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**FY 1993 REPORT ON ALUMINUM-NITRATE TESTING AT
THE ETF (U)**

by
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INTRODUCTION

The F/H-Area Effluent Treatment Facility (ETF) utilizes a submicron filtration system to remove suspended solids from the wastewater influent. The main components of the filtration system are three filter trains, each with a designed operating capacity of 100 gpm. Since commencement of operations in 1988, these filter trains have experienced difficulties processing routine and non-routine wastewater. Average flowrates were typically 20-40 gpm per filter train, and often the wastewater had to be routed to the evaporators in order to achieve any processing capability.

To achieve the designed operating capacity of the ETF, expansion of the filtration unit was proposed in late 1989. This proposal included a new cleaning system and evaporator system contained in a new building expansion, as well as additional filter area. This project became the FY94 line item "F/H ETF Filtration Upgrades" with a current estimated cost (TEC) of \$35 MM.

In early 1990, SRTC was able to identify bacteria and its decomposition products as the primary source of the filter fouling¹. Influent streams containing high bacteria concentrations were segregated and routed to the evaporator for processing. Improvement in the filtration of routine influent was noticed. Efforts were made to reduce bacteria foulants in the influents, but no feasible method could be initiated. SRTC research into methods to mitigate the biofouling resulted in a laboratory demonstration that the addition of aluminum and ferric nitrate (ANN and FeN) to wastewater simulant improved filter performance^{2,3,4}. Approval from SCDHEC was obtained and limited testing with ANN at the ETF was conducted between November 1990 and December 1991. Initial results of the testing indicated that this method of pretreatment may be very effective for routine and non-routine wastewater. The study concluded that seasonal effects on bacteria concentration need further examination along with the use of combinations of ferric nitrate and aluminum nitrate⁵.

The ETF received approval from SCDHEC, in May 1992, to continue the use of aluminum and ferric nitrate in its process. Since June 1992, it has become standard operating practice to pretreat ETF's routine feed with aluminum nitrate. This has resulted in ETF's filtration unit maintaining an average monthly throughput above 80 gpm, and no need to segregate the influents for routing to the evaporators for processing. Graph 1 shows the increasing trend in ETF's weekly average filter performance for FY93. In 1992, five tests with non-routine feed were also conducted with non-routine feed and conclusions agreed with earlier testing⁶.

SUMMARY

This report summarizes the progress of the ANN testing program at the ETF for Fiscal Year 1993. Three tests were conducted in the months of February, April, and September. The tests yielded data that validated earlier conclusions that the addition of ANN to non-routine feed has a positive effect on the performance of ETF's submicron filtration unit. Performance was observed to increase from 30 - 309%, depending on the season. The data also supports SRTC's earlier conclusion that an optimal aluminum concentration exists in the range of 30 - 40 ppm, and concentrations above this range begin to retard filtration performance⁷.

A rudimentary mathematical model that would predict Stage 1 flux was also developed during FY93. The model allowed for a more concise comparison of filter test runs, as well as increase the efficiency of the testing program by allowing shorter test runs to be conducted. It is postulated that the model can be further optimized to include aluminum concentration and time

of year as independent variables that determine Stage 1 flux. Such a model should unequivocally prove the merits of pretreating ETF's wastewater with aluminum nitrate. To proceed with the development of the model, further testing is proposed with stringent control of the aluminum concentration in the feed. In order to account for seasonal effects, one test should be conducted each month for Fiscal Year 1994.~ High Level Waste Engineering requests permission to conduct these test runs according to the following schedule: conduct tests in even numbered months beginning with October with routine influent as it is collected from normal process sewer influents and conduct tests in odd numbered months beginning with November with non-routine feed from H-Retention Basin.

DISCUSSION

Three tests were conducted using ANN as a pretreatment method during Fiscal Year 1993 in the months of February, April, and September. Each test utilized stormwater from the H-Area retention basin. It is this type of non-routine feed which has a history of being the most difficult to filter.

