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I am submitting herewith a dissertation written by Larry Willis Perkins entitled "Design and Development of a Process for Acid Hydrolysis of Excess Sludge." I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

Robert Counce, Major Professor

We have read this dissertation
and recommend its acceptance:

Paul Bienkowski, Co-Major Professor

Paul Frymier

Chris Cox

Acceptance for the Council:

Vice Provost and Dean of
Graduate Studies

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DESIGN AND DEVELOPMENT OF A PROCESS FOR ACID HYDROLYSIS OF EXCESS SLUDGE

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Larry Willis Perkins
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DEDICATION

This dissertation is dedicated to my beautiful wife Christy and our continued happiness.

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ABSTRACT

This research investigates a process called nitrolysis for treatment of excess sludge produced during wastewater treatment. Nitrolysis involves the treatment of excess sludge with nitric acid at elevated temperatures (180°C) and pressures (200 psi). This research has shown up to nearly 100% conversion of the biomass (corrected to be free of inert materials) to products. The products include acetic acid, formic acid, and carbon dioxide. The advantage of the process is the reduction in excess sludge for disposal (reduction in cost and liability) and the production of reclaimable products. This research shows a large reduction in mass and volume of excess sludge, while producing enough acetic acid to peak an interest by industrial wastewater treatment facilities. The kinetics and stoichiometry of the process were developed and a pilot plant constructed. This aided in the development of the process on a larger continuous scale, more similar to actual wastewater treatment facilities. Six publications and numerous presentations have resulted from this work.

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NOMENCLATURE

Symbol	Definition	Units
PART II		
C_A	Concentration of component A	[g/L]
C_{AO}	Initial concentration of component A	[g/L]
C_B	Concentration of component B	[g/L]
C_{BO}	Initial concentration of component B	[g/L]
k	Rate constant	[L/mole-min]
M	Constant	[-]
N_A	Moles of component A	[moles]
N_{AO}	Initial moles of component A	[moles]
r_A	Reaction rate with respect to component A	[moles/L-s]]
t	Time	[minutes]
X_A	Fractional conversion of component A	[-]
α	constant	[-]
β	constant	[-]
PART III		
C_{acid}	Concentration of nitric acid in the reactor	[mol/mL]
$C_{biomass}$	Concentration of excess sludge in the reactor	[mol/mL]
C_{sludge}	Concentration of excess sludge in the reactor	[mol/mL]
k	Reaction rate constant	$[mL/mol]^{\alpha+\beta-1}/min$
N	Number of factorial runs	[-]
$-r_{biomass}$	Reaction rate (rate of disappearance of excess sludge)	[mol/mL-min]
$-r_A$	Reaction rate (rate of disappearance of excess sludge)	[mol/mL-min]
s	Standard deviation	[-]
t	Student t statistic	[-]
X_i	Variable of interest	[same as variable]
α,β	Empirical constants or mole ratio of reactants	[-]
PART IV		
$C_{biomass}$	Concentration of excess sludge in the reactor	[mol/mL]
N	Number of factorial runs	[-]
$-r_{biomass}$	Reaction rate (rate of disappearance of excess sludge)	[mol/mL-min]
s	Standard deviation	[-]
t	Student t statistic	[-]
X_i	Variable of interest	[same as variable]
PART VI		
C_{acid}	Concentration of nitric acid	[mole/mL]
$C_{biomass}$	Concentration of biomass	[mole/mL]

COD	Chemical Oxygen Demand	[mg O_2/L]
$COD_{dissolved}$	Chemical Oxygen Demand of solids	[mg O_2/L]
$COD_{particulate}$	Chemical Oxygen Demand of liquids	[mg O_2/L]
k, k_2	Reaction rate constants	[varies]
$-r_{biomass}$	Reaction rate of biomass	[mole/mL-min]
$-r_{particulate\ COD}$	Reaction rate of particulate COD	[mole/mL-min]
$\alpha,\beta,\sigma,\omega$	Empirical constants	[-]

PART VII

$C_{biomass}$	Concentration of biomass	[mole/mL]
C_{sludge}	Concentration of excess sludge in the reactor	[mol/mL]
$COD_{dissolved}$	Chemical Oxygen Demand of solids	[mg O_2/L]
$COD_{particulate}$	Chemical Oxygen Demand of liquids	[mg O_2/L]
$-r_{biomass}$	Reaction rate of biomass	[mole/mL-min]
$-r_{particulate\ COD}$	Reaction rate of particulate COD	[mole/mL-min]
$-r_{sludge}$	Reaction rate (rate of disappearance of excess sludge)	[mol/mL-min]

PART I

INTRODUCTION

1. INTRODUCTION AND RATIONALE

The purpose of this dissertation is to serve as partial fulfillment of the requirements to obtain a PhD in Chemical Engineering. This dissertation is broken down into 8 Parts. Part 1 presents an introduction to the research including rationale for the research, the research problem, and the research objectives and deliverables. A literature review is also presented in Part I. Parts II-VII present the experimental results of this research in stand alone papers. Each one of these papers has either been published or submitted for publication and can be considered individually. Part II discusses some preliminary feasibility studies of the nitrolysis process. Parts III and IV show the results of factorial studies looking at operating parameters and reaction rates for municipal and industrial excess sludge respectively. Part V discusses the development, design, and testing of a pilot plant to continue development of the process on a larger scale. Part VI looks at the reaction rate of the process in more depth. Part VII involves a paper looking at a summary of the overall nitrolysis process, and Part VIII of the dissertation is a summary of the project. A safety summary for each phase of the work was also developed prior to any work on the project. These summaries can be found in the appendix of the dissertation.

1.1 Rationale for the Research

This research involves the treatment of excess sludge from wastewater treatment in a process called nitrolysis. The idea for this research comes from patent literature, which addresses improving the filterability of excess sludge to aid in solids removal. The patent literature[1] calls for a mild hydrolysis of the excess sludge with nitric acid

(relatively low acid-to-sludge ratio). This research looks at a severe hydrolysis (relatively high acid-to-sludge ratio) of excess sludge with the purpose of sludge conversion and product formation.

With 700 large municipalities nationwide, producing 100,000 tons of excess sludge per day[2], an improved treatment option could be potentially valuable to wastewater treatment facilities. The rationale for the project is to reduce the cost and liability associated with excess sludge treatment and disposal. The idea investigated here is to possibly produce marketable products, such as organic acids, while converting the excess sludge to biodegradable organics that may be recycled to the treatment process. The water bound in the excess sludge is released, reducing the volume of sludge. The possible production of organic acids, as well as the mass and volume reduction of sludge, contributes to the economic feasibility of the process.

1.2 Research Problem

Incineration, land farming, land disposal,[2,3,4,5] or wet air oxidation[6] are currently used to dispose of the large amounts of excess sludge produced. Current disposal techniques require high costs along with potential liability. A technique that could reduce the cost and liability associated with sludge disposal could be very useful to wastewater treatment facilities. Nitrolysis is such a process. In nitrolysis, the sludge is converted to products that may be recycled to the activated sludge process and/or reclaimed. The reduction in liability from land application as well as the reduced air pollution and cost from incineration make the nitrolysis method a disposal option of interest.

1.3 Research Objectives

The objective of this research is to develop the nitrolysis process for conversion of wastewater treatment solids. An important part of this development includes kinetic and stoichiometric data, as well as the design, construction, and operation of a pilot plant unit to demonstrate the process and provide process design data.

1.4 Summary of Deliverables

The deliverables obtained from this research include kinetic and stoichiometric models, developed from municipal and industrial excess sludge, as well as a determination of controlling parameters. The design, production, and operation of the pilot plant are also a deliverable, along with appropriate material balances. Six peer-reviewed publications were generated from this the research with numerous presentations.

2. LITERATURE REVIEW

A common bi-product of wastewater treatment is the production of excess sludge.[7] Excess sludge is made up of water, inerts, and microorganisms (living or dead) used to remove organic wastes from the wastewater. The sludge is a necessary result of the organic removal, and must be treated as a waste stream. The organics originally present react during treatment by the reaction

$$\text{ORGANICS} \rightarrow H_2O + CO_2 + \text{BIOMASS.} \qquad (1)$$

Complete organic removal is not possible without producing excess sludge.

2.1 Terminology

For the purposes of this discussion, 'excess sludge' is the term used to describe the mixture of primary solids that settle from the wastewater and the solids (excess biomass) produced during bacterial treatment (biomass normally constitutes over 90% of the solids); such material contains inert material as well as 'bound' water (96% water for the excess sludge obtained for this study). This water contributes to the Environmental Protection Agency's (EPA) estimation that primary treatment generates a stream composed of 95% water and secondary treatment generates a stream composed of 99% water on a mass basis.[3] Biomass is also referred to as 'biosolids'. 'Biosolids' is the term coined to indicate solids from wastewater treatment, which meet federal and state regulations for land application. EPA defines biosolids as "the primarily organic solid product yielded by municipal wastewater treatment processes that can be beneficially recycled." [8] EPA also states biosolids are "...solid, semi-solid, or liquid residue generated during the treatment of domestic sewage in a treatment works."[9] The term 'KUB excess sludge' represents the municipal excess sludge supplied by Kuwahee Wastewater Treatment Facility operated by the Knoxville Utility Board - KUB). The term 'industrial excess sludge' represents the industrial excess sludge obtained from an industrial secondary wastewater treatment facility. The term 'dry excess sludge', as used in this report, indicates dehydrated excess sludge.

2.2 Excess Sludge

With 5.6 million tons per year[8] (dry basis) of excess sludge generated by the 700 large municipalities in the US,[2] an alternate treatment method could prove financially

intriguing. To put this in perspective, EPA estimates 47 dry pounds of sewage sludge are produced annually by each person disposing of waste to a wastewater treatment facility.[8] The handling/management of this large amount of excess sludge accounts for as much as 50% of the water treatment cost in the United States.[7] This can be illustrated by looking at the disposal costs of excess sludge (including maintenance, equipment, electricity, labor, storage, hauling, etc.), which can reach $80-$800 per wet ton.[10] This correlates to a total cost of $2 billion per year spent treating and disposing of excess sludge.[9]

During wastewater treatment, biological oxygen demand (BOD) is removed and converted to CO_2, H_2O, and biomass. Some studies have investigated the lysis of the cells allowing the release of degradable organics. Some of these organics are converted to CO_2 and H_2O, while the rest are moved into the newly created biomass.[11]

2.3 Typical Wastewater Treatment Facility

Wastewater typically enters the treatment facility and immediately begins primary treatment. During this step, the solids are allowed to settle and are removed from the water, thereby reducing the organic load on downstream treatment units. One-half of the solids may be removed in primary treatment, but these solids are not classified as biosolids.[9] The wastewater then undergoes secondary treatment. This step utilizes bacteria to remove biodegradable organic material[9] and produce biosolids. The microorganisms remove the organics and then settle out in the bottom of the tanks where they are removed.[9] Primary and secondary sludges typically consist of ~3% solids by mass.[9]

The excess sludge is typically digested before being stabilized and sent to a

dewatering step. This digestion may be anaerobic (most common) with as a product or aerobic with carbon dioxide and water as a products.[4] The stabilization of the sludge involves the addition of lime to increase the pH and kill any living organisms[4]. The excess sludge is dewatered to remove solids from the stream (ranging in size from 1 micron to 1 mm[3]). Filter presses[3,4], drying beds[4], or centrifuges[4] are typically used to generate a cake of excess sludge, which is sent for disposal in any number of ways, such as incineration, landfilling, land farming,[2,3,4,7] or wet air oxidation.[6] Dewatered sludge is usually 20-45% solids by mass.[9] A block diagram of a typical wastewater treatment facility can be seen in Figure 1 (all figures and tables can be found in the appendix of this section).

2.3.1 Example of Excess Sludge Treatment Based On KUB'S Kuwahee WWTF

An example of a specific wastewater treatment facility can be described by looking at the Kuwahee Wastewater Treatment Facility of KUB in Knoxville, TN. Here, a device called a gravity thickener first thickens the primary solids. The secondary sludge undergoes dissolved air flotation, which involves passing air bubbles through the sludge to aid in separation. A dissolved air flotation unit typically can concentrate the solids from 1%wt to 4%wt solids. The concentrated sludges from the gravity thickening and dissolved air flotation are mixed and fed into anaerobic digesters. Bacteria in the digesters convert the sludge to a stable product, which is dewatered prior to disposal. The anaerobic digestion reduces the volume of the sludge and reduces the pathogens, making land disposal of the sludge safer for human health. The sludge is treated with lime and ferric chloride to remove any organisms still alive and is filtered through a filter

press to concentrate the sludge to about 40% solids by mass. The concentrated sludge is placed in trucks and transported to farms, where it is applied by land farming to amend the soil.[12]

2.4 Excess Sludge Disposal Techniques

Currently, several techniques are used to treat and dispose of excess sludge produced from wastewater treatment. The most common methods include incineration, land farming, and land filling. Each of these techniques have liability concerns most companies are trying to avoid. In addition, incineration (used 1/3 of the time[2]) causes concerns about air pollution. All of the methods are relatively expensive, leading to a desire for new treatment and disposal options. For example, land filling is used after the sludge is concentrated to 25%wt solids or more,[2] leaving a large volume of water which adds to the cost of land filling. Wet air oxidation has become an option of interest in recent years, but the liability and cost concerns are still present. This leads to the investigation of alternate methods to deal with the excess sludge. A table of cost comparison for each alternative can be seen in Table 1.

2.4.1 Incineration

The first disposal method discussed is incineration, which is used to reduce the mass and volume of the excess sludge.[2] During incineration, several factors must be considered, such as water content, chemical composition, and thermal value of the sludge. The incineration process first heats the sludge, evaporating the water, and then combustion occurs. The amount of water present can dictate whether the excess sludge will burn or must have some type of fuel added.[13] Biosolids containing 30% solids or

more (by mass) typically can be incinerated without the use of auxiliary fuel. It can take 1,800 to 2,500 BTU's (British Thermal Units) to simply drive off one pound of water from the waste, showing how important dewatering is to incineration. Incineration reduces the volume and weight of the sludge cake by as much as 95%.[9]

2.4.2 Land Farming

Land farming application uses sludge as a fertilizer by placing the wet substance directly on the soil.[13] After drying, it is worked into the ground by plowing.[2] Another option is to inject the sludge into the soil. This injection method avoids the possibility of removal by rainwater runoff.[13] As much as 300 tons of excess sludge per acre can be used as fertilizer,[13] but future health concerns have led to a decrease in the land application of sludge from wastewater treatment. Any problems with crops or human health related to the sludge pose severe economic hardships for the treatment facility. Sludges must pass Resource Conservation and Recovery Act (RCRA) toxicity tests in order to be land applied.[9]

2.4.3 Land Filling

Land filling involves disposing of sludge by burial at a municipal land fill or hazardous waste land fill. The practice of land filling is the most common land disposal method. A disadvantage is the high cost for transport and disposal. This increased cost makes dewatering very important.[2]

2.4.4 Wet Air Oxidation

Organics can be oxidized using elevated temperatures and pressures in the presence of oxygen by a process called wet air oxidation (currently accepted by

EPA).[14,15] Compressed air is commonly used as the source of oxygen leading to an organic conversion of 80% by mass.[14] Oxygen becomes more soluble in water at the conditions used for wet air oxidation, thus improving the reaction.

One of the big advantages of wet air oxidation is the prevention of air pollution. This advantage comes from the fact most of the wastes are in the liquid form. Several components are simultaneously oxidized, making the process even more beneficial.[13] A temperature of 149°C and a pressure of about 2000 psi typically are used, but the temperature and pressure can vary from this norm.[14] A typical reaction in wet air oxidation may look like

$$\text{Organics} + O_2 \rightarrow CO_2 + H_2O + \text{RCOOH} \qquad (2)$$

where RCOOH represents some short chain organic acids such as acetic acid. Nitrogen, in the compounds, is typically converted to ammonia and not N_2 gas, requiring further treatment by other methods.[2] A typical organics concentration treated with wet air oxidation is 5% by mass.[14]

2.4.5 Ozonation

Ozone is a possible treatment option for all organic compounds found in wastewater. Ozonation involves the absorption of gas into the liquid phase where the chemical reaction takes place.[16] Ozone is used to treat compounds in the liquid phase, such as phenols, whether by direct oxidation or indirect oxidation using radicals.[17] OH^- is the initiator resulting from the decomposition of ozone, which reacts during indirect oxidation.[18] In acidic solution, the direct oxidation is the most prevalent method.[17]

Formic and acetic acid result from ozonation of organic compounds. The reason

is reaction rate constants for carboxylic acids are commonly low. That is, acetic acid for example, reacts slowly enough (2-3 orders of magnitude slower than similar compounds[18]) that a reaction rate cannot be obtained. Such compounds reportedly "...always accumulate as final products..." It is also reported that the oxidation of organics to CO_2 is slowed when acetic acid is produced.[19]

Ozone destroys bacteria 600-3,000 times faster than chlorine,[9] while oxidizing most metals.[20] The main product of ozonation is O_2,[20] which does not produce any environmental concerns. Ozone also increases the biodegradability of wastewater but is not typically used to treat solids[21] and is not sufficient to remove enough organic matter to meet drinking water requirements.[22] Ozonation also requires longer residence times than normally encountered in drinking water treatment.[9] Even in light of the benefits, ozone is only used as a final treatment option in certain conditions (i.e. low total organic carbon (TOC) and cold temperatures).[23] In some cases, oxidation of solid particles by ozone is reported to give low yield,[18] with ozone decomposing slower with lower pH.[24] Ultimately, ozone is not an effective method to treat excess sludge from wastewater treatment.

2.4.6 Summary of Treatment and Disposal Techniques

These techniques, including aerobic digestion, anaerobic digestion, wet air oxidation, supercritical wet-oxidation, land filling, and nitrolysis were scored by a University of Tennessee report[25] in terms of economics and other 'soft issues' such as public perception. All the methods received similar scoring except for land filling, which scored lower due to public impression. Given this report,[25] nitrolysis is potentially very

useful for excess sludge treatment, due to the reduced liability and cost of treatment and disposal.

2.5 Recent Technologies

Recent technologies are somewhat parallel to the nitrolysis process. One example is thermochemical nitrate destruction introduced by Cox et al.[1] In the process, Cox et al. focus on the nitrates present in waste streams (including wastewater treatment) for denitrification. The concept calls for the introduction of formate into the waste water followed by elevating the temperature to between 200°C and 600°C for 1-120 minutes at pressures in the range 240-3,200 psi. The typical reactions reported by Cox et.al[1] include

$$5HCO_2H + 2HNO_3 \rightarrow N_2 + 5CO_2 + 6H_2O \quad (3)$$

$$3HCO_2H + 2HNO_2 \rightarrow N_2 + 3CO_2 + 4H_2O \quad (4)$$

Fasshender[26] developed a nitrogen removal process similar to the thermochemical nitrate destruction method just discussed. The technology discussed by Fasshender involves adding a nitrogen-containing compound (nitric acid) to balance the oxidized and reduced forms of the nitrogen. This process is represented by the reaction

$$C_5H_5N + 5HNO_3 + 3H_2O \rightarrow 3N_2 + 5CO_2 + 5H_2O \quad (5)$$

Still other studies have looked at the acid treatment of excess sludge to release carbon, remove metals, and increase filterability. A study by Montiel et. al[27] looked at the acid hydrolysis of sludge with sulfuric acid as a pretreatment option for sludge disposal. This work involved the adjustment of pH followed by using an autoclave at 120°C and 20 minutes for the sludge treatment. The work looked at increasing the easily

available carbon and nitrogen so cells could use the nutrients to grow and produce biopesticides. The carbon was originally difficult to metabolise but the acid hydrolysis released the nutrients.

Heavy metals are often present in urban wastewater and ultimately increase contamination of soil if the sludge is land applied.[28] Naoum et. al[29] and Cheung[30] looked at the treatment of excess sludge by hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid to remove heavy metals to the liquid phase. The acid treatment involved a 1:5 ratio of grams of sludge to mL of acid. The results showed the best removal utilizing sulfuric acid for an extended time of 60 minutes at 20% volume acid.[29] Naoum et. al[31] also looked at treating heavy metals in sludge with acid treatment. The sludge used was anaerobically stabilized sludge out of the digestion step of Figure 1. Nitric acid and hydrolchloric acid were used to treat the sludge at 20% volume acid for 30 minutes at ambient temperatures.[31] Nitric acid treatment of primary sludge was shown to remove 60% of the heavy metals in the sludge.[28]

Heat and acid/alkaline hydrolysis were studied to improve the biodegradable carbon in excess sludge. Acid hydrolysis reportedly increases the biodegradability of the primary sludge,[32] and solubilizes sludge to a stream rich in protein, carbohydrates, vitamins, and salts.[30] Elliott et. al[11] used an acidic stream from Kraft first-stage chlorination to treat the sludge at 50°C for up to 40 minutes in lab scale research. Pilot plant research was also conducted at a sludge-acid ratio of 4:1 on a volume basis. This work demonstrated a 48% decrease in the sludge production from the process and a large BOD and COD removal of 98% and 53% respectively.[11] Dewaterability was also

reportedly improved by treatment with hydrogen peroxide.[30]

Other studies have investigated the treatment of excess sludge with sulfuric acid and sodium hydroxide. Sulfuric acid reportedly gave 50-60% solubilization of the suspended solids and NaOH gave 46% solubilization of the suspended solids.[33] These tests, however, utilized a 24 hour pretreatment at room temperature by the acid or caustic, followed by a treatment at 175°C for 30 minutes.[33] The current nitrolysis process is much faster involving a 10 minute reaction time.

2.6 Organic Oxidation

The desire is to oxidize excess sludge to produce products, which would reduce the excess sludge stream from the wastewater treatment facility. The reaction for the oxidation of excess sludge in land farming can be shown as[34]

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3, \quad (6)$$

where $C_5H_7O_2N$ is a general formula commonly used to represent biomass.[34] The products of organic oxidation have been documented in other studies. Ozone, which is used to treat specific compounds in industrial wastewater and to improve taste, color, and filtration in municipal wastewater,[35] does not degrade most organics to CO_2.[36] Instead, carboxylic acids (i.e. acetic and formic) are the final products of the oxidation, due to their low reactivity.[36] Similarly, wet air oxidation ultimately results in acetic and formic acids[37] for the same reasons discussed above. The products of organic oxidation (commonly short chain organic acids) can react still further. Formic and acetic acids, for example, can both oxidize all the way to CO_2 and H_2O, as shown below[25]

$$CH_2O_2 + 0.5O_2 \rightarrow CO_2 + H_2O \quad (7)$$

$$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O \quad (8)$$

however, due to the low reactivity of these acids, they are actually viewed as final products of the reaction.[36] Reports[33] indicate oxidation of phenol results in ~20% of the carbon going to acetic and formic acids. Longer chain acids are typically not end products but intermediates that are further oxidized. Propionic acid was reported in trace quantities only, with acetic acid reportedly the "...main stable product..."[33]

Nitric acid is used in many oxidation processes, such as the oxidation of alcohols, ketones, and aldehydes. For example, 2-octonol can be oxidized by nitric acid to form 2-octanone.[38] Adipic acid is produced by the oxidation of cyclohexane using nitric acid.[39] Nitric acid has also been used to oxidize bituminous coal to form humic acids.[6] The products of such oxidations often include carboxylic acids with reacting acid concentration an important factor.[4] Any residual nitric acid can enter an anaerobic biotreatment step for conversion to N_2 and H_2O.[3]

2.7 Nitrolysis

Waste management options are typically prioritized as (1) source reduction, (2) recovery and recycle, (3) treatment, and (4) disposal.[2] This hierarchy of waste management options is favorable to nitrolysis, which reduces waste sludge and creates products from the waste. Nitrolysis involves the treatment of excess sludge from wastewater with nitric acid in an exothermic reaction[38] that substantially decreases viscosity and suspended solids. The idea of oxidizing excess sludge with nitric acid originates from the patent literature, which had a goal of improved filterability (separation of solid and liquid components)[35]. This separation required a mild

hydrolysis of the excess sludge (relatively low acid concentration of 0.4 wt% and moderate temperature of 150°C). The current research looks to treat KUB excess sludge and industrial excess sludge with a more severe hydrolysis (relatively high acid concentration of up to 11 wt% and temperatures up to 180°C). The concept is to convert the excess sludge to soluble biodegradable products, which could be recycled back to the waste treatment process or possibly be recovered as valuable organics.

There are three potential outcomes from the nitrolysis process. These results include (1) hydrolyzation of the sludge and recycle through the facility, (2) generation of products (acetic acid) for separation and resale, and (3) release of the "bound water" so the sludge can be disposed of or used in other processes.[34] A preliminary report by the University of Tennessee[25] indicates the economic potential associated with the process increases with the sludge handling rate of the facility. The overall nitrolysis reaction is represented as[38]

Excess Sludge + HNO_3 → Biodegradable organics + CO_2 + N_2. (9)

The process can also be expressed in generic terms as[25,34]

$C_5H_7O_2N + HNO_3$ → Biodegradable organics + CO_2 + N_2 . (10)

where again $C_5H_7O_2N$ is a generic formula commonly used to represent biomass from wastewater treatment. Later in this document, an experimental molecular formula will be presented for each sample of excess sludge used.

Reports[35] indicate a wastewater treatment facility may produce 50-55 tons of excess sludge per day on a dry basis. Estimating 0.15 kg of acetic acid produced per kg of dry excess sludge reacted, a typical wastewater treatment facility could produce $2.8

million per year in acetic acid ($0.44 per pound for acetic acid[36]). Another advantage of nitrolysis is the volume reduction of the sludge. The nitrolysis process releases the bound water from the excess sludge, generating a stream with a lower viscosity. This decrease in viscosity results from the release of the bound water, which allows the solids to settle and creates a smaller volume of excess sludge. These potentials add even more economic feasibility to the process.

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APPENDIX

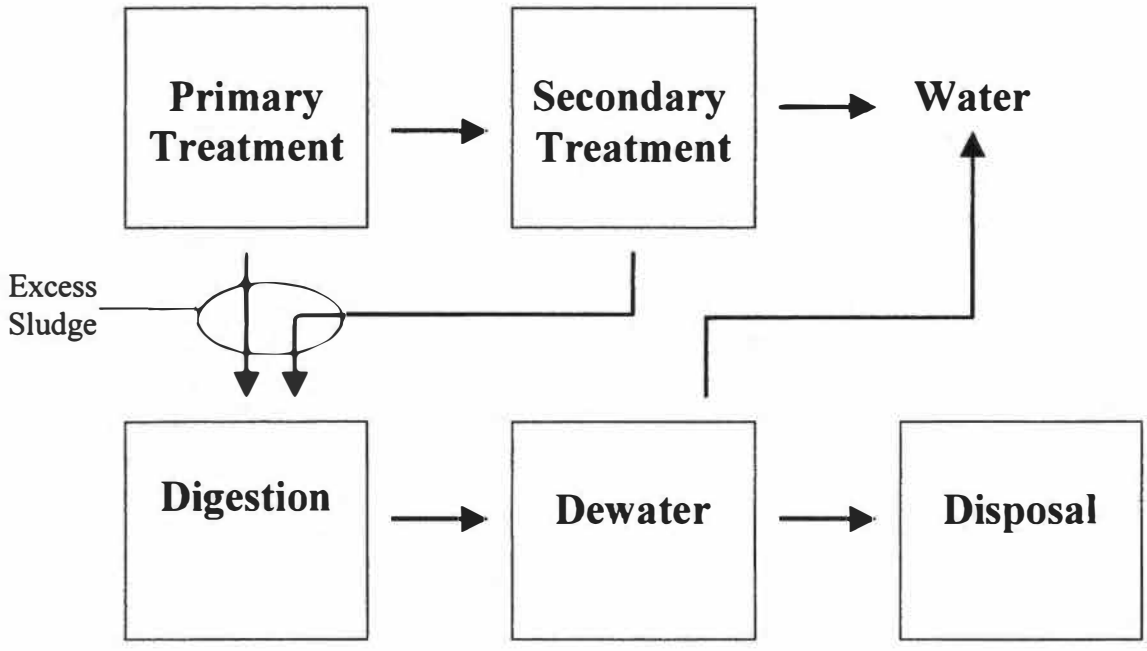

Figure 1 – Block Diagram of a Typical Wastewater Treatment Facility (WWTF)

Table 1 - Cost Comparison of Current Sludge Treatment Alternatives[15,25,40]

DISPOSAL METHOD	ESTIMATED COST
Incineration	$0.24 per pound
Land Farming	$0.12 per pound
Land Filling	$0.14 per pound
Wet Air Oxidation	$0.15 per pound
Nitrolysis	$0.08 per pound (with product recovery)

PART II

PRELIMINARY INVESTIGATION OF NITRO-HYDROLYSIS FOR WASTEWATER SLUDGE TREATMENT

Part II of this dissertation is lightly revised version of a paper by the same name originally published in the *Separation Science and Technology Journal* in 2003 by L. Perkins, K. Klasson, R. Counce, and P. Bienkowski (vol. 38 no. 12-13). The paper is reproduced with permission from the journal. (Reprinted from Ref. 03-125 p. 3271-3286 by courtesy of Marcel Dekker Inc.)

ABSTRACT

Activated Sludge waste treatment facilities generate a waste stream, in the underflow, that consists of 3 – 5 wt % biosoilds which are not readily biodegradable and must be disposed of as a solid waste. Conventional disposal methods for this biosludge consist of landfills, land farming, wet air oxidation, and incineration, all of which add substantially to the cost of operating a municipal wastewater treatment facility. Bench scale batch experiments were conducted with a 4.1 wt % biosludge stream obtained from the Knoxville Utility Board (KUB) Kuhawee treatment facility. These experiments demonstrated that treatment with dilute nitric acid at 180 ^{o}C at 200 psia initiates a hydrolysis reaction that converts 40 – 82 % of the biosolids to biodegradable substances suitable for recycle back to the treatment facility. The experimental design consisted of varying the nitric acid concentration from 1.5 to 11.2 wt% and the residence time between 5 and 20 minutes. At these conditions the initial hydrolysis reaction is rapid destroying most of the biosolids within 5 minutes. The products of this reaction consisted mainly of carboxylic acids that may be recoverable and sold commercially. The stoichiometry of the reaction was investigated and the kinetics was determined to be first order in nitric acid concentration. Results of these batch experiments performed on municipal sludge partially confirm the patent literature data that used a plug flow reactor and industrial sludge. Future work will expand this study to include a complete factorial

design of this process by investigating four possible reaction variables: residence time, reaction temperature, acid concentration, and feed solids concentration in detail with the objective of developing comprehensive kinetics for the process.

1. INTRODUCTION

The Activated Sludge process that is used by many municipalities and industries for removal of BOD from wastewater generates a solids waste stream, in the underflow, referred to as excess sludge[1]. The primary fates of the BOD are either conversion to water and carbon dioxide by cell metabolism or incorporation into the biomass.[1] The latter results in the production of an excess sludge that must be disposed of as a solid waste either by landfill, land farming, incineration,[2,3,4] or wet air oxidation.[5] It has been suggested in the patent literature[6] that contacting this waste stream with dilute nitric acid in a flow reactor at temperatures between 150 and 200 °C can convert over 90 % of the solids to biodegradable organic suitable for recycle to the Activated Sludge process. The reactor was pressurized keeping the feed streams in the liquid state. Recycle of the entire reactor effluent stream to the Activated Sludge process will make an insignificant increase in the hydraulic loading of the waste treatment plant and will substantially reduce or eliminate the solids waste removal problem. The overall reaction is:

$$\text{Sludge} + HNO_3 \rightarrow \text{Biodegradable organic} + N_2 \qquad (1)$$

The organic materials produced in the process are mainly carboxylic acids, primarily formic, acetic and propionic. It might be possible to optimize the process to economically convert this waste stream into acetic acid where a large commercial market is present.

This technology would be superior to existing methods in that it is virtually a zero discharge process which will result in considerable energy saving over incineration and eliminate the air pollution problems associated with incineration. Landfills are expensive and can lead to long term pollution concerns.[4] Land farming has risks associated which

companies may not want to take on. For example while DuPont still land farms its sludge it is actively looking for an energy efficient alternative because of potential future liability from this method. KUB currently land farms about 65,000 pounds of sludge per day (dry basis) that is transported 70 miles from the site. Because of the effects of the sludge on soil KUB has to truck its solid waste further west of Knoxville. There are over 700 large municipal treatment facilities in the United States[2] that could use this process to substantially reduce their solid waste production. In addition there are hundreds of large industrial sites with similar problems. Primary candidates are the petroleum and chemical industries; however, this process is applicable to any large industrial waste treatment process which produces excess biosolids. Companies like Tennessee Eastman may also be able to use this process to convert their waste stream to a usable product. Chemical companies have the technology to recover acetic acid from an aqueous stream and many, like Tennessee Eastman, have an internal demand for this product.

Approximately 100,000 tons of biosludge are produced in the United States each day.[2] If this material were concentrated to 12.5wt %, the concentration used by Eastman for incineration,[7] and sent to an incinerator, a net input of 4.0×10^{14} BTU/yr would be required. Approximately one third of the sludge is actually incinerated nation wide[2] resulting in an annual cost to industry and municipalities of approximately $ 662 million just for the energy needed to run the incinerators. Incineration will also lead to air pollution concerns and the capital cost of an incinerator is substantial. Chemical companies like Eastman that have the expertise to recover acetic acid from water and an internal demand for large quantities of acetic acid may be able to economically utilize

this process to convert their waste stream into a profitable product. Based on Eastman's sludge production rate of 50 – 55 tons/day,[7] dry basis, and an acetic acid price of $0.44/pound[8] there is the potential to produce $5.6 million/yr of acetic acid.

2. BACKGROUND

This process was discovered in an attempt to improve the filterability of sludge.[6] While any strong acid can be used in the sludge destruction process, nitric acid is preferred because it blends into the chemistry of the waste treatment process.[1] High molecular weight polymeric compounds make up most sludge, the sludge contains such substances as proteins, nucleic acids, lipids, etc. that degrade. An example of protein oxidation is[9]

Aspartic acid $\Leftrightarrow$ oxaloacetic acid + NH_4^+ . (2)

Proteins may make up 40%-70% (dry weight) of a cell while lipids make up 10%-15%. Carbohydrates make up 15%-35% of the cells. The products of oxidation can oxidize still further. Formic and acetic acids can both oxidize all the way to CO_2 and H_2O as shown below[9]

$CH_2O_2 + 0.5\ O_2 \rightarrow CO_2 + H_2O$ (3)

$C_2H_4O_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O$ (4)

A general equation for biomass (sludge) oxidation is [1]

$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3$ (5)

This stoichiometry estimated approximately 320 mg of acetic acid produced per gram of sludge reacted for a flow reactor using an industrial sludge. Previous research[6] indicated that as much as 96% conversion of the biosolids may be achievable. Initial tests for the

process indicated that the best performance was obtained at the reaction conditions of 200 psi and 180°C.

3. THEORY

In order to determine the reaction order for the reaction under consideration, some rate expressions must be assumed and then tested. One such rate expression would be a first-order reaction of the form

$$A \rightarrow \text{Products} \tag{6}$$

This type of reaction would then give a rate expression of

$$-r_A = \frac{-dC_A}{dt} = kC_A \tag{7}$$

By integrating this expression and substituting in the definition of fraction conversion (X_A)

$$X_A = \frac{N_{AO} - N_A}{N_{AO}} \tag{8}$$

we obtain the equation

$$-\ln(1 - X_A) = kt \tag{9}$$

In order to test the rate expression, we then perform a plot with time on the x-axis and $-\ln(1-X_A)$ on the y-axis. If the reaction is first-order with respect to the component under consideration, a straight line should be the best fit through the experimental data and should pass through the origin. The reaction may be first-order with respect to a single component of the reaction[10]

A similar test can be performed for a second-order bimolecular type reaction of

the type

$$A + B \rightarrow \text{Products} \tag{10}$$

In this case, the rate expression would be

$$-r_A = \frac{-dC_A}{dt} = \frac{-dC_B}{dt} = kC_A C_B \tag{11}$$

With appropriate substitution and integration, we obtain

$$C_{AO}(M-1)kt = (C_{BO} - C_{AO})kt \tag{12}$$

where

$$C_{BO} \neq C_{AO}$$

$$M = \frac{C_{BO}}{C_{AO}}$$

A plot of time on the x-axis and $\ln\left[\frac{M - X_A}{M(1 - X_A)}\right]$ on the y-axis should give a straight line through the experimental data that passes through the origin. If $C_{AO}=C_{BO}$, then we can represent the reaction as

$$2A \rightarrow \text{Products} \tag{13}$$

and then plot $\frac{X_A}{1 - X_A}$ versus time to test the rate expression, which is[10]

$$-r_A = \frac{-dC_A}{dt} = kC_A^{\,2} \tag{14}$$

In general,

$$-r_A = kC_A^{\,\alpha}C_B^{\,\beta} \tag{15}$$

so that by taking the logarithm of the above expression, we have

$$\ln(-r_A) = \ln k + \alpha \ln C_A + \beta \ln C_B \quad (16)$$

and the coefficients may be obtained from regression of the data.

4. EXPERIMENTAL

4.1 Equipment

The equipment used in these experiments includes a hot oil bath (National Presto Industries Inc. of Eau Claire, WI – Electric Multicooker), a pressurized batch reaction tube (fabricated by the University of Tennessee), and a calibrated thermometer. The batch reactor was 5 inches in length, with an outside diameter of 0.75 inches and a wall thickness of 1/16 inches, giving an internal volume of 25.2 cm^3. The reactor was fabricated from 316 ss tubing with a rated working pressure of 3,300 psi and a bursting pressure of approximately 8,000 psi. The reactor was sealed with 3/4 inch swagelock fittings. A fritted disk filter, a filter flask, filter paper (Whatman International Ltd. Of Maidstone, England), a 5-mL pipette and pipette bulb, a gravity filtration filter, and a graduated cylinder were utilized for analysis. Preliminary analysis on the sludge required a 600-mL beaker and a drying oven.

4.2 Materials

Great Value Vegetable Oil (Wal-Mart of Bentonville, AR) was used in the hot oil bath as the heat transfer medium. The nitric acid used had a concentration of 69.3% (Fisher Scientific of Fair Lawn, NJ). The sludge utilized in these experiments was obtained from the Knoxville Utility Board – Kuwahee Wastewater Treatment Facility in Knoxville, Tennessee. The sludge had a measured density of 1.014 g/mL and was stored

in a refrigerator, at 7°C, to prevent degradation. This sludge sample had a solids content of 4.083 ± 0.105 based on 6 replicates, a value of 4.1 wt% was used for calculation purposes.

An elemental analysis was performed on the sludge solids (Galbraith Laboratories, Knoxville Tennessee) giving the following compositions Carbon 41.14 %, Nitrogen 16.72 %, Oxygen 21.45 %, Hydrogen 12.37 % and remaining 8.32 %. The remaining probably consisted of sand, dirt, metals and other inorganics.

4.3 Procedures

The procedures used were similar to previous work.[11,12] A 100-mL sample of sludge was transferred into a beaker and weighed. The sample was then dried in an oven at 105°C to dehydrate the sample. The dried sample was then weighed to obtain the mass of dry solids in the original 100-mL sample. The fraction of the original sample that consisted of solids was then calculated. This procedure was repeated to give three replicates of the fraction solids. The average of the three tests was used as reported value. The sludge was stored in the refrigerator to preserve the properties and concentration of the sludge solution.

Preparation of a test sample included filling the batch reaction tube with 19.1 grams of the 4.1 wt % sludge slurry. A measured volume of 69.3% nitric acid was then added to the reaction tube and the cap placed tightly on to seal the reaction tube. The tube was shaken briskly to assure a good mixture of the reactants and was then submerged in the hot oil bath that had been preheated for 30 minutes and monitored to assure a constant reaction temperature of 180°C. The tube was allowed to heat up for 2

minutes and then the reaction timer was started. The tube was left submerged in the hot oil for the measured reaction time and then removed and quenched in an ice water bath for 5 minutes to stop the reaction. The tube was opened and its contents transferred to a graduated cylinder. The contents were allowed to set for about 2 minutes to allow the remaining solids to settle out and the total product volume was recorded.

Approximately 5-mL of the liquid produced was gravity filtered through filter paper (110 mm) and sent for liquid analysis. Organic acids (formic, acetic, propionic, butyric and valeric), and nitrate analyses were performed using high pressure liquid chromatography. The mobile phase (filtered 5 mM H_2SO_4) was pumped at 0.6 mL/min through a 300 mm x 7.8 mm (8μm particle size) RHM monosaccharide column (Bio-Rad Laboratories, Hercules CA) held at a temperature of 65°C. A refractive index detector (Model 240, Waters Corporation, Milford, MA) held at 40°C was used for analysis. Each Sample was pre-filtered using a Acrodisc LC 13 mm syringe filter with 0.2 μm PVDF membrane (Pall Corporation, Ann Arbor, MI). The sample injection volume was 10 μL and the resulting chromatograms were compared with injections of acids and nitrate standards. The remaining contents were vacuum filtered through a fritted disk funnel. All glassware and the reaction tube were washed into the funnel. The solids were then allowed to dry and the fraction of the solids consumed in the reaction determined.

A second order factorial design[13,14] was used for the experiments with acid concentrations of 1.5, 3.2, 6.1 and 11.2 wt % and residence times of 5, 10, 15, and 20 minutes.

5. RESULTS

5.1 Introduction

The results from this research are presented in the following section. The estimated stoichiometry is presented first, followed by a graphical test of a rate expression. The production of organic acids of interest; acetic, formic, and propionic acid are discussed. Longer chain organic acids, such as valeric acid, were analyzed for but their presence was negligible. The fractional conversion of each of the reactants as a function of reaction time, and nitric acid concentration are discussed.

5.2 Stoichiometry

The amount of sludge used in the experiments was kept constant with reaction time and initial nitric acid feed as variables. The biomass term in equation (5) was used to convert sludge to a molar basis. The analysis of the moles of sludge that react for each mole of nitric acid consumed can be found in Figure 1 (all figures can be found in the appendix of this section). Figure 1, shows a large variation in the sludge to nitric ratio, going from 8 to about 2, generally decreasing with increased reaction time, indicating that the initial step in the sludge decomposition is completed rapidly under these conditions with subsequent degradation of nitric acid. The previously estimated stoichiometry predicted 0.80 moles of nitric acid consumed per mole of sludge reacted using an industrial sludge as feed in a continuous system that consumed over 90% of the sludge. There is some scatter in the data however it appears that the actual nitric acid loading and not the concentration is the key variable.

5.3 Test for Reaction Order

In performing an initial order of reaction analysis, with respect to nitric acid a significant amount of scatter appears in the data Figure 2. As can be seen in Figure 2, the order of reaction with respect to the nitric acid gave straight lines through the data that pass nearly through the origin. This type of plot leads to the conclusion that the reaction is 1st order with respect to nitric acid. Similar graphical analysis for sludge contained a great deal of scatter and precluded any concise conclusions. Further tests are needed to determine the order of the reaction with respect to sludge.

5.4 Organic Acid Production

One objective of this work was to investigate the quantity of carboxcyclic acids produced and possibly recovered from this waste stream. The production of acetic acid with respect to the amount of sludge that reacts is presented in Figure 3. From Figure 3 increasing reaction time does not increase the amount of acetic acid produced per gram of sludge reacted. It should be noted that a small amount of acetic acid was already present in the sludge obtained from Kuwahee Wastewater Treatment Facility, the amount of acid initially present has been subtracted from the total acid present in the analysis. The acetic acid in Figure 3 is the acetic acid actually produced from the acid catalyzed hydrolysis of the sludge in the experiments. The 100 mg of acetic acid produced per gram of sludge that reacted is about one-third of the acetic acid production predicted by equation (6). Equation (6) was based on data from a flow reactor using an industrial sludge and it is unknown how much if any acetic acid was in this sludge stream prior to reaction.

The production of formic acid with respect to the amount of sludge that reacts is

presented in Figure 4. From Figure 4, the reaction time does appear to affect the formation of formic acid, as does the initial amount of nitric in the reactor. At low initial nitric acid input, as the reaction progresses the amount of formic acid produced decreases to nearly zero. As the initial input of nitric acid increases, more formic acid is produced with increased reaction time. In fact, at an initial nitric acid input of 2.6-mL (11.2 wt%), the increase in the amount of formic acid produced appears to be linearly dependent on the reaction time up to about 20-minutes (the limit of these experiments). The turning point in the formic acid production appears to occur somewhere around an initial nitric acid input of 0.65-mL (3.2 wt%). The formic acid produced is corrected for any formic acid that was already present in the sludge.

The final organic acid that appeared in detectable quantities is propionic acid. The production of propionic acid with respect to the amount of sludge that reacts is presented in Figure 5. From Figure 5, the reaction time does not appear to greatly affect the amount of propionic acid produced. The production of the propionic acid with respect to one gram of sludge reacted appears to range between 5-mg and 20-mg. The initial nitric acid input appears to increase the amount of propionic acid produced slightly in most cases. With 0.3 mL of nitric acid added to the reactor, approximately 10 mg of propionic acid are produced per gram of dry sludge. With 2.6 mL of nitric acid added to the reactor, approximately 20 mg of propionic acid are produced per gram of dry sludge.

5.5 Fractional Conversion of Reactants

The final analysis in this section will come from the fractional conversion of each of the reactants in the reaction (namely sludge and nitric acid). The fractional conversion

of the sludge with respect to the reaction time and the amount of nitric acid initially present in the reactor is presented in Figure 6. A high fractional conversion is desired. From Figure 6, with a reaction time of about 5 minutes, between 40% and 65% of the sludge that is initially present is converted. An increase in the amount of nitric acid initially present in the reactor leads to an increase in the amount of sludge that is converted. With an increased reaction time of 20 minutes, approximately 50% to 75% of the initial sludge in the reactor is converted. Based on the elemental analysis of the dried sludge 8.32 % is inert material. If the kinetics are corrected for the inert materials a maximum conversion of 82% is obtained. It appears from Figure 6 that most of the reaction is over after 5 minutes for the high initial acid concentrations.

