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PECO PROCESS FOR PRODUCING PHOSPHORIC ACID FROM FLOTATION FEED

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DISCLAIMER

PERSPECTIVE

For a great many years the potential advantages of the mono-calcium process for producing phosphoric acid have been debated. In this process phosphate rock is dissolved by phosphoric acid to form a mono-calcium phosphate solution that is reacted with sulfuric acid in a subsequent processing step to generate phosphoric acid and phosphogypsum.

It has been claimed that the mono-calcium process will produce better filtering phosphogypsum resulting in higher yields and production rates. A second claimed benefit is that less of the iron, aluminum and magnesium in the phosphate rock will be solubilized by the phosphoric acid and if the residue is removed before the sulfuric acid is added, the resulting phosphoric acid product will be purer and it will be easier to make guaranteed analysis (18-46-0) DAP (diammonium phosphate). It is also thought that less of the fluorine in the phosphate rock would appear in the phosphoric acid and/or be evolved. It has been proposed that the phosphate rock fluorine would react with the phosphoric acid and then immediately react with the calcium in solution to form insoluble calcium fluoride. Some test work has indicated that with a step-wise addition of sulfuric acid to the mono-calcium phosphate solution, the first small portion of the phosphogypsum formed would contain all of the radium from the phosphate rock and the major portion of the phosphogypsum would be radium free. Accomplishing any of these claims would also reduce the sulfuric acid consumed per ton of phosphoric acid produced.

It is apparent that the realization of any or all of these claims could significantly impact the phosphate industry from both an environmental and economic stand point. It could even positively affect mining practices by allowing the use of higher impurity phosphate rock that is not now not mined or is discarded after mining.

While there were some positive aspects of this research the results were not sufficiently encouraging to expect that there will be any interest in pursuing this processing scheme on a commercial scale.

PECO PROCESS FOR PRODUCING PHOSPHORIC ACID FROM FLOTATION FEED

Table of Contents

1.0 EXECUTIVE SUMMARY

The PECO process uses phosphoric acid to leach the phosphate from the ore, to form a monocalcium phosphate (MCP) solution which is then reacted with sulfuric acid to form phosphoric acid and gypsum. An initial sludge is removed from the MCP solution consisting of silica, clays, and an initial gypsum precipitate. The MCP solution is then reacted with sulfuric acid to produce phosphoric acid and the final precipitate of gypsum. Part of the phosphoric acid is recycled to dissolve more phosphate from the phosphate ore.

Radium contained in the phosphate ore is removed with the gypsum from the phosphoric acid process and is the source of the radiation levels of the gypsum. Since calcium has an affinity for radium, tests were conducted to determine if the major amount of radium could be removed by the initial precipitate of gypsum in the sludge, thus allowing the production of the majority of the gypsum at low, acceptable levels of radium. These tests did not confirm this hypothesis. The radium did track the calcium in the system, however it tracked not only the calcium in the gypsum but it also tracked the calcium in the monocalcium phosphate. It was therefore not possible to remove most of the radium in the initial precipitate.

The PECO process can utilize flotation feed as a source of phosphate for phosphoric acid. This would eliminate the need for a flotation operation and its capital and operating costs. In addition to saving $24.00 per ton P2O5 it would also extend the reserves of Florida by 20%, reduce the area required for slime disposal and decrease the use of fresh water by 20%. These tests showed while these objectives could be achieved, the phosphate content of the flotation feed was so low (in some cases as low as 7.4% BPL) that 3.76 times as many tons of feed would have to be transported to the phosphoric acid plant to produce the same amount of phosphate product. The transportation costs may be larger than the benefits. When this large amount of material is fed to the phosphate acid plant as a wet feed, the amount of water contained with this feed would significantly reduce the wash water on the gypsum filter resulting in unacceptable low phosphate recoveries.

The PECO process did indicate a reduction of about 30% in the iron content of the phosphoric acid.

2.0 INTRODUCTION

Phosphate mining activities in the Florida Bone Valley generally are leaving the prime area of rich deposits and moving in a more southerly direction into areas containing leaner deposits. Several years ago a feed to the beneficiation plant of 25% BPL was not uncommon, whereas current feeds to the beneficiation plant range from 15% to 18% BPL and in some cases as low as 7% Bone Phosphate of Lime (BPL). The sand tailings from the flotation plant has a 3% to 4% BPL content and it can be seen that as the feed BPL drops to the area of 7 or 8 BPL this does not afford much difference for good recovery of phosphatic material from the deposit. In some cases the amount of phosphate contained in the tailings from the flotation plant is equal to about 2/3 of the phosphate contained in the product from the beneficiation plant. As the feed becomes more lean the percent of material contained in the tailings from the beneficiation plant becomes more significant. Under current operating conditions approximately 60% of the total P2O5 in a given phosphate deposit is recovered as product. The remaining material is lost with the slimes as well as the tailings from the beneficiation plant. As the BPL of the matrix feed decreases, this recovery will also decrease.

The PECO process can use flotation feed as a raw material supply to its phosphoric acid plant. This allows for the recovery of the P2O5 normally lost in the tailings from the beneficiation plant. With such a system, a recovery of 80% of the P205 contained in the phosphate reserve is realistic. As compared to the 60% from the current beneficiation process.

A 40% cost reduction in the supply of the phosphate material to the PECO phosphoric acid plant can be realized by the complete elimination of the capitol and operating costs of the flotation system. This savings will be offset by the cost of transporting the increased tonnage of material required to the phosphoric acid plant.

This improved recovery will result in an extension of the life of the phosphate reserve in the state of Florida by approximately 25%. The amount of fresh water consumed in the beneficiation process will also be decreased by 25%, as will the area required for slimes disposal.

The PECO process produces gypsum from two different points in its phosphoric acid process. Indications are that the first gypsum precipitated from the system will contain virtually all of the radioactivity contained in the phosphate matrix. This allows for the removal of most of the radioactivity from the system by a small amount of gypsum and allowing the greater amount of gypsum to be produced at very low radioactivity levels. This lower radioactive gypsum can then be used in the construction of roads, agriculture and other types of operations. Therefore the level of radioactivity of the raw material and products were studied.

It is with these possibilities in mind that this investigation of the PECO process was performed.

3.0 PHOSPHATE DEPOSIT CHARACTERISTICS

The phosphate deposit in the state of Florida has several components which are important to this study. Which are defined as follows:

Matrix:

The term matrix, as used in this report means the ore as mined from the ground and includes all of the components. It is distinguished from overburden, which is normally discarded while the matrix is the actual ore body.

Slimes:

The term slimes as used in the phosphate industry is normally composed of clays, and other particles the size of which is less than one micron. However in the beneficiation process anything that is smaller than 100 to 200 mesh is normally considered slimes and currently is discarded. It is important that the slimes be removed from the flotation feed since slimes generally consume large amounts of reagent and makes the flotation process inefficient.

Pebble:

The pebble component of the phosphate ore is generally dictated by size and normally runs smaller than 3/8 " (10 mm) to greater than 16 mesh (1.0 mm). The pebble is separated from the other components of the matrix by screens usually of a 16 mesh size.

Flotation Feed:

After the matrix has been deslimed and the pebble has been separated from it , the remaining portion is termed flotation feed. The size of the feed is normally smaller then 16 mesh and greater then 150 mesh. In normal processing it is separated into a coarse and fine flotation feed, the separation occurring at approximately 28 to 35 mesh (500 microns). The concentration of phosphate in the flotation feed is currently about 13% to 18% BPL.

Flotation Product:

The flotation feed is directed toward flotation machines, wherein the sand is separated from the phosphate product. The sand is normally discarded and the flotation product is sent to the phosphate complex for further processing.

Flotation Tails:

The sand tails from the flotation machines are normally discarded to waste.

3.1 DISCUSSION

The matrix is mined by drag lines and the material deposited into a sump where it is disintegrated by high pressure water jets and a grizzly is used to remove large objects from the matrix such as tree stumps and other waste material. It is slurred and then pumped to the benefication plant where the plus 3/8" material is removed by trommels from the matrix feed and ground to less than 3/8" in size for further processing in the washer section of the beneficiation plant. In the washer section the pebble is removed by screens and trommels and the separation is made at about 16 mesh. The BPL of the pebble product is usually quite high, in the range of 64% to 66% BPL. It is a clean product and would be ground before it is used in a normal phosphoric acid plant. The ratio of concentrate product to pebble product usually runs about 1.1 to 1.2 tons of concentrate to a ton of pebble product.

After the pebble product has been separated, the under flow from this operation is pumped through liquid hydroclones where the slimes are removed from the material to be fed to the flotation plant. The hydroclones will separate the minus 150 mesh material from this stream and the slimes are normally disposed of to a settling area. The slimes content of the matrix is approximately 10% to 20%, contains about 7% BPL and this constitutes a rather significant loss of phosphate from the beneficiation operation. After the slimes have been removed, the flotation feed is then separated at about 28 mesh into a coarse and fine flotation feed material. It is this material when blended with an appropriate amount of pebble product, that forms a feed to the PECO phosphoric acid process. Normally flotation feed will contain approximately 13% to 15% BPL, however the material used in this investigation was much lower and ran as low as 7.4% BPL (3.4%P2O5) in the flotation feed.

Flotation Tails

This describes the material which has been removed from the flotation feed to form the flotation product. The flotation tails normally contain 4% BPL and is considered to be a loss of phosphate from the beneficiation process. The main component in flotation tails is primarily silica, which is inert to the phosphoric acid reaction system.

Flotation Product

The flotation product from the flotation machine is, as the name implies, a phosphate product and usually contains anywhere from 64% to 68% BPL. The product comes from coarse and fine flotation circuits and these are blended prior to transportation to the phosphate complex.

3.2 CONVENTIONAL BENEFICIATION PROCESS

Figure “Flot #1” shows a material balance for a current phosphate beneficiation plant. All the tonnage’s of P2O5 and BPL figures are obtained from an actual operation with the exception of those reported for matrix and slimes. The values for matrix and slimes are assumed to be 15% BPL matrix feed and 7.5% BPL slimes discharged. Using these concentrations the tons of both matrix and slimes are calculated based on the total tons of flotation feed, pebble product, flotation product, and flotation tails. The total production from this plant was 197,991 tons of P2O5 in a modern beneficiation plant operating from reserves located toward the southern part of the bone valley.

The operating plant is a modern, well designed and well operated production unit. Based on the 15% BPL matrix feed, the overall recovery of P2O5 from this unit is approximately 69%. The actual recovery of the flotation plant is 73% of the P2O5 fed to the flotation system.

This operation is helped considerably by the fact that 29% of the total P2O5 fed to the system is contained in the pebble product which requires no beneficiation what-so-ever. Most mining operations will have varying degrees of pebble in the matrix feed and some may get as low 10% pebble in the matrix fed to the beneficiation plant, This of course will adversely affect the overall recovery since most of the product will have to go through the flotation plant and consequently the amount of phosphate in the tails will take away from the production of the unit.

When the pebble and the product from the flotation plant are mixed the mixture will contain approximately 29% P2O5 or 66% BPL. The feed to the flotation unit contains 12.56% BPL which is only 5.74% P2O5. The BPL feed to the flotation unit is somewhat lower than what was experienced 10 to 15 years ago, however this is to be expected as the mining operation moves further south in the bone valley to leaner ore deposits.

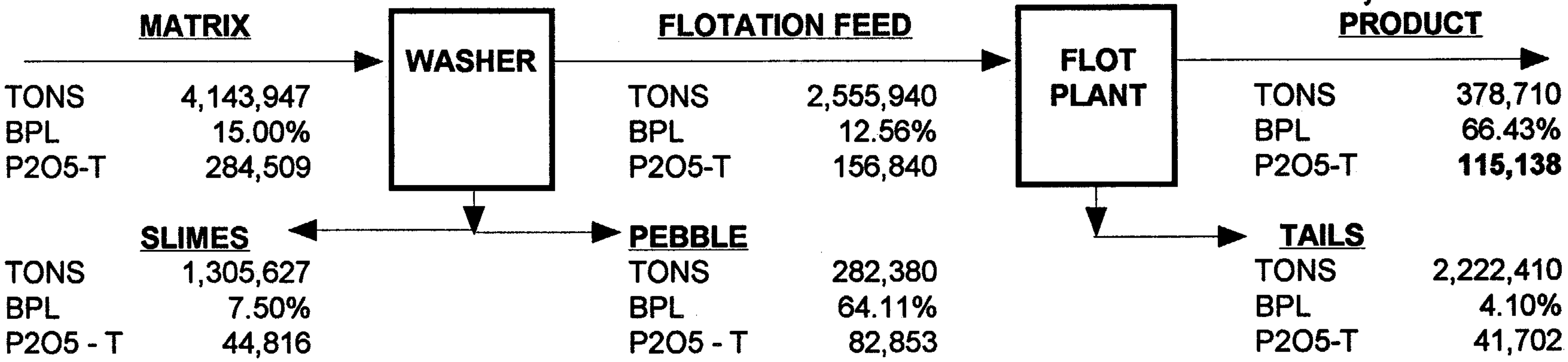
3.3 PECO PROCESS FEED

The lower half of Figure “Flot #1” shows what the beneficiation unit would look like if the material were being prepared as a source of phosphate feed to the PECO Process. The same total, 197,991 tons P2O5, is produced in both cases. In the beneficiation plant to be used for the PECO Process, the flotation plant has been totally eliminated, which eliminates the capital and operating costs for that particular unit. The amount of matrix fed to the PECO unit is reduced from 4,143,947 tons to 3,279,695 tons or only 79% of the feed required for the conventional plant to produce the same amount of the P2O5. This of course will result in extending the life of the phosphate reserves in Florida. The overall recovery in PECO benenfication process is 87% of the P2O5 fed to it in the matrix as to compared to the 73% of the conventional plant.

PECO vs 4 CORNERS BENEFICIATION COMPARISON

CURRENT PROCESS 4.10% BPL TAIL

197,991 TONS P2O5
Recovery 69.59%



MATRIX	
TONS	4,143,947
BPL	15.00%
P2O5-T	284,509

FLOTATION FEED	
TONS	2,555,940
BPL	12.56%
P2O5-T	156,840

PRODUCT	
TONS	378,710
BPL	66.43%
P2O5-T	**115,138**

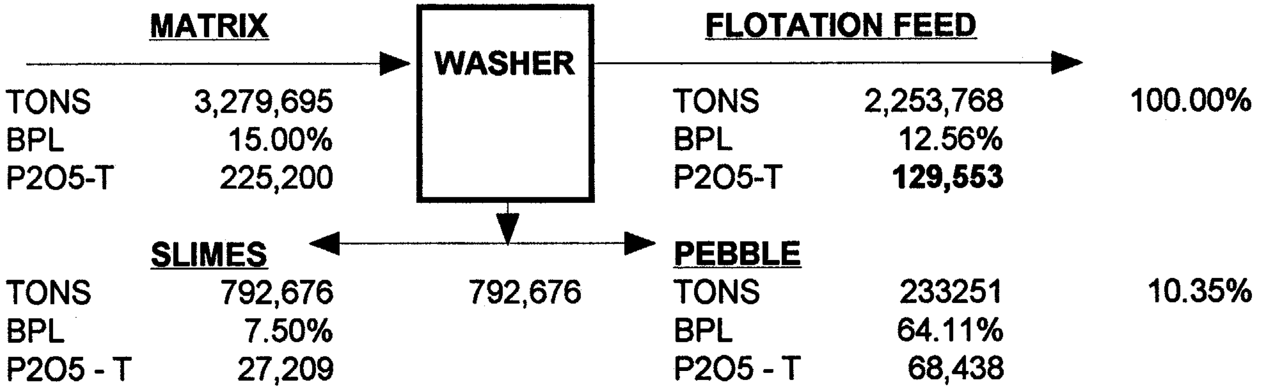
SLIMES	
TONS	1,305,627
BPL	7.50%
P2O5 - T	44,816

PEBBLE	
TONS	282,380
BPL	64.11%
P2O5 - T	82,853

TAILS	
TONS	2,222,410
BPL	4.10%
P2O5-T	41,702

PECO PROCESS FEED

197,991 TONS P2O5
Recovery = 87.92%



MATRIX	
TONS	3,279,695
BPL	15.00%
P2O5-T	225,200

FLOTATION FEED		
TONS	2,253,768	100.00%
BPL	12.56%	
P2O5-T	**129,553**	

SLIMES	
TONS	792,676
BPL	7.50%
P2O5 - T	27,209

PEBBLE		
TONS	233251	10.35%
BPL	64.11%	
P2O5 - T	68,438	

FLOT #1

In the conventional, as well as the PECO type beneficiation plant, the slimes loss is 32% of total weight pumped to the beneficiation plant and its contains 15.7% of the total P2O5 pumped to the beneficiation plant. In either type of operation, the slimes would be lost from the unit.

