PECO FLUORINE REMOVAL PROCESS PILOT PLANT

By
Jack M. Nagy, P. Eng.
Process Engineer
&
Stephen W. Hilakos
Manager of Technical Services

SF Phosphates Limited Company
515 South Highway 430
Rock Springs, Wyoming

Prepared for Presentation at

AICHE Clearwater Convention May 23, 1998

Central Florida Section
American Institute of Chemical Engineers

ABSTRACT

A process for converting the fluorine in fluosilicic acid (FSA) into calcium fluoride has been patented by Phosphate Engineering and Construction Company of Lakeland, Florida. SF Phosphates Limited Company of Rock Springs, Wyoming, has been investigating the use of a modified "PECO" process as a long term solution to reducing the ambient fluoride levels at the Rock Springs plant.

The process reacts the fluosilicic acid generated in the phosphoric acid evaporator scrubbers with phosphate rock. The fluorine is converted to calcium fluoride, a non-volatile compound. The calcium fluoride is an insoluble compound in the gypsum stack/pond water system. A byproduct of the process is a weak phosphoric acid solution. However, the phosphoric acid is defluorinated and has less metal impurities then the phosphoric acid from the conventional phosphoric acid production process.

A one-tenth scale pilot plant was built in 1997 to collect design and process information on the process so that the technical and economic feasibility of the process could be determined. This paper will discuss the operation and results to date of the pilot plant.

BACKGROUND

The Phosphate Engineering & Construction Company, Inc. (PECO) of Lakeland, Florida, has a patent titled "Process For The Production of Phosphoric Acid and Calcium Fluoride", dated July 2, 1996.

The basic chemistry of the process is:

$$3Ca_3(PO_4)_2 + 3H_2SiF_6 + 6H_2O \rightarrow 3SiO_2 + 9CaF_2 + 6H_3PO_4$$

The reaction is slightly exothermic at –8.68 kcal/mole H2SiF6 reacted.

Two other reactions that play a major part in the process are:

$$3CaCO_3 + H_2SiF_6 \rightarrow SiO_2 + 3CaF_2 + 3CO_2 + H_2O$$

$$3CaO + H_2SiF_6 \rightarrow SiO_2 + 3CaF_2 + H_2O$$

A couple of concerns about the process initially arose. PECO's testwork and patent were based on utilizing fluosilicic acid (FSA) strengths of 20-25%. The FSA available at SF Phosphates would be around 10%. The test work was also done at a reaction vessel temperature of 99 °C. Because of the altitude at Rock Springs, Wyoming, this reaction temperature would not be readily achievable. Laboratory scale test work was done at the PECO facility in Lakeland, Florida in December, 1996 to address these concerns. This work confirmed that the reaction would proceed with FSA strengths in the range of 5 - 15% and at temperatures of 90.5 - 93 °C (195 - 200 °F).

PILOT PLANT DESCRIPTION AND RESULTS

A pilot plant, one tenth the size of a full scale plant, was constructed in the spring of 1997. (Refer to the attached schematic.) Both the rock slurry and FSA are batched over once per shift. The rock slurry used is typically 68% solids. The pilot plant has a separate holding tank for the rock slurry and the FSA. The FSA is preheated to 88 °C in a graphite (Diabon F100) plate heat exchanger and enters the reactor under the liquid level. Due to the temperature limits on the graphite, we cannot use direct 35# steam on the plates. We are using a water circulating loop with direct 35# steam injection to heat the FSA.

The reactor is a 500 gallon, 316 SS, steam jacketed vessel. It has a mixer with two 20 inch turbine blades running at 175 rpm. The reactor size was chosen to give a 25 minute retention time at the maximum pilot plant flow rates. The reactor is maintained at 90.5 °C with 35# steam. The reactor then overflows to a holding tank.

Table #1 summarizes some recent test data. The %FSA feed range tested varied from 10 – 16.5% FSA. We have operated with FSA strength as low as 5% with good F conversion. The corresponding product acid %P2O5 ranged from 6 – 9%. Note that this is the thickener overflow product acid, which includes the dilution for the flocculent addition to the thickener. The key element we have found so far appears to be the Ca/F ratio of the feeds. Graphs #1 - #3 show the effect of the Ca/F ratio on the F conversion and the reactor P2O5 recovery. The indication is that there will need to be a compromise between F conversion and P2O5 recovery.