The fractional conversion of the nitric acid with respect to the reaction time and the amount of nitric acid initially present in the reactor is presented in Figure 7 and is of concern, due to requirements on the concentration of nitric acid in wastewater. Figure 7 shows that increasing the reaction time will increase the amount of nitric acid converted to product. As expected, the amount of nitric acid initially present is also an important factor. At the low initial nitric acid input of 0.3 mL nearly 95% conversion is achieved after 5 minutes of reaction time. The conversion remains constant after that indicating that the nitric acid is the limiting agent and has reacted away. If the nitric acid used is increased to 2.6 mL, the initial fractional conversion of nitric acid is about 35% at 5 minutes and then the conversion planes off to about 50% at 20 minutes. This indicates that the sludge is limiting the reaction and there is excess nitric acid present. Even though some sludge is still present in the system, the sludge does not appear to be

reacting with the acid. This could be for many reasons, one of which could be the presence of metals and other contaminates in the sludge. The sludge that is left may not react at all. The behavior exhibited in Figure 1 is explained in light of Figures 6 and 7. The initial hydrolysis of the sludge is very rapid resulting in sludge to nitric ratios of 6 – 8 in Figure 1 after 5 minutes, the nitric is then consumed as this complex reaction sequence progress and the sludge to nitric ratio continues to go down with increasing residence time.

Analysis of the reaction of wastewater treatment sludge with nitric acid to decompose the sludge to a useful product has a promising future. The sludge is being reacted away to reduce the amount of sludge that must then be disposed. The products of interest (specifically formic and acetic acid) are being produced from the reaction and an analysis of separation possibilities is needed.

In performing a carbon balance on the reactor, only 40% to 60% of the carbon is accounted for (Figure 8). The carbon accounted for is in the unreacted sludge and the organic acids produced in the reaction. The remainder of the carbon is believed to be in the form of carbon monoxide and carbon dioxide. The analysis of the off gas for these products is the topic of research that is currently underway at the University of Tennessee. Approximately 6% to 10% of the carbon that does react, appears in the organic acid products, as can be seen in Figure 9.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

- The stoichiometry for the reaction involving sludge from KUB appears to be different from the stoichiometry for the reaction involving industrial wastewater

sludge

- The reaction appears to be 1st order with respect to nitric acid
- A measurable amount of acetic acid is produced from the reaction
- A smaller but measurable amount of formic acid is produced from the reaction
- A measurable amount of propionic acid is produced from the reaction
- A significant amount of the carbon in the sludge appears to be exiting in the form of gases
- Sludge destruction is relatively high (up to 82%)
- With low initial concentrations of nitric acid, all of the nitric acid is consumed in the reaction with little to no residual
- Approximately 8.% of the reacted carbon results in organic acids
- Results indicate that at a reaction temperature of 180 °C, the initial step for sludge hydrolysis is very rapid even at low acid concentrations.

6.2 Recommendations

- Analyze off-gas from the reactor to complete a carbon balance
- Develop a factorial experimental design incorporating reaction temperature and initial sludge concentration as additional variables.
- Determine experimentally the suitability of recycling the effluent from sludge hydrolysis back to the waste treatment unit.
- Quantify the composition of the unreacted sludge.
- Build a pilot scale system for continuous operation of the reactor

7.0 ACKNOWLEDGEMENTS

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APPENDIX

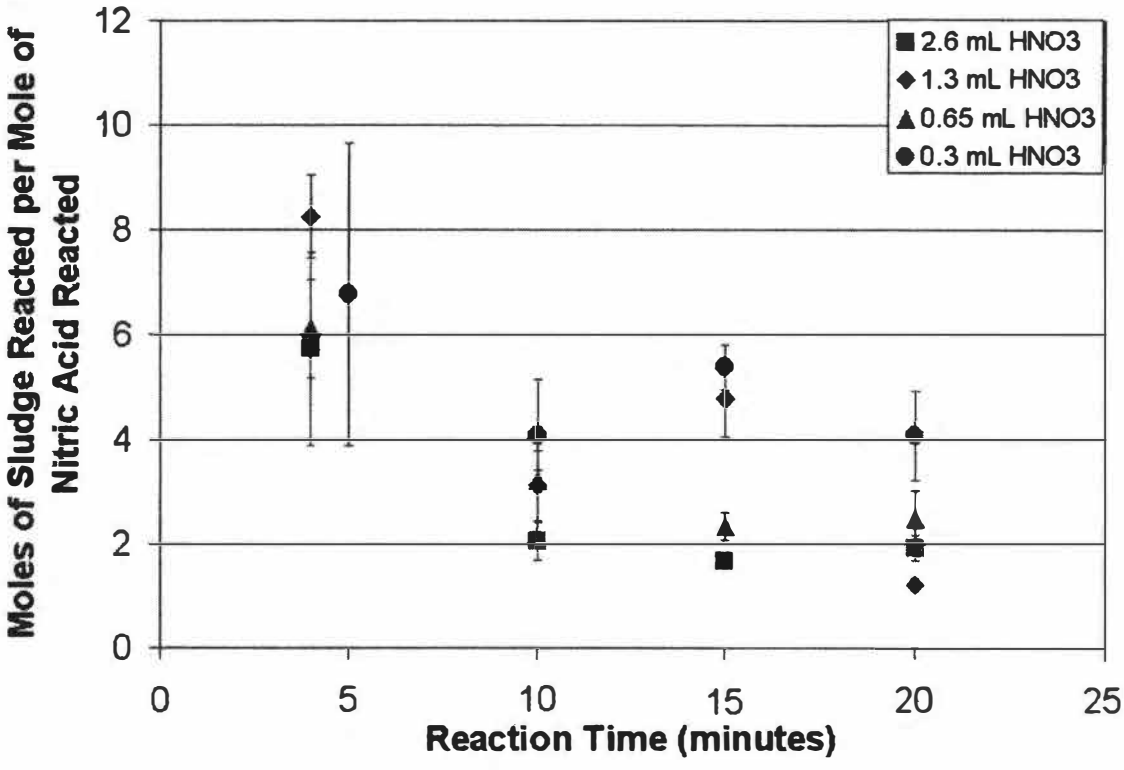

Figure 1 – Stoichiometry Estimation

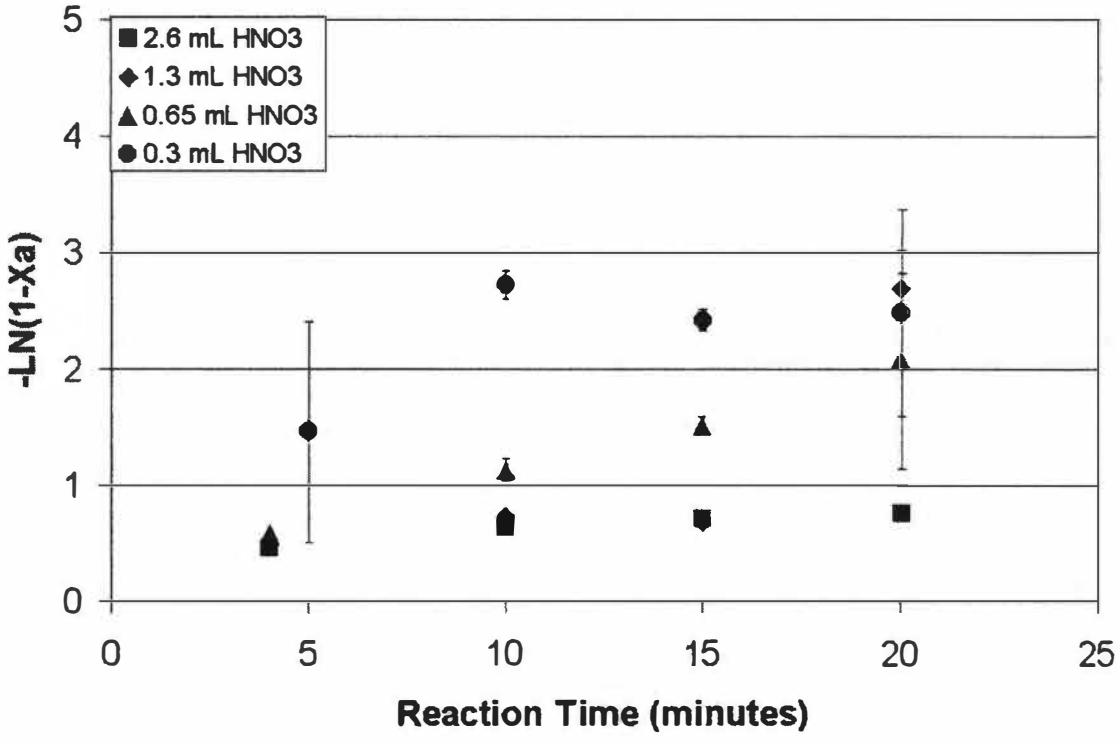

Figure 2 – 1st Order Rate Test With Respect to Nitric Acid

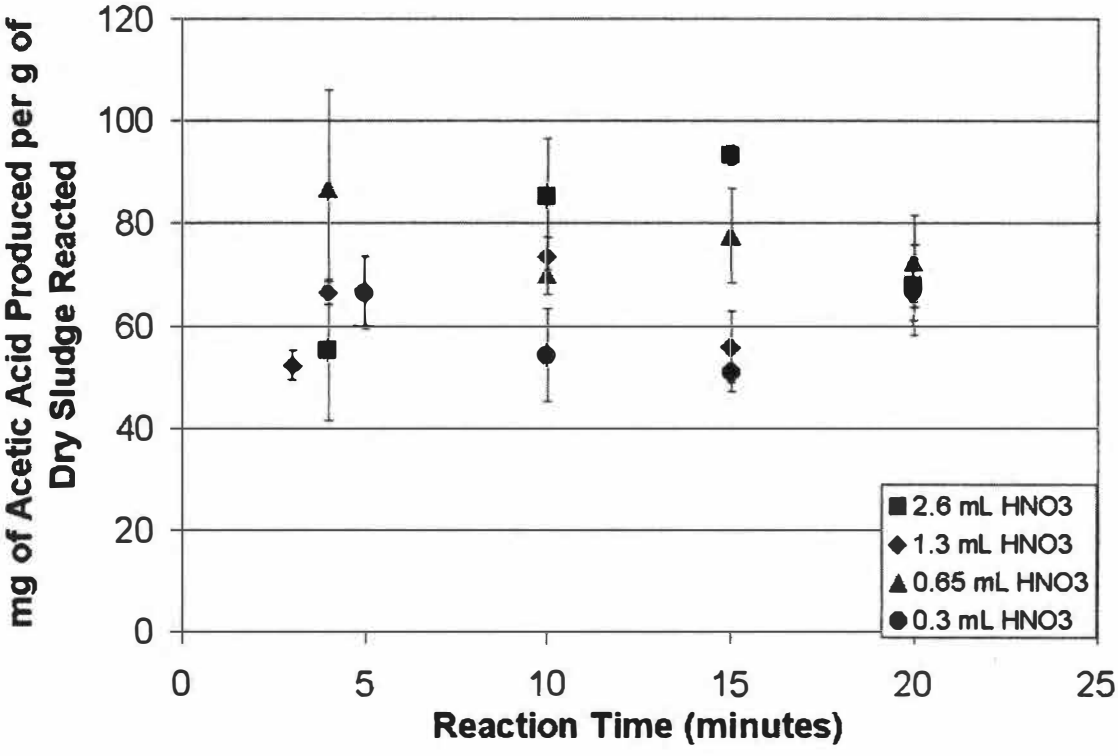

Figure 3 – Acetic Acid Production

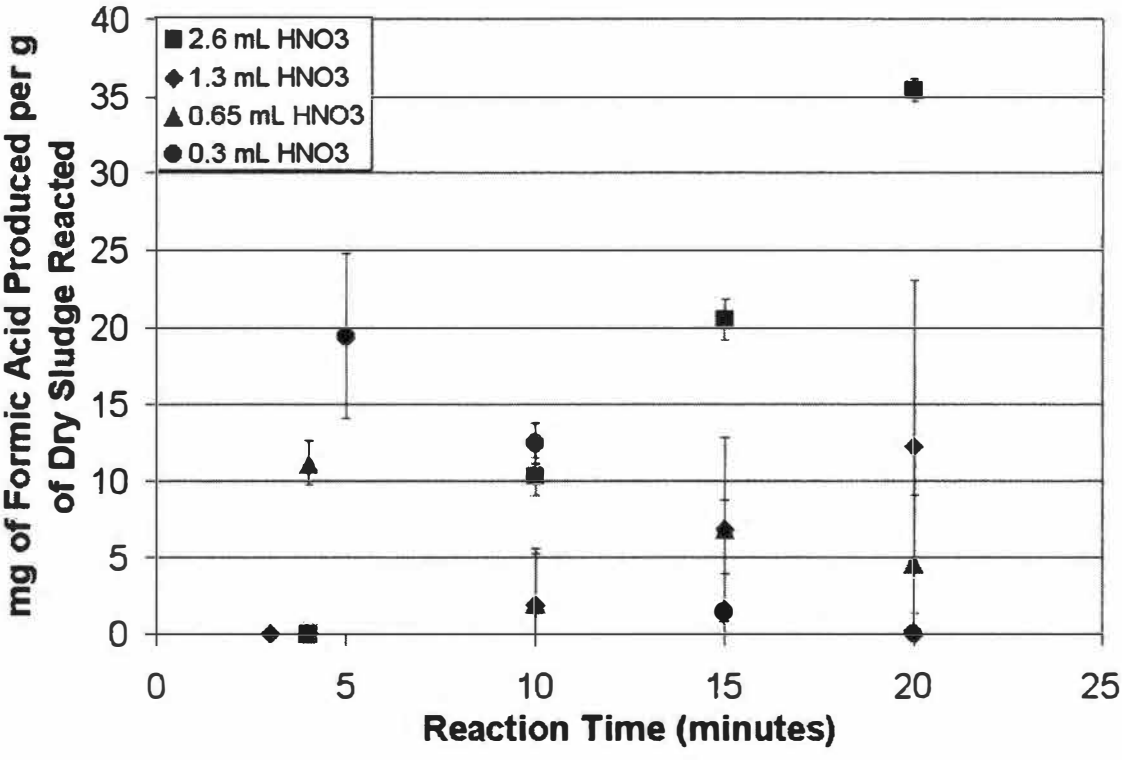

Figure 4 – Formic Acid Production

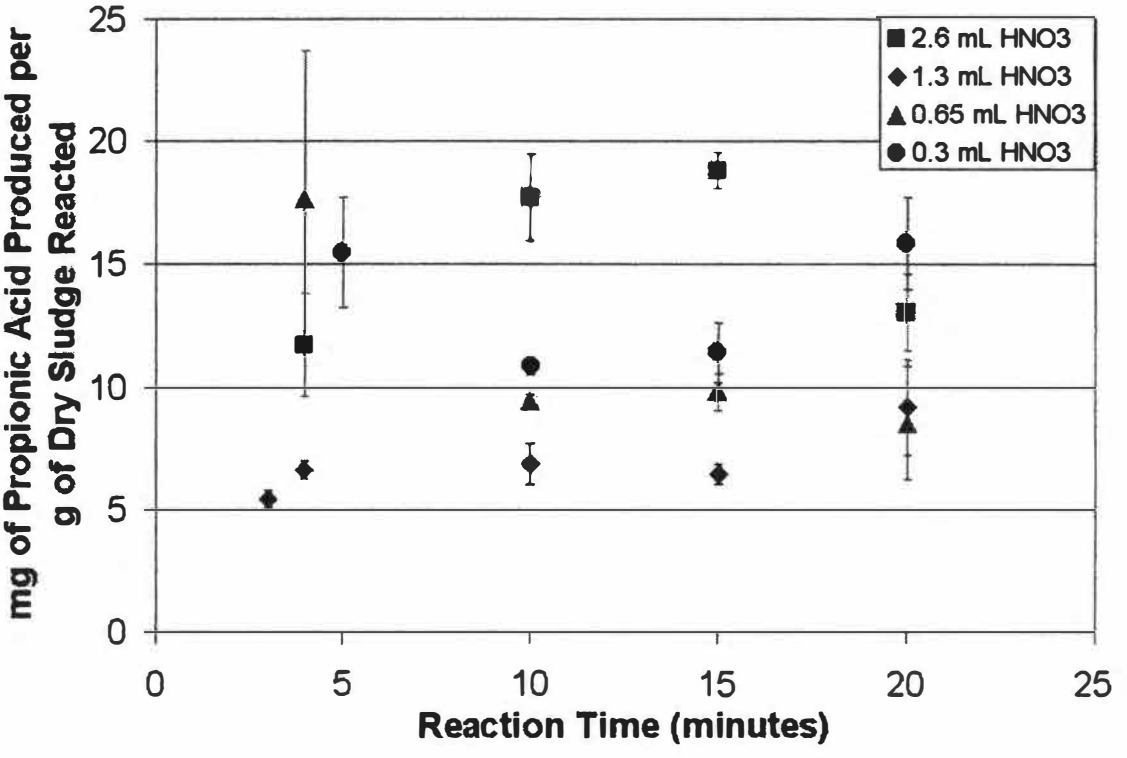

Figure 5 – Propionic Acid Production

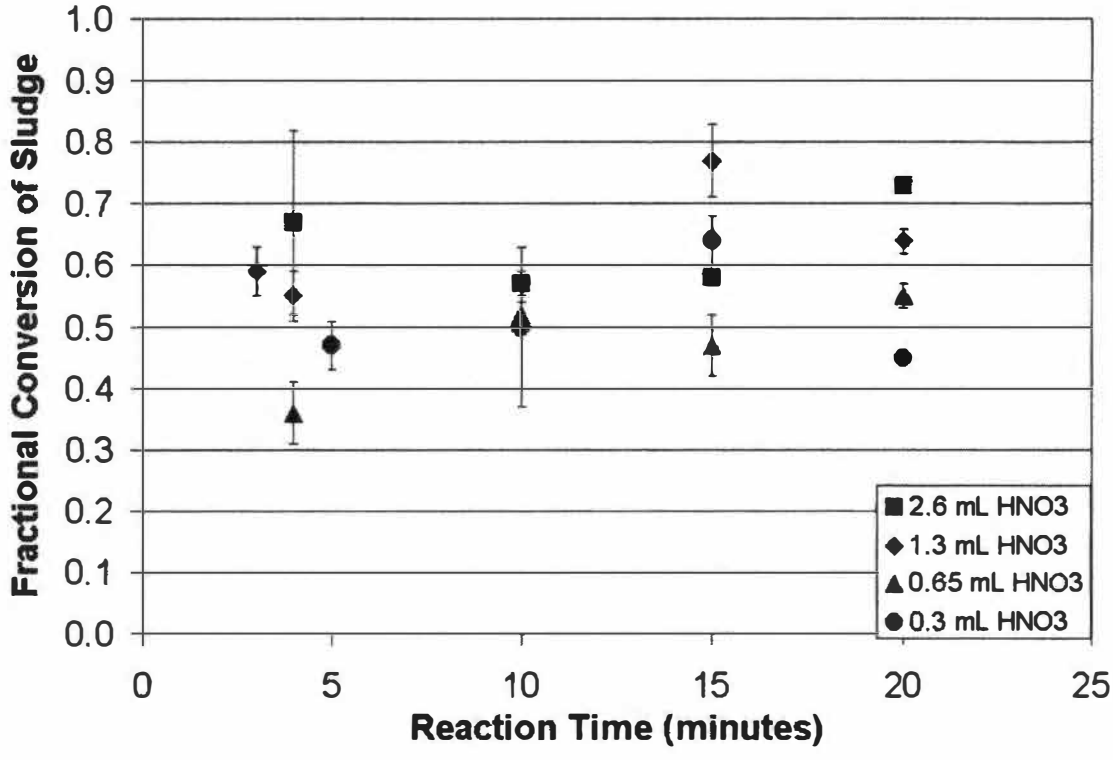

Figure 6 – Fractional Conversion of the Sludge Reactant

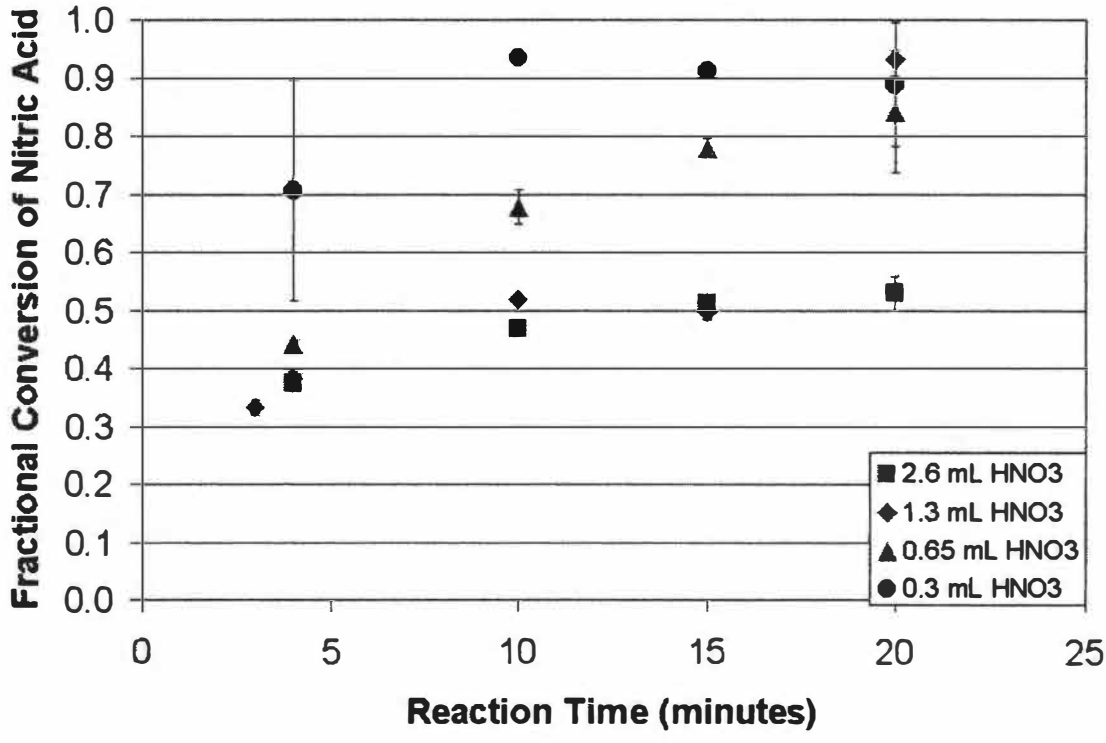

Figure 7 – Fractional Conversion of the Nitric Acid Reactant

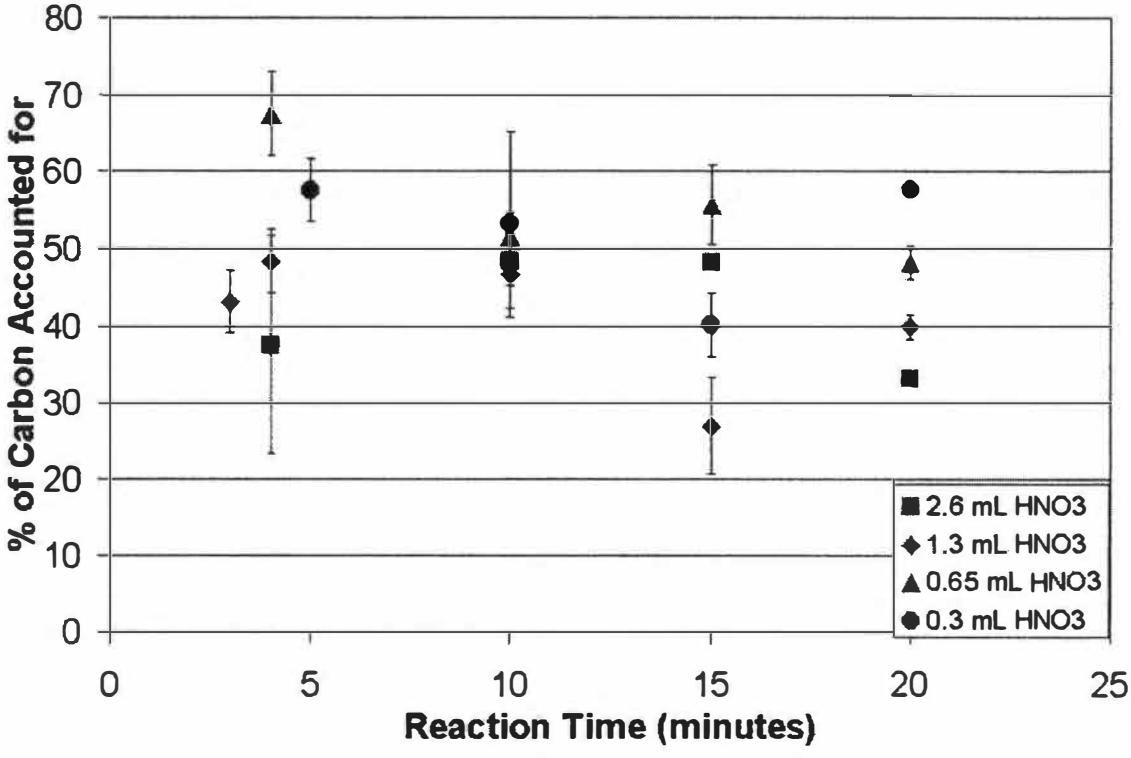

Figure 8 – Amount of Carbon That Is Accounted for in a Carbon Balance

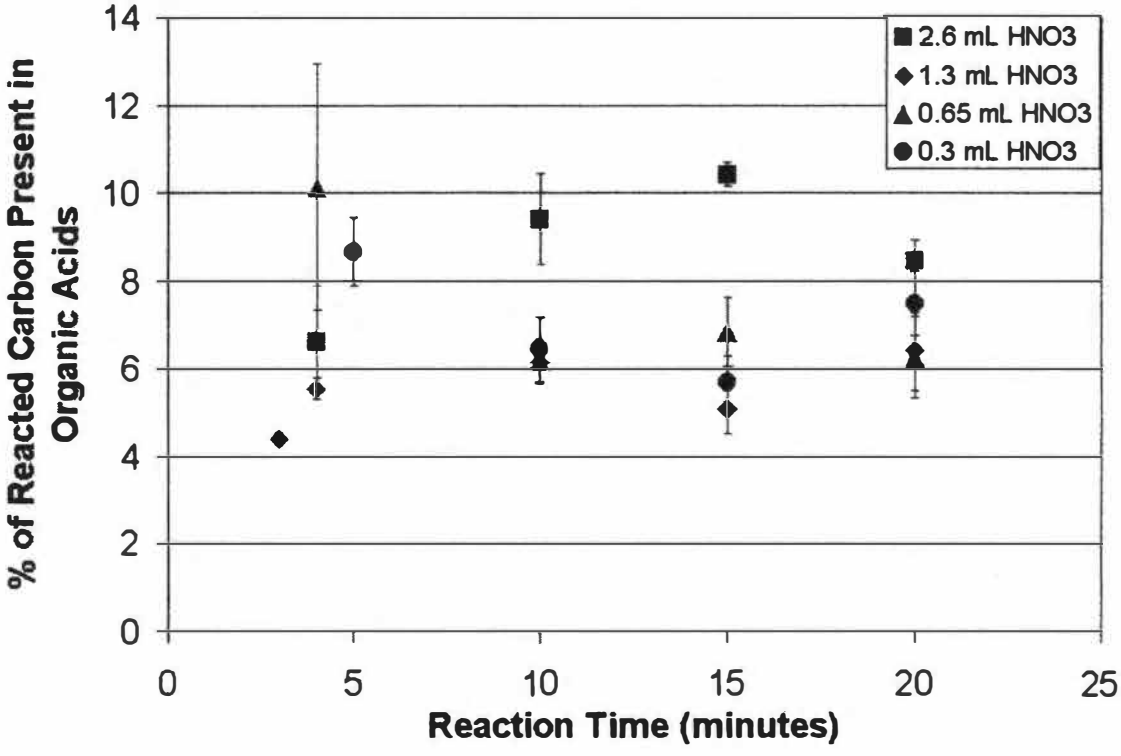

Figure 9 – Percent of Reacting Carbon that Appears in the Organic Acids

PART III

DEVELOPMENT OF NITROLYSIS FOR EXCESS SLUDGE TREATMENT: A FACTORIAL STUDY

Part III of this dissertation is a lightly revised version of a paper by the same name originally published in *Industrial & Engineering Chemistry Research* in 2003 by L. Perkins, K. Klasson, R. Counce, and P. Bienkowski. The revisions were added to include more data in the development of the rate expression and remove inert material from the development. The paper is reproduced with permission from the journal.

ABSTRACT

This research is focused on developing a process called nitrolysis for treatment of excess sludge from wastewater processing. In this process, the excess sludge is treated with nitric acid (up to 11 wt%) at an elevated temperature (greater 160°C) and pressure (100 psig). The result of this treatment is a substantial conversion of the excess sludge to soluble organic. This conversion reduces the viscosity and solids content of the excess sludge stream, thus reducing the disposal costs. The products of the reaction include biodegradable organics that may be recycled to the wastewater treatment process. Other products include potentially recoverable organic acids such as acetic. These acids are produced at about 0.15 grams per grams of dry excess sludge that reacts. This study investigates the operating parameters that could improve the conversion of excess sludge to products and/or biodegradable soluble organics. The parameters used in this study included temperature, acid concentration, sludge concentration, and reaction time. An initial factorial study of these parameters indicated that the acid and sludge concentrations were the most influential in the conversion process. Increasing the acid concentration would convert more of the excess sludge to product. Although the initial study did not show a change in conversion above 160°C, decreasing the temperature below 160°C showed a significant decrease in the excess sludge conversion from 75% to 22%. The lower acid concentration also showed a significant drop in conversion

decreasing from greater than 60% at 11.2 wt% acid to 10% at 0.4 wt% acid. Chemical oxygen demand and total organic carbon tests were used to verify the material balance around the reactor with better than 90% closure. These tests also demonstrated that the initial hydrolysis step in the biomass degradation is very rapid (less than 5 minutes).

1. INTRODUCTION

This research involves the treatment of excess sludge from wastewater treatment activities with nitric acid in a process (nitrolysis) that substantially decreases viscosity and suspended solids. The rationale for the project is to reduce the cost and liability associated with excess sludge treatment and disposal. Current disposal techniques require high costs along with potential liability. A technique that could reduce the cost and liability associated with disposal could be very useful to wastewater treatment facilities. In nitrolysis, the excess sludge is converted to soluble products that may be recycled to the treatment process and/or reclaimed. The possible production of organic acids, as well as the mass and volume reduction, contributes to the economic feasibility of the process. For the purposes of this discussion, 'excess sludge' is the term used to describe the mixture of solids that settle from the primary wastewater and the excess biomass produced during bacterial treatment (biomass normally constitutes over 90% of the solids); such material contains 'bound' water (96% water for the excess sludge obtained for this study). The release of this bound water results in the viscosity decrease. The term 'KUB excess sludge' will represent the excess sludge used in this study (supplied by Kuwahee Wastewater Treatment Facility operated by the Knoxville Utility Board - KUB).

Municipalities and industries generally produce excess sludge during waste water treatment. With approximately 700 large municipal waste water treatment facilities nation wide[1] (producing 5.6 million tons of excess sludge per year[2]), nitrolysis is an intriguing process. Disposal methods for excess sludge include incineration, landfill, land

farming (i.e. KUB),[1,3,4,5] and wet air oxidation,[6] but high cost and liabilities are concerns. These concerns have led to the investigation of alternate disposal methods.

Nitric acid is used in many oxidation processes, such as the oxidation of alcohols, ketones, and aldehydes. 2-octonol, for example, can be oxidized by nitric acid to form 2-octanone.[7] Adipic acid is produced by the oxidation of cyclohexane using nitric acid.[8] Nitric acid has also been used to oxidize bituminous coal to form humic acids.[9] The product of such oxidations often includes carboxylic acids with acid strength an important factor.[7]

The idea of oxidizing excess sludge with nitric acid originates from the patent literature with a goal of improved filterability (separation of solid and liquid components).[10] This required a mild hydrolysis (relatively low acid concentration of 0.4 wt% and moderate temperature of 150°C) of the excess sludge. The current research looks to treat KUB excess sludge with a more severe hydrolysis (relatively high acid concentration of up to 11 wt% and temperatures up to 180°C). The concept is to convert the excess sludge to soluble biodegradable products, which could be recycled back to the waste treatment process or possibly be recovered as valuable organics. These products include organic acids (such as acetic acid), which could prove economically profitable to recover. For example, a facility producing 50-55 tons of excess sludge per day on a dry basis[11] could generate $2.8 million per year in acetic acid (based on production of 0.15 kg acetic acid per kg of dry sludge and $0.44 per pound for acetic acid).[12]

The reaction for the oxidation of excess sludge in land farming can be shown as[13]

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3. \quad (1)$$

The formula $C_5H_7O_2N$ is a general formula that is commonly used to represent biomass.[14] This formula will be the basis for preliminary development of the nitrolysis process, with further stoichiometric studies using the elemental analysis given in this manuscript. The overall nitrolysis reaction is represented as[14]

$$C_5H_7O_2N + HNO_3 \rightarrow \text{Biodegradable organic} + CO_2 + N_2. \quad (2)$$

Any residual nitric acid would be recycled to the wastewater treatment process and diluted by the incoming wastewater. The nitric acid could also serve as a nutrient source during anaerobic digestion of the excess sludge.

2. EXPERIMENTAL

The KUB excess sludge utilized in these experiments was obtained from the Knoxville Utility Board – Kuwahee Wastewater Treatment Facility in Knoxville, Tennessee and stored in a refrigerator, at 7°C, to prevent degradation. An elemental analysis was performed on the KUB excess sludge (Galbraith Laboratories, Knoxville Tennessee) giving the elemental composition shown in Table 1 (all tables and figures can be found in the appendix of this section). The experimental techniques used in performing this research were developed during a previous screening and feasibility study of this process and can be found in that report.[14] Additional analysis for Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) were also performed. The COD tests were conducted using HACH 0-150 ppm COD vials, a HACH COD reactor, and a DR/700 Colorimeter all supplied by HACH Company of Loveland, CO. The TOC tests were performed using a TOC analyzer (TOC-V_{CSH}) supplied by Shimadzu

Corporation of Atlanta, GA. All procedures for the COD and TOC tests were performed according to manufacturer instructions.

3. THEORY

3.1 Reaction Rate Equation

The desire is to develop a model for the reaction rate of the nitrolysis process. In order to generate such a model, the reaction rate is represented by the form

$$-r_A = k(C_{acid})^{\alpha}(C_{sludge})^{\beta} \quad (3)$$

where

$-r_A$	is the reaction rate (rate of disappearance of excess sludge)	[mol/mL-min]
C_{acid}	is the concentration of nitric acid in the reactor	[mol/mL]
C_{sludge}	is the concentration of excess sludge in the reactor	[mol/mL]
α,β	are empirical constants	[-]
k	is the reaction rate constant.	$[mL/mol]^{\alpha+\beta-1}/min$

Equation 3 can be rewritten in the form

$$\ln(-r_A) = \ln(k) + \alpha\ln(C_{acid}) + \beta\ln(C_{sludge}). \quad (4)$$

Equation 4 can then be used to determine values for α, β, and k by fitting the parameters by statistical analysis. This model can then be used for process design purposes. The program used to generate this model was JMP supplied by SAS.[15] This program is a linear statistics program that is useful in producing models and fitting parameters. A plot of concentration (mol/mL) of sludge against reaction time was used in the model development. A polynomial was fit to the experimental data, and the slope of that curve

(dC/dt or r_A) was determined at each condition of interest. This experimental rate was then used to develop the theoretical model. The results from the model can be seen later in this document.

3.2 Parameter Effects

The variables used in this research include temperature, acid concentration, sludge concentration, and residence time. The acid concentration is the wt% acid in the reactor and the sludge concentration is the wt% solids in the original KUB excess sludge sample. The extent to which each variable affects the reaction will be examined using Equation 5 obtained from Murphy[16]

$$\text{Effect of } X_i = \frac{\sum \text{responses high } X_i - \sum \text{responses low } X_i}{\text{half the number of factorial runs}} \tag{5}$$

where X_i represents the variable of interest. This method of analysis allows all of the data in the factorial design to be included in the variable analysis, and allows the different variable effects to be compared directly.

The error in the analysis is needed to determine whether each variable effect is statistically significant (in this case with a 95% confidence interval) and is given in Equation 6 as described by Murphy[16]

$$\text{Error} = ts\sqrt{\frac{N}{4}} \tag{6}$$

where t is the student t statistic, s is the standard deviation of the data, and N is the number of factorial runs. If the variable effect is such that when the error is included, the variable range includes zero, then the effect is not statistically significant.

4. FACTORIAL DESIGN

A factorial design[16,17,18] was used in this research to assess the contribution of several variables to the nitrolysis reaction. These variables include reaction temperature, residence time, acid concentration, and sludge concentration. The range for each of these variables was determined from previous tests[14] and is shown in Table 2 with the actual set of experiments shown in Table 3.

The experiments were performed in random order and then analyzed to determine the effect of each variable on the two output variables (excess sludge conversion and product formation). The units on the developed effect are consistent with the response variable under consideration. These experiments allow a maximum amount of information to be obtained from a minimum number of experiments. The current study is an extension of previous work performed by Perkins et al,[14] which served as a screening study to assess the feasibility of the process and develop experimental procedures. This work adds additional parameters and incorporates four variables into one set of experiments.

Upon completion of the factorial study, the analysis indicated an expanded range on the variables was needed to further develop the process. Temperature was not found to have an impact on excess sludge conversion in the initial range of 160-180°C. To better characterize the effect of temperature on excess sludge conversion, a new set of experiments was conducted with a temperature range down to 100°C. The acid concentration effect was also characterized further with additional tests. These tests included runs with an acid concentration down to 0.5%wt. These data were utilized in

the yield discussion later in this paper.

5. RESULTS

5.1 Parameter Effects

The excess sludge conversion is the main response of interest in this paper and is demonstrated in Figure 1. Figure 1(a) shows the Knoxville Utility Board (KUB) excess sludge as received and Figure 1(b) shows the effluent of the nitrolysis process. In the nitrolysis reaction, nitric acid ruptures the cells of the biomass, which contain the bound water. As a result, the bound water is released from the biomass and the solids settle out more readily. The organics in the excess solids are hydrolyzed to the liquid phase and converted to products (acetic acid, formic acid, CO_2) during the reaction. The solids remaining after the reaction are mainly inert materials that do not react. These solids are free of bound water and settle out very easily as illustrated in Figure 1.

The results of the data analysis of the experimental data in the factorial study are shown in Tables 4-6. The units on the effect are the same as that of the response variable under consideration. Table 4 contains the data analysis for the effect of studied variables on the excess sludge conversion. The results of this table show that the temperature and reaction time do not affect the excess sludge conversion at a 95% confidence interval. This was particularly surprising for the temperature effect. Further tests were performed and are discussed later. The acid concentration is the variable that affects the excess sludge conversion the most. The higher acid concentrations correspond to a higher excess sludge conversion. The excess sludge concentration has the opposite affect. The higher excess sludge concentrations result in a lower excess sludge conversion represented by

the negative effect in Table 4.

The data from the factorial study were also analyzed with a response variable of acetic acid production, using a 95% confidence interval. Table 5 contains the data analysis for this response, showing the excess sludge concentration has the largest effect. The higher excess sludge concentration yields a higher formation of acetic acid. The acid concentration has the second largest effect on this response, but the error analysis shows all four variables are statistically significant. The temperature and reaction time affect the acetic acid production about half as much as the excess sludge concentration. Therefore, increasing the excess sludge and acid concentrations, should be the best method for increasing formation of acetic acid.

In order to get a more complete picture of the production of organic acid, a similar analysis was performed incorporating all acids produced. All organic acids in the effluent (including trace quantities of propionic, valeric, and butyric acids) were converted to an equivalent amount of acetic acid by calculating how much acetic acid could be produced from all of the carbon in the organic acids. The analysis was performed on the response called 'equivalent acetic acid' also given in g/L. A 95% confidence interval was again used and the results of this analysis can be seen in Table 6. These data show that the excess sludge concentration has the largest affect on the production of equivalent acetic acid and the acid concentration has the second largest affect. These data show that increasing the excess sludge and acid concentrations increases the production of equivalent acetic acid. The reaction time has the same affect as the acid concentration but to a slightly less extent. The initial factorial design showed

no temperature affect on the equivalent acetic acid produced, but further tests showed differently.

An expanded study was performed to further evaluate the temperature and acid concentration effects on the excess sludge conversion. These tests were performed at temperatures ranging from 100°C to 180°C. The results showed a nearly linear decrease in excess sludge conversion from the 72% conversion at 180°C to just 20% at 100°C. (These data can be seen in Figure 2 with an error of one standard deviation.) The result is a desired temperature for excess sludge conversion in the nitrolysis process of 160°C or above. (It should be noted that with an inert material composition of 9%, the maximum excess sludge conversion obtainable is 91%.)

The acid concentration was also investigated for maximum excess sludge conversion. The new tests were performed with a range that included 0.5%wt acid. These data can be found in Figure 3. The conversion decreased from greater than 60% for the 6.1-11.2%wt acid to 10% for the 0.5%wt acid. This decrease indicates the best acid concentration to maximize excess sludge conversion was approximately 6.1%wt acid or more.

5.2 Reaction Rate Kinetics

The reaction rate equation for the nitrolysis process was developed using Equation 4. The experimental reaction rate data and reactant concentrations data were entered into the JMP program, using the excess sludge concentration versus time plot to determine the experimental rate. The model was developed by fitting the parameters k, α, and β to the experimental reaction rate data at a 95% confidence interval. The resulting

reaction rate model becomes

$$-r_{biomass} = 0.125(C_{biomass})^{0.9}(C_{acid})^{0.2}. \quad (7)$$

Figure 4 compares the model prediction with the experimental data from previous work[14] showing agreement.

5.3 Yield Comparison and Stoichiometry

The stoichiometry and yield of the nitrolysis reaction are also of interest. The yield is defined as the moles of dry excess sludge reacted (difference in moles of dry excess sludge in and out of the reactor) per mole of nitric acid reacted. As shown in the Figure 5, the yield increases with a decrease in the reaction time. This trend can be explained by looking at the nitric acid component. The nitric acid first hydrolyzes the excess sludge as described in section 5.1. After the organics are hydrolyzed to the liquid phase, the nitric acid continues to convert the organics to other products. As the reaction time increases, the conversion does not increase but the nitric acid consumption does because the nitric acid converts the organics to shorter chain organic acids (acetic and formic acid) and eventually CO_2. This gives better insight into optimizing the operating conditions to maximize the excess sludge conversion while minimizing the cost of nitric acid. This information, along with organic acid production, should be considered in future economic studies.

Based on the elemental analysis, the molcular formula C_3H_5NO was developed for KUB excess sludge. A carbon balance around the reactor showed that approximately 10% of the carbon resulted in organic acids. Another 10-20% of the carbon was converted to the gas phase in the form of CO_2, with as much as 50% of the carbon

remaining in the residual KUB excess sludge. The balance of the carbon was accounted for in other liquid phase products. These products are not known at this time, but COD and TOC tests (discussed later) demonstrate their presence.

5.4 Material Balance and COD Tests

Chemical Oxygen Demand (COD) tests (dissolved and particulate) were performed on the effluent from the reactor to aid in closing the material balance. The dissolved COD increased significantly during the nitrolysis process, from an initial 3,700 mg/L to an effluent stream ranging from 12,000 to 16,000 mg/L, as shown in Figure 6. This result indicates the sludge is hydrolyzed, releasing more of the organics into the liquid phase. The organics are then converted to organic acids or gases. Conversely, the particulate COD (COD due to unreacted excess sludge) decreased during the reaction, as shown in Figure 7. This again, indicates that the organics in the particles are hydrolyzed, thus reducing the particulate COD. Analyzing these data, an average of 91% of the initial COD is accounted for in the effluent (dissolved COD, particulate COD, CO_2). A similar analysis was performed using TOC tests yielding similar results. Again, better than 90% closure of the material balance was obtained.

6. CONCLUSIONS

This research has shown that the conversion of excess sludge is increased with increasing acid concentration and decreased with increased excess sludge concentration. Furthermore, this work shows that biomass is hydrolyzed quickly (as shown by the increased dissolved COD and decreased particulate COD) and converted to the products of organic acids and gases more slowly. The parameter study of the nitrolysis reaction

showed the reaction time and temperature to have no statistical significance in sludge conversion in the initial study, however, an expanded range on the variables demonstrated their significance. With regards to acetic acid production, all four parameters (reaction time, temperature, acid concentration, and sludge concentration) were statistically significant at a 95% confidence interval. A reaction rate model was developed from the generated data and showed good agreement with the experimental data. COD and TOC tests also demonstrated the closure of a material balance around the reactor with better than 90% closure.

