WSRC-RP-89-1328

ANALYTICAL SUPPORT FOR A NEW, LOW-LEVEL RADIOACTIVE WASTE WATER TREATMENT PLANT (U)

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An article for publication at
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ABSTRACT

The Savannah River Site (SRS) located in Aiken, SC, is operated by Westinghouse Savannah River Company under contract with the U. S. Department of Energy. The mission of SRS is to manufacture radioisotopes for use in national defense and space exploration. The F/H Effluent Treatment Facility (ETF) is a wastewater treatment plant supporting SRS for low-level radioactive process waste streams. In order to comply with the Federal Resource Conservation and Recovery Act, the facility had to become operational by November 8, 1988.

The F/H ETF employs pH adjustment, microfiltration, organic removal, reverse osmosis, evaporation, and ion exchange to remove contaminants prior to discharge to the environment via a state-permitted outfall. Concentrated contaminants removed by these processes are diverted to other facilities for further processing. The ETF is supported by a 24 hr/day facility laboratory for process control and characterization of influent feed, treated effluent water, and concentrated waste. Permit compliance analyses reported to the state of SC are performed by an offsite certified contract laboratory.

The support laboratory is efficiently organized to provide: metal analyses by ICP-AES, alpha/beta/gamma activity counting, process ions by Ion Selective Electrode (ISE), oil and grease analyses by IR technique, mercury via cold vapor AA, conductivity, turbidity, and pH. All instrumentation is contained in hoods for radioactive sample handling.

I. SRS DESCRIPTION AND MISSION

The Savannah River Site (SRS) located in Aiken, SC is operated by Westinghouse Savannah River Company under contract with the U. S. Department of Energy. The mission of SRS is to manufacture radioisotopes for use in national defense and space exploration. Production facilities at SRS include; Reactor components fabrication, Reactor operations, and Isotope Separation facilities. The technology of the day at the time of initial operation (> 35 years ago) was to discharge the very low-level radioactive waste (i.e., evaporator overheads) from the Separations facilities to engineered seepage basins.

II. RCRA

The Federal Resource Conservation and Recovery Act (RCRA) disallowed the use of unlined seepage basins after November 8, 1988. Due to technology advances and in order to comply with RCRA, the F/H Effluent Treatment Facility (ETF) was designed and construction began in January 1987. The facility began "HOT" operations in October 1988. The ETF process treats Separation facility effluents (low-level radioactive waste streams) to meet state regulated National Pollutant Discharge Elimination System (NPDES) discharge limits and SRS radiation discharge guidelines. Permit compliance analyses reported to South Carolina Department of Health and Environmental Control (SCDHEC) are performed by an offsite certified contract laboratory.

III. ETF PROCESS DESCRIPTION

The F/H ETF employs pH adjustment, microfiltration, organic removal, reverse osmosis, ion exchange and evaporation to remove contaminates prior to discharge to the environment via a state-permitted outfall. The facility was designed for routine operation of 165 gpm influent and 200 gpm treated effluent (35 gpm internally generated). Concentrated contaminates removed by these processes are diverted to other facilities for further processing.

The F/H ETF receives wastewater from primarily Separation facility and Waste tank farm evaporator overheads into two large **Flow Equalization Tanks.** These feed tanks are 450,000 gallons each and provide continuous feed to the process and tend to dampen any waste concentration variations.

The first treatment step is **pH adjustment** to 7.5 - 8.5 for optimum filtration of iron, aluminum, and silica. Precipitated solids are then removed via **crossflow ceramic microfiltration.** Crossflow filtration allows high flow rates with the concentrate split from filtrate for further processing.

Organic removal is accomplished by passing the filtrate through two stages of carbon vessels. Microfiltration and Organic removal are pretreatment before processing through **Reverse Osmosis** (RO). RO removes dissolved ionic species and any residual colloidal matter.

Final treatment of the effluent is to pass the RO permeate and Evaporator Overhead through a two stage **Cation Exchange Column**. The purpose of cation exchange is the additional removal of ionic radioactive species such as Cs-137 and Sr-90. Treated water exiting the cation exchange columns is sampled proportionally and collected in one of three hold tanks (two currently). The treated water tanks are operated in a cyclic fashion. One is filling while the second is discharging and the third is being held for completion of analyses. Indicator analytes are analyzed within a 7-hour time limit to ensure water quality prior to discharge to the environment. As previously stated, NPDES permit compliance analyses reported to SCDHEC are performed by an offsite certified contract laboratory.

