A Concept for Wet Rock Grinding Using Pond Water

THE LANG PROCESS
(Liquid Ammonia Neutralization & Grinding)

By

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A viable alternative to two stage liming is presently in the pilot plant development stage that will permit pond water, normally treated and discharged, to be used in a wet rock grinding system. In this process, pond water is reacted with partially ground phosphate rock, oversize slurry, in the recycle loop of a closed circuit wet grinding system. The pond water replaces all of the fresh water normally used as make-up, typically up to 100 gallons per ton of rock ground.

Reaction with phosphate rock partially neutralizes the pond water. Therefore, a significantly lower "base" consumption is required to titrate the slurry to a pH suitable for grinding. P_2O_5 and other pond water constituents are recovered in the plant while closing the water balance.

Excess pond water, which now costs $8-10 or more per 1000 gallons to treat for discharge, can return $5 per 1000 gallons when recycled to the attack system via wet rock grinding using the LANG Process.

Introduction

Wet rock grinding of phosphate rock has progressed from a concept to a proven commercial process in recent years.[1] With the advent of wet grinding technology, the search for a viable method to use pond water in the slurry began. Various mechanical solutions were studied including rubber mill liners and polymer covered grinding media. These measures proved either inadequate or beyond reasonable expense and were abandoned. Chemical modification of the slurry seemed to hold particular promise when, during a DMC brainstorming session, Warren Lang suggested using the phosphate rock's natural impurities as preneutralizing agents. Experiments showed promise and patent protection was sought.

Experiments consisted of reacting pond water with phosphate rock followed by neutralization of the slurry to a pH suitable for grinding. Lime proved to be uneconomical because long reaction time and excess lime was required. Ammonia and sodium hydroxide proved to be best suited for practical plant operation. The process scheme described in this paper is based on these experiments and provides both an economically viable and desirable alternative to the present methods used to deal with excess pond water.

Current Practice

Presently, excess acidic pond water must be treated to remove the contaminant phosphate, sulphate, and fluoride ions prior to discharge from company property. The standard method of treatment, two stage liming, involves the reaction, precipitation, and removal of these anionic contaminants as calcium compounds. Although different schemes and equipment are employed, the two stage liming processes generally produce similar results.

The liming systems produce a sludge containing excess lime or limestone and this sludge can either be stored or reprocessed to reclaim the P_2O_5 values. Large settlers, or settling ponds, are required to remove the solids from the treated water prior to discharge. A typical flowsheet is shown in Figure I.

Reprocessing the sludge for P_2O_5 values is usually uneconomical because the excesses of lime or limestone used require additional sulfuric acid. Also, excess CO_2, when limestone is used, can increase foaming problems in the attack system.

The treated water must be monitored to insure that contaminant levels are below those permitted by law and, also, permits to discharge this water are difficult to obtain. Obviously, at a cost of $8-10 per 1000 gallons, two stage liming of pond water is a losing proposition.

Reclaiming Pond Water

Since wet rock grinding is presently a method for water addition to the attack system, it is an excellent candidate for pond water conversion. Moreover, since pond water is presently added to the attack system via the filter, additional pond water should not present a problem since any additional ammonium and sodium phosphates formed are soluble in the product phosphoric acid.

The major problem with pond water use in wet grinding mills is acidity and, due to this acidity, increased corrosion. Therefore, the minimum pH acceptable for grinding has a significant impact on economics. Unfortunately, most studies treat this subject on a strictly intuitive basis. We are studying this as part of our pilot studies of the process.

The flowsheet in Figure II outlines the LANG Process for using pond water in closed circuit wet rock grinding system. This is the optimum configuration since the pond water is mixed with partially ground phosphate rock and the reaction proceeds rapidly.

In the LANG Process, pond water is mixed with recycle oversize in an agitated tank and held for a specified time. Typically, mixing pond water at pH 1.5 with recycle slurry in the proper proportions for wet rock grinding results in a pH of 2.5 to 3.0. The resulting slurry is then further reacted with a suitable "base" to attain an acceptable pH for grinding and then mixed with fresh feed at the mill inlet.

One advantage of the LANG Process is the recovery of one hundred percent of the P_2O_5 in the pond water used. Since pond water has an average P_2O_5 content of 1.0 to 1.5 percent, 83 to 125 pounds of P_2O_5 are reclaimed for every 1000 gallons; a cost benefit of $7-10.[2] Also, the initial reaction with phosphate rock significantly decreases the "base" required for neutralization of the slurry to an acceptable pH for grinding. After allowing for the cost of the "base" used, a profit of $5-8 per 1000 gallons is possible depending upon the pH acceptable in the mill.