7. ACKNOWLEDGEMENTS

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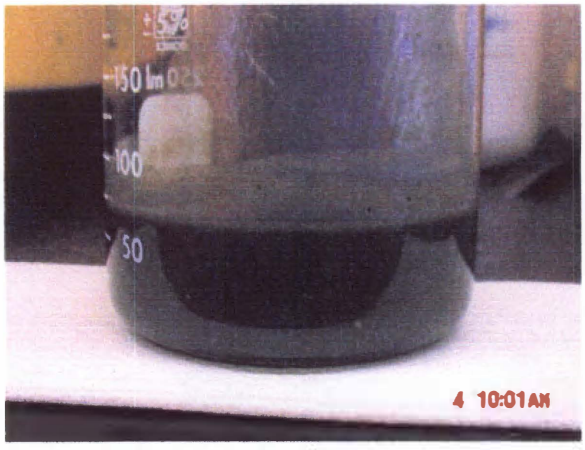
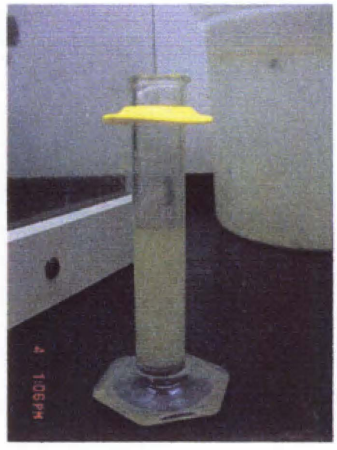
APPENDIX





(a) KUB Excess Sludge Prior to Nitrolysis (b) KUB Excess Sludge After Nitrolysis

Figure 1 – Effect of Nitrolysis Reaction on KUB Excess Sludge from Kuwahee Wastewater Treatment Facility in Knoxville, TN

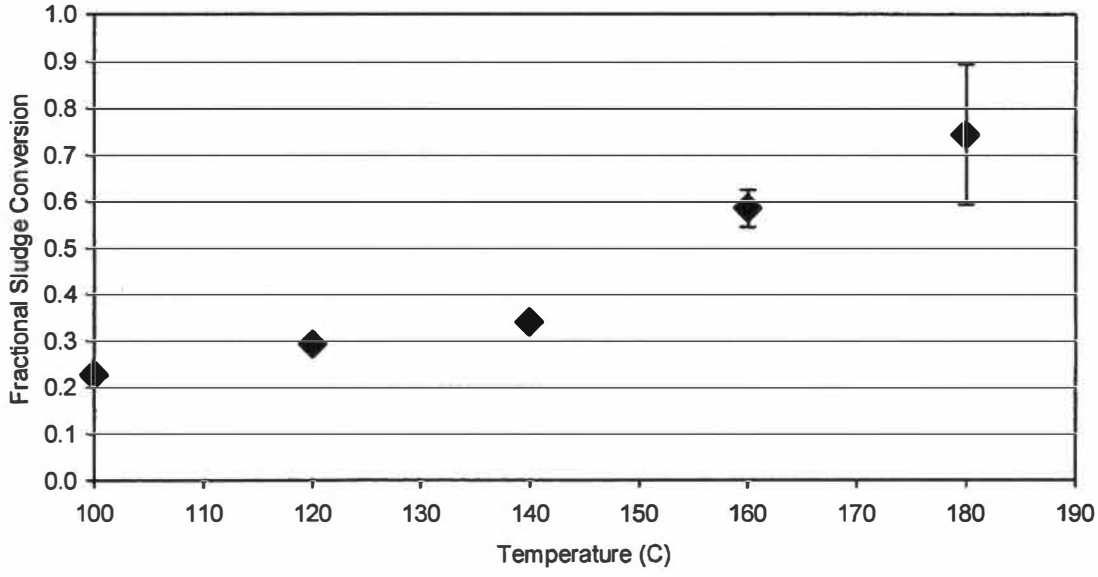


Figure 2 – Effect of Temperature on the Excess Sludge Conversion at an Acid Concentration of 11.2%wt and an Excess Sludge Concentration of 4%wt

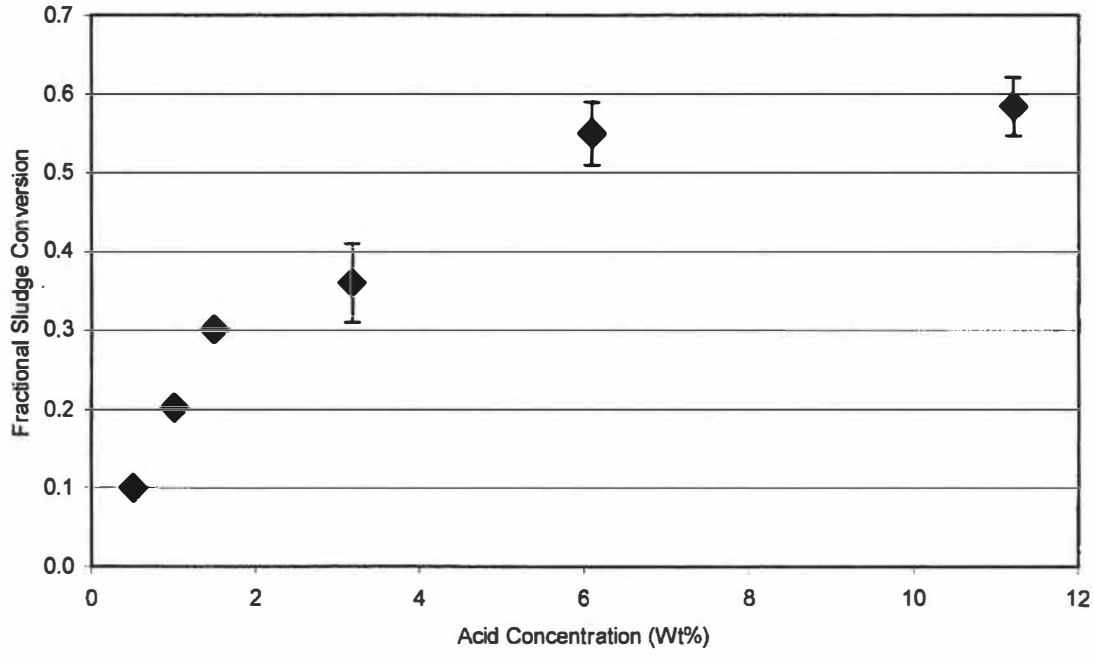


Figure 3 – Effect of Acid Concentration on Excess Sludge Conversion with a Sludge Concentration of 4% and a Temperature of 160°C

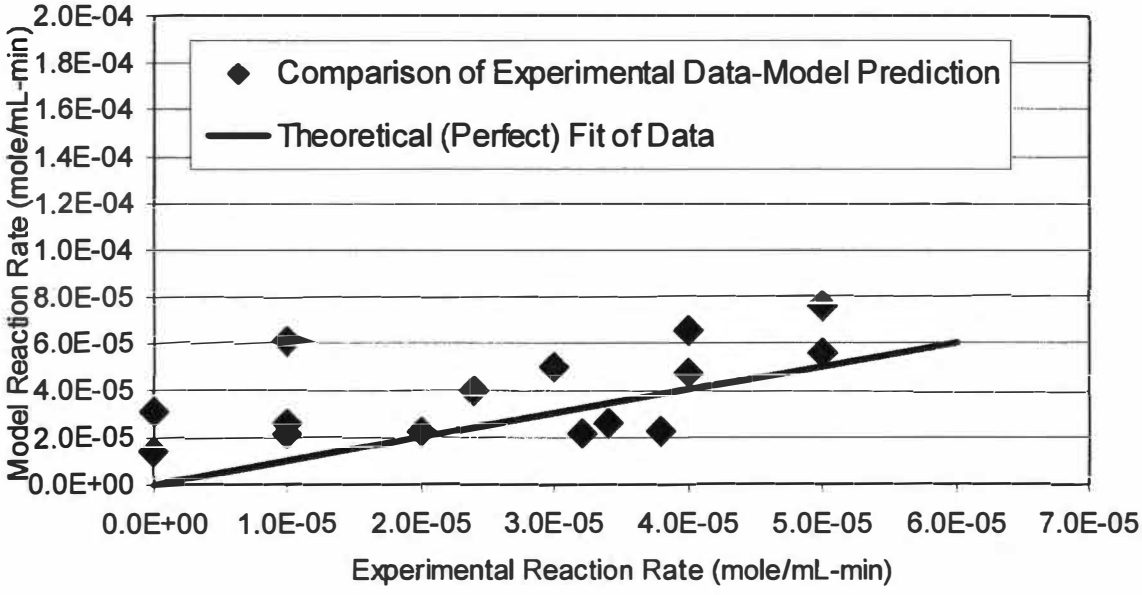


Figure 4 – Error Analysis of Reaction Rate Model Showing Actual and Model Prediction Values

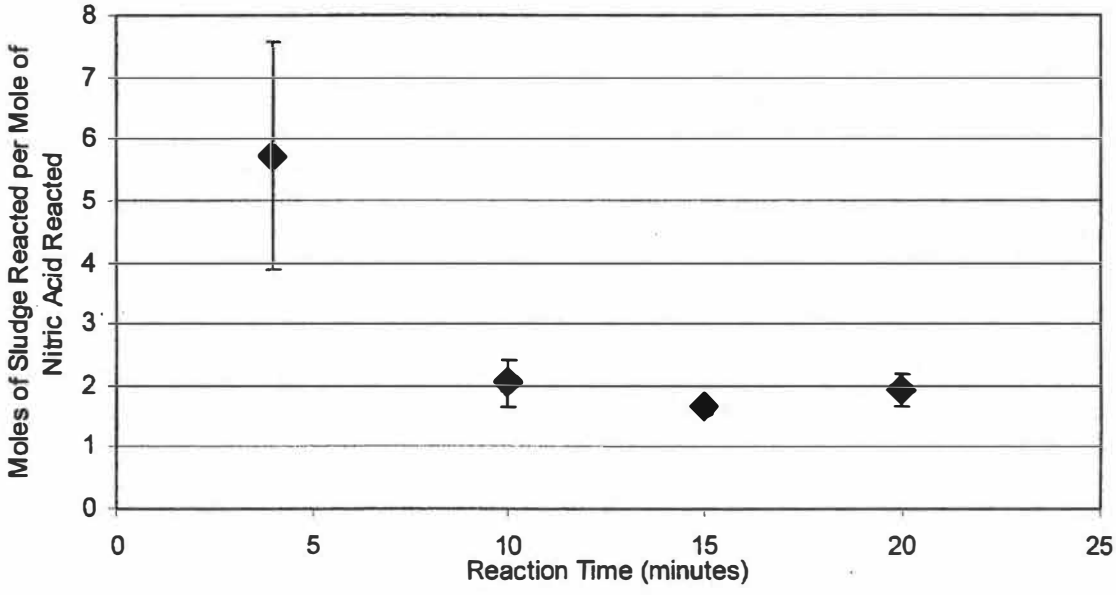


Figure 5 – Yield of Nitrolysis Process with Respect to Reaction Time for 11.2%wt Nitric Acid

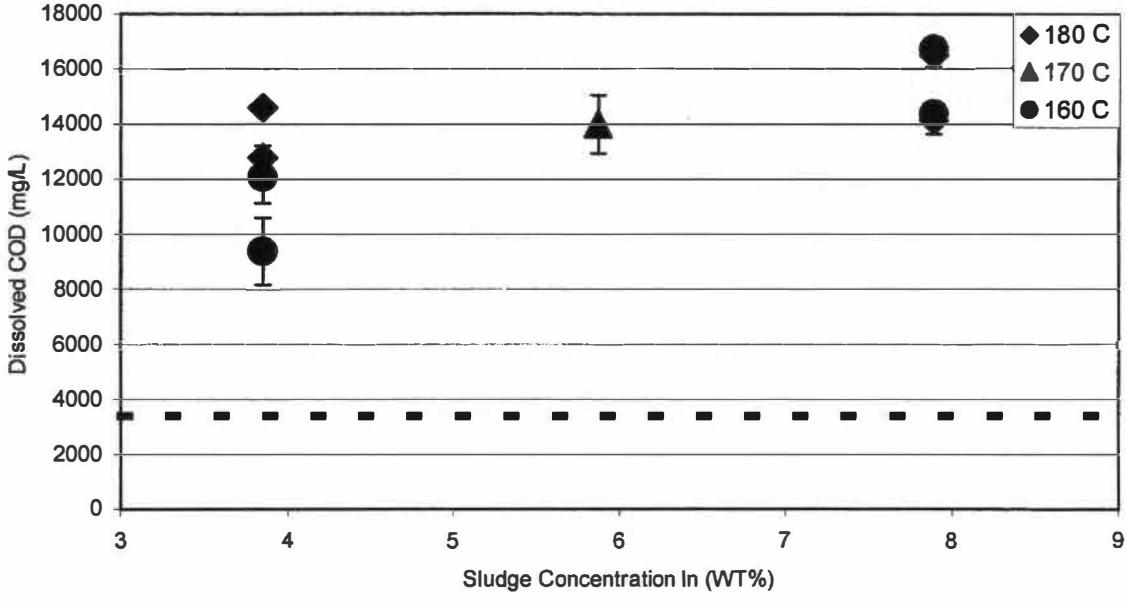


Figure 6 – Parameter Effects on Dissolved COD In Effluent

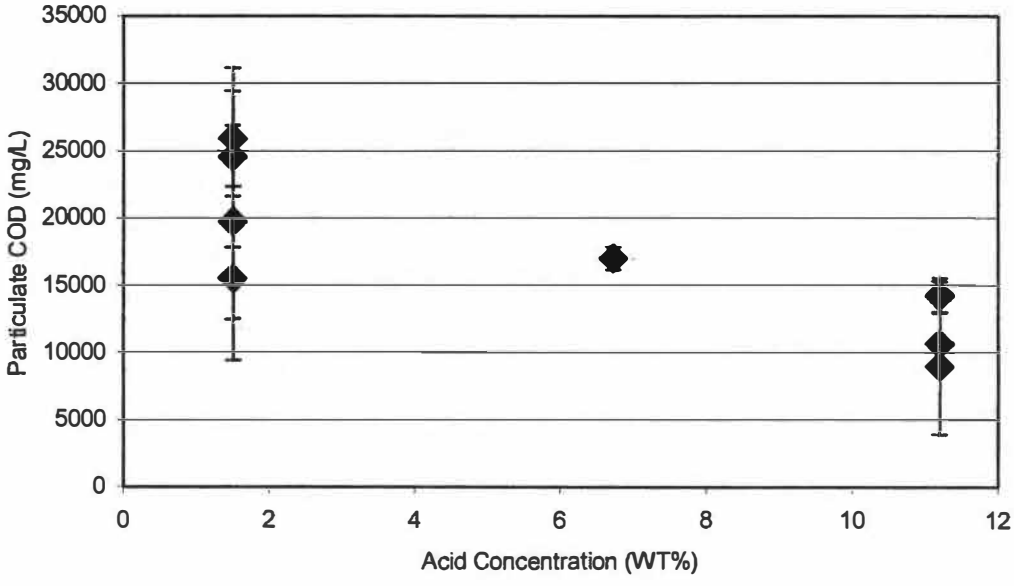


Figure 7 – Acid Concentration Effect on Particulate COD In Effluent

Table 1 – Characteristics of the KUB Excess Sludge Used in this Research

CHARACTERISTIC	VALUE	UNITS
DENSITY	1.014	g/mL
SOLIDS CONTENT (as received)	4.1	wt%
SOLIDS CONTENT (concentrated)	7.9	wt%
COMPOSITION	-	-
Carbon	41.14	wt%
Nitrogen	16.72	wt%
Oxygen	21.45	wt%
Hydrogen	12.37	wt%
Inert Material	8.32	wt%

Table 2 – Variable Ranges for Initial Factorial Design

Parameter	**Range**
Temperature	160 – 180 °C
Acid Concentration	1.5 – 11.2 %wt
Sludge Concentration	4 – 8 %wt
Residence Time	5 – 20 minutes

Table 3 – Initial Eight Run Factorial Design for Parameter Testing with KUB Excess Sludge

Runs	Temp. (°C)	Acid (wt%)	Sludge (wt%)	Time (minutes)
1	160	1.5	4	5
2	180	1.5	4	20
3	160	11.2	4	20
4	180	11.2	4	5
5	160	1.5	8	20
6	180	1.5	8	5
7	160	11.2	8	5
8	180	11.2	8	20
center	170	6.4	6	12.5

Table 4 – Parameter Effects on Sludge Conversion Based on Tables 2 and 3

Variable	**Effect & Error**	**Statistically Significant**
Temperature	0.111 ± 0.115	NO
Sludge Concentration	-0.139 ± 0.115	YES
Acid Concentration	0.309 ± 0.115	YES
Reaction Time	0.017 ± 0.115	NO

Table 5 – Parameter Effects on Acetic Acid Production Based on Tables 2 and 3

Variable	**Effect & Error**	**Statistically Significant?**
Temperature	0.382 ± 0.228	YES
Sludge Concentration	0.977 ± 0.228	YES
Acid Concentration	0.771 ± 0.228	YES
Reaction Time	0.476 ± 0.228	YES

Table 6 – Parameter Effects on Equivalent Acetic Acid Based on Tables 2 and 3 (Total Organic Acid)

Variable	**Effect & Error**	**Statistically Significant?**
Temperature	0.304 ± 0.535	NO
Sludge Concentration	1.180 ± 0.535	YES
Acid Concentration	0.860 ± 0.535	YES
Reaction Time	0.709 ± 0.535	YES

PART IV

DEVELOPMENT OF NITROLYSIS FOR EXCESS SLUDGE TREATMENT II: A FACTORIAL STUDY FOR INDUSTRIAL WASTES

Part IV of this dissertation is a lightly revised version of a paper by the same name originally submitted for publication in *Industrial & Engineering Chemistry Research* in 2003 by L. Perkins, K. Klasson, R. Counce, and P. Bienkowski. The revisions were made to make the rate expression more consistent with that of the previous paper. The paper is reproduced with permission from the journal.

ABSTRACT

Excess sludge generated in industrial wastewater treatment was converted to soluble organic products and gases in the nitrolysis reaction. The conversion of industrial excess sludge reached 80% conversion by mass (99% conversion after removing inerts from the calculation). The most instrumental operating parameters in increasing this conversion were reaction temperature and acid-sludge ratio in the reactor. The reduction in mass and volume of the excess sludge shows promise in reducing the liability and cost associated with disposal. The production of organic acids (i.e. acetic acid) was also demonstrated, leading to an even more promising treatment alternative for excess sludge. The operating parameters that affect the production of organic acids were also studied. The reaction rate of the process was compared to a previously developed model, showing good agreement. The stoichiometry of the process was investigated, showing more than 90 mg of acetic acid and more than 50 mg of formic acid produced per gram of industrial excess sludge reacted.

1. INTRODUCTION/BACKGROUND

We have investigated nitrolysis as a process using nitric acid to treat excess sludge from wastewater treatment. The result of the nitrolysis process is a decrease in the mass and volume of the excess sludge that must ultimately be disposed. The reduction in volume comes from the release of 'bound water' in the biomass as described by Perkins et al.[1] The rationale for this research is to reduce the high cost and potential liability associated with the current industrial treatment techniques such as incineration, landfill, landfarming,[2,3,4,5] and wet air oxidation[6]. The products of the nitrolysis reaction are soluble organics that may be recycled to the treatment process and/or potentially recovered (i.e., acetic acid). The term 'excess sludge', as used in this report, consists of a mixture of solids that originally settle from wastewater, excess biomass generated during bacterial treatment, inerts, and water. The term 'dry excess sludge', as used in this report, consists of dehydrated excess sludge. This work looks at extending previous work by Perkins et al.[1,7] to an industrial source of excess sludge. The excess sludge used in this study will be referred to as 'industrial excess sludge' and originates in an industrial secondary biological wastewater treatment facility.

A typical wastewater treatment facility may produce 50-55 tons of excess sludge per day on a dry basis[8] (dry excess sludge), thus generating the need for an alternate treatment method. Based on this production rate, and an estimated 0.15 kg of acetic acid produced per kg of dry excess sludge reacted, an estimated $2.8 million can be generated in acetic acid per year ($0.44 per pound of acetic acid).[9] Nitrolysis is an economically intriguing treatment option in this area, due to the reduction in the mass and volume of

the excess sludge, while possibly producing reclaimable organic acids.

The products of organic oxidation have been documented in other studies. Ozone, which is used to treat specific compounds in industry and to improve taste, color, and filtration in municipal wastewater,[10] does not degrade most organics to CO_2.[11] Instead, carboxylic acids (i.e. acetic and formic) are the final products of the oxidation, due to their low reactivity.[11] Similarly, wet air oxidation ultimately results in acetic and formic acids[12] for the same reasons discussed above. Other studies have investigated the treatment of excess sludge with sulfuric acid and sodium hydroxide. Sulfuric acid reportedly gave 50-60% solubilization of the suspended solids and NaOH gave 46% solubilization of the suspended solids.[13] These tests, however, utilized a 24 hour pretreatment at room temperature by the acid or caustic, followed by a treatment at 175°C for 30 minutes.[13] The current nitrolysis process is much faster involving a 10 minute reaction time.

Previous studies of nitrolysis by Perkins et al.[1,7] focused on the treatment of municipal excess sludge with nitric acid at elevated temperatures (180°C), demonstrating as much as 72% converison. The work indicated temperature changes at high temperatures (160-180°C) did not change the conversion, but lower temperatures (120°C) decreased the conversion. Perkins et al.[1,7] also indicated the hydrolysis of the municipal excess sludge was rapid with little to no time effect on the reaction, within the range of 5-20 minutes. The acid concentration (1.5-11.2%wt in reactor) reportedly showed the greatest effect on the conversion of the municipal excess sludge. The production of acetic acid was also investigated showing 10% of the carbon resulted in organic acids

(mainly acetic acid) with another 20% of the carbon resulting in gaseous products (i.e. CO_2) as typical results. 50-60% of the carbon typically remained in the unreacted municipal excess sludge with Chemical Oxygen Demand and Total Organic Carbon tests showing the remaining carbon to be in the liquid phase (completing a material balance around the system). A reaction rate equation for the nitrolysis of municipal excess sludge was developed by Perkins et al.[1,7] and will be utilized in this work. Refer to the papers by Perkins et al.[1,7] for more data on the nitrolysis of municipal excess sludge, as well as more background information about the nitrolysis process.

2. EXPERIMENTAL

The industrial excess sludge utilized in these experiments was obtained from a local industrial wastewater treatment facility and consists of 96.93%wt water and 3.07%wt solids. The industrial excess sludge was stored in a refrigerator, at 7°C, to prevent degradation. An elemental analysis was performed on the dried solids of the industrial excess sludge (Galbraith Laboratories, Knoxville, Tennessee) giving the elemental composition. The specific characteristics of the excess sludge, including the elemental composition can be found in Table 1. All other procedures in this work were identical to the procedures by Perkins et al.[1,7]

3. METHODS FOR INTERPRETATION OF DATA

3.1 Reaction Rate Equation

In previous studies by Perkins et. al[1,7], the desire was to develop a model for the reaction rate of the nitrolysis process on municipal excess sludge. The result was the

reaction rate equation: $-r_{biomass} = 0.125(C_{biomass})^{0.9}(C_{acid})^{0.2}$ (1)

Where $-r_{biomass}$ is the rate of disappearance of dry excess sludge and $C_{biomass}$ is the concentration of the excess sludge in the effluent from the reactor. This model can be used to compare with the current industrial excess sludge data. An estimate of the experimental reaction rate in this research was calculated by using the form

$$-r_{biomass} = \frac{\Delta \text{Concentration of Industrial Excess Sludge in the Reactor}}{\text{time}} \quad (2)$$

for the reaction rate on an inerts free basis. This estimate of the reaction rate was then used to develop a reaction rate expression to compare to the previous work[1].

3.2 Parameter Effects

The variables used in this research include temperature, acid-sludge ratio, and sludge concentration. The acid-sludge ratio is the mass ratio of nitric acid added and dry industrial excess sludge added. The sludge concentration is the wt% solids in the original industrial excess sludge sample. The extent to which each variable affects the reaction was examined using the following equation[14], where X_i represents the variable of interest.

$$\text{Effect of } X_i = \frac{\sum \text{responses high } X_i - \sum \text{responses low } X_i}{\text{half the number of factorial runs}} \quad (3)$$

The error associated with the variable effect is given in Equation 4 as described by Murphy[14] (in this case with a 95% confidence interval).

$$\text{Error} = ts\sqrt{\frac{N}{4}} \quad (4)$$

where t is the student t statistic, s is the standard deviation of the data, and N is the number of factorial runs. This error analysis allows the determination of the statistical

significance of each effect.

4. FACTORIAL DESIGN

A factorial study[1,14,15,16] was used in this research to assess the contribution of each variable to the nitrolysis reaction. These variables include reaction temperature (°C), acid-sludge ratio (mass basis), and sludge concentration (wt% originally). The range for each of these variables was derived based on previous studies[1,7] of this process involving municipal excess sludge. These ranges were 120-180°C for temperature, 0.40-3.34 for acid-sludge ratio by mass, and 3-5 wt% for sludge concentration in feed to reactor. These previous tests indicated the variables used here are the most important factors to the nitrolysis process. The ranges on each variable were also developed based on this previous work. This information was used to set up the factorial study of the research, which is shown in Table 2.

The experiments were performed in random order and then analyzed (using Equations 3 and 4) to determine the degree to which each of the variables affects the industrial excess sludge conversion and product formation. The units on the effect are the same as that of the response variable under consideration.

5. RESULTS

5.1 Parameter Effects

The primary response of interest in an industrial setting is excess sludge conversion (mass of dry solids converted to products). The results from this response are shown in Table 3. The data presented is within a 95% confidence interval, and indicates all three variables are statistically significant in excess sludge conversion. The effect

associated with the acid-sludge ratio (29.82) is the largest, nearly 1.5 times as effective as the temperature. Increasing either of these parameters increases the conversion of industrial excess sludge, as demonstrated in Figure 1. The concentration of the industrial excess sludge, while statistically significant, is considerably less effective at altering the excess sludge conversion than the other variables. In fact, the effect of the sludge concentration arguably has little to no effect.

Another response of interest in nitrolysis is the production of acetic acid as a product. Table 3, using a 95% confidence interval, shows the results of a parameter study with respect to acetic acid production. Again, this analysis shows that all three parameters in the study are statistically significant. In this case, the sludge concentration has the largest affect on the production of acetic acid. Temperature and acid-sludge ratio have the same trend, acetic acid production increases with all three parameters; however, the sludge concentration is twice as effective as the other parameters. The result shows an increase in acetic acid production can be generated by first increasing the sludge concentration (if economically feasible), then increasing the temperature and acid-sludge ratio of the reaction.

A more complete picture of the organic acid production can be obtained by looking at an 'equivalent acetic acid' production. This response is a combination of all organic acids produced into an equivalent amount of acetic acid. The results of this comparison (at a 95% confidence interval) can be seen in Table 3. From these data, again the sludge concentration is twice as effective at altering the equivalent acetic acid production, but all three variables are statistically significant. An increase in any of these

parameters will result in an increase in the amount of equivalent acetic acid produced during the reaction.

Additional tests were also performed utilizing sulfuric acid in place of nitric acid for comparison. These results indicate that low acid-sludge ratios gave the same conversion, but as the ratio of acid to sludge increased (increasing the acid concentration) the nitric acid performed better. This trend is thought to be due to the ionization of the acids. As the acid concentration increases, H_2SO_4 will not ionize completely, leading to a lower H+ concentration per mole of acid and ultimately a lower industrial excess sludge conversion.

5.2 Material Balance and COD Tests

Chemical Oxygen Demand (COD) tests were performed on the effluent from the reactor to aid in closing the material balance and to verify the movement of organics from the particulate to dissolved phase. The dissolved COD and particulate COD were both investigated in this study. The dissolved COD increased significantly during the nitrolysis process, from an initial 1,200 mg/L at 3.07%wt excess sludge (6,000 mg/L at 5.14%wt) to an effluent stream ranging from 5,000 to 13,000 mg/L at 3.07%wt (17,000 to 20,000 mg/L at 5.14%wt), as shown in Figure 2. This indicates the sludge is hydrolyzed, forcing significant amounts of the organics into the liquid phase. The organics are then converted to organic acids or gases. Conversely, the particulate COD decreased during the reaction, as shown in Figure 3. This again, indicates the organics in the particles are hydrolyzed, thus reducing the particulate COD. Analyzing these data, as much as 90% of the initial COD is accounted for in the effluent (dissolved COD, particulate COD, CO_2). A similar

analysis was performed using Total Organic Carbon (TOC) tests. An increase in the dissolved TOC in the liquid phase was also observed, with 90+% closure of the material balance.

5.3 Reaction Rate Kinetics

The focus of this work is to determine the effect of various parameters on conversion of industrial excess sludge, and to a lesser extent product formation; however, an investigation of the reaction rate is also of interest. By comparing the experimental reaction rate, as calculated by Equation 2, to the reaction rate developed by the same method as Perkins et al.,[1] a comparison of the industrial and municipal excess sludge can be made. This comparison showed some agreement between the two reaction rate expressions. The reaction rate expression for the industrial excess sludge showed good agreement with the experimental data (found in Figure 4).

5.4 Yield Comparison and Stoichiometry

The yield and stoichiometry of the nitrolysis reaction are also of interest. The yield is defined as the mass of dry industrial excess sludge reacted per mass of nitric acid reacted and is illustrated in Figure 5. (Note several more data points were taken, but these two are shown to illustrate the trend found in the entire data set.) As shown in the figure, the yield increases with a decrease in acid-sludge ratio. This gives better insight into optimizing the operating conditions to maximize the industrial excess sludge conversion while minimizing the cost of nitric acid. This information, along with organic acid production, should be considered in future economic studies.

An estimate of the stoichiometry of the reaction was also obtained. Based on the

elemental analysis, the molecular formula $C_9H_{14}NO_4$ was developed for the industrial excess sludge. A carbon balance around the reactor showed as much as 20% of the carbon was converted to organic acids. Another 5-20% (depending on operating conditions) of the carbon was converted to the gas phase, mainly in the form of CO_2. As much as 50-60% of the carbon remained in the residual industrial excess sludge, according to the elemental analysis of the unreacted industrial excess sludge. The remaining carbon was accounted for in other products in the liquid phase. These products are not known at this time, but COD and TOC tests (discussed earlier) demonstrate their presence. While excess sludge conversion is the most promising aspect of this research, the organic acid production is significant enough to consider in any economic analysis.

6. CONCLUSIONS

This work demonstrated the effectiveness of nitric acid in industrial excess sludge treatment. The results indicate the industrial excess sludge conversion increases with acid-sludge ratio and temperature. The sludge concentration had a much smaller effect. All three parameters were significant in the production of organic acids (mainly acetic acid) but the sludge concentration was the most significant. Increasing the sludge concentration increased the organic acid production. COD and TOC tests aided in closing the material balance around the reactor with as much as 90% closure. The reaction rate developed by Perkins et al.,[1] developed for municipal excess sludge, under-predicted the reaction rate of this industrial excess sludge. Future pilot plant tests will aid in further developing the reaction rate equation for the industrial excess sludge.

7. ACKNOWLEDGEMENTS

This work was funded through the Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the United States Department of Energy under contract DE-AC05-00OR22725, as well as through grants from the ORNL State Partnerships Program and the Tennessee Water Resources Center. Their support is graciously acknowledged.

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APPENDIX

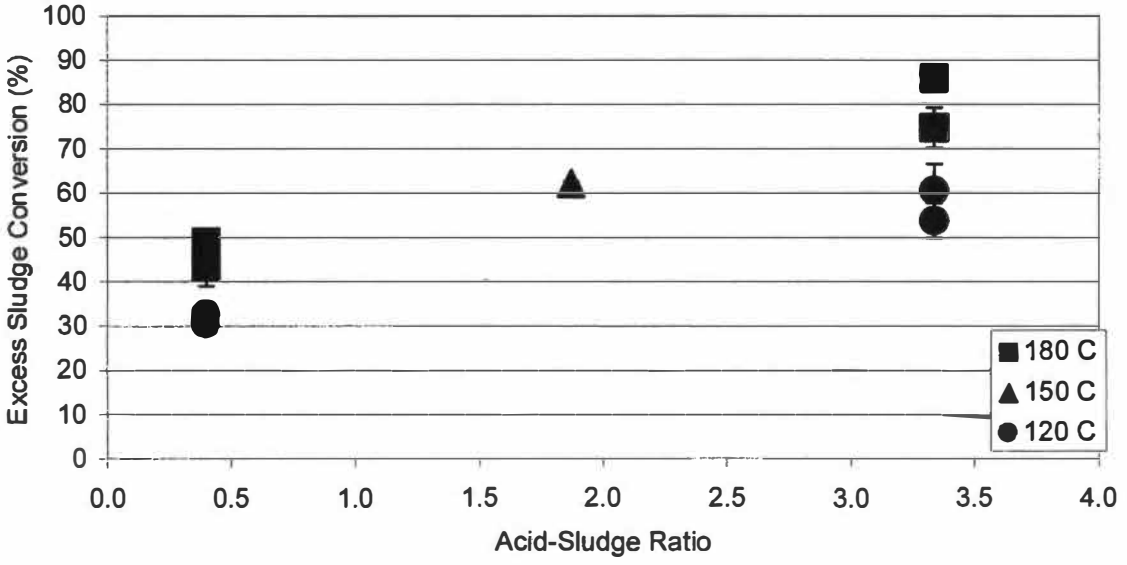

Figure 1 – Effect of Acid-Sludge Ratio and Temperature on Industrial Excess Sludge Conversion

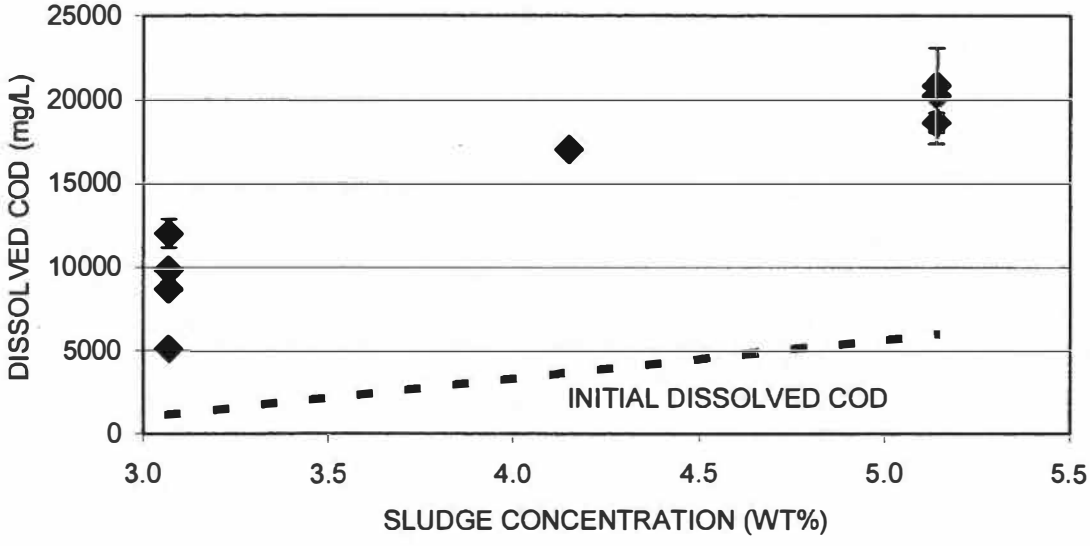

Figure 2 – Effect of Nitrolysis on Dissolved COD in Industrial Excess Sludge with Respect to Sludge Concentration

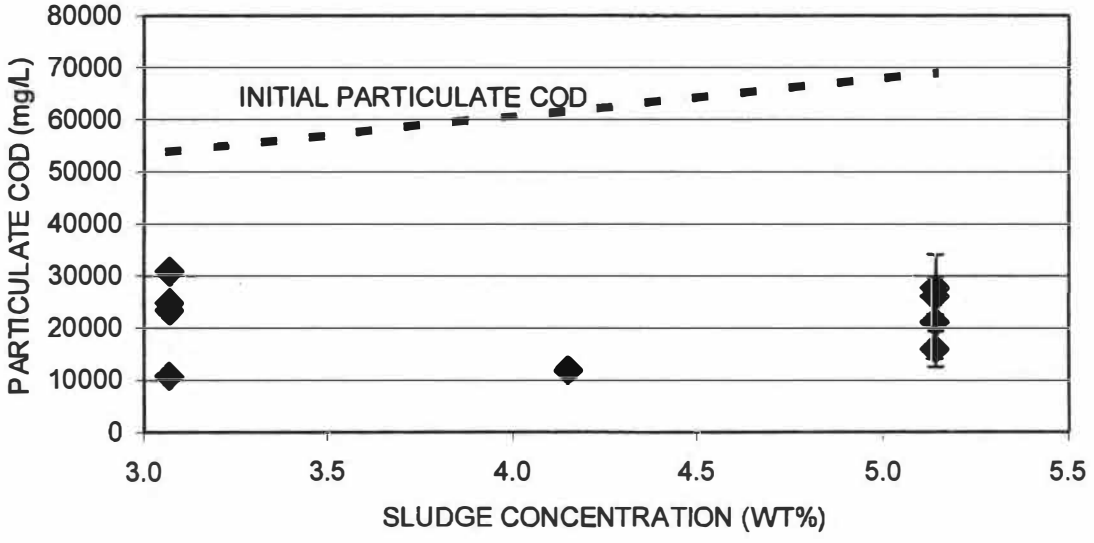

Figure 3 – Effect of Nitrolysis on Particulate COD in Industrial Excess Sludge with Respect to Sludge Concentration

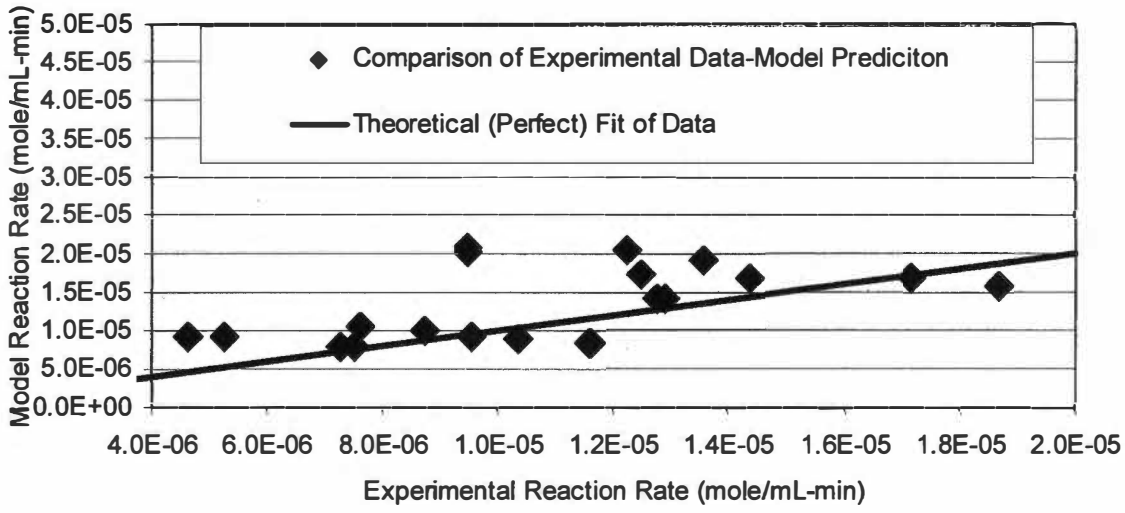

Figure 4 – Comparison of Perkins et. al Rate Equation for Nitrolysis to Industrial Excess Sludge Rate of Nitrolysis

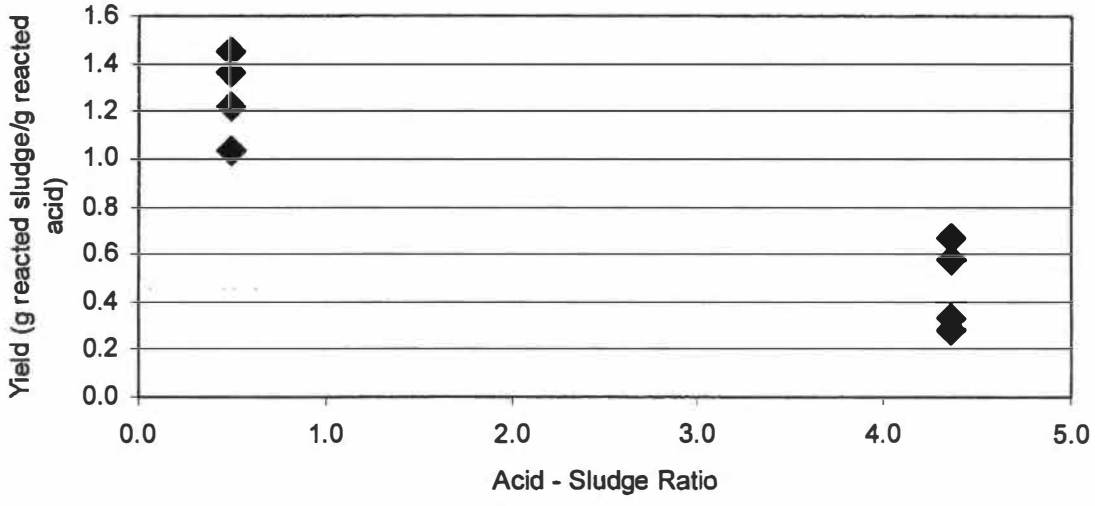

Figure 5 – Yield of the Nitrolysis Process on Industrial Excess Sludge with Respect to Acid-Sludge Ratio

Table 1 – Characteristics of the Industrial Excess Sludge Used in this Research

CHARACTERISTIC	**VALUE**	**UNITS**
DENSITY	0.969	g/mL
SOLIDS CONTENT (as received)	3.07	wt%
SOLIDS CONTENT (concentrated)	5.14	wt%
COMPOSITION	-	-
Carbon	42.78	wt%
Nitrogen	5.27	wt%
Oxygen	27.30	wt%
Hydrogen	5.56	wt%
Inerts	19.09	wt%

Table 2 – Initial Eight Run Factorial Design for Parameter Testing with Industrial Excess Sludge

Runs	Temp. (°C)	Acid-Sludge Ratio (mass)	Initial Sludge Conc. (wt%)
1	120	0.40	3
2	120	3.34	3
3	120	0.40	5
4	120	3.34	5
5	180	0.40	3
6	180	3.34	3
7	180	0.40	5
8	180	3.34	5
center	150	1.87	4

Table 3 – Parameter Effects on Industrial Excess Sludge Conversion Based on Table 2

Response	**Variable**	**Effect & Error**
Sludge Conversion	Temperature	18.789 ± 5.418
	Acid – Sludge Ratio	29.818 ± 5.418
	Sludge Concentration	-6.397 ± 5.418
Acetic Acid Production	Temperature	0.916 ± 0.314
	Acid – Sludge Ratio	0.771 ± 0.314
	Sludge Concentration	2.138 ± 0.314
Equivalent Acetic Acid	Temperature	1.578 ± 0.723
	Acid – Sludge Ratio	1.204 ± 0.723
	Sludge Concentration	3.482 ± 0.723

PART V

DESIGN AND TESTING OF A PILOT PLANT FOR DEVELOPMENT OF NITROLYSIS AS AN EXCESS SLUDGE TREATMENT ALTERNATIVE

Part V of this dissertation is a copy of a paper by the same name originally submitted for publication in *Chemical Engineering Communications* in 2003 by L. Perkins, P. Bienkowski, K. Klasson, and R. Counce. Upon submission, the authors reserved the right to publish this article in this dissertation.

ABSTRACT

This research focused on the design, construction, and operation of a pilot plant for development of the nitrolysis process for excess sludge treatment. A pilot plant was designed and constructed to demonstrate the process on a continuous larger scale than the previous batch studies. The continuous unit was used to evaluate operating parameters that affect sludge conversion and acetic acid formation, both of which make the economics of the process intriguing. This work extends previous studies to demonstrate the nitrolysis process of excess sludge treatment to a system that is more similar to an actual wastewater treatment facility. A carbon balance was also performed around the unit, with good closure. This demonstration will aid in the continued development of the process for implementation in a wastewater treatment facility, to reduce the amount of waste sludge sent for disposal and producing a potentially valuable product to reclaim.

1. INTRODUCTION

The purpose of this research was to design, construct, and test/demonstrate a pilot plant apparatus for development of the nitrolysis process. Nitrolysis involves the nitric acid treatment of excess sludge from wastewater treatment, resulting in biodegradable organics, which possibly can be recycled to the treatment process and/or recovered. The nitric acid ruptures the cells in the excess sludge and releases bound water. This release of the water allows the solids to settle out more readily and reduce the volume of the waste stream. The acid also hydrolyzes the solids (converts them to the liquid phase), thus reducing the mass of the waste stream. Previous reports[1,2,3] have shown the feasibility of the process, indicating high sludge conversion of 70% or more (at elevated temperatures of 180°C and pressures of 200 psi) with the added bonus of organic acid production. This manuscript looks at scaling up the nitrolysis process from the lab scale used in these previous reports to a larger pilot plant.

Excess sludge is generated daily by municipalities and industries during treatment of wastewater. With 5.6 million tons per year[4] of excess sludge generated by the 700 large municipalities in the US,[5] an alternate treatment method could prove financially beneficial. Wastewater typically enters the treatment facility and immediately begins primary treatment. During this step, the solids are allowed to settle and are removed from the water. The wastewater then undergoes secondary treatment. This step utilizes bacteria to produce biosolids, which are also removed from the water. The solids from primary and secondary treatment are then sent into a digestion step. This mixture of solids from primary and secondary treatment is called 'excess sludge' for the purposes of

this document and is composed of 96% water and 4% solids. The excess sludge is currently digested (typically anaerobically) and sent to a dewatering step. This dewatering removes solids from the stream (typically by filter press[6]) and generates a cake of excess sludge that is sent for disposal in any number of ways, such as incineration, landfill, land farming,[5,6,7,8] or wet air oxidation.[9] The reduction in solids may produce large savings in the dewatering and disposal aspects of the process. A block diagram of a typical wastewater treatment facility can be seen in Figure 1 (all figures can be found in the appendix of this section).

The benefit of nitrolysis, as discussed by Perkins et al.,[1,2,3] is the mass and volume reduction of excess sludge entering the digestion step. The nitrolysis reaction generates biodegradable organics that may be recycled to the treatment process. (Figure 2 illustrates a material balance with such a recycle stream.) One product of this reaction includes organic acids (mainly acetic acid). If these acids are produced in a large enough quantity, they could be profitable for separation from the waste stream. Perkins et al.[1,2,3] have demonstrated the production of such products in a quantity that warrants consideration. Reports indicate that a typical wastewater treatment facility may produce 50-55 tons of excess sludge per day on a dry basis.[10] Estimating 0.15 kg of acetic acid produced per kg of dry excess sludge reacted, a typical wastewater treatment facility could produce $2.8 million per year in acetic acid ($0.44 per pound for acetic acid[11]). Another advantage of nitrolysis is the volume reduction of the sludge. The nitrolysis process releases the bound water from the excess sludge, generating a stream with a lower viscosity. This decrease in viscosity results from the release of the bound water,

which allows the solids to settle and creates a smaller volume of excess sludge. These potentials add even more economic feasibility to the process.

2. EQUIPMENT

The equipment needed to develop and construct the pilot plant was the first concern. The reactor is a 1-liter electrically heated Fluitron (Ivyland, PA) autoclave (model 1AM-NRV-39A) with a temperature fail-safe setting on the controller and an air driven stirrer (rated at 3000 psi). An Instrument Specialties Company (Lincoln, NE) metering pump (model 314) was chosen to supply the nitric acid feed into the reactor. This pump contained the acid reservoir and the pump in the same unit with a maximum flowrate of 0.2 liters per hour. A 7.6 liters per hour positive displacement Nemo Netzsch pump (Lesson Electric Motor and Shimpo Ringcone drive model NMN0485000CAB030) was chosen to supply the excess sludge stream to the reactor. The positive displacement pump is 0.5 hp and is manufactured by Fluitron in Ivyland, PA. (Both pumps were calibrated to assure accuracy). Two Swagelock check valves (to prevent backflow), two Swagelock pressure relief valves, and several Swagelock on/off valves were selected to control the flow through the system (Swagelock of Knoxville, TN). Two 7-micron Swagelock filters were used to remove any unreacted excess sludge in the product stream. A stainless steel shell and tube heat exchanger (supplied by the University of Tennessee) was chosen to reduce the temperature of the products prior to sending them into the separation tank. A stainless steel separation tank, with a plastic sight glass, (supplied by the University of Tennessee) was used to separate the gas and liquids. A gas sampling port and flowmeter (GCC Precision Scientific) were used on the gas exhaust.