The concentrated contaminates rejected from microfiltration, reverse osmosis and cation exchange regeneration are batch processed through an **Evaporation** step for volume reduction. Concentrated contaminates removed by these processes are diverted to other facilities for further processing.

IV. ETF SUPPORT LAB MISSION

The ETF is supported by a 24-hr/day facility laboratory for process control, backup of online instruments, analyses for troubleshooting process upsets and characterization of influent feed, treated effluent water, and concentrated waste.

In addition to stream characterizations, routine process support includes analyses to determine organics loading of carbon vessels, Cs-137 loading of cation exchange columns and cold feed analyses to determine acceptability of acid and caustic receipts at the facility. Online instrumentation including pH, Density, Turbidity, and Conductivity are also backed up in the ETF laboratory. Most analyses require rapid turnaround (4-8 hours) to prevent process hold up.

V. ETF ANALYTICAL SUPPORT DESCRIPTION

The support laboratory is efficiently organized to provide: metal analyses by ICP-AES, alpha/beta/gamma activity counting, process ions by ISE, oil and grease analyses by IR technique, mercury via cold vapor AA, conductivity, turbidity, and pH. All instrumentation is contained in hoods for radioactive sample handling. Table 1 lists the key routine support the ETF laboratory provides the process.

pH

pH measurement is used throughout the process for both characterization and control parameters. pH is checked on feed material for characterization on a daily basis and can range from <1 to >12.5 pH units. Process sumps that collect rainwater are analyzed to ensure they are suitable for discharge (pH range of >6 and <9 required). The treated water effluent is batched into hold tanks and proportionally sampled prior to discharge to the environment. pH must be >6 and <9 units. Samples are also submitted from throughout the process to verify performance of online pH measurements.

An Orion Model EA940 "Expandable Ionanalyzer" is used in the measurement of both pH and other selected process ions. At the time of each use, the combination pH electrode (gel filled) is calibrated with buffer solutions traceable to the National Institute of Standard Technology (NIST).

Radioactivity Counting

Total alpha, beta (excluding tritium), and gamma radiation is determined on the feed to the ETF process (typically <10 dpm/mL alpha and <500 dpm/mL combined beta/gamma). The facilities known decontamination factor is applied to determine acceptable treatability of the feed.

Three large cation exchange (IX) columns are used as the final treatment step to remove residual Sr^{90} and Cs^{137}. Typically two IX columns are operated in series with the third as an online spare. Total gamma analyses on the IX influent and midfluent are used to determine breakthrough of the first column. This prompts operations to rotate the spare column into series while the loaded column is offline for regeneration. These daily analyses allow for uninterrupted process flow.

At the completion of the treatment process, the concentrated waste and treated water effluent are again checked for activity. The waste concentrate must be < 2x10^5 beta/gamma to be acceptable feed for further processing at facilities currently under construction. The treated water (TW) is confirmed to be <3 dpm/mL alpha and <10 dpm/mL beta/gamma (excluding tritium) prior to release to the environment. If the TW does not meet radioactivity guidelines or any of the other specified limits, the entire batch can be recirculated back to the influent Wastewater Collection tanks for further processing.

The Alpha/Beta/Gamma counting system (Canberra Model 2404F) is designed to measure low activity levels of Alpha, Beta, and Gamma radiation in environmental samples. The system discriminates between Alpha and Beta emissions with a gas flow proportional detector using P-10 counting gas (90% argon, 10% methane). Gamma radiation is detected using a sodium iodide thallium crystal. Once per shift, or prior to use, the system calibration and background level is verified with fixed standard sources traceable to NIST (Am^{241} alpha, Cs^{137} beta/gamma).

Sample preparation varies according to expected activity level, matrix and desired count time. An appropriate aliquot is mounted on a planchet and dried under a heat lamp. The sample may have first been concentrated or diluted to arrive at the desired activity and solids content deposited on the planchet. Count times vary from 15 to 45 minutes.

Oil and Grease

An Oil and Grease (O&G) analysis is provided on feed material to the plant, for characterization purposes; and on the plant treated effluent to determine discharge acceptability. Process control is also provided for the large activated carbon filled vessels whose purpose is to remove organics from the process stream prior to treatment by reverse osmosis.

Tributylphosphate (TBP) is an organic used for isotope extractions in the separations process facilities. Low levels of TBP (<150 mg/L) are therefore present in the ETF feed. TBP is known to cause degradation in certain plastics and polymers. The membranes used in the reverse osmosis trains are not compatible with TBP. This makes it necessary to remove the TBP with the activated carbon beds prior to RO.