The product acid typically has less metal impurities then conventional phosphoric production acid. The third column in the following table is from analysis of a PECO acid sample that was concentrated in the lab.

	TYPICAL PECO ACID	CONCENTRATED PECO ACID	CONVENTIONAL 28% ACID
%P2O5	6.55	28.41	25.72
PPM Al	0.63	<0.1	3224
PPM Ca	5624	15900	1552
PPM Cr	3.12	14.2	271
PPM F	1580	1590	20800
PPM Fe	98.8	341	1584
PPM Mg	657	2400	3440
PPM Na	859	3400	518
PPM Si	429	289	4160

A cyclone and a thickener were added to the pilot plant in the fall of 1997. The cyclone was added to test recycling unreacted rock back to the reactor to improve P2O5 recovery. The cyclone is a three inch Technequip, Model H3CL-AST9 neoprene lined, with a one half inch apex and three quarter inch vortex. In order to utilize the weak acid back in the conventional process, the solids need to be removed. The thickener was added because beaker tests indicated that the reactor overflow could be flocculated to allow it to settle in a thickener. The thickener installed is a six foot diameter by five foot high vessel, 316 SS.

The reactor overflow goes to a pumptank with a mixer. From there it is fed to the cyclone. The cyclone underflow can be recycled to the reactor or sent to the holding tank for disposal. The cyclone overflow either recycles to the reactor to provide level control for the pumptank, or is forwarded to the thickener.

The thickener overflow goes to the product acid holding tank. The thickener underflow goes to the holding tank for disposal. To date we have used a Nalco 8108 coagulent and a Nalco 7139 flocculent to give a clear thickener overflow. Graph #4 gives reactor P2O5 recovery verses the Ca/F feed ratio, with and without the cyclone operating. Also on the graph is a theoretical P2O5 recovery line. The indication is that the cyclone does not help improve the P2O5 recovery.

The pilot plant is controlled by a Honeywell Scan3000 system. The system utilizes a Modicon PLC and PC based graphical user interface. In addition to the control and alarming for the process, it provides process trends and printouts of the control screens.

One of the key items for getting a good conversion of H_2SiF_6 to CaF_2 is to have the correct Ca/F ratio of the reactor feed. The control system was set up to accomplish this. Mass flow meters were used for both the rock slurry and FSA feed to the reactor. The percent F of the FSA is analyzed and input into the computer each time a new batch of FSA is received. Similarly, a new analysis for the rock slurry percent Ca is also input each time a new batch of rock is received. Based on the desired Ca/F weight ratio input into the computer, the computer utilizes the above analyses and calculates the required rock mass flow setpoint based on the current FSA flow.

FUTURE PLANS

Pilot plant testing will continue until June, 1998. At that time the economics of the process will be evaluated.

A SUMMARY OF ROCK SPRINGS' FLUORIDE CONTROL – WHY PECO

SF Phosphates' Rock Springs site is the newest U.S. phosphate plant and was permitted with some of the most restrictive fluoride regulations in the U.S. Wyoming fluoride standards cover three plant classifications and four time intervals for fluoride concentration averaging. The SF site is required to continuously monitor ambient air fluoride concentrations and report average ambient air concentrations based on 12 and 24 hour intervals and 7 and 30 day rolling average intervals. The Rock Springs site did not meet the compliance standards in 1994, 1995, and 1996.

Rock Springs Compliance History

1994 – First violations of ambient air quality
Downday wash procedures and cooling tower emissions were targeted as suspect

1995 – High ambient air fluoride concentrations were observed during the annual plant turnaround. An isolated 30 acre area of concentrated pond water was targeted as the source of emissions.

1996 – Drying process gypsum identified as a major source of fluoride emissions.

1997 – Site maintained compliance by maintaining wet stack interior surface, surface limimg of exterior static surfaces, sub-surface gypsum deposition, and minimizing gypsum dike construction during high ambient temperature periods.

1998 – Plans are to repeat techniques that were successful in 1997.