Our laboratory analyses have also shown a significant reduction in soluble fluorides above a slurry pH of 3.5, which agrees well with published EPA data[2] and indicates that operation with pond water at a product slurry pH of 6 or lower may be possible. This data is supported by previous tests done to establish design requirements for two stage liming,[3] which show a minimum soluble fluoride concentration at pH 3.5 to 4.0 for single stage liming.

Laboratory Studies

At New Wales Chemicals, bench scale laboratory work was performed to evaluate process feasibility. Analyses were performed by the New Wales Quality Control and Special Projects Laboratories.

First, 500 ml samples of pond water were titrated with both a concentrated NH_4OH solution and 50% NaOH solution. The NH_4OH solution concentration, due to its volatility, was monitored by adding a 10 ml sample to 100 ml of a standardized dilute perchloric acid solution after each titration. The total was then back titrated with a 1 N solution of NaOH and compared to a control sample to obtain the concentration of the original NH_4OH solution.

Figure III is the titration curve for the pond water obtained at the New Wales facility for use in these tests. Figure IV tabulates the analysis of this pond water. The curves are typical titration curves obtained from the neutralization of pond water and agree well with those published by EPA.[2] These curves provide a basis for comparing a process against a standard neutralization process using similar "bases" or a liming process using a stoichiometric quantity of lime. The pond water used in the laboratory tests required 85 lbs of NH_3 per 1000 gallons of pond water (0.6 g mol/liter) for titration to pH 7. Similarly, 200 lbs of NaOH were required per 1000 gallons of pond water.

Samples of 68 BPL dry ground phosphate rock, wet unground phosphate rock, and ground rock slurry were obtained. The ground rock slurry was wet screened and drained then recombined to approximate the cyclone underflow size distribution: 25% + 35 mesh, 20% - 200 mesh, and 55% - 35/+200 mesh. Each rock mixture was then drained to approximately 12% moisture. A sample of each mixture was then mixed with enough pond water to make a 71% solids slurry. The pH of each of the resulting slurries was measured. Wet unground rock produced the lowest slurry pH, 2.3; wet ground recycle slurry, 3.0; and dry ground rock, the highest pH, 3.2. Using the pond water titration curve, we determined that the "base" required would be decreased by as much as 30 lbs of NH_3 (70.6 lbs of NaOH) per 1000 gallons of pond water processed with recycle slurry. Figure V compares the expected slurry titration curve with the pond water titration curve. A reduction of 35 percent in the amount of "base" used is expected when titrating to pH 7 and greater savings are obtained for lower pH slurries. For example, sixty-five percent of the base required would be saved by grinding a pH 6 slurry as opposed to pH 7.

Since little data is available relating slurry pH to ball and liner wear, these tests are part of the pilot program now underway. Mill vendors have indicated that pH 5 grinding has been practiced but actual data is inconclusive for phosphate rock with pond water.

Figure VI shows both the expected and actual results of the aforementioned experiments. Slurry condition B represents the expected results; a left shift of the original pond water neutralization curve. Slurry condition A of Figure VI represents the actual results of the test. The condition A curve indicates a lower ammonia saving than expected. Our investigation was continued and a method of operation developed whereby the curve or slurry condition B was maintained. This method of operation results in significant additional reduction savings in "base" requirement.

It has been found that, by controlling the reaction parameters of phosphate rock with the pond water, the chemical species that cause condition A on Figure VI can be suppressed. Therefore, the maximum "base" savings can be obtained and the slurry titration is as shown in the condition B curve.

Several additional effects which were observed during the laboratory tests which deserve mention are as follows:

1. As the slurry approaches the isoelectric point at pH 7, the viscosity increases, therefore operating at a pH of 6 or below may permit production at a higher percent solids slurry. The viscosity of the rock slurry at 71% solids produced in this manner is approximately 800 cp to 1000 cp at pH 6, as opposed to 2000-2500 cp at pH 7. Various advantages occur when a lower viscosity slurry is produced including possible decreases in grinding horsepower, improvement in oversize segregation for closed loop systems and lower pumping costs in addition to higher slurry concentrations.

2. When ammonia is used for neutralization, a 0.1 to 0.2% ammonia content in the 30% P_2O_5 phosphoric acid produced will occur. The final concentration depends upon the amount of ammonia required at the pH used for grinding. This ammonia will be recovered when the acid is used to make ammonium phosphates. Therefore, this portion of the ammonia used would be deducted from the operating cost of the LANG Process.

3. Effects due to ammonia in the attack tank should be no different than the effect due to ammonia in the pond water used as filter wash.[4] Again, little scientific evidence is available. New Wales will perform phosphoric acid pilot plant tests on rock slurry from our tests as part of the overall pilot program.