Several thermocouples and pressure gauges were used throughout the system for monitoring purposes. Two 55-gallon stainless steel drums were used for feed and product storage. All piping was constructed from 0.25 inch stainless steel tubing to prevent corrosion due to the nitric acid component of the feed.

3. DESIGN

The pilot plant was designed to demonstrate the nitrolysis process in a large-scale continuous environment. Figure 2 shows a diagram of the designed continuously run nitrolysis pilot plant. The feeds into the reactor consist of two streams, one of excess sludge and one of nitric acid. Pump 1 is the nitric acid feed pump and contains the feed reservoir inside the pump. Pump 2 is the excess sludge positive displacement pump, and is fed by a 55-gallon stainless steel drum (stirred). Both feed streams are fitted with check valves (V1, V2) to prevent backflow as the pressure builds in the reactor. Pressure gauge P1 is used to monitor the pressure in the nitric acid feed line to verify flow into the reactor. The reactor is a CSTR (continuously stirred tank reactor) controlled by compressed air and electrically heated. It is fitted with a sleeve that can be changed to alter the reactor volume and thus the reaction time in the reactor. The feeds enter and the products exit the reactor via ports in the top of the lid, with the system designed to operate liquid full. The reactor is fitted with a pressure relief valve (V3) and a pressure gauge (P2) to relieve and monitor the pressure in the reactor. The temperature of the reactor is monitored by a thermocouple (TC1) and controlled by a temperature setting on the reactor. The temperature at the outlet of the reactor is also monitored by a thermocouple (TC2). The effluent from the reactor is routed through a set of filters to

remove any unreacted excess sludge that may be present. The system is designed to allow the stream to be routed through one of two filters, or bypass the filter system completely by using valves V4-V8. This feature aids in cleaning plugged filters without a complete shutdown of the system. A pressure control valve (V9) is used to control the flow rate through the unit and can be adjusted during operation.

The products then pass through a shell-and-tube heat exchanger/condenser (cooled by cooling water) to cool the effluent back to room temperature. A thermocouple (TC3) is designed to measure the temperature of the stream prior to entering the heat exchanger. The products then enter the separation tank where the liquid is drained and sampled using valve V16, and the gas is sent to a set of gas sampling ports. The gas sampling portion of the apparatus is designed similar to the filtration portion of the unit, with two sampling ports and a bypass controlled by valves V10-V15. The gas then continues through a flowmeter to monitor the flow rate and is vented through a 2,000 cfm blower. Each of the safety considerations mentioned in this section are discussed in more depth in the following sections.

After design of the pilot plant and acquisition of the appropriate equipment, the pilot plant was fabricated at the University of Tennessee in Knoxville. The unit was built to be mobile for demonstration onsite at interested municipalities and/or industries. A picture of the actual unit (as constructed) can be seen in Figure 3, noting that the pumps are behind the apparatus and not visible in this picture.

4. SAFETY

Several safety considerations are vital to performing this work in a safe manner. The main areas of concern are due to elevated temperatures and pressures (180°C and 200 psi), concentrated nitric acid, and production of CO and NO_2. The unit was hydrostatically tested to assure there were no leaks in the lines, fittings, and/or reactor. The reactor was fitted with several lines of protection for the operator including a maximum temperature cutoff, above which the heater is automatically shut off. A pressure relief valve (V3) was also used to relieve excessive pressure in the reactor in the unlikely event that the reaction goes out of control. This valve was vented to the back of the unit and away from the operator. A splash shield was also placed in front of the reactor and filters, where the effluent was still at a high temperature and pressure. The temperature and pressure of the reactor, as well as the effluent streams, were monitored throughout operation. A condenser was used to cool the products soon after exiting the reactor. To address the concern or CO and NO_2 production, the gas stream was vented through a 2,000 cfm blower. CO monitors were placed throughout the laboratory to monitor for any possible gas leaks. The entire unit was enclosed in a 'fume hood' constructed by The University of Tennessee. This enclosure vented the entire unit through the blower, while also providing an added layer of protection between the operator and the unit. A picture of this enclosure can be seen in Figure 4.

The operator of the unit was also required to wear certain personal protective equipment. The operator was required to wear safety glasses (goggles during sampling) and an acid proof apron, as well as, acid proof gloves and heat resistant gloves during

operation of the unit. An eyewash station and safety shower were available to the operator if needed. A safety plan was developed to address all safety concerns for operation of the pilot plant (including emergency shutdown procedures), and all parties involved in the research were involved in a safety meeting/briefing prior to the operation of the unit. Extreme care should be taken in utilizing this process for research and/or other applications.

5. OPERATION/TESTING

The first step in running tests on the pilot scale unit was to adjust all pressure relief valves to the appropriate settings. This consisted of setting the pressure relief valve, V3, to the maximum allowable pressure in the reactor. The control valve, V9, was also set to the initial pressure needed to maintain the desired flowrate, but V9 was adjusted as needed during the experiments. The vent was turned on and checked for proper operation. The cooling water to the condenser was turned on, as well as the cooling water and compressed air to the stirrer. An inert gas, used to purge the separation vessel, was started. The next step was to charge the acid pump (Pump 1) with 40% nitric acid and set it to dispense acid into the reactor. The pump for the excess sludge (Pump 2) was started and adjusted to the appropriate flowrate. The valves in the system were used to set the flowrates and route the streams through filters, gas collectors, and into the gas/liquid separator. The heater for the reactor was turned on and the unit allowed to reach steady state before any samples are taken (typically 60 minutes). All pressure gauges and temperature gauges were monitored throughout the process for any peculiarities. After steady state was reached, liquid and gas samples were taken (in

duplicate) from the sampling ports and sent for analysis. The proper shutdown procedure for the unit can be found in the safety summary and consists of a reverse of the start up procedure described here. The liquid and gas samples were analyzed using the same method as described in Perkins et al.[1,2,3]

The actual experiments performed during this research were developed using a factorial study. The three variables of interest in this work were temperature (ranging from 120°C to 180°C), residence time (ranging from 30 minutes to 45 minutes), and nitric acid-to-sludge mass ratio (ranging from 0.3 to 1). The designed experiments can be seen in Table 1 in the appendix. The response variables were conversion and acetic acid production. Refer to previous articles by Perkins et al.[1,2,3] for a more in depth discussion of the development and analysis of experiments for a factorial study of nitrolysis.

6. RESULTS

The preliminary response of interest for the pilot plant research is the excess sludge conversion, defined as the difference in mass of solids before and after the nitrolysis reaction. The results of this study are reported at a 95% confidence interval. This work shows the effect of reaction time has the greatest effect on the sludge conversion (17.4 ± 14.3). The temperature and mass ratio of acid to sludge did not statistically affect the conversion within the limits of this study. The temperature response could be due to the temperature overshoot of the heater, and better control measures have been put in place for future studies. The other response variable studied was acetic acid production. These data showed reaction time had the greatest effect on the production of acetic acid, while reaction temperature and mass ratio of acid to sludge

did not have a statistical effect (at a 95% confidence interval).

A series of chemical oxygen demand (COD) tests were used in conjunction with gas samples to perform a carbon balance around the system. As much as 99% of the carbon was accounted for in the carbon balance, with an average of 80% closure. The COD tests also demonstrated the movement of organics from the solid to the liquid phase. The initial excess sludge had a particulate COD of about 25,000 mg/L and a negligible dissolved COD. The effluent from the reaction had an average particulate COD of 13,000 mg/L and an average dissolved COD of 12,000 mg/L.

The reaction rate kinetics was also investigated to determine the link between the previous batch studies and the current pilot plant work. The reaction rate developed using municipal excess sludge in previous work by Perkins et al. was determined to be

$$-r_{biomass} = 0.125(C_{biomass})^{0.9}(C_{acid})^{0.2} \quad (1)$$

This reaction rate was then used in a material balance around the continuous unit. The balance on the solids can be represented as

$$LC_{biomass,0} = LC_{biomass} + (-r_{biomass}) \quad (2)$$

where L is the volumetric flowrate, $C_{biomass,0}$ is the initial biomass concentration of the feed, $C_{biomass}$ is the biomass concentration at any point, and $-r_{biomass}$ is the reaction rate as developed by Perkins et al. Equation 1 was substituted into equation 2, and with some algebraic manipulation gave

$$0 = C_{biomass} - C_{biomass,0} + \theta k(C_{biomass})^{0.9}\left[C_{acid,0} - \alpha(C_{biomass,0} - C_{biomass})\right]^{0.2} \quad (3)$$

where θ is the residence time and α is an average of mole ratio of reacted nitric acid to

reacted biomass. The concentration for the biomass in the reactor can be predicted from this equation and compared to the experimental concentration, as seen in Figure 6. As can be seen in this figure, the model does a relatively good job of predicting the final concentration of biomass in the continuous system. The prediction is based on the kinetic model of equation 1, thereby allowing comparison of the model with the experimental data obtained from the pilot plant.

7. CONCLUSIONS

This research has demonstrated the nitrolysis process on a larger continuous pilot plant and the parameters affecting the conversion and acetic acid production were determined. Reaction time was determined to be effective at increasing the conversion, while reaction time and mass ratio of acid to sludge were both effective at increasing the acetic acid production. This research has served to advance the previous work of Perkins et al[1,2,3] to a unit more similar to an actual wastewater treatment facility. The developed pilot plant will aid in further study of the nitrolysis process.

8. ACKNOWLEDGEMENTS

This work was funded through grants from the Tennessee Water Resources Center and the Oak Ridge National Laboratory (ORNL) State Partnership Program. Their support is graciously acknowledged. ORNL is managed by UT-Battelle, LLC. for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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APPENDIX

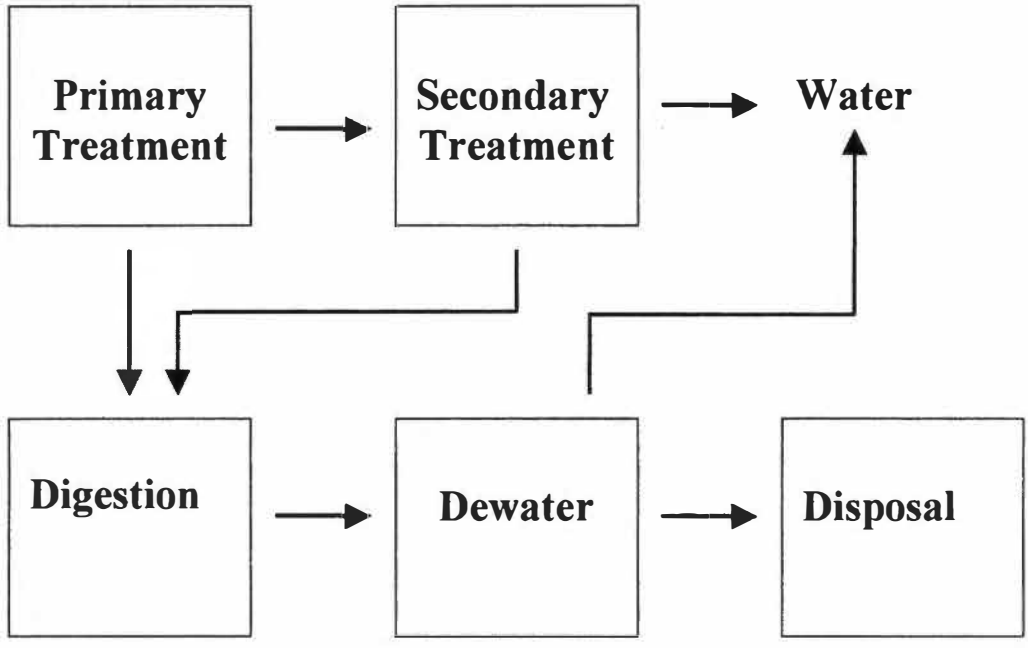

Figure 1 – Block Diagram of a Typical Wastewater Treatment Facility

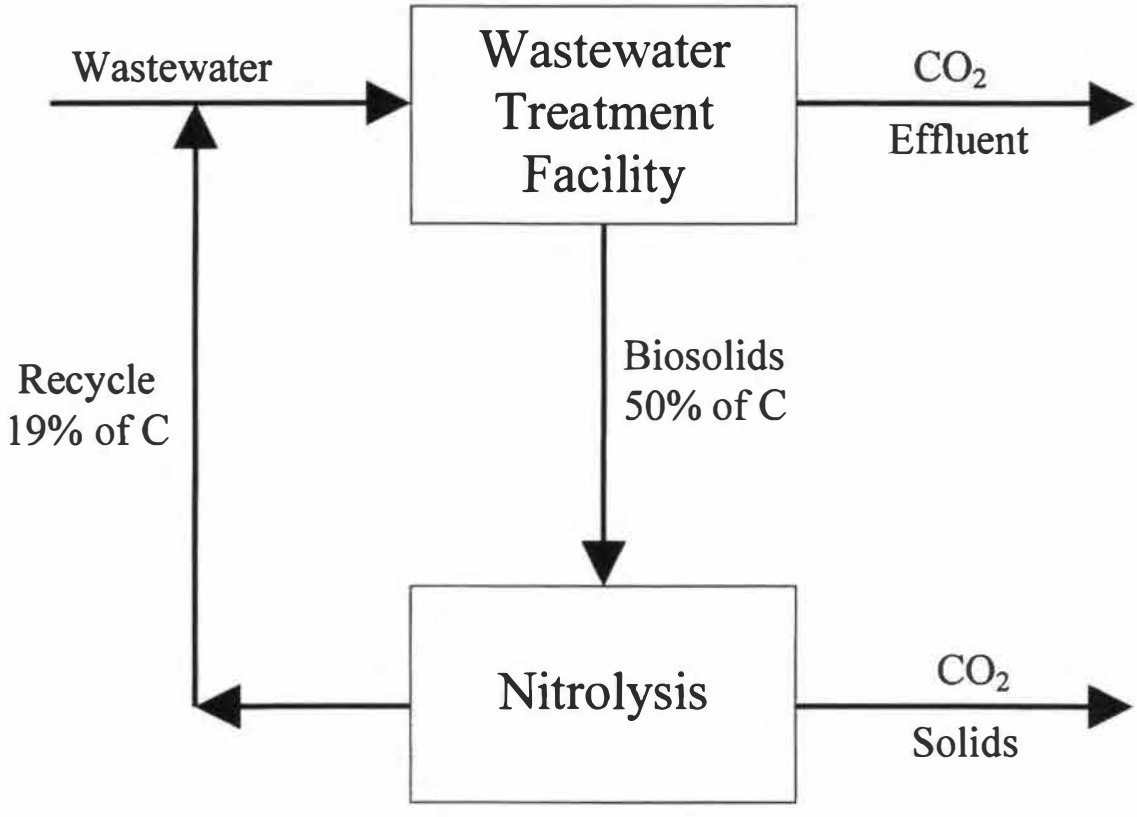

Figure 2 – Carbon Balance for Recycle of Nitrolysis Effluent to the Wastewater Treatment Process

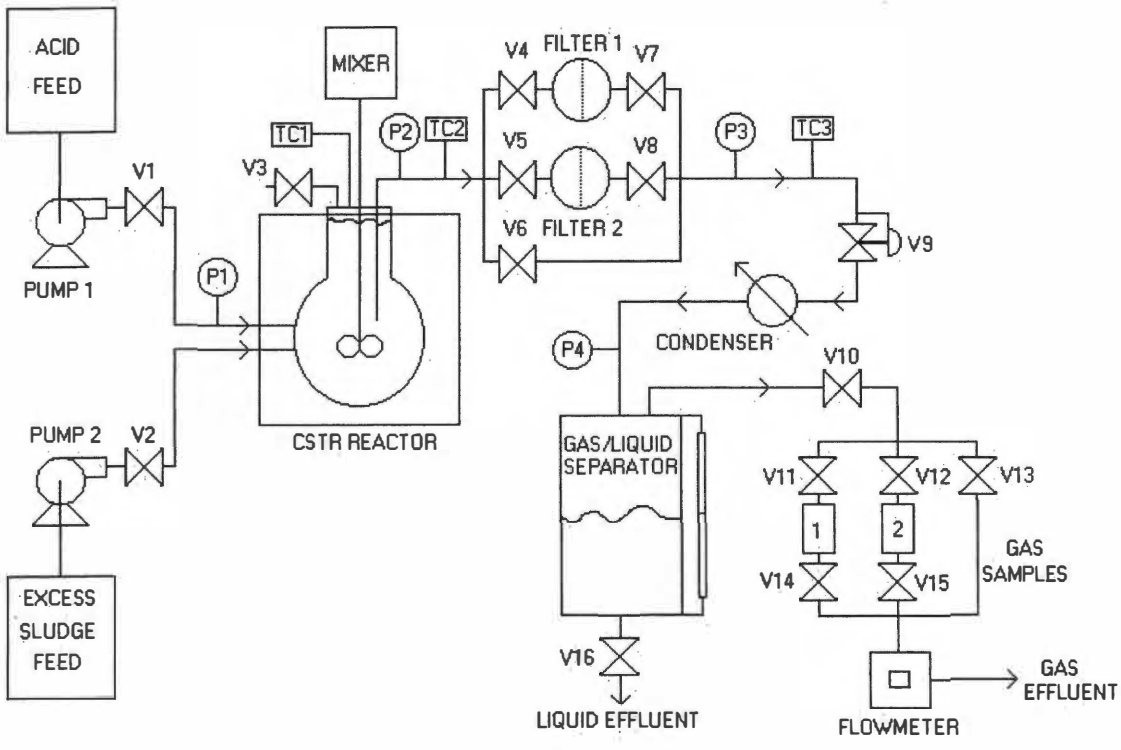

Figure 3 – Designed Continuous Pilot Plant For Development of the Nitrolysis Process

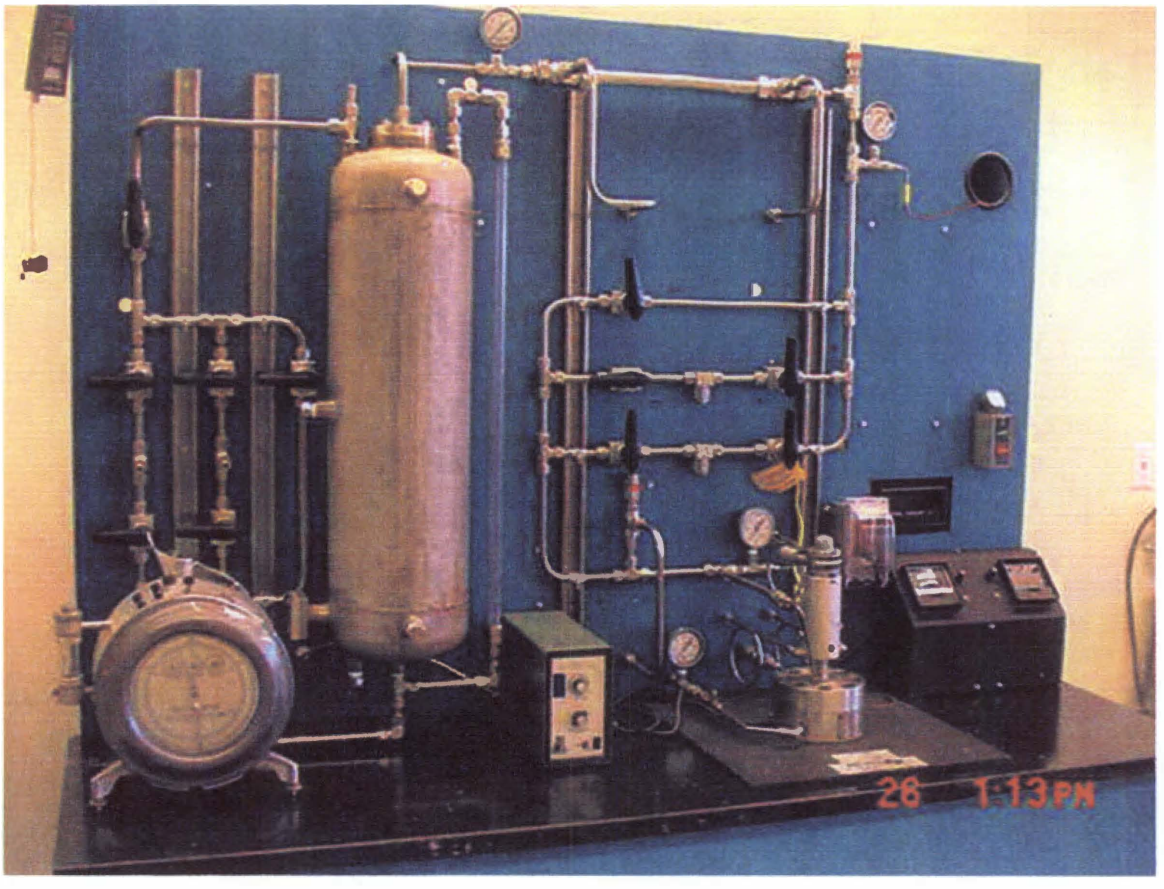

Figure 4 – Continuous Pilot Plant Unit For Development of Nitrolysis

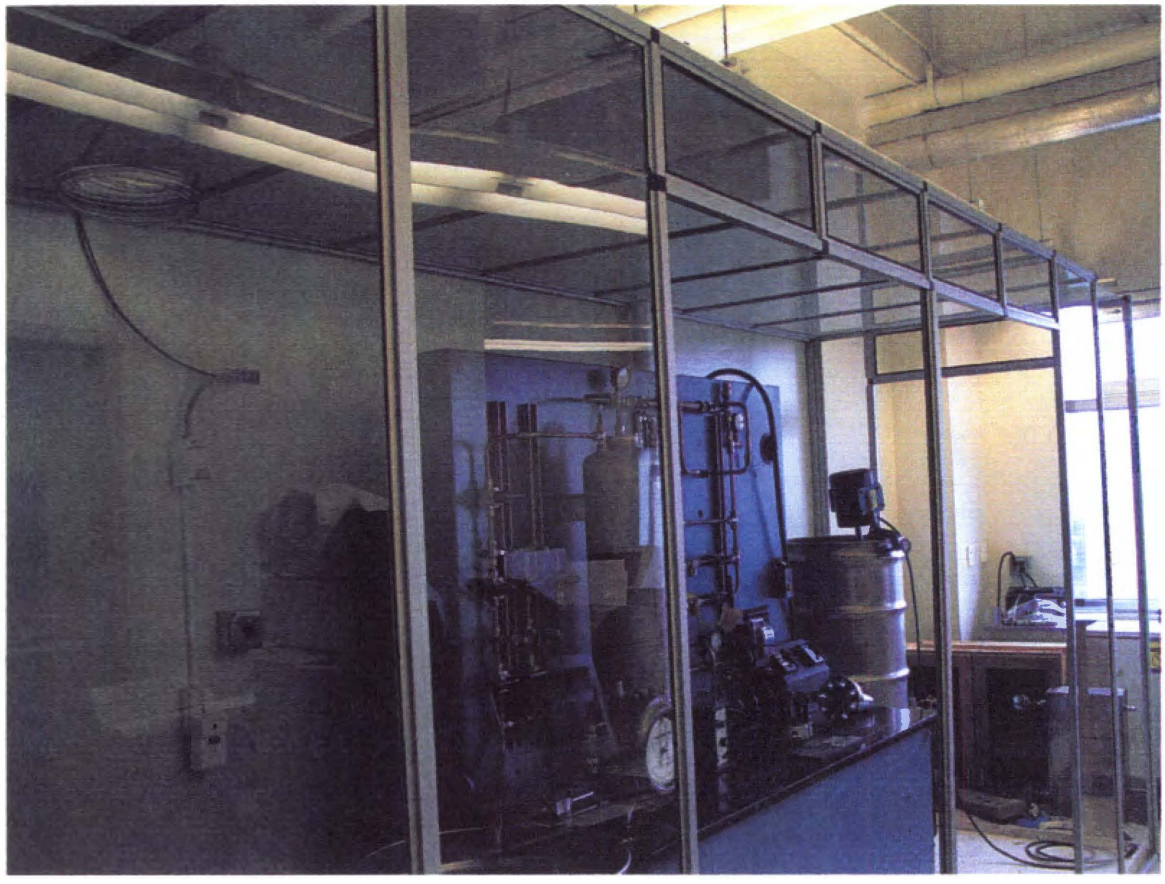

Figure 5 – Enclosure of Pilot Plant to Aid In Safety of the Operator and Reduction In Odor

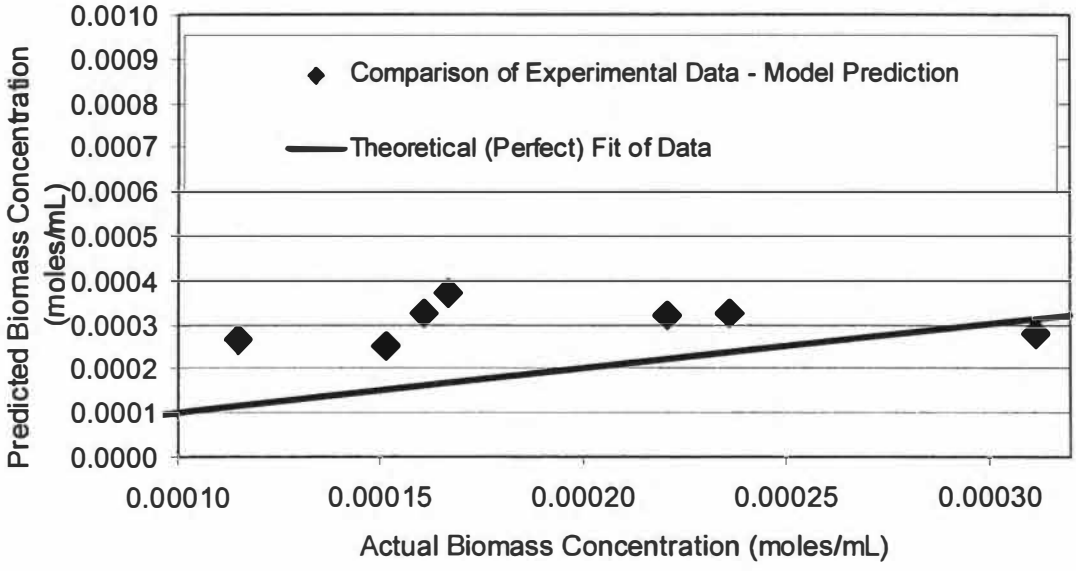

Figure 6 – Comparison of Municipal Kinetic Model to Experimental Data Obtained from a Continuous Pilot Plant System In Terms of Concentration of Biomass

Table 1 – Initial Eight Run Factorial Design for Nitrolysis of Municipal Excess Sludge In A Continuous Pilot Plant

Runs	Temp. (^{o}C)	Acid-Sludge Ratio (mass)	Reaction Time (min)
1	180	0.30	45
2	180	1.00	30
3	120	1.00	45
4	120	0.30	30
5	180	0.30	30
6	120	0.30	45
7	180	1.00	45
8	120	1.00	30
center	150	0.70	37

PART VI

REACTION RATE DEVELOPMENT AND ANALYSIS FOR THE NITROLYSIS OF MUNICIPAL AND INDUSTRIAL EXCESS SLUDGE

Part VI of this dissertation is a lightly revised version of a paper by the same name originally submitted for publication in *Chemical Engineering Communications* in 2003 by L. Perkins, K. Klasson, R. Counce, and P. Bienkowski. The revisions were included to add more data to the development of the reaction rate. The rate expressions in this paper are the same as those shown earlier, and are modified versions of the previously published papers. The paper is reproduced with permission from the journal.

ABSTRACT

This research studied the reaction rate of the nitrolysis process for excess sludge treatment. Nitrolysis is the process by which excess sludge is treated with nitric acid to reduce the amount of waste for disposal while producing a potentially valuable product. The reaction rate of this process has been studied some in the past, but this work looks at developing a reaction rate expression by considering the excess sludge without any inert material. A reaction rate expression was developed (based on inert free excess sludge) for the nitrolysis of municipal excess sludge. This rate was then compared to the reaction rate for the nitrolysis of industrial excess sludge. Good agreement with the model was demonstrated in both cases. Industrial applications are also interested in the reduction of chemical oxygen demand (COD) in the excess sludge. To this end, an expression for the reaction rate was also developed based on the disappearance of particulate COD during the nitrolysis of industrial excess sludge. Again, good agreement was found between the experimental and model reaction rates.

1. INTRODUCTION/BACKGROUND

This research investigates the development of a reaction rate expression for the process called nitrolysis. Nitrolysis is a process under development as an alternate method to treat excess sludge produced during wastewater treatment.[1,2,3] 'Excess sludge' is the term used to indicate the mixture of (1) solids that settle out from the wastewater during primary settling, (2) solids produced during bacterial treatment (biomass), and (3) bound water contained inside the cells. Specifically, excess sludge is regarded as biomass, water, and inert material. Gaudy et al.[4] identifies the biomass as $C_5H_7O_2N$. 'Biomass debris' is defined as the biomass that does not react during the nitrolysis reaction and stays in the solid phase. Grady[5] reports the biomass debris may be biodegradable, but the rate is so low the material can be considered to be inert material. 'Soluble substrate' consists of all of the materials in the liquid phase, which contribute to the chemical oxygen demand (COD). Typically, this excess sludge is dewatered during the wastewater treatment process and sent for disposal.[6,7] The dewatering step normally involves the use of a filter press, which adds significant cost to the treatment.

The excess sludge is disposed of in different ways including land fill, landfarm, incineration, [6,7,8,9] and wet air oxidation, [10] all of which have many disadvantages. The biggest problems come from high costs and liability concerns. Many industries are interested in a way to dispose of the excess sludge without the fear of it getting into the food chain and causing human health concerns.[11] The result of this concern can be higher disposal costs. These two areas of disposal costs and liability concerns are where

nitrolysis is the most intriguing.

Nitrolysis reduces the mass and volume of excess sludge, thus reducing the cost and liability concerns associated with ultimate disposal.[1,2,3] An added bonus to the nitrolysis process is the production of potentially valuable products, such as acetic acid, which may be reclaimed. In nitrolysis, nitric acid is used to rupture cells and release the bound water. In addition to the release of water, the biomass is hydrolyzed (converted from the solid phase to the liquid phase) and then converted to products.[1,2,3] The products of nitrolysis include CO_2 and organic acids (acetic acid and formic acid). The organic acids are of interest due to the possibility of reclaiming them as valuable products. Of more interest to industries, is the reduction in the mass and volume of the excess sludge. This reduction has been shown to reach 98% or more on a mass basis (inert free) and 90% or more on a volume basis,[1,2,3] using municipal and industrial sources of excess sludge. For more information on the background and results of the nitrolysis research, refer to the reports generated by Perkins et al.[1,2,3]

This document investigates the reaction rate of the nitrolysis process using both municipal and industrial sources of excess sludge. The reaction rate expression given by Perkins et al.[2,3] is modified in this paper to be on a basis that is free of inert material, but is still based on the nitrolysis of municipal excess sludge. The new reaction rate was then compared to the reaction rate obtained experimentally with the industrial source of excess sludge. Because of the concern in reducing COD for industrial excess sludge, these data were used to develop a separate reaction rate equation. This new reaction rate expression was developed based on the reduction in particulate COD during the nitrolysis process.

2. EXPERIMENTAL

The municipal excess sludge used in this work was supplied by the Knoxville Utility Board (KUB) – Kuwahee Wastewater Treatment Facility in Knoxville, Tennessee. The industrial excess sludge used was obtained from a local industrial secondary wastewater treatment facility. Both samples of excess sludge were analyzed by Galbraith Laboratories in Knoxville to determine the elemental composition. This elemental analysis can be seen in Table 1 (all tables and figures can be found in the appendix of this section). The results of that analysis led to the development of a molecular formula for each sample, which is given as C_3H_5NO for the municipal excess sludge and $C_9H_{14}NO_4$ for the industrial excess sludge.[2,3] These formulas were derived, on a basis that is free of inert material, from the elemental analysis, and were used to evaluate the reaction rate of the process. The inert material composition was found to be 8% in the municipal excess sludge and 19% for the industrial excess sludge.

For the purpose of this report, the reaction rate is defined as the disappearance of biomass (inert free solids) per unit volume per unit time. This definition indicates any biomass hydrolyzed into the liquid phase has reacted. The experimental procedures used to generate the data for this development can be found in previous papers by Perkins et al.[1,2]

3. THEORY

In order to develop a reaction rate model for the nitrolysis process, the theory used by Perkins et al.[2,3] was incorporated. The difference in this work is that this model was developed on a basis that is free of inert material, leading to a better model of the

reaction rate. An assumption was made for the form of the reaction rate as

$$-r_{biomass} = k(C_{biomass})^{\alpha}(C_{acid})^{\beta} \quad (1)$$

which can be rewritten as

$$\ln(-r_{biomass}) = \ln(k) + \alpha\ln(C_{biomass}) + \beta\ln(C_{acid}) \quad (2)$$

The reaction rate ($-r_{biomass}$), the biomass concentration ($C_{biomass}$), and the nitric acid concentration (C_{acid}) are experimental values determined from the experimental data. The reaction rate constant (k) and the empirical constants (α,β) were fit using the computer program JMP by SAS.[12] By using a 95% confidence interval, the parameters α and β were investigated to determine if the parameters were statistically significant in the reaction rate equation.

The experimental data gave the value of the parameters at specific places during the reaction. C_{acid} is the concentration of nitric acid at the end of the reaction. Likewise, $C_{biomass}$ is the concentration of biomass at the end of the reaction. The reaction rate (rate of disappearance of biomass) was calculated from the given data. In order to develop the reaction rate for municipal excess sludge, a plot of dry biomass concentration versus time was made for each reaction condition of interest. Each plot was fit to a second order polynomial equation and a slope found from that equation. The developed reaction rate was then compared to the experimental reaction rate of the industrial sludge nitrolysis tests, which were calculated by using the equation

$$-r_{biomass} = \frac{\Delta\text{Concentration of biomass}}{\text{reaction time}} \quad (3)$$

In comparison, a similar reaction rate equation was developed based on COD

values for the components of the reaction. This method for determining the reaction rate was adapted from Grady et al.[5] In this development, the nitrolysis process is represented using Figure 1, therefore, the reaction for the nitrolysis process can be represented as

$$\text{Biomass} + HNO_3 \rightarrow \text{Soluble Substrate} + \text{Biomass Debris} + CO_2. \quad (4)$$

The reaction rate based on conversion of COD was developed in a similar way to that described above. An assumption was made for the form of the reaction rate as

$$-r_{\text{particulate COD}} = k_2\left(COD_{\text{particulate}}\right)^{\sigma} \quad (5)$$

which can be rewritten as

$$\ln(-r_{\text{particulate COD}}) = \ln(k_2) + \sigma\ln(COD_{\text{particulate}}) \quad (6)$$

The experimental reaction rate ($-r_{\text{particulate COD}}$) was calculated by the equation

$$-r_{\text{particulate COD}} = \frac{\Delta\text{COD of excess sludge solids}}{\text{reaction time}}, \quad (7)$$

and the value of $COD_{\text{particulate}}$ was taken at the endpoint of the reaction.

The reaction rate constant (k_2) and the empirical constant (σ) were fit using the computer program JMP by SAS.[12]

In order to use this reaction rate, the assumption was made that COD is conserved, which is to say the reaction of COD can be represented as

$$\text{Particulate COD} \rightarrow \text{Soluble COD} + \text{negligible } CO_2. \quad (8)$$

This assumption holds for nitrolysis as indicated by Perkins et al.,[2,3] who demonstrated a COD balance around the nitrolysis reactor. The data used to develop these models can be found in Tables 2 and 3.

4. RESULTS

By using the JMP program and the municipal excess sludge nitrolysis data, values for the reaction rate constant (k) and the empirical constants (α,β) were developed. These values were determined to be

$k = 0.125$
$\alpha = 0.9$
$\beta = 0.2$

at a 95% confidence interval. The parameters α and β are unitless and the reaction rate constant (k) has units that depend on the developed model. These values for the parameters led to a reaction rate equation of

$$-r_{biomass} = 0.125(C_{biomass})^{0.9}(C_{acid})^{0.2}. \quad (9)$$

Figure 2 shows a typical plot used to determine the experimental reaction rate of the municipal nitrolysis process. The experimental reaction rate for municipal excess sludge was compared to the model of Equation 9 and gave good results. This comparison can be seen in Figure 3. The nitrolysis of industrial excess sludge was also compared to the developed reaction rate by utilizing Equation 3 and comparing the results to those generated by a similar model. Figure 4 shows that comparison. This figure also shows agreement between the experimental reaction rate of the industrial nitrolysis process and the developed reaction rate model.

Similarly, by using a 95% confidence interval, the parameters σ and k_2 in the COD reaction rate were investigated. The values of these parameters were determined to be

$k_2 = 9x10^5$

$\sigma = -0.6 \pm 0.04$

at a 95% confidence interval. These values led to a reaction rate of

$$-r_{particulateCOD} = 8x10^5 \left(COD_{particulate}\right)^{0.6} \quad (11)$$

where COD has units of mg O_2/L, k_2 has units that depend on the developed model, and the reaction rate has the units of mg O_2/L-min. Figure 5 shows a comparison of the experimental reaction rate of COD (as calculated by Equation 7) and the model of Equation 11. This model shows good agreement with the experimental reaction rates of the industrial nitrolysis process.

5. CONCLUSIONS

A reaction rate for the nitrolysis of municipal excess sludge from wastewater treatment was developed (free of inert materials). This reaction rate was then compared to the experimental reaction rate for the nitrolysis of industrial excess sludge. The model showed agreement with the experimental data in both cases. A reaction rate based on the conversion of COD from the particulate phase to the dissolved phase was also developed for the nitrolysis of industrial excess sludge. Again, good agreement was observed between the experimental data and the model. These models provide some crucial information for the development and scale up of the nitrolysis process to a larger pilot plant and eventually production size process.

6. ACKNOWLEDGEMENTS

This work was funded through grants from the Tennessee Water Resources Center and the Oak Ridge National Laboratory (ORNL) State Partnership Program.

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APPENDIX

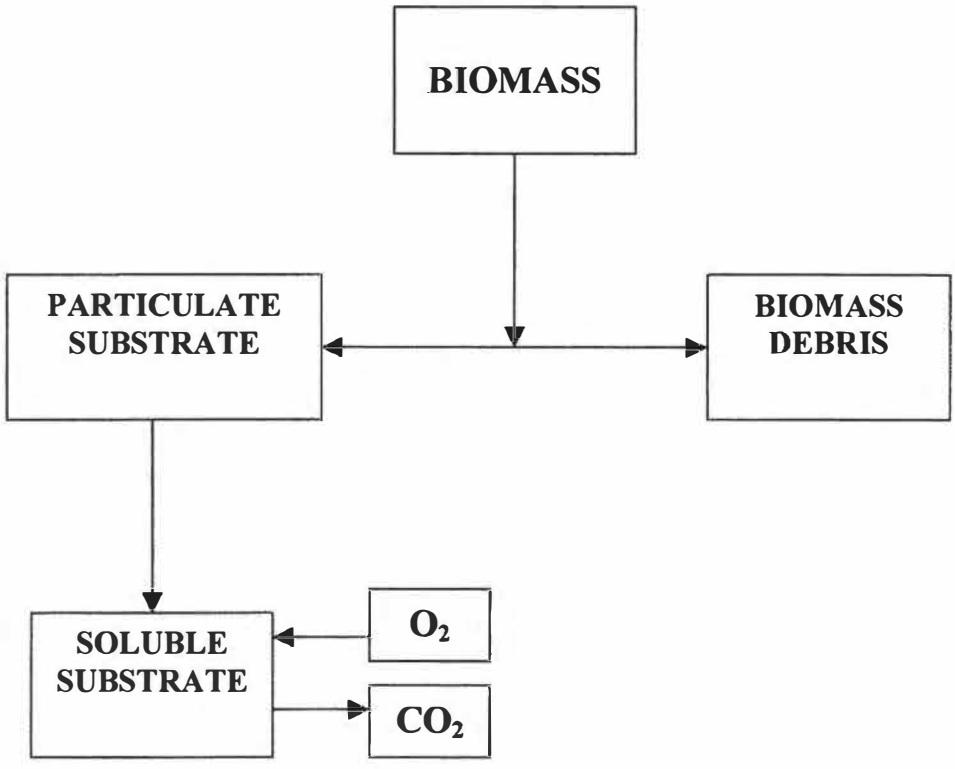

Figure 1 – Diagram for Development of a Reaction Rate Based on COD

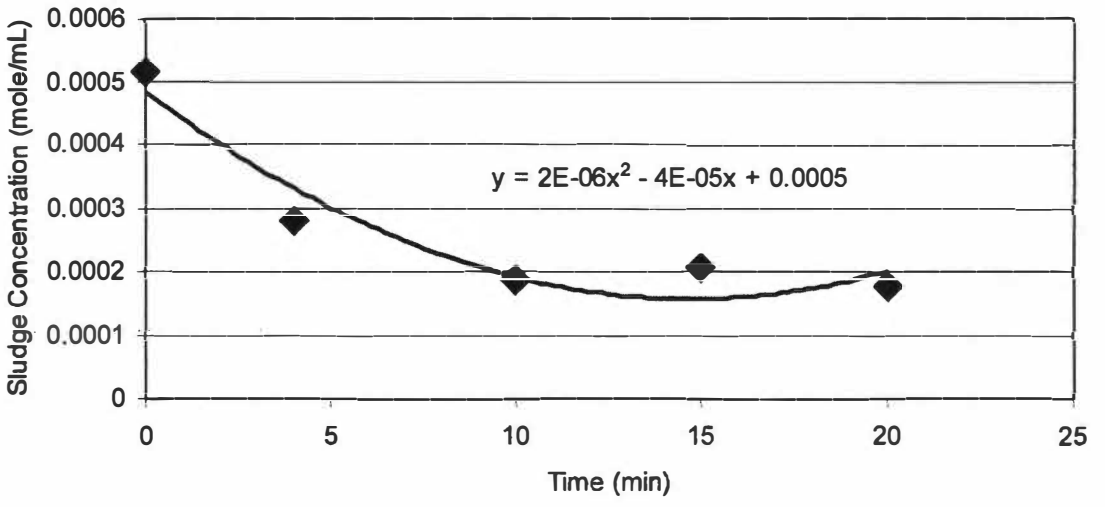

Figure 2 – Typical Figure Used to Develop a Reaction Rate for Nitrolysis of Municipal Excess Sludge (@180°C, 4.5%wt nitric acid, 4%wt municipal excess sludge and using the final concentrations)

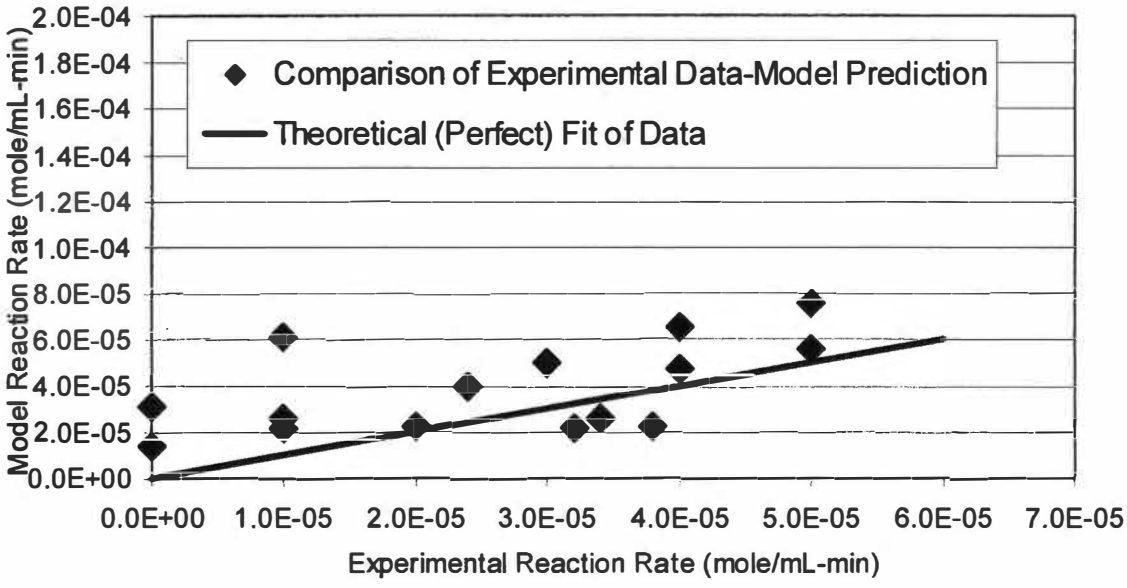

Figure 3 – Comparison of the Developed Reaction Rate Model to the Experimental Reaction Rate of Municipal Excess Sludge on an Inert Free Basis