In the PECO type operation it will be necessary to transport 3.76 times as much material to the phosphoric acid complex as it would from the conventional beneficiation plant. This is the largest deterrent to the use of this kind of operation because to get the same amount of P2O5 to the beneficiation plant it would be necessary to transport 2,487,020 tons of material for the PECO Process as compared to the conventional process transportation requirement of only 661,090 tons of material. This is a large increase in material to be transported. The BPL of the material transported from the conventional plant is 65.44% BPL, while the material transported for the PECO Process is only 17.4% BPL. This report will not attempt to investigate all the means and ways this material could be transported as well as to give economic impact of this increase in tonnage transported. Each individual operating plant will have their own individual situation such as ownership of the railroad, distance from the mine to the phosphate complex, tonnage necessary to be transported, and disposition of the sand and sludge from the phosphate complex.

3.4 BENEFICIATION COST ANALYSIS

This study is based on using a flotation feed material blended with the pebble rock normally produced by the beneficiation plant rather than using matrix alone. It is felt that if the PECO process is successful using the flotation feed then it may be applied to the matrix feed possibility.

In attempting to arrive at costs for the flotation feed material very little information is available to provide a basis for determining the flotation feed cost alone, since the mining cost and beneficiation costs are normally reported as a total mining cost. Which includes the operation of the mine as well as the washer plant and the flotation plants. There is some basic data available from The Fertilizer Institute Report of 1992 concerning the amount of material mined and beneficiated by the total phosphate industry. This data was then modified by a Zellars-Williams report issued in June of 1978 entitled "Evaluation Of The Phosphate Deposits Of Florida Using The Minerals Availability System. "In this report a breakdown of the production costs by mine, washer, flotation, product storage and waste disposal is presented." A detailed review of the method used to obtain the flotation feed costs is discussed in the Appendix of this report entitled, "PECO vs. Current Beneficiation Process Economics. Included in this section of the report are two tables; the first entitled "Flot Number 1 Costs" and the second entitled "Flot Number 2 Costs." These tables relate to the anticipated savings and production costs for the flotation balances number one and number two respectively. In these tables we have taken the total production costs, and split them into the mine and flotation costs of operation, and the “flot factor” assumed to break out the flotation costs is indicated in its respective column. The total mining cost was used to determine the production cost using the current beneficiation process and by subtracting the flot cost from the total cost we can then determine the cost to produce material for the PECO process, which does not include the flotation cost.

Approximately three times as much material is required to be transported for the PECO process as compared to the current process. No attempt has been made to determine the actual cost of this transportation due to the many factors affecting each plants operation. It would be required that each plant, on a case by case basis, be studied to determine the actual impact of these transportation costs. The Fertilizer Institute Report indicates that it costs $16.15 per ton of rock for the industry to produce phosphate feed to the phosphoric acid plant in 1992 which is the latest figure available for industry costs. Based on this cost, it will cost approximately $57.14 per ton of P2O5 to supply the phosphate material-to the phosphoric acid plant. The sequence of calculation indicated above indicates that approximately $23.12 per ton of P2O5 can be saved by utilizing the PECO process. As stated earlier, this does not take into account the cost of transporting the material to the phosphoric acid plant.

The matrix required to produce 197,991 tons of P2O5 is 4,143,947 tons for the current beneficiation process vs. 3,279,695 tons for the PECO process. This is a reduction of 21% in matrix required to produce the same amount of P2O5.

This reduction in matrix requirement has a significant impact on the life of the reserves and by using the PECO process the reserve could be extended by 21%. This reduction in matrix requirement also indicates a 20% reduction in the amount of water that would be consumed in producing the same amount of P2O5 and also the slime ponds currently used to contain the slimes from the beneficiation plant would be reduced by 21%.

These savings increase somewhat as the BPL of the feed to the flotation plant decreases. When the feed drops from 12.56% BPL down to 9.5% BPL the savings increases from $23.12 per ton of P205 to $24.07 per ton of P2O5. As indicated earlier in this report situations have presented themselves that indicate that the BPL of the flotation feed has actually decreased to as low as 7.4% BPL therefore the savings at $0.95 is realistic.

In the PECO process the only grinding required is to grind the pebble product to the size of the flotation feed material. As the BPL of the feed to the flotation plant decreases more and more of the pebble product has to be used to furnish the P2O5 in the product. Therefore as the BPL of the flotation feed drops the actual cost of grinding increases because of this increased pebble consumption. However the overall savings, due to a drop in BPL flotation feed, is still $.95 per ton of P2O5 when the flotation feed BPL drops from 12.56% to 9.5% BPL.

3.5 TEST PROGRAM

To provide a material for the PECO Process in this investigation, production material was obtained from a producing facility which is described by the current process in the “Flot 1." Pebble and flotation feed was obtained from the producing unit and blended so as to match the ratio being produced by that particular facility at that time. This resulted in a feed to the unit of approximately 18% to 20% BPL.

All the material was obtained in a wet condition and was air dried at the PECO pilot plant. It was necessary to dry this material so that it could be accurately metered into the phosphoric acid process. A given quantity of water was added to the system to approximate the wet rock feed to a normal plant, however reliance was put on the ability to calculate the affect of the increased water required by this system when 65% solids phosphate rock slurries were fed to the reactor.

The pebble product was put through a disk type grinder to give it a size which would make it about the size of the flotation feed, fed to the flotation plant. A screen analyses of the unground pebble, concentrate and the blend of the two is presented in the appendix in chart .

3.6 EFFECT OF FLOTATION FEED BPL

During the operation of the pilot unit flotation feed was obtained from the commercial flotation plant as a feed material. Several times during the course of this pilot test program the BPL of the flotation feed dropped well below the 12.5%, and in one case got as low as 7.4% BPL.

Figure “Flot #2” shows the effect of decreased BPL in the flotation feed on the overall beneficiation process. It assumes that the flotation feed BPL has dropped to 9.5% as opposed to the 12.5% assumed in the original case. In each case 197,991 tons of P2O5 are produced. The only difference is that the BPL of the flotation feed is decreased to 9.5%.

When this decrease in BPL occurs, a considerable amount of the production has to be taken over by the pebble product. At 9.5% BPL it required that 104,300 tons of pebble product be produced rather than the 82,850 tons of pebble assumed in the 12.5% case. The amount of product produced in the flot plant dropped from 115,150 tons P2O5 in the 12.5% case to 93,690 tons of the P2O5 in the 9.5% case. It should also be noted that the amount of matrix required to be fed to the overall beneficiation plant increased from the original 4.1 million tons of matrix to 5.2 million

PEBBLE & FLOTATION FEED PROPERTIES

ANALYSIS	FLOTATION FEED	PEBBLE	CONCENTRATE @ 66 BPL
CaO	9.38	44.23	44.41
P2O5	6.38	29.27	30.21
Fe2O3	0.40	1.20	1.89
Al2O3	0.36	0.85	1.70
MgO	0.08	0.65	0.36
SiO2	80.30	9.90	NA
Ra pCi/l	4.4	45.1	

PARTICLE SIZE

TYLER SCREEN	FLOTATION FEED	PEBBLE	GROUND PEBBLE
4	0.01	9.70	0.00
16	13.70	87.42	1.00
28	16.70	1.98	4.00
35	19.00	0.34	15.00
65	37.50	0.24	34.00
100	8.10	0.08	26.00
150	2.60	0.04	1.90
200	1.60	0.05	8.50
PAN	0.40	0.15	7.30
TOTAL	99.61	100.00	97.70

CHART 1

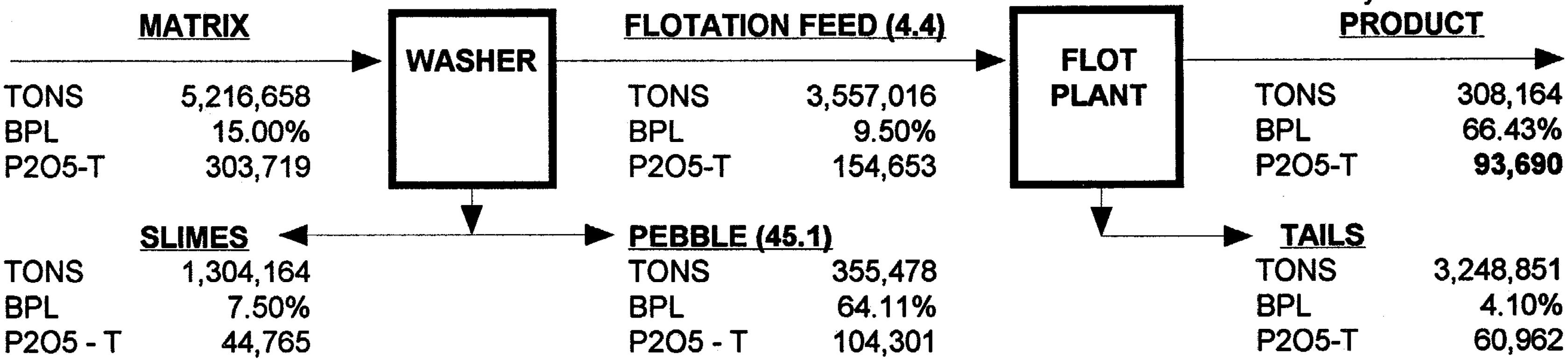
tons of matrix to produce the same number of tons of P2O5. These are some rather alarming facts. It should also be noted that only 60% of the P2O5 contained in the phosphate reserve is recovered as compared to the 69% recovered when the flotation feed BPL was 12.5%, as noted in the original case.

A similar effect was noted on the preparation of the feed for the PECO process. The amount of matrix required jumped from 3.2 million tons of matrix to 4 million tons of matrix required to produce the same of amount of P2O5. The recovery of the P2O5 in the phosphate reserve dropped from 81% to 78.5% of the P2O5 contained in the reserve.

PECO vs 4 CORNERS BENEFICIATION COMPARISON

CURRENT PROCESS 4.10% BPL TAIL

197,991 TONS P2O5
Recovery 65.19%



MATRIX

TONS	5,216,658
BPL	15.00%
P2O5-T	303,719

FLOTATION FEED (4.4)

TONS	3,557,016
BPL	9.50%
P2O5-T	154,653

PRODUCT

TONS	308,164
BPL	66.43%
P2O5-T	**93,690**

SLIMES

TONS	1,304,164
BPL	7.50%
P2O5 - T	44,765

PEBBLE (45.1)

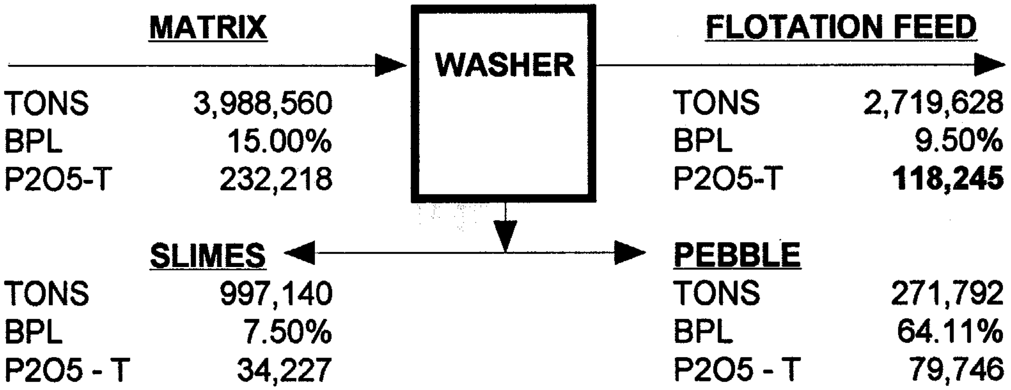
TONS	355,478
BPL	64.11%
P2O5 - T	104,301

TAILS

TONS	3,248,851
BPL	4.10%
P2O5-T	60,962

PECO PROCESS FEED

197,991 TONS P2O5
Recovery = 85.26%



MATRIX

TONS	3,988,560
BPL	15.00%
P2O5-T	232,218

FLOTATION FEED

TONS	2,719,628
BPL	9.50%
P2O5-T	**118,245**

SLIMES

TONS	997,140
BPL	7.50%
P2O5 - T	34,227

PEBBLE

TONS	271,792
BPL	64.11%
P2O5 - T	79,746

FLOT#2

4.0 PECO PROCESS DESCRIPTION

4.1 General

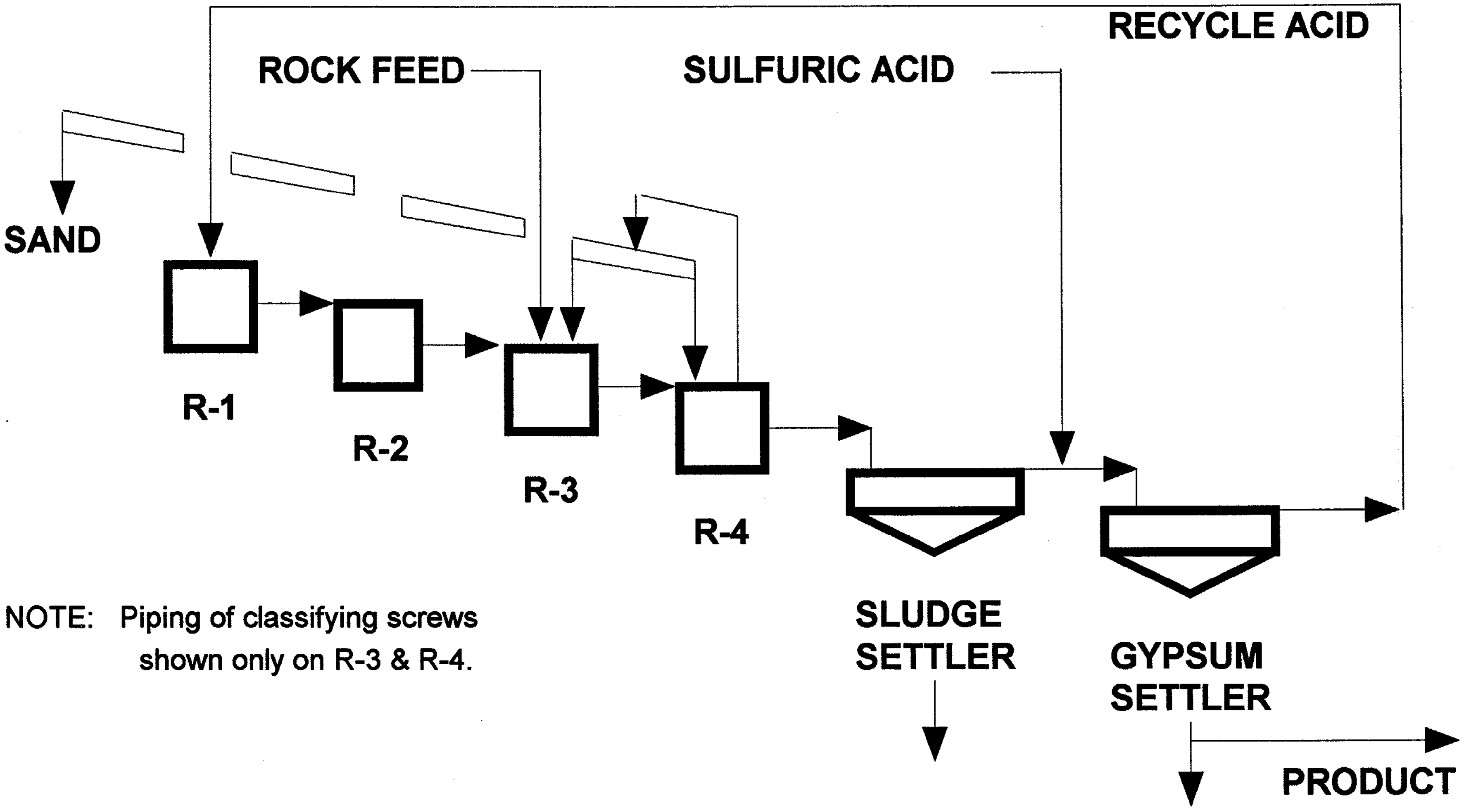
In the PECO phosphoric acid process phosphate rock, including low grade phosphate ores, is contacted with recycle phosphoric acid in a combination counter current/co-current system such that sand and sludge are individually removed from the system and the P2O5 and calcium is dissolved in a solution which is treated with sulfuric acid to produce phosphoric acid and gypsum. This process is shown in the simplified Flow Diagram "Fig. 1."

The sand is first separated from the leach system and washed to recover soluble P2O5 and to produce a saleable sand, which is also suitable for construction purposes and landfill of mined out areas. After sand removal, the slurry solution and unreacted-reacted phosphate enters the sludge thickener, where the under flow is sent to a centrifuge where a filtrate is recovered and sent back to the leach circuit. Centrifuged solids at 40-70% (weight basis) are sent back to mined out areas, sold as feed stock for brick or light weight aggregate manufacture or treated for recovery of other chemicals.