4. Much hearsay exists concerning the effects of ammonia on GTSP production. The ammonia concentration in GTSP slurry, resulting from this process, would range from 940-2000 ppm. Alternatively, NaOH may be used if this level of ammonia content would be deleterious.

Pilot Plant

Based on the bench scale data, a 1.0 STPH wet rock grinding pilot plant was built and is presently operating at New Wales Chemicals, Mulberry, Florida. The pilot plant uses a 3' x 5' ball mill to test the process on a continuous basis in a closed circuit wet grinding system. Figure VII is a schematic diagram of the pilot plant. Both caustic and ammonia are being tested in the system. Test work is scheduled for completion by July, 1981.

The pilot plant program will determine the optimum operating parameters for a closed circuit ball mill operation. Controlled experiments have been designed to produce data which will enable the operator to minimize caustic or ammonia requirements. Additional experiments are designed to detect corrosion effects and determine the minimum practical slurry pH. The pilot plant will also provide adequate amounts of slurry for phosphoric acid pilot plant use.

Economics

Any detailed economic analysis is dependent upon the pH and level of contamination of each individual pond. These are different for each plant. The economics of the LANG Process must be determined on a case-by-case basis.

Some factors to be considered in the economic evaluation are:

1. The value of the P_2O_5 recovered from the pond water.
2. The cost of liming this pond water for discharge, if used.
3. The fraction of phosphoric acid used to make ammonium phosphates.
4. Possible defoamer savings since part of the CO_2 normally released in the attack tank is now removed in the grinding circuit.
5. Added horsepower. This system requires an additional 2¢/1000 gallons of pond water.
6. Additional equipment. About 25-50¢/1000 gallons of pond water.
7. Improvements in overall plant water balance.

Typically, a savings of $10-16/1000 gallons of pond water used in the LANG Process is estimated, when compared to two stage liming.

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LIST OF FIGURES

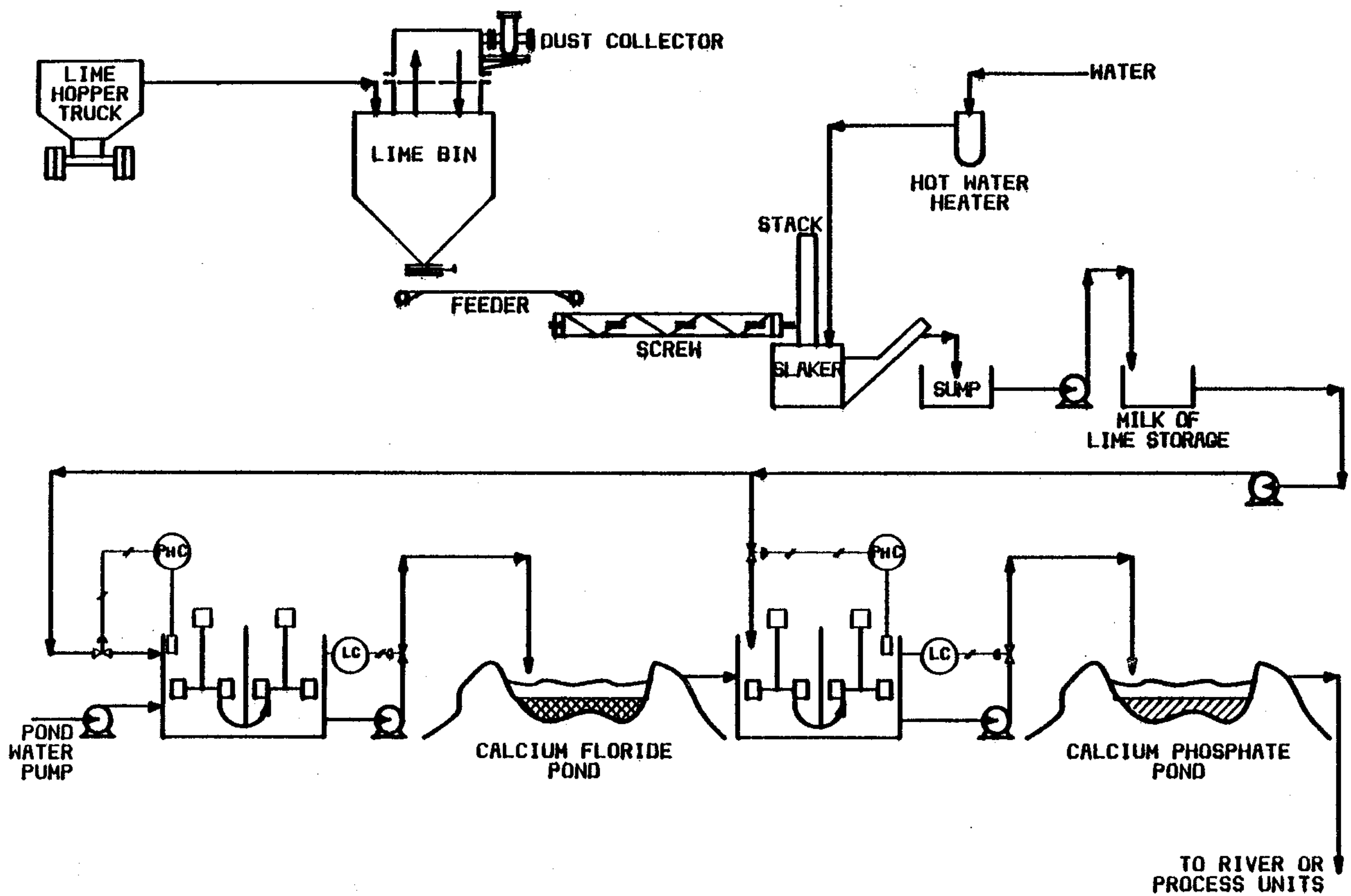
LIME HOPPER TRUCK
DUST COLLECTOR
LIME BIN
FEEDER
SCREW
STACK
SLAKER
WATER
HOT WATER HEATER
SUMP
MILK OF LIME STORAGE
PHC
LC
PHC
LC
POND WATER PUMP
CALCIUM FLORIDE POND
CALCIUM PHOSPHATE POND
TO RIVER OR PROCESS UNITS