The feed was transferred from the basin to ETF's Wastewater Collection Tanks (WWCTs) according to procedure 241-H-ETF-201C "Pumping 281-8H Basin To The ETF Via Lift Station (U)". Aluminum concentration and pH of the feed are both set by HLWE to achieve the desired test composition by procedures 241-H-ETF-192 "Transferring Aluminum Nitrate Nonhydrate (ANN) To Wastewater Collection Tanks (U)" and 241-H-ETF-170 "pH Adjusting A Wasterwater Tank Using 64% Nitric Acid (U)". All filter trains were cleaned by procedure 241-H-ETF-108B "Norton Filter Cleaning Operation Using DCS (U)" after each run. Data was obtained for the first stage of a filter train from the Distributed Control System Data Historian. All original data is retained by the ETF Computer System Cognizant Engineering group on magnetic media for a minimum of three years. The flux for Stage 1 of each filter train was calculated by dividing Stage 1 permeate flowrate by the transmembrane pressure. Transmembrane pressure is the difference between the concentrate and permeate pressure across the filter membrane. It is calculated by subtracting overall filtration permeate pressure from the average of Stage 1 pump discharge and concentrate pressures. Only Stage 1 flux was calculated because the concentrate pressures on the other two stages are not monitored. The non-steady state points (periods of backpulsing) were removed from the Stage 1 flux data set and are then plotted against time.

February 1993 Test

During this test, two baseline runs were conducted on Filter Trains #2 and #3. Run 1 was with raw basin water at a pH of 8.77 and run 2 was with basin water acidified to a pH of 1.34. This was done to validate earlier observations that preadjusting the pH of the feed increased filter performance. The test then progressed by shutting down the filtration unit and raising the aluminum concentration in the WWCT to 50 ppm. Filter operations were restarted alternately using trains #2 and #3 until the WWCT was empty. Switching between the filter trains was done when filter feed rate had dropped to 30 gpm. A sample of the feed was taken during the startup of each new filter train and the aluminum concentration analyzed. Graphs 2 and 3 depict Stage 1 flux for Filter Trains #2 and #3 respectively. The legend of each graph specifies the aluminum concentration for each run.

In previous reports, the affect of ANN on filter flux was quantified by comparing flux at startup, flux at 120 minutes, and the rate of flux decline. This method did not provide a concise and easily conveyed measurement of filter improvement. The absolute goal of the ANN testing

is to maximize the volume of water processed through the filtration unit per unit time. The best descriptor for each filter run would then be the area under the Stage 1 flux curve for a finite time interval.

A time interval of 840 minutes was selected for the filter run evaluation. This interval was chosen because at least 360 minutes are required to clean a filter train. The plant is designed to operate with two filter trains on-line with the third train proceeding through its cleaning cycle. These conditions would require a filter train to operate a minimum of 720 minutes continuously. An allowance of one hour is added for each cleaning cycle to allow for any operational delays.

An ANN filter test run typically lasts from 360 to 420 minutes due to feed volume constraints. In order to determine the area under the Stage 1 flux curve for 840 minutes, the flux needs to be projected to the end of this time interval. It was observed that the decline of Stage 1 flux resembles a simple exponential decay function as depicted in Figure 1.

Figure 1. Graphical Representation of Exponential Decay

The equation for the above decay function is:

$$F(t) = F(\infty) + [F(0) - F(\infty)]\text{EXP}(-kt)$$

Where $F(t)$ = Flux at time t
 $F(0)$ = Flux at startup ($t=0$)
 $F(\infty)$ = Flux at infinity
 k = Decay constant

To determine $F(0)$, $F(\infty)$, and k , a least squares regression was performed on the Stage 1 flux data for each filter run using the LOGEST function of Microsoft Excel®. The LOGEST function fits an array of dependent y-values to an array of independent x-values according to the following exponential curve:

$$y = b * m^x$$

The LOGEST function returns values of b , m and R^2 . The R^2 provides an objective means of assessing the validity of the model equation. A perfect model equation has a R^2 value of 1.0, though values in excess of 0.90 will generally indicate that the equation has good predictive

ability. When the model equation is rearranged to fit the form required to run LOGEST, the required LOGEST variables are defined as follows:

$$\begin{aligned} y &= F(t) - F(\infty) \\ x &= t \\ b &= [F(0) - F(\infty)] \\ m &= \text{EXP}(-k) \end{aligned}$$

The definition of y requires that the value of $F(\infty)$ be known prior to executing the LOGEST function. Since $F(\infty)$ is not known, different values were chosen and then LOGEST executed to determine R^2 . A trial-and-error method was utilized until a value for $F(\infty)$ was found that maximized R^2 .