The slurry of acid and gypsum, formed by addition of sulfuric acid to the clear overflow from the sludge thickener, is separated by the gypsum settler into a clear solution for recycle and a thickened acid-gypsum slurry to be fed to a gypsum filter. This avoids processing the full volume of solution to obtain the product acid. Product acid is recovered from the gypsum filter and the gypsum is discarded or further processed to yield additional products. The gypsum filter wash joins the clarified acid as part of the recycle acid.

4.2 Description of the Process

The phosphate bearing material, preferably naturally occurring ores, is contacted with a recycled phosphoric acid in a combination counter current/co-current leach operation using multiple reactor vessels, #1 to #4 as shown in figure 1. The feed material can be wet or dry. The coarse phosphate material is successively conveyed through the reactors, counter current to the flow of the phosphoric solution stream to dissolve and recover the phosphate. From the point of entry of the phosphate bearing material into R-3 the fine material is carried co-currently through one or more agitated vessels wherein the phosphate bearing material is reacted with phosphoric acid from the counter current stream to recover the phosphate values. The resulting slurry consists of a phosphoric acid solution containing soluble monocalcium phosphate (MCP) plus unreacted fine solids and organics from the phosphate source. This slurry leaving the digestion system passes to



NOTE: Piping of classifying screws shown only on R-3 & R-4.

PECO PHOSPHORIC ACID PROCESS FLOW SHEET

FIG. 1

a sludge settler where the unreacted fines and organics settle to produce a clean overflow solution.

The under flow from the settler is passed to a centrifuge where the liquid phase is removed from the solids and returned to the reaction system. The solids are reslurried with wash water and centrifuged a second time to recover the soluble P2O5 for return to the process, and the resulting cake is discharged as a semi-dry material for export from the system.

The clarified solution of phosphoric acid and MCP overflowing the sludge settler is sent to a crystallizer wherein sulfuric acid is added to react with the MCP and form calcium sulfate and product phosphoric acid. The resulting slurry is fed to the gypsum settler from which a more concentrated gypsum slurry is fed to the gypsum filter and a clarified overflow is obtained for recycle to the leaching process

By using counter current contact of the coarse phosphate material with the phosphoric acid solution, the size distribution of the phosphate material can be more coarse while still economically extracting the phosphate values. Since no insoluble material can occlude the phosphate particle. This allows a significant reduction in grinding costs over existing operations. Additionally, this scheme allows contact of the residual sand and unreacted phosphate bearing material with the strongest acid solution just prior to exiting the system so that the greatest extraction of P205 from the solid phase can be assured. The primary reaction is the digestion of fluorapatite by phosphoric acid to produce monocalcium phosphate solution, Sufficient phosphoric acid solution must be provided to both react with all of the fluorapatite present and to take the resulting monocalcium phosphate into solution.

The coarse material is transferred from vessel to vessel by a method which minimizes the transfer of liquid in the same direction, thus maintaining as nearly, as is practical, a counter current system. Such a method is to pump the slurry to a separating device such as a dewatering or classifying screw. The clarified liquor overflows back to the vessel from which it came, while the sand and unreacted phosphate material is extracted by the classifying screw and discharged to the next vessel.

The final separator discharges the residual sand, essentially free of unreacted phosphate, to a wash system wherein the sand is washed free of the water soluble P2O5 solution before it is discharged for disposal.

Within the leach tanks, the solids are agitated in such a manner to insure that kinetics are not limited by lack of agitation but, in such a manner as to avoid excessive carryover of coarse material in the co-current direction. Additionally, the vessels are designed to minimize such carryover in the overflowing solution.

Efficient operation of the system depends on the accurate control of the temperature. The operating temperature will depend on the reactivity of the feed material, and it has been found to be at an optimum at 170 degrees F.

For the purpose of efficiency in digesting the feed material, there is no need to maintain a low soluble calcium in the recycle acid by maintaining a high free sulfate. The quantity of recycle acid is sufficient to react with the calcium compounds in the feed material and keep the soluble calcium below the levels that cause precipitation of dicalcium phosphate. This is true provided the monocalcium phosphate is reacted stoichiometrically with sulfuric acid. Therefore, the free sulfate level in the crystallizer can be maintained at levels which are beneficial to the quality of the gypsum or to the operation of other parts of the plant. A situation may exist from time to time in the sludge washing circuit, where the sludge may become too light to settle satisfactorily. During such times, the free sulfate in the recycle acid may be allowed to rise to create gypsum in the digestion circuit. This gypsum will exit the system with the sludge, adding weight and body to the flocculated sludge and affording satisfactory settling characteristics.

4.3 Advantages of the Process

The major advantages the process offers over similar ones are in the areas of *digestion efficiency *reduction in grinding costs *recovery of soluble P2O5 form the waste streams *production of separate waste streams *versatility in operation of the gypsum crystallizer *production of a unique gypsum *reduced costs due to filtration of a portion of the liquid in the system and *production of an acid which is not black. The sludge from the centrifuge will settle, to a consistency that a jeep could be driven over the disposal area in a few days as opposed to several years for conventional disposal.

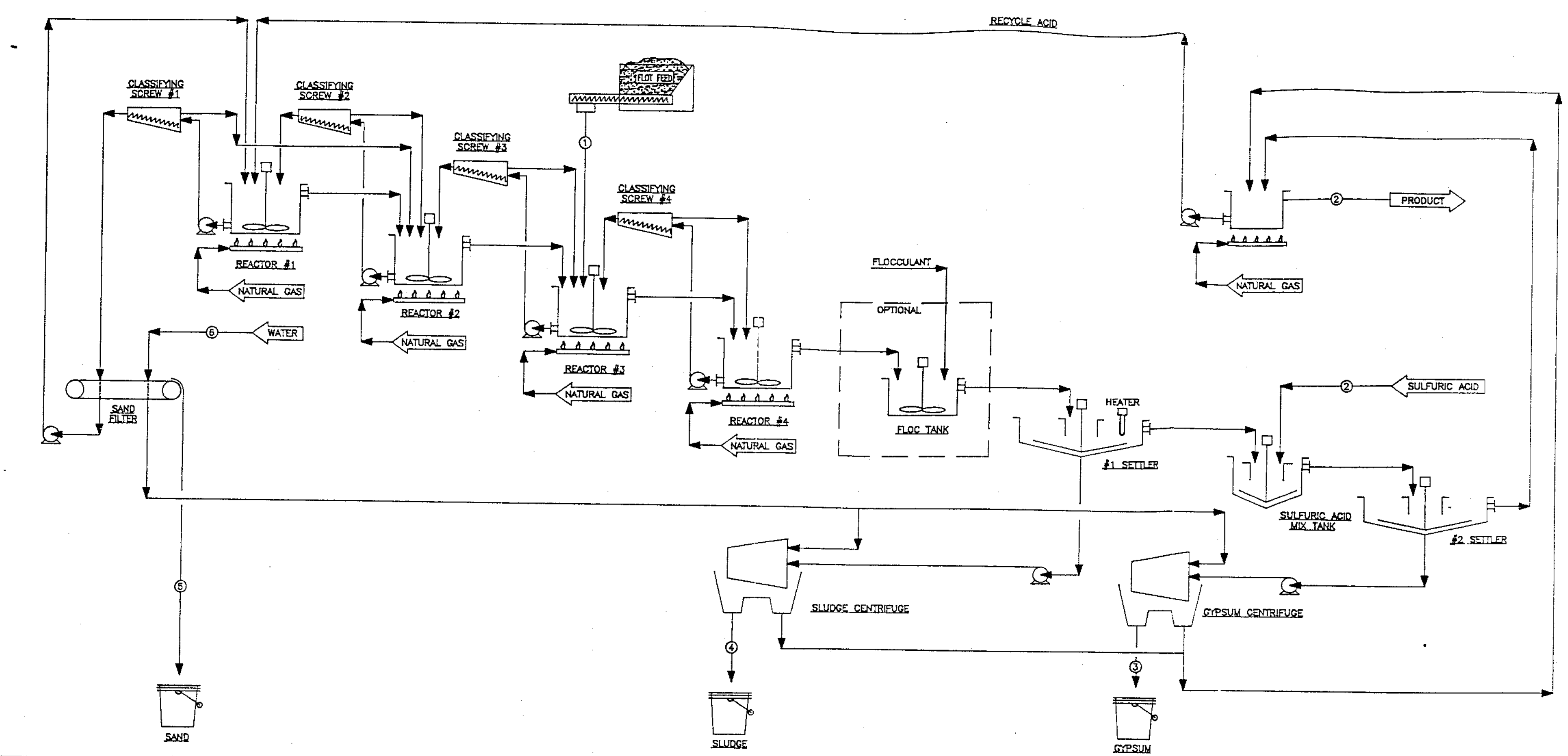
5.0 PILOT PLANT OPERATION

Drawing No. 90144-01-001 is a simplified flow sheet of the pilot plant operation in the PECO research laboratories. Reactors 1-4 are five gallon stainless steel vessels. They are arranged so that liquid overflows from reactor 1 to 2 to 3 to 4 and the solids are removed from each of these reactors and pumped up to a classifying screw. In the classifying screw between reactor 3 and 4 the solids are dewatered and conveyed from the screw into reactor 3. The liquor which is removed from the solids overflows and returns back to reactor 4. This operation is repeated between reactors 2 and 3 and reactors 1 and 2. In essence what we have accomplished here is a flow of liquor from reactor 1 through the system and exiting reactor 4. The solids on the other hand move in a counter current direction from reactor 4 towards reactor 1 and then out of the system.

The phosphoric acid from reactor 4 then goes into a sludge settler wherein the unreacted clays and rock and other inorganic ingredients are settled out of the phosphoric acid and exit the system through the sludge settler. The overflow from the sludge settler then moves to the gypsum settler where sulfuric acid is added to the monocalcium phosphate/phosphoric acid solution prior to its entering the gypsum settler, to convert the monocalcium phosphate to gypsum and phosphoric acid. The gypsum settles in the settler and is withdrawn from the bottom of the settler to be washed before disposal. The liquor overflowing the gypsum settler is recycled back to reactor 1 where it again enters the reaction system to dissolve phosphate from phosphate rock. The product is separated from the gypsum prior to washing.

The phosphate rock is fed into reactor 3 and as explained earlier the undissolved rock itself moves from reactor 3 to reactor 2 to reactor 1 and finally out the system. Any small or fine phosphate rock which overflows from reactor 3 to reactor 4 is removed and returned to reactor 3 by the previously described classifying screw operation. This affords the process a capability of keeping coarse materials in the reactor system for as long as desired so that the phosphoric acid can continue dissolving the phosphate values from the phosphate rock feed as the unreacted rock moves counter current to the phosphoric acid. The whole reaction system is maintained at a temperature of approximately 170 degrees F.

The sludge and gypsum removed from their respective settlers is then washed with water by reslurring and centrifuging as to remove as much of the soluble P2O5 from these streams as possible. This wash water is then returned and added to the recycle acid stream prior to its entrance into reactor 1. The amount of wash water which is used is whatever the maximum that can be used and still maintain a 24% to 27% P2O5 level throughout the whole system.



STREAM No.	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫
DESCRIPTION	PHOSPHATE BLEND	SULFURIC ACID	GYPSUM	SLUDGE	SAND	WASH H20	PRODUCT ACID					
WEIGHT DRY	44.82	13.09	9.40	19.01	23.91		6.69					
CAO D	7.35		3.38	4.64	0.31		0.06					
P205 D	4.90		0.15	0.21	0.07		4.32					
FE203 D	0.26		0.03	0.05	0.02		0.13					
AL203 D	0.23		0.02	0.02	0.01		0.18					
MGO D	0.07		0.00	0.01	0.00		0.08					
SIO2 D	31.00		0.89	6.61	23.36		0.11					
H2S04		13.09	5.22	7.47	0.01		0.42					
H20	0.18	0.91	6.10	8.49	1.10	34.00	10.82					
WEIGHT W	45.00	14.00	15.50	27.5	25.00	34.00	17.50					
SPG	1.932	1.828	2.003	1.000	1.603	1.000	1.275					
GYPSUM DIST.			42.1%	57.9%								

PHOSPHATE ENGINEERING & CONSTRUCTION CO., INC.
LAKELAND, FLORIDA 33811

MK	REVISION	BY	CKD	DATE	APP'D	DATE

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH
LAKELAND, FLORIDA

PECO PHOSPORIC ACID PROCESS
FOR
FLOTATION FEED

95-01-133R
90144-PFD
NONE
BEE
90144-[illegible]

Normal operation of the pilot plant is to bring the reaction to an equilibrium state and once this has been achieved the conditions of the reaction and operation are maintained for a period in excess of two and probably no more than four hours for each run. This allows all of the various streams to be sampled and analyzed during a steady state operation. During this test program three sets of operating conditions were tested. The first at 1.3% free sulfuric acid in the recycle stream, the second at 0.5% free sulfuric acid in recycle stream, and the third zero or slightly negative free sulfuric acid in the recycle stream. Each of these operations will be described individually.

6.0 DISCUSSION

6.1 Process Discussion

The basic objective of the PECO phosphoric acid process is to dissolve the P2O5 out the phosphate rock using a phosphoric acid solution. It is therefore important that we be aware of the phase diagram shown in figure 2 for the system CAO-P2O5-H2O.

This phase diagram for a 75 degree C operation indicates that the maximum amount of CAO that can be dissolved in phosphoric acid occurs at approximately 35% P2O5 and will dissolve about 5.8% CAO. Due to water balance considerations it is difficult to maintain the 35% P2O5 level in the dissolving solution; and therefore most of the test work done during this operation was done in a range of 24% to 27% P2O5. This indicates that the maximum CAO that could be dissolved is 3.9% CAO at the lower end, before a solid dicalcium phosphate is precipitated. The phase diagram shows the limits of P2O5 that can be dissolved. A solid phase monocalcium phosphate is precipitated on the right of the curve and the solid phase dicalcium phosphate precipitated on the left side of the curve. Under this curve a solution of monocalcium phosphate exists without any precipitation of phosphate.

It is therefore very important that once a concentration of P2O5 is selected as an operating point that the operation not be allowed to proceed to lower P2O5 levels. If this happens a solid phase dicalcium phosphate will be precipitated which will take P2O5 away from the solution and further reduce its P2O5 level. Resulting in more precipitation of dicalcium phosphate. This makes it very difficult to regain the original P2O5 level.

Theoretically it would be possible to dissolve the phosphate from the phosphate rock using a recirculation acid ratio of 7.5 tons of P2O5 in the phosphoric acid for each 1 ton of P2O5 to be dissolved from the phosphate rock. In actual practice it has been found that it is better to use approximately 15 tons of P2O5 as phosphoric acid to dissolve one ton of P2O5 in the rock. This gives a certain latitude required for a practical plant operation.

6.2 Rock Feed Moisture Content

As indicated above it is necessary in the PECO process to maintain P2O5 levels in the range of 24% to 26% P2O5. This then establishes that the PECO process can only tolerate so much water input to the system. If too much water is put into the system the result is a lower level of P2O5 concentration and precipitation of solid phase dicalcium phosphate can occur and result in some severe processing problems.