FIGURE I

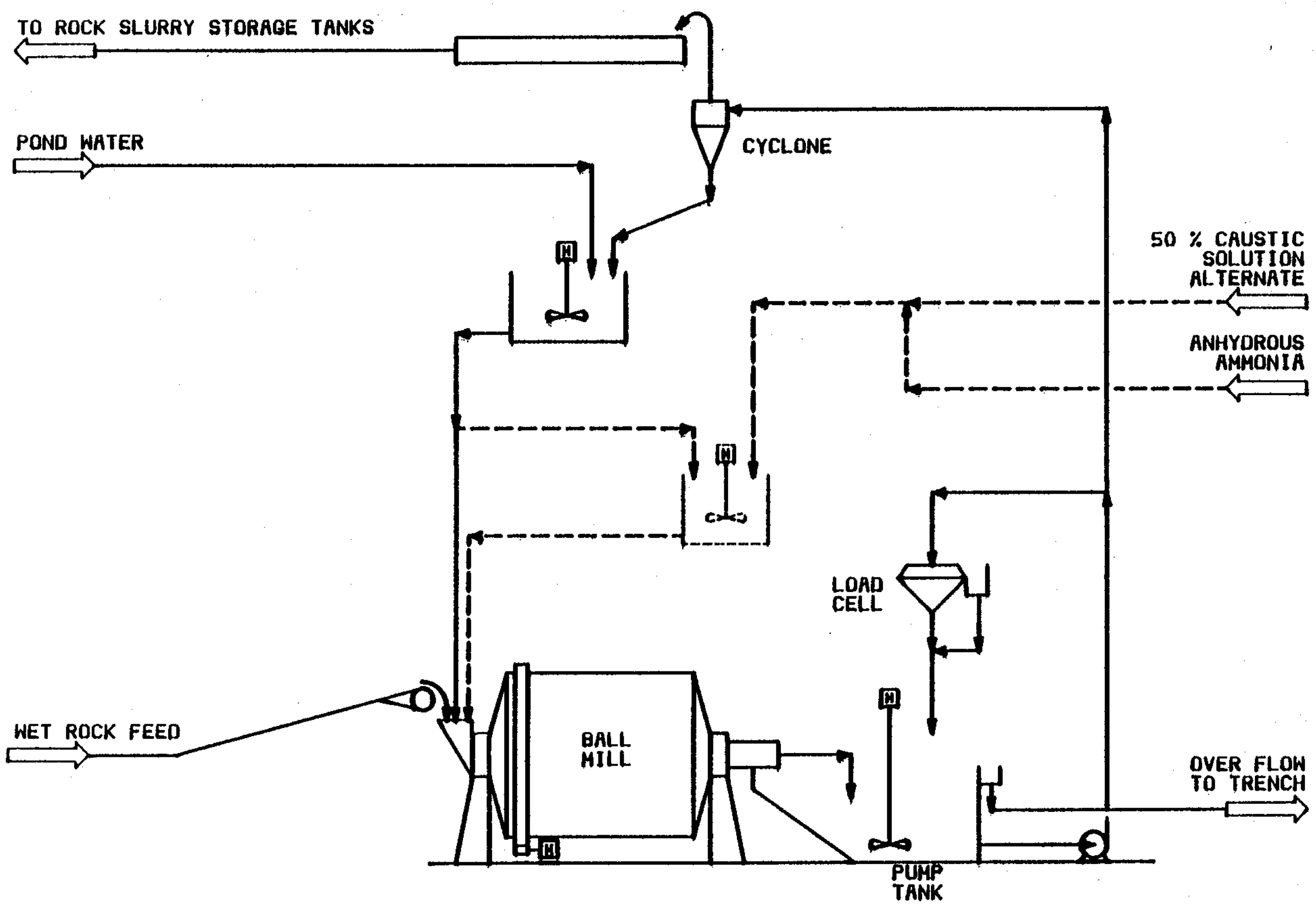
TO ROCK SLURRY STORAGE TANKS
POND WATER
CYCLONE
50 % CAUSTIC SOLUTION ALTERNATE
ANHYDROUS AMMONIA
LOAD CELL
WET ROCK FEED
BALL MILL
OVER FLOW TO TRENCH
PUMP TANK