Table 1 contains the calculated equation parameters along with each runs R^2 value. For 10 of the 11 test runs, R^2 values were well above 0.90. Only Run 1 of Filter Train #2 displayed a poor R^2 value. This appears to be the result of not maintaining the 20 psig permeate pressure for the entire run. For approximately 1.5 hours, the permeate pressure was operating at 5 psig.

Table 1. Calculated Model Equation Parameters For February 1993 Test Runs

Filter Train	Run #	Aluminum (ppm)	$F(\infty)$ (gpm/psig)	$F(0)$ (gpm/psig)	k (1/min)	R^2
2	1	0	0.035	0.130	0.00686	0.527
2	2	0	0.059	0.256	0.02929	0.993
2	3	50	0.184	0.461	0.00605	0.926
2	4	41	0.204	0.653	0.00657	0.973
2	5	39	0.182	0.689	0.00712	0.983
2	6	36	0.209	0.780	0.00656	0.985
3	1	0	0.108	0.378	0.02403	0.959
3	2	0	0.123	0.598	0.01507	0.974
3	3	44	0.299	0.826	0.01042	0.979
3	4	41	0.228	0.796	0.00682	0.987
3	5	36	0.235	0.857	0.00549	0.985

To determine the area under the Stage 1 flux curve, each model equation was integrated and evaluated at $t=840$ minutes:

$$\int F(t) = F(\infty)t - \frac{[F(0) - F(\infty)]\text{EXP}(-kt)}{k}$$

Table 2 contains the calculated Stage 1 flux area, as well as the percentage improvement based on the Run 2 of each filter. Absolute improvement is the increase in $F(\infty)$, the predominant factor that determines filter throughput.

Table 2. Percentage Improvement For February 1993 Test Runs

Filter Train	Run #	Aluminum (ppm)	Area @ Time 840	Improvement @ 840	Improvement Absolute
2	1	0	42.92		
2	2	0	56.52	Baseline	Baseline
2	3	50	200.26	254.29%	210.70%
2	4	41	239.29	323.33%	244.02%
2	5	36	223.80	295.94%	206.49%
2	6	36	261.95	363.43%	251.86%
3	1	0	102.28		
3	2	0	135.04	Baseline	Baseline
3	3	44	301.85	123.52%	142.72%
3	4	41	274.49	103.26%	84.97%
3	5	36	309.41	129.12%	90.46%

By acidifying the feed, a 32% increase in filter performance was realized thus validating earlier observations. Filter Train #2 realized an average 4.1X (309%) improvement with ANN over its acidified baseline while Filter Train #3 realized only an average 2.2X (119%) improvement with ANN over its acidified baseline. The disparity in the amount of improvement for each filter train was due the poor baseline run on Filter Train #2. Otherwise there was good agreement between the Stage 1 flux area values for each train when aluminum was present.

As in previous tests, the aluminum concentration was observed to decline as testing progressed. It is noted that this change in aluminum concentration was not a controlled variable in this experiment, therefore any conclusions about the effect of aluminum would be coincidental not causal. It is hypothesized that the aluminum concentration tends to stratify in the WWCT due to ETF's rudimentary mixing method and therefore drops as the test progresses.

April 1993 Test

For this test, it was desired to see what marginal effect on filter flux would be observed with marginal increases in aluminum concentration of the feed. Since aluminum concentration in this test was a controlled, directly manipulated factor, a causal relationship could be inferred. It was also hypothesized that an optimal concentration of aluminum exists between 30 and 40 ppm. This test method would help identify that optimal aluminum concentration. The test plan was to conduct a baseline on Filter Train #1 with acidified basin water. The filtration unit was shutdown and the aluminum concentration in the WWCT raised by 10 ppm. Six hour runs were conducted alternately on Filter Trains #2 and #1. Feed samples were taken every two hours and analyzed for pH, conductivity, and aluminum. Only two series of runs with aluminum were conducted before the feed supply was exhausted. Graphs 4 and 5 depict Stage 1 flux for Filter Trains #1 and #2 respectively. Table 3 displays each runs aluminum concentration and calculated model equation parameters. The pH remained relatively constant at 2.4 for all runs. Conductivity was 760 $\mu\text{mho/cm}$ for the baseline run and 2500 $\mu\text{mho/cm}$ for all other runs. Table 4 shows the calculated Stage 1 flux area, percentage improvement, and

marginal improvement for each run. Marginal improvement is the percentage increase over the previous run.