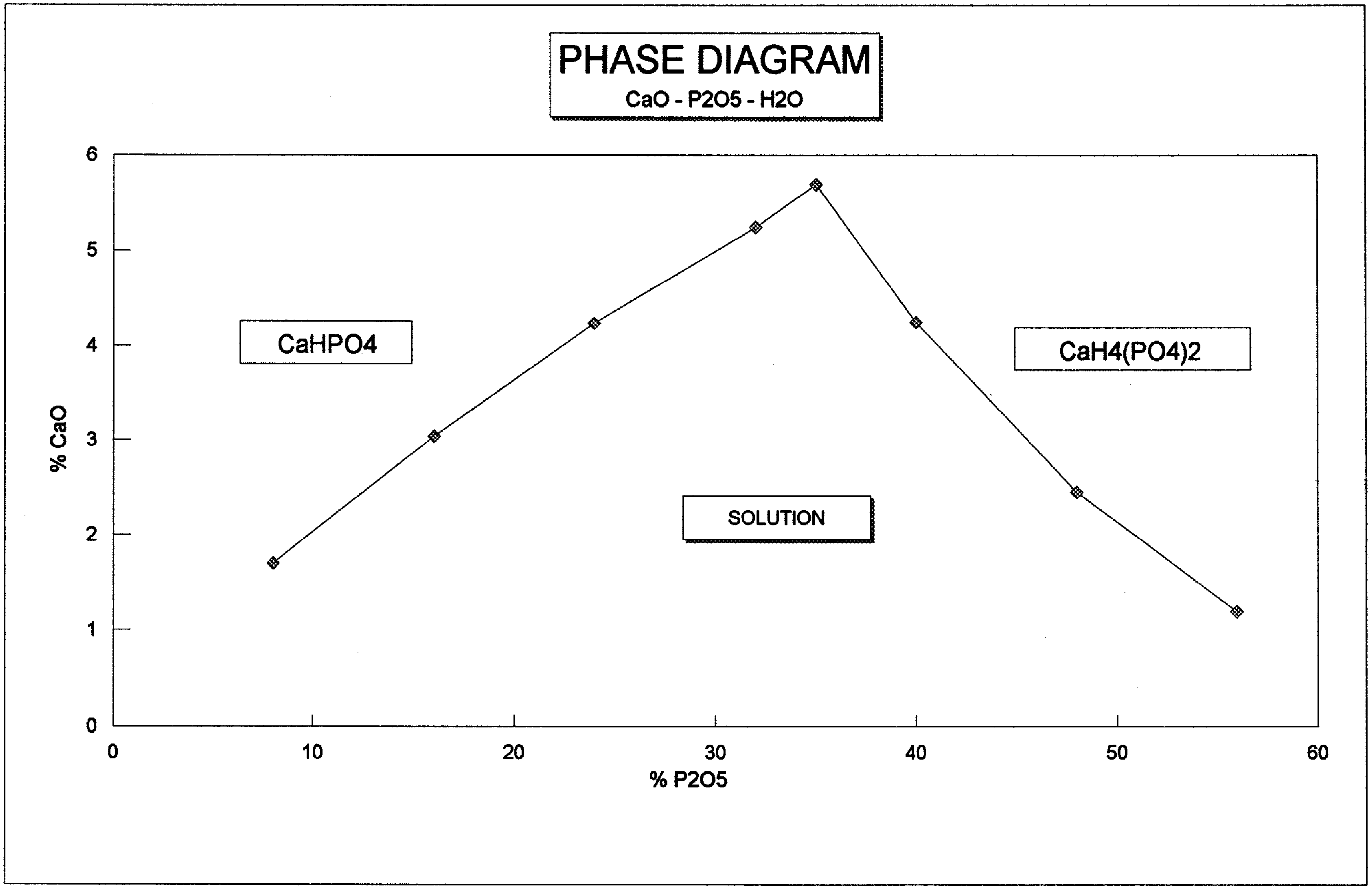

PHASE DIAGRAM
CaO - P2O5 - H2O
% CaO
0
1
2
3
4
5
6
0
10
20
30
40
50
60
% P2O5
CaHPO4
SOLUTION
CaH4(PO4)2

FIG.2

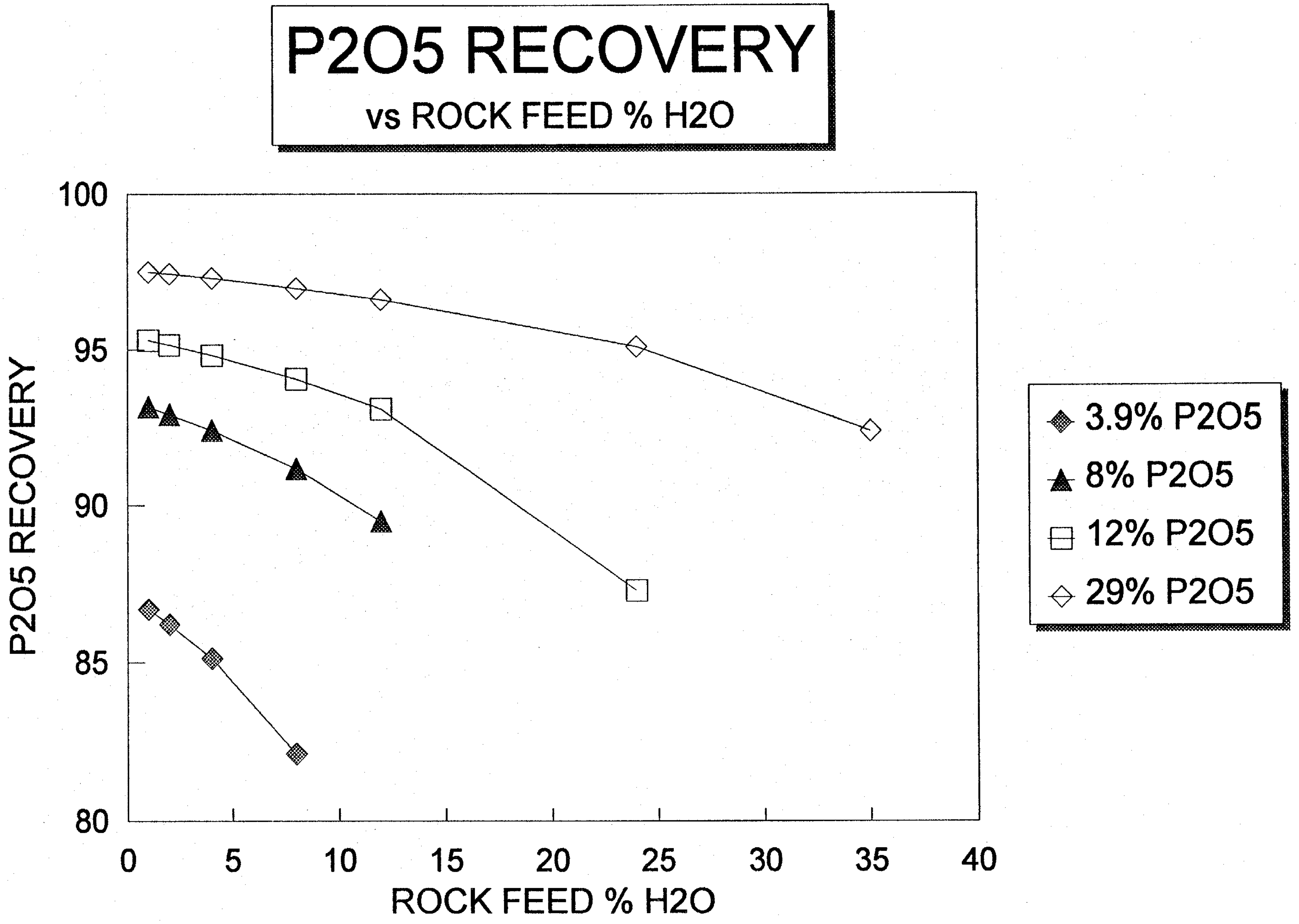

P2O5 RECOVERY
vs ROCK FEED % H2O
P2O5 RECOVERY
100
95
90
85
80
0
5
10
15
20
25
30
35
40
ROCK FEED % H2O
◆ 3.9% P2O5
▲ 8% P2O5
□ 12% P2O5
◇ 29% P2O5

FIG. 3

Figure 3 is a plot showing what effect water content of the rock fed to the PECO process has on P2O5 recovery. The top curve is for an existing operation wherein the rock feed P2O5 level is about 29% and therefore it can tolerate as much as 35% water in the feed to the phosphoric acid plant and still get recoveries in the 92% to 94% levels. As the P2O5 level of the rock decreases, which is what we are witnessing as the mining operations move further south, the amount of water that can be tolerated by the PECO process is limited. For example at a 12% P2O5 level, when the rock feed contains 25% moisture, the anticipated overall recovery decreases to about 87% P2O5. The 25% water level in the phosphate feed is significantly below the 35% level currently being utilized by most phosphate complexes in their wet rock feed system. Therefore the use of a lower P2O5 levels in the phosphate feed will result in extremely low recoveries of phosphoric acid when fed to the process as a slurry.

This situation is somewhat eleviated by the fact that concentrate and pebble, if allowed to come to an equilibrium moisture content just by standing outside in a pile will, dewater to approximately 12% moisture content. At a 12% moisture content P2O5 levels as low as 10% could be tolerated and still be able to give overall recoveries of 90% in the phosphoric acid plant. This will require that a different means of feeding the phosphate rock to the phosphoric acid reactor will have to be designed and implemented. When the P2O5 levels get much below 8% P2O5 in the phosphate rock fed to the process recoveries now drop to the lower 80's and make the process somewhat impractical to operate. Flotation feeds of 7.4 BPL (3.9% P2O5) are too dilute to be used as a feed to the phosphoric acid process. This is a very serious concern for the phosphate industry in general. Research should be instigated at this time to determine how low our phosphate feeds can be to be utilized by the phosphoric acid plant.

6.3 Gypsum Production

When the phosphoric acid is recirculated in the PECO process it contains with it a certain amount of residual free sulfuric acid. It is desirable to have as high as 2% free sulfuric acid in the final precipitation of the gypsum so that the P2O5 contained in the lattice of the gypsum crystal is reduced to a minimum. A practical level has been found to be 2% free sulfuric acid. It should be noted that if the total stream of recycle acid contains 2% free sulfuric acid. This will supply 30% to 40% of the total sulfuric acid required for the precipitation of the gypsum. When the PECO process is operated in this fashion about 30% to 40% of the gypsum will be precipitated in the first sludge settler. The remaining gypsum will be removed in the gypsum crystalizer.

It was felt that this could be used to advantage, in that by varying the amount of free sulfuric acid in the recycle phosphoric acid stream the amount of gypsum precipitated in the first settler could be controlled. Therefore we would have the possibility of precipitating approximately 15% to 25% of the total gypsum in the first settler. This would allow us to remove all of the radioactive material contained in the phosphate rock in this settler, thus allowing the production of 75% to 85% of the gypsum without any radioactivity whatsoever. The test program undertaken and described in this report indicates that this does not happen.

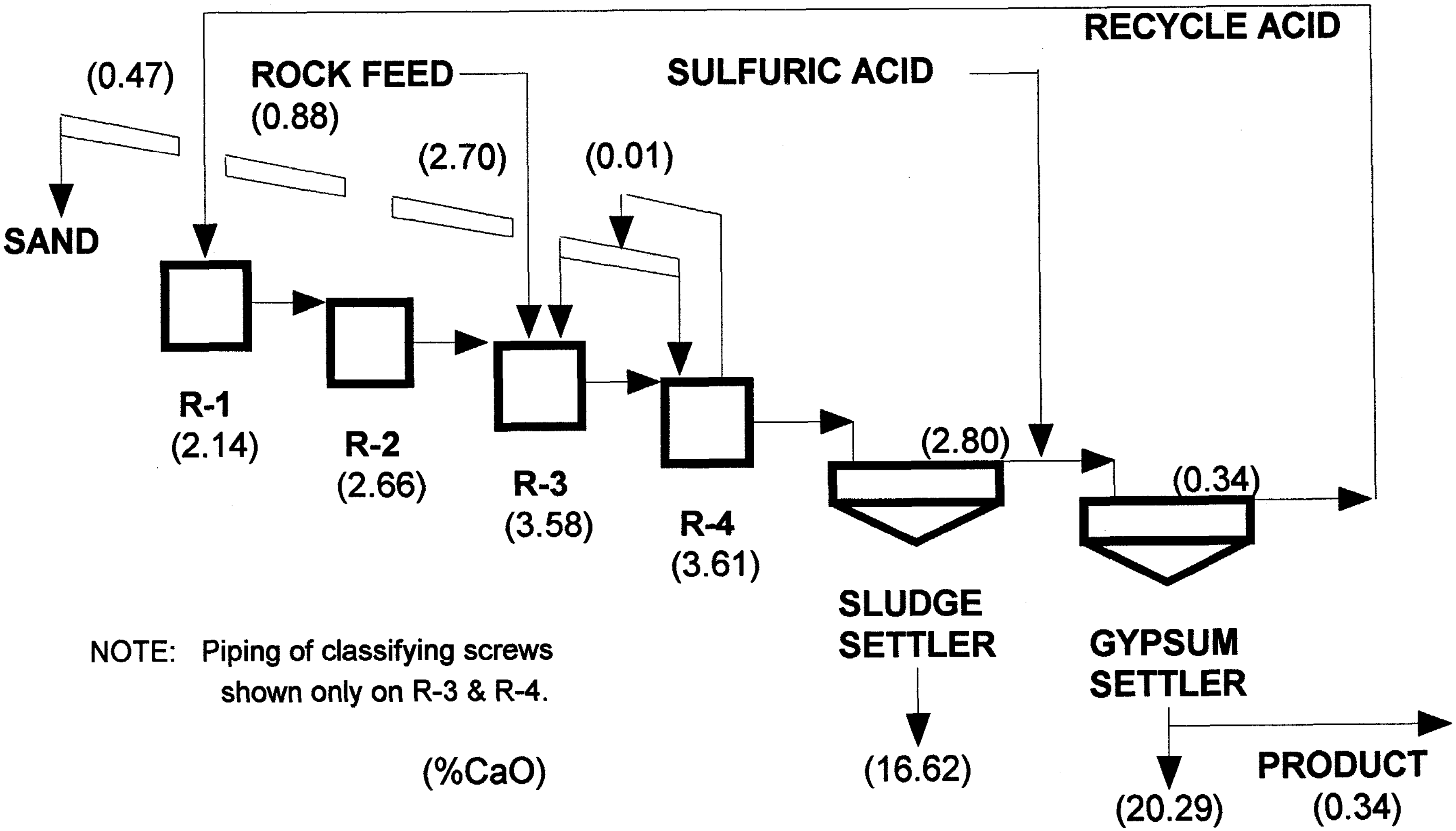
The free sulfuric acid content of the recycle acid was varied from 0.5% to 1.3% in these cases. At the 0.5% free sulfuric acid level only 30% of the gypsum was precipitated in the first settler and 70% of the gypsum precipitated in the gypsum crystallizer, while at 1.3% free sulfuric acid 60% of the gypsum is precipitated in the sludge settler and the remainder in the gypsum settler.

6.4 1.3% Free Sulfuric Acid Run

Figure 4 is a simplified flow sheet showing the conditions of this phosphoric acid run. The rock is fed into reactor 3 as seen in figure 4. The CAO content of the slurry in reactor 3 contained 3.58% CAO which overflowed into reactor 4. The CAO content in reactor 4 was slightly increased at 3.61% CAO. The rock moving from reactor 3 to reactor 3, by the classifying screw conveyor, had a citrate insoluble component of 2.7% P2O5. The rock leaving reactor 2 had its citrate insoluble component reduced to 0.88% P2O5. This rock was then discharged into reactor 1 where the citrate insoluble component was reduced to 0.47% P2O5. This indicates that the phosphate had been put into solution by its counter current recycle acid and a very good recovery of P2O5 was obtained. The very fine material that overflowed from reactor 3 to reactor 4 had all of its P2O5 dissolved from it. When it was returned to reactor 3 its citrate insoluble component was only 0.01%. This indicates a good extraction of P2O5 from the rock.

The recycle acid, having picked up as much of the calcium phosphate as possible, then enters the sludge settler wherein calcium sulfate and any unreacted material settles to the bottom of the sludge settler. The calcium component of the material settled out in the sludge contains 16.2% CAO. This quantity of CAO in the sludge indicates that approximately 60% of the total gypsum was precipitated in the sludge settler. The reason for this precipitation, as described elsewhere in this report, is due to the free sulfuric acid content of the recycle stream. At a level of 1.5% free sulfuric acid in a stream which has 20 units of P2O5 for each unit of P2O5 fed in the rock it is seen that the amount of free sulfuric is a significant component of the recycle acid stream. This results in 60% of the gypsum being precipitated in the sludge settler.

