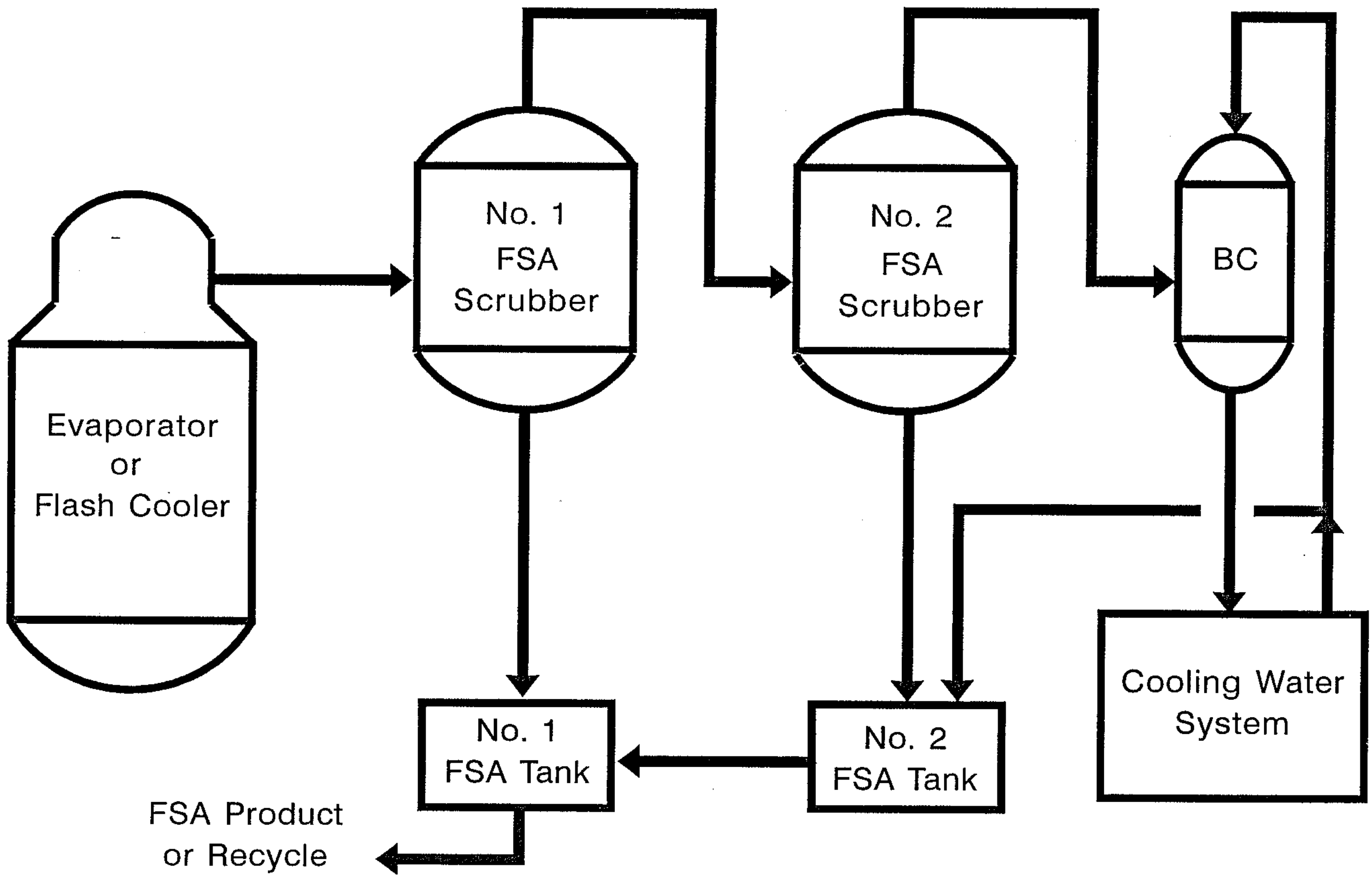


Figure X
New Non-Comingled Process

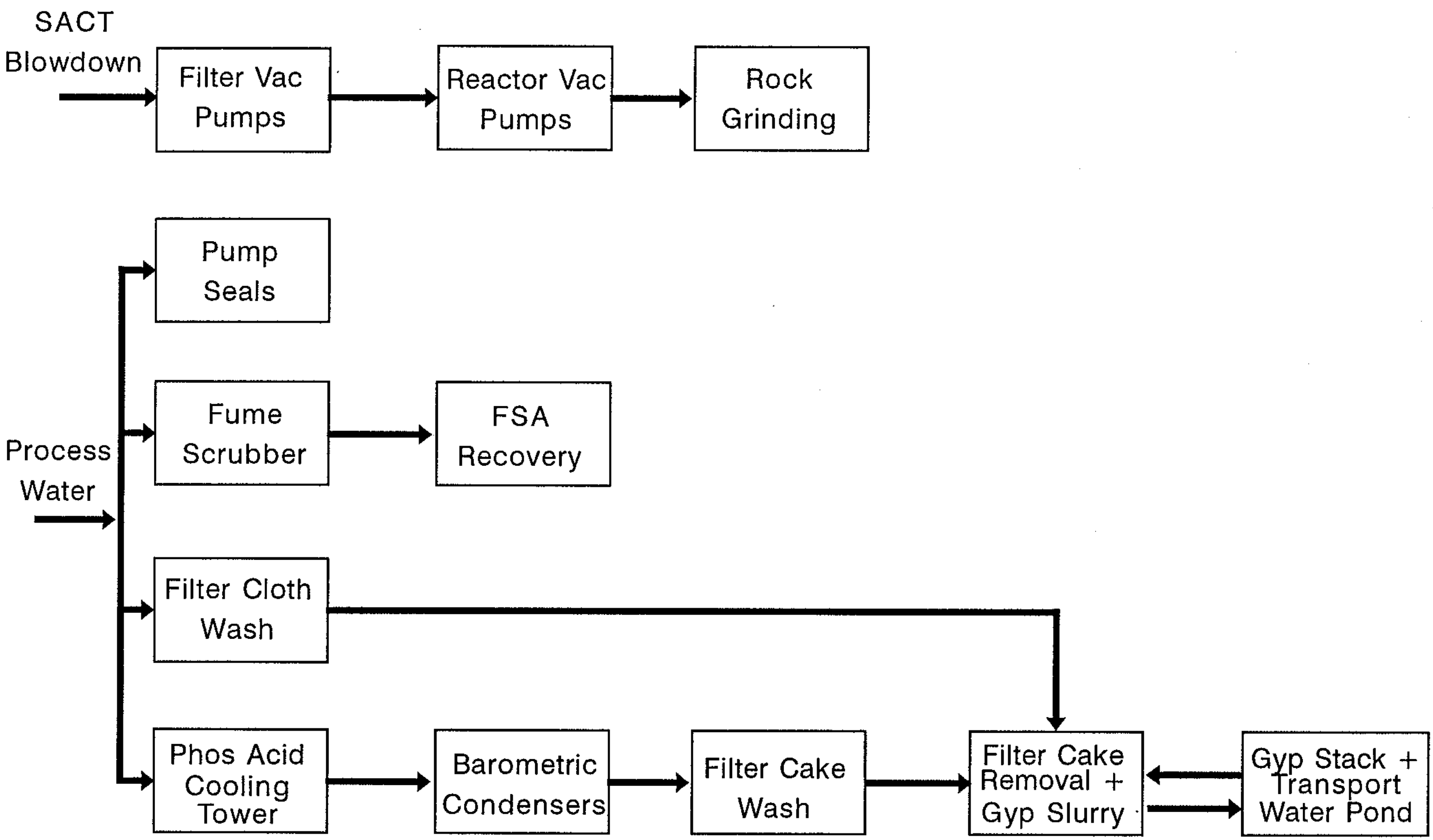


Figure XI

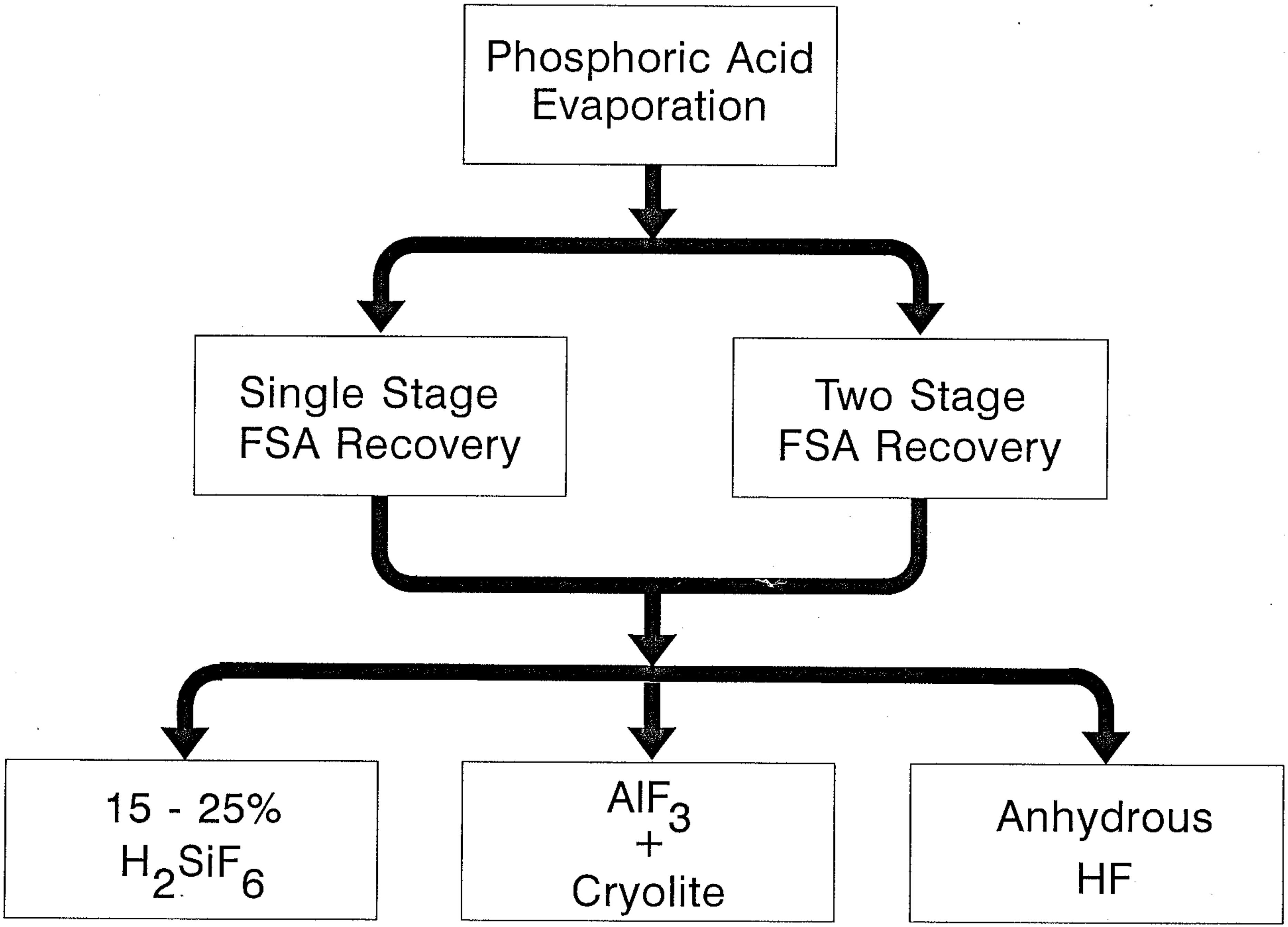

Phosphoric Acid
Evaporation
Single Stage
FSA Recovery
Two Stage
FSA Recovery
15 - 25%
H2SiF6
AlF3
+
Cryolite
Anhydrous
HF

Figure XII

Plant Water Management Alternatives

Description	Alt I	Alt II	Alt III	Alt IV
Cooling Pond	X	-	-	-
Cooling Tower w/ Direct Contact	-	X	X	-
Cooling Tower w/ Indirect Contact	-	-	-	X
FSA Scrubber - One Stage	X	X	-	X
FSA Scrubber - Two Stage	-	-	X	-
Gypsum Neutralization	X	X	X	X
PPM F - Gyp Pond	<50	<50	<50	<50
PPM F - Cooling Tower	-	>1500	<500	0