The O&G analysis used to support the carbon vessels is not specific to TBP but does indicate TBP along with other oils. The carbon vessels are operated two in series. A daily influent, midfluent and effluent analysis is used to determine column loading and breakthrough of the first vessel.

A Horiba OCMA-220 infrared O&G analyzer is used in the laboratory to measure the organic hydrocarbon content. The nondispersive infrared (MDIR) analyzer is calibrated with known TBP standards. The oil content is read directly in mg/L units on a digital panel meter expressed as "mg/L equivalent TBP". The Horiba analyzer method is based upon EPA Method 413.2, Oil and Grease, Total Recoverable, (spectrophotometric, infrared) and consists of a Freon-113 extraction followed by measurement of the absorbance of the oil in freon between 3.4 and 3.5 microns.

Low-Level Mercury

Low-level mercury analyses are performed during the daily plant feed characterizations and again for the discharge parameters on treated water. The process contains mercury removal columns just upstream of both the carbon vessels and cation exchange columns. The idea is to remove mercury selectively so that it is not adsorbed on either the carbon or IX columns. This prevents the production of what is called a mixed waste (containing both hazardous and radioactive components) and helps to minimize the complexity of disposal. These mercury removal columns are monitored weekly.

A Perkin-Elmer Mercury Analyzer model MAS-50B is used in the determination of low-level mercury. The method is based on EPA 245.1, "Mercury Analysis by Cold Vapor Flameless AA".

A Perkin-Elmer Mercury Analyzer model MAS-50B is used in the determination of low-level mercury. The method is based on EPA 245.1, "Mercury Analysis by Cold Vapor Flameless AA". Mercury in nitric-sulfuric acid medium is oxidized with permanganate to the Hg^{+2} state. The excess permanganate is reduced using hydroxylamine. Hg^{+2} is then reduced to metallic mercury with stannous chloride. The reduced mercury, in solution, is aerated to produce mercury vapor. The vapor is circulated through a closed system containing an absorption cell where the absorption of the 253.7 nanometer line is measured. Absorption at this wavelength is proportional to the quantity of mercury present. After calibration (range 2 to 10 ppb) a check sample of known mercury content is analyzed. QC samples are purchased from "Environmental Resource Associates" (ERA™) of Arvada, CO.

Conductivity

Conductivity measurements are used throughout the process as a quick assessment of plant functioning. Conductivity on samples taken both before and after a process stage are used to roughly verify decontamination factors.

Conductivity measurements are made in the lab using a YSI model 34 conductivity meter with associated conductivity dip cell and temperature probe. The cell constant is determined once per shift or just prior to use using conductance standards traceable to NIST. Sample temperature and the new cell constant are used to report conductivity relative to 25°C.

Metals by ICP-AES

Primary purpose of metals analysis is characterization of the process feed, concentrated contaminates and the treated water effluent. Typical metals of interest include Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Pb, Se, Si, Zn; ranging from trace to ppm levels. The Waste Concentrate analyses are used to determine treatability for further processing. Treated Water analyses determine acceptability for environmental discharge.

An ARL/Fissions Model 3410 Minitorch ICP-AES is used for the rapid sequential determination of metals. The spectrometer is equipped with a Maximum Dissolved Solids Nebulizer (MDSN) sample introduction system, and a dual channel peristaltic pump for sample delivery/waste removal. The instrument is calibrated for each use with multi standards prepared from NIST stock solutions. Calibration accuracy is verified with Trace metal QC samples purchased from ERA™. Waste concentrate contains high salts (up to 30 wt%) and is diluted by a factor of 10 to reduce physical limitations of high solids solutions.

Process Ions

Process ions of interest include chloride, free chlorine, and ammonium. Chloride is monitored from the evaporator bottoms and waste concentrate tanks to ensure levels do not present a corrosion problem. Free chlorine (Cl_2, HOCl, ClO^-) is a strong oxidizer and would be detrimental to the Reverse Osmosis membranes. Free chlorine is analyzed down to <0.2 mg/L to ensure it is not present. Ammonium analysis (<20 mg/L) is one of the discharge parameters for Treated Water.

Due to the space and containment limitations, Ion Selective Electrodes are the method of choice for the ions listed above. All are performed on the Orion™ model EA940 "Expandable Ionanalyzer".

range with acceptable accuracy is from 2-5000 mg/L, therefore no dilutions are required for our process concentration levels.