The liquid overflows the sludge settler and the sulfuric acid is added to this stream so as to bring the free sulfuric acid up to 1.3%. In so doing it reacts with the calcium contained in the

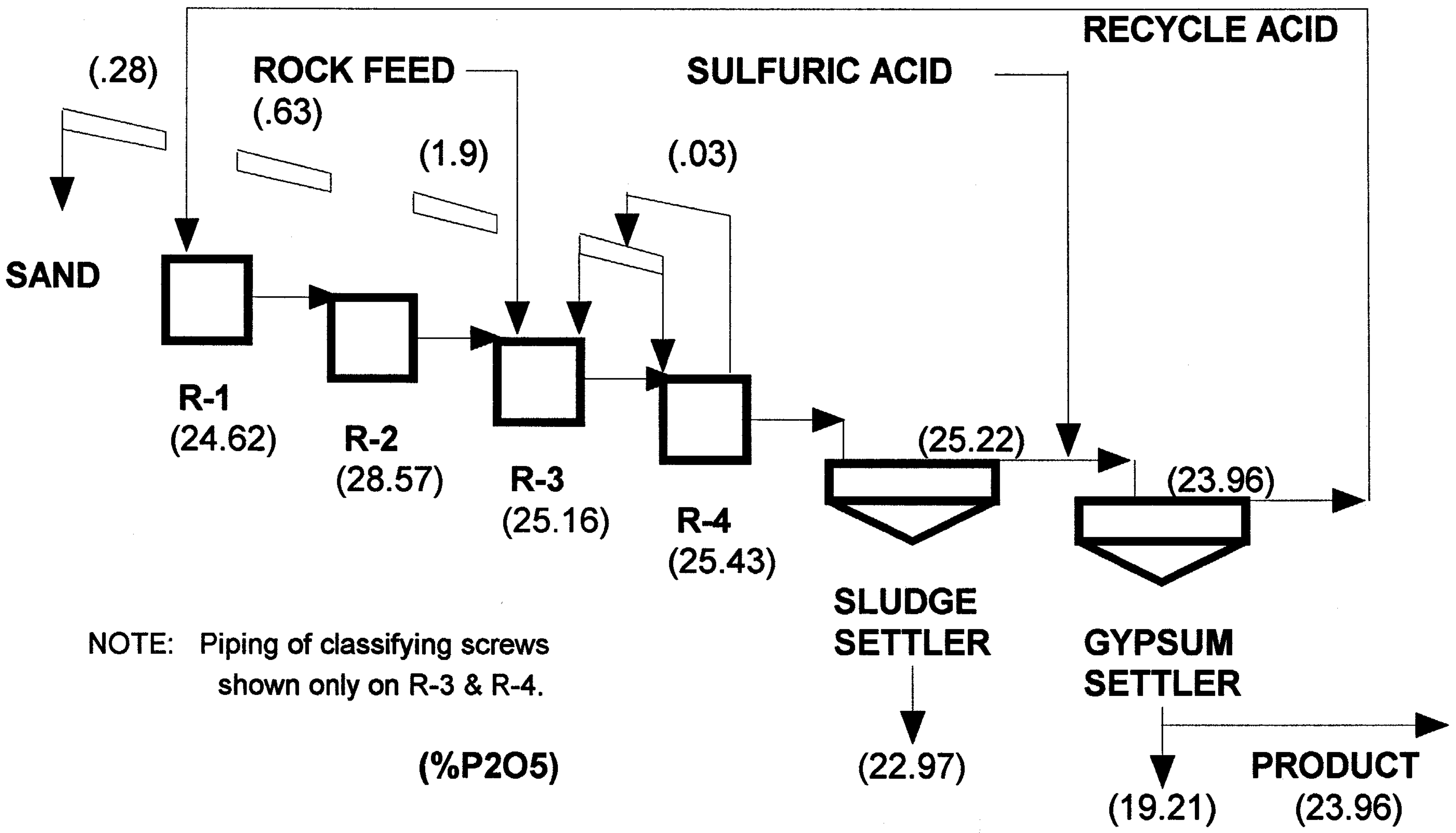


NOTE: Piping of classifying screws shown only on R-3 & R-4.

CaO CONTENT (1.3 H_2SO_4 CASE)

PECO PHOSPHORIC ACID PROCESS FLOW SHEET

FIG. 4



P2O5 CONTENT (1.3 H2SO4 CASE)

PECO PHOSPHORIC ACID PROCESS FLOW SHEET

FIG. 5

monocalcium phosphate/phosphoric acid solution and causes the CAO content to be precipitated as calcium sulfate. As shown in figure 4 the CAO content of the stream overflowing the gypsum settler contains only 0.34% CAO which is the solubility of the gypsum in the phosphoric acid.

The under flow from the gypsum settler contains 20.29% calcium as calcium sulfate however the amount of settlement from this settler is only 40% of the total gypsum produced by this system.

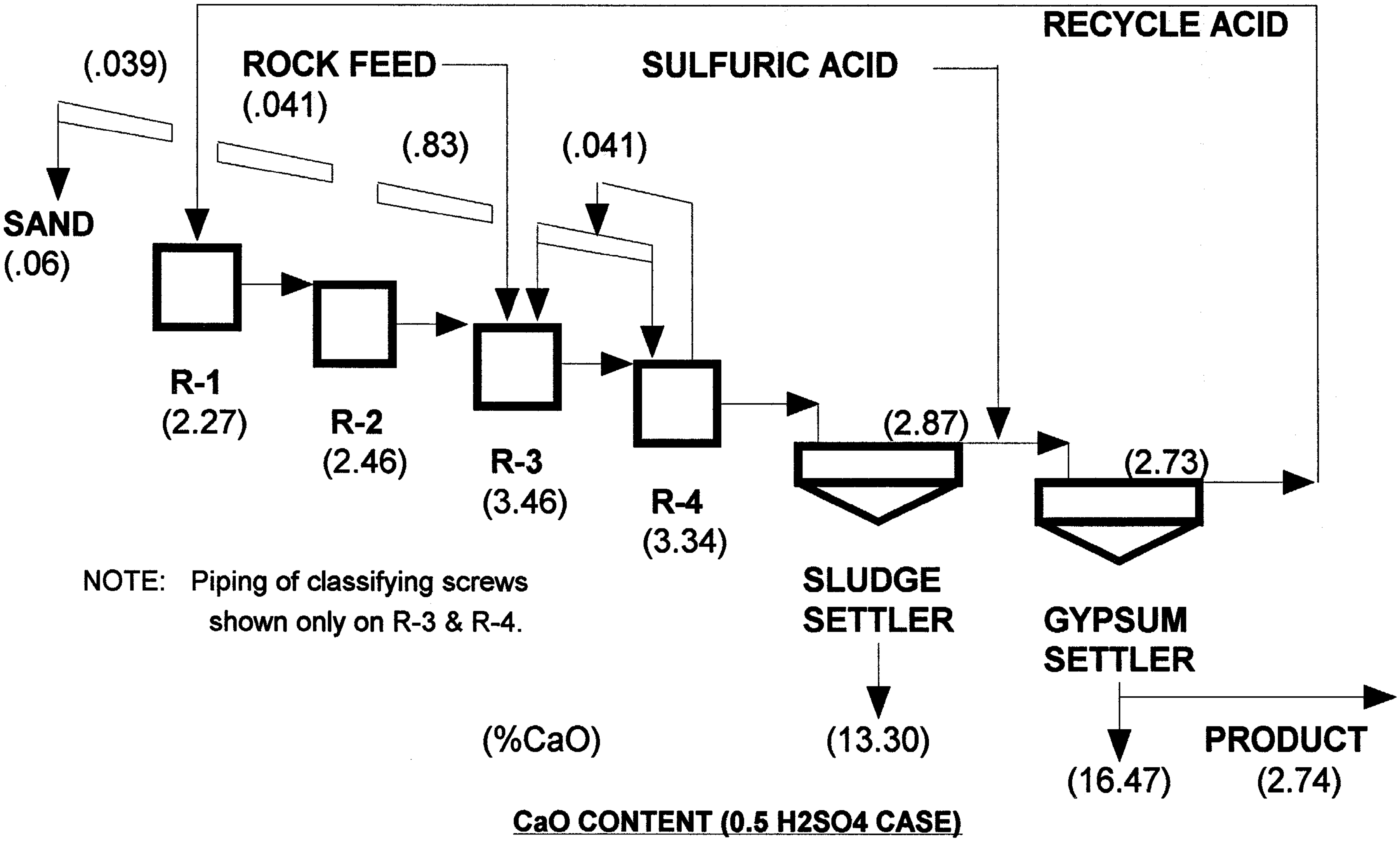
One of the objectives of this pilot plant effort was to determine if the radioactivity of this system could be removed by the first portion of gypsum produced, thereby resulting in the major portion of the gypsum produced, to contain no radioactivity. The radioactivity level of the first gypsum produced in the sludge settler was 10.8 pico curries per liter whereas the radioactive content of the gypsum removed from the gypsum settler was 14.1 pico curries per liter. In this particular case 60% of the total gypsum was removed from the sludge settler as compared to the 40% of the gypsum removed in the gypsum settler . During this run the major portion of the radioactivity was not removed by the initial calcium sulfate precipitated from this system. The radioactive level of the sand produced was 1.7 pico curries per liter. The phosphoric acid product contained 2.6 pico curries per liter and the flotation feed used in supplying phosphate to this pilot plant run measured 4.4 pico curries. The pebble used to supply phosphate to this system contained 45 pico curries per liter.

The overall recovery of P2O5 during this particular run, when comparing the P2O5 contained in the product as compared to the P2O5 contained in the rock fed to the system, was 88.2%. When one looks at the loses of P2O5 contained in the gypsum, sludge and sand, as compared to the total P2O5 fed to the system, the recoveries indicated at 91.2% recovery.

In general the level of impurities contained in the acid produced by the PECO phosphoric acid process are about the same of that encountered in a normal phosphoric acid production facility with the exception of the Fe2O3 contained in the 27% P2O5 acid. Acid produced in a normal phosphoric acid process would have 1.09% Fe2O3 contained in the phosphoric acid when using the same type of rock used in the PECO phosphoric acid process; however the iron content of the PECO acid drops to approximately 0.72% Fe2O3 or a reduction of about 30%. The other impurity levels in the PECO acid are about the same as that encountered in a conventional phosphoric acid process.

6.5 0.5% Free Sulfuric Acid Test Run

Figure 6 is a summary flow sheet of the 0.5% free sulfuric acid run. In general the reaction system in this case is about the same as that encountered in the 1.3% free sulfuric acid case. The



PECO PHOSPHORIC ACID PROCESS FLOW SHEET

FIG. 6

monocalcium phosphate/phosphoric acid solution leaving the reaction system was about the same at 3.34% CAO compared to the 3.61% for the 1.3% run. The citrate insoluble content of the sand leaving the system in this run was 0.04% P2O5 as compared to the .47% P2O5 for the 1.3% sulfuric acid run This is somewhat better, however it would be expected that both of these runs would be in the very low CI range for the sand leaving the system.

The main difference between this run and the 1.3% run is that for the 0.5% run only 35% of the gypsum was precipitated in the sludge settler as compared to the 60% of the gypsum precipitated in the sludge settler for the 1.3% free sulfuric case. The pico currie content of gypsum from the sludge settler was 9.8 pico curries per liter and the gypsum from the gypsum settler contained 10.9 pico curries per liter. It was hoped that the 35% of gypsum precipitated from the sludge settler would remove all of the radioactivity from the system, however here again this was not the case.

The radioactivity of the product was 2.6 pico curries per liter, the same as the previous run and the sand radioactivity dropped to 0.1 pico curries per liter. The radioactivity of the phosphate blend used in this run was 16.1 pico curries per liter.

The level of impurities in the product acid were about the same as those encountered in a conventional process however an approximate 30% reduction in the Fe2O3 content of the acid was noted in this run as was noted in the 1.3% run.

The overall recovery of P2O5 contained in the product as compared to the P2O5 in the phosphate rock fed to the system was 95.1%. The amount of sulfuric acid contained in the 0.5% free sulfuric acid recycle acid is approximately 30% of the total sulfuric acid required for the entire system.

6.6 Radiation Review

It has been found that the primary source of radiation in the gypsum produced by the phosphoric acid process is radium. Generally speaking the radium will follow the calcium in this system and it normally is disposed of with the calcium contained in the gypsum. Since the radium has such a high affinity for calcium it was suggested that perhaps if we precipitated the first 1/3 of the gypsum from the phosphoric acid process that it would contain virtually all of the radium and the remaining gypsum could then be precipitated relatively free of radium. This is one of the primary objectives of this study.

From the PECO process description it is apparent that the amount of gypsum contained in the first precipitation is controlled by the free sulfuric acid contained in the recycle phosphoric acid. Therefore the study was structured so that i one run the recycle acid contained 0.5% free sulfuric and another run would contain 1.3% free sulfuric acid. These different sulfuric contents in the recycle acid will cause in one case a precipitation of 35% of the gypsum as the first precipitate when the 0.5% free sulfuric acid is contained in the recycle acid and a greater amount as high as 60% to 65% of the gypsum can be precipitated as the first precipitate when the recycle phosphoric acid contains 1.3% free sulfuric acid.

Chart #8.4 entitled radioactivity comparison reports the radioactivity levels of the various raw materials, products and byproducts produced by the PECO phosphoric acid process. It can be stated that generally the radium does follow the calcium content of the various streams in the process. However the amount of radium produced in the first precipitate of gypsum, which is included in the sludge from the PECO process, carries about the same general level of radioactivity as the final precipitation of gypsum from the PECO process. The data reported in chart #8.4 has been sorted by the level of calcium contained in the various process streams. The chart indicates that the radium follows the calcium levels in each individual stream. However the first precipitate contained in the sludge did not remove most of the radioactivity from the process. This can be explained by the fact that even though 35% of the gypsum was precipitated with the sludge, there was still a lot of calcium left in the liquid phase of the overflow from the sludge settler which probably did attract the radium so that it would follow the calcium which is contained in the monocalcuim phosphate which is in solution in phosphoric acid. Therefore some of the radium was removed during the sludge settling process but an equal amount of radium was attracted to the calcium contained in the monocalcium phosphate which then was removed in the final gypsum settler. It is concluded that the partial precipitation of calcium in the initial sludge settler does not remove the radium as hoped for. The product acid in almost all cases had a low level of radioactivity of 2.6 pico curries per liter indicating that the radioactive elements did follow the calcium and leave the system with the gypsum.

FIPR/PECO

FLOTATION FEED ACIDULATION PROCESS
FLOTATION FEED

DATE: 09/25/96
FREE SULFURIC=1.3%

GIVEN:		GYP WASH	1 STAGE	PHOSPHATE FEED IS A BLEND OF 22.5% PEBBLE
ROCK WT D	44.82	CAO/P2O5	1.50 RATIO	AND 77.5%FLOTATION FEED.
EST (E)	88.17%	PROD FSUL	1.30 %	1) BLEND ANALYSIS = DRY BASIS.
GYP P2O5%	0.96	GYP CI	0.03 %	2) BLEND % -150 = 1 % (SLIME)
PROD P2O5	24.69	GYP CS	0.50 %	3) SLUDGE 69.13 % SOLIDS, 0.76 % P2O5

		BLEND (1)D	SULFURIC (2)E	GYPSUM (3)F	EVAP (4)G	SLUDGE (5)H	SAND (6)I	WASH H2O (7)J	PRODUCT (8)K	ANALYSIS (9)L		
WEIGHT	D	44.82	13.09	9.40		19.01	23.91		6.69		WEIGHT	
CAO	D	7.35		3.38		4.64	0.31		0.06	0.34	CAO%	
P2O5	D	4.90		0.15		0.21	0.07		4.32	24.69	P2O5%	
FE2O3	D	0.26		0.03		0.05	0.02		0.13	0.73	FE2O3%	
AL2O3	D	0.23		0.02		0.02	0.01		0.18	1.03	AL2O3%	
MGO	D	0.07		0.00		0.01	0.00		0.08	0.47	MGO%	
SIO2	D	31.00		0.89		6.61	23.36		0.11	0.65	SIO2%	
H2SO4			13.09	5.22		7.47	0.01		0.42		H2SO4%	
H2O		0.18	0.91	6.10	8.34	8.49	1.10	34.00	10.82	61.8	H2O%	
WEIGHT	W	45	14	15.5	8.34	27.5	25	34	17.50		WEIGHT W	
SP GR		1.923	1.828	2.003	1.000	1.000	1.603	1.000	1.275		SP GR	
GYPSUM DIST.				42.10%		57.90%						
		ANALYSIS							11.66	2.67142857		
WEIGHT	D										WEIGHT	
CAO%	D	16.34		21.79		16.89	1.25		0.34		CAO%	D
P2O5%	D	10.89		0.96		0.76	0.28		24.69		P2O5%	D
FE2O3%	D	0.57		0.18		0.19	0.07		0.73		FE2O3%	D
AL2O3%	D	0.50		0.10		0.09	0.03		1.03		AL2O3%	D
MGO%	D	0.16		0.03		0.03	0.02		0.47		MGO%	D
SIO2%	D	68.89		5.75		24.03	93.43		0.65		SIO2%	D
F%	D	1.25									F%	D
H2SO4%		0.39	93.50	33.65		27.16	0.05		2.38		H2SO4%	
H2O%		0.40	6.50	39.37	100.00	30.87	4.38	100	61.8		H2O%	
RADIUM pCi/l			0.0	14.1		10.8	1.7	0.0	2.6		RADIUM pCi	

CHART #1

FIPR/PECO

FLOTATION FEED ACIDULATION PROCESS
FLOTATION FEED

DATE: 09/25/96
FREE SULFURIC = 0.5%

GIVEN:		GYP WASH	1	STAGE
ROCK WT D	40.13	CAO/P2O5	1.50	RATIO
EST (E)	95.14%	PROD FSUL	0.50	%
GYP P2O5%	3.01	GYP CI	0.03	%
PROD P2O5	27.03	GYP CS	0.50	%

PHOSPHATE FEED IS A BLEND OF 22.5% PEBBLE AND 77.5%FLOTATION FEED.