Fluoride Chemistry – Why Rock Springs is Unique and Anticipated effects of PECO

Climate Conditions – Hot, Dry Summer Periods with low Atmospheric Pressure

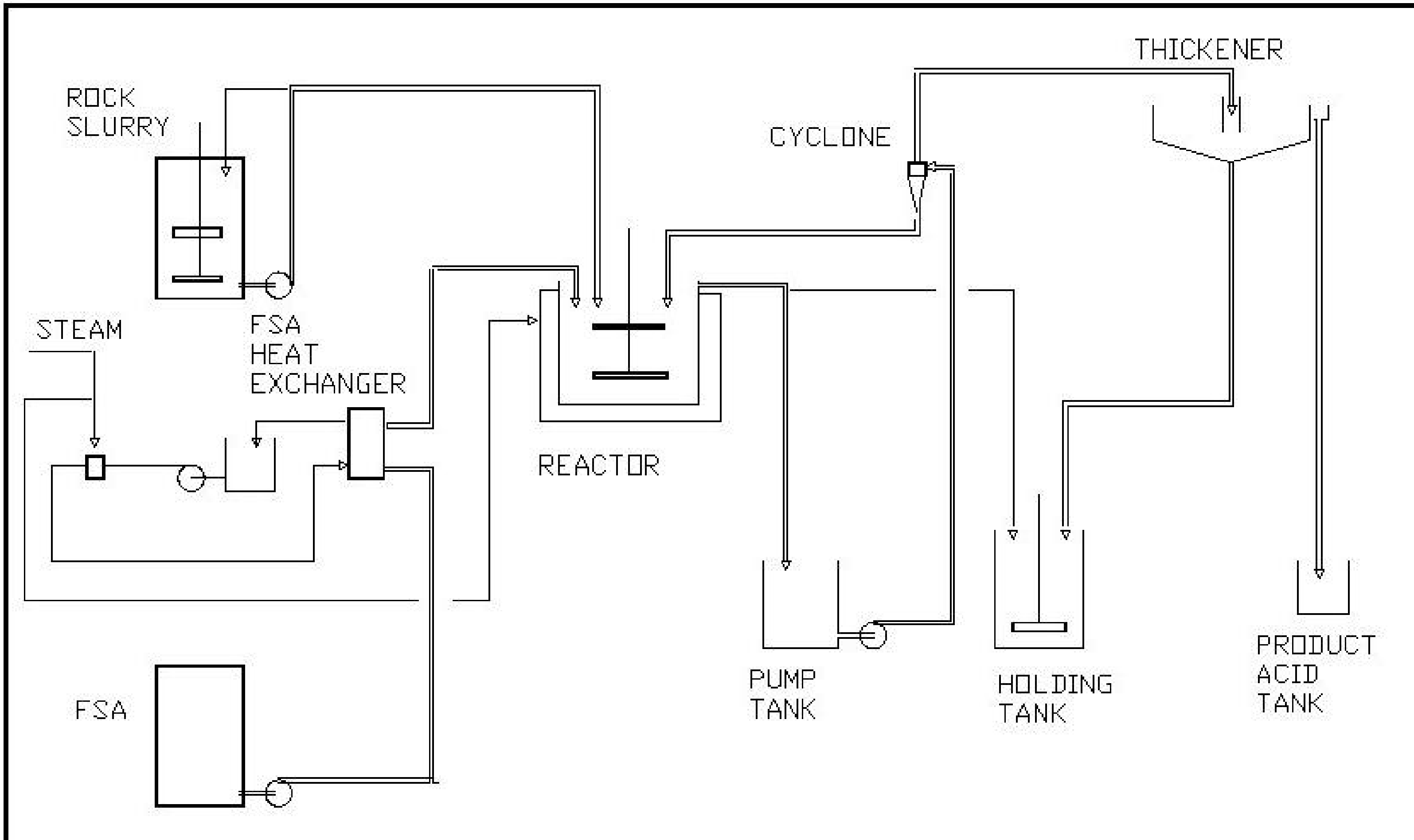
Physical Conditions – First lined gypsum stack, No water outfalls
New stack with very little height, low water percolation

Chemical Conditions – No Ammonia additions to pond water (Gran. Scrubbers)
Rock contains lower levels of Na and K

Fluorine Material Balance – Where the fluorine goes

Pore water within the Gypsum Stack
Non-soluble calcium compounds
Sodium and Potassium salt precipitates
Granular and Liquid products

Theoretical effects of PECO on the Fluorine Material Balance



REFERENCE DRAWINGS	REVISIONS	PECO PILOT PLANT	SCALE N	SF Phosphates Limited Company
		NN		A Utah Limited Liability Company
		COMPUTER NAME		ROCK SPRINGS, WY.