The method used for free chlorine analysis is derived from EPA 330.3, "Total Residual Chlorine (Iodometric)". In the chlorine electrode analysis, an acidic potassium iodide reagent is added to the sample. The electrode senses the amount of iodine released from the reaction of the potassium iodide oxidized by any free chlorine. Linear range is approximately 0.2 to 15 mg/L with calibration confirmed with QC samples purchased from ERA™.

Ammonium determination is based upon EPA 350.3, "Ammonia as Nitrogen (potentiometric, Ion Selective Electrode)." Double known standard addition is used for calibration, with ERA™ QC sample for verification. The ammonia electrode is a gas sensing electrode which measures the level of dissolved ammonia. The electrode uses a hydrophobic gas-permeable membrane separating the sample solution from the electrode internal solution. Dissolved ammonia in the sample diffuses through the membrane and changes the potential of the electrode sensing element with respect to the internal reference element.

Total Suspended Solids

Total Suspended Solids (TSS) are determined on the feed to the plant as part of the daily characterization. TSS and the other parameters measured are used to compile a data base that may be correlated to the performance of the ETF process for future trouble shooting and predictive performance. During the startup of the facility, TSS determinations were used to correlate online density measurements to the suspended solids content of concentrate rejected from the microfilters. The appropriate density setting could then be selected in the control loop for proper function of the filters.

The TSS analysis is based upon "Standard Methods 160-2, Residue, Non-filterable". A representative sample is thoroughly mixed and filtered through a binderless glass fiber filter. The residue collected is brought to a constant weight at 103°C to 105°C. The residual weight and original sample weight or volume are used to calculate wt% or mg/L TSS respectively.

Free Hydroxide

The free hydroxide content of Waste Concentrate is determined to ensure that the inhibitor levels (>1.1 M OH^-) meet storage tank specifications for limiting corrosion.

The procedure consists of two acid/base titrations, each to ph 7 units. Any carbonate is separated by addition of barium chloride; the hydroxide and aluminate are then neutralized by titration with acid. The aluminum in the formed $Al(OH_3)$ is then complexed with oxalate by addition of excess potassium oxalate releasing $3OH^-$. The reaction is forced to completion by addition of excess standard HCL which is subsequently back-titrated with standard NaOH.

A Mettler™ DL40GP Memotitrator with titration vessel and interchangeable burettes is used to automate this procedure.

Acid/Base Cold Feed Analyses

Nitric Acid and Sodium Hydroxide (sodium carbonate optional) are used in the ETF process for pH adjustment. Concentrated material is assayed upon receipt and stored in bulk (64% Nitric, 50% Caustic). Acid and caustic are diluted daily to approximately 5-10 wt% before actual use. The dilute cold feed material is sampled each day to ensure that the proper concentrations are attained.

A Mettler™ DL40GP Memotitrator is set up for the automatic analysis of both total acidity and aqueous sodium hydroxide expressed as weight%. A weighed quantity of sample is titrated potentiometrically with standardized sodium hydroxide or hydrochloric to determine total acidity or basicity respectively.

Turbidity

Online turbidity measurements at the ETF are used to monitor the performance of the crossflow microfilters. The microfilters have 0.2 micron pores and remove suspended solids from wastewater as a pretreatment for Reverse Osmosis. ETF operation specifies a filtrate turbidity of ≤0.45 Nephelometric Turbidity Units (NTU) as a measure of suspended solids remaining. The laboratory turbidity determination is used to cross check the online instrumentation and to troubleshoot individual filter housings.

A Hach™ Ratio/XR Turbidimeter is used as the lab instrument. The Ratio/XR measures the light scattered at an angle 90 degrees to the incident light. This angle is considered to be the least sensitive to variations in particle size. The instrument also measures the forward scattered light and the light transmitted through the sample. The instrument rations the light scattered at 90 degrees to the amount of forward scattered and transmitted light.

VI. ETF LABORATORY DESCRIPTION

In order to be able to provide the support described above in the time frame needed (2 to 7 hours), the laboratory was built within the facility adjacent to the processing area. The ETF Laboratory measures approximately 12 ft x 24 ft containing 12 ft bench top, 19 ft linear hood space and a sink module. Instrument gasses include Argon, Nitrogen, and P-10 counting gas. Lab operates 24 hr/day, 7 day/week, is staffed with lab supervisor, 2 chemists technical support, 1 day analyst and 8 4-shifts analysts.