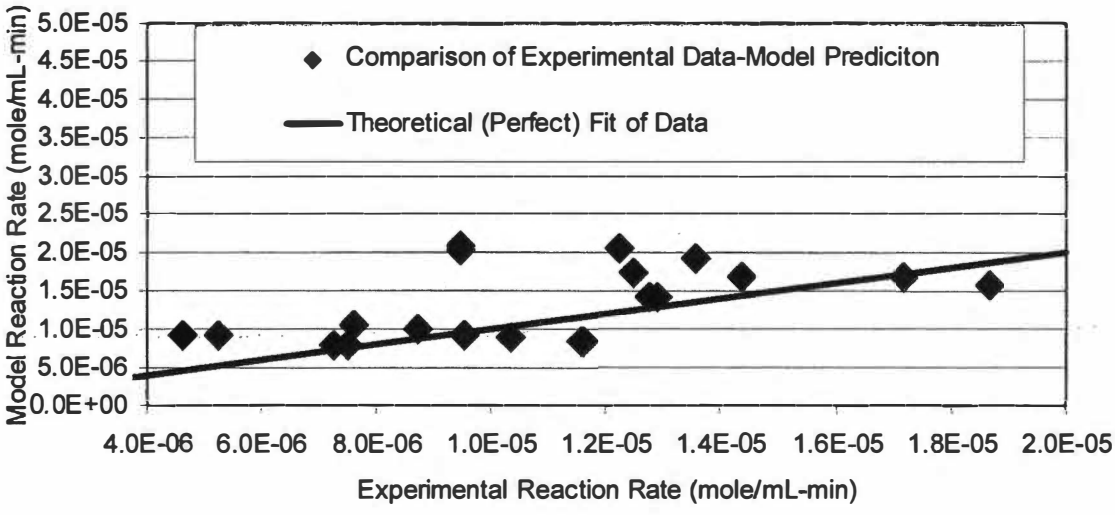

Figure 4 - Comparison of the Developed Reaction Rate Model to the Experimental Reaction Rate of Industrial Excess Sludge on an Inert Free Basis

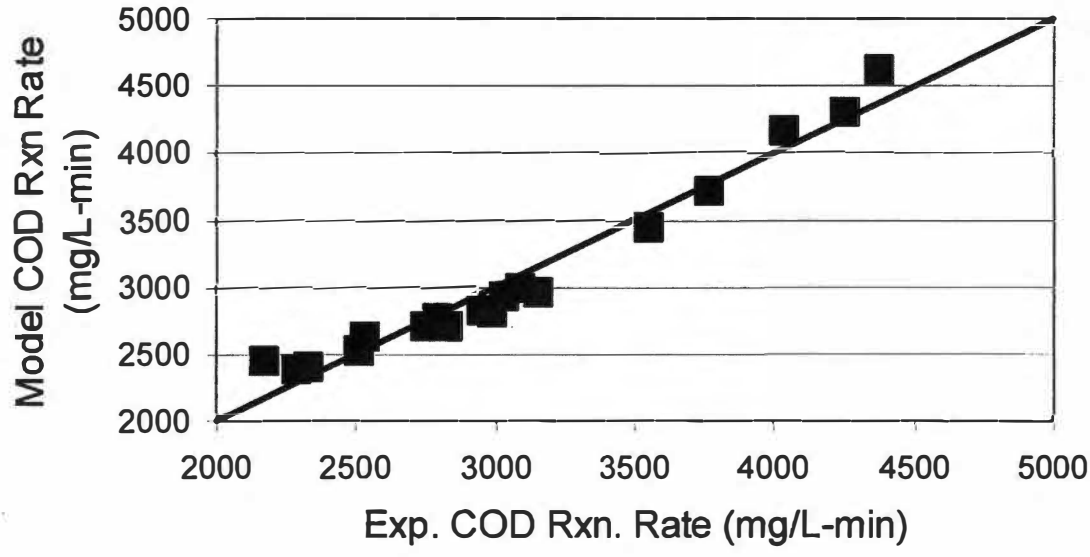

Figure 5 - Comparison of the Developed Reaction Rate Model for Disappearance of Particulate COD to the Experimental Reaction Rate of Industrial Excess Sludge

Table 1 – Elemental Analysis of Excess Sludge Samples

COMPOSITION	KUB VALUE	INDUSTRIAL VALUE	UNITS
Carbon	41.14	42.78	wt%
Nitrogen	16.72	5.27	wt%
Oxygen	21.45	27.30	wt%
Hydrogen	12.37	5.56	wt%
Inert Material	8.32	19.09	wt%

Table 2 – Experimental Data for Reaction Rate Model Development of Nitrolysis of Industrial Excess Sludge

	min	C	wt% initially	mass ratio	g/L	g/mL	mg/L	mg/L
Run	Rxn.Time	Temp.	Sludge Conc.	Acid-Sludge Ratio	Acid Conc.	Biomass Conc.	Part. COD	Diss. COD
1	10	150	3.07	2.43	60.536	0.0043	28800	10653
2	10	150	3.07	2.43	57.7	0.0026	26400	13869
3	10	180	3.07	0.5	4.494	0.0101	25600	10050
4	10	180	3.07	4.36	77.313	0.0000	31000	8844
5	10	180	3.07	0.5	4.801	0.0096	24000	9648
6	10	180	3.07	4.36	83.403	0.0000	30600	8643
7	10	120	3.07	4.36	114.693	0.0076	22400	11457
8	10	120	3.07	0.5	14.258	0.0154	10200	5226
9	10	120	3.07	4.36	119.094	0.0050	24400	12663
10	10	120	3.07	0.5	15.928	0.0143	11400	5025
11	10	120	5.14	0.5	54.692	0.0261	16200	19095
12	10	120	5.14	4.36	218.869	0.0126	13600	20904
13	10	120	5.14	0.5	38.69	0.0260	26000	18291
14	10	120	5.14	4.36	273.425	0.0155	18400	20904
15	10	180	5.14	0.5	10.782	0.0179	23000	18291
16	10	180	5.14	4.36	98.751	0.0016	28600	20301
17	10	180	5.14	0.5	10.292	0.0210	32200	22311
18	10	180	5.14	4.36	123.211	0.0049	23600	17085

Table 3 – Experimental Data for Reaction Rate Model Development of Nitrolysis of Municipal Excess Sludge

Run	min Rxn. Time	C Temp.	wt% initially Sludge Conc.	mL (19.1g sludge) Acid Added	g/L Acid Conc.	g/mL Biomass Conc.
5	3	181	4.083	1.3	60.6057	0.010428813
6	3	181	4.083	1.3	59.5545	0.013299605
2	3	179	4.083	1.3	59.0117	0.013343612
1	4	179	4.083	1.3	54.5941	0.012440122
3	4	179	4.083	1.3	53.5277	0.01447294
4	4	181	4.083	1.3	56.4652	0.015717526
7	10	181	4.083	1.3	43.5121	0.013470302
8	10	181	4.083	1.3	44.0207	0.01346354
9	10	181	4.083	1.3	43.0567	0.013987362
10	15	179	4.083	1.3	45.3072	0.003016224
11	15	179	4.083	1.3	44.1877	0.006523816
12	15	179	4.083	1.3	43.6639	0.007363309
34	20	179.5	4.083	1.3	5.47	0.011685696
35	20	179.5	4.083	1.3	6.85	0.01069353
36	20	179.5	4.083	1.3	7.04	0.010924353
13	4	181	4.083	2.6	111.0972	0.004104435
14	4	181	4.083	2.6	106.4177	0.009157145
15	4	181	4.083	2.6	108.8201	0.014700387
16	10	181	4.083	2.6	94.5311	0.010329522
17	10	181	4.083	2.6	92.3603	0.014355543
18	10	181	4.083	2.6	90.5803	0.014427985
19	15	181	4.083	2.6	83.5592	0.012226338
20	15	181	4.083	2.6	88.2804	0.013011281
21	15	181	4.083	2.6	83.3049	0.01275269
31	20	179.5	4.083	2.6	82.13	0.007809184
32	20	179.5	4.083	2.6	88.22	0.007436571
33	20	179.5	4.083	2.6	85.91	0.006826499
22	4	178	4.083	0.65	27.1661	0.024221576
23	4	178	4.083	0.65	26.5437	0.02422513
24	4	178	4.083	0.65	26.9953	0.020671965
25	10	182	4.083	0.65	13.9057	0.016648265
26	10	182	4.083	0.65	16.3953	0.017379677
27	10	182	4.083	0.68	16.4257	0.015571785
28	15	182	4.083	0.65	10.4179	0.015760207
29	15	182	4.083	0.67	11.3629	0.019794851
30	15	182	4.083	0.65	9.6930	0.017889383
37	20	179.5	4.083	0.65	2.06	0.015702491
38	20	179.5	4.083	0.65	12.98	0.015611864
39	20	179.5	4.083	0.65	9.18	0.015852924
40	5	181.8	4.083	0.3	8.9	0.022244056
41	5	181.8	4.083	0.3	1.82	0.018962074
42	5	178.9	4.083	0.3	9.95	0.017957488
43	20	178.5	4.083	0.3	5.32	0.019522354
44	21	178.5	4.083	0.3	1.06	0.019683591
45	20	178.5	4.083	0.3	1.21	0.019146723
46	15	178.9	4.083	0.3	1.93	0.012678402
47	15	178.9	4.083	0.3	1.87	0.013147083
48	15	178.9	4.083	0.3	2.19	0.009714689
49	10	178.9	4.083	0.3	1.75	0.011814741
50	10	178	4.083	0.3	1.51	0.02256452
51	10	178	4.083	0.3	1.38	0.02012496

PART VII

OVERVIEW OF THE DEVELOPMENT OF THE NITROLYSIS PROCESS FOR TREATMENT OF MUNICIPAL AND INDUSTRIAL EXCESS SLUDGE PRODUCED DURING WASTEWATER TREATMENT

Part VII of this dissertation is a copy of a paper by the same name originally submitted for publication in *Industrial & Engineering Chemistry Research* in 2003 by L. Perkins, K. Klasson, R. Counce, and P. Bienkowski. Upon submission, the authors reserved the right to publish this article in this dissertation.

ABSTRACT

This manuscript reports on nitrolysis as a treatment of excess sludge with nitric acid for the purposes of reducing the waste for disposal while producing a potentially valuable product. The product of interest is acetic acid, while the waste reduction involves both mass and volume of the excess sludge stream. This research has investigated the process (municipal and industrial sludge sources) utilizing both batch studies and continuous pilot plant studies. The work has resulted in the development of a reaction rate as well as a parameter study to determine the effect of operating parameters on the process. Chemical oxygen demand tests and total organic carbon tests were used to perform a carbon balance around the system in both the batch and pilot plant studies. The reduction of the excess sludge stream has been illustrated with in both cases, leading to an interest in the reduced cost of disposal. The production of acetic acid has been demonstrated at a concentration that is high enough to peak an interest in further developing the process. These studies have been beneficial in developing nitrolysis as an excess sludge treatment alternative.

1. INTRODUCTION/BACKGROUND

This manuscript presents an overview of the development of nitrolysis. The nitrolysis process involves the treatment of excess sludge (produced during wastewater treatment activities) with nitric acid. The organic materials are hydrolyzed during the acid treatment and moved from the solids into the liquid phase. After being hydrolyzed, the organics are then converted to products. The products of nitrolysis include organic acids. These organic acids are composed primarily of acetic acid and formic acid, with only trace amounts of longer chain organics. Gaseous products are also evolved during nitrolysis. The main gaseous product is carbon dioxide, but oxygen and nitrogen are also produced in smaller amounts. The products of most interest are the acetic and formic acids. These products are of some value, and may be profitable to reclaim from the effluent of the process. The specific feed conditions and available technology for acetic acid recovery would govern the interest in recovering the product or simply returning it to the wastewater treatment process.

The other main results of nitrolysis are a large volume and mass reduction in the excess sludge stream. The excess sludge includes water that is 'bound' in the cells. This phenomena eludes to the fact that a small mass fraction (0.04) of solids will remain opaque without the solids settling out of the sample. The nitric acid ruptures these cell walls and allows the release of the bound water. Without the bound water inside the cells, the cells (solids) settle out of the stream much more readily and allow removal of the remaining liquid. The result of this settling is a reduced viscosity of the liquid and a smaller volume waste stream that must be dewatered and sent for ultimate disposal. The

solids that settle from the excess sludge are then hydrolyzed and converted to the products discussed above. The nitrolysis process can be represented as

$$\text{Biomass} + \text{Nitric Acid} \rightarrow \text{Biodegradable Organics} + \text{Nitrogen} + \text{Carbon Dioxide} \quad (1)$$

During wastewater treatment, the water enters the treatment facility and immediately undergoes primary treatment. This process simply allows the solids to settle from the water. The remaining liquid proceeds to secondary treatment, where bacteria is used to remove organic materials from the water and produce biosolids. For the purposes of this project, 'excess sludge' was defined as the mixture of solids from primary treatment and biosolids from secondary treatment, as well as any bound water that may be in the solids. The excess sludge then enters a digester where the excess sludge is digested and then dewatered. After dewatering, the solids are typically in the range of 40% solids (60% water) by mass. This cake of solids is then sent for disposal by incineration, land filling, land farming, or wet air oxidation. Figure 1 illustrates a typical wastewater treatment facility (all figures can be found in the appendix of this section). Nitrolysis involves the treatment of this excess sludge with nitric acid to reduce the solids that are sent for disposal while producing a potentially valuable product. The liquid from the nitrolysis process would consist of approximately 1% of the flow into the facility and could be recycled. Figure 2 illustrates this concept. Refer to the previous papers by Perkins et al.[1,2,3,4,5] for more background information about the nitrolysis process.

2. EXPERIMENTAL

The nitrolysis process has been developed by Perkins et al.[1,2,3,4,5] using two sets of experimental procedures. These procedures included batch scale research, using a 25-mL pressure rated reactor. A picture of the batch reactor can be seen in Figure 3. A factorial study was performed on the nitrolysis of municipal excess sludge[2] and industrial excess sludge[3] during this batch size research. The procedures used in this research can be found in the papers by Perkins et al.[1,2,3] The process was further developed by investigating a continuously run pilot plant. This unit was designed and constructed to demonstrate the process on a larger scale, more in line with a typical wastewater treatment facility.[5] The pilot plant involved a continuously stirred tank reactor (CSTR), which was electrically heated to obtain 180°C and able to sustain the desired pressure of nearly 200 psi. The pilot plant was composed of two feed streams (acid and excess sludge) and contained numerous safety features. See the previous paper by Perkins et al.[5] for more information on the design of the pilot plant. A picture of the pilot plant can be seen in Figure 4 and the enclosure (a safety feature of the process) can be seen in Figure 5.

3. KINETIC THEORY

The theory that was used to develop the nitrolysis process comes from papers by Perkins et al.[2,3,4] These papers developed reaction rates for the nitrolysis process based on municipal and industrial excess sludge sources. The rate was first developed on a dry solids basis,[2,3] which is to say that inert material was not taken into consideration. The rate looked at the disappearance of solids during the reaction. Perkins et al.[4] then

developed a reaction rate equation based on biomass (solids free of inert material). This reaction rate is more useful because it demonstrates the rate of the nitrolysis process without inert materials, which are not going to react anyway. The inert material only skews the reaction rate. Perkins et al.[4] looked at both cases and developed reaction rates based on both municipal and industrial sources of excess sludge.

4. RESULTS

The development of the nitrolysis process has generated a significant amount of data. These results are summarized in this section, including summarizing results from several years of research. These results include the affect of operating parameters on the process, kinetic reaction rate models, stoichiometry, and demonstration of the process in a CSTR pilot plant. The operating parameters were studied with a 95% confidence interval.

4.1 Parameter Effects

The research investigated the operating parameters of the nitrolysis process and looked at acid concentration, sludge concentration, acid/sludge ratio, temperature, and reaction time. The operating parameters were studied with regards to their effect on sludge conversion, acetic acid production, and total organic acid production, when reacting municipal and industrial excess sludge in the nitrolysis process.

The municipal excess sludge results[2] showed the main operating parameters for sludge conversion are temperature, acid concentration, and sludge concentration. The research demonstrated the maximum sludge conversion is reached at reaction temperatures $\geq 160^{o}C$. Below $160^{o}C$, the conversion fell off significantly. The specific

mass conversions that illustrate this point include a sludge conversion >70% above 160°C and <20% at 100°C. The acid concentration was the other major contributor to the sludge conversion. Increasing the concentration of nitric acid in the reactor increased the conversion. With a nitric acid concentration of 0.5 wt%, the sludge conversion was only 10%, but the conversion was >60% with an acid concentration of 6 wt%. The initial sludge concentration had the opposite affect (decreased conversion with increased initial sludge concentration) indicating that the amount of sludge had 'swamped' the system, and the nitric acid was the limiting reagent. The reaction time was not an effective operating parameter for changing the conversion. The reason for this finding is the organic materials, in the excess sludge, are hydrolyzed to the liquid phase quickly (<5 min) and converted to products more slowly. The lower limit of this research (5 min) was not sufficiently low to see a change in conversion with respect to time.

The industrial excess sludge samples showed similar results,[3] with the main operating parameters of acid-sludge ratio and reaction temperature, with the acid-sludge ratio nearly 1.5 times as effective. At 180°C, the sludge conversion went from 50% at an acid-sludge ratio of 0.4 to 87% at an acid-sludge ratio of 3.4. Conversely, at an acid-sludge ratio of 3.4, the conversion went from 55% at 120°C to >85% at 180°C. These representative results illustrate the dependence of the process on the acid-sludge ratio and the reaction temperature.

The municipal excess sludge results[2] showed the main operating parameters for acetic acid production are acid concentration and sludge concentration, but an increase in reaction time and temperature also increased the amount of acetic acid produced. The

acid and sludge concentrations are about 2 times as effective at increasing the acetic acid production as the temperature and reaction time. The most effective way to increase the production of acetic acid would be to increase the acid concentration and the excess sludge concentration.

The industrial excess sludge results again showed similar results.[3] This work reported that the initial excess sludge concentration is the most important parameter for producing more acetic acid. All three parameters studied (initial excess sludge concentration, nitric acid concentration, and reaction temperature) do affect the production of acetic acid in the same way. An increase in any of these parameters increases the amount of acetic acid produced, but an increase in the initial excess sludge concentration is more than twice as affective at increasing the acetic acid production. These results indicate that an increase in the production of acetic acid can be best achieved by increasing the sludge concentration first (if feasible) and then increasing the acid-sludge ratio and temperature.

The last way of investigating this data looked at the production of 'total organic acid', which is a combination of all organic acids present (acetic, formic, propionic, valeric, and butyric) into an equivalent amount of acetic acid. The municipal excess sludge data showed similar results[2] to the acetic acid production. Increasing the sludge concentration was the most effective at increasing the total organic acid. Increases of the other parameters of reaction time and acid concentration also increased the amount of total organic acid produced, but to a lesser extent than the sludge concentration. The reaction temperature did not show an effect above 160°C. The industrial excess sludge

data showed similar results,[3] with the initial sludge concentration having the largest affect on the production of total organic acid. Larger the initial sludge concentration produces more total organic acid. The other parameters (acid-sludge concentration and reaction temperature) showed the same trend but to a much lesser extent. An increase in the initial excess sludge concentration is more than twice as effective at increasing the total organic acid produced.

4.2 Reaction Rate

A kinetic rate expression for the nitrolysis of excess sludge (municipal and industrial) was also developed during this project. This development looked at the conversion of the excess sludge, meaning any sludge that is hydrolyzed to the liquid phase has reacted. In order to develop the reaction rate, a reaction rate was assumed and the parameters were fit using the JMP program by SAS.[6] The municipal excess sludge[2] was used to develop the rate expression and then the model was compared to the experimental rate of both the municipal and industrial nitrolysis. The developed rate was first determined to be

$$-r_{biomass} = 0.125(C_{biomass})^{0.9}(C_{acid})^{0.2} \quad (2)$$

for municipal excess sludge and

$$-r_{biomass} = 0.102(C_{biomass})^{0.9}(C_{acid})^{0.2} \quad (3)$$

for industrial excess sludge. This reaction rate was compared to the experimental reaction rate for nitrolysis of both municipal[2] and industrial[3] excess sludge with good agreement. Plots illustrating this agreement can be seen in Figure 6 (municipal) and

Figure 7 (industrial) of the appendix.

The other reaction rate developed during this project was the reaction rate based on chemical oxygen demand (COD).[4] The same methodology was used to develop the reaction rate but the COD values were the areas of interest instead of the reaction of the excess sludge. The assumption was made that the particulate COD simply converted to dissolved COD, which was proven to be true with a COD balance around the process. The result of this development was

$$-r_{particulateCOD} = 8x10^{5}\left(COD_{particulate}\right)^{0.6} \quad (4)$$

Recalling a 95% confidence interval was used on all calculations.

4.3 Organic Acid Production

The amount of organic acid produced was also an interest in this research. The organic acids studied included acetic acid, formic acid, propionic acid, valeric acid, and butyric acid. In the nitrolysis process,[1] the valeric acid and butyric acid were found in trace quantities. Acetic acid was the most prevalent at greater than 100 mg/g of dry excess sludge reacted. The formic acid was produced at 35 mg/g of dry excess sludge and the propionic acid was produced at 20 mg/g of dry excess sludge. This finding, coupled with the finding that higher initial excess sludge concentrations produced more organic acids (specifically acetic acid),[2,3] made the possibility of reclaiming these products intriguing. If an industry already has the capability of separating the acetic acid, a more concentrated sludge stream could prove financially profitable. For example, an industry producing 50-55 dry tons of excess sludge per day could expect to make up to $2.8 million in acetic acid per year (at $0.44 per pound of acetic acid[7]).[3,4] This

estimation is based on the assumption that acetic acid is produced at 0.15 kg/kg of dry excess sludge (a reasonable estimate from this research). Based on these data, a chemical equation for the stoichiometry of the reaction was developed. This equation uses the term $C_4H_9N_3O_5$ to represent the soluble organic material that has not been identified (but is present according to the COD and TOC balances) and C_3H_5NO to represent the municipal excess sludge in the reaction. The other stoichiometric coefficients were determined by estimates from experimental data. The equation is given as

$$C_3H_5NO + HNO_3 \rightarrow 0.0006C_2H_4O_2 + 0.67C_4H_9N_3O_5 + 0.33CO_2 \quad (5)$$

An electron balance was also performed on the reaction to determine the movement of the electrons in the system. This balance showed the equivalent acetic acid accounted for 23% of the dissolved COD in the effluent. The remainder appears mainly in the liquid effluent (dissolved organics) and gaseous phase.

4.4 Continuous Pilot Plant

The next phase of this research focused on demonstration of the nitrolysis process on a larger continuous pilot scale unit.[5] This work involved the design, construction, and operation of the pilot plant. Significant safety features were incorporated into the pilot plant, including a formal safety review and meeting prior to startup. The design included pressure release valves, emergency cutoffs, multiple layers of protection for the operator, and several pieces of personal protective equipment. Figure 5 shows the actual pilot plant with safety precautions (such as the enclosure) in place.

The results of this work showed reaction time to be effective at increasing the sludge conversion, with reaction time and mass ratio of acid to sludge both effective at

increasing the acetic acid production. COD tests on the effluent of the reactor were used to close a carbon balance around the unit with up to 99% closure. The concentration of the acetic acid in the effluent reached 1.3 g/L (2.0 g/L total organic acid). A more concentrated sludge feed could potentially produce more acetic acid (possibly enough to separate and reclaim). This study also illustrated the nitrolysis process on a scale and system more similar to an actual wastewater treatment facility.

The reaction kinetics developed by Perkins et al.[2] were also compared to the experimental data obtained from the pilot plant research. The rate expression was used to predict the conversion of the biomass in the reactor. This prediction was then compared to the experimental conversion of biomass. Figure 8 shows the comparison of the experimental and predicted conversions. This figure shows good agreement with the model from the previous work. The predicted from the model was very similar to the actual conversion calculated from the experimental data. See the previous work by Perkins et al.[2] for more information on the development of the prediction from the kinetic expression.

5. CONCLUSIONS

The development of the nitrolysis process has been developed through batch studies and pilot plant studies. The results of these studies have shown up to 85% conversion (by mass) can be achieved (99% after accounting for inert material). COD tests have been used to perform a carbon balance around both systems. As much as 2.4 g/L acetic acid was produced in the batch studies and 1.3 g/L in the pilot plant (2.0 g/L total organic acid). A reaction rate was developed for the process and tested using both

municipal and industrial excess sludge feeds. Continuing work with the pilot plant will yield additional valuable data, including the possible use of a slip-stream from an actual wastewater treatment facility as the sludge feed to the unit.

6. ACKNOWLEDGEMENTS

This work was funded through grants from the Tennessee Water Resources Center and the Oak Ridge National Laboratory (ORNL) State Partnership Program. Their support is graciously acknowledged. ORNL is managed by UT-Battelle, LLC. For the U.S. Department of Energy under contract DE-AC05-00OR22725.

REFERENCES

REFERENCES

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APPENDIX

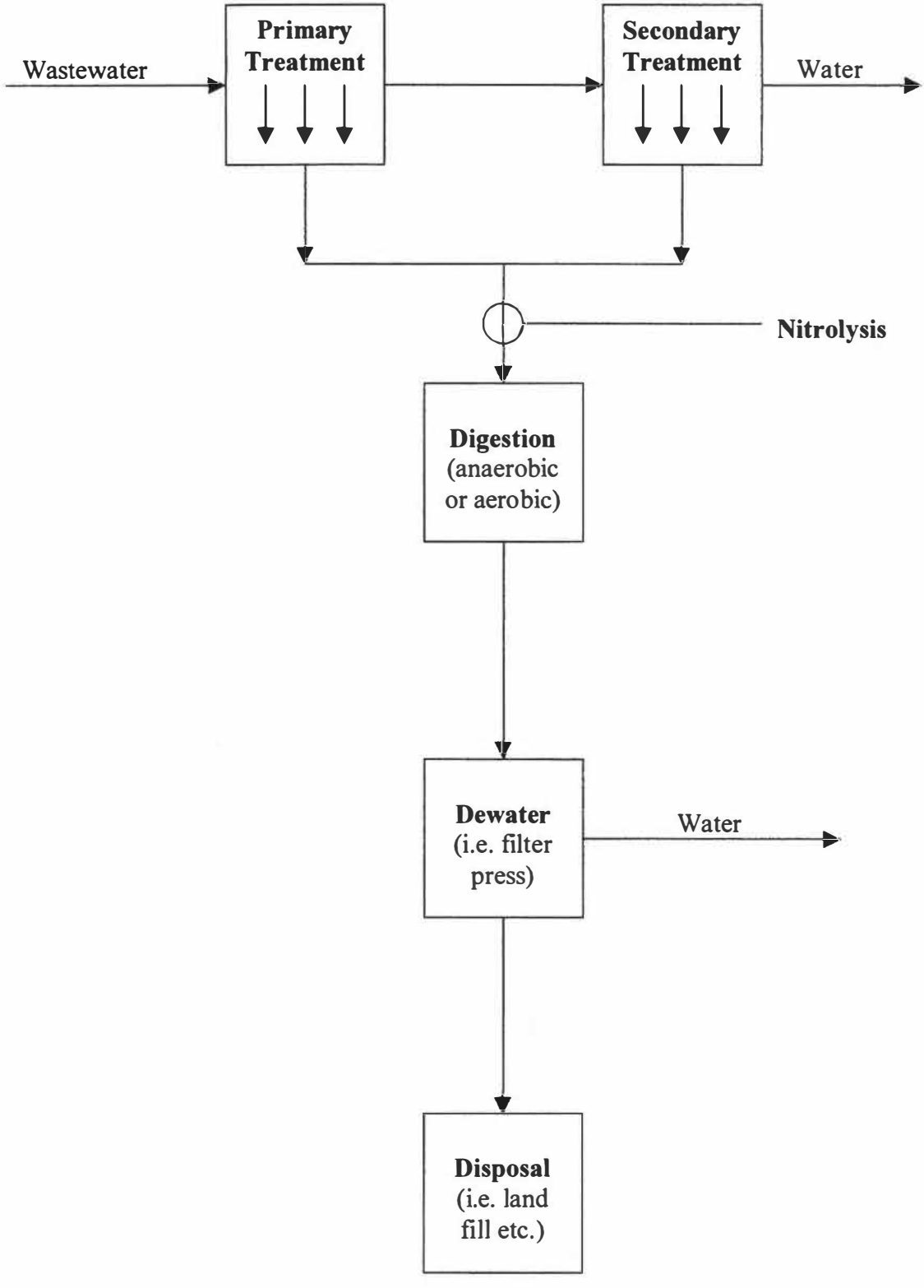


Figure 1 – Illustration of a Typical Wastewater Treatment Facility

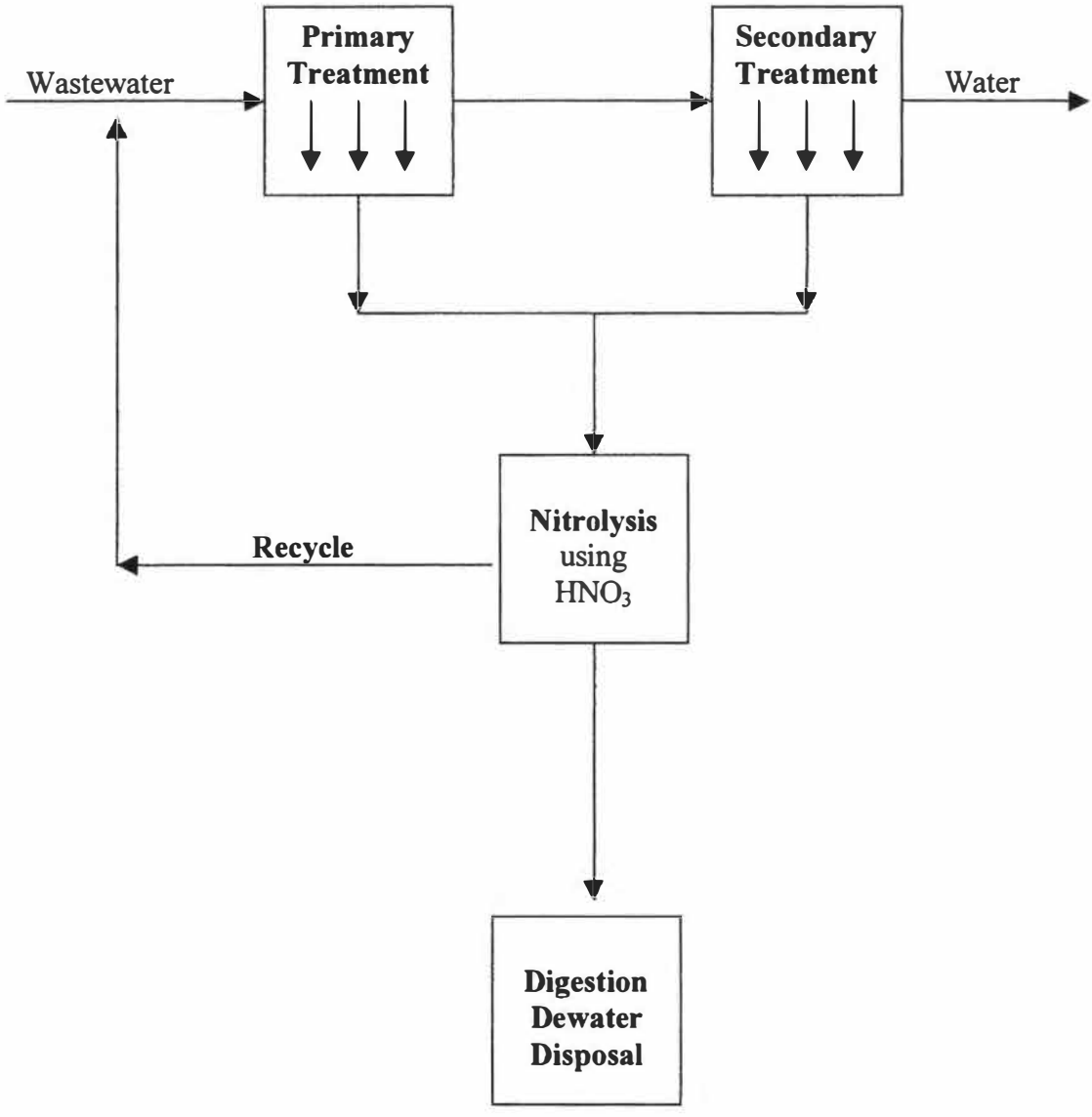


Figure 2 – Concept of Nitrolysis Incorporated Into a Wastewater Treatment Facility

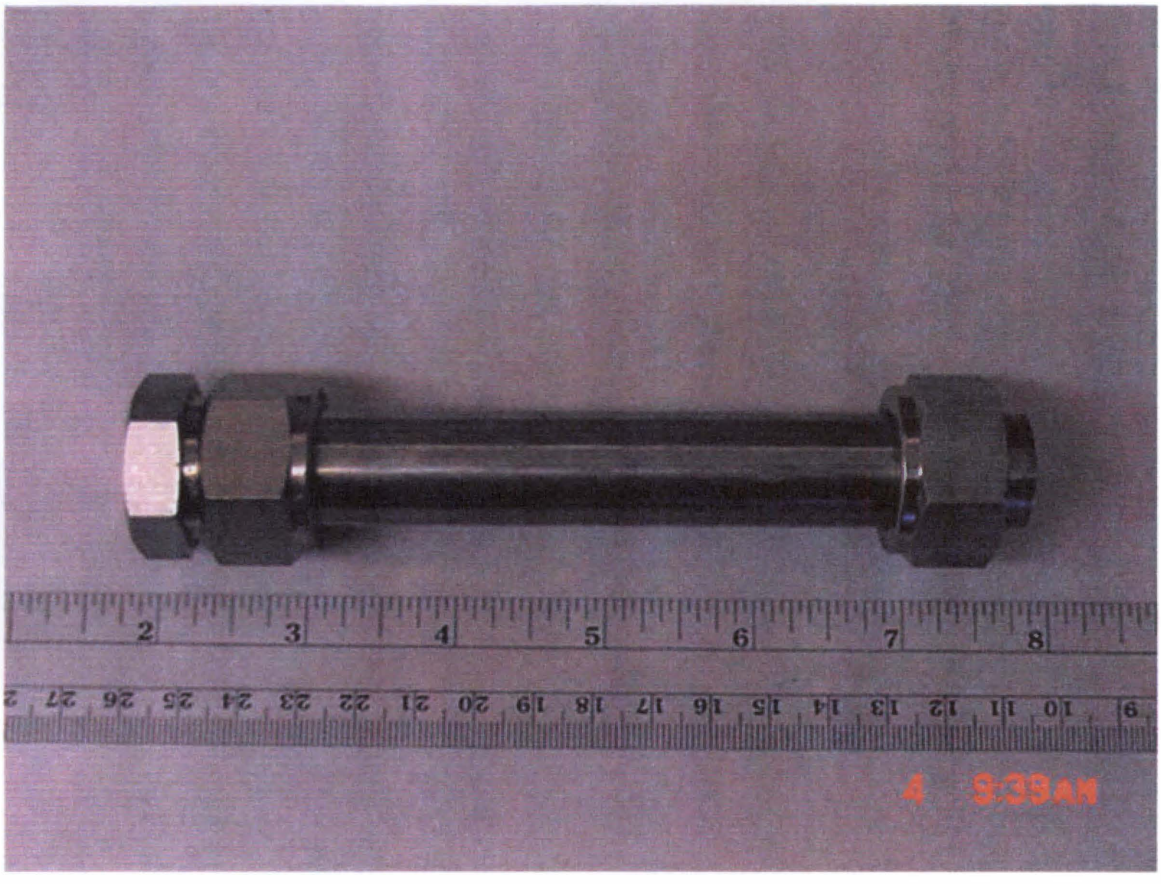


Figure 3 – Pressure Rated 25-mL Batch Nitrolysis Reactor



Figure 4 – Continuously Stirred Tank Pilot Plant Nitrolysis System

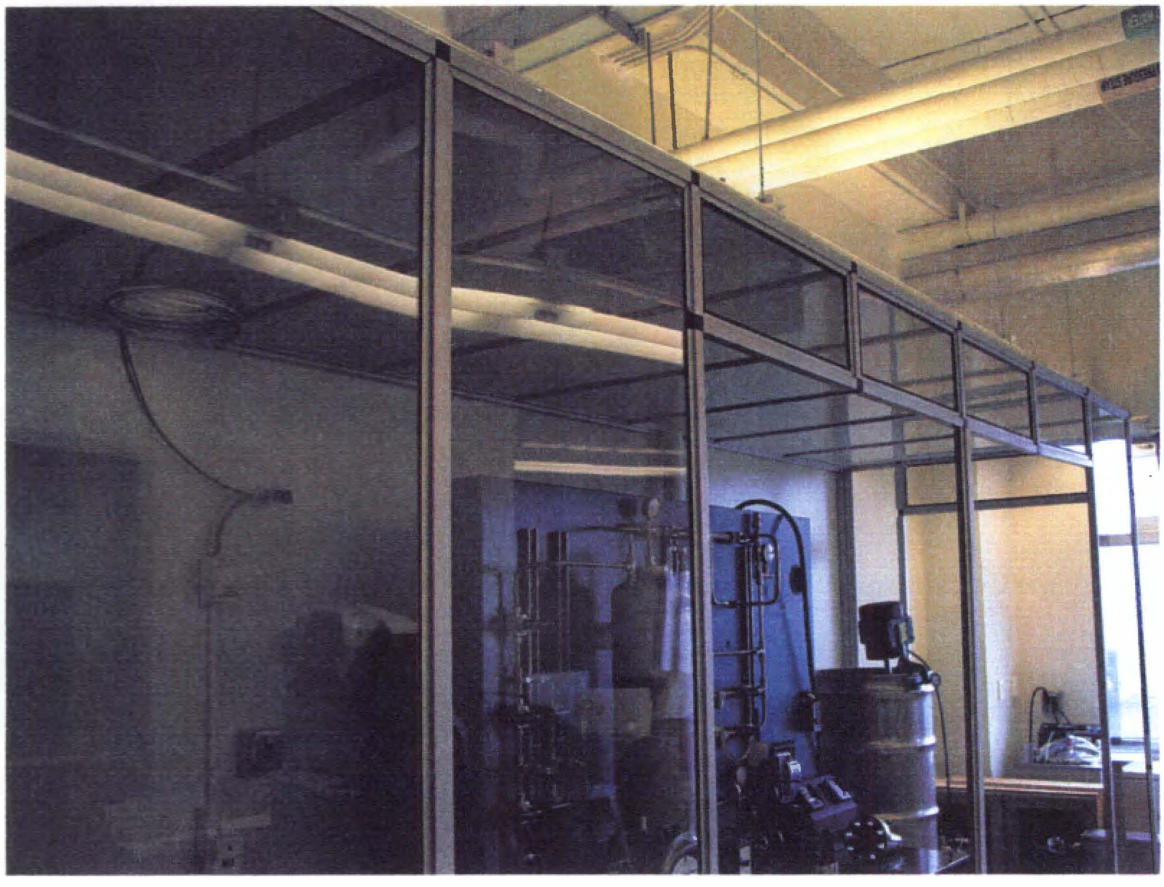


Figure 5 – Safety Enclosure for Continuously Stirred Tank Pilot Plant Nitrolysis System

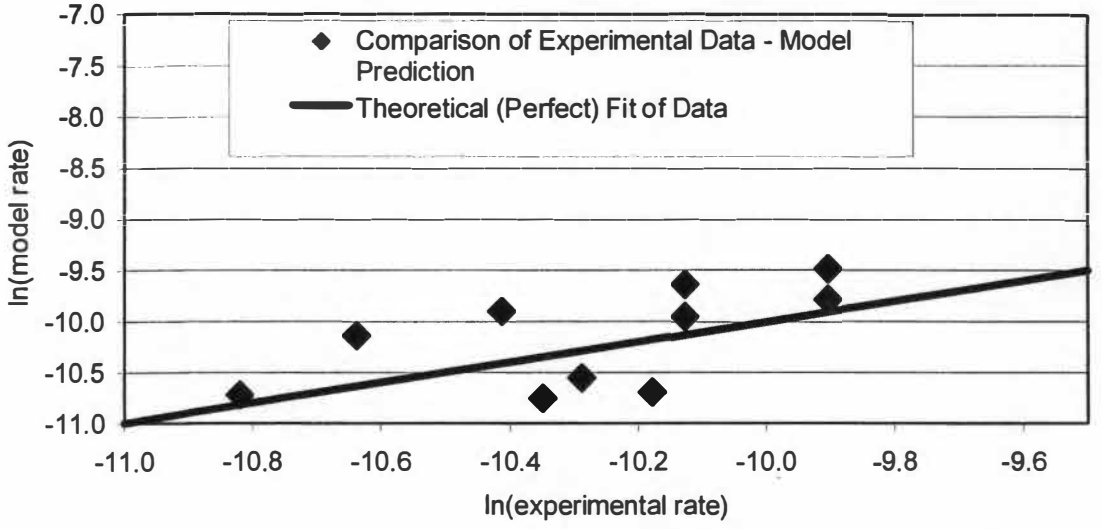


Figure 6 – Comparison of Experimental Reaction Rate to Model Reaction Rate for Nitrolysis of Municipal Excess Sludge

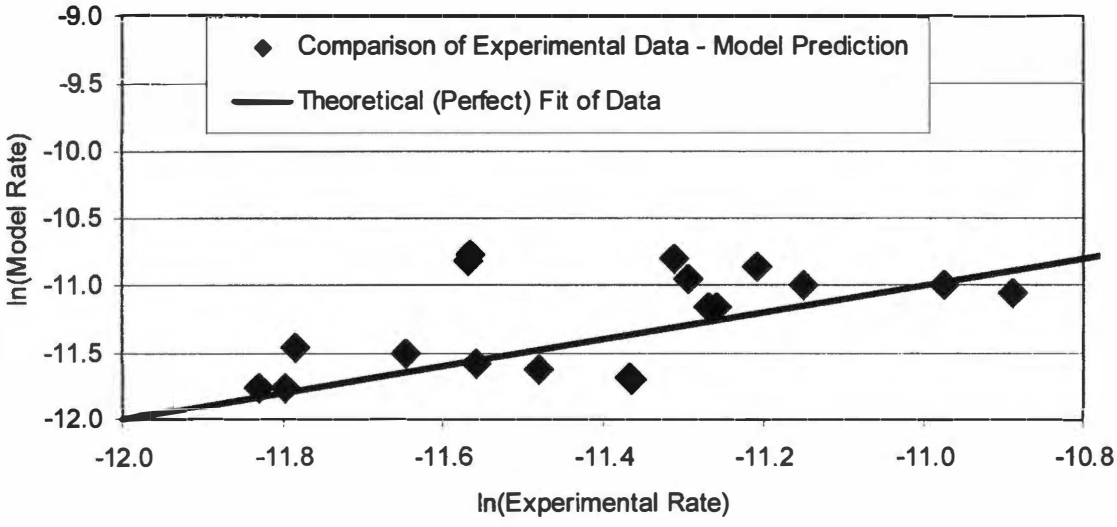


Figure 7 – Comparison of Experimental Reaction Rate to Model Reaction Rate for Nitrolysis of Industrial Excess Sludge

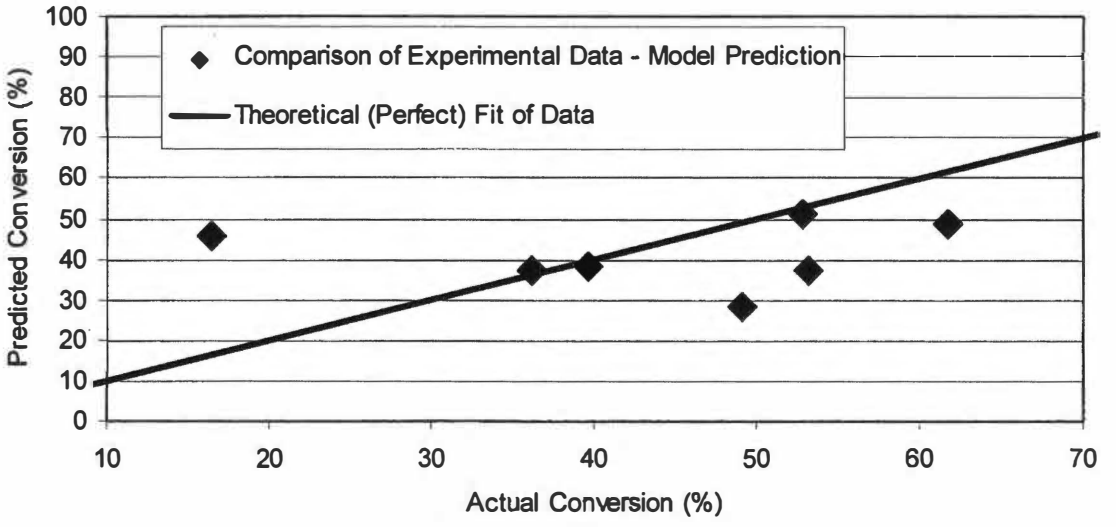


Figure 8 – Comparison of Municipal Kinetic Model to Experimental Data Obtained from a Continuous Pilot Plant System In Terms of Conversion of Biomass

PART VIII

CONCLUSIONS

1. SUMMARY AND CONCLUSIONS

The nitrolysis process has been developed and demonstrated on both a laboratory scale and a pilot plant scale. The process has been shown to reduce the volume and mass of excess sludge, as well as produce potentially valuable products such as acetic acid. Nitrolysis has been developed in both batch and continuous experiments, corresponding to the lab and pilot plant studies. The following discussions give a brief summary of each part of this dissertation. For a more in depth assessment of each paper, please refer to the specific part earlier in the dissertation.

Part 2 showed the mass reduction in the excess sludge reached better than 80%. The production to acetic acid, and to a lesser extent, formic acid and propionic acid was illustrated. The concentration of these organic acids was high enough to peak an interest in their production from nitrolysis. The production of gases was also found in this preliminary investigation of the process. The reaction rate of nitrolysis was investigated briefly, but no reaction rate expression was developed during this initial evaluation phase. Approximately 8% (by mass) of the carbon was shown to result in organic acids. This study showed good separation of the remaining solids and liquids after nitrolysis and demonstrated a very fast hydrolysis of the excess sludge. This study also showed that all of the nitric acid could be reacted at low acid concentrations, but some residual nitric acid remained if larger nitric acid concentrations were used.

Part 3 showed the development of the nitrolysis reaction utilizing municipal excess sludge. This paper showed a parameter study (factorial study) of the nitrolysis process to determine which operating parameters affected the hydrolysis of the municipal

excess sludge, as well as which operating parameters affected the production of potentially valuable organic acids. The process showed that increasing nitric acid concentration increased the mass reduction of the excess sludge, but also left a larger nitric acid residue in the effluent. All four operating parameters (acid concentration, sludge concentration, reaction time, and reaction temperature) were shown to affect the production of organic acids, however the reaction time was not found to affect the hydrolysis of the excess sludge. This finding illustrated the fact that during nitrolysis, the excess sludge is hydrolyzed to the liquid phase quickly, and then converted to products (organic acids and CO_2) more slowly. A reaction rate expression was developed for the nitrolysis of municipal excess sludge that compared to the experimental data with good agreement. A material balance based on COD was also performed around the reactor (liquid effluent, solid residual, and gases) with better than 90% closure. Similar results were found for TOC material balances. The gas products were also analyzed showing that the largest component of the gaseous phase was CO_2.