TABLE #1 PECO TEST SUMMARY

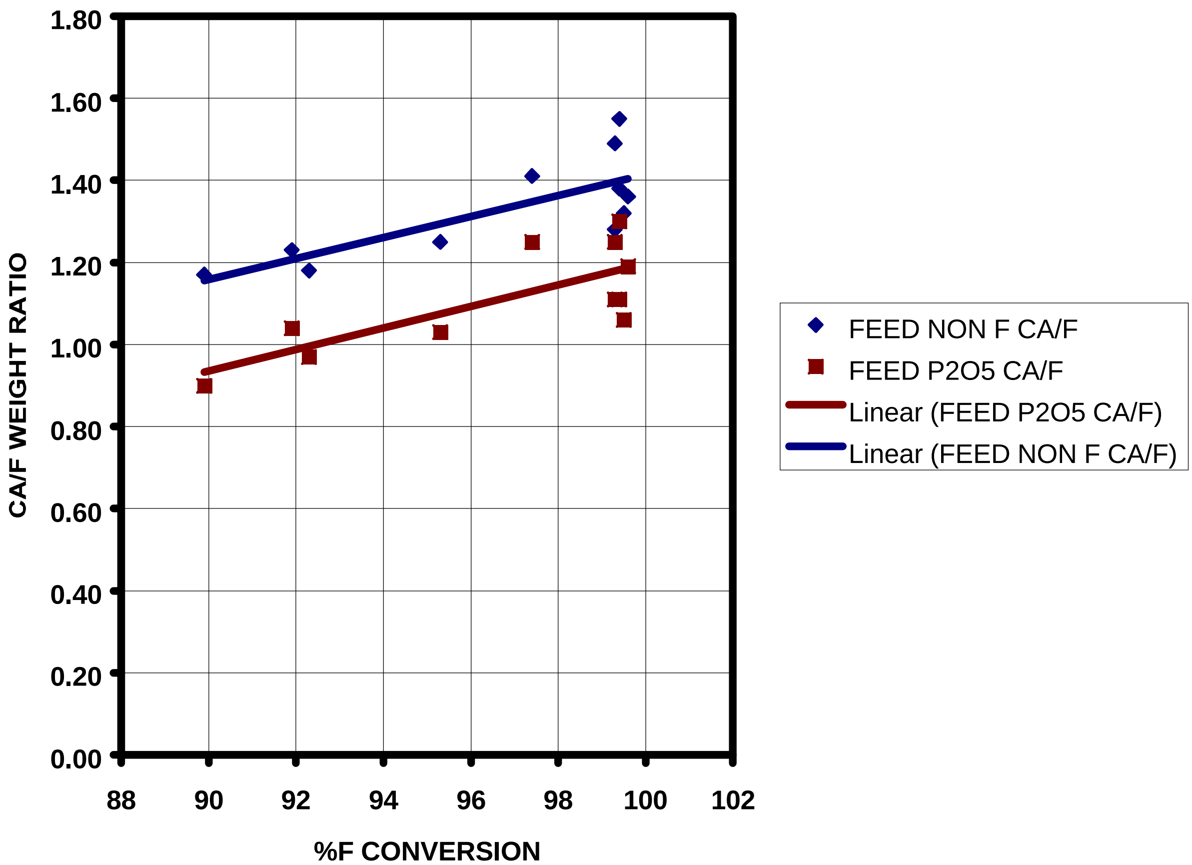
NO CYCLONE OPERATING

	98-01-30	98-02-02	98-02-16	98-02-20	98-03-19
% FSA FEED	12.1	9.95	16.56	12.89	12.77
% P2O5 PRODUCT (THICKENER OVERFLOW)	7.8	6.15	8.89	7.86	6.93
FEED NON F CA/F WEIGHT RATIO	1.55	1.49	1.17	1.25	1.38
FEED P2O5 CA/F WEIGHT RATIO	1.30	1.25	0.90	1.03	1.11
F CONVERSION TO CAF2	99.4	99.3	89.9	95.3	99.4
REACTOR P2O5 RECOVERY	68.7	65.8	81	80.7	69
P2O5 RECOVRED TO THICKENER OVERFLOW	64.2	60.4	72.8	73.7	63