1) BLEND ANALYSIS = DRY BASIS.

2) BLEND % -150 = 1 % (SLIME)

3) SLUDGE 72.55 % SOLIDS, 1.43 % P2O5

	BLEND (1)D	SULFURIC (2)E	GYPSUM (3)F	EVAP (4)G	SLUDGE (5)H	SAND (6)I	WASH H2O (7)J	PRODUCT (8)K	ANALYSIS DELTA	
WEIGHT D	40.13	9.78	12.71		10.16	21.51	0	5.95	-0.43	WEIGHT D
CAO D	6.00		3.12		1.86	0.02		0.39	0.61	CAO% D
P2O5 D	4.01		0.57		0.20	0.03	0	3.81	-0.61	P2O5% D
FE2O3 D	0.19		0.03		0.02	0.00		0.10	0.03	FE2O3% D
AL2O3 D	0.21		0.03		0.02	0.00		0.15	0.01	AL2O3% D
MGO D	0.06		0.02		0.01	0.00		0.06	-0.03	MGO% D
SIO2 D	27.19		2.71		3.70	21.58		0.10	-0.91	SIO2% D
H2SO4	0.18	9.78	5.20		3.13	0.01	0	0.66	0.95	H2SO4%
H2O	0.17	0.72	6.29	8.34	3.84	4.49	29.70	8.15	-0.51	H2O%
WEIGHT W	40.3	10.5	19	8.34	14	26	29.7	14.10	-0.94	WEIGHT W
SP GR	1.923	1.828	2.003	1.000	1.000	1.603	1.000	1.275		SP GR
GYPSUM DIST.										
	ANALYSIS		62.65%		37.35%			2.56		
WEIGHT D										WEIGHT D
CAO% D	14.89		16.44		13.30	0.06		2.74		CAO% D
P2O5% D	9.94		3.01		1.43	0.11		27.03		P2O5% D
FE2O3% D	0.46		0.18		0.14	0.01		0.72		FE2O3% D
AL2O3% D	0.52		0.17		0.11	0.01		1.07		AL2O3% D
MGO% D	0.14		0.08		0.05	0.00		0.45		MGO% D
SIO2% D	67.46		14.28		26.46	83.00		0.71		SIO2% D
F% D	1.25									F% D
H2SO4%	0.44	93.10	27.36		22.35	0.05		4.69		H2SO4%
H2O%	0.42	6.90	33.08	100.00	27.45	17.26	100	57.8		H2O%
RADIUM pCi/l	16.1	0.0	10.9		9.8	0.1	0.0	2.6		RADIUM pCi/l

CHART #2

FIPR/PECO

FLOTATION FEED ACIDULATION PROCESS
FLOTATION FEED

DATE: 09/25/96
FREE SULFURIC = NEG

GIVEN:		GYP WASH	1	STAGE
ROCK WT D	96.88	CAO/P2O5	1.49	RATIO
EST (E)	71.03%	PROD FSUL	-.17	%
GYP P2O5%	1.19	GYP CI	0.07	%
PROD P2O5	23.84	GYP CS	0.54	%

PHOSPHATE FEED IS A BLEND OF 22.5% PEBBLE
AND 77.5%FLOTATION FEED.
1) BLEND ANALYSIS = DRY BASIS.
2) BLEND % -150 = 1 % (SLIME)
3) SLUDGE 69.6 % SOLIDS, 1.76 % P2O5

	BLEND (1)D	SULFURIC (2)E	GYPSUM (3)F	EVAP (4)G	SLUDGE (5)H	SAND (6)I	WASH H2O (7)J	PRODUCT (8)K	ANALYSIS (9)L	
WEIGHT D	96.88	17.47	27.00		16.70	57.13	0	14.44	-0.94	WEIGHT
CAO D	19.99		6.89		3.32	4.87		1.75	3.16	CAO%
P2O5 D	13.43		0.57		0.42	2.19	0	9.54	0.71	P2O5%
FE2O3 D	0.72		0.28		0.14	0.20		0.26	-0.16	FE2O3%
AL2O3 D	0.55		0.29		0.14	0.10		0.36	-0.34	AL2O3%
MGO D	0.20		0.11		0.05	0.03		0.15	-0.14	MGO%
SIO2 D	67.17		5.76		9.39	50.67		0.32	1.04	SIO2%
H2SO4		17.47	10.59		4.49	0.05	0	2.30	0.03	H2SO4%
H2O	0.40	1.23	21.00	8.34	7.30	2.87	63.40	25.56	-0.03	H2O%
WEIGHT W	97.5	18.7	48	8.34	24	60	63.4	40.00	-0.74	WEIGHT W
SP GR	1.923	1.828	2.003	1.000	1.000	1.603	1.000	1.275		SP GR
GYPSUM DIST.			67.45%		32.55%					
ANALYSIS								1.83	2.152152875	
WEIGHT D										WEIGHT D
CAO% D	20.50		14.35		13.85	8.11		4.37	3.06	CAO% D
P2O5% D	13.77		1.19		1.76	3.65		23.84		P2O5% D
FE2O3% D	0.74		0.59		0.58	0.34		0.65		FE2O3% D
AL2O3% D	0.56		0.60		0.57	0.17		0.91		AL2O3% D
MGO% D	0.20		0.22		0.20	0.05		0.38		MGO% D
SIO2% D	68.89		11.99		39.13	84.45		0.79		SIO2% D
F% D	1.25									F% D
H2SO4%	0.41	93.40	22.07		18.71	0.08		5.75		H2SO4%
H2O%	0.64	6.60	43.74	100.00	30.40	4.78	100	63.9		H2O%
RADIUM pCi/l		0.0	18.5		15.7	2.7	0.0	2.6		RADIUM pCi/l

CHART #3

8.4 RADIOACTIVITY COMPARISON

SAMPLE ID	pCi/l	% Ca
Flotation Concentrate	4.4	
Sand - 0.5% H2SO4 Run	0.10	0.06
Sand - 1.3% H2SO4 Run	1.70	1.25
Product Acid	2.60	2.50
Sand - NEG H2SO4 Run	2.70	9.78
Sludge - 0.5% H2SO4 Run	9.80	13.30
Sludge - NEG H2SO4 Run	15.70	13.85
Rock Blend #14	16.10	14.89
Gypsum - NEG Run	18.50	15.50
Gypsum - 0.5% H2SO4 Run	10.90	16.44
Sludge - 1.3% H2SO4 Run	10.80	16.89
Gypsum - 1.3% H2SO4 Run	14.10	21.79
Phosphate Pebble	45.10	43.65

8.5 PHOSPHORIC ACID IMPURITY COMPARISION OF PECO vs NEW WALES

	N. WALES	1.3	0.5	NEG
CAO	0.082	0.34	2.74	4.37
P2O5	27.87	24.69	27.03	23.84
FE2O3	1.09	0.73	0.72	0.65
AL2O3	1.12	1.03	1.07	0.91
MGO	0.51	0.47	0.45	0.38
SIO2	1.15	0.65	0.71	0.79
F	1.98	0	0	0
H2SO4		2.38	4.69	5.75
H2O		61.8	57.8	63.9
SP GR	1.34	2.6	2.6	2.6

7.6 APPENDIX

PECO VS. CURRENT BENEFICIATION PROCESS ECONOMICS

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PECO vs CURRENT BENEFICIATION PROCESS ECONOMICS

The PECO process is one that can make phosphoric acid from flotation feed material thus eliminating the losses associated with the flotation operation. This memorandum presents a comparison of the current beneficiation process and that required for the PECO process. This comparison indicates the following:

1. The current beneficiation process produces 789,412 tons of P205 in 1,717,346 tons of 66.71 BPL and 1,158,400 tons of a 50% BPL pebble rock for an annual cost of $41,499,000.

2. The same beneficiation plant, by-passing the flotation operation produces the same 789,412 tons of P205 in 8,624,326 tons of 18.18% BPL product and 862,433 tons of a 50% BPL pebble rock for an annual cost of $24,555,000.

3. The current plant consumes 16.6 million tons of matrix to produce the 789,412 tons of P205, while the PECO process consumes only 12.36 million tons of matrix.

4. A savings of $16,944,000 is saved by the PECO process, FOB the beneficiation plant, when producing the same amount of P205.

5. The PECO operation requires that 9,486,759 tons of product be transported to the phosphoric acid plant as compared to 2,875,792 tons for the current operation. This cost has not been estimated in this report since some companies have their own railroad, may desire to transport the material hydraulically, may be close to the phosphoric acid plant, or can work out an arrangement whereby the rail costs for the shipping of the finished product may include the transportation of the intermediate product.

6. When the BPL content of the tails from the current process rise to 8% BPL the savings of the PECO process increases to an estimated $23,144,663 per year.

7. Should the BPL of the matrix feed drop below the assumed 17.45% the advantage of the PECO process will increase significantly.

8. Approximately 3 million gallons of deep well water are consumed each day by the current beneficiation plant. Since the PECO process needs much less matrix than the current process the deep well water requirement will decrease to 2 1/4 million gallons per day.

9. Slime ponds will be reduced by one-quarter due to the decreased amount of matrix required for a given P_2O_5 production.

10. Since the PECO process uses less matrix for a given production of P_2O_5, the reserve life of the Florida deposit will be extended by 25%.

EVALUATION BASIS

This comparison is based on supplying the phosphoric acid plant with the a normal phosphate rock of 66.71% BPL and the equivalent amount of a 50% BPL pebble rock as compared to supplying the same amount of P2O5 in the form of a flotation feed of only 15.00% BPL and its equivalent pebble product. Since the amount of slime and the amount of pebble product contained in the matrix is the same in either case, these items will be treated as constants. It will be assumed that 20% of the matrix P2O5 will be lost in the slime and that 20% of the P2O5 in the matrix will be contained in the 50% BPL pebble product. This will allow this comparison to be directed toward the flotation feed.

The PECO process requires only a flotation feed as a phosphatic raw material, therefor the cost of the flotation operation will be deducted from the total beneficiation plant costs.

CONVENTIONAL BENEFICIATION PROCESS

The conventional beneficiation process begins with clearing the overburden followed by mining the matrix with large draglines and pumping the ore to the beneficiation plant for processing. Processing begins with a washer operation consisting of scalping, separation of the pebble, attrition scrubbing, sizing and desliming. Great care must be taken to remove all slimes from the flotation feed or high reagent costs will be encountered in the flotation circuit. The washed pebble maybe considered product or may be added to the concentrate as product while the slimes are pumped to a slimes holding pond. For this evaluation the pebble product is added to the product. The sized material is sent to the flotation plant as a coarse or fine flotation feed. This sizing operation is not required for the PECO process. In the flotation plant the sand is separated from the phosphate by flotation. The sand tailings are discharged as a waste material and the phosphate product is sent to drain bins where the water is drained off and dropped into rail cars for transport to the phosphoric acid plant.

Basic data for this economic evaluation was obtained from The Fertilizer Institute Production Cost Survey of December 31, 1992.

This report indicates that the weighted average annual production of a beneficiation plant during 1992 was 2,585,616 tons of 66.71% BPL product. This production was achieved by the mining and processing of 8,765,000 cubic yards of matrix. No information is given in this report about the overall recovery or cost of the flotation operation.

The flotation operation basically takes the flotation feed and separates it into a phosphate product and silica tails. Little information is available on the split of these two materials in the report by TFI, therefor a mathematical model was constructed to relate these streams. This model was used to determine the overall recovery of P205 values as a function of flotation feed BPL, tails BPL, product BPL and quantity of each stream. Table 1 is a plot of % recovery of the P205 in the flotation feed as it is affected by BPL of the feed, BPL of the tails and BPL of the product.

This model indicates that when a flotation plant operates on a feed of 15% BPL and a tailings of 6% BPL, 1,717,346 tons of a 66.71% BPL product is obtained and 9,867,113 tons of an 6% BPL tailings are produced for each 11,584,459 tons of 15% BPL feed. A phosphate recovery of 65.9% is expected. Assuming a slime BPL content of 20% by weight of the matrix and the production of 1,158,446 tons of a 50% BPL pebble containing 20% of the matrix P205 this operation will require the mining and transport of 16,599,091 tons of 17.45% BPL matrix. The annual cost of this operation is $41,499,000. The annual cost of the benefication plant without the flotation plant, producing the same amount of P2O5 to be delivered to the pac plant is $24,555,000. The annual savings, FOB the plant gate is estimated to be $16,944,000.

The amount of BPL contained in the tails is very important in this calculation. Should the tails BPL go up to 8% BPL, the over all recovery will drop from 65.9% to 53.0%. This will increase the amount of matrix required to produce the same amount of product from 16,599,100 tons to 19,079,400 tons, an increase of 2,480,300 tons per year or about 15%%. The annual savings of the PECO process FOB the plant gate will then increase to $23,144,600.

Similar increases in the current method production costs will be encountered should the matrix BPL content drop below the 17.45% used as the base case.

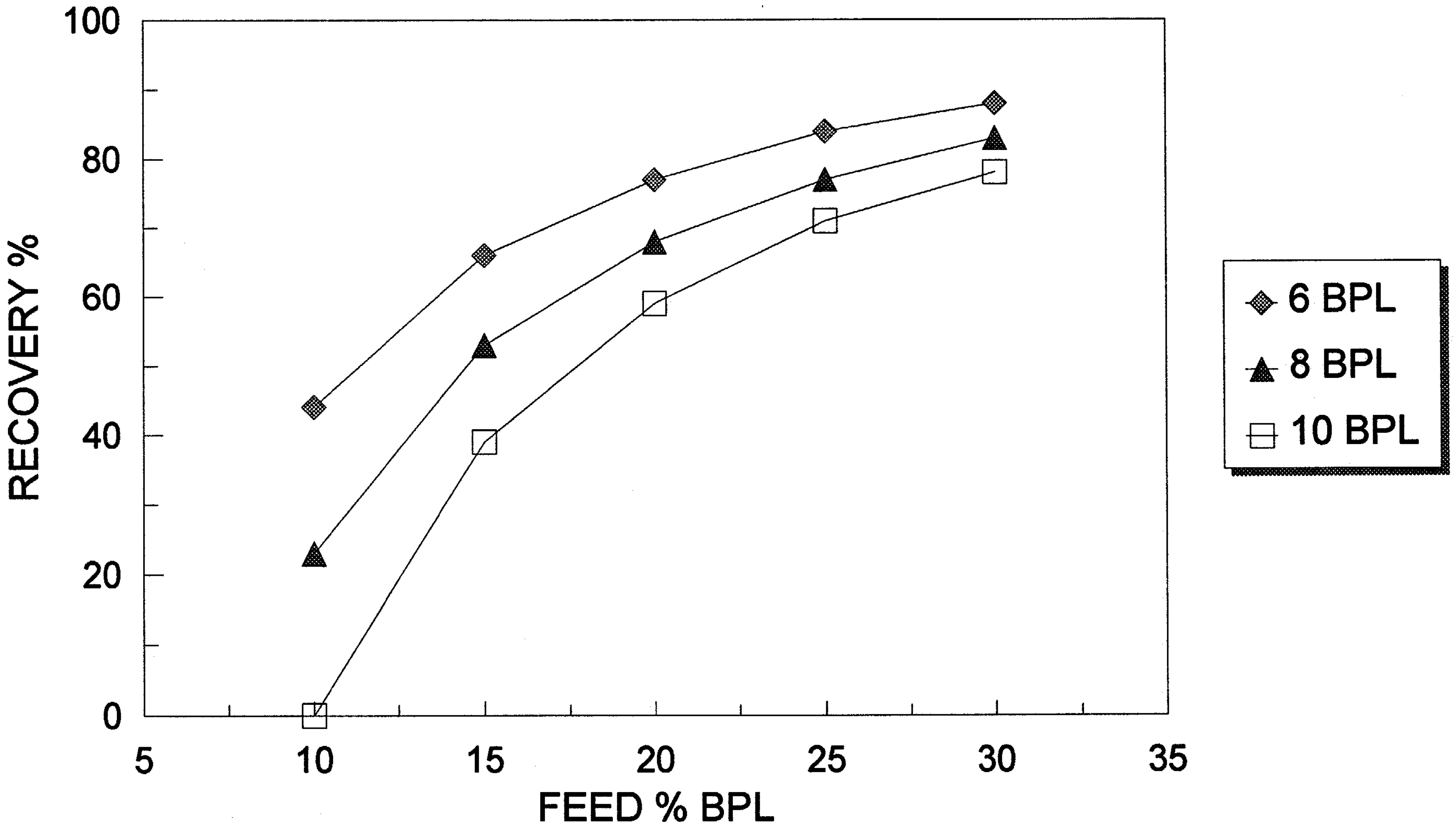
PECO PROCESS

Since this evaluation concerns itself with the cost of the feed to the flotation plant it is necessary that the cost of the flotation operation be deducted from the current total production costs. To be able to do this it was necessary to use the excellent report by Zellars-Williams issued in June of 1978 entitled, "Evaluation of the Phosphate Deposits of Florida Using the Minerals Availability System". Included in this report is a breakdown of the production cost by mine, washer, flotation, product storage and waste disposal.