Part 4 showed the development of the nitrolysis reaction utilizing industrial excess sludge obtained from a secondary wastewater treatment facility. This paper showed a parameter study (factorial study) of the nitrolysis process to determine which operating parameters affected the hydrolysis of the industrial excess sludge, as well as which operating parameters affected the production of potentially valuable organic acids. The operating parameters in this study were included sludge concentration, reaction time, and nitric acid-sludge ratio (mass basis). The results indicated that increasing the acid-sludge ratio increased the conversion of industrial excess sludge. The results showed that

increasing any of the operating parameters increased the organic acid production. The reaction rate expression developed in Part 3 was compared to the experimental reaction rate for nitrolysis of industrial excess sludge. The comparison showed the model under-predicted the experimental reaction rate for the nitrolysis of the industrial excess sludge. Again, better than 90% closure was demonstrated on a COD material balance. Similar results were found for a TOC material balance.

Part 5 showed a more in depth development of the reaction rate expression of the nitrolysis process and compared reaction rates of nitrolysis of both municipal and industrial excess sludge. The reaction rate expression was developed considerins inert material, and thus gave a better reaction rate model than that developed in Part 3. The nitrolysis of both municipal and industrial excess sludge showed agreement with the model developed in this part of the project. A similar reaction rate was developed on a COD basis. This model also showed good agreement with the experimental reaction rates, and will be useful to industries and municipalities interested in incorporating this process into the wastewater treatment process. It should be noted, the reaction rates determined in this study are limited to the operating parameters discussed, and should be further investigated if the operating parameters are altered outside this range.

Part 6 showed the design, construction, and operation of a pilot plant for development of the nitrolysis process on a larger continuous scale. This study demonstrated the thought and work that went into the design of the pilot plant. The finished product was illustrated and the nitrolysis process was demonstrated in the CSTR. The experimental data from this work was also compared to the reaction rate developed

in Part 3. This study demonstrated the process on a larger and continuous scale, which is more consistent with a typical wastewater treatment facility, and aided in the development of the process.

Part 7 showed an overall summary and review of the nitrolysis process and the status of the process upon completion of this project. This summary illustrated the advances and knowledge that has been gained during the research effort. The development of reaction rate expressions and the study of the reaction stoichiometry were discussed. The production of potentially valuable products and the advantage of excess sludge hydrolysis were also discussed.

APPENDIXES

APPENDIX A

PROJECT SAFETY SUMMARY
ACID CATALYZED HYDROLYSIS OF SLUDGE
PHASE I

PROJECT SAFETY SUMMARY

DATE: August 14, 2001
PROJECT NAME: Acid Catalyzed Hydrolysis of Sludge – Phase I
LOCATION: Science and Engineering Facility Room 716

Larry Perkins
University of Tennessee
Chemical Engineering Department
Science and Engineering Research Facility - Room 716
Knoxville, TN 37996
(865) 974-8303 (work)
(865) 882-5358 (home)

Robert Counce
University of Tennessee
Chemical Engineering Department
Dougherty Engineering Building – Room 509
Knoxville, TN 37996
(865) 974-5318 (work)
(865) 584-5986 (home)

Paul Bienkowski
University of Tennessee
Chemical Engineering Department
Dougherty Engineering Building – Room 516
Knoxville, TN 37996
(865) 974-1618 (work)
(865) 938-0586 (home)

Signatures:

Larry Perkins (Engineer in Charge)	*Date*
Robert Counce (Professor in Charge)	*Date*
Paul Bienkowski (Safety Officer)	*Date*
John Collier (Department Head)	*Date*

Emergency Shutdown Procedure

1. Kill the power by unplugging the hot oil bath.
2. Close the fume hood.

HEALTH AND SAFETY PLAN FOR UNIVERSITY OF TENNESSEE RESEARCH PROJECT: ACID CATALYZED HYDROLYSIS OF SLUDGE PHASE I

Company Name: University Of Tennessee/Chemical Engineering
Address: Knoxville, Tennessee
Date: August 14, 2001

I. Introduction and Summary Description

The University of Tennessee is a four year educational institution for higher learning. The Chemical Engineering Department runs chemical experiments for research and development.

The project will have a total of five people involved within the project.

II. Key Personnel (include reporting relationships; include phone and pager numbers for Section III.F)

Position	Name	Phone	Pager	Reports to:
Senior Management	Dr. Robert M Counce	974-5318	N/A	Dr. John Collier
Safety and Health Officer	Dr. Paul Bienkowski	974-1618	N/A	Dr. John Collier
Emergency Response Coordinator	Dr. Paul Bienkowski	974-1618	N/A	Dr. John Collier

III. Site Safety Requirements

A. Emergency Management Responsibilities

By mutual agreement of both University of Tennessee and the City of Knoxville, the City of Knoxville will respond to emergency needs to include: fire protection, spill response and clean-up, and medical emergencies will be supplied by the University of Tennessee Hospital.

The University of Tennessee Emergency Response point of contact identified in section II above will coordinate company resources to provide pertinent information to both emergency responders and company management. In the event that an emergency may impact other companies appropriate communications will be made per the mutual aid agreements.

B. Reporting/Notifications and Emergencies

Reporting of emergencies should be made by calling 911. Report the nature, exact location, and extent of the emergency.

C. Record Keeping and Documentation

University of Tennessee will keep all safety records and documentation as required per the OSHA requirements. This includes 29 CFR (OSHA) records such as the OSHA 200 Log, documentation of equipment / facilities inspections (as required), and documentation of employee training (as required). These records will be kept at a location consistent with 29 CFR requirements.

D. Alarm Signals, Emergency Notification (Public Address) System, Employee Response

Alarm signals, emergency notification, and employee response are covered in the initial training. In the event of an emergency, employees are expected to pay attention to announcements made over the public address system, and to take appropriate protective actions as directed.

E. Medical Treatment

Emergency medical treatment is available by calling 911. For non-emergency medical needs, notify University of Tennessee management discussed above and a decision will be made on a case-by-case basis whether to use medical facilities.

F. Key Phone Numbers/Contacts

See Section II for primary information.

G. Assembly Locations

In the event of a building evacuation, employees should report outside the front door.

H. Weather Alerts

In the event of severe weather, weather alerts may be made by personal communications. Employees should pay attention to these alerts, and take appropriate protective actions.

I. Traffic Rules

All employees are expected to abide by the State of Tennessee Department of Transportation requirements, including posted speed limits and established and no parking zones.

J. Radiological Protection

This project involves no radiological materials. Any employee questions regarding radiological protection should be directed to the University of Tennessee Radiological Protection Safety Officer, who can then pursue additional information from appropriate representatives.

K. Fitness for Duty

While on the job, employees are expected to remain in an unimpaired state, both mentally and physically, appropriate for their job responsibilities. Supervisors are responsible for ensuring that employees reporting to them meet this level of fitness for duty.

L. Floor Plans of Facility With Emergency Exits

Floor plans for all buildings, with emergency paths identified, are located in appendix A of this document. This project will be located in SERF 716.

IV. Hazards

A. Define Scope of Work

The scope of this work is to react sludge generated from wastewater with nitric acid. This acid catalyzed hydrolysis of biosolids will generate products including acetic acid and formic acid that can then be sold to create a profit. This phase of the research is a scoping phase to aide in the determination of kinetics and stoicheometry for the reaction. The research will include the variables of residence time, acid-to-sludge ratio, and temperature. The small batch reactor will be charged with the reactants and submerged in a hot oil bath. After the appropriate reaction time, the tube will be removed from the oil and quenched in an ice water bath. The reactor will then be opened and the contents separated and analyzed. The reactor will be heated to 150-200°C and operated at approximately 200 psig. The liquid products produced include formic acid, acetic acid, alanine, and water, which will be gravity filtered to remove any residual solids prior to analysis. The gases produced are nitrogen, carbon monoxide, carbon dioxide, and nitrous oxide, which may be collected and analyzed to help close the material balance on the reactor. Ammonium and nitrate ions will also be produced in solution. The unreacted sludge will be vacuum filtered and allowed to dry prior to analysis.

B. Hazard Identification

(Check all that apply)

1. Physical Hazards
___ Cold Stress
___ Heat Stress
___ Noise
_X_ Slip/Trip/Fall
___ Enclosed Space
___ Confined space
___ Oxygen Deficient
___ Oxygen Enriched
___ Ergonomics
_X__ Manual Lifting
_X__ Compressed Gases/Cylinders
_X__ Pressurized Systems
_X__ High Pressure*
___ Compressed Air
___ Explosive/Flammable
___ Vibration/Shock sensitive
___ Mechanical/Moving Parts
_X__ Sharp Edges/Corners
___ Inclement Weather
___ Work on or near water
___ Moving Equipment/Vehicles

2. Safety/Construction Hazards
___ Demolition
___ Drum Handling
___ Elevated Work
_X__ Hazardous Energy (electrical/ hydraulic/ pneumatic/ steam/ etc.)
___ Concealed/Underground Hazards
___ Excavation/Penetration
___ Hoisting/Rigging
___ Overhead Hazards
___ Welding/Cutting/Burning
___ Other _____

3. Utility Hazards
___ Electrical
___ Gas
___ Plumbing
___ Telephone
___ Overhead utility lines
___ Septic/Sewer
___ Other Concealed/ Underground utilities
___ Other _____

4. Chemical Hazards*
___ Asbestos
___ Lead
___ Manmade Mineral Fibers
___ Mercury
___ Metals
_X__ Toxic
_X__ Incompatible Chemicals
___ PCBs
___ Inorganic
_X__ Volatile Organic
_X__ Corrosive
___ Carcinogen
___ Mutagen
___ Reproductive Toxicant
_X__ Reactive
___ Pyrophoric
___ Other _____

5. Ionizing Radiological Hazards*
___ External Exposure
___ Internal Exposure
___ Contamination
___ Fissionable Material

6. Non-Ionizing Radiological Hazards
___ High Voltage
___ RF
___ Laser
___ Microwave
___ Ultra Violet

7. Biological/Vector Hazards
_X__ Bacterial/Fungi
___ Plants (Allergens)
___ Medical Waste
___ Wildlife
___ Parasites
___ Rodents (Hantavirus)
___ Insects, snakes, spiders, etc.

8. Hazardous Waste*
Waste code (If known)
_____
Metals:
___ Arsenic
___ Barium
___ Cadmium
___ Chromium
___ Lead
___ Mercury
___ Selenium
___ Silver
___ Other _____
Volatiles:
___ Benzene
___ 2-Butanone
___ 1,4 Dichlorobenzene
___ Ethylbenzene
___ Tetrachloroethylene
___ Toluene
___ 1,1,1-Trichloroethane
___ Trichloroethylene
___ Xylene
Other:
___ Asbestos
___ PCBs
___ Soil Debris
___ Hydrocarbon Impacted Waste
Waste Characteristics
_X__ Corrosive
___ Exothermic reaction
___ Ignitable
_X__ Reactive
_X__ Toxic (CO)
Waste Categories
___ Bio-Hazard
___ Mixed
___ Radiological
___ RCRA
___ Sanitary Industrial
___ TSCA

9. Others
___ Type _____
___ Type _____
___ Type _____
___ Type _____

B. **Identification and Assessment of Effectiveness of the Controls in Place to Prevent or Mitigate Accidents That Could Occur From the Hazards Identified.** (Controls may include but are not limited to engineered safeguards, use of industry standards and company procedures and safe work practices, employee training, emergency response, personal protective equipment, etc.) See pictures of

equipment in Appendix A.

V. Training

A. Site Access Training

All employees are required to take access training.

B. Required OSHA Training

Employees may be involved in the activities checked below, and therefore may require further training under 29 CFR (OSHA) regulations:

___ Crane usage
___ Fork-truck usage
___ Use of powered platforms or lifts
_X__ Working with chemical products
___ Exposure to noise
___ Working at heights
___ Use of respirator
___ Working with hazardous waste
_X__ Working with hazardous materials
_X__ Use of compressed gases
___ Welding/cutting
___ Entry into confined spaces
_X__ Lockout/tagout activities
___ Electrical activities
___ Excavation
___ Asbestos work
___ Other _____
___ Other _____
___ Other _____

VI. Medical Surveillance (include frequency of medical exams, exposure monitoring, air sampling, and possible signs and symptoms of overexposure to site-specific hazards)

Employees Covered (i.e. shop worker, foreman, etc.)	**Reason for and Type of Surveillance/Exam**	**Frequency**
N/A		

VI. Contingency Plans

In the event of an emergency, call 911. During the emergency, the University of Tennessee Emergency Response Coordinator identified in this plan should be available to provide information needed by emergency responders. Any legally required notifications to federal, state, or local agencies remain the responsibility of the University of Tennessee.

For medical emergencies arising from injury or illness, call 911. Report the nature, exact location, and extent of the emergency.

For hazardous chemical spills or material releases, alert people in the immediate vicinity, and evacuate the area. Report the emergency by calling 911 as soon as safely possible. A decision regarding the need for assistance in cleanup of the spill/release will be made on a case-by-case basis by company management.

For fire emergencies, alert people in the immediate vicinity, and evacuate the area. Report the emergency by calling 911 as soon as safely possible. Fire fighters arriving on the scene should be informed of any toxic, hazardous, or flammable materials involved with or in the vicinity of the fire.

Startup Procedure

1. Turn on heater to hot oil bath and allow to set for 20 minutes.
2. Add appropriate amounts of sludge and acid to the reaction tube.
3. Seal the reaction tube.
4. Shake the tube to ensure good mixing.

Shutdown Procedure

1. Unplug the hot oil bath.
2. Allow several minutes for the oil to cool.

Liquid Sampling Procedures

1. Decant products to a graduated cylindar.
2. Allow solids to settle out.
3. Pipett the liquid phase off.
4. Gravity filter the liquid phase to remove any residual solids.
5. Analysis at Oak Ridge National Laboratory.

Vapor Sampling Procedures

1. Attach the vapor collection device.
2. Open the valve on the reaction tube.
3. Allow the collection device to fill with vapor.
4. Close the valve on the reaction tube.
5. Analysis at Oak Ridge National Laboratory.

Solid Sampling Procedures

1. Vacuum filter solids through filter paper.
2. Allow solids to dry.

Safety Precautions

1. Operate in fume hood to remove gases
2. Pressure rated test tubes (screw caps)
3. Shield to deflect any leaks of tubes for heat or acid under pressure
4. Heat and acid resistant gloves
5. Acid proof safety goggles
6. Acid proof apron
7. Tubes are immediately quenched in an ice water bath after removal from hot oil
8. Forceps to remove tubes from hot oil
9. Eye wash station (Located in SERF 716, clearly marked on the sink.)
10. Safety shower (Located in the hall in front of SERF 718, clearly marked on attached floor plan.)
11. Samples analyzed at Oak Ridge

Small Lab Scale Experiments at UTK

Variables

Temperature

Sludge concentration

Amount of feed or nitric acid (HNO_3)

Reaction time

Measurements

Solids fraction consumed

Nitrate fraction consumed

Acetic acid

Formic acid

Total Organic Carbon (TOC) or (COD)

Temperature Range 160°C to 200°C in 20° increments (3 points)

Sludge Concentration Range 4% and 40% (2 points)

Amount of nitric acid (HNO_3) in feed ¼, ½, estimated stoicheometric amount, and 2 times (4 points)

Reaction Time 5 minute to 20 minutes in 5-minute increments (4 points)

Repeat each point 3 times

288 Total Data Points

Lab Scale Research Description

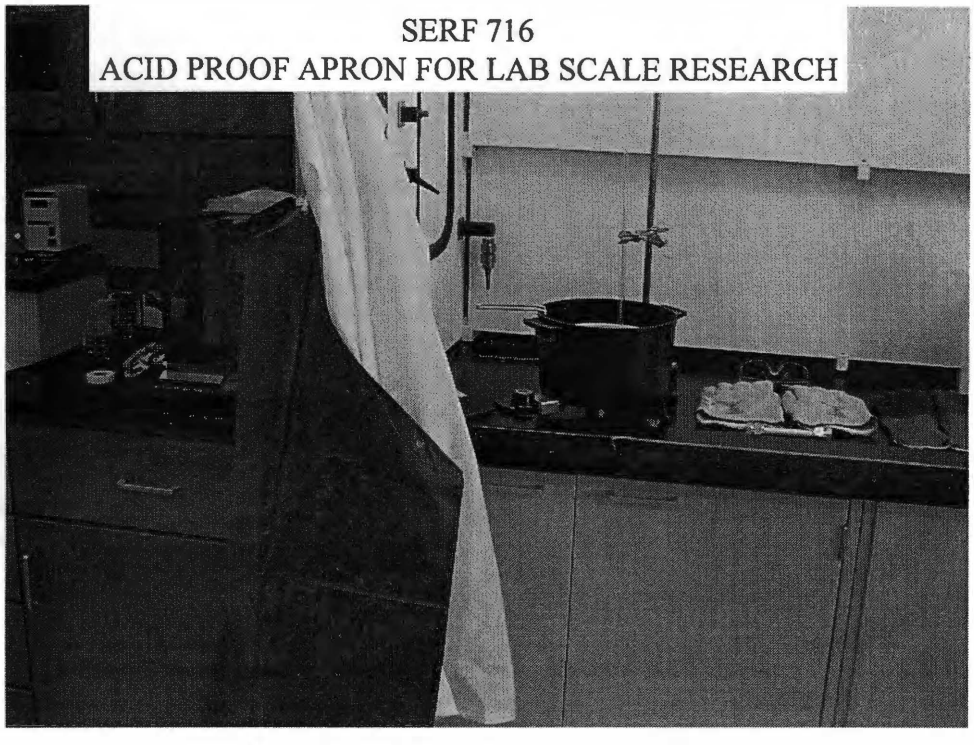
A small lab scale experiment will be conducted at the University of Tennessee to study the stoicheometry and product distribution of this type of reaction. The research will be conducted in room 716 of the Science and Engineering Research Facility. The research will be conducted inside a fume hood equipped with a 2500 cfm blower to remove any dangerous or toxic gases. The equipment involved in this research will include a hot oil bath, pressure rated test tubes, forceps, and the appropriate reactants. The variables of interest in this study will include temperature, feed ratio of reactants, concentration of sludge fed (% solids versus % water), and reaction time. The reactants will be placed in a pressure rated test tube, the tube sealed, and the tube placed in the hot oil bath. The cap for the pressure rated test tube is Teflon coated to prevent any reaction with the reactants or products of the reaction. After the appropriate residence time, the tube will be removed from the hot oil bath (using forceps) and immediately quenched in an ice water bath. The products will be stored in sample vials for storage and eventual transport to Oak Ridge National Laboratory for analysis. Other safety equipment used in this lab scale research will include acid proof apron, acid proof goggles, acid and heat resistant gloves, splash shield to protect against splashes or leaks of hot, pressurized, and/or acidic solutions, eye wash station, and safety shower. The products of this research will be analyzed for the fraction of solids consumed, the fraction of nitrate consumed, the total organic carbon, the acetic acid formed, and the formic acid formed.

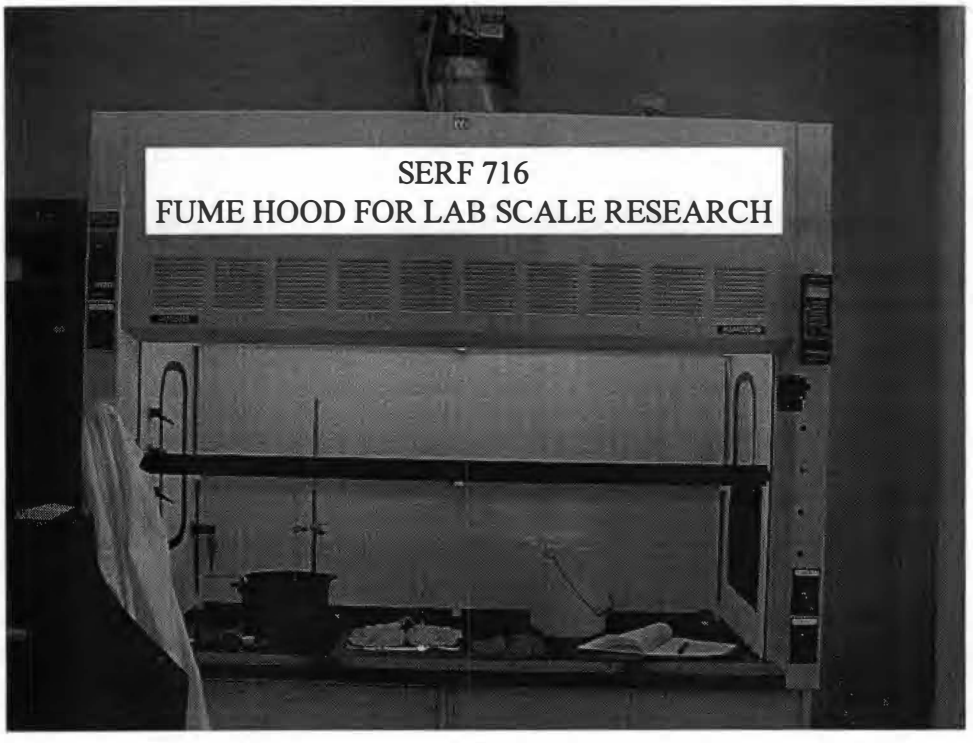
PHOTOGRAPHS AND FLOOR PLAN

SERF 716
EQUIPMENT FOR LAB SCALE RESEARCH

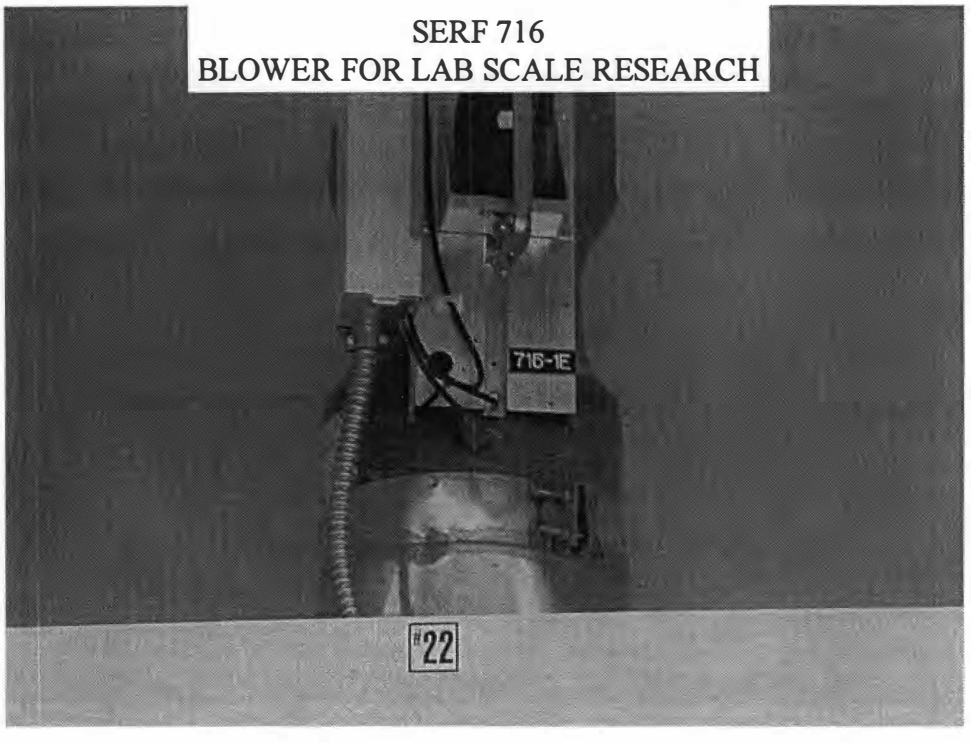


SERF 716
ACID PROOF APRON FOR LAB SCALE RESEARCH



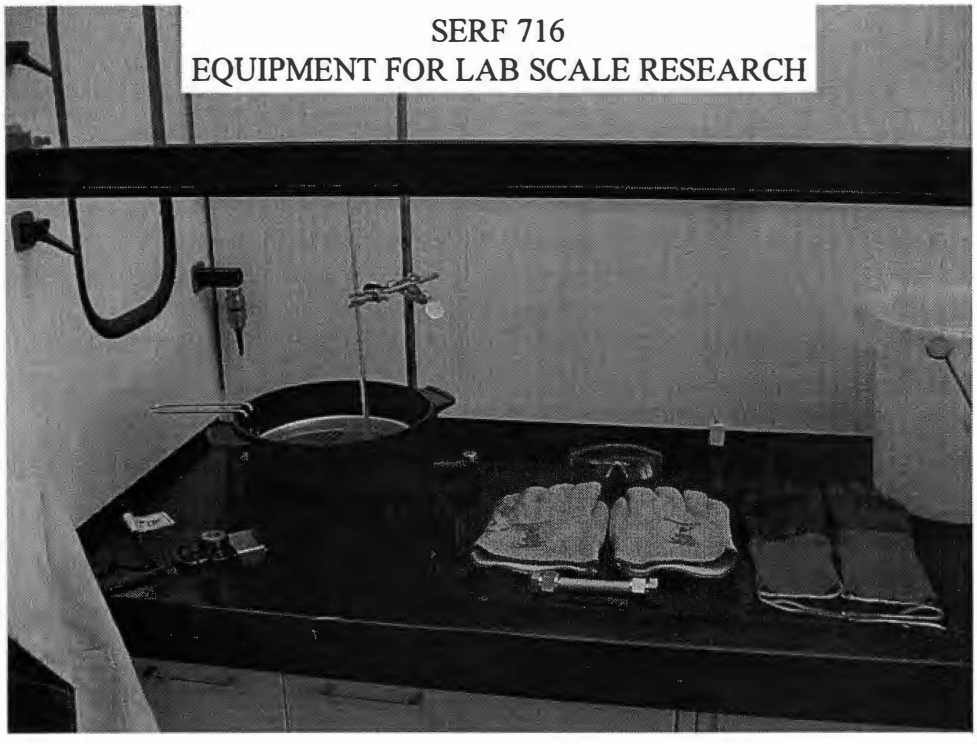


SERF 716
FUME HOOD FOR LAB SCALE RESEARCH



SERF 716
BLOWER FOR LAB SCALE RESEARCH

SERF 716
EQUIPMENT FOR LAB SCALE RESEARCH



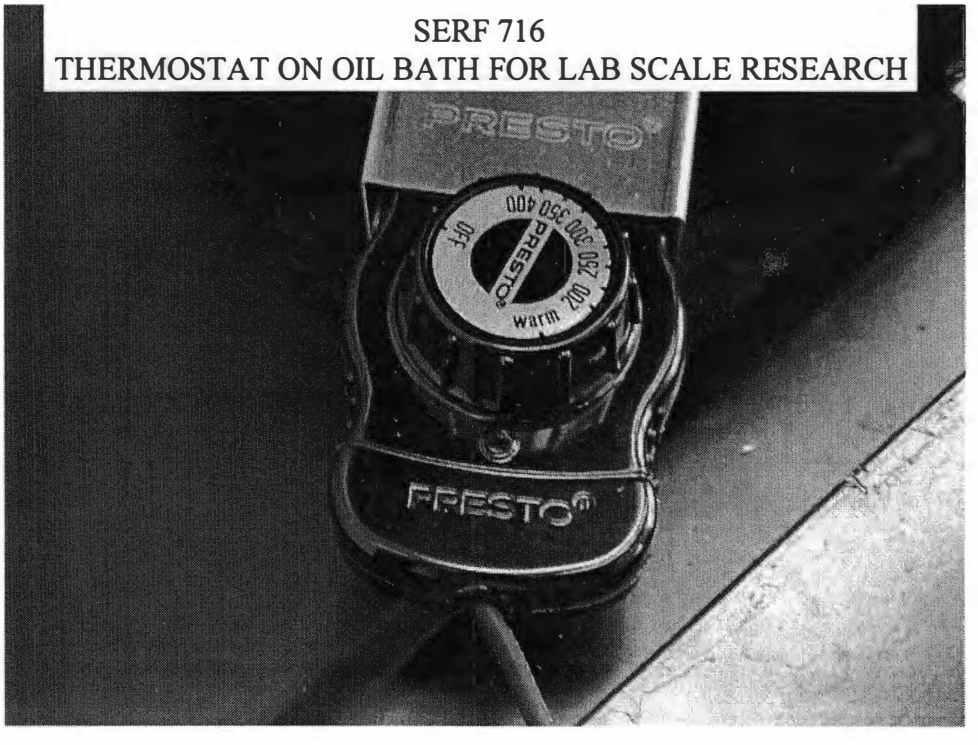
SERF 716
HOT OIL BATH FOR LAB SCALE RESEARCH



SERF 716
HOT OIL BATH FOR LAB SCALE RESEARCH



SERF 716
THERMOSTAT ON OIL BATH FOR LAB SCALE RESEARCH



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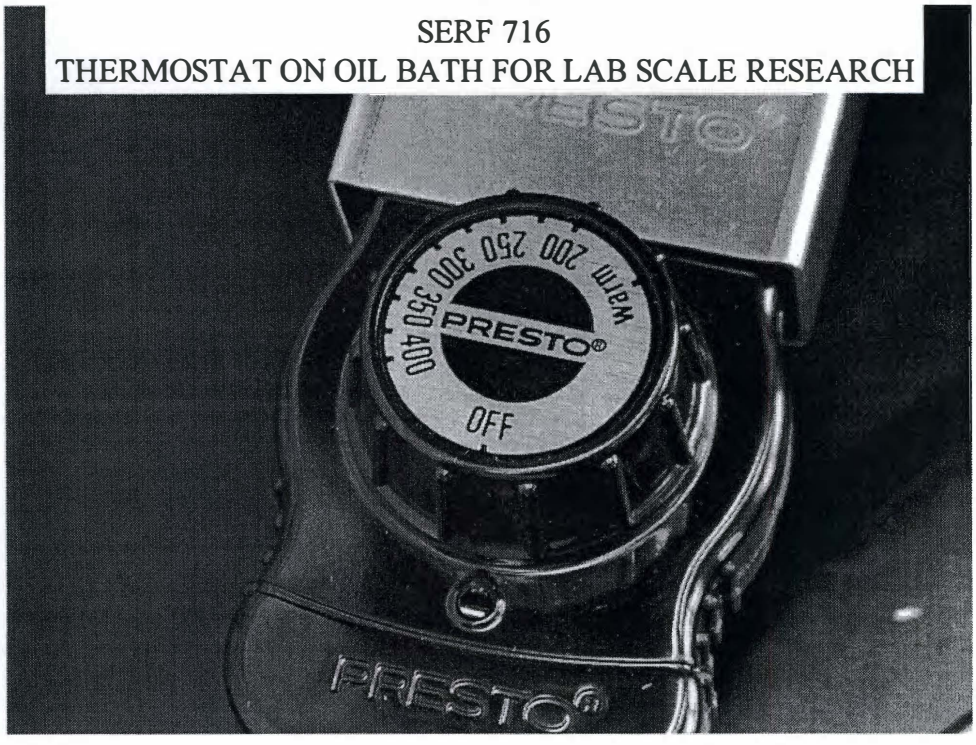
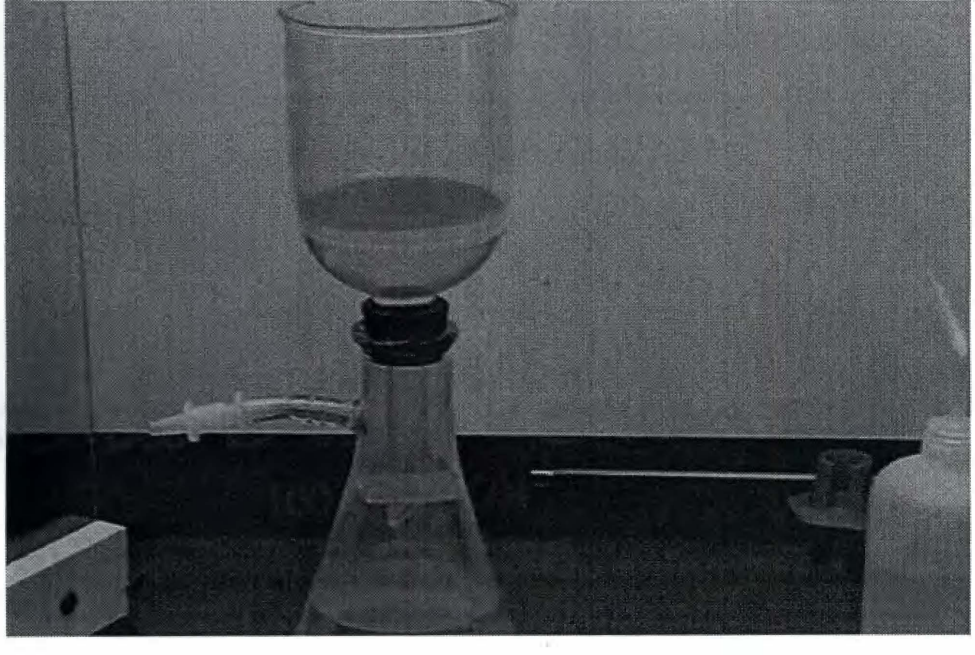
THERMOSTAT ON OIL BATH FOR LAB SCALE RESEARCH



SERF 716
VACUUM FILTRATION FUNNEL FOR LAB SCALE RESEARCH



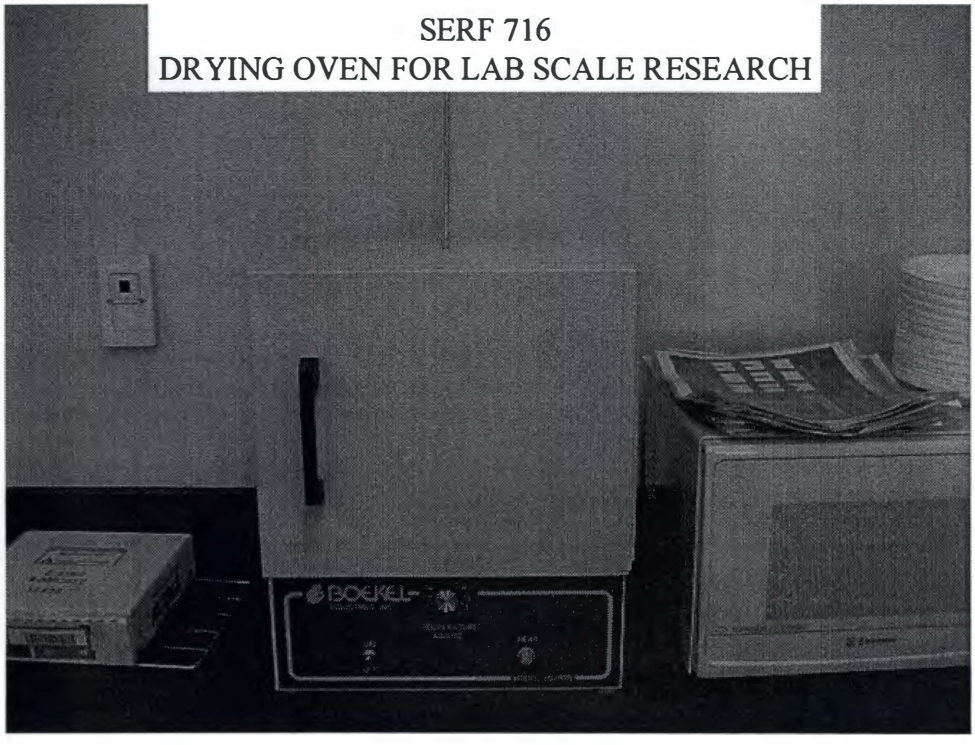
SERF 716
DIGITAL SCALE FOR LAB SCALE RESEARCH



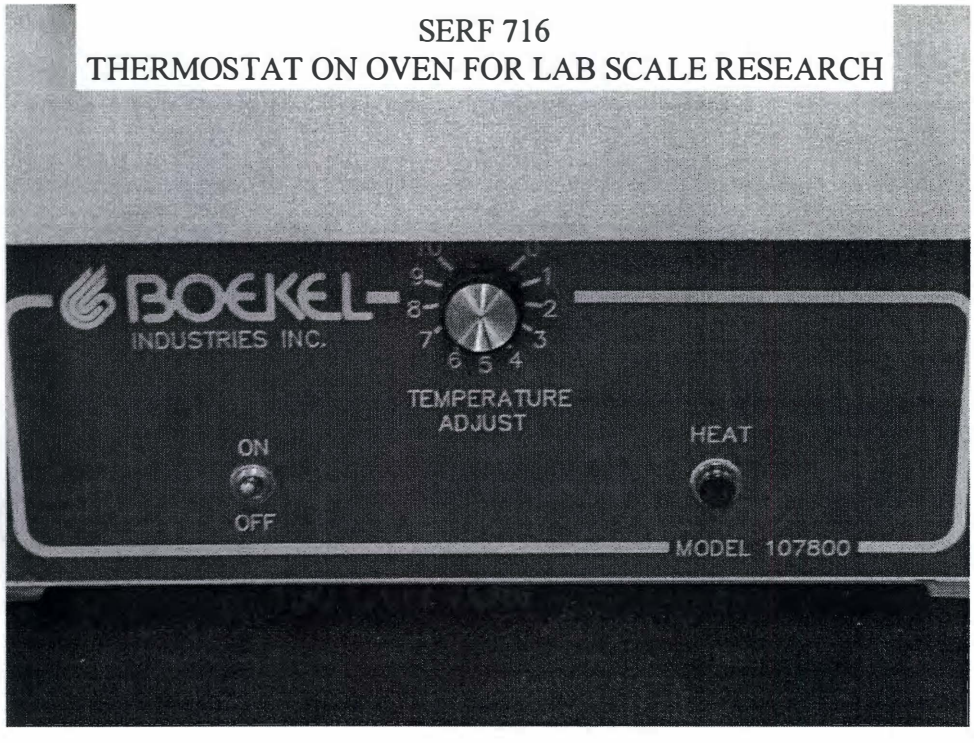
SERF 716
DIGITAL SCALE FOR LAB SCALE RESEARCH



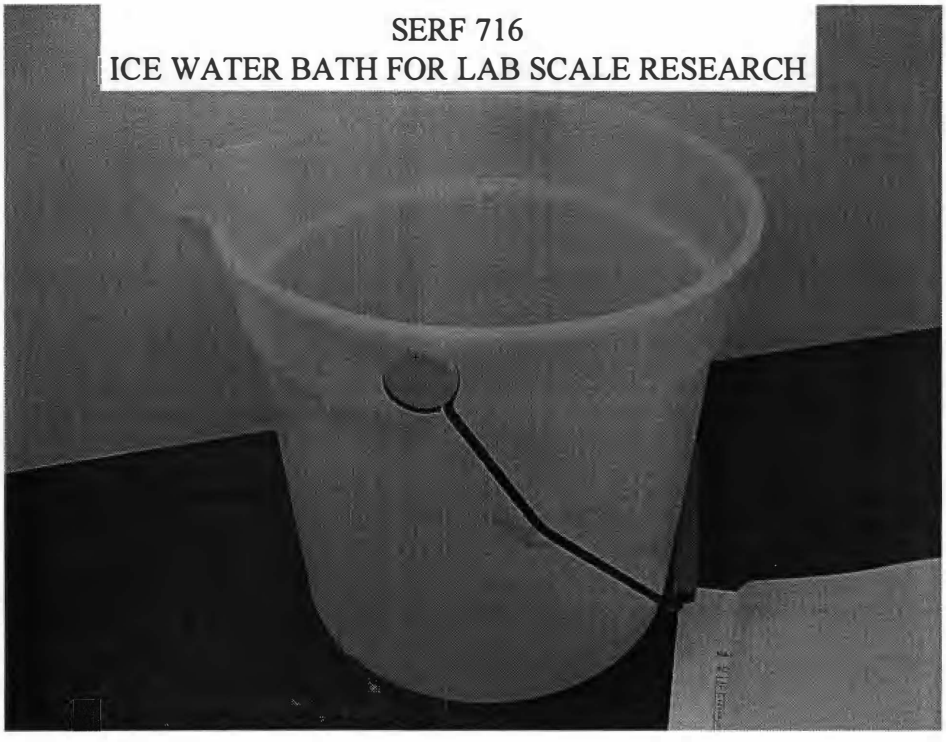
SERF 716
DRYING OVEN FOR LAB SCALE RESEARCH



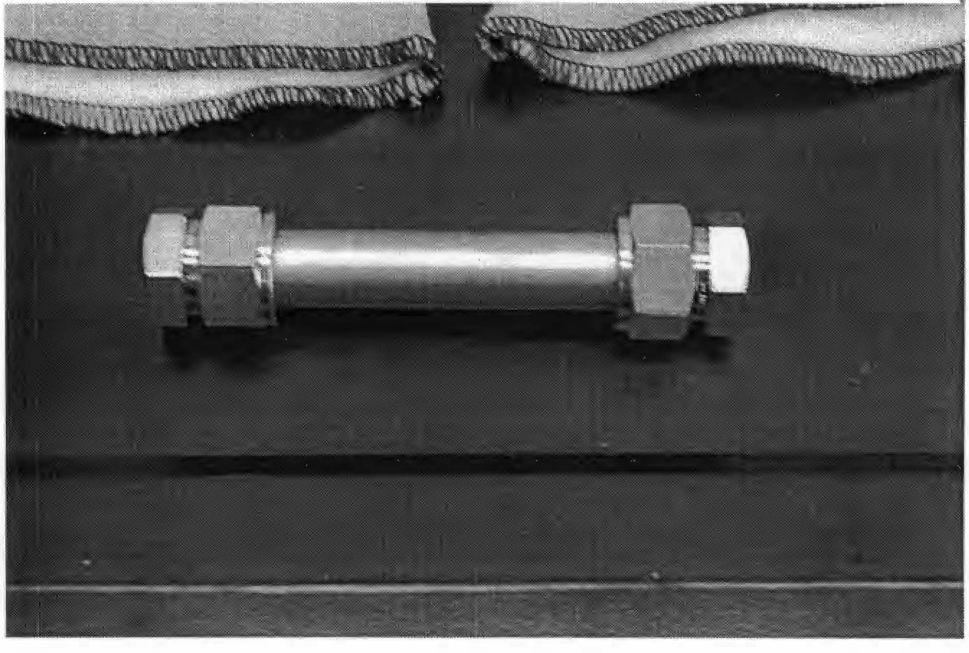
SERF 716
THERMOSTAT ON OVEN FOR LAB SCALE RESEARCH



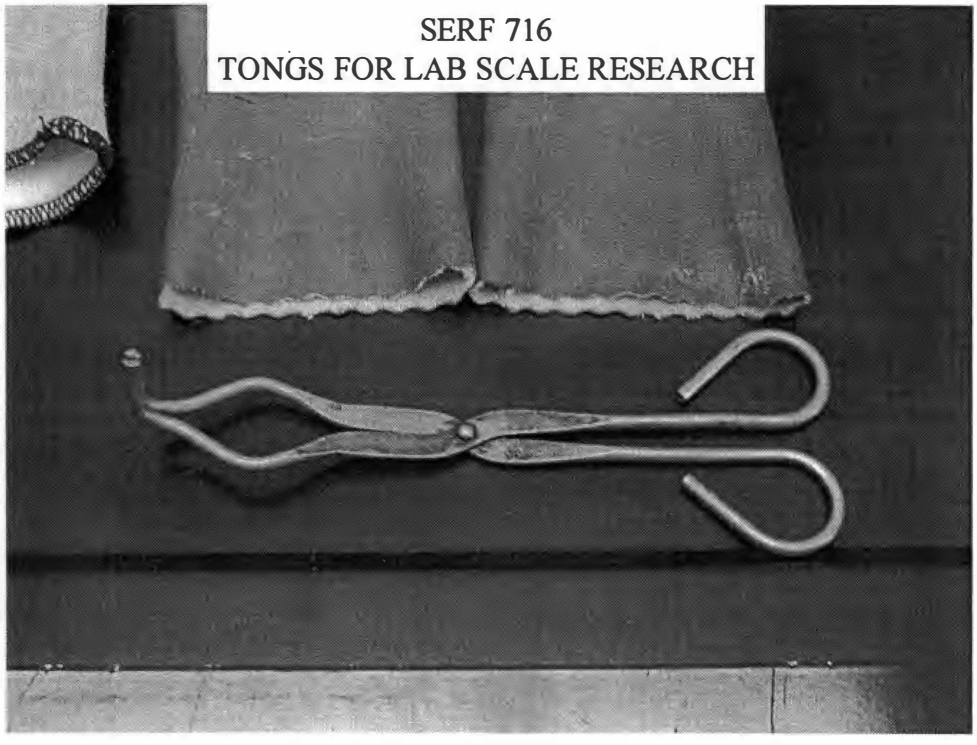
SERF 716
ICE WATER BATH FOR LAB SCALE RESEARCH