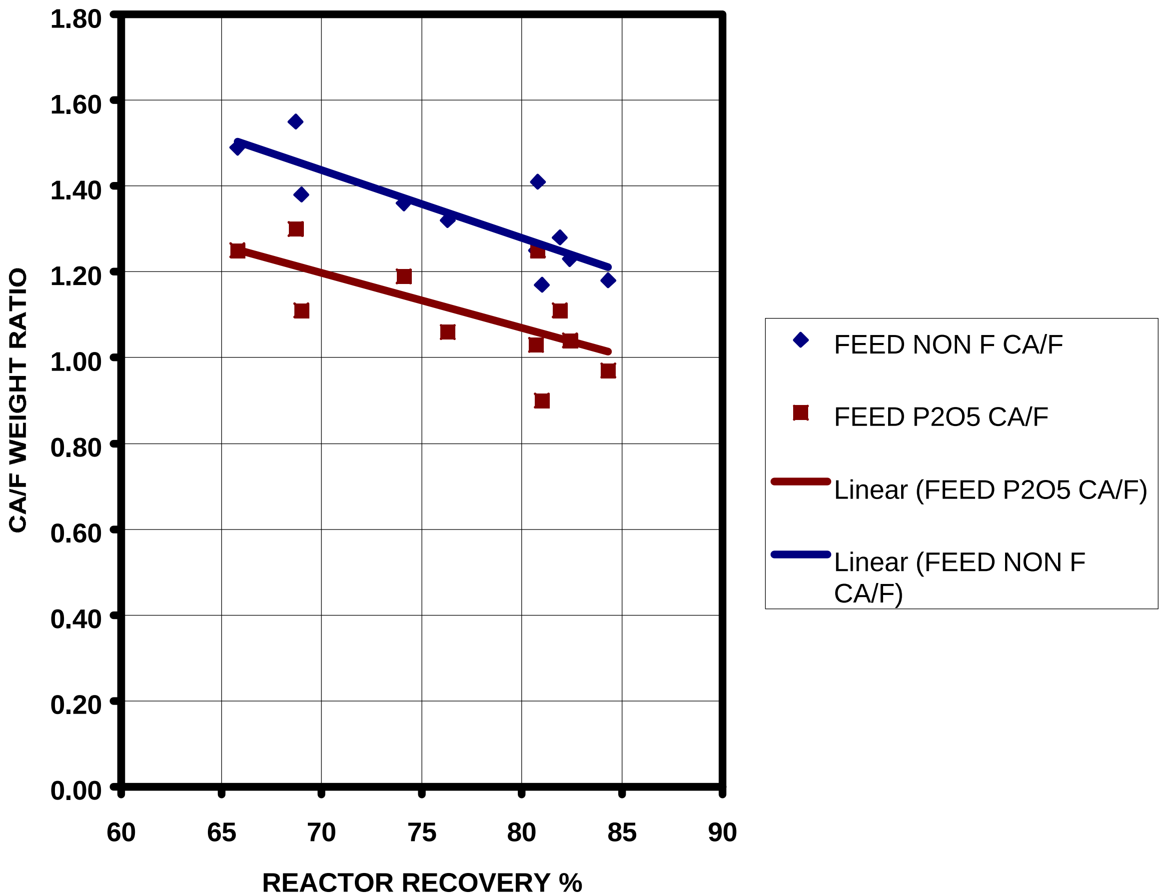
CYCLONE OPERATING

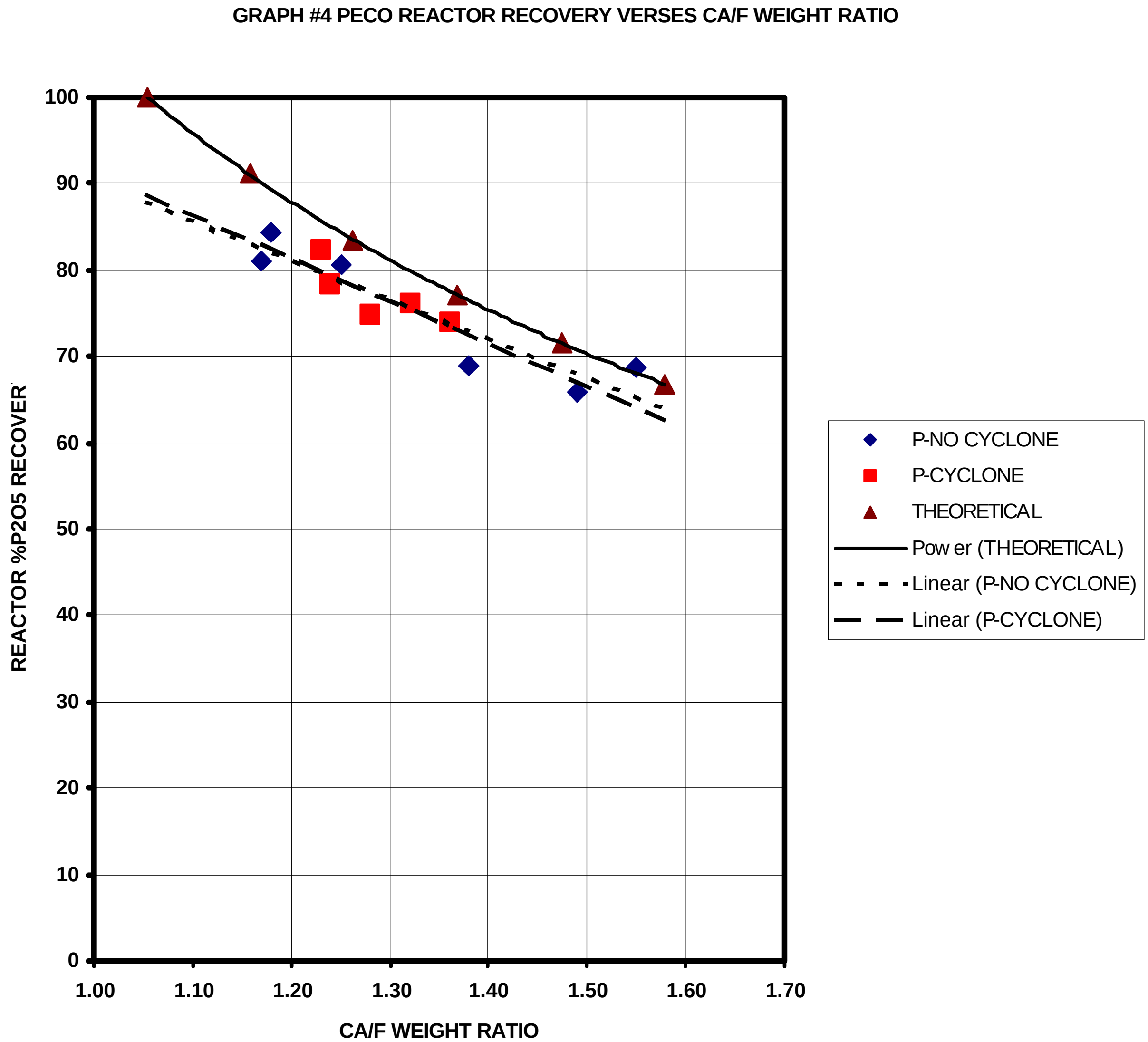
	98-02-06	98-03-20	98-03-22	98-04-07#1	98-04-07#2
% FSA FEED	13.54	12.00	11.94	10.35	11.62
% P2O5 PRODUCT (THICKENER OVERFLOW)	8.5	6.65	7.57	6.62	7.21
FEED NON F CA/F WEIGHT RATIO	1.36	1.23	1.24	1.28	1.32
FEED P2O5 CA/F WEIGHT RATIO	1.19	1.04	1.09	1.11	1.06
F CONVERSION TO CAF2	99.6	91.9	97.6	99.3	99.5
REACTOR P2O5 RECOVERY	74.1	82.4	78.4	74.9	76.3
P2O5 RECOVRED TO THICKENER OVERFLOW	66.6	77.2	71.8	68.8	69.8

GRAPH #1 PECO REACTOR F CONVERSION VERSES FEED CA/F WEIGHT RATIO



GRAPH #2 PECO REACTOR RECOVERY VERSES FEED CA/F WEIGHT RATIO




GRAPH #4 PECO REACTOR RECOVERY VERSES CA/F WEIGHT RATIO
REACTOR %P2O5 RECOVERY
CA/F WEIGHT RATIO
100
90
80
70
60
50
40
30
20
10
0
1.00
1.10
1.20
1.30
1.40
1.50
1.60
1.70
P-NO CYCLONE
P-CYCLONE
THEORETICAL
Power (THEORETICAL)
Linear (P-NO CYCLONE)
Linear (P-CYCLONE)

GRAPH #3 PECO EFFICIENCY VERSES Ca/F FEED WEIGHT RATIO