Figure 1 illustrates the laboratory layout of the equipment summarized from the analytical descriptions above. A descriptive narrative of the ETF laboratory follows and proceeds around the lab perimeter in a counterclockwise direction, starting at the entrance.

Mounted above the sink to the right of the entrance is the system providing reagent water. A Millipore™ combination RO and 4-bowl cartridge filter system provides DI water from the process water supplied. Water supply and drain are plumbed under the sink to maintain housekeeping.

The radioactivity level of the samples is low; <100 nCi/mL tritium, <3x10^3 dpm/mL Alpha and <2x10^5 dpm/mL Beta/Gamma (other than tritium). For personnel safety all samples, along with the associated equipment, are handled in exhaust hoods with minimum face velocity of 150 Lfm. Due to the limited hood space available and the wide variety of analyses required, installation of most of the equipment was nonroutine. The lab equipment was selected to be compact and provide the rapid turnaround time required.

The first 4-ft hood is used for sample preparations consisting of volume reductions, drying, and acid digestions. This hood contains a water bath, infrared drying lamp, and small microwave oven mounted on an elevated stand.

The next 4-ft hood contains the equipment for conductivity, turbidity, pH and Ion Selective measurements. The conductivity and pH/ISE meters are mounted horizontally on the hood walls to maximize hood floor space.

The last hood along the right hand wall is 8 linear ft. It contains instrumentation for Mercury Cold Vapor, infrared Oil and Grease analyzer, solids filtration equipment, and an autotitrator in conjunction with the adjacent bench top. The autotitrator microprocessor and reagent delivery system is stationed on the bench top with the titration stand remoted into the hood.

Along the opposite lab wall is the reagents preparation bench. Next to this bench is the Canberra simultaneous alpha, beta, and gamma counter. This instrument is equipped with dual detection for alpha/beta and gamma respectively. Alpha/beta detection is with a top-down gas flow proportional counter; gamma is detected from under the sample dish with a sodium iodide crystal.

The last piece of instrumentation is a contained Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The ARL model 3410 Minitorch™ is a sequential spectrometer controlled by an IBM PS/2 model 30. The equipment was modified slightly for containment. The cosmetic metal panels enclosing the plasma torch stand were removed along with the exhaust chimney. A specially built 3-ft-square plexiglass (sides) and stainless steel (top and bottom) hood was built onsite. A hole was cut in the left hood wall configured to match the contour of the instrument and allow the free standing torch stand to slide in, with the spectrometer butted up against the hood.

The spectrometer is equipped with a Maximum Dissolved Solids Nebulizer (MDSN) sample introduction system, and a dual channel peristaltic pump for sample delivery/waste removal. Because of the containment required for radioactive material, the normal gravity feed of ICP sample waste to a reservoir on the floor was unacceptable. Instead, the sample pump was upgraded to two channels, one of which is used to transfer the sample waste from a small gravity feed receptacle under the spray chamber to a large waste receptacle in the back of hood. The small waste receptacle under the spray chamber always contains some liquid to provide backpressure to the spray chamber to maintain proper argon flows.