FIGURE II

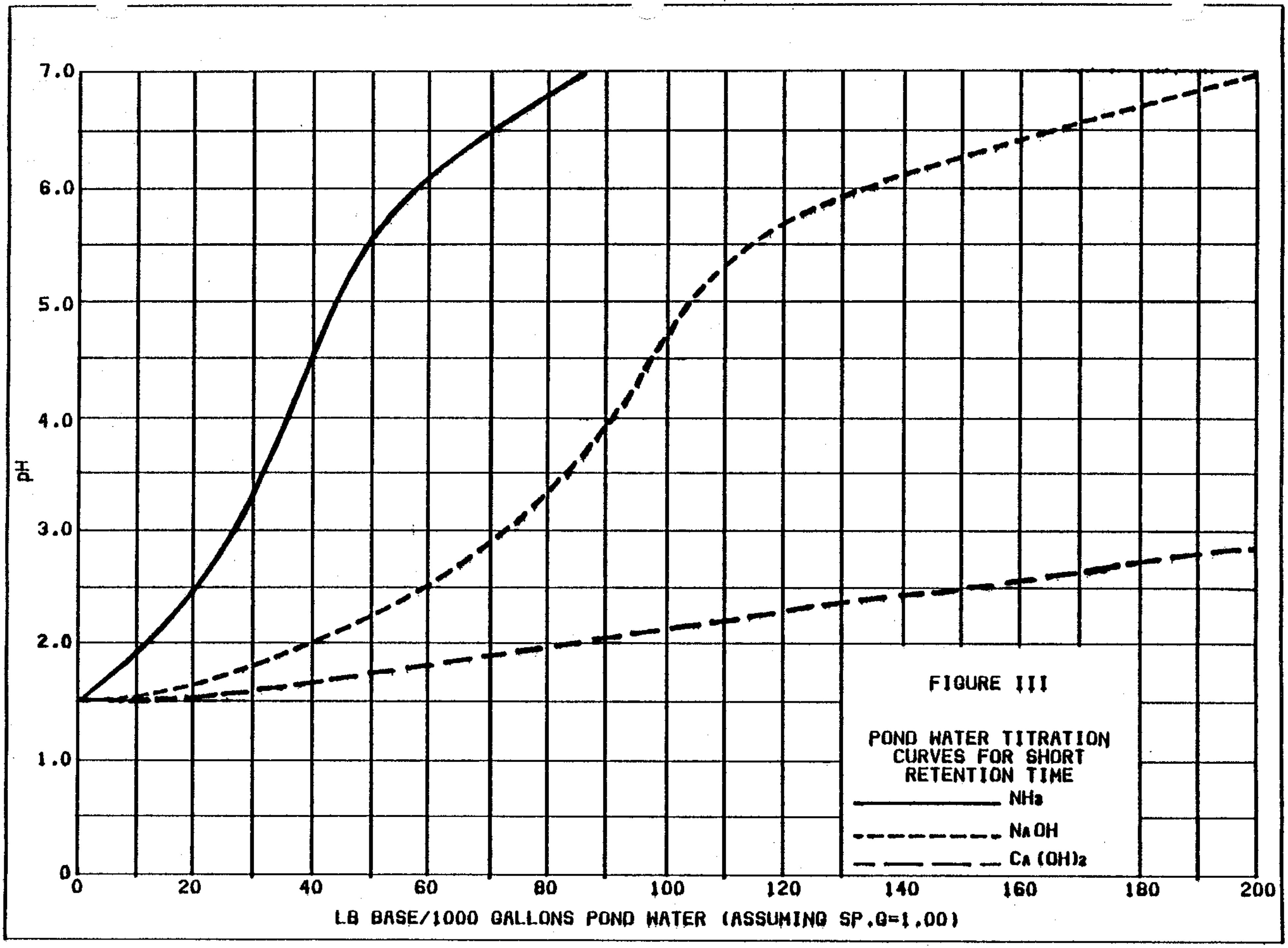
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
pH
0
20
40
60
80
100
120
140
160
180
200
LB BASE/1000 GALLONS POND WATER (ASSUMING SP.G=1.00)
FIGURE III
POND WATER TITRATION
CURVES FOR SHORT
RETENTION TIME
NH3
NaOH
Ca (OH)2