SERF 716
HIGH PRESSURE REACTION TUBE FOR LAB SCALE RESEARCH



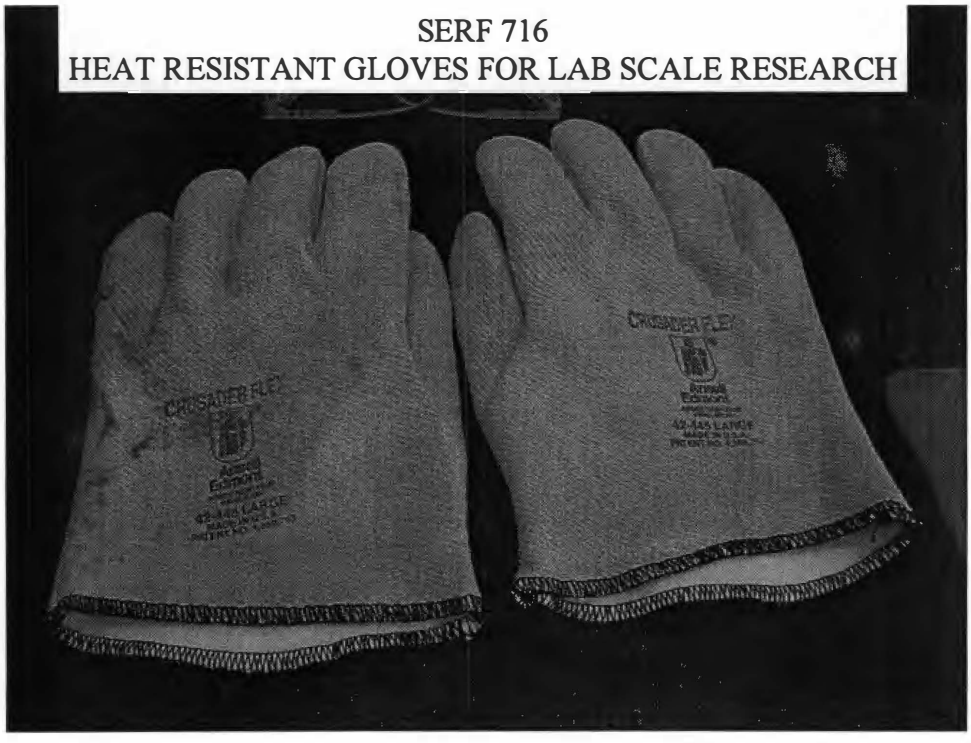
SERF 716
TONGS FOR LAB SCALE RESEARCH



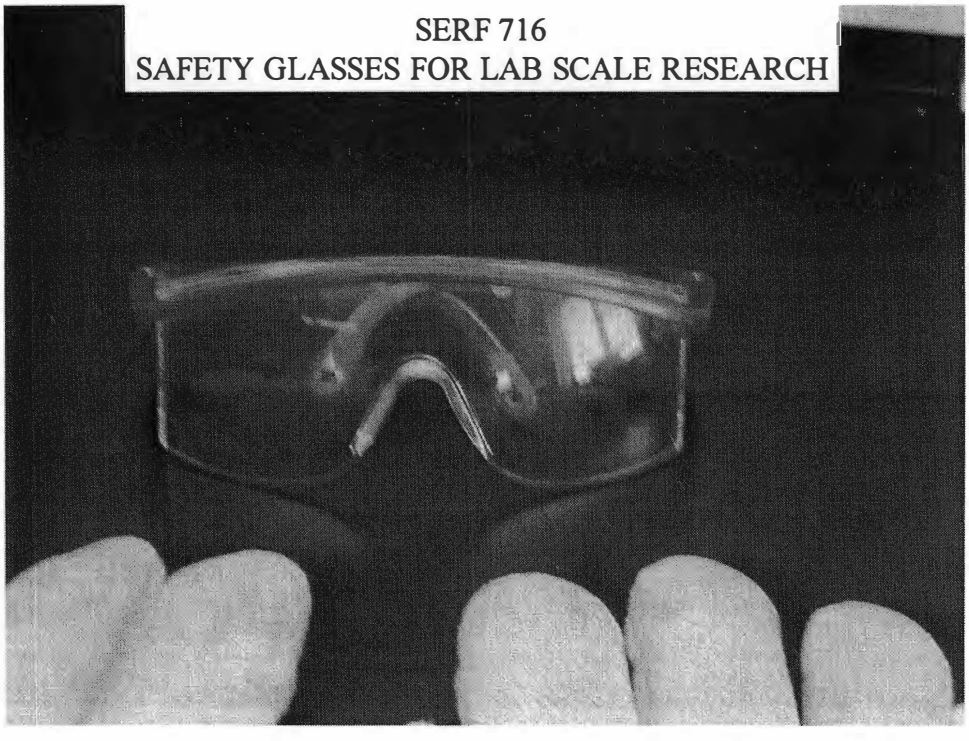
SERF 716
ACID PROOF GLOVES FOR LAB SCALE RESEARCH



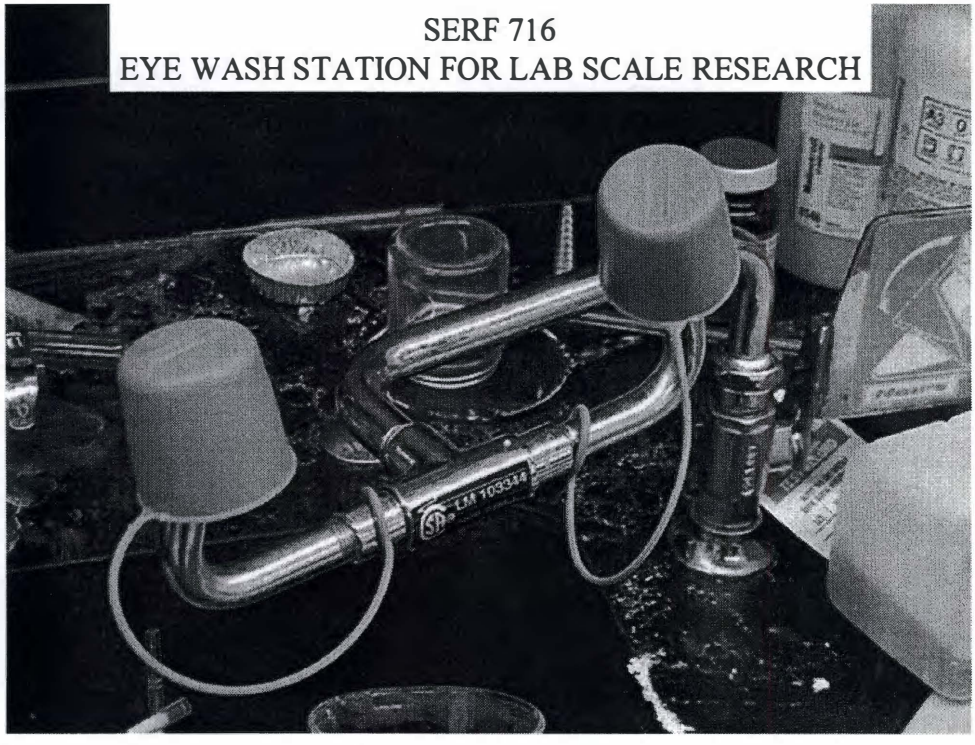
SERF 716
HEAT RESISTANT GLOVES FOR LAB SCALE RESEARCH



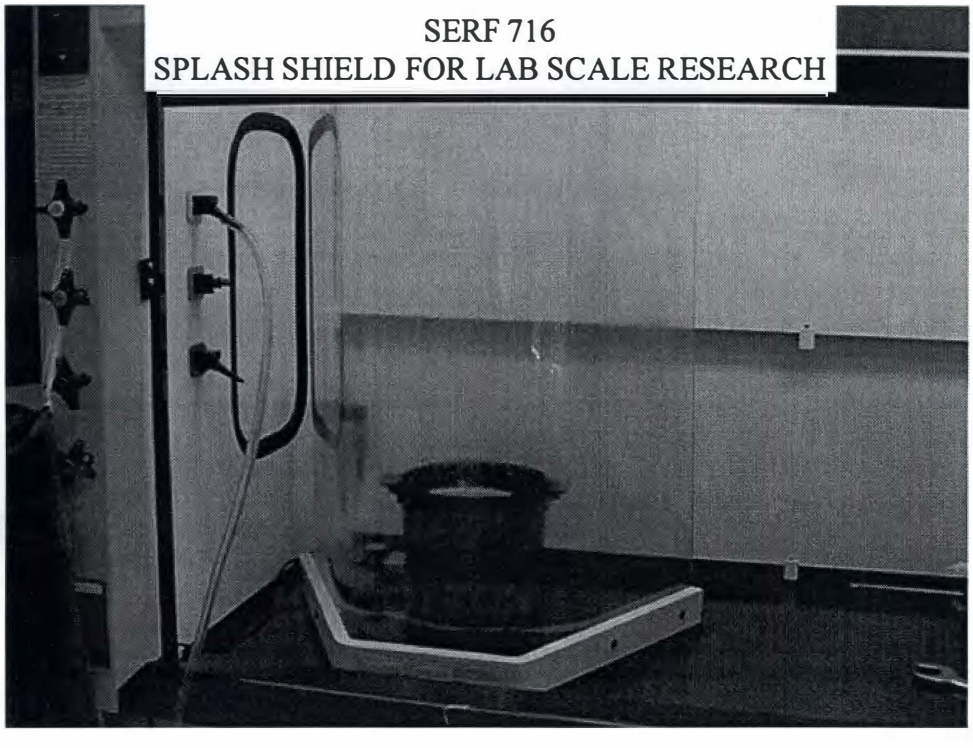
SERF 716
SAFETY GLASSES FOR LAB SCALE RESEARCH



SERF 716
EYE WASH STATION FOR LAB SCALE RESEARCH



SERF 716
SPLASH SHIELD FOR LAB SCALE RESEARCH



SERF 716
SPLASH SHIELD FOR LAB SCALE RESEARCH

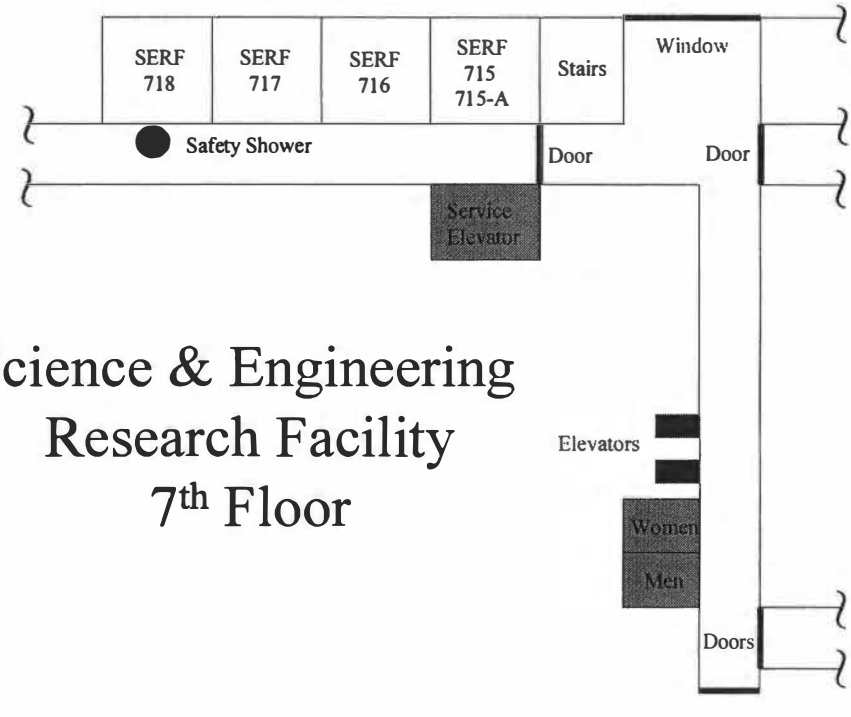


SERF 718
SAFETY SHOWER FOR RESEARCH PROJECT



SERF 718
SAFETY SHOWER FOR RESEARCH PROJECT





Science & Engineering Research Facility
7th Floor

APPENDIX B

PROJECT SAFETY SUMMARY
ACID CATALYZED HYDROLYSIS OF SLUDGE
PHASE II

PROJECT SAFETY SUMMARY

DATE: August 14, 2001
PROJECT NAME: Acid Catalyzed Hydrolysis of Sludge – Phase II
LOCATION: Science and Engineering Facility Room 715-A

Larry Perkins
University of Tennessee
Chemical Engineering Department
Science and Engineering Research Facility - Room 716
Knoxville, TN 37996
(865) 974-8303 (work)
(865) 882-5358 (home)

Robert Counce
University of Tennessee
Chemical Engineering Department
Dougherty Engineering Building – Room 509
Knoxville, TN 37996
(865) 974-5318 (work)
(865) 584-5986 (home)

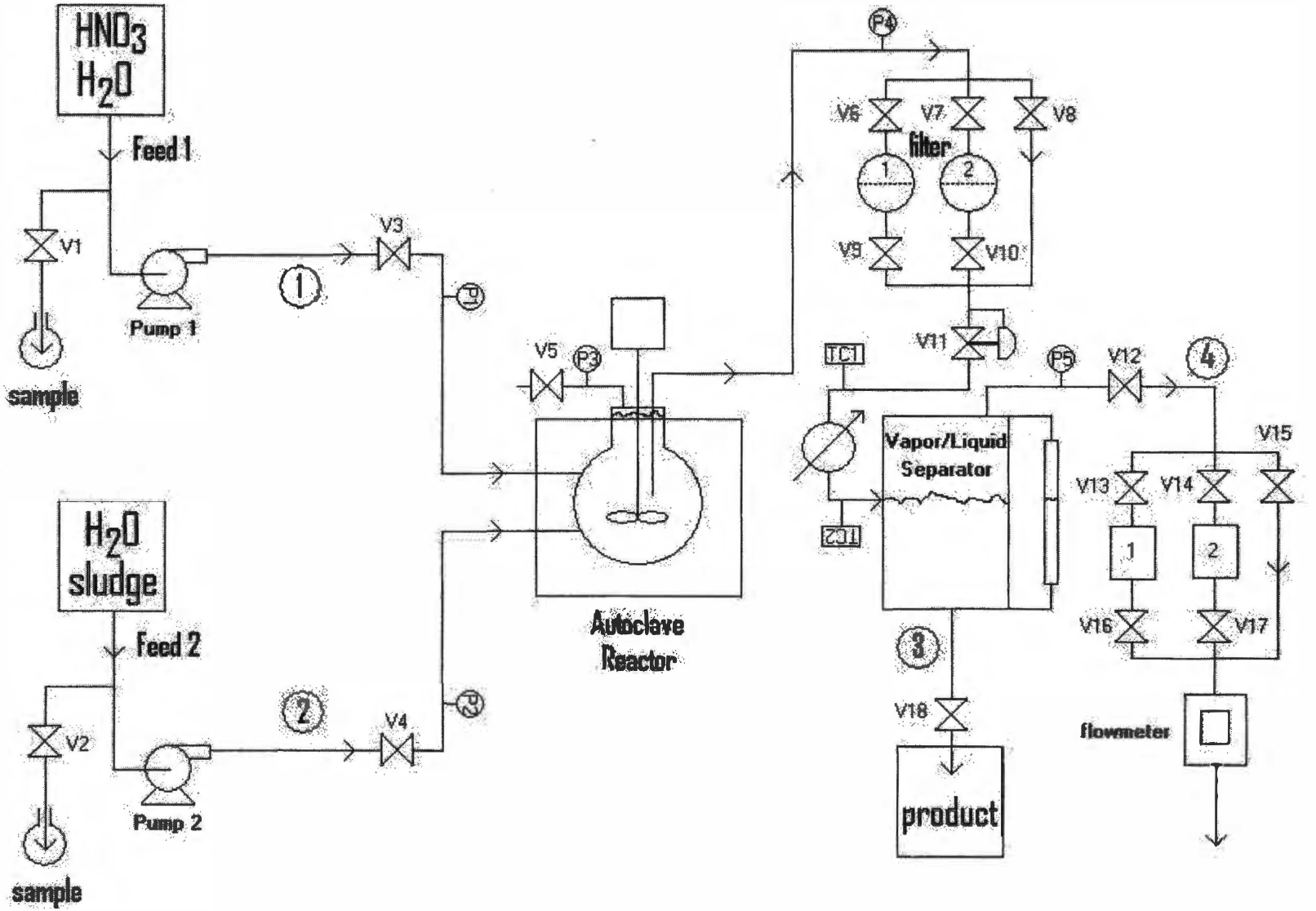
Paul Bienkowski
University of Tennessee
Chemical Engineering Department
Dougherty Engineering Building – Room 516
Knoxville, TN 37996
(865) 974-1618 (work)
(865) 938-0586 (home)

Signatures:

Larry Perkins (Engineer in Charge)	*Date*
Robert Counce (Professor in Charge)	*Date*
Paul Bienkowski (Safety Officer)	*Date*
John Collier (Department Head)	*Date*

Emergency Shutdown Procedure

1. Kill the power switch. (Clearly marked on the experimental apparatus [red].)
2. Leave the blower on.
1. Leave the water on.
2. Cutoff the air to the stirrer. (Clearly marked on the experimental apparatus.)
3. Monitor pressure gauges. (Clearly marked on the experimental apparatus.)


HNO3
H2O
Feed 1
V1
Pump 1
sample
V3
P1
1
V5
P3
Autoclave
Reactor
P4
V6
V7
V8
filter
1
2
V9
V10
V11
TC1
TC2
P5
V12
4
Vapor/Liquid
Separator
V15
V13
V14
1
2
V16
V17
flowmeter
3
V18
product
H2O
sludge
Feed 2
V2
Pump 2
sample
2
V4
P2

HEALTH AND SAFETY PLAN FOR UNIVERSITY OF TENNESSEE RESEARCH PROJECT: ACID CATALYZED HYDROLYSIS OF SLUDGE PHASE II

Company Name: University Of Tennessee/Chemical Engineering
Address: Knoxville, Tennessee
Date: August 14, 2001

I. Introduction and Summary Description

The University of Tennessee is a four-year educational institution for higher learning. The Chemical Engineering Department runs chemical experiments for research and development.

The project will have a total of five people involved within the project.

II. Key Personnel (include reporting relationships; include phone and pager numbers for Section III.F)

Position	Name	Phone	Pager	Reports to:
Senior Management	Dr. Robert M Counce	974-5318	N/A	Dr. John Collier
Safety and Health Officer	Dr. Paul Bienkowski	974-1618	N/A	Dr. John Collier
Emergency Response Coordinator	Dr. Paul Bienkowski	974-1618	N/A	Dr. John Collier

III. Site Safety Requirements

A. Emergency Management Responsibilities

By mutual agreement of both University of Tennessee and the City of Knoxville, the City of Knoxville will respond to emergency needs to include: fire protection, spill response and clean-up, and medical emergencies will be supplied by the University of Tennessee Hospital.

The University of Tennessee Emergency Response point of contact identified in section II above will coordinate company resources to provide pertinent information to both emergency responders and company management. In the event that an emergency may impact other companies appropriate communications will be made per the mutual aid agreements.

B. Reporting/Notifications and Emergencies

Reporting of emergencies should be made by calling 911. Report the nature, exact location, and extent of the emergency.

C. Record Keeping and Documentation

University of Tennessee will keep all safety records and documentation as required per the OSHA requirements. This includes 29 CFR (OSHA) records such as the OSHA 200 Log, documentation of equipment / facilities inspections (as required), and documentation of employee training (as required). These records will be kept at a location consistent with 29 CFR requirements.

D. Alarm Signals, Emergency Notification (Public Address) System, Employee Response

Alarm signals, emergency notification, and employee response are covered in the initial training. In the event of an emergency, employees are expected to pay attention to announcements made over the public address system, and to take appropriate protective actions as directed.

E. Medical Treatment

Emergency medical treatment is available by calling 911. For non-emergency medical needs, notify University of Tennessee management discussed above and a decision will be made on a case-by-case basis whether to use medical facilities.

F. Key Phone Numbers/Contacts

See Section II for primary information.

G. Assembly Locations

In the event of a building evacuation, employees should report outside the front door.

H. Weather Alerts

In the event of severe weather, weather alerts may be made by personal communications. Employees should pay attention to these alerts, and take appropriate protective actions.

I. Traffic Rules

All employees are expected to abide by the State of Tennessee Department of Transportation requirements, including posted speed limits and established and no parking zones.

J. Radiological Protection

This project involves no radiological materials. Any employee questions regarding radiological protection should be directed to the University of Tennessee Radiological Protection Safety Officer, who can then pursue additional information from appropriate representatives.

K. Fitness for Duty

While on the job, employees are expected to remain in an unimpaired state, both mentally and physically, appropriate for their job responsibilities. Supervisors are responsible for ensuring that employees reporting to them meet this level of fitness for duty.

L. Floor Plans of Facility With Emergency Exits

Floor plans for all buildings, with emergency paths identified, are located in appendix A of this document. This project will be located in SERF 715-A.

IV. Hazards

A. Define Scope of Work

The scope of this work is to react sludge generated from wastewater with nitric acid. This acid catalyzed hydrolysis of biosolids will generate products including acetic acid and formic acid that can then be sold to create a profit. The nitric acid and sludge will be fed into a 1-liter heated reactor. The reactor will be operated liquid full with an approximate residence time of 10 minutes. The flow rates of reactants will be 0.025-gpm sludge feed

and a nitric acid feed of approximately 4-mL per minute. The reactor will be heated to 150-200°C and operated at approximately 200 psig. The products exiting the reactor will have the unreacted sludge removed by inline filtration and the products cooled by a condenser. The products will then pass through a control valve to control the flow from the reactor. The products will then go into a vapor/liquid separator to separate the vapors and liquids. The liquids will be collected in a product drum and the gases will be vented through a blower. The liquid products produced include formic acid, acetic acid, alanine, and water. The gases produced are nitrogen, carbon monoxide, carbon dioxide, and nitrous oxide. Ammonium and nitrate ions will be produced in solution. The total operating time per run will be approximately 1.5 hours.

B. Hazard Identification

(Check all that apply)

1. Physical Hazards
___ Cold Stress
___ Heat Stress
___ Noise
_X_ Slip/Trip/Fall
___ Enclosed Space
___ Confined space
___ Oxygen Deficient
___ Oxygen Enriched
___ Ergonomics
_X__ Manual Lifting
_X__ Compressed Gases/Cylinders
_X__ Pressurized Systems
_X__ High Pressure*
_X__ Compressed Air
___ Explosive/Flammable
___ Vibration/Shock sensitive
_X__ Mechanical/Moving Parts
_X__ Sharp Edges/Corners
___ Inclement Weather
___ Work on or near water
___ Moving Equipment/Vehicles

2. Safety/Construction Hazards
___ Demolition
_X__ Drum Handling
___ Elevated Work
_X__ Hazardous Energy (electrical/ hydraulic/ pneumatic/ steam/ etc.)
___ Concealed/Underground Hazards
___ Excavation/Penetration
___ Hoisting/Rigging
___ Overhead Hazards
___ Welding/Cutting/Burning
___ Other _____

3. Utility Hazards
___ Electrical
___ Gas
___ Plumbing
___ Telephone
___ Overhead utility lines
___ Septic/Sewer
___ Other Concealed/ Underground utilities
___ Other _____

4. Chemical Hazards*
___ Asbestos
___ Lead
___ Manmade Mineral Fibers
___ Mercury
___ Metals
_X__ Toxic
_X__ Incompatible Chemicals
___ PCBs
___ Inorganic
_X__ Volatile Organic
_X__ Corrosive
___ Carcinogen
___ Mutagen
___ Reproductive Toxicant
_X__ Reactive
___ Pyrophoric
___ Other _____

5. Ionizing Radiological Hazards*
___ External Exposure
___ Internal Exposure
___ Contamination
___ Fissionable Material

6. Non-Ionizing Radiological Hazards
___ High Voltage
___ RF
___ Laser
___ Microwave
___ Ultra Violet

7. Biological/Vector Hazards
_X__ Bacterial/Fungi
___ Plants (Allergens)
___ Medical Waste
___ Wildlife
___ Parasites
___ Rodents (Hantavirus)
___ Insects, snakes, spiders, etc.

8. Hazardous Waste*
Waste code (If known)
_____
Metals:
___ Arsenic
___ Barium
___ Cadmium
___ Chromium
___ Lead
___ Mercury
___ Selenium
___ Silver
___ Other _____
Volatiles:
___ Benzene
___ 2-Butanone
___ 1,4 Dichlorobenzene
___ Ethylbenzene
___ Tetrachloroethylene
___ Toluene
___ 1,1,1-Trichloroethane
___ Trichloroethylene
___ Xylene
Other:
___ Asbestos
___ PCBs
___ Soil Debris
___ Hydrocarbon Impacted Waste
Waste Characteristics
_X__ Corrosive
___ Exothermic reaction
___ Ignitable
_X__ Reactive
_X__ Toxic (CO)
Waste Categories
___ Bio-Hazard
___ Mixed
___ Radiological
___ RCRA
___ Sanitary Industrial
___ TSCA

9. Others
___ Type _____
___ Type _____
___ Type _____
___ Type _____

B. **Identification and Assessment of Effectiveness of the Controls in Place to Prevent or Mitigate Accidents That Could Occur From the Hazards Identified.** (Controls may include but are not limited to engineered safeguards, use of industry standards and company procedures and safe work practices, employee training, emergency response, personal protective equipment, etc.) See pictures of equipment in Appendix A.

V. Training

A. Site Access Training

All employees are required to take access training.

B. Required OSHA Training

Employees may be involved in the activities checked below, and therefore may require further training under 29 CFR (OSHA) regulations:

___ Crane usage
___ Fork-truck usage
___ Use of powered platforms or lifts
_X__ Working with chemical products
___ Exposure to noise
___ Working at heights
___ Use of respirator
___ Working with hazardous waste
_X__ Working with hazardous materials
_X__ Use of compressed gases
___ Welding/cutting
___ Entry into confined spaces
_X__ Lockout/tagout activities
___ Electrical activities
___ Excavation
___ Asbestos work
___ Other _____
___ Other _____
___ Other _____

VI. **Medical Surveillance** (include frequency of medical exams, exposure monitoring, air sampling, and possible signs and symptoms of overexposure to site-specific hazards)

Employees Covered (i.e. shop worker, foreman, etc.)	**Reason for and Type of Surveillance/Exam**	**Frequency**
N/A		

VII. Contingency Plans

In the event of an emergency, call 911. During the emergency, the University of Tennessee Emergency Response Coordinator identified in this plan should be available to provide information needed by emergency responders. Any legally required notifications to federal, state, or local agencies remain the responsibility of the University of Tennessee.

For medical emergencies arising from injury or illness, call 911. Report the nature, exact location, and extent of the emergency.

For hazardous chemical spills or material releases, alert people in the immediate vicinity, and evacuate the area. Report the emergency by calling 911 as soon as safely possible. A decision regarding the need for assistance in cleanup of the spill/release will be made on a case-by-case basis by company management.

For fire emergencies, alert people in the immediate vicinity, and evacuate the area. Report the emergency by calling 911 as soon as safely possible. Fire fighters arriving on the scene should be informed of any toxic, hazardous, or flammable materials involved with or in the vicinity of the fire.

Startup Procedure

1. Charge the acid pump (pump 1) with 70% nitric acid (HNO_3).
2. Purge the system with nitrogen (N_2).
1. Start the blower on the gas exit.
2. Check that ventilation affecting the experiment is operable to insure safe operation
3. Start the water through the condenser.
4. Open valve V4.
5. Start pump 2.
6. Open valve V3.
7. Start pump 1.
8. Start heater on the reactor.
9. Start the air driven stirrer.
10. Start the water cooling the stirrer.
11. Open valve V6.
12. Open valve V9.
13. Close valve V7.
14. Close valve V8.
15. Close valve V10.
16. Adjust valve V11 to the desired exit flowrate.
17. Open valve V15.
18. Adjust valve V18 to the desired level in the Vapor/Liquid Separator.

19. Open valve V12.

20. Close valve V13.

21. Close valve V14.

22. Monitor pressure gauges.

23. Monitor temperature gauges.

24. If valve V5 opens due to excessive pressure, shutdown the system immediately.

Shutdown Procedure

1. Open valve V15.
2. Close valve V13.
1. Close valve V14.
2. Open valve V6.
3. Open valve V9.
4. Shutoff heat to the reactor.
5. Shutoff pump 1.
6. Shutoff pump 2.
7. Close valve V3.
8. Close valve V4.
9. Shutoff air to stirrer.
10. Monitor pressure in reactor.
11. Monitor temperature in reactor.
12. Release pressure on reactor.
13. Allow several minutes for venting.
14. Shutoff water to stirrer.
15. Shutoff water to condenser.
16. Wait several minutes for venting.
17. Shutoff blower.

Liquid Sampling Procedures

1. Collect liquid exiting valve V18 in sample bottle.
2. Place lid on sample bottle.
3. Analysis in Oak Ridge.

Vapor Sampling Procedures

1. Close valve V16 (or V17).
2. Close valve V15.
3. Open valve V13 (or V14).
4. Allow vapor to enter the sample vial.
5. Close valve V13 (or V14).
1. Open valve V15.
2. Remove sample vial.
3. Store sample vial appropriately.
4. Analysis in Oak Ridge.

Solid Sampling Procedures (collected over entire run)

1. Open valve V7.
2. Open valve V10.
3. Close valve V9.
4. Close valve V6.
5. Remove filter 1.
4. Remove sand from filter 1.

5. Collect sand in sample vial.

6. Replace filter 1 (repeat as necessary).

Safety Precautions

1. CO monitors

2. 2500 cfm blower

3. Acid proof safety goggles

4. Acid proof gloves

5. Acid proof apron

6. Operator shall wear long pants (no shorts)

7. Pressure monitors (gauges)

8. Temperature gauges

9. Pressure release valve on reactor

10. Shield to deflect any hot or acidic leaks

11. Sight glass on vapor/liquid separator

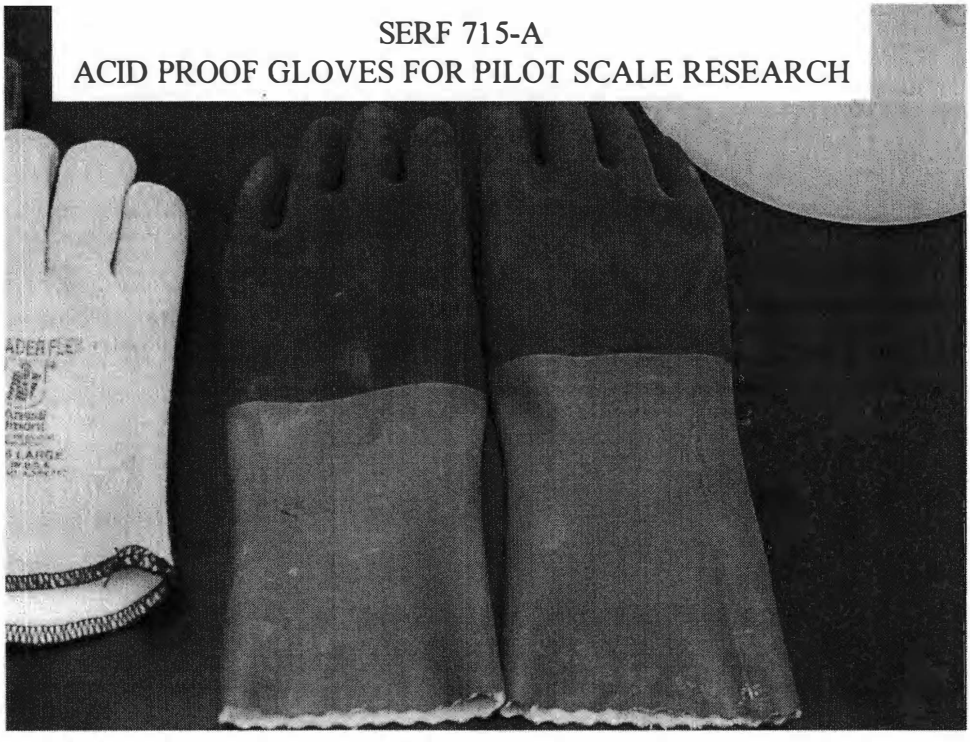
12. Exposure limits (TOSHA, etc.)

13. Safety shower (Located in the hall in front of SERF 718, clearly marked on attached floor plan.)

14. Eye wash station (Located in SERF 715-A, clearly marked on attached floor plan.)

PHOTOGRAPHS AND FLOOR PLAN

SERF 715-A
ACID PROOF GLOVES FOR PILOT SCALE RESEARCH



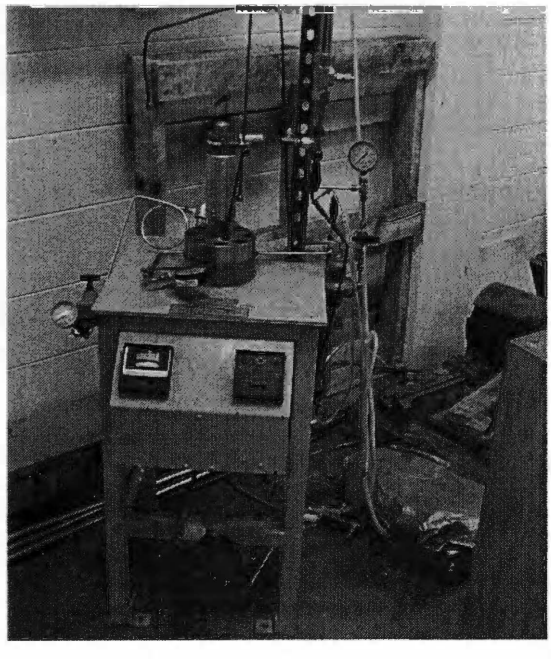
SERF 715-A
HEAT RESISTANT GLOVES FOR PILOT SCALE



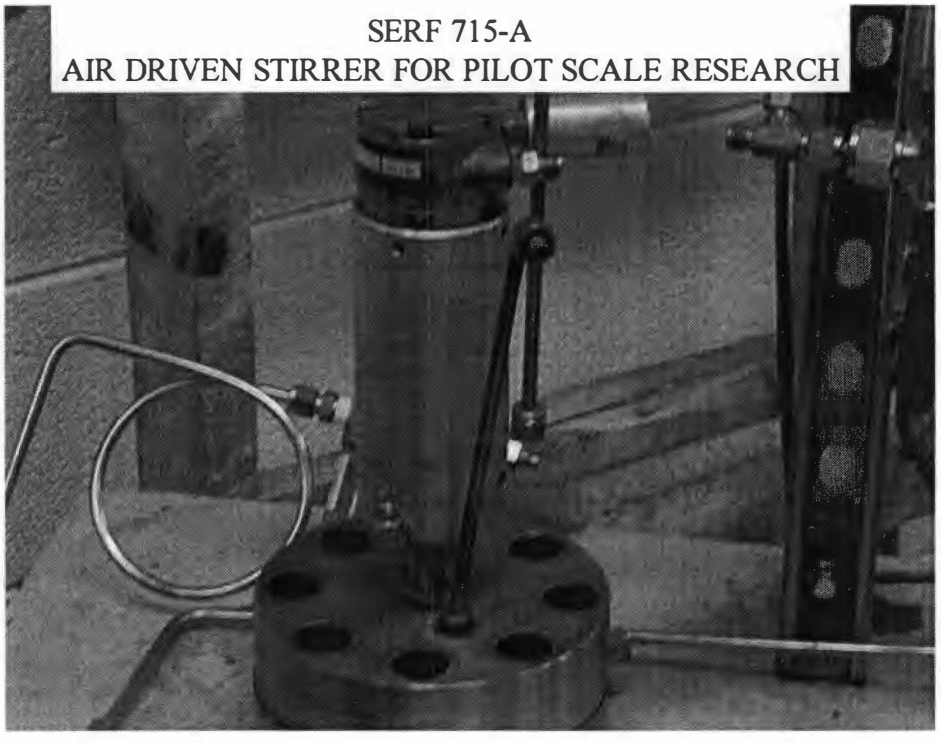
SERF 715-A
SAFETY GLASSES FOR PILOT SCALE



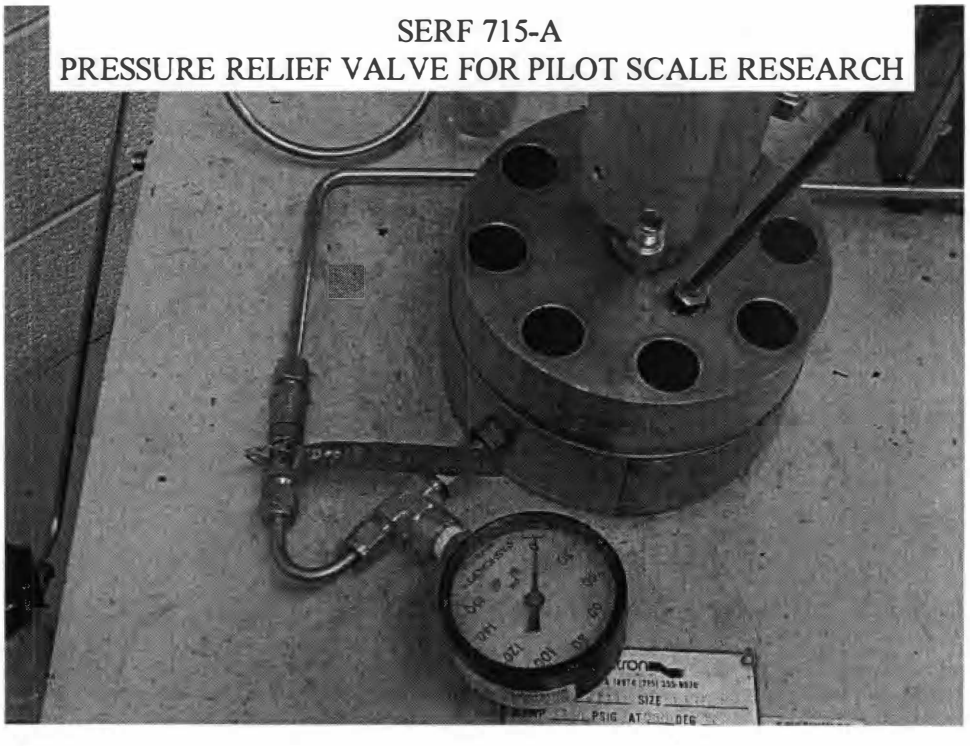
SERF 715-A
STIRRED REACTOR FOR PILOT SCALE RESEARCH



SERF 715-A
AIR DRIVEN STIRRER FOR PILOT SCALE RESEARCH



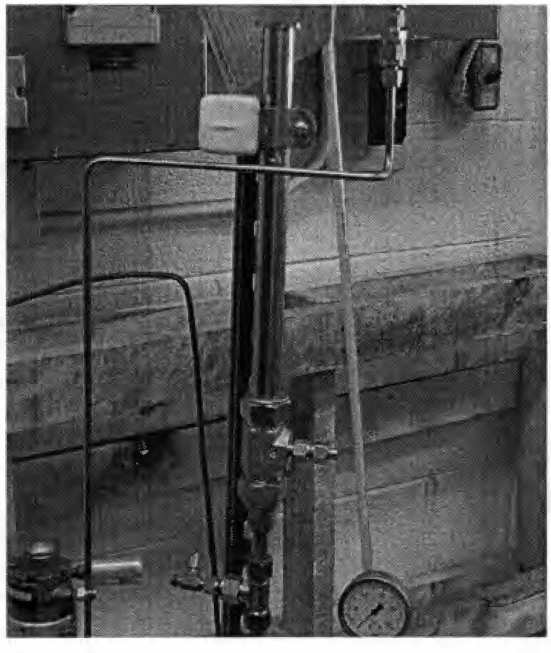
SERF 715-A
PRESSURE RELIEF VALVE FOR PILOT SCALE RESEARCH



SERF 715-A
PRESSURE CONTROLLER OF AIR FOR PILOT SCALE RESEARCH



SERF 715-A
CONDENSOR FOR PILOT SCALE RESEARCH



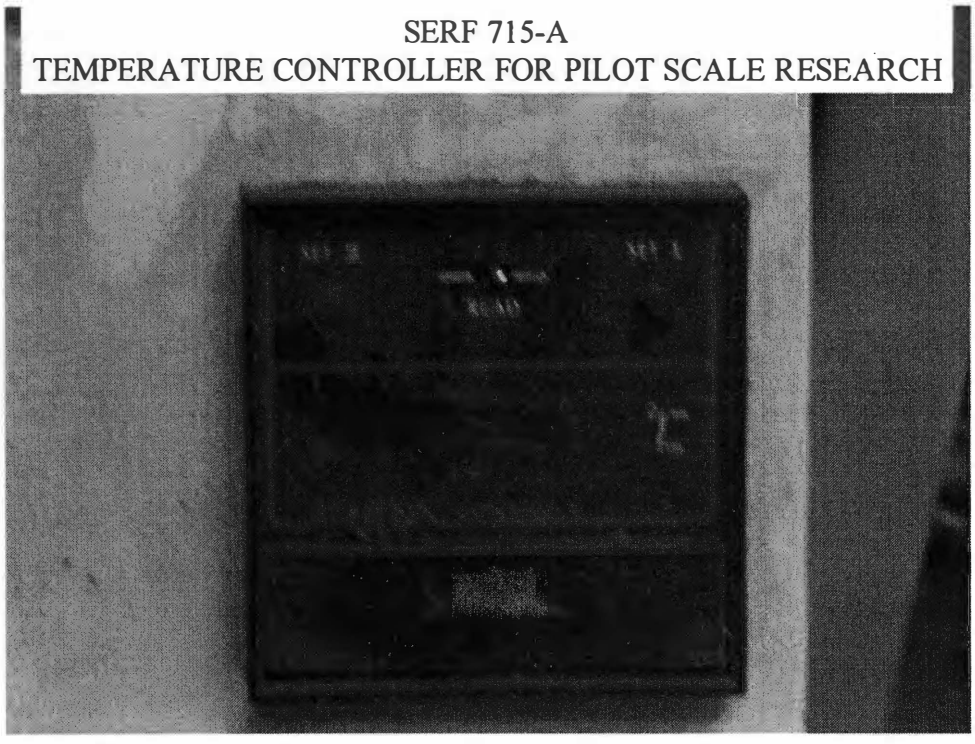
SERF 715-A
CONDENSOR FOR PILOT SCALE RESEARCH



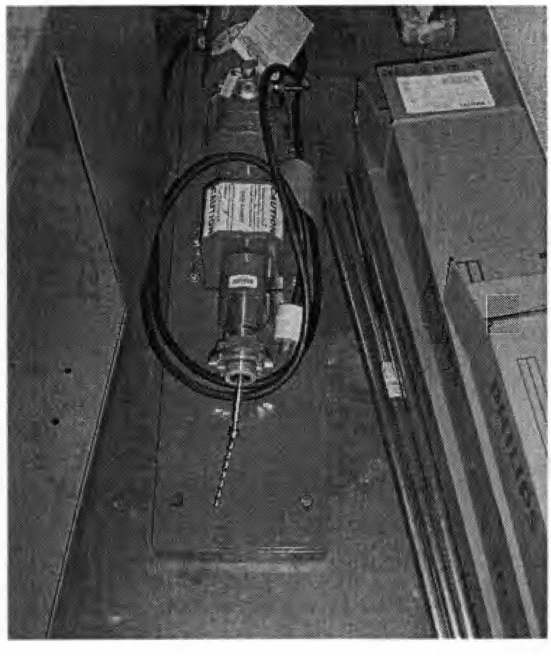
SERF 715-A
TEMPERATURE CONTROLLER FOR PILOT SCALE RESEARCH



SERF 715-A
TEMPERATURE CONTROLLER FOR PILOT SCALE RESEARCH



SERF 715-A
SLUDGE PUMP FOR PILOT SCALE RESEARCH



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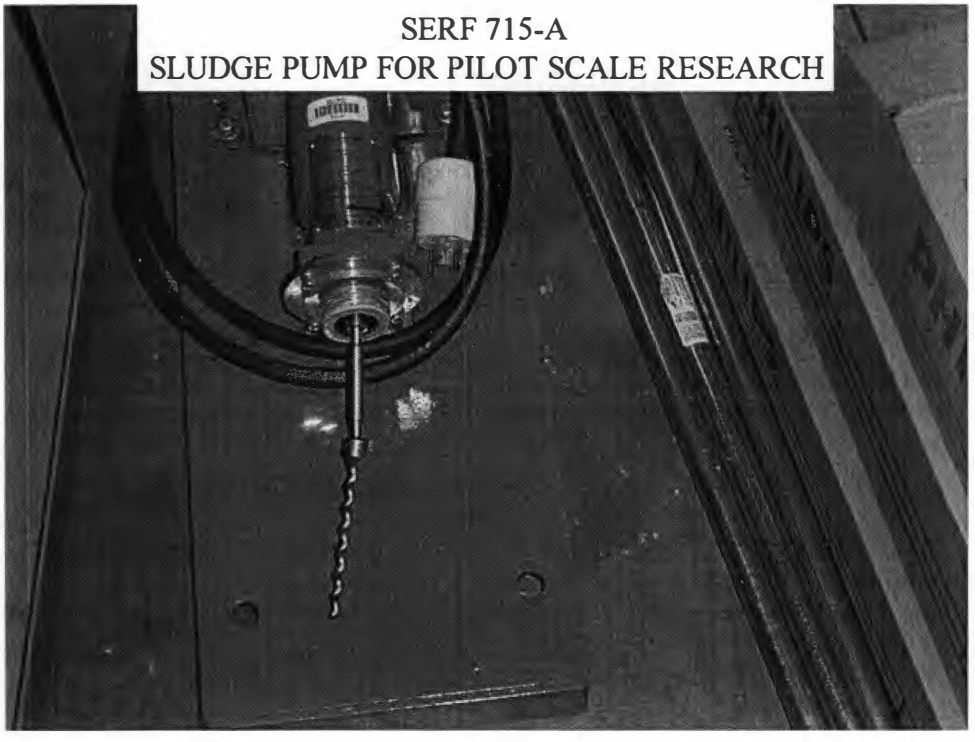
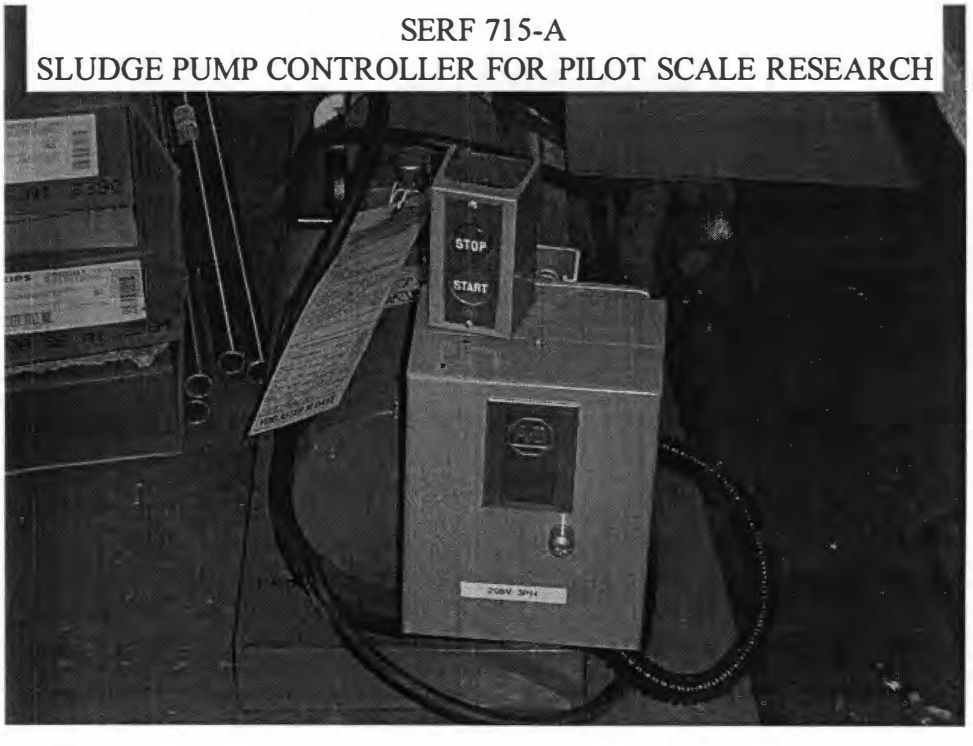
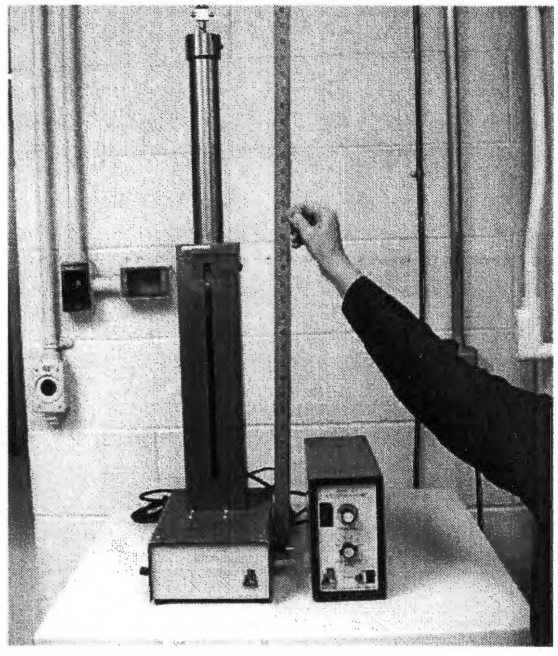
SLUDGE PUMP FOR PILOT SCALE RESEARCH



