CHAPTER 1

Introduction

This verification report describes the nature and scope of an environmental evaluation of one of ThermoEnergy Corporation’s wastewater treatment technologies. ThermoEnergy Environmental Corporation, a joint venture of Foster Wheeler Environmental Corporation (FWENC) and ThermoEnergy Corporation, in association with Battelle Memorial Institute, has developed an alternative process for the recovery and beneficial reuse of ammonia from municipal wastewater. The treatment process is called the Ammonia Recovery Process (ARP) and it is designed to take advantage of the high concentration of ammonia that exists in the centrate obtained in centrifuging an anaerobically digested sludge. ARP removes the ammonia and recycles it into an agricultural fertilizer. The centrate from an anaerobically digested sludge typically contains 20–40% of the total nitrogen load in a wastewater plant.

The evaluation process and the creation of this report was overseen and coordinated by the Environmental Technology Evaluation Center (EvTEC), a service center of the Civil Engineering Research Foundation (CERF), the research and technology transfer arm of the American Society of Civil Engineers (ASCE). EvTEC is operated through a cooperative agreement with the U.S. Environmental Protection Agency (USEPA).

A pilot scale ARP treatment facility was constructed and tested at the Oakwood Beach Water Pollution Control Plant (WPCP) in Staten Island, New York, and tested from September through December of 1998. For the purposes of this EvTEC verification, the ARP system was run in a batch-mode operation while the full-scale version would operate under a continuous-mode. The evaluation was conducted using centrate produced by the Oakwood Beach WPCP’s anaerobically digested sludge dewatering operations. The main objective was to test the effectiveness, economy, and reliability of the ARP process for treating a typical municipal centrate stream. Another important objective of the pilot study was to determine the relevant design parameters for use in scaling up the ARP process to full scale.

The goal of this report is to provide potential users and purchasers of the ThermoEnergy ARP with the information needed to make informed decisions about ARP for their local treatment works.

1.1 Technical Background

The ARP process recovers ammonia from aqueous streams for subsequent reuse as ammonium sulfate fertilizer. Theoretically and ideally, the ARP first concentrates the ammonia from an influent ammonia concentration of approximately 1,000 parts per million (ppm) up to a resin-loaded value of approximately 15,000 ppm by using a specially prepared ion exchange resin. During this
project, ACCUTEST® measured influent ammonia concentrations ranging from just over 100 ppm to a high of 500 ppm NH₃-N. EvTEC’s off-site contract laboratory, ACCUTEST® did not record values of influent ammonia concentrations in the 1,000 ppm range (see Table 3-1 Ammonia Concentrations and Section 3-1) and the off-site laboratory did not record an ammonia regeneration solution value approaching 15,000 ppm (see Appendix A). One reason for not recording regeneration values as high as 15,000 ppm is that ACCUTEST®’s random trip visits did not correspond to a day that the regeneration solution was high enough to move it to the crystallization process.

A solution of zinc sulfate and sulfuric acid is used to regenerate the exchange column. The ammonia-laden spent regeneration solution is then concentrated with an evaporator to approximately 60,000 ppm ammonia. This concentrated solution is then cooled until zinc ammonium sulfate crystals form. The crystals are collected and roasted to drive off ammonia. The resultant ammonia gas is recovered in a packed-bed scrubber where ammonium sulfate forms. The recovered ammonium sulfate crystals are dried and bagged for use as fertilizer. The zinc sulfate crystals remaining in the roaster are recirculated and used to prepare fresh column regeneration solution.

The ARP technology is a reversible chemisorption process. The sorbent is regenerated by stripping the ammonia with a strong acid and zinc salt solution such as ZnSO₄/H₂SO₄. The ZnSO₄/H₂SO₄ regenerant is recovered by crystallization of the ammonium zinc sulfate double salt, subsequent ammonia desorption in a thermal treatment step and recovery of the gas phase ammonia with a H₂SO₄ scrubber. Figure 1-1 provides a schematic of the ARP process. Following is a systematic description of the process chemistry.