Several of the tables used from that report are appended to this report for reference. These factors were used to subtract the cost of the flotation operation from the total production cost given in the TFI report of 1992. Table 3 shows what factors were used for each category given in the TFI report to arrive at the cost of operating the beneficiation plant without the flotation operation. While each of these factors may be debated, they are presented so that the reader may substitute other factors to see the effect of the change.

PHOSPHATE RECOVERY

vs FEED & TAILS % BPL



DISCUSSION

This analysis uses the amount of P2O5 supplied to an average phosphoric acid plant as a basis. Current beneficiation plants supply 2,585,617 tons of 66.74% BPL rock and 1,158,446 tons of a 50% BPL pebble rock to the plant while the PECO process requires 8,624,326 tons of a 15% BPL flotation feed and 862,433 tons of a 50% BPL pebble rock for the same P2O5 capacity. Surprisingly, when the PECO process is used, the amount of matrix which has to be mined and processed by the beneficiation plant drops from 16,599,100 tons to 12,357,600 tons or a reduction of 4.2 million tons of matrix (25%) while producing the same amount of feed to the phosphoric acid plant.

The total operating cost of $41,500,000 for the current operation drops to $24,555,000 per year, for the PECO process, a savings of $16,950,000 per year, a reduction of 40.8% in the cost of supplying the phosphoric acid plant with its raw material. This is a significant drop in the cost of the phosphate feed to the phosphoric acid plant.

The cost of transporting this increased tonnage to the phosphoric acid plant will be sizable and is difficult to estimate, at this time, since some companies have their own railroad, or may desire to transport this material hydraulically or can work out an arrangement whereby the rail costs associated with the shipping of the finished product may include the intermediate product. This report presents an indication of the savings in out right production cost may be achieved and the affect it will have on the life of the phosphate reserve.

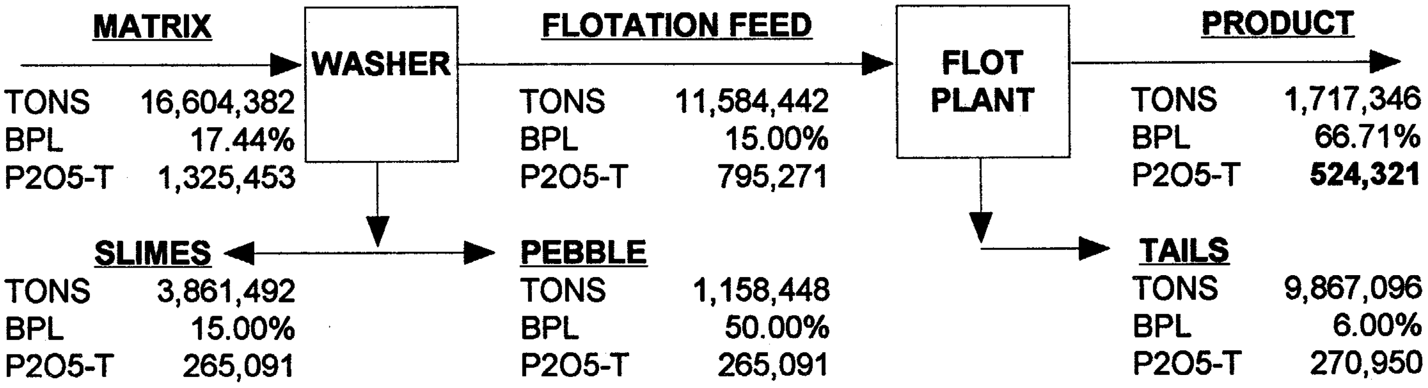
Current beneficiation processes use about 3 million gallons of deep well water every day. Since the PECO process uses only 74.4% of the matrix, one could conclude that the deep well water consumption would drop by 3/4 million gallons per day. When the BPL of the tails goes up to 8%, or the BPL of the matrix drops from the assumed 17.45%, this reduction will be in the range of 1.0 million gallons per day.

The PECO process does not require ground phosphate rock. This results in a savings of $4.91 per ton of P2O5 in the cost of grinding.

The silica produced by the PECO process is clean since it has been acid washed. It certainly can be used in cement, concrete blocks and many other construction products such as sand-lime brick. If it can be sold for $1.00 per ton, a new profit center can be established which could decrease the cost per ton of P2O5 by $15.05. No credit has been taken for this new profit center which could generate a profit of $7,890,000 per year.

PECO vs CURRENT BENEFICIATION COMPARISON

CURRENT PROCESS 6% TAIL



MATRIX

TONS	16,604,382
BPL	17.44%
P2O5-T	1,325,453

FLOTATION FEED

TONS	11,584,442
BPL	15.00%
P2O5-T	795,271

PRODUCT

TONS	1,717,346
BPL	66.71%
P2O5-T	**524,321**

SLIMES

TONS	3,861,492
BPL	15.00%
P2O5-T	265,091

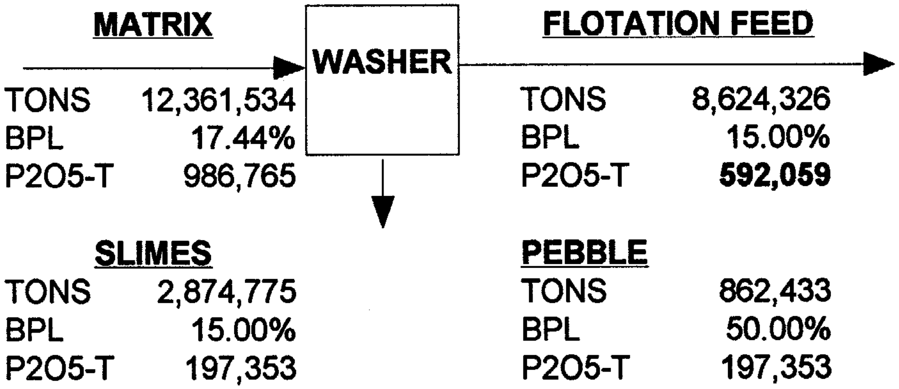
PEBBLE

TONS	1,158,448
BPL	50.00%
P2O5-T	265,091

TAILS

TONS	9,867,096
BPL	6.00%
P2O5-T	270,950

PECO PROCESS FEED



MATRIX

TONS	12,361,534
BPL	17.44%
P2O5-T	986,765

FLOTATION FEED

TONS	8,624,326
BPL	15.00%
P2O5-T	**592,059**

SLIMES

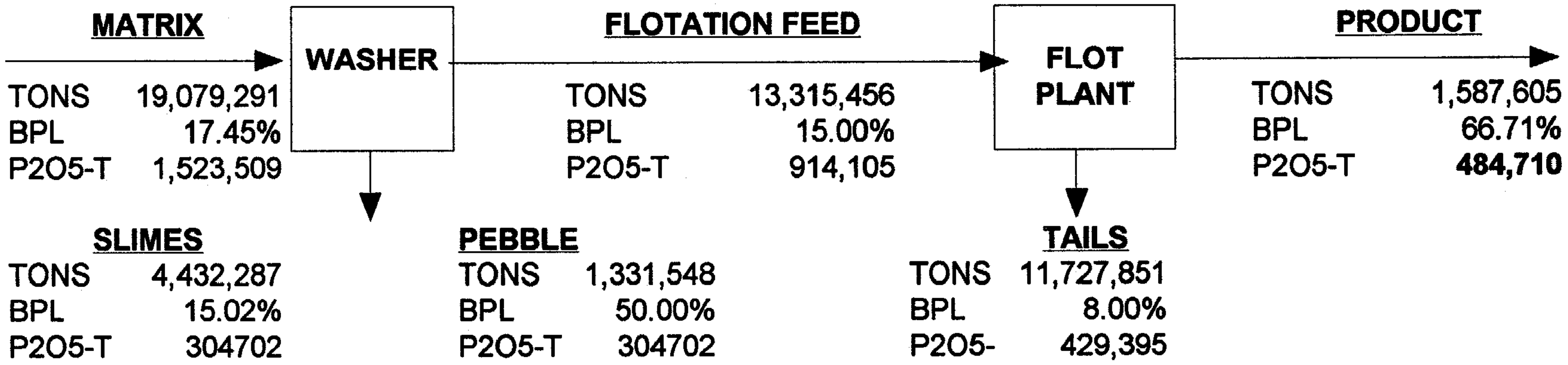
TONS	2,874,775
BPL	15.00%
P2O5-T	197,353

PEBBLE

TONS	862,433
BPL	50.00%
P2O5-T	197,353

PECO vs CURRENT BENEFICIATION COMPARISON

CURRENT PROCESS 8% TAIL



MATRIX

TONS	19,079,291
BPL	17.45%
P2O5-T	1,523,509

FLOTATION FEED

TONS	13,315,456
BPL	15.00%
P2O5-T	914,105

PRODUCT

TONS	1,587,605
BPL	66.71%
P2O5-T	**484,710**

SLIMES

TONS	4,432,287
BPL	15.02%
P2O5-T	304702

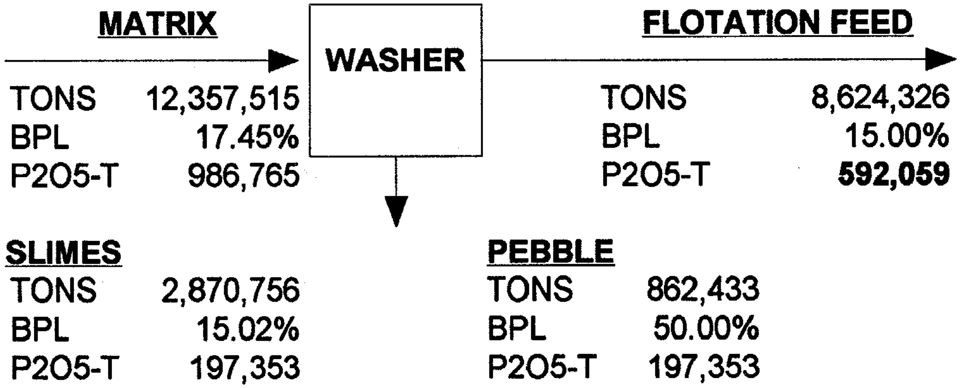
PEBBLE

TONS	1,331,548
BPL	50.00%
P2O5-T	304702

TAILS

TONS	11,727,851
BPL	8.00%
P2O5-	429,395

PECO PROCESS FEED



MATRIX

TONS	12,357,515
BPL	17.45%
P2O5-T	986,765

FLOTATION FEED

TONS	8,624,326
BPL	15.00%
P2O5-T	**592,059**

SLIMES

TONS	2,870,756
BPL	15.02%
P2O5-T	197,353

PEBBLE

TONS	862,433
BPL	50.00%
P2O5-T	197,353

1992 PRODUCTION COST PER TON FOB MINE
BASIS: 2,585,616 TONS PER YEAR

			6% BPL TAILS		
		TOTAL	MINE	FLOT	FLOT FACTOR
1	ELECTRICITY	$2.37	1.849	0.521	22.00%
2	REAGENTS	0.83	0.000	0.830	100.00%
3	SEVERANCE TAX	1.57	1.570	0.000	0.00%
4	LAND RECLAIMATION	0.58	0.580	0.000	0.00%
5	DAM BUILDING	0.4	0.400	0.000	0.00%
6	EMPLOYMENT COSTS - OPERATIONS	1.67	1.169	0.501	30.00%
7	MAINTENANCE - CONTRACT	0.45	0.392	0.059	13.00%
8	MAINTENANCE - LABOR & OVERHEAD	1.31	1.140	0.170	13.00%
9	MAINTENANCE - MATERIALS	1.59	1.383	0.207	13.00%
10	OPERATING SUPPLIES	0.58	0.406	0.174	30.00%
11	OPERATING SERVICES	0.73	0.511	0.219	30.00%
12	AUTOS AND TRUCKS	0.08	0.080	0.000	0.00%
13	INSURANCE	0.07	0.046	0.025	35.00%
14	TAXES	0.36	0.234	0.126	35.00%
15	MINE OVERHEAD	1.33	1.330	0.000	0.00%
16	OTHER	0.06	0.039	0.021	35.00%
17	DEPRECIATION	1.26	0.819	0.441	35.00%
18	DEPLETION/ROYALTIES	0.81	0.810	0.000	0.00%
		$16.05	$12.76	$3.29	
	TOTAL COST PER YEAR '000 DOLLARS	$41,499	$32,984	$8,515	

		CURRENT PROCESS		PECO
		6% TAILS	8% TAILS	PROCESS
TONS P2O5 IN PRODUCT		789,412	789,412	789,412
TONS MATRIX REQUIRED		16,599,091	19,079,407	12,357,587
TONS PRODUCT PRODUCED		2,585,616	2,585,616	9,486,759
PRODUCT % BPL		66.71%	66.71%	18.18%
TOTAL COST PER TON OF MATRIX PROCESSED		$2.50	$2.50	$2.50
TOTAL ANNUAL COST	($,000)	$41,499	$47,700	$24,555
WASHER ANNUAL COST	($,000)	$32,984	$37,912	$24,555
FLOTATION PLANT ANNUAL COST	($,000)	$8,515	$9,788	0
COST PER TON P2O5		$52.57	$60.42	$31.11
MINE & BENEFICIATION PLANT ANNUAL SAVINGS		$0.00	($6,201,001)	$16,943,662
ROCK GRINDING COST ($1.50/TON ROCK)		$3,878,424	$3,878,424	$0.00
CREDIT FOR SALE OF CLEAN SAND				NONE TAKEN
CREDIT FOR 25% INCREASE IN RESERVE				NONE TAKEN
NET SAVINGS		$0.00	($6,201,001)	$20,822,086
NET SAVINGS DOLARS PER TON P2O5				$26.38

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LABOR COST DISTRIBUTION

(By area, as % of total labor cost)

