

US EPA ARCHIVE DOCUMENT

Materials and Methods



Exterior Photograph of Centrate Settling Tank and Processing Trailer

2.1 General Pilot Plant Process

The pilot plant was designed in a decoupled, modular fashion using standard water treatment and fertilizer industry process equipment. Figures 2-1 through 2-4 show some of the key unit operations for ARP. The decoupled modular design philosophy was incorporated to allow the isolation of each unit operation, thus allowing observation and analysis of each unit operation independently.

In practice, the ARP process was incorporated into a workable pilot process. The centrate was pumped from the centrate wet well to a settling tank where solids were settled for approximately one hour. The settling tank was added after construction and processing began, and it was not part of the original design. Settled centrate was pumped from the settling tank through a basket filtration system (75-micron filter in series with a 10-micron filter) to an equalization/storage tank (i.e., centrate head tank). Filtered centrate was pumped from the centrate head tank through the ARP absorption columns and returned to the head of the wastewater treatment plant. The flow rate, ammonia concentration, zinc concentration, iron concentration and pH of the centrate influent and effluent from the ion exchange columns were monitored.

2.2 ARP Adsorption Columns

The adsorption system consisted of two fiberglass vessels filled with zinc-impregnated ion-exchange media. Each vessel was two feet in diameter and six feet tall with a two-foot resin depth. Each absorption column contained 181 liters of ion exchange resin. The vessels were typically operated with one unit on-line while the other was off-line for backwashing or regeneration, although, both columns were run concurrently during several processing runs. The ion exchange backwash system consisted of two 300-gallon polyethylene tanks and a backwash pump. Backwash operations were manually controlled and typically involved approximately 200 gallons of water. The primary purpose of the backwash system was to remove any solids build-up on the resins. The backwash tanks were provided with level controls, which terminated the backwash operation on a low-level condition in the backwash tanks. Backwash flow rates were monitored.

Following exchange media exhaustion, a regeneration solution consisting of 0.5 M ZnSO_4 in 5% H_2SO_4 was pumped through the columns to regenerate the media. The regeneration solution flowed upward through the media and was returned to the regeneration solution storage tanks. The regeneration system consisted of two 300-gallon capacity polyethylene tanks and a regeneration pump, and like the backwash system, these tanks were typically filled with 200 gallons of regeneration solution. The regeneration solution storage tanks were provided with level control switches that terminated operation of the regeneration pump when a low

level condition was sensed. Regeneration operations were manually controlled. When the regeneration solution reached an appropriate ammonia concentration, it was pumped to the regeneration solution processing system, i.e., the crystallization process.

2.3 Double Salt Crystallization Process

The regeneration solution processing system consisted of an evaporator, a crystallizing unit, a batch furnace and an ammonia scrubber. The regeneration solution processing system was operated on a batch basis and processed approximately 200 gallons of solution per batch. The evaporator was used to concentrate the regeneration solution. The evaporation system consisted of a glass lined jacketed stainless steel evaporator and a mobile steam generator.

The concentrated regeneration solution is pumped from the evaporator to the crystallizer where the solution was chilled to approximately 1°C (34°F) to promote the formation of ammonium-zinc sulfate crystals. The crystallization system consisted of a jacketed stainless steel crystallizer and a mobile chiller unit. A chilled ethylene glycol solution was pumped through the tank jacket. When the concentrated regeneration solution reached a temperature of about 1°C (34°F) resulting in the proper degree of crystallization, it was pumped through a basket filtration system. The crystals were retained in stainless steel wire mesh basket filters and the filtrate solution was returned to the regeneration solution storage tanks for reuse.

2.4 Ammonium Sulfate Purification Process

The crystals recovered from the basket filters were placed in stainless steel drying trays and placed in a furnace held at approximately 400°C (750°F) for approximately one hour to drive off ammonia, leaving ZnSO₄ crystals. The ZnSO₄ crystals derived from the process were mixed with 5% H₂SO₄ solution and reused as an ion exchange regenerate. During the crystallization operations there were two heatings of these wet crystals: 1) to remove and vaporize H₂O; and 2) a more extreme heating to convert NH₄⁺ to NH₃ and remove the NH₃ as a gas and send it to the scrubber unit. This was done to

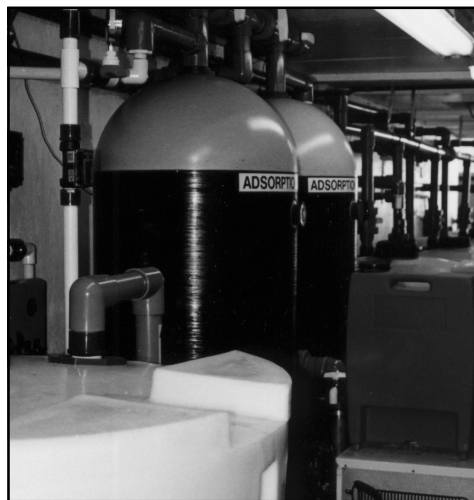


Figure 2-1. ARP Adsorption Columns



Figure 2-2. Regeneration Solution Evaporator



Figure 2-3. Crystal Furnace



Figure 2-4. Crystallizer Unit

obtain separate mass balance numbers for the amounts of water and ammonia volatilized during the purification process.