![Figure 1-1. Ammonia Recovery Process Schematic](image-url)
Ammonia Equilibrium Chemistry on Columns

In Water Solution
\[ \text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+ \] (pK_a is approximately 9.3 for 25°C solution)

Ammonia Adsorption onto Column Resin
\[ \text{R-Zn}^{+2} + 2\text{NH}_3 \rightarrow \text{R-Zn}^{+2}:(\text{NH}_3)_2 \]

Column Regeneration with Sulfuric Acid and Zinc Sulfate

Ammonia Stripping from Columns
\[ \text{R-Zn}^{+2}:(\text{NH}_3)_2 + \text{H}_2\text{SO}_4 \rightarrow \text{R-Zn}^{+2} + 2\text{NH}_4^+ + \text{SO}_4^{2-} \]

Zinc Adsorption Equilibrium Column:
\[ \text{R-2H}^+ + \text{ZnSO}_4 \leftrightarrow \text{R-Zn}^{+2} + 2\text{H}^+ + \text{SO}_4^{2-} \]

Zinc Chemistry

Getting the Ammonia out of Solution by precipitating (ppt) the Double Salt:
\[ 2\text{NH}_4^+ + \text{Zn}^{+2} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \leftrightarrow (\text{NH}_4)_2\text{SO}_4\text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \text{ ppt} \]

Solubility of 42gms/100gms @ 80°C
Solubility of 7gms/100gms @ 0°C

This precipitation occurs at a very low pH (approximately pH=2); \([\text{NH}_4^+]/\text{NH}_3\]’s pK_a = 9.3, meaning the majority of the available aqueous ammonia-nitrogen is in the protonated form.

Separating and Recovering the Ammonia and Zinc

Roast the Double Salt Crystals:
\[ (\text{NH}_4)_2\text{SO}_4\text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \text{ (s)} + \text{heat} \rightarrow 2\text{NH}_3(g) + \text{ZnSO}_4(\text{s}) + \text{SO}_3(\text{g}) + 7\text{H}_2\text{O}(\text{g}) \]

Form Ammonium Sulfate:
\[ \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) \]

2\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s})

Dehydrate (NH_4)_2SO_4 and Crystallize

1.2 Project Goals

At the outset of the project, the Technical Evaluation Panel members, developed a set of issues regarding the ARP technology. From this list, several primary objectives were established to test and evaluate the technology. Accordingly, the ThermoEnergy ARP was evaluated by the EvTEC Expert Panel to determine:

- The reduction of centrate ammonia concentrations through the treatment process;
- Process implementation, including ease of operation and maintainability;
- Short-term effectiveness;
- Long-term effectiveness (where possible); and,
- Cost (capital, operation, and maintenance)

In addition, the following issues and questions specifically raised by the EvTEC Evaluation Panel were addressed during the evaluation testing:

- The effect of iron on the resin used in the ARP process;
- The maximum solids concentrations influent to the ARP process;
- Soluble zinc concentrations in the effluent from the ARP process
- The effects of polymer use in the dewatering centrifuges upstream of the ARP process;
- Crystal growth and dusting;
- Potential for biofouling of ammonium sulfate crystals;
- The effect of contaminants on the ARP resin and in the crystallization streams; and,
- Struvite formation.

1.3 Summary/Overview of Pilot Plant Operation

The pilot scale ARP treatment facility was operated for approximately 3 months. Centrate produced as part of the daily WPCP operations was used as pilot plant influent during the 3-month period. Besides the independent verification testing provided by the EvTEC-contracted laboratory, the pilot plant was routinely sampled and analyzed by both the New York City Department of Environmental Protection (NYC-DEP) and FWENC. EvTEC utilized the services of ACCUTEST®, Dayton, New Jersey, and NYC-DEP used the on-site laboratory located at the Oakwood WPCP. While data were collected by all three entities, and apart from the crystal production and cost data provided by ThermoEnergy and FWENC in Section 3.6 and Appendix C, only the EvTEC-collected data are referenced and used for verification purposes within the context of this report.
During the EvTEC evaluation, FWENC completed forty-eight (48) processing runs removing ammonia from 25,200 gallons (95,382 liters) of centrate. EvTEC’s contracted laboratory, ACCUTEST®, sampled 16 of the forty-eight processing runs. The plant processed the centrate under normal day-to-day conditions at the WPCP, and no special operational considerations were undertaken at the centrifuges to accommodate the ARP pilot plant. The Oakwood WPCP was operated exactly the way it would have been had the ARP technology not been in place. The pilot plant was subject to weather extremes from 90°F days in September to 25°F days in December.