Table 3. Calculated Model Equation Parameters For April 1993 Test Runs

Filter Train	Run #	Aluminum (ppm)	F(∞) (gpm/psig)	F(0) (gpm/psig)	k (1/min)	R ²
1	1	1	0.335	1.058	0.00198	0.977
1	2	11	0.378	0.694	0.00348	0.986
1	3	21	0.546	1.119	0.00213	0.986
2	1	11	0.477	0.989	0.00223	0.978
2	2	21	0.460	0.974	0.00189	0.976

Table 4. Percentage Improvement For April 1993 Test Runs

Filter Train	Run #	Aluminum (ppm)	Area @ Time 840	Improvement @ 840	Marginal Improvement
1	1	1	577.06		
1	2	11	403.53	-30.07%	
1	3	21	682.80	18.32%	69.20%
2	1	11	594.96	3.10%	
2	2	21	602.97	4.49%	1.35%

An anomalous run was observed with Run 2 of Filter Train #1 for this test. This appears to be due to difficulty in controlling filter permeate pressure. For the entire length of this run, filter permeate pressure averaged 16.4 psig with a standard deviation of ± 3.1 . The DCS controller was programmed to hold a setpoint of 20 psig, which was achieved on the other runs with data averaging 19.9 psig with a standard deviation of ± 1.2 . Failure to maintain the 20 psig setpoint was attributed to operator intervention of manually controlling the level in the Organic Removal feed tank, the recipient of filtration permeate.

September 1993 Test

Because the April test resulted in so few good runs, the experimental method utilized was repeated. A larger volume of feed allowed for test runs to be conducted up to an aluminum concentration of 48 ppm. Graphs 6 and 7 depict Stage 1 flux for Filter Trains #1 and #2 respectively. Table 5 displays each run's aluminum concentration and calculated model equation parameters. The pH and conductivity remained relatively constant for all runs at 2.2 and 3500 $\mu\text{mho/cm}$, respectively. Table 6 shows the calculated Stage 1 flux area, percentage improvement, and marginal improvement for each run.

Table 5. Calculated Model Equation Parameters For September 1993 Test Runs

Filter Train	Run #	Aluminum (ppm)	$F(\infty)$ (gpm/psig)	$F(0)$ (gpm/psig)	k (1/min)	R^2
1	1	1	0.582	0.774	0.00577	0.862
1	2	11	0.487	0.999	0.00362	0.990
1	3	22	0.684	1.082	0.00408	0.956
1	4	31	0.566	1.131	0.00177	0.961
2	1	11	0.499	0.888	0.00448	0.942
2	2	22	0.453	1.057	0.00230	0.977
2	3	31	0.211	1.117	0.00107	0.949
2	4	48	0.710	1.072	0.00294	0.910

The R^2 values show that all the Stage 1 flux models are good except for Run 1 of Filter Train #1. This low value was attributed to difficulty in the DCS controlling the filter feed pH. For this run, the pH would oscillate by almost 1 pH unit around the programmed setpoint of 7.5. For the rest of the runs, pH oscillated by less than 0.1 pH units. The large oscillation was considered to be due to a low buffering ability of the wastewater. The addition of ANN increased the buffering capability and subsequently dampened the pH oscillations.