FIGURE IV
POND WATER ANALYSIS

SPECIE	CONCENTRATION (WT PERCENT)
P_2O_5	1.28
F	1.08
SiO_2	0.56
NH_3	.0813
CaO	0.22
SO_3	0.47

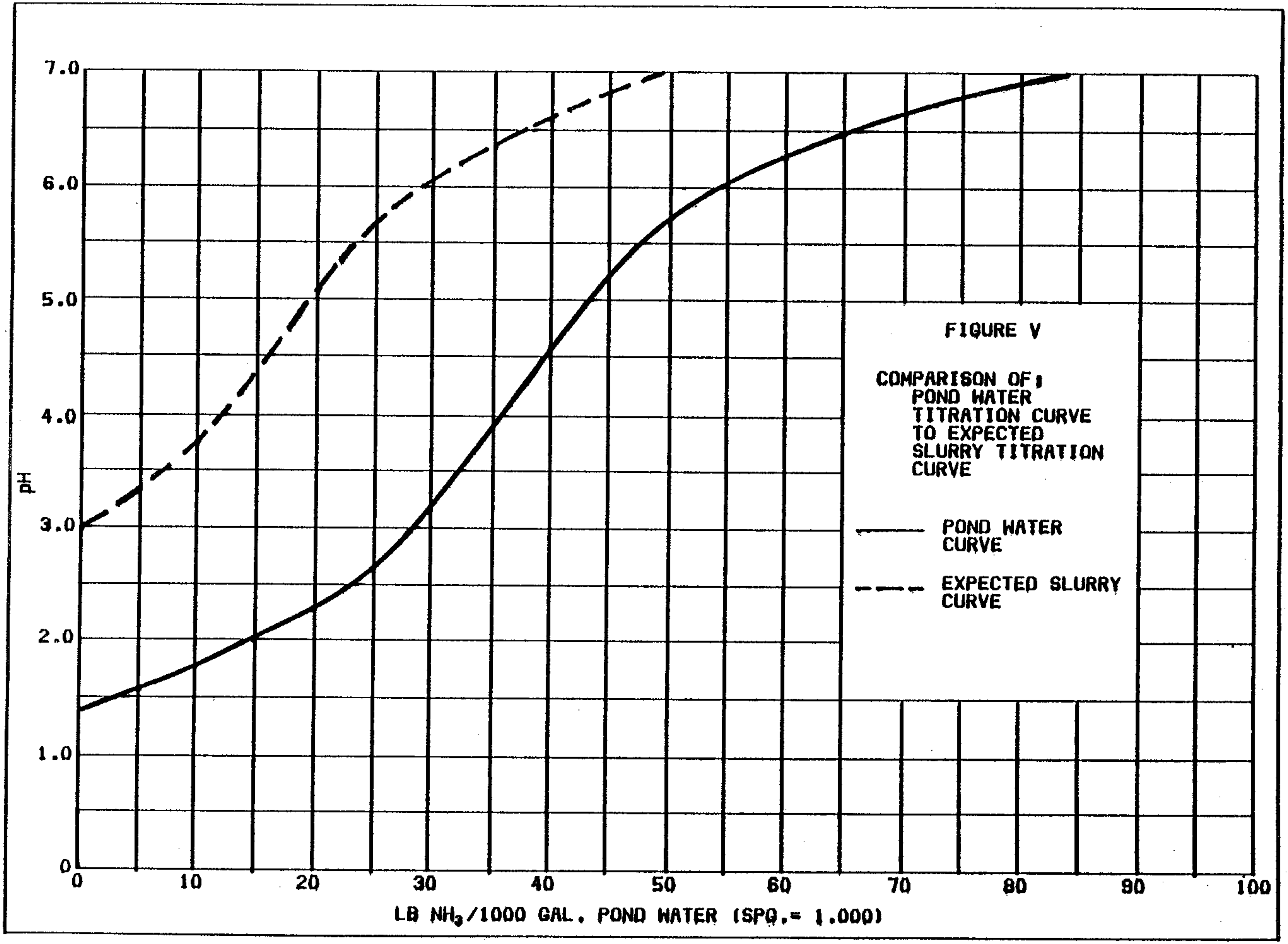
FIGURE V
COMPARISON OF:
POND WATER
TITRATION CURVE
TO EXPECTED
SLURRY TITRATION
CURVE
POND WATER CURVE
EXPECTED SLURRY CURVE
pH
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
10
20
30
40
50
60
70
80
90
100
LB NH_3/1000 GAL. POND WATER (SPG.= 1.000)