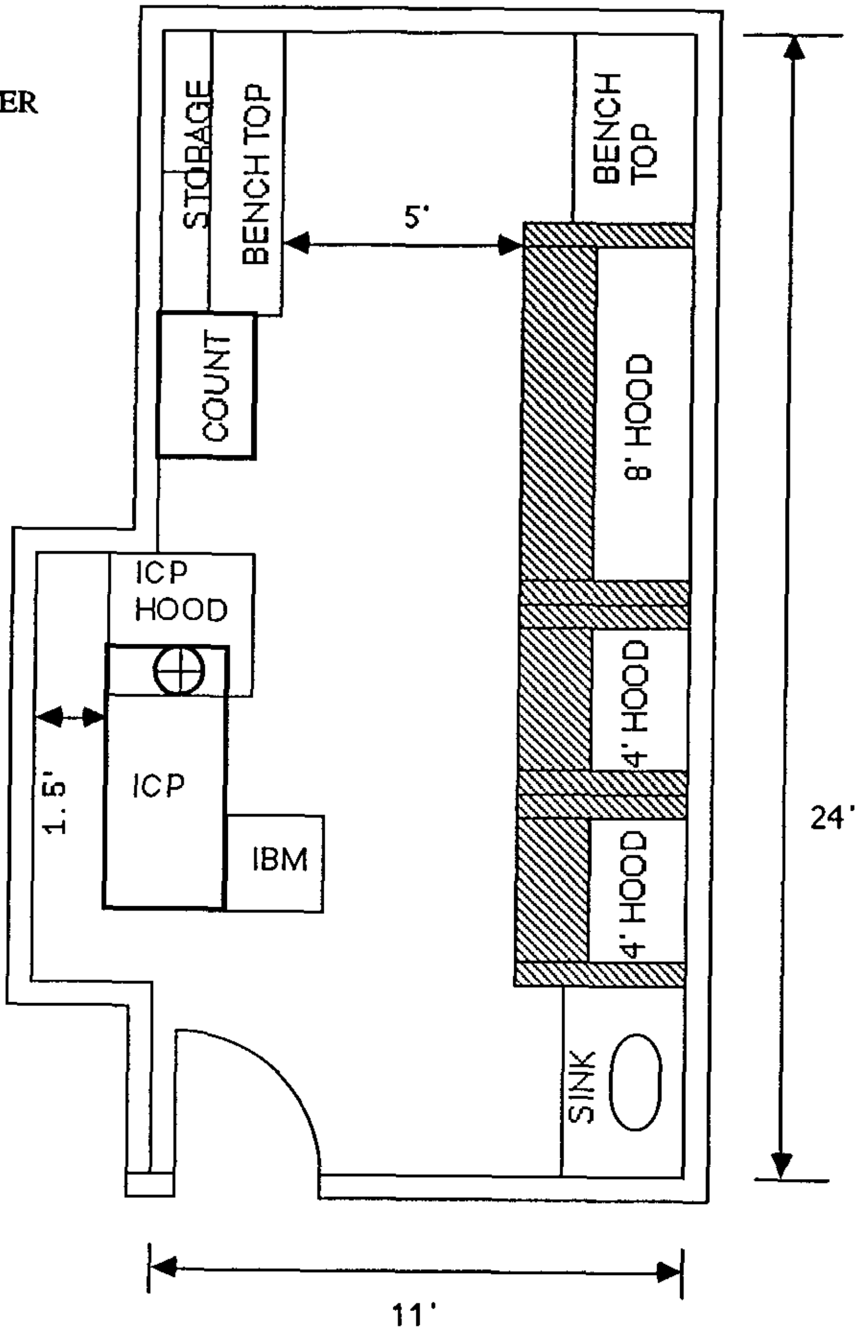
ACKNOWLEDGMENT

The information contained in this article was developed during the course of work done under Contract No. DE-AC09-88SR18035 with the U. S. Department of Energy.

TABLE 1. ETF LAB GENERAL PROCESS SUPPORT

SAMPLE	pH	*a* d/m/ml	*b/g* d/m/ml	O/G mg/L	HG mg/L	COND UMHOS/CM	ICP mg/L	Cl- mg/L	NH4+ mg/L	TRC mg/L	TSS	TITRATOR %/M	TURB NTU
PROCESS FEED	X	X	X	X	X	X	Cr Pb Cu Zn Al Si Fe				X		
ORGANIC REMOVAL CARBON BEDS				X									
PRE-CARBON BED MERCURY REMOVAL					X								
PRE-ION EXCHANGE MERCURY REMOVAL					X								
CATION EXCHANGE COLUMNS			X										
COMBINED FILTER PERMEATE										X			X
EVAPORATOR BOTTOMS				X				X	X				
EVAPORATOR OVERHEADS	X			X		X			X				
WASTE CONCENTRATE	X		X	X			As Ba Cd Pb Hg Se Ag Cr	X	X		TSS VOL% X	OH- X	
ACID/CAUSTIC RECEIPT & DILUTIONS												HNO3 NaOH	
TREATED WATER	X	X	X	X	X	X	Cr Pb Cu Zn		X				

FIGURE 1. UTILIZATION OF ETF LABORATORY



<u>EQUIPMENT LIST</u>

ICP-AES
ALPHA-BETA-GAMMA COUNTER

<u>8' HOOD AND BENCH</u>
AUTO TITRATION
SOLIDS FILTRATION
OIL AND GREASE
HG - LOW LEVEL

<u>4' HOOD</u>
CONDUCTIVITY
TURBIDITY
pH/ISE

<u>4' HOOD</u>
SAMPLE PREP
*Waterbath
*Microwave
*Drying Lamp

<u>STAFF</u>
1 Supervisor
2 Chemists
9 Analysts

<u>SAMPLE LOAD/Mnth</u>
> 1000 Samples
up to 10,000 Determinations