SERF 715-A
SLUDGE PUMP CONTROLLER FOR PILOT SCALE RESEARCH



SERF 715-A
ACID PUMP FOR PILOT SCALE RESEARCH



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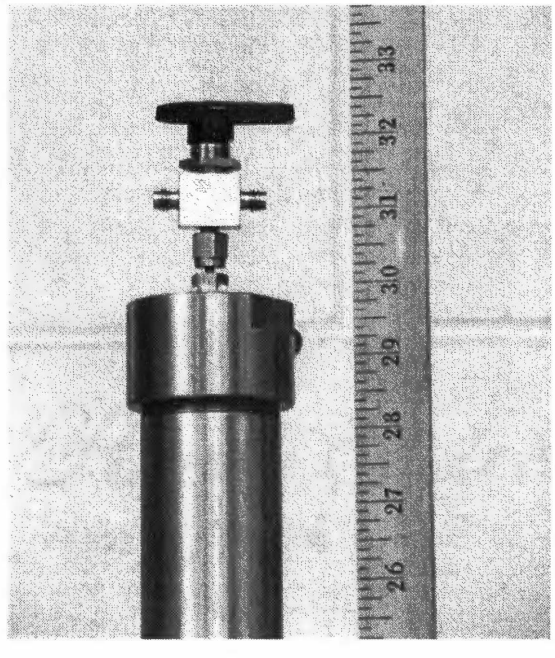
ACID PUMP FOR PILOT SCALE RESEARCH



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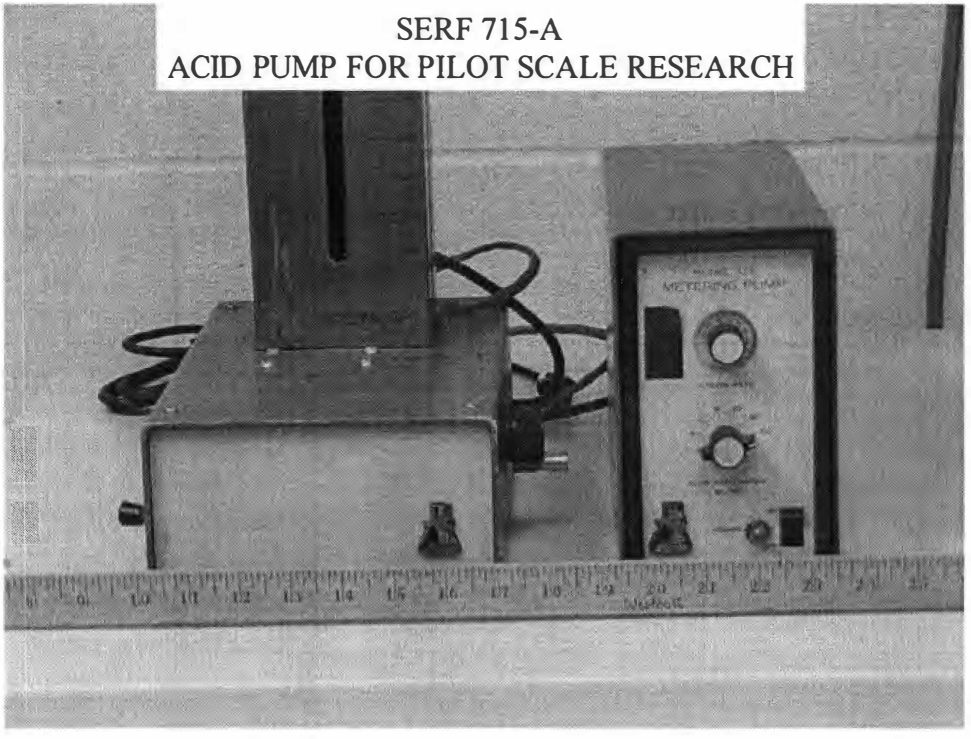
ACID PUMP FOR PILOT SCALE RESEARCH



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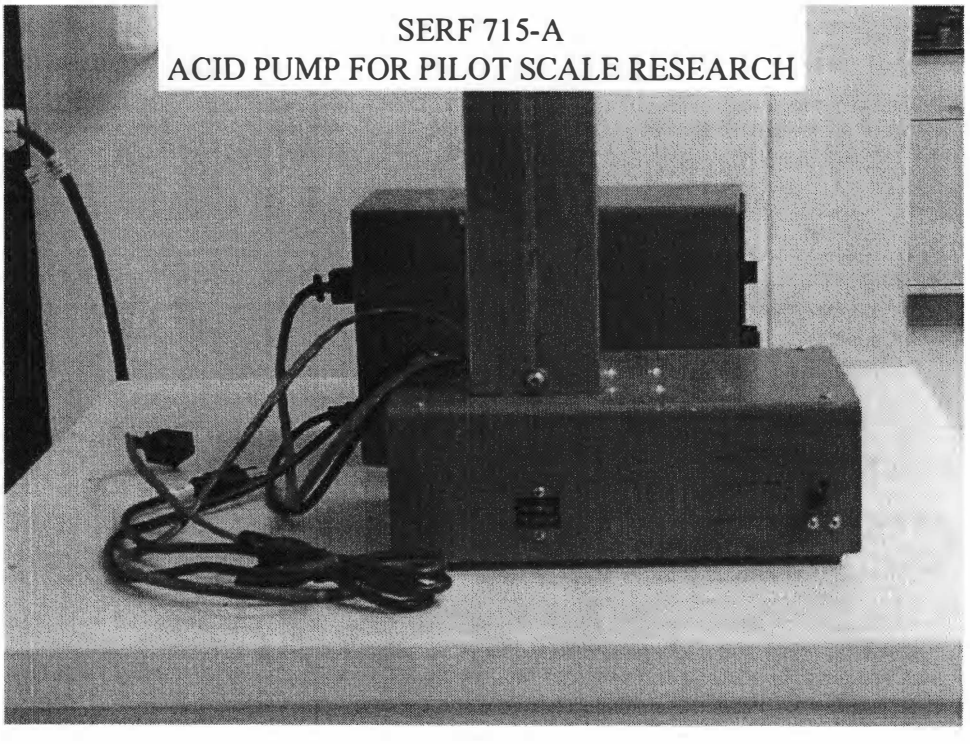
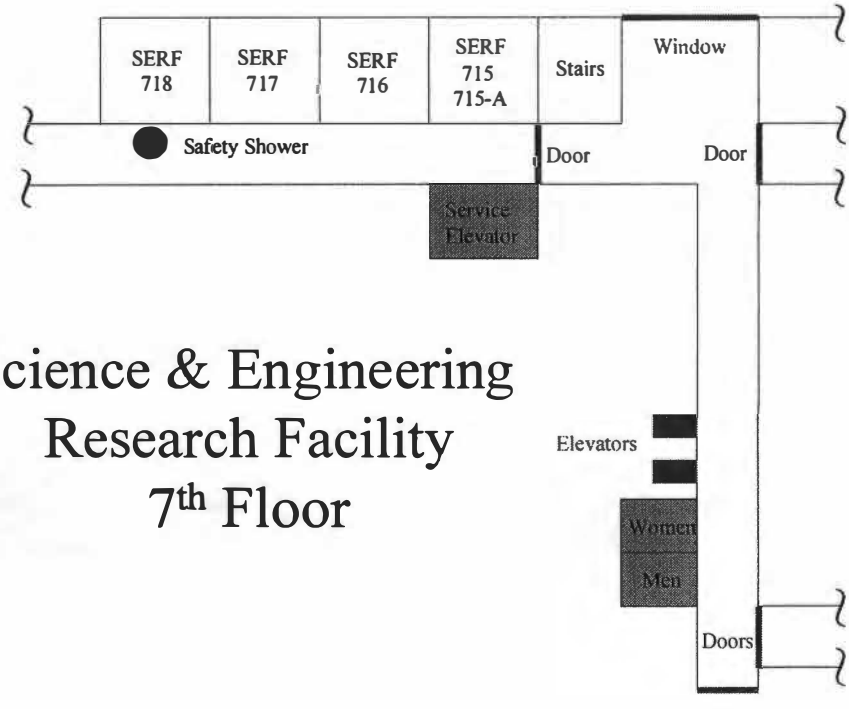
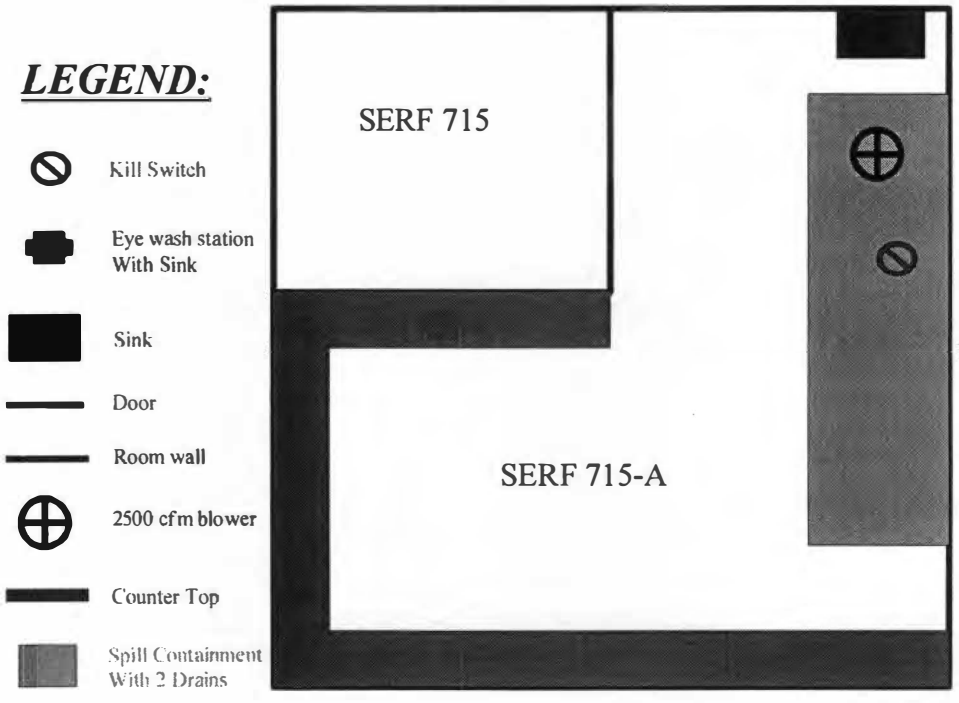
ACID PUMP FOR PILOT SCALE RESEARCH

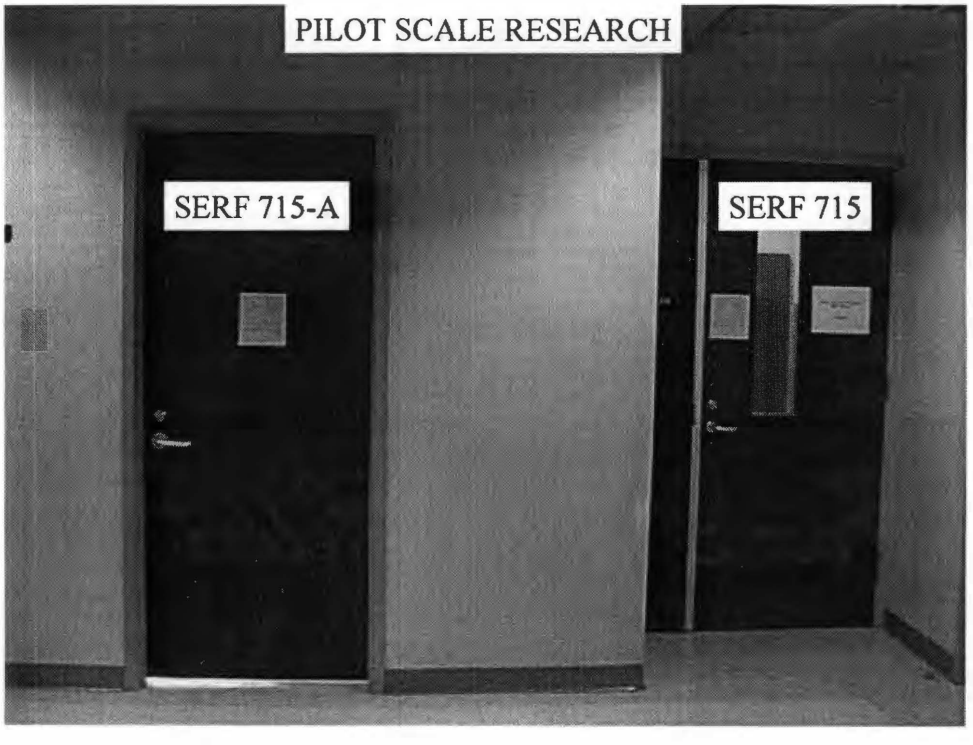


SERF 715-A
ACID PUMP CONTROLLER FOR PILOT SCALE RESEARCH





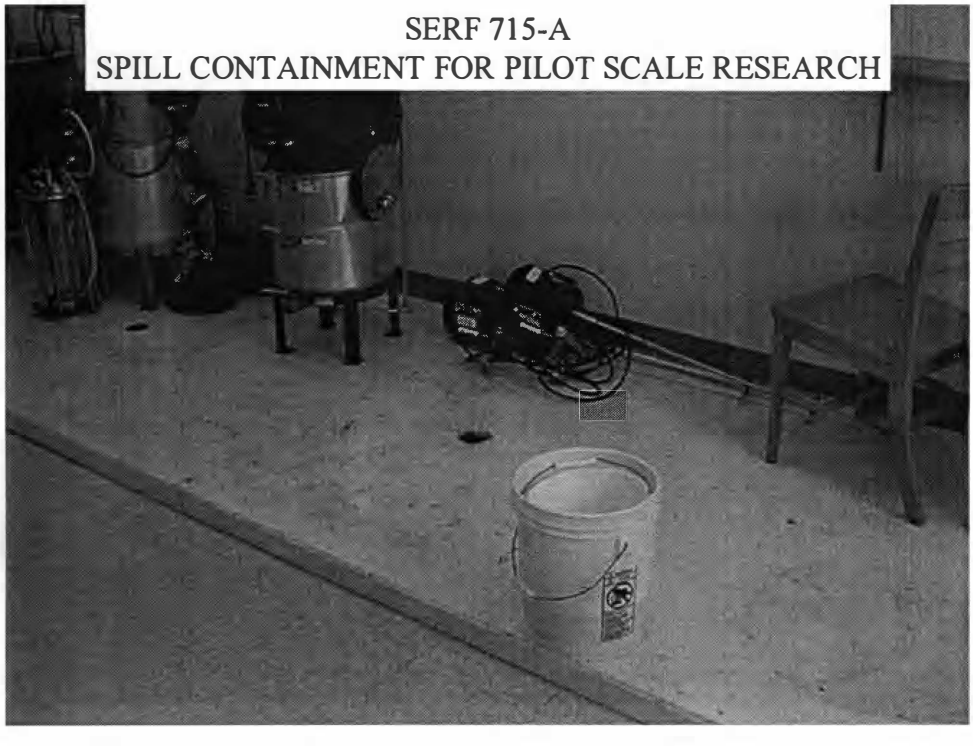

LEGEND:
Kill Switch
Eye wash station With Sink
Sink
Door
Room wall
2500 cfm blower
Counter Top
Spill Containment With 2 Drains
SERF 715
SERF 715-A


PILOT SCALE RESEARCH
SERF 715-A
SERF 715

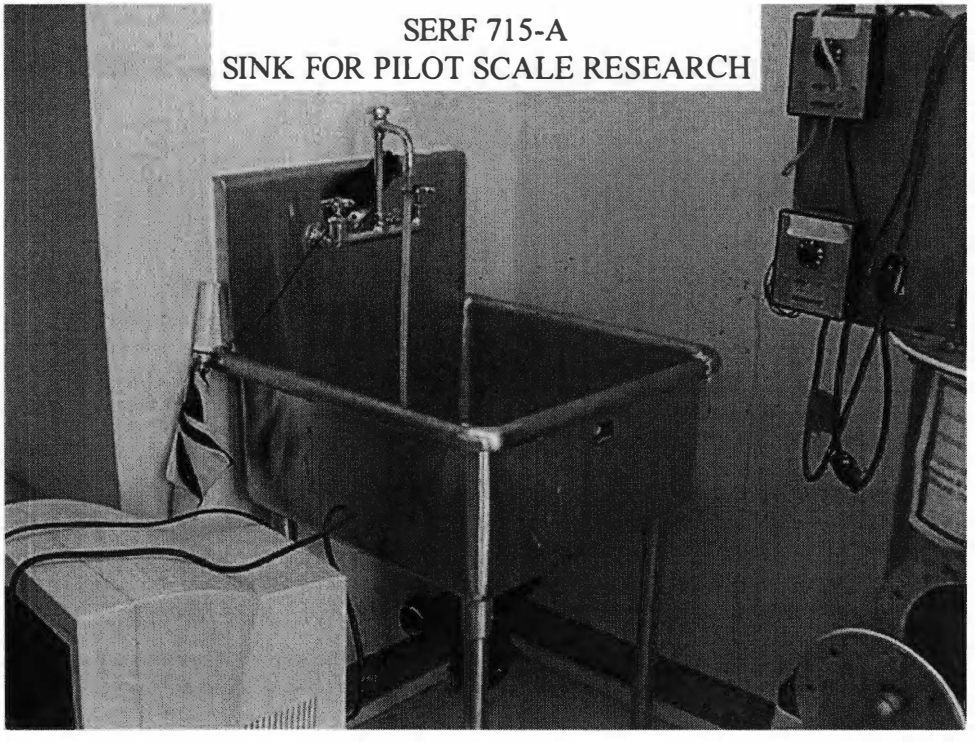
SERF 715-A
PILOT SCALE RESEARCH AREA



SERF 715-A
SPILL CONTAINMENT FOR PILOT SCALE RESEARCH



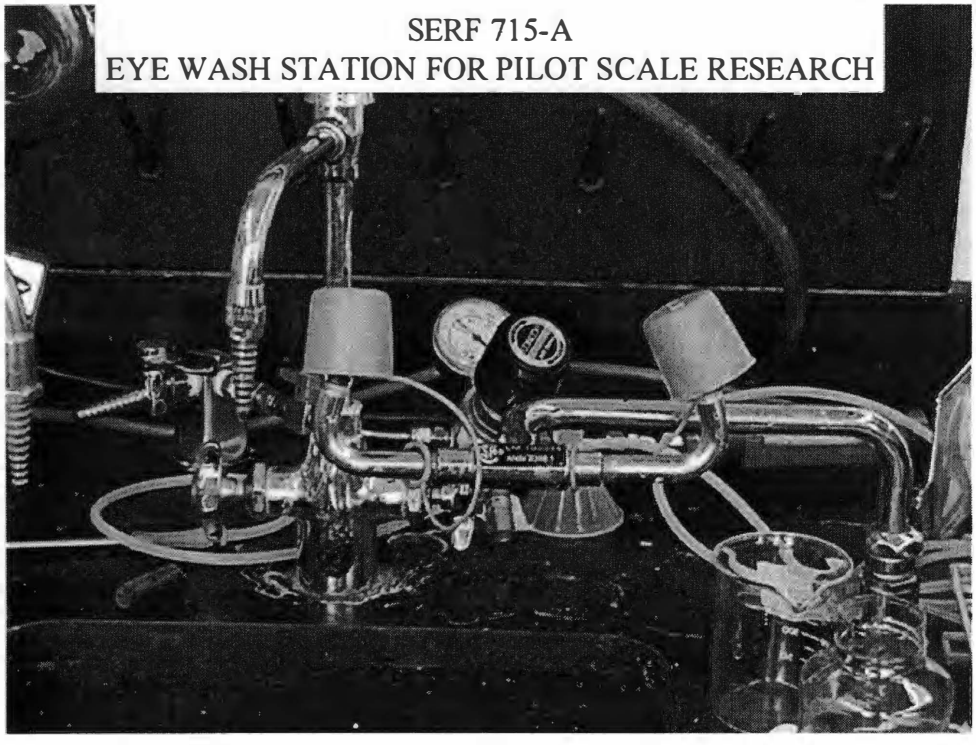
SERF 715-A
SINK FOR PILOT SCALE RESEARCH



SERF 715-A
BLOWER FOR PILOT SCALE RESEARCH



SERF 715-A
EYE WASH STATION FOR PILOT SCALE RESEARCH



SERF 715-A
SPLASH SHIELD FOR PILOT SCALE RESEARCH



SERF 718
SAFETY SHOWER FOR RESEARCH PROJECT



SERF 718
SAFETY SHOWER FOR RESEARCH PROJECT



APPENDIX C

EXPERIMENTAL DATA FOR INDUSTRIAL BATCH STUDIES

	wt%	C		g	g	g
Sample	Sludge Conc.	Temperature	Acid-Sludge Ratio	Sludge In (wet)	Sludge In (dry)	Carbon In
1	3.07	150	2.43	19.1367	0.5875	0.251331084
2	3.07	150	2.43	19.1270	0.5872	0.251203689
3	3.07	180	0.5	19.1747	0.5887	0.251830155
4	3.07	180	4.36	19.1807	0.5888	0.251908956
5	3.07	180	0.5	19.1484	0.5879	0.251484745
6	3.07	180	4.36	19.0935	0.5862	0.250763719
7	3.07	120	4.36	19.1656	0.5884	0.251710641
8	3.07	120	0.5	19.0642	0.5853	0.250378908
9	3.07	120	4.36	19.1187	0.5869	0.251094682
10	3.07	120	0.5	19.1683	0.5885	0.251746101
11	5.14	120	0.5	19.2690	0.9904	0.423704499
12	5.14	120	4.36	19.1435	0.9840	0.42094489
13	5.14	120	0.5	19.1832	0.9860	0.42181785
14	5.14	120	4.36	19.2041	0.9871	0.422277419
15	5.14	180	0.5	19.2279	0.9883	0.422800755
16	5.14	180	4.36	19.1844	0.9861	0.421844237
17	5.14	180	0.5	19.2100	0.9874	0.422407153
18	5.14	180	4.36	19.1500	0.9843	0.421087818
19A	4.15	150	1.8	19.1158	0.7933	0.339376178
20A	4.15	150	1.8	19.1460	0.7946	0.33991234
H2SO4 SULFURIC ACID TESTS						
19	3.07	150	1.87	19.1644	0.5883	
20	3.07	180	0.5	19.1470	0.5878	
21	3.07	180	4.36	19.1834	0.5889	
22	3.07	120	4.36	19.1724	0.5886	
23	3.07	120	0.5	19.1495	0.5879	

						reading			
						dissolved	actual		
mL	g	g	g		mL	mg/L	mg/L	mL	grams
Volume out	Paper mass	Paper+sludge mass	Sludge Out	Sludge Conversion	Dilution	COD	COD	Dilution	sludge
19.1	0.8961	1.0899	0.1938	67.0126	200	53	10653	400	0.0216
19.2	0.8896	1.0509	0.1613	72.5306	200	69	13869	400	0.0204
18.0	0.9150	1.2199	0.3049	48.2047	200	50	10050	400	0.0227
19.1	0.9285	1.0111	0.0826	85.9726	200	44	8844	200	0.0358
15.5	0.8810	1.1762	0.2952	49.7836	200	48	9648	400	0.0199
17.4	0.9253	1.0084	0.0831	85.8232	200	43	8643	200	0.0376
18.9	0.8812	1.1377	0.2565	56.4060	200	57	11457	400	0.0209
15.0	0.9050	1.3108	0.4058	30.6646	200	26	5226	200	0.0447
19.9	0.9287	1.1352	0.2065	64.8178	200	63	12663	400	0.0224
16.5	0.9231	1.3073	0.3842	34.7117	200	25	5025	200	0.0390
	0.8681	1.5543	0.6862	30.7167	200	95	19095	200	0.0375
	0.9072	1.334	0.4268	56.6250	200	104	20904	400	0.0200
	0.9265	1.6103	0.6838	30.6502	200	91	18291	200	0.0350
	0.9302	1.4134	0.4832	51.0481	200	104	20904	200	0.0379
	0.8862	1.4154	0.5292	46.4543	200	91	18291	200	0.0363
	0.9244	1.1428	0.2184	77.8517	200	101	20301	200	0.0419
	0.9029	1.492	0.5891	40.3379	200	111	22311	200	0.0428
	0.9000	1.1803	0.2803	71.5232	200	85	17085	200	0.0398
	0.9039	1.2078	0.3039	61.6919	400	86	34486	200	0.0196
	0.9308	1.2295	0.2987	62.4068	400	84	33684	200	0.0196
19.0	0.9418	1.2839	0.3421	41.8540	200	58	11658	200	0.0371
18.0	0.9358	1.2273	0.2915	50.4094	400	53	21253	200	0.0220
18.5	0.9081	1.1296	0.2215	62.3894	400	82	32882	200	0.0190
15.8	0.9250	1.335	0.4100	30.3423	200	41	8241	200	0.0466
17.6	0.9054	1.3283	0.4229	28.0647	200	20	4020	200	0.0436

	reading									
	particulate	actual								
grams	mg/L	mg/L	micro-moles	micro-moles	micro-moles	micro-moles	micro-moles	micro-moles	g/L	g/L
sludge	COD	COD	CO2	O2	N2	CO	H2	CH4	Acetic Acid	Formic Acid
0.0216	72	28800	585.24	0	1743.63	0	0	28.52	1.488	0.359
0.0204	66	26400	1447.97	34.63	2094.3	0	0	30.32	1.664	0.423
0.0227	64	25600	1.67	17.56	78.77	0	0	0	1.396	0.72
0.0358	155	31000	4825.87	0	2411.86	0	0	0	2.35	0.37
0.0199	60	24000	899.65	0	968.23	0	0	15.17	1.323	0.389
0.0376	153	30600	6173.75	0	3160.95	0	0	0	2.317	0.066
0.0209	56	22400	1.29	0.69	17.17	0	0	0.23	1.382	0.418
0.0447	51	10200	38.12	19.87	246.9	0	0	4.6	0.716	0.217
0.0224	61	24400	481.61	0	939.42	0	0	15.15	1.456	0.145
0.0390	57	11400	27.37	82.68	434.54	0	0	0	0.718	0.248
0.0375	81	16200	0	157	523	0	0	0	3.122	1.015
0.0200	34	13600	455	117	2214	0	0	0	3.323	0.869
0.0350	130	26000	42	56	704	0	0	0	2.713	0.95
0.0379	92	18400	0	91	295	0	0	0	3.115	0.537
0.0363	115	23000	2109	7	2103	0	0	0	3.533	1.214
0.0419	143	28600	2293	0	1505	0	0	0	4.917	0.876
0.0428	161	32200	2325	8	2386	0	0	0	3.602	1.191
0.0398	118	23600	3363	0	1962	0	0	0	4.433	0.907
0.0196	58	11600	4	240	744	0	0	0	2.107	0.873
0.0196	61	12200	1233	7	1756	0	0	0	2.56	1.124
0.0371	121	24200	92.55	97.21	300.04	0	187.6	9.44	0.958	0
0.0220	65	13000	16.85	79.75	309.19	0	7.39	0	0.801	0.2
0.0190	70	14000	301.51	0	561.12	0	2793.77	8.93	1.568	0.416
0.0466	151	30200	101.03	50.24	186.8	0	189.94	4.45	0.764	0
0.0436	53	10600	9.37	33.32	130.73	0	3.21	0	0.602	0

				(acetic acid equivalent)	
g/L	g/L	g/L	g/L	g/L	g/L
Formic Acid	Propionic Acid	Valeric Acid	Butyric Acid	TOTAL ORGANIC ACID	Nitric Acid remaining
0.359	0.006	0	0.134	1.912155005	60.536
0.423	0.021	0	0.153	2.174046469	57.7
0.72	0.189	0	0.068	2.188157355	4.494
0.37	0.422	0	0.337	3.564093046	77.313
0.389	0.178	0	0	1.793182139	4.801
0.066	0.32	0	0.123	2.91695994	83.403
0.418	0.153	0	0	1.840689777	114.693
0.217	0.152	0	0	1.042386604	14.258
0.145	0.122	0	0	1.698943596	119.094
0.248	0.152	0	0	1.064603995	15.928
1.015	0.502	0	0.163	4.61676979	54.692
0.869	0.457	0	0.294	4.846459032	218.869
0.95	0.498	0	0.101	4.075968166	38.69
0.537	0.093	0	0.705	4.539689136	273.425
1.214	0.477	0	0.206	5.185783356	10.782
0.876	0.789	0.096	1.331	8.404075413	98.751
1.191	0.471	0	0.221	5.252940605	10.292
0.907	0.653	0	0.898	7.043256383	123.211
0.873	0.009	0	0.248	3.02547559	112.568
1.124	0.16	0	0.276	3.864001709	114.233
0	0.042	0	0	1.009081081	65.373
0.2	0.212	0	0	1.18927262	12.259
0.416	0.547	0	0.045	2.565938254	108.234
0	0.122	0	0	0.912378378	111.721
0	0.13	0	0	0.760108108	16.385

APPENDIX D

EXPERIMENTAL DATA FOR MUNICIPAL BATCH STUDIES

Sample Number	Temperature (oC)	Sludge Concentration (% solids)	Acid Added (mL)	Warm Up Time (min)
1	180	3.853	0.3	1
2	180	3.853	2.6	1
3	180	3.853	2.6	1
4	180	3.853	0.3	1
5	160	3.853	2.6	1
6	160	3.853	0.3	1
7	160	3.853	2.6	1
8	160	3.853	0.3	1
9	160	7.889	0.3	1
10	160	7.889	2.6	1
11	160	7.889	0.3	1
12	160	7.889	2.6	1
13	180	7.889	2.6	1
14	180	7.889	0.3	1
15	180	7.889	2.6	1
16	180	7.889	0.3	1
17	170	5.917	1.45	1
18	170	5.917	1.45	1
19 (run 11 redo)	160	7.889	0.3	1

Reaction Time (min)	Cool Dow n Time (min)	Wet Sludge Added (g)	Dry Sludge Added (g)	Volume Out (mL)
20	5	19.1555	0.738061415	15.5
5	5	19.1375	0.737367875	14.3
5	5	19.1481	0.737776293	18.8
20	5	19.2009	0.739810677	15.1
20	5	19.138	0.73738714	18.4
5	5	19.1184	0.736631952	18.1
20	5	19.1271	0.736967163	18.7
5	5	19.1373	0.737360169	18
20	5	19.1471	1.510514719	17.1
5	5	19.2898	1.521772322	17.5
20	5	19.1969	1.514443441	-
5	5	19.2033	1.514948337	17.9
20	5	19.1451	1.510356939	18.7
5	5	19.2335	1.517330815	18
20	5	19.1914	1.514009546	18.8
5	5	19.1739	1.512628971	18
12.5	5	19.1755	1.134566396	18.8
12.5	5	19.1684	1.134146307	16.8
20	5	19.1381	1.509804709	17.2

Jar Mass (empty) (g)	Jar Mass (dried sludge) (g)	Mass of Sludge remaining (g)	Acetic Acid (g/L)
113.6992	114.1708	0.4716	0.892
114.0029	114.2714	0.2685	1.629
113.0791	113.1888	0.1097	1.393
113.7017	114.1817	0.48	0.857
113.8919	114.1789	0.287	1.843
113.8073	114.3204	0.5131	0.7
114.6426	114.9681	0.3255	1.641
113.0129	113.5302	0.5173	0.701
113.0672	114.3013	1.2341	2.195
113.8515	114.7168	0.8653	2.43
112.8974	-	-	2.074
113.7717	114.5300	0.7583	2.305
113.3403	113.8815	0.5412	3.955
113.8245	114.9279	1.1034	2.389
113.3167	113.7846	0.4679	3.864
113.4576	114.4778	1.0202	2.526
114.1458	114.532	0.3862	2.335
113.8492	114.1937	0.3445	2.472
114.1504	115.1237	0.9733	2.634

Formic Acid (g/L)	Propionic Acid (g/L)	Butyric Acid (g/L)	Valeric Acid (g/L)	Nitric Acid (g/L)	Oxygen (μ moles)
0.228	0.369	0	0	4.292	182
0.409	0.338	0	0	90.881	15
0.318	0.249	0	0	85.934	0
0.149	0.375	0	0	3.087	298
0.57	0.468	0.135	0.301	82.89	20
0.198	0.376	0	0	11.318	209
0.327	0.381	0	0	83.268	13
0.202	0.377	0	0	11.248	55
0	1.021	0.145	0	5.252	388
0.211	0.739	0.128	0	134.873	15
0	0.885	0	0	6.326	129
0	0.736	0	0	94.163	16
0	0.625	0.242	0	65.888	70
0	0.615	0.358	0	9.887	58
0.881	0.626	0.237	0	65.008	29
0	0.642	0.377	0	9.426	148
0	0.366	0.169	0	47.656	46
0.154	0.367	0.133	0	43.56	72
0	0.663	0.346	0	8.84	44

Nitrogen (m moles)	Carbon Dioxide (m moles)			
1144	935			
3350	5413			
2929	5685			
1471	767			
3449	2394			
800	341			
2223	1511			
403	252			
1448	0			
1247	1601			
511	21			
3121	3577			
3539	6878			
225	4			
4937	10747			
1200	414			
2914	3210			
2848	3892			
1187	777			

	(oC)	(minutes)	(minutes)	(minutes)	(grams)
Sample #	Temperature	Heating Time	Reaction Time	Cooling Time	Mass of Sludge In (wet)
5	181	2	3	2	19.0802
6	181	2	3	2	19.0785
2	179	2	3	2	19.0595
1	179	2	4	2	19.0661
3	179	2	4	2	19.3388
4	181	2	4	2	19.1926
7	181	2	10	5	19.1648
8	181	2	10	5	19.2350
9	181	2	10	5	19.1523
10	179	2	15	5	19.2136
11	179	2	15	5	19.0919
12	179	2	15	5	19.1558
34	179.5	2	20	5	18.99
35	179.5	2	20	5	19.16
36	179.5	2	20	5	19.07
13	181	2	4	5	19.1057
14	181	2	4	5	19.1810
15	181	2	4	5	19.1409
16	181	2	10	5	19.0874
17	181	2	10	5	19.1030
18	181	2	10	5	19.1686
19	181	2	15	5	19.1584
20	181	2	15	5	19.0923
21	181	2	15	5	19.0710
31	179.5	2	20	5	19.11
32	179.5	2	20	5	19.05
33	179.5	2	20	5	19.27
22	178	2	4	5	19.1924
23	178	2	4	5	19.1105
24	178	2	4	5	19.1136
25	182	2	10	5	19.1290
26	182	2	10	5	19.1912
27	182	2	10	5	19.1758
28	182	2	15	5	19.1342
29	182	2	15	5	19.1469

(mL)	(mL)	(grams)	(grams)	(grams)
Volume of HNO3 In	Total Product Volume Out	Filter Paper	Filter Paper + Sludge	Mass of Sludge Out
1.3	20.7	0.9219	1.2001	0.2782
1.3	20.3	0.8968	1.2291	0.3323
1.3	20.5	0.9059	1.2417	0.3358
1.3	20.5	0.9191	1.2364	0.3173
1.3	21.0	0.9245	1.2916	0.3671
1.3	20.5	0.8665	1.2514	0.3849
1.3	20.2	0.9314	1.2661	0.3347
1.3	20.0	0.9254	1.2575	0.3321
1.3	20.5	0.9300	1.2793	0.3493
1.3	21.0	0.9029	1.029	0.1261
1.3	20.5	0.9293	1.1254	0.1961
1.3	21.0	0.9058	1.123	0.2172
1.3	19.5	0.9538	1.2437	0.2899
1.3	19.2	0.9191	1.187	0.2679
1.3	19.7	0.9331	1.2106	0.2775
2.6	21.0	0.9004	1.0490	0.1486
2.6	21.3	0.9324	1.1901	0.2577
2.6	21.1	0.9237	1.2964	0.3727
2.6	21.1	0.9399	1.2202	0.2803
2.6	21.1	0.9245	1.2898	0.3653
2.6	21.0	0.9091	1.2747	0.3656
2.6	21.3	0.9031	1.2261	0.323
2.6	21.0	0.9109	1.2465	0.3356
2.6	21.0	0.9417	1.2718	0.3301
2.6	19.5	0.9264	1.1411	0.2147
2.6	20.1	0.9519	1.1636	0.2117
2.6	21	0.9126	1.1189	0.2063
0.65	19.0	0.9042	1.4271	0.5229
0.65	19.0	0.9256	1.4483	0.5227
0.65	19.0	0.9289	1.3841	0.4552
0.65	19.0	0.8780	1.2568	0.3788
0.65	19.0	0.8714	1.2643	0.3929
0.68	19.7	0.8985	1.2679	0.3694
0.65	19.6	0.9167	1.2881	0.3714
0.67	19.7	0.9077	1.3602	0.4525

(%)		(g/L)	(g/L)	(g/L)
Conversion of Sludge	Fractional Conv. Sludge	Acetic Acid Conc.	Propionic Acid Conc.	Butyric Acid Conc.
64.29	0.64	1.563	0.514	0.259
57.34	0.57	1.548	0.514	0.254
56.85	0.57	1.557	0.493	0.239
59.24	0.59	1.833	0.529	0.239
53.51	0.54	1.697	0.509	0.235
50.88	0.51	1.720	0.524	0.256
57.23	0.57	2.037	0.560	0.239
57.71	0.58	1.974	0.532	0.232
55.33	0.55	2.003	0.535	0.241
83.93	0.84	1.889	0.567	0.249
74.84	0.75	2.013	0.569	0.244
72.23	0.72	2.038	0.561	0.233
62.61	0.63	2.144	0.637	0.254
65.75	0.66	1.93	0.604	0.251
64.36	0.64	2.267	0.68	0.285
80.95	0.81	1.639	0.664	0.442
67.09	0.67	1.695	0.662	0.427
52.31	0.52	1.719	0.643	0.434
64.03	0.64	2.078	0.746	0.372
53.17	0.53	2.181	0.749	0.358
53.29	0.53	2.190	0.743	0.347
58.71	0.59	2.425	0.796	0.353
56.95	0.57	2.310	0.765	0.346
57.61	0.58	2.353	0.768	0.343
72.48	0.72	2.387	0.813	0.383
72.78	0.73	2.383	0.782	0.355
73.78	0.74	2.154	0.691	0.316
33.27	0.33	1.706	0.716	0.426
33.01	0.33	1.783	0.694	0.395
41.67	0.42	1.524	0.600	0.341
51.50	0.52	1.820	0.610	0.280
49.86	0.50	1.830	0.617	0.284
52.82	0.53	1.958	0.601	0.277
52.46	0.52	1.858	0.602	0.257
42.12	0.42	1.864	0.580	0.246

(g/L)	(g/L)	(% by mass)	(g/L)	
Valeric Acid Conc.	Nitric Acid Conc.	Conversion of HNO3	Formic Acid Conc.	
0.0880	60.6057	0.316		
0.0840	59.5545	0.340		
0.0808	59.0117	0.340		
0.0830	54.5941	0.389		
0.0826	53.5277	0.387		
0.0861	56.4652	0.369		
0.0840	43.5121	0.520		
0.0800	44.0207	0.520		
0.0821	43.0567	0.518	0.121	
0.0912	45.3072	0.481	0.148	
0.0815	44.1877	0.506	0.233	
0.0796	43.6639	0.500	0.205	
0.0651	5.47	0.942	0	
0.0768	6.85	0.928	0.554	
0.0869	7.04	0.924	0.405	
0.260	111.0972	0.364	0	
0.219	106.4177	0.382	0	
0.165	108.8201	0.374	0	
0.164	94.5311	0.456	0.212	
0.150	92.3603	0.468	0.21	
0.117	90.5803	0.481	0.225	
0.116	83.5592	0.515	0.473	
0.128	88.2804	0.494	0.415	
0.118	83.3049	0.523	0.423	
0.132	82.13	0.563	1.031	
0.107	88.22	0.516	0.976	
0.0929	85.91	0.508	0.997	
0.283	27.1661	0.437	0.131	
0.125	26.5437	0.450	0.168	
0.107	26.9953	0.440	0.197	
0.0706	13.9057	0.712	0	
0.0777	16.3953	0.660	0	
0.0722	16.4257	0.663	0.128	
0.0663	10.4179	0.777	0.236	
0.0634	11.3629	0.763	0.152	

	(oC)	(minutes)	(minutes)	(minutes)	(grams)
Sample #	Temperature	Heating Time	Reaction Time	Cooling Time	Mass of Sludge In (wet)
30	182	2	15	5	19.1109
37	179.5	2	20	5	19.08
38	179.5	2	20	5	19.12
39	179.5	2	20	5	19.11
40	181.8	2	5	5	19.22
41	181.8	2	5	5	19.07
42	178.9	2	5	5	19.19
43	178.5	2	20	5	19.16
44	178.5	2	21	5	19.12
45	178.5	2	20	5	19.02
46	178.9	2	15	5	19.25
47	178.9	2	15	5	19.18
48	178.9	2	15	5	19.11
49	178.9	2	10	5	19.07
50	178	2	10	5	19.11
51	178	2	10	5	19.1

(mL)	(mL)	(grams)	(grams)	(grams)
Volume of HNO3 In	Total Product Volume Out	Filter Paper	Filter Paper + Sludge	Mass of Sludge Out
0.65	19.2	0.8780	1.2839	0.4059
0.65	18.9	0.9356	1.2947	0.3591
0.65	17.4	0.9741	1.3082	0.3341
0.65	18.5	0.9507	1.3064	0.3557
0.3	17.7	0.9579	1.4144	0.4565
0.3	18.2	0.9484	1.3558	0.4074
0.3	18.4	0.9191	1.3122	0.3931
0.3	18.6	0.9439	1.3696	0.4257
0.3	18.5	0.9198	1.3464	0.4266
0.3	18.9	0.9505	1.3745	0.4240
0.3	18.9	0.9516	1.2541	0.3025
0.3	18.7	0.9186	1.2271	0.3085
0.3	19	0.9251	1.1721	0.2470
0.3	18.3	0.9132	1.1917	0.2785
0.3	17.5	0.949	1.4063	0.4573
0.3	18.5	0.96	1.3947	0.4347

(%)		(g/L)	(g/L)	(g/L)
Conversion of Sludge	Fractional Conv. Sludge	Acetic Acid Conc.	Propionic Acid Conc.	Butyric Acid Conc.
47.98	0.48	1.875	0.592	0.250
53.90	0.54	2.067	0.6	0.248
57.20	0.57	2.061	0.619	0.263
54.41	0.54	2.271	0.679	0.298
41.83	0.42	1.802	0.761	0.499
47.68	0.48	1.793	0.775	0.502
49.83	0.50	1.68	0.705	0.449
45.58	0.46	1.795	0.766	0.468
45.35	0.45	1.584	0.696	0.43
45.40	0.45	1.663	0.71	0.432
61.51	0.62	1.624	0.685	0.42
60.61	0.61	1.804	0.747	0.462
68.34	0.68	1.836	0.73	0.432
64.23	0.64	1.618	0.717	0.464
41.39	0.41	1.541	0.654	0.419
44.26	0.44	1.532	0.634	0.398

(g/L)	(g/L)	(% by mass)	(g/L)	
Valeric Acid Conc.	Nitric Acid Conc.	Conversion of HNO3	Formic Acid Conc.	
0.0694	9.6930	0.797	0	
0.0591	2.06	0.958	0.199	
0.0617	12.98	0.754	0.123	
0.0725	9.18	0.815	0	
0.159	8.9	0.628	0.245	
0.156	1.82	0.922	0.466	
0.145	9.95	0.567	0.47	
0.137	5.32	0.766	0	
0.114	1.06	0.954	0	
0.112	1.21	0.946	0	
0.116	1.93	0.914	0	
0.126	1.87	0.917	0.108	
0.107	2.19	0.902	0	
0.129	1.75	0.924	0.305	
0.114	1.51	0.938	0.255	
0.108	1.38	0.940	0.233	

VITA

Larry Willis Perkins was born in Richlands, VA on August 12, 1977. He attended high school at Harriman High School in Harriman, TN. He continued his education by attending Roane State Community College where he obtained an Associate of Science degree. He then attended Tennessee Technological University in Cookeville, TN, where he graduated with a Bachelor of Science degree in Chemical Engineering in 1999. He received the Master of Science degree in Chemical Engineering from The University of Tennessee, Knoxville in 2001. From there, Larry continued his education and received a Doctor of Philosophy degree with a major in chemical engineering from the University of Tennessee in 2003. He is a member of the American Institute of Chemical Engineers, as well as the American Chemical Society.

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