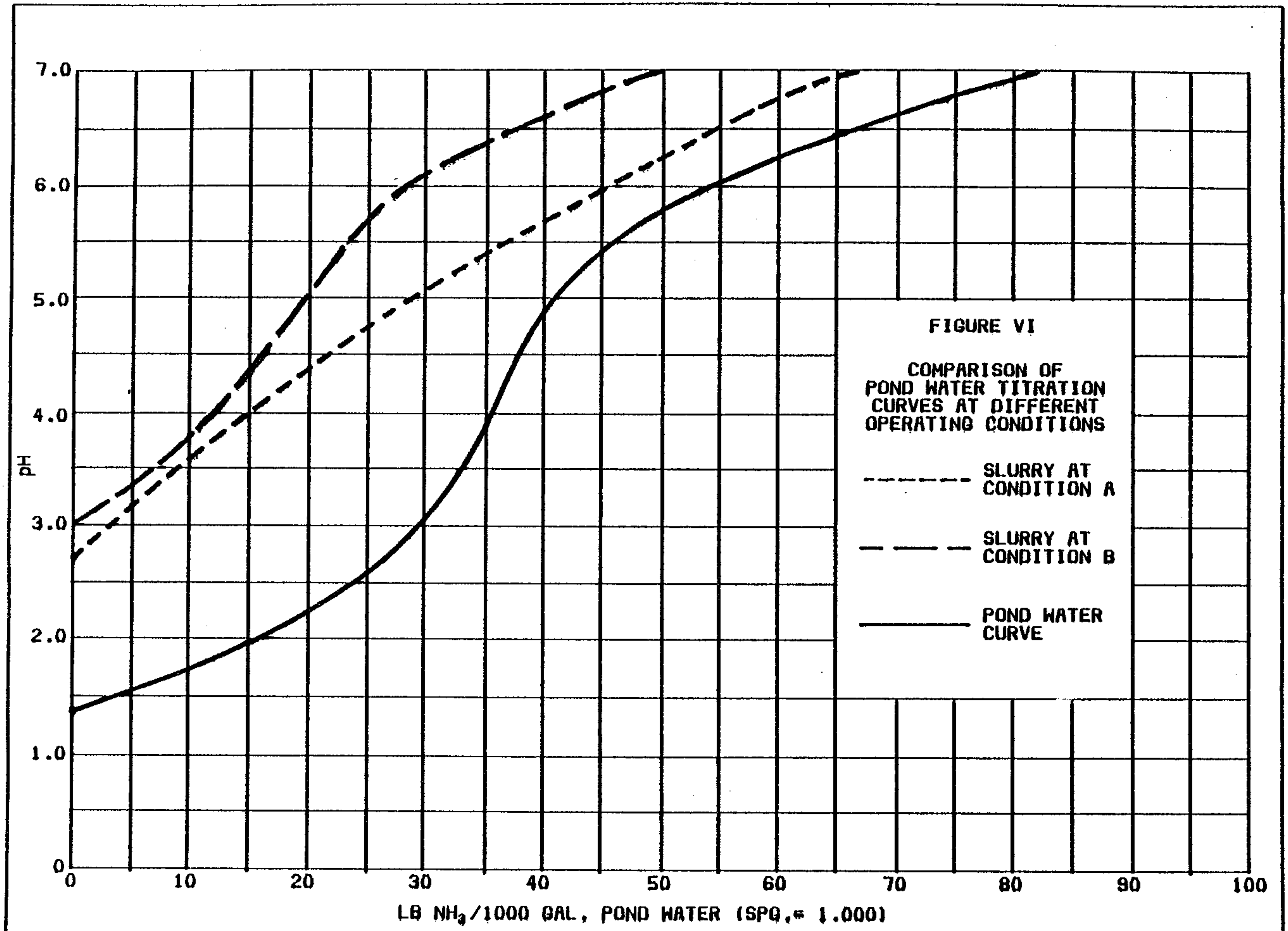
FIGURE VI
COMPARISON OF POND WATER TITRATION CURVES AT DIFFERENT OPERATING CONDITIONS
SLURRY AT CONDITION A
SLURRY AT CONDITION B
POND WATER CURVE
pH
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
10
20
30
40
50
60
70
80
90
100
LB NH_3/1000 GAL, POND WATER (SPG.= 1.000)