Gases derived from the furnace, ammonia, sulfur trioxide and water, are captured in the scrubber system. The ammonia scrubber system consisted of a stainless steel wet scrubber, chemical addition system and blower. Desorbed ammonia was recovered in the packed bed scrubber using a H_2SO_4 solution held at a pH of 2.0 to 3.0 to capture the ammonia, sulfur trioxide and water as ammonium sulfate at a temperature of $40^{\circ}C$ to $70^{\circ}C$ ($100^{\circ}F$ to $140^{\circ}F$). The resulting ammonium sulfate solution was transferred to the batch crystallizer to lower the temperature to about $10^{\circ}C$ to $20^{\circ}C$ ($50^{\circ}F$ to $70^{\circ}F$) to grow and precipitate ammonium sulfate crystals. The remaining solution was returned to the scrubber and fresh H_2SO_4 was added as necessary to replace the amounts used to adsorb the ammonia. The crystals were then removed in the basket filters and dried in the furnace in the same manner as the ammonium zinc sulfate crystals.

2.5 Analytical Methods

The methods listed in Table 2-1 were used by the EvTEC-contracted laboratory, ACCUTEST[®], during the ThermoEnergy ARP evaluation. ACCUTEST[®] laboratory personnel were responsible for adding chemical preservatives and storing the samples at the proper temperature (i.e., $4^{\circ}C$) until the analytical work was performed. ACCUTEST[®] personnel followed the procedures outlined in the Evaluation Plan for the ARP for sample collection and handling.

Total Kjeldahl Nitrogen (TKN) values were collected because the added laboratory costs were minimal and TKN is a good indicator of how well the anaerobic digestors are performing upstream of the ARP columns. TKN is a measurement for the organic-nitrogen and the ammonia-nitrogen levels within an aqueous sample.

2.6 Sampling Locations and Frequency

Table 2-2 below outlines where and how often samples were taken by the independent laboratory, ACCUTEST[®], for the analysis of the ThermoEnergy ARP.

The EvTEC evaluation plan called for the sampling collection to be performed over an 8 week period. ACCUTEST[®] traveled

Parameter	U.S. EPA Method No.
Total Suspended Solids (TSS)	160.2
Total Kjeldahl Nitrogen (TKN)	351.2
Ammonia-Nitrogen	350.2
Zinc	200.7
Iron	200.7
Calcium	200.7
Magnesium	200.7
Alkalinity, Total	310.1
Phosphorus, Total	365.3

Table 2-1. Laboratory Analytical Methods

to the site 16 times over approximately 12 weeks and took split samples from Foster Wheeler’s automatic composite samplers around the ion exchange unit (i.e., influent and effluent points of the ARP columns), discrete samples from the wet well located before the filtering units and from the regeneration solution. Although the ammonia sulfate crystals were planned to be sampled during the pilot plant operations,

system problems with the scrubber unit did not allow for laboratory analysis of these crystals.

Over the course of the EvTEC evaluation, ACCUTEST® personnel would arrive at the ARP pilot plant site unannounced and take composite or grab samples from the ARP port locations described above. ACCUTEST® was responsible for all aspects of the EvTEC testing.

Location/Analyte	TSS	TKN	NH3-N	Total Zinc	Total Iron	pH, Temperature, Flow
Centrate Wet Well	2/week – Grab	2/week - Grab	2/week - Grab	2/week - Grab	2/week - Grab	N/A
Centrate Head Tank	2/week – Daily Composite	2/week - Daily Composite	2/week - Daily Composite	2/week - Daily Composite	2/week - Daily Composite	4/day - Meter
ARP Effluent	2/week – Daily Composite	2/week - Daily Composite	2/week - Daily Composite	2/week - Daily Composite	2/week - Daily Composite	4/day - Meter
Ammonia Sulfate Crystals	N/A	N/A	1/week - Grab	1/week - Grab	1/week - Grab	N/A
Regeneration Solution	N/A	N/A	1/week - Grab	1/week - Grab	1/week - Grab	Meter per event
<i>ACCUTEST Totaled 16 trip visits and 288 sampling events during the course of the EvTEC Evaluation Testing</i>						
<i>FWENC performed pH, Temperature, and Flow measurements</i>						

Table 2-2. Sampling Locations and Frequency