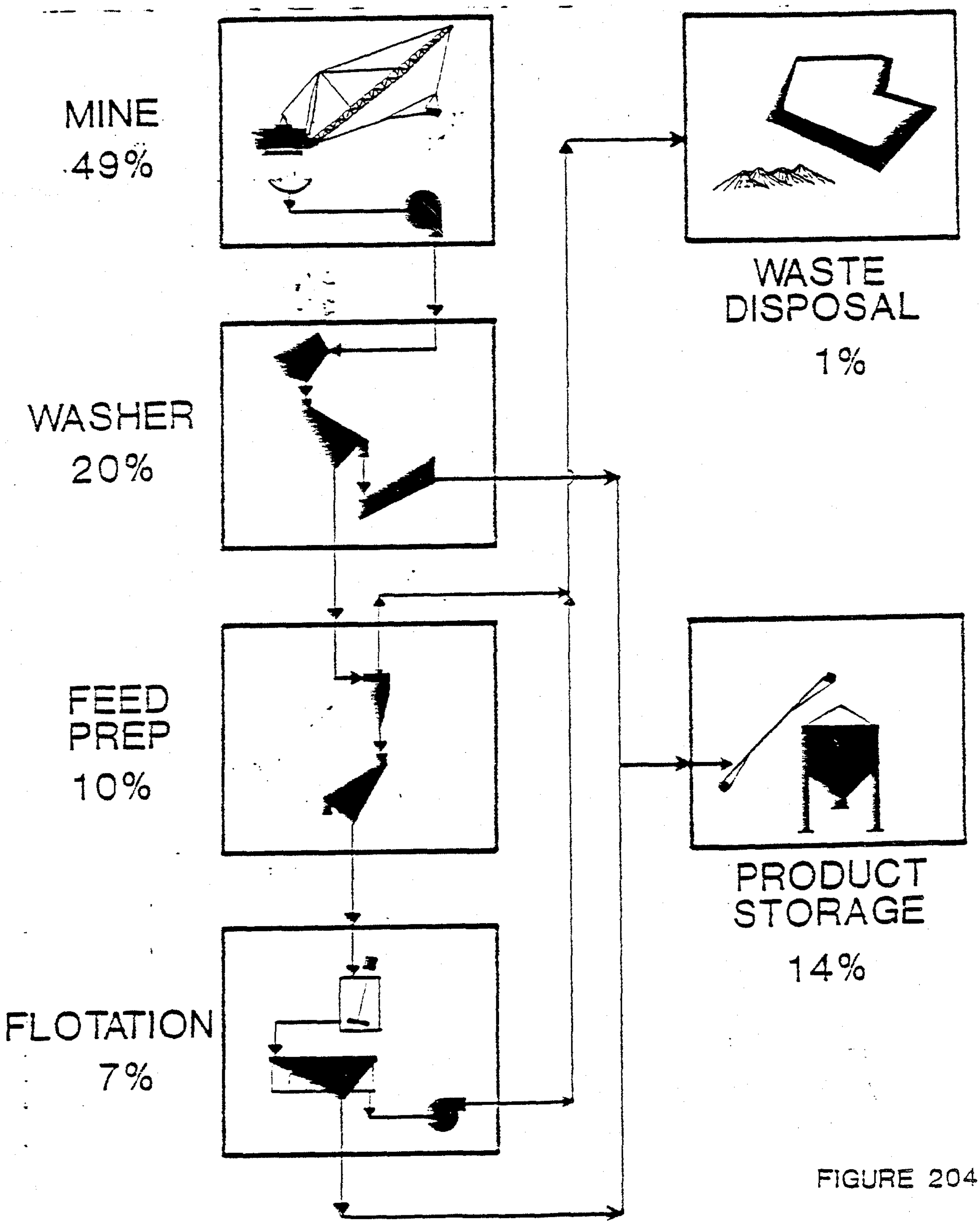

FIGURE 204.3

OPERATING COST, BY AREA

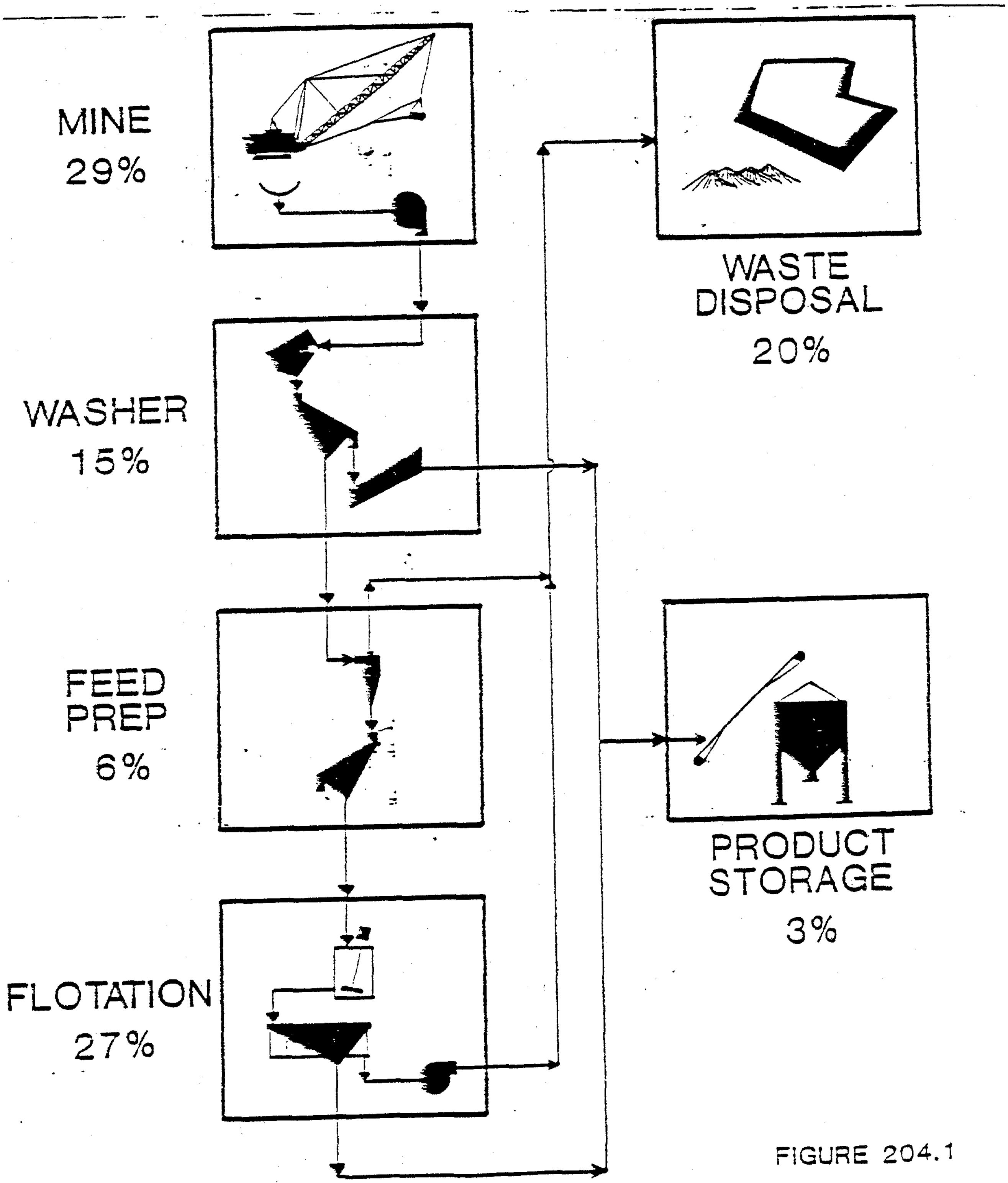

FIGURE 204.1

ELECTRICAL POWER COST

(By area, as % of total power cost)

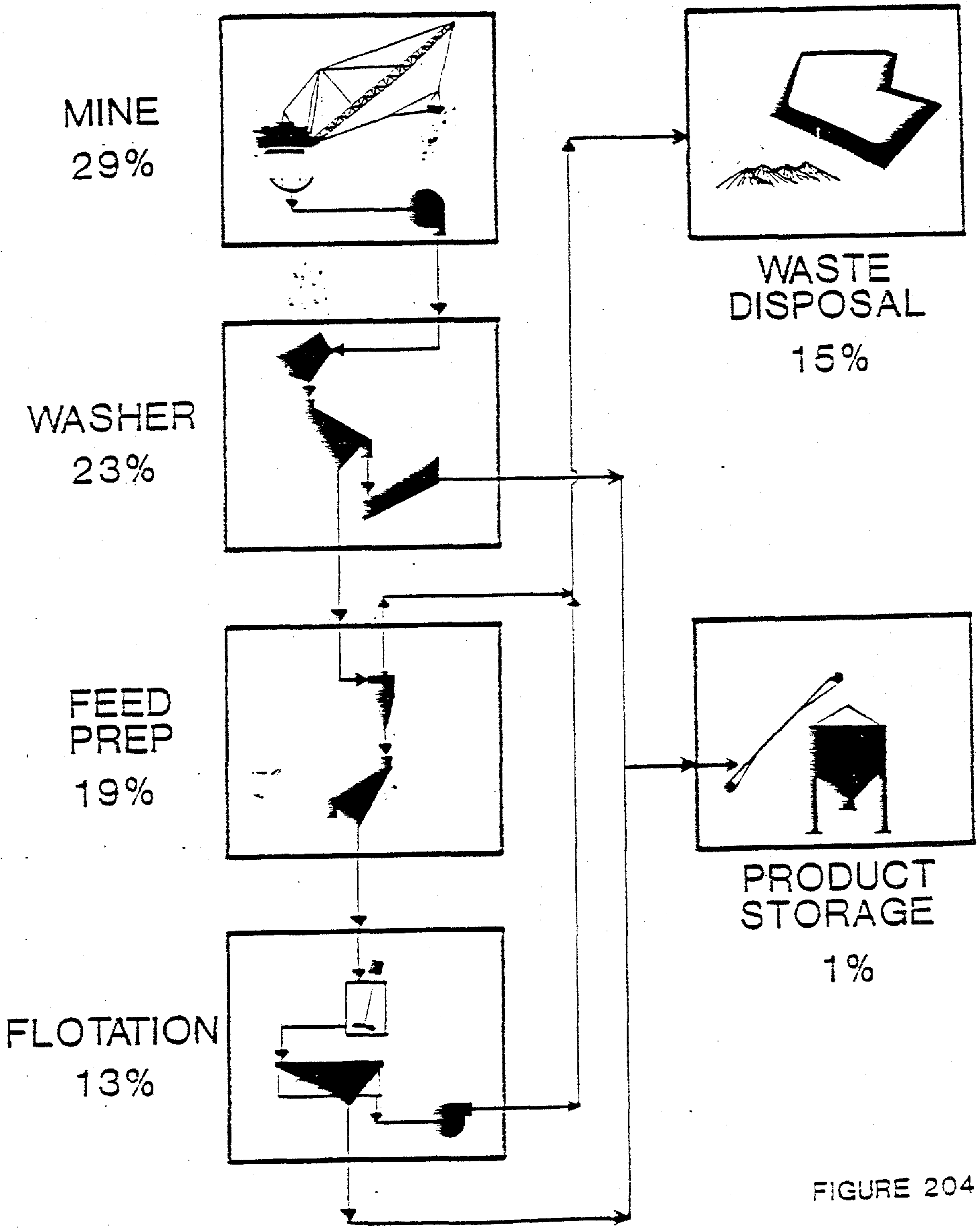

FIGURE 204.2

MAINTENANCE SUPPLIES COST

(By area, as % of total maintenance supplies)

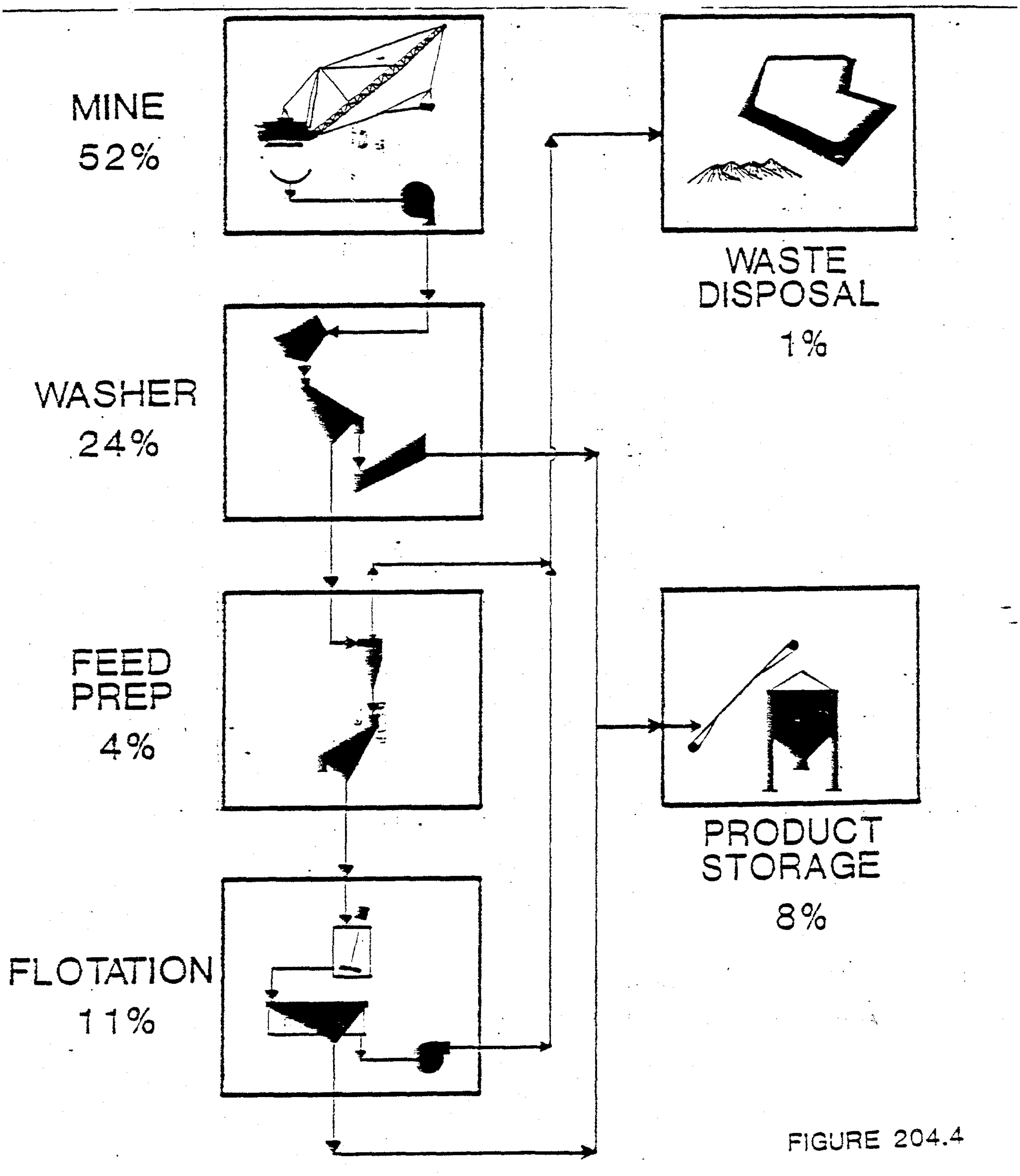

FIGURE 204.4

PERCENT COST BY AREA

WASHING	23
FEED PREP	20
FLOTATION	22
REAGENT	3
WET ROCK STORAGE	15
OFFSITES	17
	100%

FIGURE 206.6

TYPICAL OPERATION

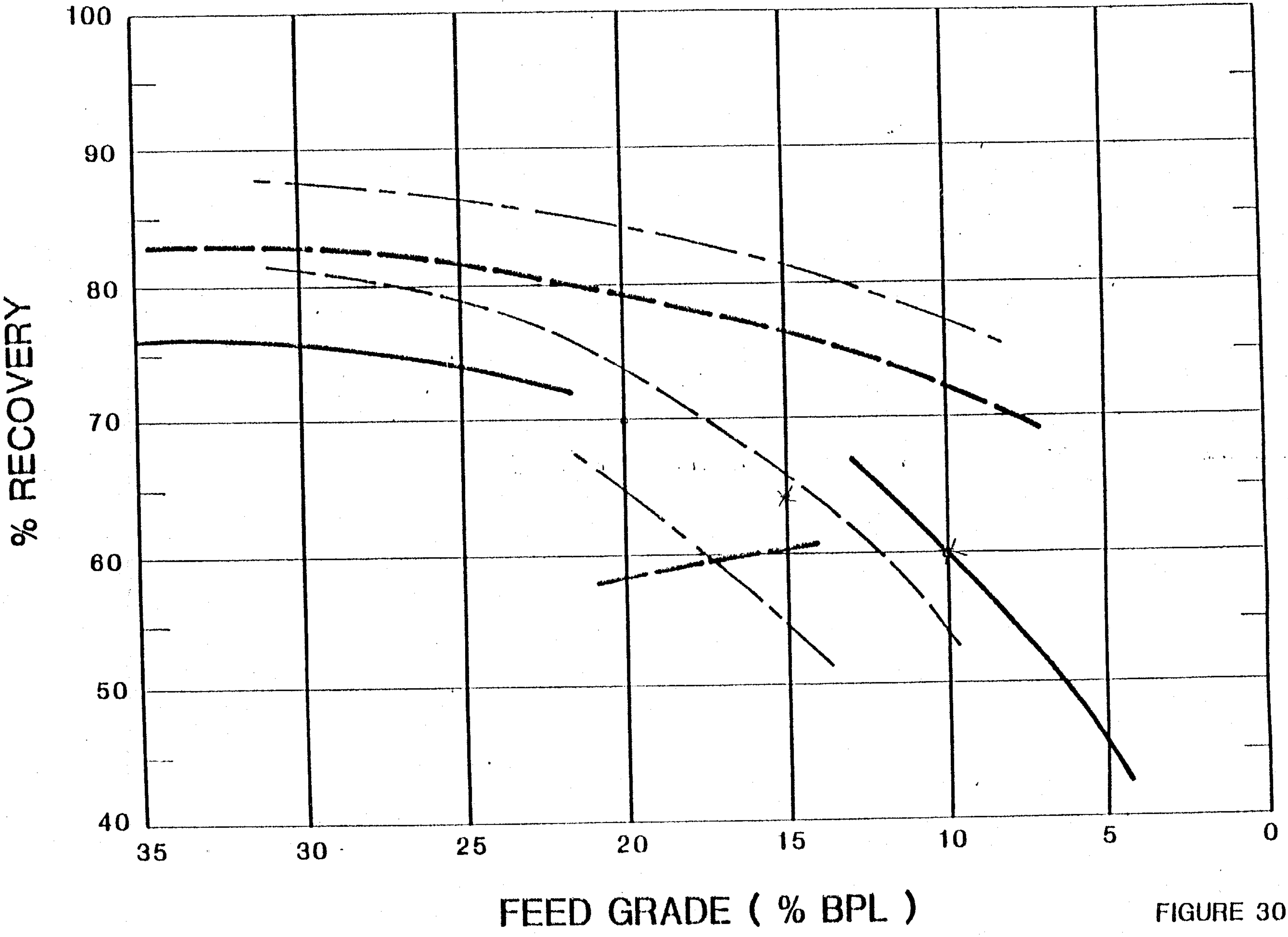

FIGURE 303.2