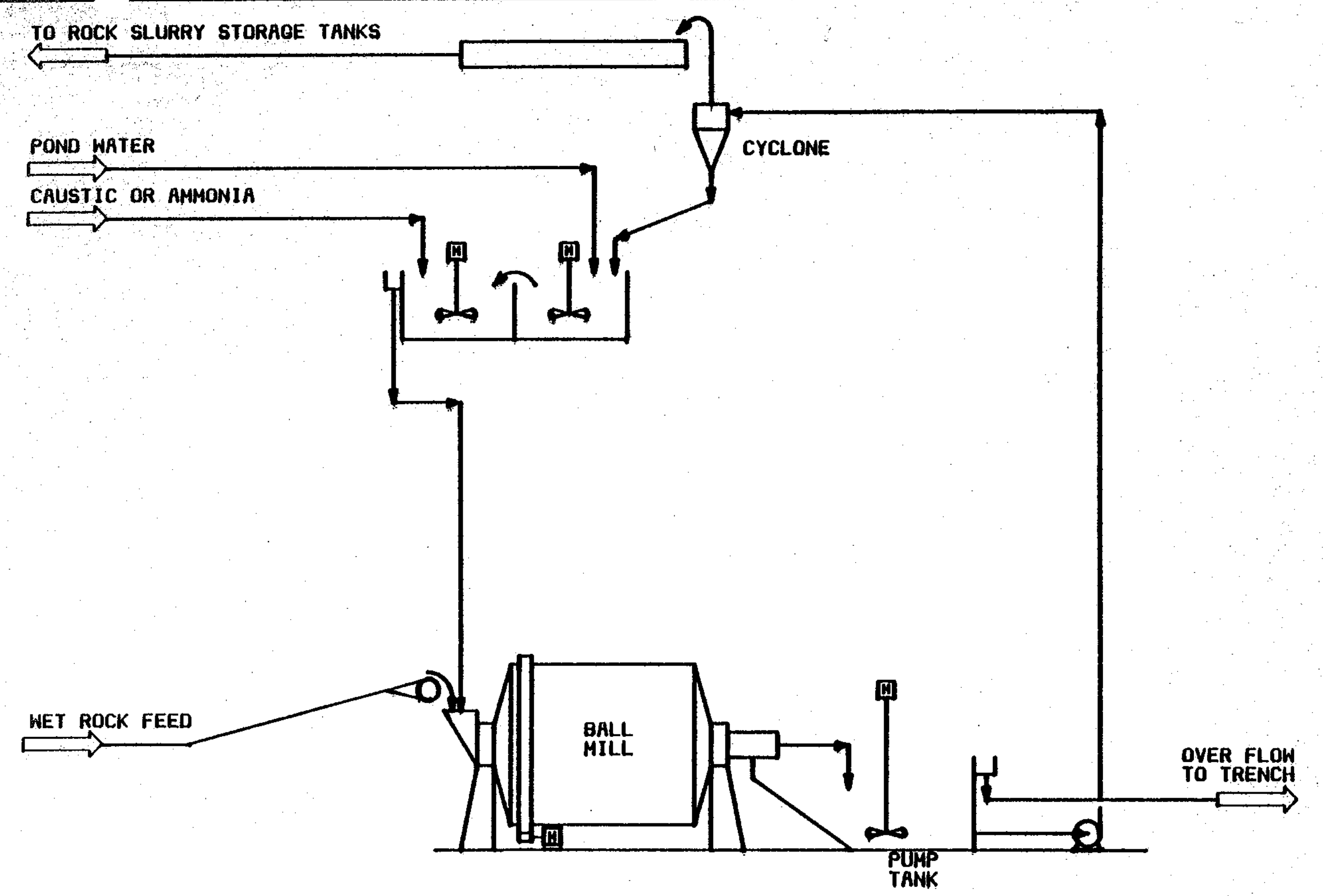
TO ROCK SLURRY STORAGE TANKS
POND WATER
CAUSTIC OR AMMONIA
CYCLONE
WET ROCK FEED
BALL MILL
PUMP TANK
OVER FLOW TO TRENCH

FIGURE VII