Table 6. Percentage Improvement For September 1993 Test Runs

Filter Train	Run #	Aluminum (ppm)	Area @ Time 840	Improvement @ 840	Marginal Improvement
1	1	1	522.21		
1	2	11	543.50	4.08%	
1	3	22	668.96	28.10%	23.08%
1	4	31	722.01	38.26%	7.93%
2	1	11	504.19	-3.45%	
2	2	22	604.67	15.79%	19.93%
2	3	31	679.72	30.16%	12.41%
2	4	48	708.97	35.76%	4.30%

The experimental data in this test supports the typical hypothesis. As the aluminum concentration increased, the area under the Stage 1 flux increased till the aluminum concentration reached 48 ppm. At this point, there appeared to be a leveling off or down turn in the area value.

ANALYSIS ISSUES

While the currently used model seems to reflect the general shape of the flux decay curve, there is concern that this model does not accurately fit the data. This is especially troublesome because the results from 360 to 420 minute runs are being extrapolated to 840 minutes. A high R^2 value indicates an overall proximity of the data to the fitted model, but does not mean the model is unbiased. Analysis of the residual values, the difference between observed and predicted Stage 1 flux, demonstrates the current model has a definite pattern of under predicting and over predicting the expected values. Graph 8 is representative of the typical pattern of residual values.

Since the current model is similar to

$$\ln(f(t)) = \beta_0 + \beta_1 t$$

the following variations were proposed:

$$\ln(f(t)) = \beta_0 + \beta_1 t + \beta_{11} t^2$$

$$\ln(f(t)) = \beta_0 + \beta_1 t + \beta_{11} t^2 + \beta_{111} t^3$$

While each of these fit the data more accurately where data was available, both suffer from extreme deviations from the expected curve shape when extrapolated. Figure 2 demonstrates how the quadratic form increases dramatically and the cubic form drops off abruptly when extrapolated. Previous long runs show that neither of these situations occur.

Figure 2. Graphical Demonstration of Model Fit to Observed Data

An alternative hypothesis is that the curvature observed in the initial part of the run is related to the startup of the filter train and that after the process reaches a stable state, the filter capacity decays at a linear rate. This allows for two alternatives for the modeling process. The first method is to fit both the startup portion and the linear portion of the process and link them in a single function of time as follows:

$$f(t) = \begin{cases} f(t)_{startup} : t \leq t_{transition} \\ f(t)_{linear} : t > t_{transition} \end{cases}$$

The second method is to fit only the linear portion and extrapolate back through the startup period. The second method would underestimate flux for the startup period, giving a lower bound to the flux during startup. Since additional flow during startup would be small compared to the total capacity of the run, the overall estimate of run capacity should be close to the actual and the bias comparable from test to test.

CONCLUSION

The addition of ANN to the wastewater demonstrated a marked improvement in the performance of the submicron filter's Stage 1 flux over performance without ANN. The September test results support previous conclusions that an optimal concentration of aluminum lies in the range of 30 to 40 ppm, and that concentrations beyond 40 ppm begin to hinder performance. The February test results also support the latter conclusion. As the aluminum concentration dropped from 50 ppm, there was a positive trend in Stage 1 flux performance.

Stage 1 flux performance was observed to follow a definite pattern similar to an exponential decay function. Each filter run's data was fit to an exponential decay model, with typically good R^2 values. But based on operational history and further analysis of the model's predicting quality, the model is considered to be systematically flawed. Further research needs to be conducted in developing the model. Once an acceptable modeling method has been achieved for a single run, the data from all tests will be incorporated into a single data set and compared to determine the optimal aluminum concentration and any seasonal variances.

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F/H EFFLUENT TREATMENT FACILITY FILTER PERFORMANCE HISTORY - FY93

Weekly Average

GRAPH 1

ANN Test Runs 02/93
Feed: H-Retention Basin
Filter Train 2

GRAPH 2

ANN Test Runs 02/93
Feed: H-Retention Basin
Filter Train 3

GRAPH 3

ANN Test Runs 04/93
Feed: H-Retention Basin
Filter Train 1

GRAPH 4

ANN Test Runs 04/93
Feed: H-Retention Basin
Filter Train 2

GRAPH 5

ANN Test Runs 09/93
Feed: H-Retention Basin
Filter Train 1

GRAPH 6

ANN Test Runs 09/93
Feed: H-Retention Basin
Filter Train 2

GRAPH 7

Difference Between Observed Flux and Predicted Flux
ANN Test Runs 02/93
Run 6 of Filter Train 2

GRAPH 8

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